Doctoral Thesis

Relation between surface properties and catalytic behaviour of a specific family of aluminosilicates materials
Towards the rational design of new aluminosilicates solids

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Relation between surface properties and catalytic behaviour of a specific family of aluminosilicate materials: towards the rational design of new aluminosilicate solids

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

presented by

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Summary

Amorphous aluminosilicates (ASAs) are widely used as catalyst support in the oil refining industry, especially in the conversion of heavy fractions. These mixed oxides provide the moderate acidity required for cracking and isomerization reactions of carbonaceous molecules. Thus, they can convert the residual fractions of crude oil towards middle-distillates, for which demand is continuously increasing. The deposition of a reduced or sulfided metal on the surface of ASAs gives a mesoporous catalyst that can selectively crack and hydro/dehydrogenate large molecules. However, because characterization is difficult on such amorphous materials, little is known about the distribution, at different scales, of silicon and aluminium atoms in ASAs, while a great number of synthesis techniques leads to very dissimilar materials. Since the surface structure and chemistry has a direct impact on the acidity and catalytic properties, the comprehension of the relation between these parameters to optimize the catalytic performance of ASAs is crucial. Although extensively studied, the structure of ASAs and, more particularly, the nature, localization and number of the sites at the origin of their acidity remain largely debated.

In order to solve these issues, a model family of ASAs was obtained by grafting. Al/SiO$_2$ and Si/Al$_2$O$_3$ materials were synthesized by depositing, in controlled conditions of water content and temperature, aluminium isopropoxide (Al(OiPr)$_3$) and tetraethyl orthosilicate (Si(OEt)$_4$) on silica and γ-alumina, respectively. The aim was to obtain a set of model ASAs covering a wide range of composition and surface structure that may be compared to commercial ASAs and materials stemming from classic synthesis paths (e.g. cogelation).

It was found that the yield of grafting depended on the density of surface OH groups of the support. For low OH density of the support, grafting was limited to one precursor molecule per OH. If the density of OH groups was high enough, the size of the precursor
molecule became the limiting factor and deposition was saturated when the surface of the support was fully covered with precursor molecules ($\approx 3.5 \text{ nm}^2$). In such a case, the grafting of new species was only possible after calcination and consequent recovering of hydroxyl groups. If water was added to the reaction mixture or at grafting temperature above $200^\circ\text{C}$, the continuous hydrolysis or decomposition of the alkoxy groups of the precursor molecules allowed unlimited grafting. $^{29}\text{Si}$ and $^{27}\text{Al}$ NMR, ToF-SIMS (time-of-flight secondary ion mass spectrometry) and TEM revealed that excess water favoured heterogeneous deposition and the presence of single oxide domains. High temperature in gas-phase grafting also led to inhomogeneous deposition of silicon species. Conversely, anhydrous conditions during synthesis enabled a regular distribution of surface species.

The adsorption of ethanol on ASAs enabled to calculate the percentage of exposed surface aluminium species on ASAs by comparing the amount of ethanol adsorbed to a scale (from 0 to 100%) where silica was the minimum and $\gamma$-alumina was the maximum. The evolution of the temperature at which the dehydration of ethanol took place, associated to the investigation of surface OH groups and acid sites by IR-adsorbed CO studies, showed that the grafting of silicon species on $\gamma$-alumina in mild conditions (up to $250^\circ\text{C}$) was selective to the facets of the support. Grafting preferentially took place first on the (100) surface, which lowered the number of active sites for ethanol dehydration. Then, the (110) surface was grafted, which created both strong Lewis acid sites and Brønsted acid sites. The latter were formed by interaction of a silanol and a tri-coordinated aluminium atom; these Brønsted sites were active in both ethanol dehydration and $m$-xylene isomerization, a Brønsted-demanding reaction. The stoichiometric dehydration of ethanol to ethylene enabled the quantification of the number of Brønsted acid sites and the calculation of their turnover frequency (TOF) for $m$-xylene isomerization: $1.4 \times 10^{-3} \text{ s}^{-1}\text{site}^{-1}$ at $350^\circ\text{C}$. At high coverage of the (110) surface, silicon was deposited on the first layer of deposited species, which consumed Brønsted acid sites and formed more strong Lewis acid sites.

The grafting of aluminium on the silica surface created Brønsted acid sites, as proven by infrared spectroscopy of adsorbed CO and ethanol adsorption and dehydration followed by thermogravimetry. The Lewis acid sites that also formed were associated to the presence of clusters of aluminium species, which were particularly present on the catalysts prepared under aqueous conditions. The Brønsted sites showed higher ethanol dehydration temperature than for Si/Al$_2$O$_3$ materials. The calculation of their TOF for $m$-xylene isomerization showed lower value ($4.3 \times 10^{-4} \text{ s}^{-1}\text{site}^{-1}$) and confirmed a lower strength of the Brønsted sites than for Si/Al$_2$O$_3$ materials. The Brønsted sites of both Si/Al$_2$O$_3$ and Al/SiO$_2$ were weaker than those
of a H-USY zeolite with very few extra-framework aluminium species, for which the TOF for m-xylene isomerization was $3.14 \times 10^{-2} \text{s}^{-1} \text{site}^{-1}$.

Evidence was given of the non-unique nature of Brønsted acid sites of ASAs. An ASA made by cogelation, i.e. mixing of molecular precursors of silicon and aluminium species, possessed zeolitic Brønsted acid sites, as indicated by the ethanol dehydration temperature (ca. 210°C) which was common to several types of zeolites. The detailed study of adsorbed CO by infrared spectroscopy yielded the stretching vibration of the Brønsted acid sites of Si/Al$_2$O$_3$ (3600 cm$^{-1}$) and Al/SiO$_2$ materials (3640 cm$^{-1}$) and proved that their number decreased when increasing the activation temperature from 250°C to 450°C. The same characterization techniques were applied to a commercial ASA (Siralox 30, 30 wt.% SiO$_2$, Sasol). The acidity features of this commercial ASA (ethanol dehydration temperature, number of Lewis acid sites, isosurface rate of conversion of m-xylene), obtained by impregnation of alumina (prepared by hydrolysis of an aluminium alkoxide) with orthosilicic acid, were similar to those of Si/Al$_2$O$_3$ materials prepared by grafting. The deposition of silicon species was also selective to the facets of alumina. This demonstrated that synthesis by grafting may convincingly describe the synthesis of commercial ASAs, despite strong differences in the preparation method. The infrared study of adsorbed ethanol on γ-alumina showed that the active sites of γ-alumina for ethanol dehydration were either OH groups or Lewis sites of the (100) surface depending on the activation temperature, and it confirmed the selective grafting of silicon species on the facets of γ-alumina.

The behaviour of Si/Al$_2$O$_3$ and Al/SiO$_2$ towards steaming, i.e. heating at high temperature in gaseous water flow, was evaluated. On Si/Al$_2$O$_3$, steaming had a limited effect and led to the redistribution of surface silicon species, with a better coverage of the alumina surface, yet lower on the (100) surface. Part of the Brønsted acid sites of the (110) surface were disrupted or covered, which led to a greater number of strong Lewis acid sites. On Al/SiO$_2$, both the surface aluminium species and the silica support sintered and collapsed, which led to a much smaller number of Brønsted sites by agglomeration of the dispersed aluminium species.

The thermogravimetric study of the adsorption, desorption and dehydration of ethanol has proven to be a simple, reliable, and reproducible technique for both the surface and the acidity characterization, and which can be applied to a great diversity of ASAs and zeolites. Its implementation with mass spectroscopy or gas chromatography could provide even further information on the catalytic processes. The unique disclosure of the selective grafting of silicon species on the facets of γ-alumina opens the way to new research on the optimization
of the ratio of facets, the study of molecular precursors reactivity, and the optimization of the synthesis parameters (water content, amount of precursor) to even more finely tune the surface properties. This thesis has contributed to the comprehension of the Brønsted acidity of ASAs: The comparison of various ASAs and zeolites has demonstrated the non-unique nature of Brønsted acid sites on ASAs, which can be either different or similar to those found on zeolites. The choice of grafting to synthesize the materials was consistent with the characterization techniques and greatly helped to rationalize the problematics.
Résumé

Les aluminosilicates amorphes (ASAs) sont fréquemment utilisés en tant que supports de catalyseur dans l'industrie du raffinage du pétrole, et plus spécifiquement pour la conversion des charges lourdes. Ces oxydes mixtes possèdent une acidité modérée à même de craquer et d'isomériser les composés carbonés. Ils permettent ainsi la valorisation de la fraction résiduelle issue de la distillation atmosphérique en distillats moyens, dont la demande ne cesse de croître. Un catalyseur mésoporeux bifonctionnel, possédant en plus d’une fonction craquante une fonction hydro/déshydrogénante, peut être obtenu par dépôt d'une couche de métal réduit ou sulfuré en surface de l’ASA. Cependant, la caractérisation de tels matériaux amorphes est difficile. Malgré la variété des techniques de synthèse conduisant à des matériaux très divers, les informations concernant la distribution des espèces siliciques et aluminiques au sein des ASAs sont rares. Afin d’optimiser les performances des ASAs, la compréhension entre chimie de surface, structure de surface et activité catalytique est pourtant cruciale. Bien que régulièrement étudiés, le nombre, la nature ainsi que la localisation des sites acides des ASAs restent l'objet de débats.

Afin de répondre à cette problématique, une famille modèle d’ASAs a été synthétisée par greffage en conditions contrôlées de teneur en eau et de température : Al/SiO₂ (isopropoxyde d'aluminium (Al(O'Pr)₃) sur silice) et Si/Al₂O₃ (tétra-éthoxy-silane (Si(OEt)₄) sur alumine γ). Il s’agissait de disposer d’une famille d’ASAs couvrant une gamme large de composition et structure de surface et qui puisse être comparée à des ASAs commerciales et/ou issues de voies de synthèse plus classiques (cogélation par exemple).

L’impact de la densité surfacique de groupements hydroxyles du support sur le rendement de greffage et a été mis en évidence. À faible teneur en OH de surface, le greffage maximal se limite à une molécule de précurseur par OH. Si la teneur en OH est suffisante, c’est la taille de la molécule de précurseur qui fixe le rendement maximal du greffage ; celui-
ci est atteint lorsque la surface du support est recouverte d'une monocouche de molécules précurseur (≈ 3.5 nm²). Le greffage de nouvelles espèces n'est alors possible qu'après calcination et formation de nouveaux groupes hydroxyles. En présence d'eau ou pour des températures supérieures à 200°C, l'hydrolyse ou la décomposition régulières des groupements alcoxy du précurseur autorisent le greffage de nouvelles espèces en continu. La structure du dépôt de surface a été évaluée par RMN ²⁹Si et ²⁷Al, ToF-SIMS (time-of-flight secondary ion mass spectrometry) et MET (microscopie électronique en transmission). Un excès d'eau lors du greffage favorise un dépôt hétérogène et la présence de zones oxyde simple. À l'inverse, des conditions anhydres permettent une distribution régulière et homogène des espèces greffées en surface.

Le suivi thermogravimétrique de l'adsorption d'éthanol sur les ASAs a permis de calculer le pourcentage de surface occupé par les espèces aluminiques et siliciques : la quantité d'éthanol adsorbé est reportée à une échelle (de 0% à 100%) où la silice et l'alumine sont les minimum et maximum respectifs. Des résultats convergents basés sur l'évolution de la température de déshydratation de l'éthanol et la caractérisation des OH de surface et des sites acides par adsorption du CO suivie par spectroscopie infrarouge, ont montré que le greffage des espèces siliciques à température modérée (jusqu'à 250°C) était sélective aux facettes cristallographiques de l'alumine. Dans un premier temps, le greffage se fait préférentiellement sur la face (100) et conduit à une baisse du nombre de sites actifs pour la déshydratation de l'éthanol. Ensuite, la face (110) est greffée, ce qui entraîne la formation de sites acides forts de Lewis et de sites acides de Brønsted. Ces derniers correspondent à l’interaction d'un silanol et d'un aluminium trivalent de la même surface ; ils sont actifs à la fois pour la déshydratation de l'éthanol et l'isomérisation du m-xylène. La déshydratation stœchiométrique de l'éthanol en éthylène permet la quantification du nombre de sites acides de Brønsted et le calcul de leur TOF (turnover frequency) pour l'isomérisation du m-xylène : 1.4.10⁻³ s⁻¹ site⁻¹ à 350°C pour les matériaux Si/Al₂O₃. Lorsque la face (110) est saturée, les espèces siliciques se déposent sur la première couche greffée, recouvrant ainsi les sites acides de Brønsted précédemment formés et conduisant à plus de sites acides forts de Lewis.

Les mêmes techniques de caractérisation d’acidité appliquées aux matériaux Al/SiO₂ ont montré que le greffage d'espèces aluminiques sur silice créait des sites acides de Brønsted. Des sites de Lewis sont également formés en raison de la présence de clusters d'espèces aluminiques, particulièrement présents sur les catalyseurs préparés en conditions aqueuses. La température de déshydratation de l'éthanol est plus élevée que celle constatée pour les matériaux Si/Al₂O₃. Leur plus faible TOF pour l'isomérisation du m-xylène (4.3.10⁻⁴ s⁻¹ site⁻¹)
confirme que les sites acides de Brønsted de ces matériaux sont moins forts que ceux des Si/Al₂O₃. Les sites de Brønsted des Si/Al₂O₃ comme des Al/SiO₂ demeurent toutefois plus faibles que ceux d'une zéolithe, comme par exemple une H-USY dépourvue d'aluminium extra-réseau, pour laquelle le TOF pour l'isomérisation du m-xylène est de 3,14.10⁻² s⁻¹site⁻¹.

En réalité, il n’existe pas de modèle unique de site acide de Brønsted des ASAs. La température de déshydratation de l’éthanol obtenue sur une ASA préparée par cogélation, c’est-à-dire mélange de précursors moléculaires de silicium et d'aluminium, est identique à celle des zéolithes (environ 210°C) et confirme la présence de sites acides de Brønsted zéolithiques sur ces matériaux. Sur les ASAs obtenues par greffage, l'étude détaillée de l'adsorption du CO suivie par infrarouge a donné accès à la fréquence de vibration des sites acides de Brønsted des matériaux Si/Al₂O₃ (3600 cm⁻¹) et Al/SiO₂ (3640 cm⁻¹). Le nombre de ces sites diminue lorsque la température d'activation augmente de 250°C à 450°C. Ces résultats ont été comparés à une référence ASA commerciale (Siralox 30, 30% poids SiO₂, Sasol). Les propriétés d'acidité de cette ASA (température de déshydratation de l'éthanol, nombre de sites acides de Lewis, vitesse de conversion isosurface du m-xylène), préparée par imprégnation d'une alumine (obtenue par hydrolyse d'un alcoxyde d'aluminium) avec de l'acide orthosilicique, sont similaires à celles de matériaux Si/Al₂O₃ préparés par greffage. Le dépôt d'espèces siliciques est ainsi sélectif aux facettes de l'alumine. Les phénomènes observés lors du greffage peuvent donc être étendus à une certaine diversité de protocoles de synthèse d’ASAs commerciales, en dépit de conditions opératoires différentes. L'étude par infrarouge de l'adsorption de l'éthanol a démontré que les sites actifs de l'alumine γ pour la déshydratation de l'éthanol étaient soit des groupes OH de la face (100), soit des sites acides de Lewis de la même surface, en fonction de la température d'activation. Elle est également venue confirmer le caractère sélectif du greffage des espèces siliciques sur les facettes de l'alumine γ.

Le comportement des Si/Al₂O₃ et Al/SiO₂ dans des conditions de steaming, c'est-à-dire chauffage à haute température sous flux d'eau vaporisée, a été évalué. Sur Si/Al₂O₃, l'effet du steaming est limité et engendre principalement une redistribution des espèces siliciques de surface, menant à un plus grand degré de couverture de l'alumine, quoique moindre sur la face (100). Une partie des sites acides de Brønsted, situés sur la face (110), est perturbée ou recouverte, ce qui entraîne une augmentation du nombre de sites acides de Lewis forts. Sur Al/SiO₂, aussi bien les espèces aluminiques de surface que la structure du support silicique frittent et/ou s'effondrent partiellement, conduisant à un nombre de sites de Brønsted
bien plus faible après steaming, du fait de l'agglomération des espèces aluminiques initialement dispersées.

L'étude thermogravimétrique de l'adsorption et la déshydratation de l'éthanol s'est révélée être une méthode simple de mise en œuvre, fiable et répétable pour la caractérisation de l'état de surface et de l'acidité, applicable à tous types d'ASAs ou de zéolithes. Son implémentation par ajout d'un spectromètre de masse ou d'une colonne de chromatographie gazeuse pourrait fournir des informations complémentaires quant au processus catalytique. Le caractère inédit de la découverte du mécanisme de greffage des facettes de l'alumine γ ouvre la voie à des recherches portant sur l'optimisation du ratio de ces facettes et des paramètres de greffage (teneur en eau, quantité de précurseur) afin d'ajuster encore plus finement les propriétés de surface. Cette thèse a contribué à la compréhension de l'acidité de Brønsted des ASAs. Comme l’a démontré la comparaison de plusieurs ASAs et zéolithes, différents types de sites acides de Brønsted coexistent dans la catégorie des aluminosilicates amorphes, qu’ils soient similaires ou différents à ceux des zéolithes. Le choix du greffage comme technique de synthèse des matériaux modèles s'est révélé judicieux et pertinent vis-à-vis des techniques de caractérisation employées, et a grandement aidé à rationaliser la problématique de départ.
Chapter 1

General introduction

1.1 Nature of amorphous aluminosilicates (ASAs) and their use

Although the world demand for gas-oils is accelerating,[1] the typical composition of imported crude oils cannot satisfy the needs for middle-distillates; therefore the refining industry has to adapt. Middle-distillates (C_{13-25} fraction), originally resulting from the separation of the 150-350°C cut of crude oil by atmospheric distillation, can also be produced by conversion of low-value heavy oil feedstocks stemming from the residual fraction of atmospheric distillation of crude oil, which corresponds to the middle-distillate effluent of vacuum distillation (Vacuum Gas-Oil, VGO). Amorphous aluminosilicates (ASAs) can serve as catalysts supports for this operation, since they possess the moderate acidity required for the primary cracking of heavy molecules, which leads to good selectivity in the C_{13-25} fraction, and mesoporous channels that enable large molecules to react with the surface and prevent from over-cracking. These aluminosilicates provide the acidic function enabling the breaking of C-C bonds, while deposited metals (Pt, Pd) or sulfide metals ensure the hydrogenation/rehydrogenation role in hydrocracking, i.e. cracking under hydrogen pressure.

Many synthesis routes are available for ASAs preparation.[2] What differ between each of them are the hydration/condensation state of the precursors and their relative quantity; therefore the resulting materials have variable levels of structural homogeneity. The cogelation method (also known as coprecipitation), where precursors are molecules, is thought to lead to the most homogeneous mixed oxides because it supposedly enables the best dispersion and condensation of silica and alumina precursors throughout the volume of the reactor. Generally speaking, the characterization of the repartition and the detailed structure of the silicon and aluminium species in amorphous aluminosilicates is challenging, because the different synthesis methods lead to very dissimilar structures.[2]
This high level of structural heterogeneity has prevented unequivocal identification of the surface species that are responsible for acidity: These structures may have acid sites with a very different architecture. On the contrary, zeolites have a well-defined crystalline structure and porosity, and defined Brønsted acid sites consisting of a hydroxyl group bridging an aluminium and a silicon atom. The question as to the exact structure of the active site in ASAs is of primary importance if we are to understand the relationship among surface chemistry, acidity, and catalytic activity. Although extensively studied the nature, localization and number of the sites originating the acidity of ASAs remain largely debated.

The first suggestions for the nature of acid sites in ASAs, formulated in the 1940-1950's, remain popular today. The acidic protons $H^+$ were supposed to be formed due to compensation of the negative charge induced by the presence of aluminium atoms inserted in the silica network, like in zeolites. Nonetheless, to explain the specific behaviours of ASAs in catalytic reactions, especially the low performances compared to zeolites, other theories emerged. For some of them, ASAs and zeolites possess different concentrations of the same type of acid sites; while for others the acid sites of ASAs and zeolites have distinct architectures. The characterization of the acidity itself is challenging and comparison of results is difficult because of the variety of techniques used for this purpose.

1.2 Synthesis routes

An extensive number of patents have been published so far to describe the synthesis techniques of ASAs. A large combination of properties (structure, texture and composition) can be obtained provided that experimental conditions are carefully chosen. The most common synthesis techniques of ASAs are cogelation (or coprecipitation), co-sequenced technique and grafting or impregnation.\(^2,3\) Table 1.1 gives the main categories of synthesis techniques. The variety of routes for ASA synthesis is mostly due to the hydrolysis/condensation state of each of the precursors, but other factors such as pH, temperature of the reaction, or nature of the alkoxide groups in the case of a molecular precursor, all contribute to design a unique structure formed by nano-assembling of silicon and aluminium atoms. The cogelation consists in the controlled gelation or precipitation of a mixture of aluminium and silicon molecular precursors, maintained at a given pH.\(^2,4\) The co-sequenced techniques consists in mixing a pre-hydrolyzed silicon or aluminium precursor suspension (i.e. oligomers) with a molecular precursor solution of the complementary component.\(^2\) In grafting or impregnation, a molecular precursor of silicon or aluminium is
deposited on a solid oxide (alumina or silica, respectively); the term “grafting” is used in the case of an accurate deposition.

The mesoporosity of ASAs is mostly due to the presence of interstitial spaces between dense primary particles of silica, alumina or aluminosilicates. The main characteristics of the mesoporosity (surface area, diameter of the pores, total pore volume) depend on the synthesis route. Either the formation of the primary particles takes place in course of synthesis or a solid single oxide, possessing its own porosity, is used as one of the precursors, which does not lead to the same results.\textsuperscript{[2]}

The textural parameters can be tuned post-synthesis by applying specific thermal or hydrothermal treatments, such as steaming or calcination.\textsuperscript{[5]}

## 1.3 The acidity of ASAs

### 1.3.1 Characterization of acidity

The acidity of solids results from the presence of defects on the surface, which are commonly associated with electronic charge issues such as incomplete dehydration or unsaturated coordination of atoms. Simple oxides usually display two types of acid sites, which existence depends on the temperature and the nature of the oxide:

- Lewis acid sites (LAS): exposed surface metallic cations,
- Brønsted acid sites (BAS): hydroxyl (OH) surface groups.

The adsorption of basic probe molecules is used to distinguish the nature, strength and amount of acid sites on ASAs.\textsuperscript{[6]} The adsorption of these molecules on the surface of the

| Table 1.1 Synthesis techniques of amorphous aluminosilicates (ASAs).\textsuperscript{[2]} |
|-----------------------------------|---------------------------------|-----------------|-----------------|
| **Liquid phase**                  | **Solid phase**                 | **Isolated SiO\textsubscript{2}** |
| Molecular precursor of SiO\textsubscript{2} | Sol of SiO\textsubscript{2} | SiO\textsubscript{2} gel/precipitate | Isolated SiO\textsubscript{2} + molecular precursor or sol of Al\textsubscript{2}O\textsubscript{3},xH\textsubscript{2}O (e.g. grafting) |
| Sol of Al\textsubscript{2}O\textsubscript{3},xH\textsubscript{2}O | Cogelation/coprecipitation | Co-sequenced | Isolated SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3},xH\textsubscript{2}O gel/precipitate |
| Isolated Al\textsubscript{2}O\textsubscript{3},xH\textsubscript{2}O | Isolated Al\textsubscript{2}O\textsubscript{3},xH\textsubscript{2}O + molecular precursor or sol of SiO\textsubscript{2} (e.g. grafting) | Isolated Al\textsubscript{2}O\textsubscript{3},xH\textsubscript{2}O + SiO\textsubscript{2} gel/precipitate | Co-malaxing |
oxides is monitored by spectroscopic means and yields the nature of sites; the modulation of the temperature gives the strength of the adsorption; the quantification of the adsorption and desorption of molecules may be measured by thermogravimetry.\[7\] The adsorption depends on both the basic strength (\(n\)-butylamine > ammonia > pyridine for example) and sterical issues. Various sites such as acidic protons, acceptor electron sites, or even neutral hydroxyl groups can be probed. Since all molecules do not adsorb on the same type of sites, cross-checking can be made for evaluating the surface using different basic probes. Thanks to microcalorimetry, the adsorption energy can be measured.\[8\] CO, for example, can be used as a probe molecule: Its adsorption followed by infrared spectroscopy yields the nature and strength of the acidic sites (BAS, weak and strong LAS) of ASAs\[6,9,10\] based on the CO stretching frequency. The hydroxyl groups of ASAs can be made to react with deuterated molecules and monitored by IR spectroscopy, which stresses the role of these OH groups in the adsorption of molecules and further reaction. Similarly, deuterated aluminosilicates surface previously exchanged with deuterated water can react with alkene molecules, which forms cracked or isomerized products observed by mass spectrometry.\[11\]

The study of the conversion of a model molecule provides information regarding the acidic behaviour of a catalyst in a complete catalytic cycle; it is thus complementary to the adsorption of probe molecules. Methyl benzene\[12\] molecules or cumene\[13\] are example of species used in catalytic model reactions. Numerous articles also report the use and characterization of ASAs for catalytic reactions such as alcohol dehydration,\[14-20\] positional or skeletal 1-butene isomerization.\[21,22\] The assessment of the catalytic performance of ASAs can be achieved based on the isomerization of \(m\)-xylene to \(o\)- and \(p\)-xylene, catalyzed by acid solids such as ASAs and zeolites.\[23,24\] BAS catalyze the isomerization from \(m\)- to \(o\)- and \(p\)-xylene through formation of a benzenium ion intermediate.\[23\]

### 1.3.2 Nature of the acid sites

Figure 1.1 gives the main hypothetic structures of acid sites in ASAs. Tamele\[25\] and Thomas\[26\] propose a structure based on the difference between the valence of silicon and aluminium atoms. The acidity of both zeolites and ASAs results from the positively charged and labile protons that compensate the negative charge induced by the presence of aluminium atoms in tetrahedral coordination embedded in a silica environment (Figure 1.1.a). However, the typical bridged structure associated to these sites have been only found on zeolites, and characterized by a peak around 3600 cm\(^{-1}\) in IR spectroscopy, but not in ASAs.\[3\]
Hansford\cite{27} postulates that aluminium hydroxide groups located in the vicinity of silanol groups are responsible for the Brønsted acidity of ASAs, thanks to proton transfer occurring between the catalyst and the hydrocarbon molecule. This proton transfer is enabled by the weakening of the O-H bond thanks to the presence of an aluminium atom (Figure 1.1.b).

Based on CO adsorption followed by IR spectroscopy, Daniell et al.\cite{6} observe the changes in the chemical nature of an ASA surface (Siral, Sasol) when increasing the silica loading. They describe BAS of ASAs resembling those of zeolites, i.e. silanol groups bridging neighbouring aluminium atoms (Figure 1.2). The isomorphous substitution of silicon by aluminium atoms in tetrahedral environment also forms strong LAS. These sites are located in a mixed aluminosilicate phase. The bridged Si-O(H)-Al sites are much less numerous on ASAs than on zeolites, which explains the absence of a characteristic IR band at 3600 cm\(^{-1}\).

Trombetta et al.\cite{28} use pyridine and acetonitrile adsorption to compare zeolites (FER and HZSM-5), ASAs (commercial ASA and silicated alumina Si/Al\(_2\)O\(_3\)), silica and alumina. Zeolites have a stronger acidity than ASAs and the acidity of the simple oxides is very weak. Moreover, silanol groups differing from those of pure silica are observed on ASAs. Because of a more flexible structure than that of zeolites, the BAS of ASAs only form upon protonation of a basic molecule, by bridging of the Si-O-Al bond between a silanol and a coordinatively unsaturated aluminium atom (Figure 1.1.c). The negative charge of the Si-OH group is transferred to the aluminium atom only when H protonates a basic molecule. This explains the absence of an IR resonance corresponding to permanent bridged sites in ASAs.

According to Crépeau et al.,\cite{9} based on pyridine, lutidine and CO adsorption followed by IR spectroscopy, the BAS of ASAs also correspond to silanol groups in the vicinity of coordinatively unsaturated aluminium atoms. These (SiOH, Al\(^{IV}\)) paired sites are the most acidic of three types of OH groups (A1, A2, B). The higher the number of neighbouring Al\(^{IV}\) atoms, the stronger the acidity. Thanks to CO adsorption frequencies and comparison with zeolites, they propose a non-bridging structure of site (Figure 1.1.d) where the silanol alone is acidic, thanks to its chemical environment. Therefore, there may be many types of BAS on ASAs, depending on the technique used for their synthesis, hence the local environment of surface aluminium and silicon atoms. The formation of an “OH chain” by H bonding between neighbouring silanols may confer a small charge defect, hence acidity, to the chain-ending silanol (Figure 1.1.e). The well-mixing and distribution of silicon and aluminium atoms at the atomic scale on the surface of materials prepared by cogelation may enable the formation of zeolitic Al\(^{IV}\)-O-SiOH sites (Figure 1.1.f), like Thomas et al. and Tamele et al. suggest. The
formation of the Lewis acid sites of ASAs is also explained: They appear upon water desorption by heating, and correspond to Al\textsuperscript{3+} surface atoms. Using NMR arguments, Huang et al.\cite{29} also show that silanols in the vicinity of tetra-coordinated aluminium atoms form BAS of moderate strength, and that the interaction of these BAS with penta-coordinated aluminium atoms increases their strength.

According to Hensen et al.\cite{3} the incorporation of tetrahedral aluminium atoms in the silica framework in ASAs, leading to zeolitic BAS, is limited to a very low amount of aluminium atoms, hence the lower acidity of ASAs. A detailed study of the same author, based on the adsorption of basic molecules followed by IR spectroscopy, NMR and the catalytic isomerization of \textit{m}-xylene, show that BAS of lower strength also exist; they might be associated to the interaction between silanols and strong LAS.\cite{30} According to Cairon, based on CO adsorption studies, there is a high diversity of OH groups on both ASAs and zeolites.\cite{31} An additional A0 category of OH groups is specifically detected on zeolites.

Chizallet and Raybaud\cite{32,33} obtain an aluminosilicate surface by simulating the deposition of silicon species on a model of γ-alumina surface ((100) surface) previously established by Digne et al.\cite{34}, and built by DFT (Density Functional Theory) calculations. Starting with a full dehydrated surface, its progressive hydration leads to the appearance of so-called Pseudo-Bridging Silanols (PBS), i.e. silanol groups interacting with a neighbouring aluminium atom (Figure 1.1.g). These sites show Brønsted acidity and form a bridged structure only when protonating a basic molecule. The main difference with the structure proposed by Trombetta et al. is the coordination of the aluminium atom: In the case of a PBS it is tetra-coordinated (penta-coordinated when closing the bridge), since tri-coordinated aluminium species are not found at such hydration state of the surface. The flexibility of the BAS, the variable angles and bond length, are responsible for their lower acid strength than those of zeolites. Zeolitic bridged BAS are also observed on the model ASA surface, but at a lower concentration than PBS.

Based on the comparison of calorimetric measurements of propane adsorption on ASAs and zeolites, Xu et al.\cite{35} show that the energy of adsorption of reactant molecules also has an impact on the catalytic conversion. A lower energy of adsorption on ASAs than on zeolites leads to a lower coverage of the surface, hence lower conversion. Besides, the lower number of active sites on ASAs contributes to their lower activity.
Introduction

Figure 1.1 Hypotheses for Brønsted acid sites in ASAs: a) Isomorphous substitution by Al atom in a silica lattice;\textsuperscript{[26]} b) Al hydroxide group in the closeness of a silanol group;\textsuperscript{[27]} c) Bridging Si-O-Al bond upon basic molecule (L) protonation;\textsuperscript{[28]} d) Non-bridging SiOH and Al\textsuperscript{3+} upon basic molecule (L) protonation;\textsuperscript{[9]} e) SiOH weak acidity by SiOH chain formation;\textsuperscript{[8]} f) Bulk Al\textsuperscript{IV}-O-SiOH acidic site (ASAs obtained by cogelation);\textsuperscript{[8]} g) Pseudo-Bridging Silanol formed upon adsorption of a basic molecule (L).\textsuperscript{[32,33]}

Figure 1.2 Brønsted acid sites of zeolites: permanently bridged structure.\textsuperscript{[6,28]}
1.4 Aim of the thesis

The multiplicity of techniques for ASA synthesis, the variety of composition accessible, and the dissimilarity of structures (i.e. the repartition of silicon and aluminium atoms through the particles), reflect the development of ASAs through trial and error. They also contribute to their high diversity, and thus render their characterization difficult in the absence of a “model ASA”. The hypothetical structures for BAS found in the literature cannot be compared since each of them is associated to a given synthesis technique. When it is mentioned, the diversity of preparation methods for ASA synthesis is associated to a potential and parallel diversity of acid sites, without further detail. Due to lack of understanding of the acid site architecture, optimization of the acidic properties, by tuning the repartition of silicon and aluminium atoms and by controlling the local structure of the site, is difficult.

The present thesis proposes to rationalize the diversity of ASAs using a model technique for ASA synthesis: grafting. Starting from pure alumina and silica, it aims at covering a wide range of accessible Si/Al composition as a first step by depositing the complementary material (silica and alumina, respectively), and then making the structure of the materials more complex by tuning the parameters of synthesis (temperature, water content). Thanks to this technique, the mixed-oxide phase is restricted to the surface, which simplifies the interpretation of characterization results. Investigation of the surface structure and chemistry (NMR, IR, etc.) and of the acidic properties (adsorption of probe molecules, catalytic test of model molecules, etc.) is directly related to the presence of the deposited species. Eventually, a fine correlation can be established between the surface species and the nature of acid sites, to finally disclose the origin of Brønsted acidity in ASAs. The results for grafted ASAs can be compared to the results for ASAs synthesized by other techniques, including commercial references, to better understand their surface structure and catalytic properties.
Chapter 2

Synthesis of amorphous aluminosilicates by grafting

2.1 Preparation of ASAs by grafting

The grafting technique corresponds to the deposition of molecular species on an oxide surface, to obtain a mixed oxide upon calcination of the deposited species. Grafting is also referred as deposition or functionalization, alluding to the modification of surface properties induced by the anchorage of molecules.

Grafting takes place in a biphasic environment, using a solid support oxide. The molecular precursor of the second oxide can react on the solid either in liquid phase (CLD: Chemical Liquid Deposition) or in gas phase (CVD: Chemical Vapour Deposition). There is an example of Al/SiO$_2$ materials prepared in supercritical medium.[36]

2.1.1 Chemical Liquid Deposition

CLD is a variant of the sol-gel process, i.e. the mixing of aluminium and silicon precursors in liquid state at moderate temperatures. In liquid phase grafting, silicon and aluminium precursors having distinct hydrolysis/condensation states are introduced in the reactor:

- support (SiO$_2$ or Al$_2$O$_3$): major component, introduced in its oxidized and polymerized form, solid-state,
- precursor (aluminium and silicon, leading respectively to Al/SiO$_2$ and Si/Al$_2$O$_3$): molecular species, either in a liquid or solid state. The relative amounts of precursor and support, and their mutual reactivity determine the yield of grafting,
- most of the times, a solvent is added to the mixture for homogenization and dilution of the precursor. Sometimes the liquid phase is the precursor itself. There is no rule concerning the order of introduction of the components.
In Al/SiO$_2$ grafting, the aluminium precursors are typically salts (AlCl$_3$, NaAlO$_2$, etc.) and alkoxides (aluminium isopropoxide, aluminium sec-butoxide, etc.). Supports are either mesostructured silica support, having ordered porosity, or silica without ordered porosity. The latter is preferred in industrial processes. Si/Al$_2$O$_3$ grafting usually takes place over γ-alumina: it is a good compromise between reactivity (the γ-alumina surface has a high hydroxyl density), crystalline character (useful for characterization) and textural properties, compared to other polymorphs of alumina. Moreover, γ-alumina is extensively used in the refining industry. The silicon precursors usually are alkoxides such as TEOS (tetraethyl orthosilicate), or TMOS (tetramethyl orthosilicate).

The maximum grafting temperature corresponds to the boiling point of the solvent. At such temperature, the reaction takes place under reflux. Generally speaking, the grafting temperature does not exceed 150°C when grafting is performed in liquid media. The choice of the solvent and, thus, the maximum temperature can affect the support and precursor relative reactivity.

2.1.2 Chemical Vapour Deposition

In CVD, the molecular precursor is brought to the support in gas phase. Contrary to CLD, a wide range of deposition temperatures is accessible. The grafting temperature must be higher than the precursor boiling point (e.g. TEOS: 166-169°C); CVD is not suitable for temperature-sensitive supports and/or precursors.[37] There are different CVD setups.

2.1.2.1 Static or sequenced CVD

The static CVD consists in the repetition of cycles alternating evacuation and admission steps:[20]

- evacuation: The first step is for desorption of surface water under vacuum and at a given temperature. During grafting cycles: desorption of residual species stemming from the decomposition of the alkoxide (alcohol or ether molecules) in order to "re-activate" the oxide surface,
- admission: After evacuation, the vapours of the silicon precursor, coming from an evaporator maintained at 0 °C (for control of the vapour pressure), are aspiried by vacuum up to the oxide chamber where the support is heated at a given temperature,
- repetition of evacuation and admission steps as long as necessary,
- admission of water at the end of grafting for hydrolysis of the chemisorbed species
Synthesis of ASAs by grafting

- calcination: decomposition of the carbonaceous components at high temperature in air, leading to a purely inorganic catalyst.

Figure 2.1 gives the scheme of the set-up. The amount of deposited species depends on the number of evacuation/admission cycles. The weight gain during deposition is measured by a microbalance.

![Figure 2.1 Setup for static CVD](image)

2.1.2.2 Continuous CVD

In continuous CVD, a carrier gas passes through a reservoir containing the precursor and maintained at a given temperature for control of its evaporation before reaching the reactor containing the solid oxide (Figure 2.2.a). The precursor can also be introduced in the liquid state directly in the reactor (Figure 2.2.b). Due to the furnace temperature, the precursor is vaporized before contacting the support bed. A gas flow drags the precursor molecules through the catalysts grains. This technique is also referred as pulsed CVD.

The contact between particles of the solid oxide and precursor molecules can be enhanced using fluidized-bed CVD (FB-CVD). In that case, part of the carrier gas is used to suspend the particles, which then behave as a liquid.

To our knowledge, there is no attempt of grafting aluminium on non-ordered amorphous silica in gas phase to modify acidity. However, aluminium has been successfully deposited on mesostructured silica by pumping the aluminium precursor under vacuum and passing the molecules through the silica bed maintained at a given temperature.
2.2 Impact of grafting on the final properties of ASAs

2.2.1 Al/SiO$_2$

2.2.1.1 Surface structure

NMR (Nuclear Magnetic Resonance) provides insight on both the bulk and surface structure of the materials. $^{27}$Al NMR is a tool of interest to investigate the coordination of the deposited aluminium atoms. Four-coordinated (Al(IV) or tetrahedral) aluminium atoms are usually located at around 60 ppm and six-coordinated (Al(VI) or octahedral) aluminium atoms are located at around 0 ppm. Another signal can be observed at around 30 ppm, it corresponds to five-coordinated aluminium atoms (Al(V)) or four-coordinated aluminium located in a distorted environment. Both Al(IV) and Al(VI) species are typically found in alumina-grafted samples.

The grafting of aluminium first leads to the appearance of tetrahedral aluminium atoms which adopt the coordination of the surface silicon species. A small number or the main part of these Al(IV), or even the totality of the Al(IV) may correspond to species inserted in the silica network and substituting silicon atoms. The emergence of hexa-coordinated aluminium atoms when increasing the alumina loading causes the decrease of the Al$^{IV}$/Al$^{VI}$ ratio. This is consistent with the growth of a purely aluminated phase being either aluminium hydroxide or alumina.
2.2.1.2 Acidity

Pure silica does not show any acidity.\textsuperscript{[57]} The appearance of a Lewis acidity upon grafting is directly related to the presence of surface aluminium species.\textsuperscript{[54,57-59]} The number of Lewis acid sites (LAS) of Al/SiO\textsubscript{2} grafted materials does not exceed the number of LAS of pure alumina. Brønsted acid sites (BAS) also appear.\textsuperscript{[55]} When the alumina loading increases even more, the Brønsted acid sites are progressively covered and the catalyst eventually behaves like pure alumina at high aluminium loading.\textsuperscript{[54,58]}

The BAS may form by isomorphous substitution of silicon atoms by Al(IV) in the silica framework.\textsuperscript{[3,49,54,55,60-63]} According to Hensen et al.\textsuperscript{[3]} only few Al(IV) atoms diffuse in the silica network; thus, the number of BAS hardly depends on the alumina loading. Similarly, Corma et al.\textsuperscript{[61]} (by pyridine adsorption followed by IR spectroscopy) and Mokaya et al.\textsuperscript{[63]} (based on pyridine adsorption and cumene cracking) show that the impact of the alumina loading on the appearance of a medium-strength Brønsted acidity is low; however they consider that all the Al(IV) are inserted in the silica network and form a BAS.

2.2.2 Si/Al\textsubscript{2}O\textsubscript{3}

2.2.2.1 Surface structure

Depending on the grafting temperature, the deposition of silicon species on alumina does not lead to the same surface structure. At low temperatures, by CLD, only low silica loadings are accessible because of the lack of reactivity of the precursor molecules.\textsuperscript{[64,65]} After calcination, a new grafting step enables to increase the silica loading. In the case of successive grafting steps, islet-like deposits grow vertically.\textsuperscript{[21,66]} Between 200°C and 400°C, by CVD, the control on the deposition process enables the progressive formation of a monolayer, and even a bilayer if the first layer is reactive enough.\textsuperscript{[20,39,67-69]} The reactivity of alumina under CVD conditions is enhanced due to the continuous desorption of residual molecules (physisorbed H\textsubscript{2}O or alcohol molecules resulting from the alkoxide decomposition) of the alumina surface. Above 400°C, grafting fails to fully cover the surface because silicon precursor molecules agglomerate inhomogeneously.\textsuperscript{[38,67]}

2.2.2.2 Acidity

Pure alumina possesses LAS which are formed by dehydroxylation of the surface. Upon silica deposition LAS disappear and stronger BAS than the hydroxyls of pure alumina appear.\textsuperscript{[22,21,70-74]}
There is no unique optimum silica loading that leads to the best catalytic properties. For instance, the optimum silica loading of Si/Al$_2$O$_3$ prepared by CVD that leads to the best activity in 1-butene isomerization may be $7 \text{ Si nm}^2$ \cite{70} or $12-13 \text{ Si nm}^2$ \cite{20,39}. The active sites for 1-butene isomerization may be located at the border between the spot deposits of bilayers of silica and the alumina surface.\cite{70} Alternatively, a complete monolayer might be required to form BAS: These would be silanol groups (belonging to the deposit) attached to aluminium atoms belonging to the surface (i.e. Al-O-SiOH species).\cite{20,38,68,69,75} At low silica loading, for dispersed silicon species on alumina, the Brønsted acidity is low.\cite{38,67,70} The building of a silica network is a prerequisite for generating BAS; however, these BAS are not strong enough to catalyze the cracking of cumene when compared to commercial ASAs.\cite{20} At higher silica loading the Brønsted acidity decreases\cite{20} because the access to the Si/Al interface is blocked.\cite{40}

Since the silica network builds on the alumina surface, it is strained due to the difference of angles and bond length between Si-O and Al-O bonds. This strained structure, differing from that of silica, associated to electronic charge effects and structural issues, might explain the appearance of BAS.\cite{20,38,67,69,75} According to Finocchio et al.,\cite{76} Si/Al$_2$O$_3$ materials are active in catalytic reactions performed at moderate to high temperatures because the silanols, contrary to the OH groups of alumina, do not immediately dehydroxylate upon temperature increase: the acidic OH groups remain present and active on the surface.
Chapter 3

Experimental

3.1 Description of the experimental set-ups

3.1.1 Chemical Liquid Deposition

The set-up consists in a reflux assembly (Figure 3.1): The support and the precursor are diluted in a solvent, put under magnetic stirring and heated to reflux of the solvent. Vapours are condensed by fresh water circulating in the condenser.

![Figure 3.1 Set up for Chemical Liquid Deposition (CLD).](image)

3.1.2 Chemical Vapour Deposition

The set-up is similar to that of Katada et al.[39] (Figure 3.2): A carrier gas, charged in vapours of the precursor, passes through the oxide bed maintained at a given temperature in a furnace. The system is equipped with two three-way valves enabling the carrier gas to go through two lines:

- line 1: The precursor reservoir is by-passed. This is dedicated to pretreatment steps, i.e. heating of the oxide bed under gas flow,
The gas flow passes through the precursor reservoir, which is heated at a given temperature in an oil bath in order to facilitate evaporation (by increasing the vapour pressure of the precursor). Consequently, all upstream lines are heated at a slightly higher temperature than the reservoir in order to avoid condensation of the precursor before reaching the oxide bed.

The furnace temperature is controlled by a thermocouple measuring the temperature inside the oxide bed. Effluent (non-reacted precursor, residual organic molecules stemming from the grafting of alkoxides, etc.) are condensed downstream.

![Figure 3.2 Set-up for Chemical Vapour Deposition (CVD).](image)

### 3.2 Synthesis of the materials

#### 3.2.1 Si/Al₃O₃

Si/Al₂O₃ samples were synthesized either by CLD or by CVD. Gamma-alumina (236 m²/g) – resulting from calcination of boehmite Pural SB3 (Sasol) at 540°C – and silicon – obtained from tetraethylorthosilicate (TEOS, Si(OCH₂CH₃)₄, Aldrich) were used as support and precursor, respectively. Anhydrous CLD on alumina consisted of vacuum pretreating the alumina at 40°C (10⁻² mbar) for 4 h to eliminate physisorbed water from the surface (referred as “normal” Si/Al₂O₃ pretreatment further in the document). Then the appropriate amount of precursor, TEOS, was added under inert atmosphere (argon) together with dry toluene (< 5 ppm water) so that the solvent volume (mL):alumina weight (g) ratio was 10. The mixture was stirred under reflux (110°C) for 5 h. The solvent, the excess precursor molecules which
did not react, and the organic molecules stemming from alkoxide decomposition, were eliminated by filtration and washing with dry toluene. Washing was repeated three times to ensure that no non-grafted TEOS molecules were remaining. The obtained impregnated gel was dried under a flow of argon, then the remaining solvent was eliminated by pumping under vacuum. The powder was kept in open air overnight, which allowed hydrolysis of the alkoxy groups grafted on the surface. The material was then dried at 100°C during 24 h and finally calcined in a muffle furnace at 550°C for 4 h under air. Repetition of the grafting following the same procedure was done on part of the resulting material.

In aqueous CLD a controlled amount of water was added after the pretreatment step and mixed for one hour. Thus, the water to precursor molar ratio was precisely known: 4 and 12 for Si/Al₂O₃; 1 and 3 for Al/SiO₂ (vide infra).

CVD samples were prepared following a method close to that previously described by Katada et al.³⁹ Nitrogen or air (4 L.h⁻¹ g⁻¹ support⁻¹) was passed through a saturator containing TEOS and maintained at 70°C. All lines downstream of the TEOS saturator were insulated and heated to avoid deposition of TEOS. The Si-containing flow then reached a quartz reactor containing the γ-alumina support heated between 200 and 400°C, i.e. above the TEOS boiling point (166-169°C). Prior to grafting, the alumina support was pretreated under an argon flow at 250°C to eliminate physisorbed water. Similar to the CLD procedure, samples were finally exposed to air moisture overnight and calcined at 550°C for 4 h under air flow. The amount of precursor during grafting depended on the vapour pressure of TEOS – at the saturator temperature, the flow rate of the carrier argon and the length of grafting.

### 3.2.2 Al/SiO₂

The preparation of Al/SiO₂ samples in liquid media followed the same procedure as for Si/Al₂O₃ in case of both anhydrous and aqueous grafting, but using silica ground into powder (silica gel beads from Grace, 552 m²g⁻¹) and aluminium isopropoxide (Al(OiPr)₃) as support and precursor, respectively. Silica was pretreated under vacuum (10⁻² mbar) at 30°C (referred to as “normal” Al/SiO₂ pretreatment further in the document). To evaluate the role of the support hydroxyl density, the silica support was either rehydroxylated by refluxing the silica powder in water or partially dehydroxylated by increasing the pretreatment temperature to 110°C.
3.2.3. List of samples

The main characteristics of the materials used in this thesis and their synthesis conditions are given in Table 3.1. The temperature of grafting, the water content, and the amount of the alkoxide precursor were adapted to obtain materials displaying a wide range of compositions and surface structures. Further details on the preparation of each sample are given in the chapters.

### Table 3.1 Synthesis conditions and main characteristics of Si/Al₂O₃, Al/SiO₂, and other amorphous aluminosilicates and zeolites evaluated in this thesis.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample nature</th>
<th>Sample name</th>
<th>wt.% Al₂O₃</th>
<th>wt.% SiO₂</th>
<th>S₅₅₀ (m²/g)</th>
<th>Synthesis technique</th>
<th>Pretreatment conditions (temperature, mode)</th>
<th>Synthesis conditions (temperature, media)</th>
<th>Amount of precursor introduced (mmol g⁻¹ precursor)</th>
<th>Chapters</th>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>Si/Al₂O₃</td>
<td>SA(7/anh)</td>
<td>92.7</td>
<td>7.3</td>
<td>200</td>
<td>CLD anhydrous</td>
<td>40°C, vacuum</td>
<td>110°C, toluene from 1.4 to 12.9</td>
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<td>4-8</td>
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<td>12.2</td>
<td>180</td>
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<td>110°C, toluene</td>
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<td>17.1</td>
<td>160</td>
<td>CLD anhydrous (x3)</td>
<td>40°C, vacuum</td>
<td>110°C, toluene</td>
<td>40.9</td>
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<td>SA(17/4eqW)</td>
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<td>16.5</td>
<td>175</td>
<td>CLD aqueous (4 eq. water)</td>
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<td>175</td>
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<td>110°C, toluene</td>
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<td>4</td>
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<td>165</td>
<td>CVD</td>
<td>250°C, air flow</td>
<td>250°C, air</td>
<td>2.9, 5.8</td>
<td>4, 5, 7</td>
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<tr>
<td>(9)</td>
<td>Al/SiO₂</td>
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<td>19.4</td>
<td>165</td>
<td>CVD</td>
<td>250°C, air flow</td>
<td>250°C, air</td>
<td>6.7, 7.3</td>
<td>4, 5</td>
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<td>14.8</td>
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<td>300°C, air</td>
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<td>CVD</td>
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<td>4, 5</td>
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<td>400°C, N₂</td>
<td>7.9</td>
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<tr>
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<td>Pure silica</td>
<td>0.0</td>
<td>100.0</td>
<td>550</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(16)</td>
<td>Al/SiO₂</td>
<td>AS(3/ah)</td>
<td>2.8</td>
<td>97.2</td>
<td>505</td>
<td>CLD anhydrous</td>
<td>30°C, vacuum</td>
<td>110°C, toluene</td>
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<td>4, 6</td>
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<tr>
<td>(17)</td>
<td>Al/SiO₂</td>
<td>AS(6/ah)</td>
<td>5.7</td>
<td>94.3</td>
<td>460</td>
<td>CLD anhydrous</td>
<td>30°C, vacuum</td>
<td>110°C, toluene</td>
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</tr>
<tr>
<td>(18)</td>
<td>Al/SiO₂</td>
<td>AS(10/ah)</td>
<td>10.3</td>
<td>89.7</td>
<td>430</td>
<td>CLD anhydrous</td>
<td>30°C, vacuum</td>
<td>110°C, toluene</td>
<td>2.0</td>
<td>4, 6</td>
</tr>
<tr>
<td>(19)</td>
<td>Al/SiO₂</td>
<td>AS(15/ah)</td>
<td>15.0</td>
<td>85.0</td>
<td>400</td>
<td>CLD anhydrous</td>
<td>30°C, vacuum</td>
<td>110°C, toluene</td>
<td>3.7, 6.1</td>
<td>4, 6, 8</td>
</tr>
<tr>
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<td>Al/SiO₂</td>
<td>AS(25/ah)</td>
<td>24.8</td>
<td>75.2</td>
<td>330</td>
<td>CLD anhydrous</td>
<td>30°C, vacuum</td>
<td>110°C, toluene</td>
<td>6.4</td>
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</tr>
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<td>AS(34/ah)</td>
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<td>66.5</td>
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<td>30°C, vacuum</td>
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<td>(22)</td>
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<td>AS(35/anh)</td>
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<td>65.1</td>
<td>185</td>
<td>CLD anhydrous</td>
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<td>AS(16/1eqW)</td>
<td>16.1</td>
<td>83.9</td>
<td>420</td>
<td>CLD aqueous (1 eq. water)</td>
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<td>110°C, toluene</td>
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<td>420</td>
<td>CLD aqueous (3 eq. water)</td>
<td>30°C, vacuum</td>
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<td>3.8</td>
<td>4, 6</td>
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<td>CLD anhydrous</td>
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<td>Al/Re/O₂</td>
<td>SA(13/rehyd)</td>
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<td>87.4</td>
<td>340</td>
<td>CLD anhydrous</td>
<td>30°C, vacuum</td>
<td>110°C, toluene from 3.8 to 6.4</td>
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<td>SA(12/steam)</td>
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<td>87.8</td>
<td>170</td>
<td>Steaming of (3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8</td>
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<td>Al/Re/O₂</td>
<td>SA(15/steam)</td>
<td>15.0</td>
<td>85.0</td>
<td>170</td>
<td>Steaming of (19)</td>
<td>-</td>
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<td>SA(cogel)</td>
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<td>20.0</td>
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<td>ASA(comm.)</td>
<td>70.0</td>
<td>30.0</td>
<td>315</td>
<td>Impregnation of alumina with silica gel</td>
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<td>H-USY</td>
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<td>94.6</td>
<td>780</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7</td>
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</tbody>
</table>

[a] Bold values refer to the sample for which the other characteristics are detailed.
3.3 Characterization

This paragraph describes the characterization methods that are common to several chapters. Characterization techniques which are specific to a given chapter are described in the chapter itself.

3.3.1 Texture

Textural features, such as pore volume, average pore diameter and surface area, were determined by nitrogen adsorption performed on a Micrometrics ASAP 2420 apparatus. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was determined thanks to the BJH (Barrett-Joyner-Halenda) method applied to the N\textsubscript{2} desorption branch of the isotherm. The pore volume was determined at the maximum relative pressure of nitrogen. The density of grafted atoms (nm\textsuperscript{-2}) was calculated with respect to the surface area of the initial support (silica or alumina).

3.3.2 Composition

X-ray fluorescence was employed to determine the elemental composition, which is expressed in weight % of grafted Al\textsubscript{2}O\textsubscript{3} respectively SiO\textsubscript{2} for Al/SiO\textsubscript{2} and Si/Al\textsubscript{2}O\textsubscript{3}.

3.3.3 Hydroxyl density

Hydroxyl density of the parent supports (silica and alumina) was obtained by means of thermogravimetric analysis (TGA). Samples were heated from room temperature until 1000°C at a rate of 10°C.min\textsuperscript{-1}. Weight loss after dehydration (i.e. removal of adsorbed water) was ascribed to dehydroxylation, and the surface hydroxyl density (expressed in OH.nm\textsuperscript{-2}) was calculated basing on the BET surface area.

3.3.4 CO adsorption followed by infrared spectroscopy (IR)

IR spectra were recorded by a Nexus Fourier transform instrument. Samples (self-supported pellets of compressed powder) were pretreated \textit{in situ} under vacuum (\approx 10\textsuperscript{-5} mbar) for 10 h at 450°C (heating rate of 5°C.min\textsuperscript{-1}) including a plateau at 150°C for 1 h. CO adsorption was achieved by adding increasing amounts of CO to the sample at liquid nitrogen temperature.
3.3.5 \textit{m}-xylene isomerization

The \textit{m}-xylene isomerization test consisted of reacting a catalyst bed of 0.5 g with gaseous \textit{m}-xylene (0.6 cm$^3$ h$^{-1}$). Catalysts were first preheated in an air flow at 350°C, followed by xylene conversion at 350°C in a flow of nitrogen. Analysis of the products was performed by on-line gas chromatography by means of a Hewlett Packard 6850 apparatus, equipped with a flame ionization detector (FID) and an FFAP column. \textit{m}-xylene was isomerized to \textit{p}- and \textit{o}-xylene or disproportionated to toluene and isomers of trimethylbenzene. In the latter case, the reaction of trimethylbenzene with toluene or xylene may also lead to the formation of isomers of xylene by a bimolecular mechanism (Figure 3.3). The rate of \textit{m}-xylene conversion measured after the first 10 min of reaction was given by:

$$\text{Rate molecule.h}^{-1}\text{nm}^{-2} = \frac{\sum_{i} A_i \times \text{number of carbon}}{\text{number of carbon}_i} \times \frac{\text{flow rate (cm}^3\text{h}^{-1}) \times \text{density}_{\text{m-xylene}} (\text{g cm}^{-3})}{\text{M}_{\text{m-xylene}} (\text{g mol}^{-1}) \times \text{M}_{\text{catalyst}} (\text{g})} \times \frac{N_A}{S_{\text{BET}} (\text{nm}^2\text{g}^{-1})} \quad (3.1)$$

where $A_i$ is the area of the GC peak of species $i$ (\textit{i} = toluene, \textit{p}-xylene, \textit{o}-xylene, trimethylbenzenes), $N_A$ the Avogadro number (6.02×10$^{23}$ mol$^{-1}$), and $S_{\text{BET}}$ the surface area of the catalyst.

![Figure 3.3 Scheme for \textit{m}-xylene isomerization](image)

3.3.6 Ethanol adsorption and desorption followed by thermogravimetry (TGA)

TGA experiments were carried out with a Mettler Toledo apparatus (TGA/SDTA851e) according to the procedure of Kwak et al.\cite{18} Before the measurements, the samples were pretreated in a flow of helium (60 mL.min$^{-1}$) at 200 and 500°C respectively, 10°C.min$^{-1}$, for 2 h to eliminate physisorbed water from the surface and/or to activate sites.
Samples were cooled to room temperature. Helium was passed through a saturator containing ethanol at room temperature for approx. 30 min, and the increase in the weight of the sample was determined. Weakly bonded ethanol molecules were evacuated by means of a helium purge at room temperature for 1 h. Temperature-programmed desorption of ethanol (TPD) was performed at a rate of 10°C.min⁻¹ until 400°C. The intensity of the desorption features was measured by calculation of the first derivative of weight loss during TPD with respect to temperature, and normalized by the surface area of the sample. The release of ethanol and ethylene was confirmed by mass spectrometry. The amount of dehydrated ethanol determined from the TGA results was calculated as follows:

\[
\text{Ethanol dehydrated } \text{nm}^{-2} = \frac{\text{Ethanol retained after purge (nm}^{-2}) \times \frac{A_{\text{peak ethylene}}}{A_{\text{peak ethylene}} + A_{\text{peak ethanol}}}}{A_{\text{peak ethylene}} + A_{\text{peak ethanol}}}
\]  

(3.2)

where \(A_{\text{peak } i}\) is the area of the peak corresponding to the desorption of species \(i\) when calculating the derivative of the weight loss of ethanol during TPD.
Chapter 4

Synthesis of amorphous aluminosilicates by grafting: tuning the building and final structure of the deposit by selecting the appropriate synthesis conditions

4.1 Introduction

The synthesis method of ASAs impacts the degree of intimacy of aluminium and silicon atoms, and their general repartition throughout the particles. The high level of structural heterogeneity in ASAs has prevented unequivocal identification of the surface species that are responsible for acidity. To rationalize this, ASAs can be synthesized in a more controlled way, e.g. by grafting. Either silicon or aluminium containing species (alkoxides) are deposited on the complementary oxide, to prepare Si/Al$_2$O$_3$ or Al/SiO$_2$ materials, respectively.

Aluminium deposition on silica proceeds by anchoring the aluminium species onto the hydroxyl groups of silica. Thanks to potentiometric and TGA measurements, Iengo et al. identified that grafted species can be either preferentially monodentately – at low Al(OR)$_3$ concentration – or bidentately bound to the surface. This is a first indication of the role played by synthesis parameters on the nature of the grafted deposit. Similarly, the temperature pretreatment, the media in which grafting takes place, and, especially, the water content all impact the support hydroxyl density, leading to different aluminium incorporation into the silica network. Yet, generally limited information is available regarding the size and shape of the aluminic deposit and the degree of coverage of the silica surface. Very similar conclusions can be drawn for silicon deposition on alumina, such as the importance of the initial amount of precursor molecules and the consumption of hydroxyl groups of the alumina support as observed in IR spectra of the grafted samples.
The temperature at which the grafting takes place, as showed by the differences between liquid-phase (CLD) and gas-phase (CVD) grafting, affects the building of the deposit and the reactivity of the alumina support anchoring sites. Benzonitrile ammonia titration, BAT, is based on the specific adsorption and quantification of benzonitrile on aluminium sites and allows one to determine the ratio of remaining bare alumina surface.

Solid-state magic-angle spinning (MAS) NMR of $^{27}$Al and $^{29}$Si nuclei is an efficient tool to investigate the deposit structure of, respectively, Al/SiO$_2$ and Si/Al$_2$O$_3$ materials. Hensen et al., for example, ascribed four-, five- and six-coordinated aluminium atoms as detected by $^{27}$Al NMR to certain positions within the aluminium containing deposit. While six-coordinated aluminium atoms belong to a pure aluminium oxide phase, four-coordinated and five-coordinated species would be located, respectively, in a mixed silica-alumina phase and at the interface between this mixed phase and the pure aluminic domains. Conversely, Goldbourt et al. considered the alumina deposit to display the same ratio of tetrahedral to octahedral aluminium atoms of 1/3 as in transition aluminas. If a higher ratio is found, the excess Al(IV) atoms are supposedly inserted into the silica matrix in a similar way as in zeolites. Due to the rareness of the $^{29}$Si isotope, $^{29}$Si NMR spectra of Si/Al$_2$O$_3$ often display low signal-to-noise ratios which render interpretation difficult. CP (cross-polarization) NMR allows enhancement of the signal by polarization of the nuclei by neighbouring protons. Sato et al. noticed that the loading of alumina with silicon atoms at 240°C, using CVD, progressively leads to the accumulation of up to three layers of silica, by successive completion of silica monolayers. Such assertions are based on the characteristic NMR chemical shifts of the Si/Al$_2$O$_3$ materials, ranging between -70 (isolated SiO$_4$ species) and -110 ppm (SiO$_4$ in siliceous environment). There is a clear impact of the grafting temperature, but opinions differ regarding the formation process of the deposit. Precursor molecules can be randomly grafted onto the alumina surface or previously deposited species, rather than first forming a uniform monolayer.

This chapter aims at describing the parameters governing the deposition of alumina, respectively silica species on silica and alumina to obtain aluminosilicates as reference materials for ASAs. To cover a wide range of elemental composition, both Al/SiO$_2$ and Si/Al$_2$O$_3$ grafting techniques have been used. To modify the deposit structure, water has been added to the reaction mixture, to embody different hydrolysis/condensation states of the precursors and the temperature has been varied; CLD/CVD techniques have been employed to assess the role of the grafting technique. Comprehension of the phenomena occurring on the surface during grafting allows one to understand the processes giving rise to a given deposit.
4.2 Experimental

4.2.1 Nuclear magnetic resonance (NMR)

$^{27}$Al and $^{29}$Si MAS NMR spectra were recorded using a rotation speed of 12 kHz on a Bruker Avance 400 spectrometer equipped with a 4-mm probe head. $^{29}$Si CP-MAS experiments were carried out with a rotation speed of 10 kHz. 2D 3QMAS $^{27}$Al experiments were performed on Al/SiO$_2$ samples using a 700 MHz Bruker spectrometer. Samples were put in 2.5-mm rotors and spun at 20 kHz.

4.2.2 Transmission electron microscopy (TEM)

TEM images were taken on a Tecnai F30 ST (FEI, FEG, 300 kV).

4.2.3 Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS measurements were performed with an IONTOF V spectrometer (IONTOF GmbH, Münster, Germany). The samples were bombarded with a pulsed Bi$_3^+$ ion beam (30 keV). The analyzed area used in this work was a square of 500 x 500 µm and the data acquisition time was 60 s. Charge effects were compensated by means of an interlaced pulsed electron flood gun ($E_k = 20$ eV). With these parameters, the primary ion dose density was lower than $10^{11}$ Bi$_3^+$ cm$^{-2}$. The powders were supported by pressing them onto the adhesive side of “Post-it®” pieces.

4.3 Results

4.3.1 Surface reactivity

4.3.1.1 Al/SiO$_2$

Single CLD grafting of aluminium on silica after pretreatment in vacuum at 30°C (entry 19) or 110°C (entry 25), yields 3.8 and 3.1 Al.nm$^{-2}$ at maximum, respectively (Figure 4.1.a). This indicates that the hydroxyl density of the support is a limiting factor for grafting of species under these conditions. Grafting after rehydroxylation (entry 27) leads to 3.8 Al.nm$^{-2}$ at maximum, the same as after a pretreatment at 30°C. Thus, new hydroxyl groups created upon rehydroxylation of silica (4.0 vs. 3.3 OH.nm$^{-2}$) do not allow to graft a higher
amount of aluminium. Repetition of the grafting in anhydrous conditions allows the deposition of new aluminium species (entries 20-22).

Precursor molecules used in this study are alkoxides, which hydrolyze and/or condensate in the presence of water. In the case of Al(OiPr)₃, three water molecules are theoretically required to fully hydrolyze one precursor molecule. Yet, if only one out of the three alkoxy groups of the precursor molecule is hydrolyzed, it can still condensate. Adding one respectively three water eq. per precursor molecule (which amount was the same as for entry 19) yielded the highest possible amount of precursor molecules that can be grafted in one step in anhydrous CLD (entries 23 and 24, respectively).

![Figure 4.1](image)

**Figure 4.1** Amount of atoms initially introduced vs. surface density of grafted atoms for Al/SiO₂ (a) and Si/Al₂O₃ (b). The maximum grafting yield (---) corresponds to the full grafting of all precursor molecules initially present in the reaction mixture. Numbers in brackets correspond to entries in Table 3.1.

4.3.1.2 Si/Al₂O₃

Desorption of physisorbed water requires a higher temperature than on silica, but the hydroxyl density on the alumina surface still exceeds that of silica (10.5 vs. 3.3 OH.nm⁻²). Yet, saturation of deposition in anhydrous Si/Al₂O₃ CLD occurs at 3.5 Si.nm⁻² (Figure 4.1.b, entry 2), which is quite close to Al/SiO₂ which saturates at 3.8 Al.nm⁻² (Figure 4.1.a). Similarly to what was observed for Al/SiO₂ grafting, repetition of the grafting steps (entries 3 and 4) yields higher coverages, up to 9.0 Si.nm⁻².

During aqueous CLD with four (entry 5) and twelve (entry 6) water equivalent per TEOS molecule, all the precursor molecules are grafted, whatever their initial amount. Full or nearly full grafting of TEOS can also be achieved under CVD conditions. Similar to CLD, repetition of the grafting steps is possible (Figure 4.1.b-Figure 4.2). Figure 4.2 shows that above 200°C, a grafting yield between 75 and 90% is achieved (entries 8-14). When the
amount of introduced TEOS exceeds 4 mmol per gram of alumina, the grafting yield decreases.

![Graph](image)

**Figure 4.2.** Comparison between Si/Al₂O₃ CLD and CVD techniques on the yield after one grafting step. Numbers in brackets correspond to entries in Table 3.1.

### 4.3.2 Texture

Irrespective of grafting, all samples show type IV N₂ adsorption/desorption isotherms (Figure 4.3), meaning that the mesoporosity of the initial silica and alumina supports is retained. Figure 4.4 shows that the pore volume (Vp) continuously decreases upon grafting of species.

![Graph](image)

**Figure 4.3** N₂ adsorption/desorption isotherms: (a) Al/SiO₂ grafted samples; (b) Si/Al₂O₃ grafted samples. Numbers in brackets correspond to entries in Table 3.1.
Similarly, surface areas ($S_{BET}$) (Figure 4.5) and mean pore diameters ($D_p$) (Figure 4.6) decrease, which is line with previous observations in the literature. $^{[3,4,7,8,3]}$ Figure 4.7 shows the evolution the mean pore diameter upon grafting. For both Al/SiO$_2$ and Si/Al$_2$O$_3$, the pore diameter decreases upon grafting. This is due to the growth of the deposit, perpendicular to the channel surface. The rehydroxylation of silica (Figure 4.7.a, entry 26) caused an increase of its pore diameter.

Figure 4.5 Evolution of the surface area ($S_{BET}$): (a) Al/SiO$_2$ grafted samples; (b) Si/Al$_2$O$_3$ grafted samples. Numbers in brackets correspond to entries in Table 3.1.
The role of water is also noteworthy: in the case of Al/SiO$_2$ grafting, the more water is added during synthesis, the lower the pore volume loss (Figure 4.4.a). It is likely that the interparticle arrangement of silica particles changes in these conditions. Thus, the Vp loss normally ascribed to grafting is compensated and larger mesopores are created (Figure 4.6.b).

In fact, part of the surface area and pore volume loss is due to the weight gain associated to the grafting of non-porous species on porous oxides. It mathematically causes the decrease of the surface area per weight unit. Calculation of the theoretical surface area allows one to determine whether the surface area loss can only be ascribed to the weight gain effect:

$$S_{\text{BET}}^{\text{theoretical}} = \frac{S_{\text{BET}}^{\text{oxide}}}{1 + \frac{X_{\text{deposited}}}{100 - X_{\text{deposited}}}}$$  \hspace{1cm} (4.1)

where X is the weight percentage of deposited material (SiO$_2$ or Al$_2$O$_3$).

In that case, theoretical $S_{\text{BET}}$ equals the experimental value. Otherwise, it means that access to part of the pores has been blocked ($S_{\text{BET}}$ th. $>$ $S_{\text{BET}}$ exp.) or that a new porosity has been created ($S_{\text{BET}}$ th. $<$ $S_{\text{BET}}$ exp.). Figure 4.8 shows the results of the calculation. All of our materials (Al/SiO$_2$ and Si/Al$_2$O$_3$) show theoretical values higher than experimental ones. This indicates that grafting does not only leads to the coating of the walls of the pore channels, but also systematically leads to the filling or blocking of part of the pores, probably the smallest ones.
Figure 4.8 Evolution of the difference between theoretical (based on the weight gain due to the deposition of non-porous species) and experimental values of the surface area: (a) Al/SiO₂ grafted samples; (b) Si/Al₂O₃ grafted samples. Numbers in brackets correspond to entries in Table 3.1.

4.3.3 Structure of the deposit

4.3.3.1 Al/SiO₂

²⁹Si MAS NMR of silica (Figure 4.9.a) shows three main peaks at around -90, -100 and -110 ppm respectively associated to Q², Q³, and Q⁴ species.⁸⁴ Possible assignment of resonances in ²⁹Si NMR to the environment of silicon atoms is summarized in Table 4.1. Grafting of aluminium species causes, already at the lowest loading (AS(3/an), entry 16), a decrease of the relative intensity of the -90 ppm peak and a downfield shift of the -100 ppm peak (indicated by red arrows on Figure 4.9.b). Such a 4-6 ppm downfield shift can be ascribed to the grafting of an aluminium atom to the silica surface by consumption of a silanol group:⁷⁰,⁸⁵

Si(3Si, 1H) → Si(3Si, 1Al)

The decrease of the -90 ppm peak results from the grafting of vicinal silanol groups (Table 4.1):

Si(2Si, 2H) → Si(2Si, 1Al, 1H) → Si(2Si, 2Al)

Yet in that case the resonances of the resulting species overlap strongly with those of other species. Another striking feature is the appearance of a broad signal between -78 and -90 ppm after loading an excess of 10.3% Al₂O₃ (indicated by red arrows on Figure 4.9.d-g). This signal can result from the appearance of silanol groups located in an aluminous environment (Table 4.1) such as:

Si(2Al, 2H) or Si(3Al, 1H) or Si(1Si, 1Al, 2H)
Finally, the absolute signal intensity progressively decreases with the aluminium content, which is consistent with the progressive coverage of the silica surface with aluminium species.

**Table 4.1** Assignment of the resonances in $^{29}$Si NMR spectra.$^{[70,84,85]}$

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Possible environments of the silicon atoms (most probable for Al/SiO$_2$)</th>
<th>Possible environments of the silicon atoms (most probable for Si/Al$_2$O$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-75</td>
<td>Si(1Al, 3H)</td>
<td>Si(1Al, 3H)</td>
</tr>
<tr>
<td>-80</td>
<td>Si(1Si, 3H) (Q1)</td>
<td>Si(2Al, 2H)</td>
</tr>
<tr>
<td>-85</td>
<td>Si(1Si, 1Al, 2H)</td>
<td>Si(3Al, 1H) or Si(1Si, 1Al, 2H)</td>
</tr>
<tr>
<td>-90</td>
<td>Si(2Si, 2H) (Q2)</td>
<td>Si(2Si, 2H) (Q2) or Si(1Si, 2Al, 1H)</td>
</tr>
<tr>
<td>-95</td>
<td>Si(2Si, 1Al, 1H)</td>
<td>Si(1Si, 3Al) or Si(2Si, 1Al, 1H)</td>
</tr>
<tr>
<td>-100</td>
<td>Si(3Si, 1H) (Q3) or Si(2Si, 2Al)</td>
<td>Si(3Si, 1H) (Q3) or Si(2Si, 2Al)</td>
</tr>
<tr>
<td>-105</td>
<td>Si(3Si, 1Al)</td>
<td>Si(3Si, 1Al)</td>
</tr>
<tr>
<td>-110</td>
<td>Si(4Si) (Q4)</td>
<td>Si(4Si) (Q4)</td>
</tr>
</tbody>
</table>

**Figure 4.9** $^{29}$Si MAS NMR spectra of Al/SiO$_2$ samples prepared by anhydrous CLD: (a) pure silica; (b) AS(3/anh) (c) AS(6/anh); (d) AS(10/anh); (e) AS(15/anh); (f) AS(25/anh); (g) AS(35/anh). Numbers in brackets correspond to entries in Table 3.1.
Al MAS NMR spectra of Al/SiO\textsubscript{2} samples (Figure 4.10) display three main peaks corresponding to three different aluminium coordinations. Peaks located at around 0 and 60 ppm are ascribed to six- and four-coordinated aluminium, respectively. The resonance at 30 ppm (more pronounced for highest aluminium loadings (Figure 4.10.e-f)) corresponds to five-coordinated aluminium.\textsuperscript{[44]} The pure alumina spectrum only displays the peaks corresponding to four- and six-coordinated aluminium (Figure 4.10.g). Loadings between 2.8\% Al\textsubscript{2}O\textsubscript{3} (0.6 Al.nm\textsuperscript{-2}, entry 16) and 15.0\% Al\textsubscript{2}O\textsubscript{3} (3.8 Al.nm\textsuperscript{-2}, entry 19) (Figure 4.10.a-d), i.e. for materials derived from one grafting step, yield spectra that are dominated by the peaks of four-coordinated and six-coordinated aluminium. AS(3/anh) (entry 16) shows a spectrum similar to that of γ-alumina (entry 1), except for the position of the four-coordinated aluminium. At higher loading (entries 17-19), the four-coordinated/six-coordinated aluminium ratio increases. As the hydroxyl density on silica is a limiting factor for grafting, these aluminium species might essentially be isolated – certainly for AS(3/anh). In spectra of samples with 5.7\% Al\textsubscript{2}O\textsubscript{3} and higher loadings (entries 17-19), a small contribution of five-coordinated aluminium is visible as the signal does not go back to the baseline between the two main peaks. A distinct five-coordinated aluminium peak clearly shows up only for samples resulting from two successive graftings (entries 20 and 22). For these samples, the structure of the deposit clearly differs from that of γ-Al\textsubscript{2}O\textsubscript{3}. The presence of such five-coordinated species could then be related to the deposition of aluminium atoms over the first layer of aluminium species, connecting isolated species, and to the geometrical constraints favouring the stabilization of this five-coordinated aluminium species. The chemical shift of the four-coordinated aluminium peak varies with the aluminium loading: The more aluminium atoms are deposited on the surface, the higher is the chemical shift (indicated by red arrows on Figure 4.10). The position of the four-coordinated aluminium peak then indicates whether tetrahedral aluminium atoms are in an aluminous (≈ 65 ppm) respectively siliceous (≈ 50 ppm) environment.\textsuperscript{[86,87]} At a loading below 10\% Al\textsubscript{2}O\textsubscript{3}, the four-coordinated aluminium peak is dominantly in a siliceous environment.
Figure 4.10 $^{27}$Al MAS NMR spectra of Al/SiO$_2$ samples prepared by anhydrous CLD (1 step): (a) AS(3/anh) (b) AS(6/anh); (c) AS(10/anh); (d) AS(15/anh); (e) AS(25/anh); (f) AS(35/anh); (g) pure $\gamma$-alumina. Numbers in brackets correspond to entries in Table 3.1.

Figure 4.11 compares $^{27}$Al and $^{29}$Si MAS NMR spectra of Al/SiO$_2$ samples ($\approx$ 15-17% Al$_2$O$_3$) obtained by anhydrous (AS(15/anh), entry 19) and aqueous (AS(17/3eqW), entry 24) CLD. The $^{29}$Si NMR spectra are quite similar (top panel). Yet, water during synthesis leads to slightly less silicon atoms in an aluminous environment, indicated by lower intensity of the
peak at -90 ppm (as evidenced by a red arrow in Figure 4.11, upper panel). The $^{27}$Al NMR spectra in contrast point out to dissimilar aluminium coordinations. Water favours the formation of hexa-coordinated aluminium atoms rather than tetra- and penta-coordinated ones.

![Figure 4.11](image.png)

Figure 4.11 $^{29}$Si MAS NMR (upper panel) and $^{27}$Al MAS NMR (lower panel) of Al/SiO$_2$ samples ($\approx$ 15-17\% Al$_2$O$_3$) prepared by CLD (1 step): (a) AS(17/3eqW); (b) AS(15/anh). Numbers in brackets correspond to entries in Table 3.1.

The 2D 3QMAS NMR spectra of AS(17/3eqW) (Figure 4.12) shows that the broad four-coordinated aluminium band originates from two different environments at around $\approx$ 65 ppm and $\approx$ 55 ppm in reflecting aluminium in aluminous, respectively siliceous environment.
Surface structure of grafted ASAs

Figure 4.12 $^{27}$Al 2D 3QMAS NMR of AS(17/3eqW) (entry 24 in Table 3.1).

The electron micrographs of samples up to 15% Al$_2$O$_3$ loading displays the typical features of silica (Figure 4.13.a-b), i.e. small spheres of about 10 nm. A homogeneous aluminium and silicon composition of the grafted sample is also confirmed by EDXS (energy dispersive X-ray spectroscopy). Grafting in the presence of water (Figure 4.13.c) leads to inhomogeneously dispersed alumina platelets.

Figure 4.13 TEM micrographs: (a) pure silica (entry 15 in Table 3.1); (b) AS(15/anh) (entry 19); (c) AS(17/3eqW) (entry 24).

In TOF-SIMS, ionic species are detached from the outermost surface of the materials under the effect of Bi$_3^+$ bombardment and then analyzed by mass spectrometry. To allow
comparisons between the different samples, the relative contribution of fragments of interest is calculated. For example, aluminium-containing anions are inspected in the case of Al/SiO$_2$ and their intensity is normalized by the total count of anions. The presence of ions containing more than one atom of aluminium evidences the presence of Al-O-Al bonds on the surface of the materials, either in the form of dimeric, oligomeric, polymer or crystalline AlO$_x$ species. The data reported in Figure 4.14 correspond to the relative contribution to the total intensity (in %) of fragments having at least two aluminium atoms (poly-Al), which are more representative of the deposit than the isolated monomers (mono-Al). These data provide qualitative insight into the distribution of species at the surface, as it can be seen as a measure of the degree of condensation of alumina surface species. The percentages indicated are the average of the values obtained after repeating the test three times. Figure 4.14 evidences a higher ratio of aluminium species on the surface of Al/SiO$_2$ when grafting is performed in the presence of water. In anhydrous conditions (entries 17-19), the more aluminium species are deposited, the more they are found under a polymeric form: The part of poly-Al containing at least seven aluminium atoms among poly-Al and mono-Al increases from 0.7% (entry 16) to 1.7% (entry 19) (not shown here).

**Figure 4.14** ToF-SIMS of Al/SiO$_2$ samples: percentage of fragments containing at least two aluminium atoms (poly-Al) among the total intensity of all fragments. Numbers in brackets correspond to entries in Table 3.1.

In agreement with NMR and TEM, ToF-SIMS results indicate that at a given aluminium loading, the presence of water during synthesis (AS(17/3eqW)) favours the condensation of aluminium species. These alumina platelets are thus the first ones to be
removed from the surface during ion bombardment in ToF-SIMS experiments. Dry deposition leads to a regular deposition throughout the silica surface.

4.3.3.2 Si/Al₂O₃

Figure 4.15 shows the $^{29}$Si CPMAS spectra of all Si/Al₂O₃ materials prepared by anhydrous CLD. CP-MAS had to be used as MAS spectra showed poor resolution, due to the low amount of silicon species.

![Figure 4.15](image)

**Figure 4.15** $^{29}$Si CPMAS NMR spectra of Si/Al₂O₃ samples prepared by anhydrous CLD: (a) SA(7/anh); (b) SA(12/anh); (c) SA(17/anh); (d) pure silica. Numbers in brackets correspond to entries in Table 3.1.

At low silica loading (Figure 4.15.a), a broad peak is located between -70 and -100 ppm, centred at around -85 ppm. This corresponds to monomeric and dimeric silicon species monodentately, bidentately, and tridentately attached to the alumina surface (Table 4.1). At a higher silica loading (12.2% SiO₂), (Figure 4.15.b), the peak is shifted high-field (as indicated
Chapter 4

by red arrows) and is centred at around -90 ppm. This coincides with the increase of dimeric silicon species. At 17.1% SiO₂, the peak is centred at around -95 ppm and extends until -110 ppm (Figure 4.15.c).

This indicates the presence of oligomers of silica. Yet, even at this high silicon loading, the structure of the deposit differs from that of pure silica (Figure 4.15.d). Even though CPMAS minimizes the amount of Q⁴ species because their signal is less enhanced than that of other groups, little or no signal accounting for such species is visible on the spectra.

27Al MAS NMR spectra of Si/Al₂O₃ prepared by anhydrous CLD show only minor differences with increasing the silicon loading (not shown here). Surface effects due to silicon deposition are hidden by the signal resulting from the alumina bulk. The main difference is the relative amount of six-coordinated aluminium atoms, which slightly decreases as soon as silicon atoms are deposited on the alumina surface.

Figure 4.16 illustrates the role of water and temperature on the structure of the silicon deposit. Figure 4.16.b shows that the spectrum of SA(17/4eqW) is similar to that of SA(17/anh) (Figure 4.16.a). This is indicative of the same nature and distribution of silicon species on the surface. A higher amount of water during synthesis (SA(17/12eqW), Figure 4.16.c), leads to a very different spectrum, thus a different distribution of species. The peak is wider and can be divided into two domains. One between -70 and -95 ppm corresponds to species bound to the alumina surface, and is similar to what was observed in Figure 4.15.b (SA(12/anh)). The other between -95 and -110 ppm corresponds to a silica-like deposit consisting of multilayers of silica (Si(4Si), -110 ppm).

The spectrum of SA(17/CVD250) (Figure 4.16.d) shows a markedly decreased peak around -85 and -90 ppm compared to that of SA(17/anh), because it has less monomeric and dimeric species. The signal between -100 and -110 ppm is more intense and indicates a higher amount of oligomeric silica species, and even multilayers of silica. Thus, CVD at 250°C leads to less monomeric and dimeric silicon species, and more oligomeric species than CLD at 110°C. As for SA(17/CVD250), the spectrum of SA(17/CVD400) (Figure 4.16.e) shows a lower amount of monomeric and dimeric species (at around -90 ppm) than the SA(17/anh). The part of oligomeric silicon species, yet, is similar. A common feature of samples prepared at high temperature is thus the lower amount of mono- and dimeric species compared to a grafting in CLD conditions (110°C).
Figure 4.16 $^{29}$Si CPMAS NMR spectra of Si/Al$_2$O$_3$ samples ($\approx$ 17% SiO$_2$): (a) SA(17/anh); (b) SA(17/4eqW); (c) SA(17/12eqW); (d) SA(17/CVD250); (e) SA(17CVD400). Numbers in brackets correspond to entries in Table 3.1.

As for samples prepared by anhydrous CLD, the $^{27}$Al MAS NMR of the samples prepared by other techniques are very similar, except for a small decrease of the six-coordinated aluminium peak compared to pure alumina (not shown here).

Figure 4.17 shows the TEM micrographs of pure alumina (a) and Si/Al$_2$O$_3$ samples prepared by anhydrous (SA(17/anh)) and aqueous (SA(17/12eqW)) CLD, respectively (Figure 4.17.b and c). Figure 4.17.a shows the typical platelet structure of alumina particles. Figure 4.17.b and Figure 4.17.c show that this structure is hidden by the deposition of large amounts of silica. A homogeneous Si/Al composition of the Si/Al$_2$O$_3$ samples is confirmed by EDXS.
Figure 4.17 TEM images: (a) pure alumina (entry 1); (b) SA(17/anh) (entry 4); (c) SA(17/12eqW) (entry 6).

Figure 4.18 shows the ToF-SIMS results (relative contribution of poly-Si fragments, i.e. silicon-containing anions comprising at least to silicon atoms among all the fragments) of various Si/Al₂O₃. With increasing silica loading, the percentage of poly-Si increases, indicative of a larger surface density of silicon species. Similarly, the part of poly-Si among Si-containing fragments increases with the silica loading (12.4% for entry 2, 15.5% for entry 4), which is indicative of a higher part of polymeric species and agrees with the NMR results.

Figure 4.18 ToF-SIMS of Si/Al₂O₃ samples: percentage of fragments containing at least two silicon atoms (poly-Si) among the total intensity of all fragments. Numbers in brackets correspond to entries in Table 3.1.

The part poly-Si fragments of SA(17/12eqW) is similar to that of SA(12/anh) despite a higher silica loading. This also fits with the NMR results indicating that both samples have a similar distribution of monomeric and dimeric silicon species. SA(17/CVD250) shows, within the margin of error, results similar to those of SA(17/anh). SA(17/CVD400) shows a lower
part of poly-Si than SA(17/CVD250) and SA(17/anh). Both SA(17/CVD250) and SA(17/CVD400) display a high part of poly-Si among Si-containing fragments (around 20%).

Figure 4.19 shows the ToF-SIMS results (poly-Al among all fragments) of Si/Al₂O₃ with ≈ 17% SiO₂. They follow the same trend as those given by Figure 4.18: SA(17/12eqW) shows high alumina surface left uncovered. Conversely, little alumina surface is still uncovered on SA(17/CVD250). Results for SA(17/anh) and SA(17/CVD400) are closer, the former showing the highest alumina coverage by silicon species of the two.

![Figure 4.19 ToF-SIMS of Si/Al₂O₃ samples: percentage of fragments containing at least two aluminium atoms (poly-Al) among the total intensity of all fragments. Numbers in brackets correspond to entries in Table 3.1.](image)

**4.4 Discussion**

**4.4.1 Key parameters of grafting**

Observations regarding the grafting of aluminium, respectively silicon species, on silica and alumina are summarized in Table 4.2. In anhydrous Al/SiO₂ CLD, less aluminium species are deposited on a dehydroxylated surface (left column) because at least one hydroxyl group is required to react with one precursor molecule. Al(O’Pr)₃ is grafted on the surface without forming Al₂O₃ aggregates before reaching the surface. The maximum grafting yield is reached once every hydroxyl group has been grafted.
Table 4.2 Determination of the limiting factors for Al/SiO₂ and Si/Al₂O₃ grafting according to the synthesis conditions.

### Al/SiO₂

<table>
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<tr>
<th>CLD anhyd.</th>
<th>Max. amount of aluminium precursor deposited (nm²)</th>
<th>Limiting factor when ↗ the amount of precursor molecules</th>
<th>Amount of precursor ↓ Hydroxyl density</th>
<th>Amount of precursor ↓ Size of the prec. molecule</th>
<th>Amount of precursor ↓ Size of the prec. molecule</th>
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<td>3.3</td>
<td>3.8</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

### Si/Al₂O₃

<table>
<thead>
<tr>
<th>CLD anhydrous</th>
<th>Max. amount of silicon precursor deposited (nm²)</th>
<th>Limiting factor when ↗ the amount of precursor molecules</th>
<th>Amount of precursor ↓ Size of the prec. molecule</th>
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</thead>
<tbody>
<tr>
<td>CLD anhydrous</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>CLD aqueous (+14 or +12 eq. water)</td>
<td>No apparent limitation</td>
<td>No apparent limitation (continuous hydrolysis)</td>
<td></td>
</tr>
<tr>
<td>CVD (250 or 400°C)</td>
<td>No apparent limitation</td>
<td>No apparent limitation (continuous decomposition)</td>
<td></td>
</tr>
</tbody>
</table>

The higher hydroxyl group density after rehydroxylation of silica (right column) does not lead to a higher amount of aluminium deposits. Similarly, excess precursor molecules are not grafted above a certain concentration (middle and right columns). Scheme 4.1, based on the experimental results, suggests a schematic view of the grafting process depending on the synthesis conditions. Scheme 4.1.a-c illustrates that, when the hydroxyl group density is not the limiting factor, the size of the precursor molecule determines the maximal amount of deposit. More species can be deposited after calcination and recovering of the hydroxyl groups.

A similar mechanism takes place in the case of grafting silicon (Si(OEt)₄) onto alumina. Yet, in that case, the surface hydroxyl density of the support, 10.5 OH.nm⁻², is no longer a limiting factor, and deposition is also saturated at 3.5 molecules.nm⁻² in anhydrous conditions. Such a value is close to that in Al/SiO₂ grafting (3.8 Al.nm⁻²), and thus confirms the strong influence of the precursor molecule size (Al(O’Pr)₃ or Si(OEt)₄) in the grafting yield (Scheme 4.1.d). Beguin et al. noted the influence of the precursor molecule size in Si/Al₂O₃ grafting.⁶¹ Yet they found a higher saturation density, 4.6 vs. 3.5 Si.nm⁻², which might result from less drastic synthesis conditions, especially concerning the water content, as ethanol was used as a solvent. The presence of water in aqueous CLD grafting leads to hydrolysis of the alkoxy groups of the precursor molecules, hence reducing their size, and even forming multilayers in large excess of water. Water present during synthesis increases the density of grafted atoms (Scheme 4.1.e). The equilibrium between surface grafting on
Si(OH)x(OEt)y/SiO2 (1st grafting)

Al(OiPr)3/Al(OSi)x(OiPr)y/SiO2 (2nd grafting)

dehydroxylated SiO2

pure SiO2

Si(OEt)y/SiO2 (1st calcination)

Si2Al1(OEt)y/Al2O3 (2nd calcination)

Si(OEt)y(OH)x/Al2O3 (1st hydration)

Scheme 4.1 Schematic view of the surface reactivity of the support surface: (a) Al/SiO2 on dehydroxylated silica; (b) Al/SiO2 in “normal” pretreatment conditions (4 h at 30°C, 10^-2 mbar); (c) Al/SiO2 on rehydroxylated silica; (d) Si/Al2O3 in “normal” (4 h at 40°C, 10^-2 mbar) pretreatment conditions (anhydrous CLD); (e) Si/Al2O3 after addition of water (aqueous CLD). One circle stands for precursor molecules; one circle attached to two smaller ones corresponds to water molecules. According to the synthesis conditions, the size of the precursor molecule (hence the corresponding circle) can be reduced (by hydrolysis in the presence of water or by alkoxy decomposition during calcination). Numbers in brackets correspond to entries in Table 3.1.
alumina and condensation of TEOS molecules is closely related to the TEOS/water ratio in the reaction mixture. The role of precursor decomposition on the grafting yield is visible in the CVD syntheses, which show no limitation of the grafting yield (Scheme 4.1.e). In CVD synthesis, TEOS readily reacts with the alumina surface: TEOS thermal decomposition starts at 600 K in inert atmosphere and at 450 K in the presence of oxygen. Such high loadings are further favoured by the elimination of adsorbed by-products resulting from grafting, such as ethoxy species.

**4.4.2 Impact of the experimental conditions of grafting**

Deposition of species reduces the surface area and the average pore diameter, even blocking the smallest ones. The textural properties and the TEM-EDXS results indicate that species are deposited all over the surface of the support. Yet, according to the amount of deposited species and synthesis parameters, the deposit may be more or less homogeneous, showing different degrees of coverage of the oxide surface, and up to several layers of guest atoms.

Scheme 4.2 depicts the schematic distribution of surface species with respect to the synthesis conditions, according to the structural results given by TEM, NMR and ToF-SIMS. Aluminium deposition on silica occurs, for low amounts of precursor, via grafting of Al(O\(^\text{\textsuperscript{iPr})}_3\) on silanols. Depending on the configuration of the grafting site, aluminium atoms adopt upon calcination, a four- or six-coordination. There is no clear trend concerning the repartition between four- or six-coordinated aluminium atoms until 15.0% Al\(_2\)O\(_3\) (entries 16-19), and five-coordinated species are detected (vide infra) (Figure 4.10.a-d, Scheme 4.2.a). According to Hensen et al., at such low concentrations, four-coordinated species correspond to bipodal species while six-coordinated species are monopodal surface species. At low loading, aluminium is in a siliceous environment, at higher loading in a more aluminous one. Repeated grafting leads to loadings in excess of 15.0% Al\(_2\)O\(_3\). Precursor molecules are then grafted onto the first layer of aluminium species. This coincides with the substantial increase of the five-coordinated aluminium peak (Figure 4.10.e-f, Scheme 4.2.a) which could be associated with the newly deposited aluminium, connecting the previously deposited species.

Aqueous grafting of aluminium species onto silica results in the presence of two different four-coordinated species belonging to aluminium in an aluminous respectively siliceous environment (AS(17/3eqW), entry 24). Water thus leads to the formation of purely aluminous domains even at relatively low loading, besides aluminium atoms at the interface.
of the deposit and the silica surface (Scheme 4.2.a). Some four-coordinated aluminium atoms are thus close to the silica surface, and are part of an alumina deposit strongly constrained by the silica surface – thus also leading to the existence of five-coordinated aluminium. Other four-coordinated aluminium atoms are associated to an alumina-like structure, where the atoms are less constrained, and adopt a structure which is closer to that of γ-alumina. Platelets of alumina are visible on TEM images (Figure 4.13) and account for the high intensity of poly-Al in ToF-SIMS (Figure 4.14). That is not really surprising as the calcination of materials is 550°C, i.e. within the temperature range where γ-alumina is usually obtained from calcination of boehmite.\[34\]

As for Al/SiO$_2$ grafting, the first silicon atoms to be deposited by anhydrous CLD Si/Al$_2$O$_3$ are essentially isolated (Scheme 4.2.b), as indicated by $^{29}$Si NMR results. Yet, the width of the NMR signal indicates a certain distribution of species. The more silicon is introduced, the more oligomerized the silica network becomes and the rarer the isolated monomers and dimers of silicon are. In anhydrous CLD, some Q$^4$ species start to appear at 17.1% SiO$_2$ loading (Si(17/anh), entry 4). This indicates a heterogeneity of the silica deposit, displaying a variable thickness, with parts of alumina surface remaining uncovered, while what is usually claimed in the literature is a uniform silica deposit.\[70,89\] Since the Si(17/anh) sample is obtained after three successive grafting steps, silicon precursor molecules (TEOS) are more likely to attach to the first layer of silica deposit, thus growing silica “islets” instead of filling the remaining free alumina surface. A similar deposit is obtained in the presence of water after a one-step grafting (Si(17/4eqW), entry 5) (Scheme 4.2.b). An excess of water (Si(17/12eqW), entry 6) leads to a non-controlled deposition: a large part of the alumina surface remains uncovered (Figure 4.19) and TEOS polymerizes (Scheme 4.2.b).

Scheme 4.2 Summary view of the distribution of species according to the synthesis conditions and loading of guest species: (a) Al/SiO$_2$; (b) Si/Al$_2$O$_3$. The darker the band, the higher the probability of finding the species in the material. Numbers in brackets correspond to entries in Table 3.1.
Si/Al$_2$O$_3$ grafting at 250°C by CVD (Si(17/CVD250), entry 8) leads to the most homogeneous deposition according to NMR and ToF-SIMS results, and little alumina surface remains uncovered (Figure 4.19). Conversely, grafting at 400°C (Si(17/CVD400), entry 12) leaves more alumina surface exposed in agreement with ref.[20,38,67-69] (Figure 4.19). Temperature thus affects the structure of the silica deposit on alumina.

4.5 Conclusion

The synthesis of aluminosilicates by grafting of silicon respectively aluminium alkoxides on the complementary oxides follows some basic rules, which further determines the nature of the layer of deposited species. When the density of OH groups of the support is no longer the limiting factor, above ≈ 3.5 OH.nm$^{-2}$, the maximum grafting yield is determined by the size of the precursor molecule. In anhydrous liquid conditions, deposition is saturated when the surface of the support oxide has been completely covered with a monolayer of precursor molecules. Non-reactive alkoxy groups do not allow the deposition of excess molecules, and the grafting of new species is only possible after calcination and consequent recovering of hydroxyl groups. Conversely, the decrease of the precursor molecule size and its activation via hydrolysis of the alkoxy groups allow unlimited grafting of species. Temperature and water/precursor ratio then control the structure of the deposit.

Water largely favours the presence of pure silica domains on Si/Al$_2$O$_3$ materials. However, an excess of water has to be used (water to precursor molar ratio of 12) to observe significant changes in the structure of the deposit. High temperature in gas-phase grafting also leads to inhomogeneous deposition of silicon species.

Al(OiPr)$_3$ is very sensitive to water, and condensates as soon as water is present in the reaction mixture at a water to precursor molar ratio of 1, initiating the growth of alumina nanoparticles. Deposition of aluminium species on silica in anhydrous conditions leads to the formation of an amorphous and regular deposit, which is characterized by the presence of numerous five-coordinated aluminium species after repetition of the grafting step. Fine tuning of the conditions enables to have control of the structure of the deposit.

The wide range of composition and surface structure obtained on these reference ASAs constitutes a valuable starting point for further characterization of the relation between structure and acidity, and disclosure of the nature of acid sites on ASAs
Chapter 5

Quantification of Brønsted acid sites of grafted amorphous silica-aluminas and their turnover frequency in m-xylene isomerization

5.1 Introduction

Because of their moderate acidity and mesoporosity, ASAs are tailored for the conversion of large hydrocarbon molecules to middle distillates during the oil-refining process. Moreover, numerous articles also report the use and characterization of alumina for catalytic reactions such as alcohol dehydration. Kwak et al. showed that the (100) surface of γ-alumina catalyzes the dehydration of ethanol to ethylene. Upon thermogravimetric analysis after ethanol adsorption on the surface of alumina, they found that the active sites are either Al(VI)-OH groups (Brønsted acid sites (BAS)) or coordinatively unsaturated Al(V) (Lewis acid sites (LAS)) belonging to the (100) surface. The dehydration temperature depends on the type of site involved. Roy et al. applied the same technique to ethanol and other alcohols and compared the results to DFT (density functional theory) calculations. They found no evidence that BAS are involved in alcohol dehydration, which they proposed to be exclusively catalyzed by LAS. The nature of the alcohol determines the temperature of dehydration. The BAS specific to zeolites also catalyze the dehydration of ethanol.

Infrared spectroscopy enables the differentiation of the different OH groups (stretching region, \(\approx 3000 \text{ cm}^{-1} \) to \(4000 \text{ cm}^{-1}\)) that make up the surface of alumina, silica, and aluminosilicates. Based on DFT calculations, Digne et al. assigned the typical IR bands in the OH stretching region of γ-alumina. This model improves the previous assignment by Knøzinger et al.
Chapter 5

The adsorption of probe molecules, especially CO, followed by infrared spectroscopy yields the nature and strength of the acidic sites (BAS, weak and strong LAS) of ASAs\textsuperscript{[6,9,10,99-101]} based on the CO stretching frequency.

We developed a series of aluminosilicates by grafting (Chapter 4). The materials, with a considerable variation in the Si/Al ratio and the surface structure, were synthesized by the deposition of Si(OEt)\textsubscript{4} (TEOS) on γ-alumina and Al(OiPr)\textsubscript{3} on silica. \textsuperscript{27}Al and \textsuperscript{29}Si NMR, time-of-flight secondary ion mass spectrometry (ToF-SIMS), and TEM results indicate that the type of deposit on the oxide support depends strongly on the temperature of grafting and the water content of the reaction mixture.

The present chapter determines the acidity of γ-alumina, silica, and Si/Al\textsubscript{2}O\textsubscript{3}. Assessment of their catalytic performance was achieved based on the isomerization of \textit{m}-xylene to \textit{o}- and \textit{p}-xylene, catalyzed by acid solids such as ASAs and zeolites.\textsuperscript{[23,24]} BAS catalyze the isomerization from \textit{m}- to \textit{o}- and \textit{p}-xylene through formation of a benzenium ion intermediate.\textsuperscript{[23]} Infrared spectroscopy measurements were performed before and after CO adsorption to monitor the development of BAS and LAS. Ethanol adsorption and thermogravimetric analysis were employed to assess the nature and the number of sites that are active for dehydration. The comparison between the dehydration temperature and the IR spectra of the OH stretching region for Si/Al\textsubscript{2}O\textsubscript{3} samples, prepared under various conditions, shows the selective grafting of silicon species onto surfaces (100) and (110) of alumina, and their relationship to the formation of LAS and BAS. BAS are active in both \textit{m}-xylene isomerization and ethanol dehydration. Because the amount of BAS is quantified, we were uniquely able to determine the turnover frequency (TOF) in \textit{m}-xylene isomerization over BAS.

5.2 Results

5.2.1 Preferential adsorption of ethanol on alumina surfaces

5.2.1.1 Ethanol adsorption on γ-alumina and silica

Figure 5.1 gives an example of the weight evolution of γ-alumina (entry 1 in Table 3.1) during a TGA experiment with pretreatment at 500°C. Weight loss during pretreatment is ascribed to both dehydration and dehydroxylation of the alumina surface. The uptake of ethanol is characterized by a steep increase in weight until saturation of the surface. The room temperature purge results in weight loss because of desorption of the weakly bonded ethanol. The TPD is marked by a two-stage weight loss; at the end of the TPD, the weight of the sample is the same as that after pretreatment.
Selective grafting of the facets of $\gamma$-alumina

Figure 5.1 Weight evolution during a TGA experiment (example: $\gamma$-alumina pretreated at 500°C).

Figure 5.2 gives the derivative of the weight loss of alumina (entry 1) and silica (entry 15) during TPD, after pretreatment at 200°C and 500°C. Both samples show a first weight loss, between 30°C and approx. 150°C, at around 80°C, which corresponds to desorption of medium strong bound ethanol.\textsuperscript{[4]} The second main desorption feature, only visible for alumina, relates to the formation and desorption of ethylene. The desorption temperature decreases when the pretreatment temperature increases, which is consistent with previous observations.\textsuperscript{[4]} Pretreatment at 500°C leads to a larger amount of desorbed ethanol. Silica pretreated at 200°C shows a greater amount of desorbed ethanol than at 500°C pretreatment, in agreement with a high-temperature weight loss corresponding to dehydroxylation.

Figure 5.2 Derivative of the TPD weight loss of ethanol on silica and alumina after pretreatment at 200°C and 500°C. Numbers in brackets correspond to entries in Table 3.1.
Table 5.1 gives the amounts of adsorbed and desorbed ethanol (per surface unit) at different stages of the TGA experiment on pure alumina and silica. Following the proposal of Golay et al.\textsuperscript{[102]} the adsorption sites of ethanol fall into three categories:

- weak adsorption sites: ethanol desorbs at room temperature. Ethanol desorbs from these sites during purge,
- medium strong adsorption sites: ethanol desorbs below 200°C,
- dehydration sites: ethanol remains adsorbed and is dehydrated to ethylene at a temperature above 200°C. These sites are found on alumina, but not on silica.

The total amount of adsorbed ethanol on alumina is significantly higher than on silica (col. 2). The high-temperature treatment on silica decreases the total amount of adsorbed ethanol (col. 2) and weakens its adsorption sites (col. 3 and 4). Conversely, the high-temperature treatment on alumina increases the total amount of adsorbed ethanol (col. 2) and increases the amount of medium strong adsorption sites and dehydration sites (col. 4 and 5).

Table 5.1 Surface density of adsorbed ethanol (nm\(^{-2}\)) at different stages of TPD depending on the pretreatment conditions on pure alumina and silica.

<table>
<thead>
<tr>
<th>Pretreatment temperature (°C)</th>
<th>Total([a]) (col. 2)</th>
<th>Amount of EtOH adsorbed (nm(^{-2}))</th>
<th>On weak sites([b]) (col. 3)</th>
<th>On medium sites([c]) (col. 4)</th>
<th>On dehydration sites([d]) (col. 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alumina</td>
<td>Silica</td>
<td>Alumina</td>
<td>Silica</td>
<td>Alumina</td>
</tr>
<tr>
<td>200°C</td>
<td>3.5</td>
<td>3.2</td>
<td>1.2</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>500°C</td>
<td>3.8</td>
<td>3.0</td>
<td>1.0</td>
<td>1.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\([a] = [b] + [c] + [d]\)

5.2.1.2 Fraction of the alumina surface covered by silicon species on Si\(_2\)Al\(_2\)O\(_3\)

Table 5.2 gives the amount of ethanol retained, i.e. still adsorbed on the surface after the purge on various Si/Al\(_2\)O\(_3\) after pretreatment at 500°C. All the Si/Al\(_2\)O\(_3\) samples retained a smaller amount of ethanol than pure alumina (entry 1). Values for SA(17/CVD250), SA(17/4eqW), and SA(17/CVD400) are close to that of SA(17/anhy). Despite its high silica loading, the level of ethanol adsorption of SA(17/12eqW) is similar to that of SA(12/anhy) with less silicon. The amount of ethanol left on SA(28/CVD400) is comparable to that on silica. Ethanol adsorption values in Table 5.2 confirm the results in Table 5.1, showing the preferential adsorption of ethanol on alumina surfaces. Deposited silica lowers the number of ethanol adsorption sites (vide infra).
Selective grafting of the facets of $\gamma$-alumina

Table 5.2 Surface density of ethanol retained after purge (nm$^{-2}$) following pretreatment at 500°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Ethanol retained after purge (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$\gamma$-alumina</td>
<td>2.8</td>
</tr>
<tr>
<td>(2)</td>
<td>SA(7/anh)</td>
<td>2.4</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>2.2</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>1.7</td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>1.8</td>
</tr>
<tr>
<td>(6)</td>
<td>SA(17/12eqW)</td>
<td>2.2</td>
</tr>
<tr>
<td>(8)</td>
<td>SA(17/CVD250)</td>
<td>1.6</td>
</tr>
<tr>
<td>(13)</td>
<td>SA(17/CVD400)</td>
<td>1.8</td>
</tr>
<tr>
<td>(14)</td>
<td>SA(28/CVD400)</td>
<td>1.3</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>1.3</td>
</tr>
</tbody>
</table>

From the values in Table 5.2, it is possible to estimate the ratio of exposed surface aluminium species by comparing the amount of ethanol retained after the purge of each sample to the minimum and maximum values obtained on pure silica (1.3 EtOH.nm$^{-2}$) and pure alumina (2.8 EtOH.nm$^{-2}$), respectively:

Experimental density of surface Al atoms $\% = \frac{\text{Amount of adsorbed ethanol}}{2.8-1.3} \times 100$ (5.1)

The amount of deposited silicon atoms on Si/Al$_2$O$_3$ (Si.nm$^{-2}$) allows the calculation of the theoretical density of exposed surface aluminium atoms (eq. (5.2))$^*$. On $\gamma$-alumina, this value was estimated to be between 9.3 Al.nm$^{-2}$ and 14.5 Al.nm$^{-2}$\cite{70,89}; we chose it as 12.5 Al.nm$^{-2}$.

Theoretical density of surface Al atoms $\% = \frac{\text{Density of Al atoms on alumina (nm$^{-2}$)} - \text{Density of grafted Si (nm$^{-2}$)}}{\text{Density of Al atoms on alumina (nm$^{-2}$)}} \times 100$ (5.2)

Figure 5.3 gives the plot of the relative amount of adsorbed ethanol after purge at room temperature in % (eq. (5.1)), reflecting the experimental surface density of aluminium atoms (Y-axis) versus the theoretical density (eq. (5.2), X-axis). When the theoretical density of surface aluminium atoms equals the experimental density (dashed line), each deposited silicon atom covers one adsorption site of alumina. Si/Al$_2$O$_3$ samples prepared under anhydrous conditions (entries 2-4) show this behaviour. The results for SA(17/4eqW) (entry 5) are similar to those of SA(17/anh) (entry 4). The deposition of silicon species by chemical vapour deposition (SA(17/CVD400) (entry 13) and SA(17/CVD250) (entry 8) is less regular but remains close to the ideal line. Due to the large excess of water during deposition, the silicon species form aggregates on SA(17/12eqW) (entry 6), maintaining a large fraction of

$^*$ Equations 5.1&5.2 are valid, because the number of sites formed by Si deposition that are active for EtOH dehydration and $m$-xylene isomerization is at most 5% of the exposed Al atoms; for exposed Si atoms the value is only half of that.
accessible alumina. The surface of SA(28/CVD400) (entry 14) has the same available adsorption sites as silica (entry 15). This corresponds to a complete coverage of the alumina surface by silicon species.

**Figure 5.3** Fraction of the alumina surface accessible to ethanol adsorption and retained after purging: theoretical X values (based on the composition data) vs. experimental Y values (based on ethanol adsorption). Numbers in brackets correspond to entries in Table 3.1.

### 5.2.2 Dehydration of ethanol

Figure 5.4.a gives the derivative of the weight loss during TPD on alumina and on Si/Al₂O₃ prepared under anhydrous conditions. All the samples show similar ethanol desorption features at around 80°C and dissimilar ethanol dehydration peaks between 200°C and 280°C. At silica loadings below 12% (SA(7/anh) and SA(12/anh), entries 2 and 3), the intensity of the ethanol dehydration peak is lower and is shifted towards a higher temperature compared to that of pure alumina (entry 1). At higher loadings (17% SiO₂: SA(17/anh), entry 4) the intensity of the dehydration peak intensity is lower but has shifted back towards a lower temperature.

Figure 5.4.b. gives the results for samples prepared by CVD and by CLD in the presence of water. SA(17/4eqW) (entry 5) and SA(17/CVD250) (entry 8) show similar ethanol dehydration peaks (both the intensity and temperature) as that of SA(17/anh). Conversely, SA(17/12eqW) (entry 6) and SA(17/CVD400) (entry 13) show higher intensities than SA(17/anh) but still significantly lower than for alumina. The position of the ethanol dehydration peak of SA(17/CVD400) is very similar to that of pure alumina (around 250°C) while that of SA(17/12eqW) has shifted (Table 5.3).
Selective grafting of the facets of $\gamma$-alumina

Figure 5.4 Derivative of TPD weight loss of ethanol on Si/Al$_2$O$_3$ grafted samples after pretreatment at 500°C: (a) prepared by anhydrous CLD; (b) prepared by various methods (around 17% SiO$_2$). The intensities are normalized by the surface area of each sample. Numbers in brackets correspond to entries in Table 3.1.

Table 5.3 gives the amount of dehydrated ethanol. Si/Al$_2$O$_3$ prepared in anhydrous conditions, in the presence of four water equivalent per TEOS molecule, and by CVD at 250°C (entries 1-8), show a decrease in the amount of ethanol that undergoes dehydration when the free alumina surface decreases. SA(17/CVD400) is an exception: although its alumina surface is mainly covered by silicon species, it dehydrates a large amount of ethanol per surface unit. Fifteen percent of the ethanol remaining after the purge undergoes dehydration, which, though 50% less than on pure alumina, is significantly higher than on the other Si/Al$_2$O$_3$ (col. 6). Entries 1 to 8 first show a decrease (entries 1-3 and 6) and then an increase (entries 4, 5, and 8) in the amount of dehydrated ethanol per exposed aluminium (col.
5) when the free alumina surface decreases. SA(17/CVD400) clearly follows a different trend than the other Si/Al₂O₃.

**Table 5.3** Ethanol dehydration over Si/Al₂O₃ grafted samples as function of the percentage of free aluminium species.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Percentage of free alumina surface (%)</th>
<th>EtOH undergoing dehydration</th>
<th>Fraction of ethanol dehydrated (%)</th>
<th>Position of the ethanol dehyd. peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(col. 2)</td>
<td>(col. 3)</td>
<td>(col. 4)</td>
<td>(col. 5)</td>
</tr>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td>100</td>
<td>0.83</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>(2)</td>
<td>SA(7/anh)</td>
<td>70</td>
<td>0.27</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>57</td>
<td>0.23</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>29</td>
<td>0.17</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>34</td>
<td>0.20</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>(6)</td>
<td>SA(17/12eqW)</td>
<td>61</td>
<td>0.22</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>(8)</td>
<td>SA(17/CVD250)</td>
<td>17</td>
<td>0.16</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>(13)</td>
<td>SA(17/CVD400)</td>
<td>35</td>
<td>0.27</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>0</td>
<td>0.00</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

[a] based on the total surface area.  
[b] based on the fraction of alumina not covered by silicon species.  
[c] relative to total EtOH desorbed during TPD.

### 5.2.3 *m*-xylene isomerization

Table 5.4 gives the rates of *m*-xylene isomerization per gram of catalyst and per surface area of alumina, silica, and Si/Al₂O₃ and per exposed aluminium atom. All the catalysts deactivate over time; hence the conversion data in Table 5.4 were obtained after only 10 min in *m*-xylene stream. Entries 1 to 8 first show an increase and then a decrease in the rate of *m*-xylene conversion when the fraction of free alumina surface decreases. The highest rates are reached when about 30% of the alumina surface is still uncovered. Once again, SA(17/CVD400) (entry 13) does not follow the same trend and exhibits a rate of conversion

**Table 5.4** Conversion of *m*-xylene over Si/Al₂O₃ grafted samples and wavenumber in the CO region corresponding to the first CO adsorption on OH groups.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>Isoweight (×10⁻² mmol.h⁻¹g⁻¹ cat⁻¹)</th>
<th>Rate of <em>m</em>-xylene converted @ 10 min (×10⁻² molecule.h⁻¹nm⁻²)</th>
<th>First-pulse wavenumber of CO band (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td>3</td>
<td>7.9</td>
<td>2162</td>
</tr>
<tr>
<td>(2)</td>
<td>SA(7/anh)</td>
<td>7</td>
<td>21.8</td>
<td>2170</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>16</td>
<td>54.0</td>
<td>2172</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>25</td>
<td>94.1</td>
<td>2173</td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>29</td>
<td>98.3</td>
<td>2175</td>
</tr>
<tr>
<td>(6)</td>
<td>SA(17/12eqW)</td>
<td>16</td>
<td>55.4</td>
<td>2173</td>
</tr>
<tr>
<td>(8)</td>
<td>SA(17/CVD250)</td>
<td>22</td>
<td>78.1</td>
<td>2175</td>
</tr>
<tr>
<td>(9)</td>
<td>SA(19/CVD250)</td>
<td>17</td>
<td>64.2</td>
<td>2171</td>
</tr>
<tr>
<td>(13)</td>
<td>SA(17/CVD400)</td>
<td>7</td>
<td>24.9</td>
<td>2166</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>3</td>
<td>2.9</td>
<td>2156</td>
</tr>
</tbody>
</table>

[a] based on the total surface area.  
[b] based on the fraction of alumina not covered by silicon species.  
[c] upon CO adsorption on OH groups.
Selective grafting of the facets of γ-alumina

...four times lower than expected for such coverage of the alumina surface. Data normalized by the density of the exposed aluminium atoms follow the same trend as the isoweight and isosurface data.

5.2.4 CO adsorption followed by infrared spectroscopy

5.2.4.1 Infrared spectra of the OH stretching region

Figure 5.5 gives the OH stretching vibrations between 3200 cm\(^{-1}\) and 4000 cm\(^{-1}\) of alumina and Si/Al\(_2\)O\(_3\) prepared under anhydrous conditions. Entry 1 (γ-alumina) has five main contributions. The assignment of the peaks to local Al-OH structures is based on the computational study by Digne et al., as shown in the figure.\(^{[34]}\) The 3590 cm\(^{-1}\) and the 3770 cm\(^{-1}\) bands correspond to the Al-OH groups on the (100) surface of alumina. The 3671 cm\(^{-1}\) and the 3730 cm\(^{-1}\) peaks as well as the 3793 cm\(^{-1}\) shoulder are Al-OH groups on the (110) surface. The deposition of the first silicon atoms on SA(7/anh) causes the 3770 cm\(^{-1}\) band to disappear and the attenuation of the 3590-600 cm\(^{-1}\), the 3670-80 cm\(^{-1}\), and the 3790-93 cm\(^{-1}\) bands. The 3730 cm\(^{-1}\) band remains, and a new band at 3740 cm\(^{-1}\), corresponding to isolated silanol, appears.\(^{[96]}\) The only remaining feature of alumina on SA(12/anh) is the attenuated 3730 cm\(^{-1}\) shoulder. A broad absorption band becomes visible at around 3600 cm\(^{-1}\). It is often visible on silicated aluminas and other ASAs and sometimes ascribed to Al-OH groups, rendered inaccessible to probe molecules due to the deposition of silicon species, and to Si-OH and Al-OH groups interacting with each other and with water.\(^{[9,20,35,82]}\) A computational study by Leydier et al.\(^{[98]}\) indicates the presence of pseudo-bridging silanols (PBS, i.e. silanol groups bridging aluminium atoms under certain conditions) and other H-bonded groups between 3600 cm\(^{-1}\) and 3700 cm\(^{-1}\). Zaki et al. also locate the origin of the acidity of ASAs in the broad band at around 3600 cm\(^{-1}\).\(^{[95]}\) On SA(17/anh) there are no longer any visible OH groups of alumina; apart from the isolated silanols, the main feature is the broad band at 3600 cm\(^{-1}\).
Figure 5.5 Infrared spectra (OH region) of Si/Al$_2$O$_3$ prepared by anhydrous CLD: (a) γ-alumina; (b) SA(7/anh); (c) SA(12/anh); (d) SA(17/anh). Top of the figure: ascriptions of the vibrational stretching frequencies of Al-OH and Si-OH groups$^{[9,11]}$ (x): entries in Table 3.1; (100) or (110): surfaces of γ-alumina.

Figure 5.6 gives the infrared spectra of Si/Al$_2$O$_3$ (≈ 17% SiO$_2$) prepared under various conditions. The spectrum of SA(17/4eqW) (entry 5) is similar to that of SA(17/anh) (entry 4) and only shows the peak corresponding to isolated silanols (3745 cm$^{-1}$) and a broad band at around 3600 cm$^{-1}$; there is no visible characteristic signal of the pure alumina surfaces. The spectrum of SA(17/12eqW) (entry 6) is dominated by the peak of the silanols. The peaks at 3681 cm$^{-1}$, 3730 cm$^{-1}$, and 3795 cm$^{-1}$ are still visible and are the last remaining features of the (110) surface of alumina. The spectrum of SA(17/CVD250) (entry 8) is close to that of
Figure 5.6 Infrared spectra (OH region) of Si/Al₂O₃ prepared by various grafting techniques: (a) γ-alumina; (b) SA(17/anh); (c) SA(17/4eqW); (d) SA(17/12eqW); (e) SA(17/CVD250); (f) SA(17/CVD400). Top: ascriptions of vibrational stretching frequencies of Al-OH and Si-OH groups \(^{9,11}\) (x): entries in Table 3.1; (100) or (110): surfaces of γ-alumina.
SA(17/anh) and SA(17/4eqW) except for the lower intensity of the broad band at 3600 cm\(^{-1}\). Of the Si/Al\(_2\)O\(_3\), SA(17/CVD400) (entry 13) is the only material with a remaining peak at 3771 cm\(^{-1}\), characteristic of the (100) surface of alumina. Peaks at 3672 cm\(^{-1}\) and 3795 cm\(^{-1}\) are also visible; the 3730 cm\(^{-1}\) band has disappeared and the silanol peak is visible. It is not clear whether the broad signal at around 3600 cm\(^{-1}\) is a remaining band of the alumina support or the OH signal similar to those for entries 4 to 5 and 8.

5.2.4.2 Infrared spectra of the CO stretching region upon CO adsorption

Figure 5.7 gives the characteristic CO stretching region after stepwise dosing of CO and saturation on alumina and Si/Al\(_2\)O\(_3\). On pure alumina (entry 1), two peaks are visible. One, located between 2175 cm\(^{-1}\) and 2215 cm\(^{-1}\), is red-shifted with increasing CO dosing; it corresponds to CO adsorption on medium-strength Lewis acid sites (LAS).\(^{[9,10,99,103]}\) Digne et al.\(^{[34]}\) and Zecchina et al.\(^{[103]}\) agree on the tetrahedral coordination of the aluminium atoms of these sites. The progressive shift of the peak (2209 cm\(^{-1}\) \(\rightarrow\) 2182 cm\(^{-1}\)) is associated with the adsorption on sites of lower strength.\(^{[103]}\) The other peak, at around 2160 cm\(^{-1}\), ranks second in the order of CO adsorption and is ascribed to weaker LAS formed by octahedrally\(^{[103]}\) or penta-coordinated\(^{[34]}\) aluminium atoms, to low-acidic OH groups,\(^{[9,104]}\) or to hydrogen-bonding to Al-OH groups.\(^{[95]}\) Adsorption of CO on pure silica (entry 15) (see Chapter 6) also leads to a peak from 2150 cm\(^{-1}\) to 2160 cm\(^{-1}\). Thus, it is attributed to CO adsorption on weak OH groups rather than on LAS.\(^{[6,105]}\)

SA(7/anh) (entry 2) shows a 2200 cm\(^{-1}\) peak of low intensity and a shoulder at around 2135 cm\(^{-1}\) to 2140 cm\(^{-1}\), corresponding to physisorption on silanols.\(^{[6,9,34,103-105]}\) This is consistent with the consumption of the alumina surface and the grafting of silicon species. The OH peak is red-shifted (\(\approx\) 6 cm\(^{-1}\)), indicative of a stronger H-bond donor or, generally, of a stronger acidity.\(^{[9,31,34,95,103,104]}\)

SA(12/anh) (entry 3) is also characterized by a less intense 2200 cm\(^{-1}\) peak and a more intense peak at 2135 cm\(^{-1}\). However, the first CO molecules adsorbed cause the appearance of a low-intensity peak at around 2230 cm\(^{-1}\), which is usually not related to the presence of silicon species but to the existence of strong LAS on the \(\gamma\)-alumina surface,\(^{[6,9]}\) viewed as surface defects.\(^{[103]}\) Based on thermodynamic calculations, these sites can probably be formed only upon high-temperature dehydroxylation of alumina and correspond to tri-coordinated aluminium species.\(^{[34]}\) Wischert et al. showed, however, that the optimal temperature for obtaining such tri-coordinated species was around 700°C.\(^{[106]}\) In the present study, strong LAS
Selective grafting of the facets of $\gamma$-alumina

are not observed on pure $\gamma$-alumina, but only after the grafting of a certain number of silicon species.

SA(17/anh) (entry 4) shows more intense peaks at 2230 cm$^{-1}$ and 2135 cm$^{-1}$ and a less intense peak at 2200 cm$^{-1}$. This is in line with the tendency observed on SA(12/anh). The position of the peaks of the OH groups is approximately the same as for SA(7/anh) and SA(12/anh).

**Figure 5.7** Infrared spectra (CO region) of increasing doses of CO adsorbed on Si/Al$_2$O$_3$ prepared by anhydrous CLD: (a) $\gamma$-alumina; (b) SA(7/anh); (c) SA(12/anh); (d) SA(17/anh). LAS: Lewis acid sites. Numbers in brackets correspond to entries in Table 3.1.

Figure 5.8 gives the effect of the synthesis conditions of Si/Al$_2$O$_3$ on the adsorption of CO. The CO stretching region of SA(17/4eqW) (entry 5) is similar to that of SA(17/anh)
With a larger fraction of the alumina surface uncovered, SA(17/12eqW) (entry 6) shows a higher amount of weak and medium LAS and a less intense silanol shoulder. SA(17/CVD250) (entry 8) is characterized by a large amount of strong LAS; the silanol shoulder is comparable to the shoulders of SA(17/anh) and SA(17/4eqW). Even though SA(17/CVD400) (entry 13) also has a silanol shoulder similar to those of entries 4, 5, and 8, the amount of weak and medium LAS is significantly higher, and it shows fewer strong LAS.

**Figure 5.8** Infrared spectra (CO region) of increasing doses of CO adsorbed on Si/Al\textsubscript{2}O\textsubscript{3} prepared by various grafting techniques: (a) SA(17/anh); (b) SA(17/4eqW); (c) SA(17/12eqW); (d) SA(17/CVD250); (e) SA(17/CVD400). LAS: Lewis acid sites. Numbers in brackets correspond to entries in Table 3.1.
Selective grafting of the facets of $\gamma$-alumina

The peaks for CO adsorbed on OH groups of the silica, alumina, and Si/Al$_2$O$_3$ samples (around 2150 cm$^{-1}$ to 2160 cm$^{-1}$) do not show the same evolution with increasing amounts of adsorbed CO. Some of the red-shift is due to the interaction of neighbouring CO molecules,$^6$ and some also depends on the wavenumber for the first CO doses on the OH groups (Table 5.4, col. 6). The higher the wavenumber, the stronger the acidic character. The highest wavenumbers for the first CO doses on the OH groups are obtained for SA(17/4eqW) and SA(17/CVD250), the lowest for pure silica and alumina. The values increase from SA(7/anh) to SA(17/anh). Although higher than for pure alumina, the wavenumber for SA(17/CVD400) is markedly lower than for the other Si/Al$_2$O$_3$. The higher the wavenumber of CO on OH groups, the higher the rate of conversion of $m$-xylene (Table 5.4). High conversion rates are thus associated with OH groups with the strongest acidity.

The integration of the 2230 cm$^{-1}$ and 2200 cm$^{-1}$ peaks yields an estimate of the amounts of weak, medium, and strong LAS. Normalization of the data by the weight of the sample wafer and the surface area enables a comparison of the surface density of LAS of the different samples. The absorption coefficients for each type of LAS are similar,$^{107}$ thus, the fraction of strong LAS among the total amount of LAS can be estimated as follows:

$$\text{Fraction of strong LAS in total LAS} = \frac{A_{\text{peak strong LAS}}}{A_{\text{peak strong LAS}}+A_{\text{weak & medium LAS}}} \quad (5.3)$$

$A_i$: area of the CO peak of species $i$, normalized by the weight of the wafer and the surface area of the material ($i =$ strong LAS: peak at 2230 cm$^{-1}$, or weak and medium LAS: peak at 2200 cm$^{-1}$).

The plot of the fraction of strong LAS among the total LAS vs. the free alumina surface is given in Figure 5.9. There is no strong LAS on $\gamma$-alumina and SA(7/anh) (entry 2). Strong LAS appear at higher silica loadings (entries 3-8), and their percentage correlates with the area of uncovered alumina. Again, SA(17/CVD400) (entry 13) deviates and shows a much lower percentage of strong LAS than SA(17/4eqW) (entry 5).
Figure 5.9 Evolution of the percentage of strong Lewis acid sites (LAS) as a function of the available alumina surface. Numbers in brackets correspond to entries in Table 3.1.

5.3 Discussion

5.3.1 Surface occupancy and distribution of silicon species on γ-alumina

The amount of ethanol adsorbed and retained at room temperature enables the calculation of the fraction of the alumina support occupied by silicon species (Figure 5.3). Data show a regular deposition of silicon species for samples prepared under anhydrous conditions (entries 2-4), with four equivalents of water per precursor molecule (entry 5), and for those prepared by CVD at 250°C (entry 7). In these cases, the coverage of the alumina surface is proportional to the amount of deposited silicon. High heterogeneity is observed on SA(17/12eqW) (entry 6) prepared in excess water, in agreement with our previous data.\(^19\) This confirms the relevance and accuracy of ethanol adsorption as a probe for determining the fraction of occupied and unoccupied alumina surface. In particular, the data reveal the similarity between the surface states of SA(12/anh) and SA(17/12eqW), despite the different silica loading, as also detected by\(^{29}\)Si NMR (Chapter 4).

5.3.2 Active sites for ethanol dehydration and m-xylene isomerization

5.3.2.1 Stepwise grafting of silicon atoms on the facets of γ-alumina by CLD and CVD-250°C

Infrared spectroscopy (Figures 5.5 and 5.6) demonstrates the uneven decrease in the alumina OH stretching absorption bands when silicon is grafted to its surface. The first silicon atoms are grafted on the (100) facet, as indicated by the disappearance of the band at 3770 cm\(^{-1}\) (Al(VI)-OH). Kwak et al. showed the preferential grafting of BaO on the (100) facet of γ-alumina.\(^{18,108}\) On SA(12/anh), Al(IV)-OH and (Al(VI))\(_2\)-OH are no longer visible, and the
intensity of the Al(V)-OH band is notably reduced. This means that silicon is also grafted on the (110) facet. A further increase in silica loading results in the complete covering of the alumina surface. Thus, the infrared data reveal that the grafting is selective with regard to the facets, the (100) one being grafted first, the (110) afterwards, while the adsorption of ethanol suggested the progressive and regular coverage of the alumina surface by silicon species.

The grafting of silicon species in aqueous CLD follows the same rules (Figure 5.6). When a small amount of water is added to the reaction mixture (SA(17/4eqW), entry 5), no difference is found compared to the equivalent prepared under anhydrous conditions (SA(17/anh), entry 4): IR shows high coverage of the alumina surface. When a larger amount of water is added (SA(17/12eqW), entry 6), some of the TEOS polymerizes, and a smaller fraction of the alumina surface is covered (39%). As a consequence, the distribution of the alumina OH groups on the surface, visible in IR, is close to that of SA(7/anh) (70% alumina uncovered) and SA(12/anh) (57% alumina uncovered) (respectively entries 2 and 3 in Figure 5.5): The (100) surface is grafted and the (110) surface is partially grafted.

The IR spectrum of SA(17/CVD250) (entry 8, Figure 5.6) shows a general pattern which is similar to that for SA(17/anh) and SA(17/4eqW) but with a more intense silanol peak, which is associated to a higher degree of coverage and more regular deposition of silicon species on the surface, thus maximizing the density of surface SiOH. On SA(17/CVD400) (entry 13, Figure 5.6), all of the OH groups of the alumina support are equally affected, which is evidence of the non-selective grafting of the silicon species under such conditions, irrespective of the alumina facets.

Thus, for samples prepared by CLD or by CVD at 250°C (entries 2-8), silicon species are first grafted on the (100) surface and only at higher coverage on the (110) surface. It is noteworthy that strong LAS appear only above a certain amount of grafted silicon (Figure 5.9), and they are located on the (110) surface, as confirmed by a computational study of the γ-alumina surface, which shows that the “defect sites” or strong LAS are located on the (110) surface.\textsuperscript{[34,106]} Here, they are not visible on γ-alumina and result from the change in the nature of the (110) surface after the grafting of the silicon species.

### 5.3.2.2 Nature of the active sites for ethanol dehydration respectively m-xylene isomerization

Figure 5.10.a gives the amount of dehydrated ethanol (per surface unit) as a function of uncovered alumina surface and the nature of the grafted facet ((100) or (110)) for CLD and CVD-250-prepared Si/Al₂O₃ (entries 1-8). The grafting of silicon on the (100) facet is accompanied by a strong decrease in the amount of dehydrated ethanol. In agreement with the
conclusions of Kwak et al., this confirms that the sites of alumina that are active for ethanol dehydration are on the (100) facet.\textsuperscript{[18]} According to infrared spectra of the OH stretching region, these active sites are, thus, the hydroxylated or dehydroxylated form of Al(VI)-OH or (Al(VI))\textsubscript{2}-OH, visible at 3770 cm\textsuperscript{-1} and 3600 cm\textsuperscript{-1}, respectively.

Figure 5.10.b gives the evolution of the number of weak/medium and strong LAS as a function of the alumina coverage and the nature of the grafted facet. As the (100) surface is covered by silicon species, the number of weak and medium LAS decreases, while strong LAS and BAS do not form. Weak and medium LAS on the (100) surface thus are, depending on the activation temperature, the sites of γ-alumina that are active for ethanol dehydration.

![Figure 5.10](image)

Figure 5.10 Impact of grafting mode of silicon on catalytic performance (a) and amount (per surface unit) of weak/medium and strong Lewis acid sites (LAS) (b) of Si/Al\textsubscript{2}O\textsubscript{3} prepared by CLD or CVD-250°C (entries 1-8). BAS: Brønsted acid sites; (100) and (110): surfaces of alumina. Numbers in brackets correspond to entries in Table 3.1.

Covering the (110) surface with silicon species hardly leads to a change in ethanol dehydration (Figure 5.10.a). However, there are still dehydration sites on the surface, despite the full coverage of the (100) surface; thus, these sites form by deposition of silicon on the (110) surface. When this occurs, the ethanol dehydration peak shifts back towards lower temperature (entries 4, 5 and 8 in Figure 5.4). The coverage of the (110) surface is associated with a loss of the weak and medium LAS, especially between SA(7/anh) (entry 2) and SA(12/anh) (entry 3) (Figure 5.10.b). Strong LAS form as a result of the deposition of silicon on the (110) surface. SA(17/CVD250) shows the largest amount of strong LAS but the smallest number of dehydration sites, indicating that strong LAS on the (110) surface are not the active sites.
Selective grafting of the facets of γ-alumina

Figure 5.10.a also shows the development of the rate of m-xylene conversion (per surface unit) for CLD and CVD-250°C-prepared Si/Al₂O₃ (entries 1-8). The rate per surface unit remains low when the (100) surface undergoes grafting. Thus, (nearly) no active sites for m-xylene conversion are formed. The rate increases strongly as soon as silicon is deposited on the (110) surface, which indicates that active sites for m-xylene isomerization are on the (110) surface and that they require the presence of silicon. The isomerization of m-xylene requires Brønsted acidity, and it takes place over zeolites such as HZSM-5, zeolite Beta, and mordenite.\[12,23,109-111\] The correlation between the wavenumber at the lowest CO coverage on the OH groups (Table 5.4, col. 6) and m-xylene isomerization reactivity (Table 5.4, col. 4) suggests that these OH sites catalyze the reaction.

Similarly, and in accord with the IR data, we associate the remaining sites for ethanol dehydration with the same BAS on the (110) surface of γ-alumina, formed following deposition of the silicon species. The formation of BAS is accompanied by the formation of strong Lewis acidity on the same surface (Figure 5.10.b). However, as mentioned above, the strong LAS are not responsible for EtOH or m-xylene conversion.

When the surface is almost fully covered by silicon species (entries 4, 5, and 8), the rate of conversion of m-xylene passes the maximum (Figure 5.10.a). At the same time, there is a slight decrease in the amount of dehydrated ethanol. We ascribe these evolutions to the grafting of precursor molecules to the BAS, thus removing the active site. Once the TEOS molecules are grafted to the (100) and (110) surfaces of γ-alumina, anchorage sites for new precursor molecules become fewer and it is likely that TEOS is grafted to the most reactive of the available OH groups, hence decreasing the number of BAS. Conversely, the deposition of the same amount of silicon in one step and in the presence of water (SA(17/4eqW) (entry 5)) leaves more of the BAS ungrafted because of the uncontrolled deposition. The grafting to BAS explains the decrease in the rate of m-xylene conversion between SA(17/CVD250) and SA(19/CVD250) (Table 5.4, col. 4). Thus, there is an optimum γ-alumina coverage, between 70% and 80%, above which deposition of silicon species no longer takes place exclusively on alumina, but leads to the consumption of BAS in anhydrous CLD or CVD-250°C. As BAS are grafted, the number of strong LAS increases further (Figure 5.10.b).

Scheme 5.1 shows the evolution, on the (110) surface, of the sites that are grafted and of the active sites, depending on the coverage of alumina by silicon species. On γ-alumina (top panel), Al(VI)-OH sites on the (100) surface are the first to dehydroxylate with increasing temperature;\[34\] they can readily dehydroxylate to form LAS which are active in ethanol dehydration. Conversely, Al(IV)-OH sites on the (110) surface are not
dehydroxylated. When silicon is deposited on the (110) surface (Scheme 5.1, middle panel), Al(V)-OH sites (3730 cm\(^{-1}\) in IR) disappear due to grafting. Strong LAS, which were not present on \(\gamma\)-alumina, form; they probably are three-coordinated\(^{[34]}\). Interaction of these strong LAS with silanol, provided that the coordination of the aluminium is flexible, form BAS, according to the hypothesis of Trombetta et al.\(^{[28]}\). In contrast to zeolites, the silanol does not permanently bridge the aluminium atom, but rather pseudo-bridging occurs, according to the definition of Chizallet et al.\(^{[32]}\). Depending on the SiOH-Al distance, angle, and activation temperature, either BAS or strong LAS are detected. Since all these parameters probably have a large spread, it is impossible to detect a clear stretching frequency of OH in the IR. Above 70% coverage of alumina by silicon species, new species are grafted to the BAS (low panel). The number of strong LAS, which are no longer in interaction with silanols, increases.

\[
\text{Si/Al}_2\text{O}_3 \quad (110) \\
\text{BAS} \\
\Rightarrow \\
\text{TEOS} \\
\text{Si/Al}_2\text{O}_3 \quad (110) \\
< 30\% \text{ free} \\
\text{alumina} \\
\]

**Scheme 5.1** Nature of the anchorage active sites of the (110) surface depending on the coverage of \(\gamma\)-alumina by silicon species.

### 5.3.2.3 Turnover frequency in \(m\)-xylene isomerization

Based on the stoichiometric adsorption and desorption of ethanol, it is possible to calculate the total density of ethanol dehydration sites (Table 5.5, col. 3). Once the whole (100) surface is grafted (entries 4, 5 and 8), both the dehydration of ethanol and \(m\)-xylene isomerization take place exclusively on the BAS. The number of BAS equals the amount of ethanol dehydration sites, which is known. As the isosurface rate of \(m\)-xylene conversion is also known, the turnover frequency (TOF) of BAS, expressed in \(s^{-1}\text{site}^{-1}\), can be calculated as follows:
Selective grafting of the facets of \(\gamma\)-alumina

\[
\text{TOF } \text{s}^{-1}\text{site}^{-1} = \frac{\text{Rate of m-xylene converted at 10 min} \ (\text{h}^{-1}\text{nm}^{-2})}{\text{EtOH dehydration sites} \ (\text{nm}^{-2})} \times \frac{1}{3600} \tag{5.4}
\]

Table 5.5 (col. 4) gives the TOF for entries 4, 5, and 8. The entries yield similar results, about \(1.4 \times 10^{-3} \text{ s}^{-1}\) per BAS, which indicates that they have similar BAS. This value is approximately 22 times lower than that (\(3.1 \times 10^{-2} \text{ s}^{-1}\) per BAS\(^*\)) obtained over a USY zeolite, that has no or few extra-framework aluminium (CBV720 from Zeolyst, entry 32).\(^{[112]}\)

Assuming that all the samples have the same TOF, the number of BAS (per surface unit) of the other Si/Al\(_2\)O\(_3\) can be estimated based on the average TOF for entries 4, 5, and 8 (Table 5.5, col. 5):

\[
\text{BAS } \text{nm}^{-2} = \frac{\text{Rate of m-xylene converted at 10 min} \ (\text{h}^{-1}\text{nm}^{-2})}{1.4 \times 10^{-3} \text{ s}^{-1}\text{site}^{-1}} \times \frac{1}{3600} \tag{5.5}
\]

The number of BAS for entries 4, 5 and 8 is equal to the number of ethanol dehydration sites. Other samples show a smaller number of BAS than of dehydration sites, which means that some of the dehydration sites are still on the (100) surface, in general agreement with the characterization of the sample (Chapter 4).

The density of the BAS is low with respect to the exposed aluminium and silicon (Table 5.5, col. 6-7). Figure 5.11 shows the density of BAS per exposed silicon (a) and aluminium (b) as a function of the fraction of accessible alumina. The density per atom of the (110) surface is calculated by estimating that the (100) and (110) surfaces represent 20% respectively 75% of the total \(\gamma\)-alumina surface\(^{[34]}\) and by determining the coverage of the (100) surface (vide infra). Figure 5.11.a shows that among the silicon atoms grafted on the whole alumina surface, the percentage of silicon atoms which form the BAS reaches a maximum (2%) when the (110) surface is grafted. This value is even lower at the initial grafting of silicon on the (100) surface. Around 4% of the silicon atoms that are grafted on the (110) surface give rise to BAS. Thus, most of the grafted silicon atoms do not form BAS. When grafting to the BAS occurs, at high coverage of the alumina surface, the density of the BAS per silicon atom decreases. Figure 5.11.b shows that, at most, 7% of the total exposed aluminium atoms, and 8% of the aluminium atoms of the (110) surface, relate to a BAS (on SA(17/CVD250)). The deposition of silicon species by CVD-400°C is much less efficient when it comes to the formation of BAS than when it occurs by CLD and CVD-250°C.

\* The number of BAS of this sample was determined by ethanol dehydration (yield 0.18 BAS.nm\(^{-2}\)), which is virtually identical to the value obtained by the temperature-programmed desorption of pyridine.
Especially for samples with only partial coverage of alumina surfaces, the difference between the number of ethanol dehydration sites and the number of BAS enables the calculation of the percentage of free (100) surface (Table 5.5, col. 10):

$$\text{Part of } 100 \text{ uncovered}(\%) = \frac{\text{EtOH dehydration sites (nm}^{-2}) - \text{BAS (nm}^{-2})}{\text{EtOH dehydration sites of alumina (0.83 nm}^{-2})}$$  \hspace{1cm} (5.6)

and the fraction of BAS of the total number of ethanol dehydration sites (Table 5.5, col. 8):

$$\text{Fraction of BAS in EtOH dehydration sites(\%) = } \frac{\text{BAS (nm}^{-2})}{\text{EtOH dehydration sites (nm}^{-2})}$$ \hspace{1cm} (5.7)

These data prove the preferential deposition of the first silicon species, at early stage of the grafting, under relatively mild synthesis conditions, on the (100) surface of γ-alumina (entries 1-8): the degree of coverage of the (100) surface is always higher than that of the whole alumina surface. There are virtually no BAS on pure alumina. On SA(7/anh), most of the dehydration sites are still on the (100) surface. SA(12/anh) and SA(17/12eqW) show that some of the dehydration sites on the (100) surface are still present while some BAS appear. On SA(17/anh), SA(17/4eqW), and SA(17/CVD250), the (100) surface is completely covered.
Selective grafting of the facets of γ-alumina

Table 5.5 Comparison of the density of m-xylene conversion sites and ethanol conversion sites over Si/Al₂O₃-grafted samples and the degree of coverage of the (100) surface of alumina by silicon species.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>EtOH dehyd. sites (nm²)</th>
<th>TOF (×10⁻³, s⁻¹ site⁻¹)</th>
<th>Isosurface (nm²)</th>
<th>BAS Per Al atom (×10⁻³, Al exposed)</th>
<th>BAS Per Si atom (×10⁻³, Si exposed)</th>
<th>Fraction of BAS in EtOH dehyd. sites (%)</th>
<th>Fraction of free alumina surface (%)</th>
<th>Fraction of free (100) surface (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td>0.83</td>
<td>-</td>
<td>0.02</td>
<td>0.1</td>
<td>2</td>
<td>100</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>SA(17/anh)</td>
<td>0.27</td>
<td>-</td>
<td>0.04</td>
<td>0.5</td>
<td>12</td>
<td>16</td>
<td>70</td>
<td>27</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>0.23</td>
<td>-</td>
<td>0.11</td>
<td>1.5</td>
<td>2.0</td>
<td>47</td>
<td>57</td>
<td>14</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>0.17</td>
<td>1.5</td>
<td>0.19</td>
<td>5.2</td>
<td>2.1</td>
<td>≈100</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>0.20</td>
<td>1.3</td>
<td>0.20</td>
<td>4.5</td>
<td>2.4</td>
<td>≈100</td>
<td>34</td>
<td>1</td>
</tr>
<tr>
<td>(6)</td>
<td>SA(17/12eqW)</td>
<td>0.22</td>
<td>-</td>
<td>0.11</td>
<td>1.4</td>
<td>2.2</td>
<td>50</td>
<td>61</td>
<td>13</td>
</tr>
<tr>
<td>(8)</td>
<td>SA(17/CVD250)</td>
<td>0.16</td>
<td>1.3</td>
<td>0.16</td>
<td>7.2</td>
<td>1.5</td>
<td>≈100</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>(13)</td>
<td>SA(17/CVD400)</td>
<td>0.27</td>
<td>-</td>
<td>0.05</td>
<td>1.1</td>
<td>0.6</td>
<td>18</td>
<td>35</td>
<td>26</td>
</tr>
</tbody>
</table>

[a] calculated on the basis of an average TOF value of 1.4×10⁻³ s⁻¹ site⁻¹ calculated for SA(17/anh), SA(17/4eqW) and SA(17/CVD250) for m-xylene conversion. Values are obtained by assuming that all the ethanol dehydration sites of the materials are BAS (eq. (5.5)).
[b] calculated on the basis of the fraction of alumina surface covered/not covered by silicon species.
[c] calculated by dividing the number of BAS by the total number of dehydration sites (eq. (5.7)).
[d] (100) surface of γ-alumina. Calculated by dividing the difference between the number of ethanol dehydration sites and the number of m-xylene conversion sites by the number of ethanol dehydration sites on γ-alumina, where they are exclusively located on the (100) surface (eq. (5.6)).

5.3.3 Non-selective grafting of silicon atoms on the facets of γ-alumina by CVD-400°C

The process of grafting differs in the case of CVD-400°C. Despite the similar coverage of the alumina surface as SA(17/anh), SA(17/4eqW), or SA(17/CVD250), shown by the amount of ethanol bound to the surface (Figure 5.3) and consistent with our previous data (Chapter 4), SA(17/CVD400) (entry 13) has a smaller number of BAS and strong LAS. The IR spectrum shows a non-preferential decrease in the alumina OH bands (Figure 5.6); the position of the ethanol dehydration peak is similar (although less intense) to that of γ-alumina. This indicates that, at high grafting temperature, the facets of γ-alumina are non-selectively grafted by the silicon species. By calculating the percentage of the free (100) surface (Table 5.5), we confirm that the value (26%) is close to the overall percentage of the free alumina surface (35%). The remaining sites on the (100) surface allow the dehydration of ethanol in a similar way as on γ-alumina.

5.4 Conclusion

Silicon grafting on γ-alumina takes place preferentially on the (100) surface when grafting occurs under mild conditions. When this whole surface is covered, the (110) surface is grafted. At almost complete coverage of the (110) surface, silicon is grafted on the previously deposited silicon species. Lewis acid sites (LAS) on the uncovered γ-alumina (100) surface are the active sites for ethanol dehydration; these sites are hydroxylated or dehydroxylated forms of Al(VI)-OH or (Al(VI))₃-OH. Brønsted acid sites (BAS) and strong LAS are created by silicon grafting on the (110) surface. These BAS are responsible for m-
xylene isomerization and are also active in the dehydration of ethanol. Because the Brønsted active sites are the same for ethanol dehydration and \textit{m}-xylene isomerization, we were able to determine the TOF in \textit{m}-xylene isomerization: $1.4 \times 10^{-3}$ s$^{-1}$site$^{-1}$. This value is 22 times lower than obtained over the BAS of a USY zeolite with very few extra-framework aluminium.
Chapter 6

Creation of Brønsted acidity by grafting aluminium isopropoxide on silica in controlled conditions: determination of the number of Brønsted sites and their turnover frequency in \(m\)-xylene isomerization

6.1 Introduction

We have described the synthesis of ASAs by grafting in Chapter 4. Al/SiO\(_2\) were obtained by depositing Al(O\(_i\)Pr)\(_3\) on an amorphous silica gel under controlled conditions. Such Al/SiO\(_2\) have a Brønsted acidic character, which is not the case of the parent support.\(^{54-56,60,63,113}\) For example, Al/SiO\(_2\) materials catalyze the cracking of cumene.\(^{54,62,113}\) The deposition of Pd leads to bifunctional catalysts, which function in hydrogenation/dehydrogenation.\(^{3,55,60}\) Hensen et al. found that the Brønsted acidity of Al/SiO\(_2\), prepared by homogeneous deposition-precipitation of aluminium nitrate on silica, results from the diffusion of a limited amount of tetrahedral aluminium atoms through the silica lattice, leading to negative charge compensation by labile acidic protons, hence Brønsted acidity, similar to what occurs in zeolites.\(^3\) The choice of method for the synthesis of ASAs – cogelation, grafting, etc. – strongly influences the spread of silicon and aluminium atoms through the particles and can lead to dissimilar structures.\(^2\)

The nature of the OH groups upon the grafting of aluminium can be monitored by observing the OH stretching region (\(\approx 3000\) cm\(^{-1}\) to \(4000\) cm\(^{-1}\)) in infrared spectroscopy. The adsorption of CO leads to changes in the range \(2100\) cm\(^{-1}\) to \(2250\) cm\(^{-1}\) (CO stretching); each peak thus obtained is ascribable to a specific type of acidic site.

The dehydration of ethanol to ethylene is catalyzed by the Lewis acid sites (LAS) of \(\gamma\)-alumina and the Brønsted acid sites (BAS) of zeolites and ASAs.\(^{18,19,91-94}\) We already
demonstrated the relevance of ethanol adsorption followed by thermogravimetry to evaluate the development of BAS on Si/Al₂O₃ ASAs (Chapter 5). Knowing the number of BAS enables the calculation of the turnover frequency (TOF) in Brønsted-demanding reactions, such as \( m \)-xylene isomerization. On Si/Al₂O₃ the turnover frequency is \( 1.4 \times 10^{-3} \text{ s}^{-1} \text{site}^{-1} \), and on a USY zeolite with very few extra-framework aluminium \( 3.1 \times 10^{-2} \text{ s}^{-1} \text{site}^{-1} \).

The present chapter determines the acidity of Al/SiO₂ obtained by grafting aluminium isopropoxide on silica. The catalytic activity to \( m \)-xylene isomerization was measured and indicated the emergence of Brønsted acidity upon grafting of silica with aluminium species. This was confirmed by taking infrared spectra of the CO stretching region after CO adsorption. We performed the adsorption of ethanol followed by thermogravimetry. This enables the determination of the surface coverage of aluminium species, similar to Si/Al₂O₃ (Chapter 5). The TOF of Al/SiO₂ for \( m \)-xylene isomerization was calculated.

6.2 Experimental: Adsorption of 2,6-lutidine followed by infrared spectroscopy

For 2,6-lutidine adsorption, samples were first pre-heated at 300°C under secondary vacuum for 10 h comprising a 150°C plateau for 1 h. Lutidine was then introduced at 25°C under vacuum and progressively desorbed by increasing temperature at 100°C for 1 h, 200°C for 1 h and 300°C for 30 minutes. Fourier-Transform IR spectra are recorded at each temperature.

6.3 Results

6.3.1 Adsorption of ethanol followed by thermogravimetry

6.3.1.1 Surface coverage of aluminium species on Al/SiO₂

Following a pretreatment at 500°C, ethanol was adsorbed at room temperature, and weakly bonded molecules were desorbed by purge. With increasing alumina content (Table 6.1, entries 16-22) a higher amount of ethanol was retained after the purge. Similar to our previous observations in Chapter 5, this indicates a greater number of strong ethanol adsorption sites on alumina surfaces. Despite a similar aluminium loading, entries 23 and 24, synthesized in the presence of water, show a smaller amount of retained ethanol than entry 19, which was prepared under anhydrous conditions.
Table 6.1 Surface density of ethanol (nm$^2$) retained after purge following a pretreatment at 500°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Ethanol retained after purge (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>1.3</td>
</tr>
<tr>
<td>(16)</td>
<td>AS(3/anh)</td>
<td>1.3</td>
</tr>
<tr>
<td>(17)</td>
<td>AS(6/anh)</td>
<td>1.5</td>
</tr>
<tr>
<td>(18)</td>
<td>AS(10/anh)</td>
<td>1.6</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>2.0</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>2.2</td>
</tr>
<tr>
<td>(22)</td>
<td>AS(35/anh)</td>
<td>2.6</td>
</tr>
<tr>
<td>(23)</td>
<td>AS(16/1eqW)</td>
<td>1.6</td>
</tr>
<tr>
<td>(24)</td>
<td>AS(17/3eqW)</td>
<td>1.4</td>
</tr>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td>2.8</td>
</tr>
</tbody>
</table>

As for Si/Al$_2$O$_3$ materials, the surface coverage by aluminium species on Al/SiO$_2$ materials can be calculated by comparing the amount of ethanol retained after the purge to the minimum and maximum amounts on pure silica (1.3 EtOH.nm$^2$), and pure alumina (2.8 EtOH.nm$^2$)

In the plot of the experimental density of aluminium atoms (Y-axis) versus the theoretical plot (X-axis) (Figure 6.1), dashed line corresponds to the experimental density being the same as the theoretical density, as found when aluminium atoms are deposited uniformly on the surface. Thus, samples that are prepared under anhydrous conditions (entries 17-22) display a homogeneous deposition of species. The higher the surface density of aluminium atoms, the higher the amount of strong adsorption sites for ethanol. Conversely, entries 23 and 24 show inhomogeneous deposition, which confirms previous observations (Chapter 4). The higher the water content during synthesis, the lower the density of the
aluminium atoms accessible to ethanol, which is indicative of the presence of clusters of alumina species. The difference of ethanol retained after purge between silica and AS(3/anh) is not accurate enough to calculate the surface ratio of surface aluminium; thus, it is not reported in Figure 6.1 and the surface ratio of aluminium species of AS(3/anh) used further in the document corresponds to the theoretical one.

6.3.1.2 Dehydration of ethanol

The derivative of the weight loss of silica, γ-alumina, and various Al/SiO$_2$ (prepared under anhydrous conditions) during the TPD of adsorbed ethanol from room temperature to 400°C shows a desorption feature at around 80°C, associated with ethanol desorption from medium strong sites, visible for all materials (Figure 6.2.a). Above 200°C, ethylene desorbs from dehydration sites.\cite{18,102} Dehydration occurs only on materials possessing surface aluminium species, the amount increasing with the aluminium content. The dehydration peak of Al/SiO$_2$ is constantly located at around 270°C, except for AS(3/anh) (entry 16), whose dehydration temperature is slightly higher (275°C). The dehydration temperature is notably higher than that of γ-alumina (entry 1), which is indicative of a different surface.

For Al/SiO$_2$ prepared in the presence of water (Figure 6.2.b), the higher the water content during synthesis, the higher the dehydration temperature (280°C for AS(16/3eqW), entry 24) and the lower the intensity. Compared to that of AS(16/anh) (entry 19), the dehydration peak of AS(16/3eqW) is particularly asymmetric.

For samples prepared under anhydrous conditions, high aluminium loading is associated to a higher amount of dehydrated ethanol (Table 6.2, col. 4). Entries 23 and 24, prepared by aqueous grafting, have fewer dehydration sites than entry 19. At low aluminium loading (AS(3/anh), entry 16), one fifth of the exposed atoms form a dehydration site (col. 5). At a higher aluminium loading (entries 17-22), the number of dehydration sites per exposed aluminium atoms decreases. Consistent with their low amount of exposed aluminium, AS(16/1eqW) and AS(17/3eqW) show a large number of dehydration sites per exposed atom, especially AS(17/3eqW), for which one third of the exposed aluminium atoms are associated to a dehydration site. For entries 16 to 20 and 23 to 24, the more aluminium atoms are present on the surface, the greater the percentage of adsorbed ethanol molecules that undergo dehydration (col. 6). For AS(35/anh) (entry 22) only 20% of the ethanol is dehydrated: it means that the number of aluminium atoms that form medium strong adsorption sites (where ethanol is adsorbed but does not react) increases more than the number of aluminium atoms that form dehydration sites.
Figure 6.2 Derivative of the TPD weight loss of ethanol on Al/SiO\(_2\) grafted samples after pretreatment at 500°C: (a) prepared by anhydrous CLD; (b) prepared by various methods with similar loading (around 15-17% Al\(_2\)O\(_3\)). The intensities are normalized by the surface area of each sample. Numbers in brackets correspond to entries in Table 3.1.

Table 6.2 Ethanol dehydration over Al/SiO\(_2\) grafted samples as function of the surface coverage of aluminium species.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Surface coverage of aluminium species (%) (col. 3)</th>
<th>IsoSurface (nm(^2)) (col. 4)</th>
<th>EtOH undergoing dehydration (col. 5)</th>
<th>Per Al atom (exposed Al(^{+}))(^{[a]})</th>
<th>Fraction of ethanol dehydrated (%)(^{[c]}) (col. 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>0</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>(16)</td>
<td>AS(3/anh)</td>
<td>(\approx 5^{[b]})</td>
<td>0.12</td>
<td>(\approx 0.2^{[b]})</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>(17)</td>
<td>AS(6/anh)</td>
<td>11</td>
<td>0.20</td>
<td>0.15</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>(18)</td>
<td>AS(10/anh)</td>
<td>15</td>
<td>0.26</td>
<td>0.14</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>46</td>
<td>0.45</td>
<td>0.08</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>56</td>
<td>0.61</td>
<td>0.09</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>(22)</td>
<td>AS(35/anh)</td>
<td>83</td>
<td>0.65</td>
<td>0.05</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>(23)</td>
<td>AS(16/1eqW)</td>
<td>21</td>
<td>0.38</td>
<td>0.14</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>(24)</td>
<td>AS(17/3eqW)</td>
<td>7</td>
<td>0.27</td>
<td>0.33</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td>100</td>
<td>0.83</td>
<td>0.07</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

\(^{[a]}\) based on the surface ratio of aluminium species.

\(^{[b]}\) based on the theoretical density of grafted atoms, by considering a uniform deposition.

\(^{[c]}\) relative to total EtOH desorbed during TPD.
6.3.2 CO adsorption followed by infrared spectroscopy

6.3.2.1 Infrared spectra of the OH stretching region

In Figure 6.3, pure silica (entry 15) shows a main peak at 3745 cm\(^{-1}\), corresponding to isolated silanols.\(^{[96]}\) The low-wavenumber tail between 3400 cm\(^{-1}\) and 3700 cm\(^{-1}\) corresponds to weakly interacting silanol groups,\(^{[96]}\) which is consistent with the high density of surface OH groups (3.3 OH.nm\(^{-2}\)). The first deposited aluminium atoms (entry 16) do not change the global shape of the spectra, except for a small bump at around 3600 cm\(^{-1}\), which is also detected at higher loading (entry 19). A broad peak of low intensity at around 3850 cm\(^{-1}\), also visible for entry 18, corresponds to a torsional mode resonance of silanols.\(^{[96]}\) Increasing the aluminium loading (entries 17-22) causes a decrease in the tail from 3400 cm\(^{-1}\) to 3700 cm\(^{-1}\) and, hence, less bonding between silanol groups. At the same time, a broad band centred at around 3650 cm\(^{-1}\) increases. This was observed for our Si/Al\(_2\)O\(_3\) materials and corresponds to interacting Al-OH and Si-OH groups. The acidic hydroxyl groups of ASAs could be located in this area.\(^{[95,98]}\) Even at high loadings, the band corresponding to isolated silanols is still visible.

Figure 6.4 gives the spectra for AS(16/1eqW) and AS(17/3eqW), which were prepared in the presence of water. The spectrum of AS(16/1eqW) (entry 23) is similar to that of entry 18 (with 10% Al\(_2\)O\(_3\)) in Figure 6.3, which has a similar coverage of aluminium species (Figure 6.1). Similarly, the spectrum of AS(17/3eqW) (entry 24) is close to that of entry 16 (with 3% Al\(_2\)O\(_3\)). Both samples show a small bump at around 3600 cm\(^{-1}\).
Figure 6.3 Infrared spectra of Al/SiO$_2$ prepared by anhydrous CLD: (a) silica; (b) AS(3/anh); (c) AS(6/anh); (d) AS(10/anh); (e) AS(15/anh); (f) AS(25/anh); (g) AS(35/anh). Numbers in brackets correspond to entries in Table 3.1.
6.3.2.2 Infrared spectra of the CO stretching region upon CO adsorption

Upon progressive dosing of CO until saturation on pure silica, the CO stretching region displays two main peaks (Figure 6.5.a). In the CO stretching region, the higher the CO stretching frequency on OH groups, which are characterized by bands in the 2140 cm\(^{-1}\) to 2180 cm\(^{-1}\) region, the higher the acidity.\[^{10}\] CO adsorption first causes an increase in the peak at around 2155 cm\(^{-1}\). This corresponds to adsorption on weak OH groups.\[^{9}\] Further CO adsorption yields a shoulder at around 2140 cm\(^{-1}\), corresponding to physisorption on silanols.\[^{6,9,103,105}\] CO adsorption on the sample with the lowest number of grafted aluminium (AS(3/anh), entry 16) causes the appearance of a peak at 2179 cm\(^{-1}\), which corresponds to CO adsorption on strong BAS.\[^{9}\] Such high wavenumber is usually obtained for the strong BAS of zeolites.\[^{31}\] Thus, for this sample, BAS are the only sites that differ from the sites of pure silica. Higher aluminium loading (entries 17-22) induces the appearance of strong (2230 cm\(^{-1}\)) then weak/medium (≈ 2200 cm\(^{-1}\)) LAS.\[^{6,9}\] Their number increases with the aluminium content. At the same time, CO adsorption on BAS increases, and CO physisorption on silanols decreases.
Figure 6.5 Infrared spectra of CO adsorbed on Al/SiO$_2$ prepared by anhydrous CLD: (a) silica; (b) AS(3/anh); (c) AS(6/anh); (d) AS(10/anh); (e) AS(15/anh); (f) AS(25/anh); (g) AS(35/anh). BAS: Brønsted acid sites. LAS: Lewis acid sites. Numbers in brackets correspond to entries in Table 3.1.

Order of adsorption:
str. LAS $\rightarrow$ w. & med. LAS $\rightarrow$ BAS $\rightarrow$ OH groups $\rightarrow$ SiOH physisorption

strong LAS

weak and medium LAS

increasing doses of CO

weak OH groups

physisorption on SiOH

Wavenumber (cm$^{-1}$)
AS(16/1eqW) and AS(17/3eqW), prepared in the presence of water, are characterized by the presence of strong and weak/medium LAS and BAS, even at the first doses of CO (Figure 6.6). The number of strong LAS on AS(16/1eqW) is particularly high. The peak corresponding to BAS is similar in both samples. The peak corresponding to CO physisorption on silanols is better defined on AS(17/3eqW) than on AS(16/1eqW).

The integration of the peaks for CO adsorption on strong LAS (2230 cm\(^{-1}\)) and weak/medium LAS (2200 cm\(^{-1}\)), normalized by the weight of the pellet and the surface area of the sample, yields a comparative estimate of the number of sites. The fraction of strong LAS of the total LAS is estimated according to Equation 5.3 (Chapter 5).

Materials stemming from anhydrous synthesis show a decrease in the fraction of strong LAS as coverage by aluminium species increases (Figure 6.7). Under such preparation conditions, the first LAS are strong (entries 16 and 17). At high aluminium loading, the percentage of strong LAS remains constant and low. The percentage of strong LAS of AS(16/1eqW) (entry 23) is consistent with its coverage of aluminium species. Given its even

**Figure 6.6** Infrared spectra of CO adsorbed on Al/SiO\(_2\) prepared in the presence of water: (a) AS(16/1eqW); (b) AS(17/3eqW). BAS: Brønsted acid sites. LAS: Lewis acid sites. Numbers in brackets correspond to entries in Table 3.1.

Order of adsorption:
- strong LAS → weak and medium LAS → BAS → OH groups → physisorption on SiOH

![Infrared spectra of CO adsorbed on Al/SiO\(_2\)](image-url)
lower coverage, the structure of the alumina deposit of \( \text{AS}(17/3\text{eqW}) \) (entry 24) differs, with a low percentage of strong LAS. Pure \( \gamma\text{-Al}_2\text{O}_3 \) (entry 1) shows no strong LAS.

![Figure 6.7](image-url) Evolution of the fraction of strong Lewis acid sites (LAS) of the total number of LAS. Numbers in brackets correspond to entries in Table 3.1.

### 6.3.3 \( m \)-xylene isomerization

The grafting of aluminium species under anhydrous conditions first leads to an increase (entries 16-20) and then to a decrease (entry 22) in the isosurface rate of \( m \)-xylene conversion (Table 6.3, col. 3). AS(16/1eqW) and AS(17/3eqW) show values consistent with their surface ratio of exposed aluminium. The rates per exposed aluminium atom (col. 4) decrease continuously with increasing surface coverage of aluminium species. The highest rate is obtained on AS(17/3eqW).

#### Table 6.3 \( m \)-xylene conversion over Si/Al\(_2\)O\(_3\) grafted samples.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Isosurface (( \times 10^2 ) molecule.h(^{-1})nm(^{-2}))</th>
<th>Rate of ( m )-xylene converted @ 10 min (( \times 10^2 ) molecule.h(^{-1})exposed Al(^{3+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>(16)</td>
<td>AS(3/anhy)</td>
<td>20.7</td>
<td>34.5</td>
</tr>
<tr>
<td>(17)</td>
<td>AS(6/anhy)</td>
<td>31.2</td>
<td>23.6</td>
</tr>
<tr>
<td>(18)</td>
<td>AS(10/anhy)</td>
<td>47.1</td>
<td>25.0</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anhy)</td>
<td>59.1</td>
<td>10.3</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(23/anhy)</td>
<td>78.9</td>
<td>11.2</td>
</tr>
<tr>
<td>(22)</td>
<td>AS(35/anhy)</td>
<td>42.2</td>
<td>4.1</td>
</tr>
<tr>
<td>(23)</td>
<td>AS(16/1eqW)</td>
<td>43.7</td>
<td>16.3</td>
</tr>
<tr>
<td>(24)</td>
<td>AS(17/3eqW)</td>
<td>30.8</td>
<td>37.4</td>
</tr>
<tr>
<td>(1)</td>
<td>( \gamma )-alumina</td>
<td>7.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

[a] based on the total surface area.

[b] based on the surface ratio of aluminium species.
6.4 Discussion

6.4.1 Surface occupancy and distribution of aluminium species on silica

Anhydrous conditions during synthesis yield regular and uniform deposition of aluminium species on silica: The coverage is proportional to the surface density of grafted species. Infrared spectra of the CO stretching region also show the disappearance of silanols physisorbing CO, which is directly related to the coverage of aluminium species. Water during synthesis, even at low concentration (one equivalent per precursor molecule), favours the polymerization of the precursor to aggregates, which causes a lower coverage of the silica surface. The higher the water concentration, the higher the degree of aggregation. These findings agree with our previous findings based on TOF-SIMS, NMR, and TEM data (Chapter 4).

IR spectra of the OH stretching region (Figure 6.3) show that the grafting of the silica surface causes the disruption of H-bonding among silanols. Considering a “chain” model of silanols that interact with each other, the grafting of aluminium species not only consumes silanols by condensation with the OH groups, but also disturbs the long-distance interaction of these groups. When this occurs, the remaining silanols are, for the most part, isolated; they remain visible even at high aluminium loading, confirming that the coverage onto silica is not complete. New OH groups, typically found on ASAs, become visible in the OH region upon the grafting of enough aluminium. Interestingly, three of the samples (entries 16, 23, and 24), which have low alumina coverage, show bumps at about 3600 cm\(^{-1}\) to 3650 cm\(^{-1}\), emerging from a broader band of OH groups. These may result from the interaction of deposited aluminium with the silanols of the silica support.

6.4.2 Brønsted acid sites as active sites for ethanol dehydration and m-xylene isomerization

6.4.2.1 The active sites for ethanol dehydration and m-xylene isomerization

As probed by CO, the grafting of the first aluminium species (entry 16) causes a steep increase in the number of BAS (Figure 6.8.a). With increasing aluminium loading, the number of BAS increases more slowly.

For samples prepared under anhydrous conditions, the number of strong LAS first increases (particularly pronounced between entry 16 (3% Al\(_2\)O\(_3\)) and entry 17 (6% Al\(_2\)O\(_3\))), then decreases above 10 wt.% Al\(_2\)O\(_3\). Up to 10 wt.% Al\(_2\)O\(_3\), no weak/medium LAS are visible. While the number of strong LAS decreases, weak and medium LAS appear and their number increases. Thus, increasing the aluminium loading causes the weakening of the LAS.
Contrary to BAS, the evolution of the number of LAS is strongly related to the structure of the deposit. Samples prepared in the presence of water show a high number of LAS and display strong LAS, even at low coverage. γ-Al2O3 (entry 1) shows neither BAS nor strong LAS but a large number of weak LAS.

![Figure 6.8](image)

**Figure 6.8** Evolution of the number of (a) Brønsted acid sites (BAS) and (b) strong Lewis acid sites (LAS) (solid line) and weak or medium LAS (dashed line) of Al/SiO2, probed by CO adsorption followed by infrared spectroscopy. Numbers in brackets correspond to entries in Table 3.1.

The isomerization of m-xylene requires BAS.\(^{12,23,109-111}\) This is confirmed by the good correlation for entries 16 to 20, 23, and 24 between the rate of m-xylene conversion and the number of BAS as a function of the coverage of aluminium species (Figure 6.9): BAS of Al/SiO2 are responsible for m-xylene isomerization. γ-Al2O3, which has no BAS, does not catalyze m-xylene isomerization. At high aluminium loading, AS(35/anh) (entry 22) shows discrepant results: While the number of BAS probed by CO still increases, the rate of conversion of m-xylene decreases. The reason for this is not immediately clear.

The dehydration of ethanol can take place on both Lewis acid sites of alumina and Brønsted acid sites of Si/Al2O3 (Chapter 5). AS(3/anh) (entry 16) is active in both ethanol dehydration and m-xylene isomerization (Figure 6.9), despite the absence of weak LAS and a low number of strong LAS (Figure 6.8.b). Conversely, the number of BAS of this sample is high, despite its low aluminium loading (Figure 6.8.a). Although entries 16 and 17 do not have weak LAS, these materials still dehydrate ethanol (Figure 6.9). This shows that ethanol dehydration can be done on sites other than weak LAS. The evolution of the number of strong LAS, which is highest at around 10% Al2O3, does not parallel the amount of dehydrated ethanol, which is highest at around 25% Al2O3. Thus, strong LAS cannot be the exclusive sites for ethanol dehydration.
It can, thus, be postulated that the ethanol dehydration sites are a combination of BAS and LAS. Figure 6.9 gives a good correlation between the number of BAS and the amount of ethanol dehydration sites for entries 16 to 20, 23, and 24.

In Chapter 5, we showed that, on Si/Al₂O₃, the temperature of the ethanol dehydration peak is associated with the nature of the active site. In the present chapter, all the samples prepared under anhydrous conditions show similar ethanol dehydration temperatures (around 270°C). Thus, the ethanol dehydration sites of entry 16, with BAS but almost no LAS, are the same as those of entries 17 to 20. Furthermore, the dehydration temperature is higher than that of γ-Al₂O₃ (252°C) where ethanol dehydration occurs on LAS (Chapter 5). Therefore, we assume that the BAS of Al/SiO₂, detected by CO adsorption and probed by ethanol dehydration, are the active sites for \( m \)-xylene isomerization and that for samples 16 to 20 their number is probed by the amount of dehydrated ethanol.

Figure 6.9 Evolution of the \( m \)-xylene isomerization conversion rate (solid line), the amount of dehydrated ethanol (dashed line), and the number of Brønsted acid sites (BAS), as probed by CO (dotted line). Numbers in brackets correspond to entries in Table 3.1.

6.4.2.2 Turnover frequency for \( m \)-xylene isomerization

We already showed that the BAS of ASAs dehydrate ethanol, which enabled us to estimate their number and to calculate their turnover frequency (TOF) for \( m \)-xylene isomerization (Chapter 5). Based on the number of ethanol dehydration sites (Table 6.5, col. 3), and assuming that they are exclusively BAS, the turnover frequency of BAS in s\(^{-1}\)site\(^{-1}\) is calculated according to Equation 5.4.
Entries 16 to 20, i.e. materials showing consistent results between the number of BAS probed by CO, the amount of dehydrated ethanol, and the rate of conversion of \textit{m}-xylene (Figure 6.9), and having similar ethanol dehydration temperatures (Figure 6.2.a), yield comparable TOF (Table 6.4, col. 4), the average of which (4.3×10⁻⁴ s⁻¹ per BAS) is approximately 75 times lower than that obtained for a USY zeolite with very few extra-framework aluminium (CBV720 from Zeolyst, entry 32): 3.1×10⁻² s⁻¹ per BAS. Assuming that all the Al/SiO₂ materials have the same TOF, this average value enables the calculation of the number of BAS (col. 5). The number of BAS in entries 16 to 20 is the same as the number of ethanol dehydration sites. For entries 22 to 24, the number of dehydration sites is higher than the number of BAS. A non-negligible percentage (24% to 45%, col. 8) of the ethanol dehydration sites of these materials is not active in \textit{m}-xylene isomerization (vide infra).

On AS(35/anh) (entry 22), this difference might be due to the accessibility of the reactant molecules to the active sites: Figure 6.9 shows that although CO probes a higher number of BAS when the alumina loading increases from 25% (entry 20) to 35% Al₂O₃ (entry 22), ethanol dehydration and \textit{m}-xylene isomerization indicate an opposite trend. The adsorption of 2,6-lutidine, with a similar size to that of \textit{m}-xylene, followed by infrared spectroscopy, also shows a decrease in the number of BAS when the alumina loading increases from entry 20 to entry 22 (Figure 6.10). The number of BAS was calculated by integrating the areas of the absorption bands corresponding to lutidine adsorption on Brønsted acid sites at around 1610 cm⁻¹ to 1650 cm⁻¹ in infrared, normalized by the weight of the pellet and the surface area of the sample.

![Figure 6.10](image-url)  
**Figure 6.10** Evolution of the number of Brønsted acid sites (BAS) of Al/SiO₂, determined by infrared spectroscopy after 2,6-lutidine adsorption. Numbers in brackets correspond to entries in Table 3.1.
AS(16/1eqW) (entry 23) and AS(17/3eqW) (entry 24) both show a higher ethanol dehydration temperature than the materials prepared under anhydrous conditions as well as asymmetric ethanol dehydration peaks. This indicates that the active sites for ethanol dehydration are different to those of entries 16 to 22. We assume that these samples have additional sites, other than BAS, that dehydrate ethanol and contribute to a composite ethanol peak resulting from their combined effects. These sites might be LAS, which are more numerous on water-prepared samples than on the other samples (Figure 6.8b). Nonetheless, BAS are major active sites and represent between 73% and 76% of the dehydrated ethanol.

Columns 6 and 7 give the density of BAS per surface aluminium and silicon atoms. When the surface density of aluminium species increases, the density of silicon atoms decreases; thus, the number of BAS per surface silicon increases. Since the number of surface aluminium species increases faster than the number of BAS, the number of BAS per surface aluminium decreases. At low aluminium loading (AS(3/anhy)), one out of five aluminium atoms is related to a BAS.

There is a strong correlation, even for samples with a dissimilar surface structure (entries 16-20, 23, and 24), between the number of BAS, probed by different means, and the coverage by aluminium species (Figure 6.9 and Table 6.4). Conversely, despite a similar coverage, the number of LAS is higher on materials with alumina clusters (entries 23 and 24) than on materials with well-dispersed aluminium species (entries 17 and 18) (Figure 6.8b). Thus, BAS are associated with well-dispersed aluminium species, while clusters favour the presence of LAS.

Table 6.4 Density of m-xylene conversion sites and ethanol conversion sites over Al/SiO₂ grafted samples.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>EtOH dehydration sites (nm⁻²)</th>
<th>TOF (×10⁻⁴ s⁻¹site⁻¹)</th>
<th>Isosurface (nm⁻²)</th>
<th>BAS Per Al atom (10⁻² Al exposed 1⁻¹)</th>
<th>Part of EtOH sites in dehyd. (%)</th>
<th>Surface ratio of aluminium species (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(16)</td>
<td>AS(3/anhy)</td>
<td>0.12</td>
<td>4.7</td>
<td>0.14</td>
<td>22.5</td>
<td>≈100</td>
<td>≈5</td>
</tr>
<tr>
<td>(17)</td>
<td>AS(6/anhy)</td>
<td>0.20</td>
<td>4.4</td>
<td>0.20</td>
<td>15.4</td>
<td>≈100</td>
<td>11</td>
</tr>
<tr>
<td>(18)</td>
<td>AS(10/anhy)</td>
<td>0.26</td>
<td>5.0</td>
<td>0.31</td>
<td>16.3</td>
<td>≈100</td>
<td>15</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anhy)</td>
<td>0.45</td>
<td>3.6</td>
<td>0.39</td>
<td>6.7</td>
<td>≈100</td>
<td>46</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anhy)</td>
<td>0.61</td>
<td>3.7</td>
<td>0.52</td>
<td>7.3</td>
<td>≈100</td>
<td>56</td>
</tr>
<tr>
<td>(22)</td>
<td>AS(35/anhy)</td>
<td>0.50</td>
<td>-</td>
<td>0.28</td>
<td>2.7</td>
<td>≈100</td>
<td>83</td>
</tr>
<tr>
<td>(23)</td>
<td>AS(16/1eqW)</td>
<td>0.38</td>
<td>-</td>
<td>0.29</td>
<td>10.7</td>
<td>76⁻⁶</td>
<td>21</td>
</tr>
<tr>
<td>(24)</td>
<td>AS(17/3eqW)</td>
<td>0.27</td>
<td>-</td>
<td>0.20</td>
<td>24.5</td>
<td>73⁻³</td>
<td>7</td>
</tr>
</tbody>
</table>

[a] calculated based on an average TOF value of 4.25×10⁻⁴ s⁻¹site⁻¹ obtained on samples (16-20) for m-xylene conversion. These values are obtained by assuming that all the ethanol dehydration sites of these materials are BAS (equation 5.5).
[b] calculated based on the surface ratio of aluminium species.
[c] < 100 due to accessibility: a higher number of sites is accessible to ethanol than to m-xylene.
[d] < 100 due to the composite nature of the ethanol dehydration sites.
6.4.3 Comparison with Si/Al₂O₃ grafting and zeolite

Table 6.5 gives a comparison between the main features of Al/SiO₂ and those of Si/Al₂O₃ from Chapter 5, and of a H-USY that is free of extra-framework aluminium species (EFAL) (entry 32). In both Si/Al₂O₃ and Al/SiO₂ the number of BAS decreases at high loading of grafted species, but for different reasons: On Si/Al₂O₃ new species are grafted on top of the BAS at the highest loadings, whereas on Al/SiO₂, the accessibility of large molecules, such as m-xylene, to BAS might be difficult when the alumina deposit is too thick. The number of BAS per nm² is generally higher on Al/SiO₂ than on Si/Al₂O₃, but these sites are less active: The TOF for m-xylene isomerization is 3.3 times lower than on Si/Al₂O₃ and 75 times lower than on a USY zeolite with very few EFAL. This is also reflected by the average ethanol dehydration temperature (269°C), which is higher than that of the BAS of Si/Al₂O₃ (248°C) and much higher than that of the zeolite (211°C). The dehydration peak is also broader on Al/SiO₂, suggesting a larger spread in local structure. On γ-alumina, the LAS on the (100) surface are responsible for the large number of ethanol dehydration sites. The calculation of the rates of m-xylene conversion per unit of surface stresses the impact of the high surface area of zeolites: the isoweight rate of the USY zeolite is 61 and 91 times higher than on Al/SiO₂ and Si/Al₂O₃, respectively.

Table 6.5 The main catalytic properties of Al/SiO₂ and Si/Al₂O₃ materials prepared under anhydrous conditions and H-USY with very few extra-framework aluminium (EFAL).

<table>
<thead>
<tr>
<th></th>
<th>Al/SiO₂</th>
<th>Si/Al₂O₃</th>
<th>H-USY w/o EFAL (CBV720)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evolution of the number of BAS when grafting guest species under mild conditions</td>
<td>increases</td>
<td>goes through a maximum</td>
<td>-</td>
</tr>
<tr>
<td>Maximum number of BAS (nm⁻²)</td>
<td>0.52 (AS(25/anh))</td>
<td>0.18 (Sa(17/4eqW))</td>
<td>0.18</td>
</tr>
<tr>
<td>Maximum number of ethanol dehydration sites (nm⁻²)</td>
<td>0.61 (AS(25/anh))</td>
<td>0.83 (Pure γ-alumina)</td>
<td>0.18</td>
</tr>
<tr>
<td>TOF for m-xylene isomerization (s⁻¹ active site⁻¹)</td>
<td>4.3×10⁻⁴</td>
<td>1.4×10⁻³</td>
<td>3.1×10⁻²</td>
</tr>
<tr>
<td>Maximum rate of m-xylene converted @ 10 min (×10⁻² mmol.h⁻¹g⁻¹)</td>
<td>43 (AS(25/anh))</td>
<td>29 (Sa(17/4eqW))</td>
<td>2640</td>
</tr>
<tr>
<td>Average ethanol dehydration temperature (when exclusively catalyzed by BAS) (°C)</td>
<td>269</td>
<td>248</td>
<td>211</td>
</tr>
</tbody>
</table>

6.5 Conclusion

Controlled deposition of aluminium species on silica occurs under anhydrous conditions and creates Brønsted acid sites, whose number increases with the aluminium loading. Ethanol dehydration followed by thermogravimetry, combined with infrared after CO adsorption, yields the number of Brønsted acid sites and the turnover frequency of these sites for m-xylene isomerization: 4.3×10⁻⁴ s⁻¹site⁻¹. This value is 3.3 times lower than that of
Si/Al$_2$O$_3$ and 75 times lower than that of a USY zeolite with very few extra-framework aluminium. This confirms that the nature of the Brønsted acid sites strongly depends on the method of ASA synthesis. Strong Lewis acid sites also appear during grafting; they become weaker as the concentration of guest species increases. Under aqueous conditions, the grafting is less controlled and alumina agglomerates form, which possess weak and medium Lewis acid sites but no Brønsted acidity.
Chapter 7

The variety of Brønsted acid sites in amorphous aluminosilicates and zeolites

7.1 Introduction

Thermogravimetry analysis after ethanol adsorption is a relevant tool for investigating the surface ratio of silicon and aluminium species (Chapters 5 and 6).\textsuperscript{[93,94,102,114]} It enables the quantification of the number of Brønsted acid sites, which enables to calculate the turnover frequency of Brønsted catalyzed reactions, such as the isomerization of $m$-xylene. This gives the intrinsic acidity of the Brønsted acid sites. On grafted Si/Al$_2$O$_3$ the turnover frequency is $1.4 \times 10^{-3}$ s$^{-1}$site$^{-1}$, on grafted Al/SiO$_2$ $4.3 \times 10^{-4}$ s$^{-1}$site$^{-1}$ and on a H-USY zeolite with very few extra-framework aluminium (entry 32) $3.1 \times 10^{-2}$ s$^{-1}$site$^{-1}$ (Chapter 6).

IR spectroscopy enables the characterization of the surface hydroxyl groups of ASAs and zeolites. The IR spectroscopy of adsorbed CO yields the nature and relative amount of Brønsted acid sites and strong and weak/medium Lewis acid sites.\textsuperscript{[6,9,10,31]} Sites of similar strength were found in ASAs and steamed zeolites,\textsuperscript{[10]} acknowledging the complexity of the Brønsted acidity in ASAs and zeolites.\textsuperscript{[31]} By evaluating ASAs (Siral from Sasol, ex Condea) from 0 to 100% wt.% SiO$_2$, a mixed silica-alumina phase was found for compositions below 30 wt.% SiO$_2$, possessing bridged zeolitic Brønsted acid sites, as well as the encapsulation of the alumina surface by silicon species above 30 wt.% SiO$_2$ with decreasing acidity.

In this chapter, we demonstrate the variety of Brønsted acidities in zeolites and ASAs. The model Si/Al$_2$O$_3$ and Al/SiO$_2$ ASAs that were previously prepared by grafting and characterized are compared to ASAs prepared by cogelation. A cogel ASA (entry 30), prepared by mixing molecular precursors of both aluminium (aluminium sulfate) and silicon (sodium metasilicate), followed by washing, drying and calcination at 550°C, and whose structure is expected to differ from that of the grafted samples, shows a heterogeneous
structure and the presence of zeolitic sites that are not found in the ASAs made by grafting. A Siralox reference from Sasol (Siralox 30, 30 wt.% SiO₂, entry 31), obtained by impregnation of alumina with a silica gel, is compared to Si/Al₂O₃ samples that we made by grafting. We uniquely give evidence of the presence of specific structures for the BAS of ASAs made by grafting thanks to CO and ethanol adsorption followed by IR.

7.2 Results

7.2.1 Ethanol adsorption and dehydration followed by thermogravimetric analysis

Figure 7.1 gives the derivative of the weight loss during TPD on various ASAs and H-USY. The first peak at around 80°C corresponds to the desorption of ethanol; its position is the same for all samples. The second peak above 150°C corresponds to the release of ethylene from dehydration of ethanol (Chapters 5 and 6). On Si/Al₂O₃ materials prepared under anhydrous conditions (Figure 7.1.a), the ethanol dehydration peak first shifts to higher temperatures, then to lower temperatures, which is indicative of the consumption of LAS and to the formation of BAS, respectively (Chapter 5). In terms of intensity and position of the peaks, ASA(comm.) (entry 31) shows ethanol and ethylene desorption features very similar to those of SA(12/anh) (entry 3). Figure 7.1.b gives the results for ASAs and H-USY. The increasing ethanol dehydration temperature from H-USY to SA(17/anh) and AS(25/anh), for which ethanol dehydration takes place exclusively on BAS, relate to a decreasing strength of the BAS (Chapter 6). ASA(cogel) shows a low amount of ethanol desorbing, and its ethanol dehydration peak has the same position as that of H-USY. The weight loss above 250°C is ascribed to dehydroxylation.

Table 7.1 gives the amount of ethanol retained after purge, and the amount of ethanol undergoing dehydration. ASA(cogel) and γ-alumina show, respectively, the minimum and maximum values of ethanol retained after purge (col. 3). The calculation of the percentage of free alumina surface, in column 4, is based on the preferential adsorption of ethanol on alumina surfaces compared to the silica surface (Chapters 5 and 6). Given its specific crystalline structure, this calculation has no meaning for H-USY. The low amount of ethanol retained on ASA(cogel) is evidence of a highly dehydroxylated surface, without sites typical of alumina, such as LAS. Except for silica, all samples possess ethanol dehydration sites (col.5). We demonstrated that these sites are LAS on alumina, BAS on AS(25/anh), SA(17/anh) and H-USY, and a sum of LAS and BAS on SA(7/anh) and SA(12/anh) (Chapters 5 and 6).
Figure 7.1 Derivative of TPD weight loss of ethanol on ASAs and H-USY after pretreatment at 500°C: (a) Si/Al$_2$O$_3$ prepared by anhydrous CLD and commercial reference; (b) Si/Al$_2$O$_3$ (entry 4), Al/SiO$_2$ (entry 20), and cogel (entry 30) ASAs and H-USY (entry 32). Numbers in brackets correspond to entries in Table 3.1.

Table 7.1 Surface density of ethanol retained after purge and undergoing dehydration (nm$^2$) after pretreatment at 500°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Ethanol retained after purge (nm$^2$)$^{[a]}$ (col. 3)</th>
<th>Percentage of free alumina surface (%) (col. 4)</th>
<th>Ethanol undergoing dehydration (nm$^2$)$^{[a]}$ (col. 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$\gamma$-alumina</td>
<td>2.8</td>
<td>100</td>
<td>0.83</td>
</tr>
<tr>
<td>(15)</td>
<td>silica</td>
<td>1.3</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>(2)</td>
<td>SA(7/anh)</td>
<td>2.4</td>
<td>70</td>
<td>0.27</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>2.2</td>
<td>57</td>
<td>0.23</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>1.7</td>
<td>29</td>
<td>0.17</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>2.2</td>
<td>56</td>
<td>0.61</td>
</tr>
<tr>
<td>(30)</td>
<td>ASA(cogel)</td>
<td>1.1</td>
<td>0</td>
<td>0.12</td>
</tr>
<tr>
<td>(31)</td>
<td>ASA(comm.)</td>
<td>2.1</td>
<td>55</td>
<td>0.27</td>
</tr>
<tr>
<td>(32)</td>
<td>H-USY</td>
<td>1.4</td>
<td>-</td>
<td>0.18</td>
</tr>
</tbody>
</table>

$^{[a]}$ based on the total surface area.
7.2.2 Infrared spectroscopy

7.2.2.1 Infrared spectra of the OH stretching region upon ethanol adsorption

Figure 7.2 gives the difference spectra of the IR stretching region, recorded after adsorption of ethanol on alumina and Si/Al$_2$O$_3$ samples, following a pretreatment at 200°C. Ethanol adsorption on the OH groups of the support causes a decrease of intensity in the OH stretching region (3600 cm$^{-1}$ to 3800 cm$^{-1}$), and the appearance of peaks in the CH$_2$-CH$_3$ stretching region (2800 cm$^{-1}$ to 3000 cm$^{-1}$).$^{102}$ H-bonding between ethanol molecules and hydroxyl groups of the support is characterized by a broad positive band in the 3000 cm$^{-1}$ to 3600 cm$^{-1}$.$^{115}$ On alumina, ethanol molecules are mainly adsorbed on Al(VI)-OH groups of the (100) surface, as indicated by the negative peak at 3770 cm$^{-1}$. Upon heating and dehydration of ethanol, these OH groups are restored (not shown here). These observations confirm the role of the (100) surface of γ-alumina in the dehydration of ethanol, as demonstrated in Chapter 5.$^{118}$ To a lesser extent, Al-OH groups of the (110) surface (at 3790 cm$^{-1}$ and 3730 cm$^{-1}$) also contribute to the adsorption of ethanol. On SA(7/anh), ethanol adsorption takes place on silanol groups (3745 cm$^{-1}$) and OH groups of the (110) surface of alumina (3730 cm$^{-1}$). The OH groups of the (100) surface are grafted with silicon species and can no longer adsorb ethanol, hence the absence of a negative peak at 3770 cm$^{-1}$. On SA(12/anh), due to grafting of the (110) surface with silicon species, the intensity of the negative bands corresponding to the OH groups of the (110) surface (3790 cm$^{-1}$ and 3730 cm$^{-1}$) decreases. The ethanol dehydration sites of SA(17/CVD250) are exclusively BAS. On SA(17/CVD250), silanols are the main adsorption sites, but the negative band extends until 3650 cm$^{-1}$.

On alumina, the CH$_2$-CH$_3$ stretching region is characterized by four main peaks. The peaks at 2967 cm$^{-1}$ and 2926 cm$^{-1}$ are ascribed to the asymmetric stretching vibration of CH$_3$ ($\nu_a$(CH$_3$)) and CH$_2$ ($\nu_a$(CH$_2$)), respectively; the peaks at 2895 cm$^{-1}$ and 2868 cm$^{-1}$ are ascribed to the symmetric stretching vibration of CH$_2$ ($\nu_s$(CH$_2$)) and CH$_3$ ($\nu_s$(CH$_3$)), respectively.$^{102}$ H-bonding confirms the adsorption of ethanol on OH groups. From alumina to SA(7/anh), the four peaks are blue-shifted, and the intensity of $\nu_s$(CH$_3$) decreases. When the silica loading increases, $\nu_a$(CH$_3$) is red-shifted, the intensity of $\nu_a$(CH$_3$) decreases, and H-bonding is more pronounced.
Brønsted acidity of zeolites and ASAs

Figure 7.2 Infrared spectra (OH and CH$_2$-CH$_3$ stretching region) of Si/Al$_2$O$_3$ after adsorption of ethanol, following pretreatment at 200°C. (x): entries in Table 3.1; (100) or (110): surfaces of γ-alumina.

The temperature of activation of alumina impacts the type of adsorption of ethanol (Figure 7.3). Upon ethanol adsorption after a pretreatment at 400°C, no-H-bonding is visible. The negative signal in the OH region only appears for high ethanol coverage, and it is not centered at 3770 cm$^{-1}$, which indicates that most of the ethanol molecules are not adsorbed on OH groups. The absence of disturbances, in the OH stretching region, between 3750 cm$^{-1}$ and 3800 cm$^{-1}$, confirms that the (100) surface has no hydroxyl group. In fact, upon dehydroxylation of the (100) surface by pretreatment at high temperature, LAS form and become the adsorption sites of ethanol instead of OH groups. However, whatever the activation temperature, the four peaks in the CH$_2$-CH$_3$ stretching region have the same ratios of intensity and the same positions. This means that the shape of the CH$_2$-CH$_3$ stretching
region is not sensitive to the nature of the adsorption site (BAS or LAS), but rather to the local environment of the site (aluminium or silicon atoms).

**Figure 7.3** Infrared spectra (OH and CH\textsubscript{2}-CH\textsubscript{3} stretching region) of γ-alumina (entry 1 in Table 3.1) after adsorption of ethanol, following pretreatment at 200°C and 400°C.

Figure 7.4 compares the results of ethanol adsorption on ASAs (SA(17/CVD250) and AS(25/anh)) to that on a zeolite (H-USY), following a pretreatment at 200°C. On AS(25/anh), the OH and CH\textsubscript{2}-CH\textsubscript{3} stretching regions are very similar to that of SA(17/CVD250), and silanols are the main adsorption sites of ethanol. On H-USY, ethanol first adsorbs on OH groups of the supercages (SiOHAl HF, 3630 cm\textsuperscript{-1}) and sodalite cages (SiOHAl LF, 3564 cm\textsuperscript{-1}),\textsuperscript{116} then finally on silanols, which confirms that ethanol is a good probe of the BAS. As for ASAs, H-bonding of ethanol is visible and the CH\textsubscript{2}-CH\textsubscript{3} stretching region is dominated by the peak of $\nu_a$(CH\textsubscript{3}). Thus, this stretching region has a characteristic shape when ethanol is adsorbed on BAS of ASAs and zeolites. However, contrary to H-USY, there is no wavenumber specific to the OH stretching of BAS of ASAs. These might be hidden because of the appearance of the broad H-bonding band.
7.2.2.2 Infrared spectra of the OH stretching region and CO stretching region upon CO adsorption

Figure 7.5 gives the evolution of the OH and CO stretching regions of H-USY upon CO adsorption following a pretreatment at 450°C. Due to the formation of the OH-CO bond, the stretching wavenumber of the adsorbing OH groups is shifted towards lower values. On a difference spectrum, the wavenumber shift due to adsorption on OH groups results in a negative peak indicating the original wavenumber of the OH group, and a positive band at lower wavenumber relating to the new OH-CO complex.\(^{31}\) The intensity of the shift (\(\Delta v\)) is proportional to the acidic strength of the OH group.\(^{10}\) CO first adsorbs on strong Lewis acid sites (2230 cm\(^{-1}\), ①) (Figure 7.5.a). This causes a shift of the OH stretching peak of isolated silanols (3745 cm\(^{-1}\)) and SiOHAl HF (3632 cm\(^{-1}\)) towards higher wavenumbers. This phenomenon was observed by Crépeau et al. and it was ascribed to thermal effects caused by the temperature gap between CO and the temperature of the cell.\(^9\) One can also postulate that silanol groups are disturbed due to the introduction of the first CO molecules. Further
adsorption of CO molecules is characterized by a peak at 2180 cm\(^{-1}\) (CO-OH(a)) in the CO region (②). The simultaneous appearance of a negative band at 3632 cm\(^{-1}\) in the OH stretching region confirms the adsorption on strong BAS (SiOHAl HF, OH(a)). Upon CO adsorption, this OH band is shifted to 3280 cm\(^{-1}\) (CO-OH(a)). The CO adsorption on silanols (③) causes the appearance of several peaks in the CO stretching region (CO-OH(b) and (c)). The silanol peak (OH(b-c)) is shifted to 3660 cm\(^{-1}\) (CO-OH(b-c)) upon CO adsorption.

**Figure 7.5** Progressive adsorption of CO on H-USY (entry 32) followed by infrared spectroscopy after pretreatment at 450°C.

Figure 7.6 gives the parallel evolution of the OH and CO stretching region of AS(25/anh) upon the adsorption of CO following a pretreatment at 450°C. The first CO molecules are adsorbed on strong (2230 cm\(^{-1}\), ①) then weak/medium LAS (2200 cm\(^{-1}\), ②)
(Figure 7.6.a).\textsuperscript{[6,9,10,103]} Further CO adsorption causes the appearance of a peak at 2177 cm\textsuperscript{-1}, which is associated to adsorption on BAS (3).\textsuperscript{[9]} As for zeolites (Figure 7.5), negative and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Progressive adsorption of CO on Al/SiO\textsubscript{2} (AS/25/anh, entry 20) followed by infrared spectroscopy after pretreatment at 450°C.}
\end{figure}
positive bands are visible in the OH stretching region. Studies about ASAs have shown the presence of positive bands corresponding to perturbed OH bands, but they have failed to locate the original wavenumber of BAS, which has led to various hypotheses aiming at explaining its absence: structure of BAS differing from that of zeolites\textsuperscript{9,28} or low number of bridged sites,\textsuperscript{6} for example. Here, we observe both the shifted wavenumber of the CO-OH complex starting at around 3400 cm\textsuperscript{−1} (CO-OH(A)), the original wavenumber of the BAS at 3640 cm\textsuperscript{−1}, (OH(A)) and the stretching frequency of CO on BAS at 2177 cm\textsuperscript{−1} (CO-OH(A)). In agreement with the observations of Cairon et al. and Crépeau et al.,\textsuperscript{9,10} CO is then chemisorbed on weaker OH groups (④), hence higher wavenumber for CO-OH(B) (3550 cm\textsuperscript{−1}) and lower wavenumber for CO-OH(B) (2157 cm\textsuperscript{−1}). The right part of the silanol peak (3745 cm\textsuperscript{−1}) becomes negative, which suggests that weak-acidic silanols in interaction with each other are the adsorbing sites (OH(B)). Physisorption of CO causes the appearance of a third component in the OH stretching region (CO-OH(C), 3660 cm\textsuperscript{−1}) and in the CO stretching region (CO-OH(C), 2135 cm\textsuperscript{−1}). The global silanol peak becomes negative, which shows that both isolated and interacting silanols undergo the physisorption of CO.

The OH and CO stretching regions of SA(17/anh), SA(17/4eqW) and SA(17/CVD250) (entries 4, 5, and 8, respectively) upon CO adsorption after pretreatment at 450°C are similar to the OH and CO stretching region of AS(25/anh). However, no negative band for BAS in the OH region nor specific peak for BAS in the CO region is detected.

The relative number of LAS and BAS of each sample are compared by integrating the corresponding band, in the CO stretching region, at saturation of its intensity. The values, reported in Table 7.2, are normalized by the weight of the wafer and the surface area. Entries 3 to 5 and 31 show no peak that can be exclusively ascribed to BAS, hence no values are reported. ASA(comm.) has the same number of strong LAS as SA(12/anh) and the same amount of weak/medium LAS as SA(17/anh). Consistent with its low amount of extra-framework aluminium species, H-USY shows almost no LAS.

Table 7.2 Number of sites probed by CO (a.u. isosurface data: intensity of the band in the CO region after integrating and dividing by the weight of the wafer and the surface area of the sample).
Brønsted acidity of zeolites and ASAs

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Activation temperature (°C)</th>
<th>Strong LAS</th>
<th>Weak/medium LAS</th>
<th>BAS[a]</th>
<th>Silanols</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>450</td>
<td>39</td>
<td>374</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>450</td>
<td>76</td>
<td>272</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>250</td>
<td>34</td>
<td>333</td>
<td>-</td>
<td>605</td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>450</td>
<td>73</td>
<td>441</td>
<td>-</td>
<td>802</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>250</td>
<td>88</td>
<td>219</td>
<td>781</td>
<td>468</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>450</td>
<td>27</td>
<td>152</td>
<td>547</td>
<td>456</td>
</tr>
<tr>
<td>(31)</td>
<td>ASA(comm.)</td>
<td>450</td>
<td>38</td>
<td>278</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(32)</td>
<td>H-USY</td>
<td>450</td>
<td>8</td>
<td>14</td>
<td>1250</td>
<td></td>
</tr>
</tbody>
</table>

[a] Entries 3-5 and 31: no peak specific to BAS. Entry 32: integration of all the bands corresponding to CO adsorption on OH groups.

On ASAs, there is an impact of the activation temperature of the sample on the amount of CO adsorbed on BAS and LAS. Figure 7.7 gives the results for AS(25/anh) and SA(17/4eqW), which possess the highest number of BAS of Si/Al₂O₃ and Al/SiO₂, respectively (see Chapters 5 and 6), on the OH and CO stretching regions. At high activation temperature, the number of LAS (2180 cm⁻¹ to 2240 cm⁻¹) and BAS (OH(A)) of AS(25/anh) (Figure 7.7.a) is lower; physisorption (OH(C)) is constant. Integration of the peaks (Table 7.2) confirms a lower number of strong LAS (-69%), weak/medium LAS (-31%), and BAS (-30%) at 450°C versus 250°C. Although their quantification is more difficult in the absence of a proper peak to integrate in the CO region, the number of silanol groups of SA(17/4eqW) (Figure 7.7.b), measured during physisorption of CO, is constant whatever the activation temperature. On SA(17/4eqW), the number of strong and weak/medium LAS increases (+115% and +32%, respectively) when the activation temperature increases; the number of silanol groups of SA(17/4eqW) also increases (≈ +30%). The negative peak at around 3600 cm⁻¹ in the OH stretching region indicates the presence of BAS at a lower wavenumber than for AS(25/anh) (3640 cm⁻¹), and which are hardly visible at high activation temperature. The CO dose which is adsorbed on the BAS of SA(17/4eqW) leads to a more intense CO-OH(A/B) band in the CO region, at a higher wavenumber than for the following CO doses (2173 cm⁻¹ vs. 2156 cm⁻¹), as observed in Chapter 5.
7.2.3 Isomerization of m-xylene

Figure 7.7 Impact of the activation temperature on CO adsorption: (a) AS(25/anh); (b) SA(17/4eqW). Dotted lines correspond to CO adsorption on BAS.

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Table 7.3 gives the rates of conversion of \(m\)-xylene. These and the turnover frequency (TOF) of the BAS of Si/Al\(_2\)O\(_3\) (entries 2, 3, and 4), Al/SiO\(_2\) (entry 20), and H-USY (entry 32) were determined based on the amount of ethanol dehydration exclusively occurring on BAS, as calculated in Chapters 5 and 6. ASA(cogel) shows the highest isoweight and isosurface rates of conversion, and the highest TOF of the ASAs. However, compared to SA(17/anh) and AS(25/anh), showing the best catalytic performance of their respective category, the number of BAS per surface unit is low. Furthermore, the level of conversion and the TOF are much lower than for H-USY. The isosurface conversion rate of ASA(comm.) is intermediary between that of SA(12/anh) and that of SA(17/anh); but due to a higher surface area, its isoweight conversion rate is much higher. Considering that the surface structure of ASA(comm.) can be rationalized as that of a Si/Al\(_2\)O\(_3\) material (vide infra), hence by using the same TOF, the number of BAS per surface unit can be estimated. The value is, again, between those of SA(12/anh) and SA(17/anh).

### Table 7.3 \(m\)-xylene conversion over ASAs and zeolites.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Rate of (m)-xylene converted @ 10 min</th>
<th>TOF ((\times 10^3) s(^{-1}) site(^{-1}))</th>
<th>BAS (nm(^2))[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>SA(7/anh)</td>
<td>21.8</td>
<td>1.4</td>
<td>0.04</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>54.0</td>
<td>1.4</td>
<td>0.11</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>94.1</td>
<td>1.4</td>
<td>0.19</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>78.9</td>
<td>0.4</td>
<td>0.52</td>
</tr>
<tr>
<td>(30)</td>
<td>ASA(cogel)</td>
<td>259.6</td>
<td>6.0</td>
<td>0.12</td>
</tr>
<tr>
<td>(31)</td>
<td>ASA(comm.)</td>
<td>80.0</td>
<td>(1.4^{[a]})</td>
<td>0.16</td>
</tr>
<tr>
<td>(32)</td>
<td>H-USY</td>
<td>2034.8</td>
<td>31.4</td>
<td>0.18</td>
</tr>
</tbody>
</table>

[a] based on the hypothesis that ASA(comm.) is similar to Si/Al\(_2\)O\(_3\) material, for which the TOF is \(1.4\times 10^{-3}\) s\(^{-1}\) site\(^{-1}\).

[b] based on the TOF.

### 7.3 Discussion

#### 7.3.1 Zeolitic Brønsted acid sites in ASAs

Table 7.4 summarizes the main conclusions about Brønsted acidity of ASAs and zeolite. The ethanol dehydration temperature of ASA(cogel) is lower than that of other ASAs and equal to that of H-USY. It means that, contrary to the other ASAs, ASA(cogel) has BAS of zeolitic strength. The presence of such strong BAS was already demonstrated in ASAs prepared by cogelation and homogeneous deposition of aluminium on silica using selective poisoning of these site by lutidiline during \(m\)-xylene isomerization.\[^{[30]}\] However, the TOF for \(m\)-xylene isomerisation of ASA(cogel) is five times lower than that of H-USY. ASA(cogel) and H-USY have the same intrinsic activation energy for catalytic reactions but different rates because of different surface structures affecting the adsorption and the number of active
sites.\textsuperscript{35} The higher pore diameter of ASA(cogel) (ca. 20 nm) compared to the micropores of the zeolite and amorphous structure, resulting in a lower confinement and fitting of the reactant molecule to the pore and the active site, lowers the heat of adsorption. The low amount of ethanol retained on the surface of ASA(cogel) after purge (Table 7.2) and the large amount of water lost during pretreatment (20\% of the total sample weight) indicate that the surface of the sample is sensitive to heating and highly dehydroxylated upon activation at 500\°C. The study of the OH stretching region in IR spectroscopy confirms the low number of silanol groups (not shown here). Moreover, the surface contains almost no aluminium species that form LAS, which would retain ethanol even after dehydroxylation. Thus, the cogelation synthesis does not lead to a homogeneous polymerization of species, and most of the minor component (silicon species) ends up on the outermost surface of the material. The core contains the major component (aluminium species), which explains the high pore diameter and low surface area. The few aluminium species on the surface might be incorporated in the silica matrix, and would lead to zeolitic BAS (Table 7.4), by bridging silanols.\textsuperscript{3,117} In contrast, the surface of H-USY is more stable against thermal deactivation (10\% weight loss during activation) and shows a higher amount of ethanol retained after purge (Table 7.1); thus, its surface silanols condensate to a lesser extent than those of ASA(cogel) upon heating. The stretching frequency of the BAS of ASA(cogel) could not be determined upon CO adsorption followed by IR spectroscopy; this can be the consequence of the low surface area and number of BAS, and the high amount of water despite pretreatment.

Table 7.4 Main conclusions on the BAS of grafted and commercial ASAs and zeolites.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>Type of Brønsted acid site (BAS)</th>
<th>Evolution of the number of BAS with increasing temperature</th>
<th>Characteristic wavenumber in IR (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>ASA (Si/Al\textsubscript{2}O\textsubscript{3})</td>
<td>decreases (upon heating, formation of a strong Lewis acid site and a silanol)</td>
<td>3600\textsuperscript{[a]}</td>
</tr>
<tr>
<td>(5)</td>
<td>SA(17/4eqW)</td>
<td>ASA (Si/Al\textsubscript{2}O\textsubscript{3})</td>
<td>decreases</td>
<td>3640</td>
</tr>
<tr>
<td>(8)</td>
<td>SA(17/CVD250)</td>
<td>ASA (Si/Al\textsubscript{2}O\textsubscript{3})</td>
<td>decreases</td>
<td>3630\textsuperscript{[b]}</td>
</tr>
<tr>
<td>(31)</td>
<td>ASA(comm.)</td>
<td>ASA (Si/Al\textsubscript{2}O\textsubscript{3})</td>
<td>stable</td>
<td>3640</td>
</tr>
<tr>
<td>(20)</td>
<td>AS(25/anh)</td>
<td>ASA (Si/Al\textsubscript{2}O\textsubscript{3})</td>
<td>decreases</td>
<td>3630\textsuperscript{[b]}</td>
</tr>
<tr>
<td>(32)</td>
<td>H-USY</td>
<td>zeolitic</td>
<td>stable</td>
<td>3630\textsuperscript{[b]}</td>
</tr>
<tr>
<td>(30)</td>
<td>ASA(cogel)</td>
<td>ASA (Si/Al\textsubscript{2}O\textsubscript{3})</td>
<td>decreases</td>
<td>3640</td>
</tr>
</tbody>
</table>

\[a\] as found in SA(17/4eqW), which contains the highest number of active sites, following a pretreatment at 250\°C before CO adsorption.

\[b\] the stretching frequency of Brønsted acid sites of ASA(cogel) is supposed to be the same as that of H-USY, but no evidence was found in IR-CO.

### 7.3.2 Diversity of Brønsted acid sites in zeolites and ASAs

In all ASAs other than ASA(cogel), the ethanol dehydration temperature is higher than that of H-USY, which indicates higher activation energy and lower strength of the site. Hence, they are of a different nature (Table 7.4). Such ASAs may, however, catalyze the
isomerization of \textit{m}-xylene to its products. This proves that sites other than zeolitic BAS and weaker than zeolitic BAS may catalyze the isomerization of \textit{m}-xylene, which contradicts former results.\textsuperscript{30}

Based on computational data, sites that are specific to ASAs have been proposed.\textsuperscript{32} The temperature range in which these pseudo-bridging silanols (PBS) can be obtained is narrow, as a certain hydration state of the surface is required. In the present study, CO adsorption on Si/Al\textsubscript{2}O\textsubscript{3} after activation at 250°C or 450°C shows that the number of both strong LAS and silanols increases and BAS are less visible when the activation temperature increases (Figure 7.7.b). Basing on our model of BAS for Si/Al\textsubscript{2}O\textsubscript{3} exposed in Chapter 5, it means that the interaction between the aluminium species and the silicon species, which can be assimilated to a PBS structure, is weaker at high temperatures, leaving the two species isolated and causing the increase of the strong Lewis acidity and the decrease of the Brønsted acidity. On Al/SiO\textsubscript{2}, the number of both LAS and BAS decreases when increasing the activation temperature, while the number of silanols remains constant (Figure 7.7.a). There is no clear explanation for this observation, but it confirms the role of the hydration state of the surface in the number of BAS. NMR on AS(25/anh) showed no change in the distribution of coordination of the aluminium atoms upon adsorption of ethanol, as it is expected for PBS.

In the OH stretching region of the infrared spectra of AS(25/anh) upon CO adsorption, a Brønsted acid site with a stretching frequency of 3640 cm\textsuperscript{-1} can be identified in Al/SiO\textsubscript{2} (Figure 7.6). Because of the lower surface area of AS(25/anh), the negative peak observed during CO adsorption is less intense than those of H-USY. As a consequence, this peak is hidden by the H-bonding following the adsorption of ethanol (Figure 7.4). The broadness of the band at 3640 cm\textsuperscript{-1} in IR-CO indicates a certain variety of sites, which correlates to a broad ethanol dehydration peak (Figure 7.1.b), contrary to H-USY. The lower wavenumber of the BAS of Si/Al\textsubscript{2}O\textsubscript{3} (3600 cm\textsuperscript{-1}) and the lower ethanol dehydration temperature (Figure 7.1.b) confirm a different nature and environment of the sites between the two types of ASAs.

On H-USY, we show that both the dehydration of ethanol and the adsorption of CO followed by IR probe the BAS of the supercages. These sites show constant ethanol dehydration temperature and amount of ethanol dehydrated whatever the pretreatment temperature. The number of BAS probed by CO adsorption is similar after activation at 250°C and 450°C (not shown here), which confirms the high stability to temperature of the bridged BAS of H-USY. The shift of the OH band (\(\Delta\nu\)) upon CO adsorption is higher for the BAS of H-USY (\(\Delta\nu = 352\) cm\textsuperscript{-1}) than for the BAS of AS(25/anh) (\(\Delta\nu = 240\) cm\textsuperscript{-1}) and for the silanol groups (\(\Delta\nu = 85\) cm\textsuperscript{-1} for both H-USY and AS(25/anh)), which is consistent with a
higher acidity of the BAS of the zeolite.\textsuperscript{10} A similar conclusion had been obtained by calculating the turnover frequencies (TOF) of the BAS of these materials for \textit{m}-xylene isomerization (Chapter 6).

We found no impact of the type of zeolite (H-USY with and with very few EFAL, H-ZSM-5) nor of the activation conditions (200°C or 500°C) on the dehydration temperature of ethanol (ca. 210°C, Figure 7.8.). Figure 7.8 gives the derivative of the weight loss during TPD on various zeolites. The values of the derivatives are normalized by the surface area of each sample. The first peak at around 80°C corresponds to the desorption of ethanol. The second peak at around 210°C corresponds to ethylene stemming from the dehydration of ethanol. The nature of the zeolite (H-ZSM-5 or USY) and the aluminium content impact the amount of ethanol dehydrated, but the dehydration temperature is the same for all samples and activation temperatures. Table 7.5 gives the number of Brønsted acid sites (BAS), quantified by the amount of ethanol dehydrated. One every two aluminium atoms of H-ZSM-5 forms a BAS and one every four or five aluminium atoms of USY forms a BAS. CBV 712, which possesses extra framework aluminium species (EFAL), shows the lower ratio of BAS per aluminium atom.

![Figure 7.8](image)

**Figure 7.8** Impact of the activation temperature on CO adsorption: (a) AS(25/anh); (b) SA(17/4eqW). Dotted lines correspond to CO adsorption on BAS.

However, the nature of the intermediate leading to ethylene, either a carbenium ion\textsuperscript{92} or an alkoxy\textsuperscript{93}, is debated. On alumina, the reactivity of ethanol depends on the activation temperature of the catalyst. After a pretreatment at 500°C, ethanol is adsorbed at room temperature on the LAS of the (100) surface, and is further dehydrated upon heating at ca.
Table 7.5 Number of Brønsted acid sites (BAS) on various zeolites.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Isosurface (nm²)</th>
<th>BAS Per Al atom (Al atom⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>0.75</td>
<td>0.51</td>
</tr>
<tr>
<td>H-USY CBV 760</td>
<td>0.11</td>
<td>0.24</td>
</tr>
<tr>
<td>H-USY CBV 720</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>NH₄-USY CBV 712</td>
<td>0.45</td>
<td>0.20</td>
</tr>
</tbody>
</table>

250°C according to a mechanism of the E₂-type, i.e. concerted.¹⁹ Our results show that after a pretreatment at 200°C, ethanol is adsorbed on the Al(VI)-OH groups of the (100) surface. Contrary to the OH groups of silica, these sites are strong enough not to desorb ethanol upon heating at 200°C. Above 200°C LAS are formed, which enables the formation of ethoxy species. These species are further transformed into ethylene upon heating at ca. 270°C. In a recent study, Phung et al. claim that the formation of ethoxy species on alumina occurs whatever the hydroxylation state of the surface.¹¹⁸ However, the more silicon atoms are grafted on the surface of alumina, the smaller the effect of the pretreatment temperature on the ethanol dehydration temperature. This confirms that the active Lewis acid sites of the bare alumina surface are responsible for the lower ethanol dehydration temperature after pretreatment at 500°C. On Al/SiO₂ materials, this effect of the pretreatment temperature is limited (between 1°C and 7°C).

7.3.3 Grafted ASAs as a model for the variety of commercial ASAs

Our ASA(comm.) is prepared by impregnation of alumina, obtained by hydrolysis of an aluminium alkoxide, with orthosilicic acid.¹¹⁹ The results obtained for this sample (percentage of free alumina surface, position of the ethanol dehydration peak, number of strong and weak/medium LAS, and isosurface rate of conversion of m-xylene) are systematically close to those of SA(12/anh), despite dissimilar synthesis techniques. Thus, the deposition of silicon species must proceed in a similar way, that leads to the stepwise grafting of the γ-alumina facets. Assuming that ASA(comm.) has the same BAS as Si/Al₂O₃ materials (Table 7.4), hence the same turnover frequency for m-xylene isomerization (TOF), the distribution of species on the surfaces can be calculated (Table 7.6). The results confirm the partial coverage of the facets of ASA(comm.) in a similar way as SA(12/anh). This conclusion confirms and provides further clarification on the deposition process of silicon species in Siral materials as described by Daniell et al.⁶ These materials do not possess bridged zeolitic BAS.
Table 7.6 Percentage of free (100) and (110) surfaces on Si/Al₂O₃ and ASA(comm.).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Part of free (100) surface (%)</th>
<th>Part of free (110) surface (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>SA(7/anh)</td>
<td>27</td>
<td>81</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td>(4)</td>
<td>SA(17/anh)</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>(31)</td>
<td>ASA(comm.)</td>
<td>14</td>
<td>65</td>
</tr>
</tbody>
</table>

7.4 Conclusion

Zeolitic-like Brønsted acid sites are found on an ASA prepared by cogelation (20% SiO₂), despite a heterogeneous core-shell structure exhibiting essentially silicon surface species. Grafted ASAs possess specific Brønsted acid sites that differ from those of zeolites, with high sensitivity to temperature. The grafting approach of Si/Al₂O₃ materials that we previously described, including stepwise grafting of silicon species on the facets of γ-alumina, is convincingly extended to a commercial ASA reference (Siralox). We confirm the relevance of ethanol as a probe of the Brønsted acid sites of ASAs and zeolites and OH and Lewis acid sites of γ-alumina.
Chapter 8

The behaviour of amorphous aluminosilicates towards aging by high-temperature steaming

8.1 Introduction

The use of amorphous aluminosilicates (ASAs) is very common in catalysis due to their Brønsted acidity. However, when submitted to harsh thermal and mechanical conditions in reactors, these catalysts can undergo structural changes that alter their properties. From an industrial point of view, maintaining the catalytic properties at a high level over time and temperature is a major issue. Paradoxically, the changes in structure and texture induced by a thermal or hydrothermal treatment can also be a way to improve the selectivity, stability, and catalytic activity of catalysts: There are many examples of hydrothermal dealumination of zeolites to improve their stability, such as the so-called ultrastable Y zeolites (USY). Roy et al. found that the catalytic activity of a Fe-ZSM-5 zeolite is enhanced due to the dealumination and consecutive formation of oxygen vacancies that change the properties of the iron species. Steaming, i.e. post-treatment in the presence of water at high temperature, is also used to create hierarchical porosity in zeolites, which associates both micro- and mesoporosity to enable a greater access of the reactants to the active sites.

The grafting of silicon species on alumina enhances its stability during thermal and hydrothermal treatments by limiting the diffusion of surface aluminium species that are precursors of sintering. Similarly, the collapse of the silica structure during steaming is limited when depositing aluminium species on its surface by avoiding diffusion of Si4+ species or dehydroxylation.

In this chapter, we compare the effect of steaming on Si/Al2O3 and Al/SiO2 materials prepared by grafting. We chose a Si/Al2O3 sample with only partial coverage of the γ-alumina facets, especially the (110) surface where Brønsted acid sites are created by the deposition of
silicon species (Chapter 5). The steaming of SA(12/anh) (entry 3) and AS(15/anh) (entry 19) was performed in a vertical furnace at 850°C for 2 h under air and gaseous water flow, and led to SA(12/steam) (entry 28) and AS(15/steam) (entry 29), respectively. We followed the evolution and texture (N₂ adsorption) and structure (NMR) after steaming. The catalytic activity tom-xylene isomerization was evaluated, and the evolution of the nature and amount of acid sites was estimated by CO adsorption followed by IR spectroscopy.

8.2 Results

8.2.1 Adsorption of ethanol followed by thermogravimetry

The amount of retained ethanol after purge depends on the ratio of aluminium and silicon surface species. The values reported in Table 8.1 (col. 3) enable the calculation of the percentage of surface alumina species, by comparing the amount of ethanol adsorbed to a scale (from 0 to 100%) where silica is the minimum (1.3 EtOH·nm⁻²) and γ-alumina is the maximum (2.8 EtOH·nm⁻²) (col. 4). The percentage of surface alumina species decreases by one fourth after steaming of SA(12/anh) (43% vs. 57%). The amount of ethanol retained on AS(15/steam) is even lower than that on silica, so that its surface has no aluminium species, contrary to AS(15/anh) for which half of the surface possesses aluminium species.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>Ethanol retained after purge (nm⁻²)</th>
<th>Percentage of surface aluminium species (%)</th>
<th>Isosurface (nm⁻²)</th>
<th>EtOH undergoing dehydration (×10⁻², exposed Al⁻¹)</th>
<th>Percentage of ethanol dehydrated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td>2.8</td>
<td>100</td>
<td>0.83</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>1.3</td>
<td>0</td>
<td>0.00</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>2.2</td>
<td>57</td>
<td>0.23</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>(28)</td>
<td>SA(12/steam)</td>
<td>1.9</td>
<td>43</td>
<td>0.22</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>2.0</td>
<td>46</td>
<td>0.45</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>(29)</td>
<td>AS(15/steam)</td>
<td>0.9</td>
<td>0</td>
<td>0.10</td>
<td>-</td>
<td>11</td>
</tr>
</tbody>
</table>

[a] based on the total surface area.
[b] calculated on the basis of the density of accessible surface aluminium atoms.
[c] relative to total EtOH desorbed during TPD.

Figure 8.1 gives the derivative of the weight loss during TPD of ethanol on Si/Al₂O₃ and Al/SiO₂ materials, normalized by the surface area of each sample. The first peak at ca. 80°C corresponds to the desorption of ethanol and the second peak, above 200°C, corresponds to the release of ethylene after dehydration of ethanol. On silica, there is no peak associated to the release of ethylene. The ethanol peak of AS(15/steam) is smaller than that of silica, which is indicative of a dehydroxylated surface and had been measured by the low amount of
ethanol retained after purge, and it has no ethylene peak contrary to AS(15/anh). The ethylene peak of SA(12/steam) is less intense than that of SA(12/anh), and its maximum temperature is slightly higher (272°C vs. 270°C). The temperature of the ethylene peak of alumina is the lowest of all samples.

![Figure 8.1](image)

**Figure 8.1** Derivative of TPD weight loss of ethanol on alumina, silica, and ASAs, before and after steaming, after activation at 500°C. Numbers in brackets correspond to entries in Table 3.1.

The amount of ethanol dehydrated (Table 8.1) is calculated basing on the surface area of each sample (col. 5) and on the percentage of surface aluminium species (col. 6). Maximum amounts are obtained on pure alumina, where the dehydration sites are LAS. Moreover, alumina has the highest percentage of ethanol dehydrated of the total ethanol retained after purge (col. 7). After steaming of SA(12/anh), the amount of ethanol dehydrated is stable, despite the loss of surface aluminium species. Only 11% to 12% of the ethanol retained after purge is dehydrated. The amount of ethanol dehydrated on AS(15/steam) is considerably reduced compared to AS(15/anh) (-78%) and the percentage of ethanol converted diminishes. However, this is more than silica, for which no dehydration of ethanol occurs.

### 8.2.2 m-xylene isomerization

Table 8.2 gives the results of m-xylene conversion obtained after 10 min on stream and calculated basing on the surface area and the percentage of surface aluminium of each sample. Alumina and silica show the lowest conversion values. The isosurface conversion rate of SA(12/steam) is lower than that of SA(12/anh), but due to a lower percentage of surface
aluminium species, the conversion rate per aluminium atom is higher. The conversion rate of AS(15/anh) decreases after steaming (-44%).

Table 8.2 m-xylene conversion.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>Isosurface (\times10^{-2}) molecule.h^{-1}nm^{-2}[^{[a]}]</th>
<th>Rate of m-xylene converted @ 10 min (\times10^{-2}) molecule.h^{-1}exposed Al^{-1}[^{[b]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(\gamma)-alumina</td>
<td>7.9</td>
<td>0.6</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>54.0</td>
<td>7.6</td>
</tr>
<tr>
<td>(28)</td>
<td>SA(12/steam)</td>
<td>45.6</td>
<td>8.4</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>59.1</td>
<td>10.3</td>
</tr>
<tr>
<td>(29)</td>
<td>AS(15/steam)</td>
<td>32.9</td>
<td>-</td>
</tr>
</tbody>
</table>

[^{[a]}]: based on the total surface area.
[^{[b]}]: based on the surface density of aluminium species.

8.2.3 Texture

The three main textural features of the materials before and after steaming (Table 8.3, entries 3, 28, 19, and 29) are compared to the textural properties of the original supports (entries 1 and 15). The steaming of SA(12/anh) leads to a slight decrease of the surface area (-6%), while the pore volume increases but remains lower than that of alumina (also visible in Figure 8.2.a). Conversely, the mean pore diameter of SA(12/steam) is larger than that of SA(12/anh) and alumina: The whole pore size distribution of alumina is retained after grafting and steaming (Figure 8.3.a), but SA(12/steam) has a higher fraction of larger mesopores and a lower fraction of smaller mesopores than SA(12/anh). The steaming of AS(15/anh) causes a sharp decrease of the surface area (-58%). The pore diameter is higher than that of AS(15/anh) and silica: The whole pore size distribution is deeply modified and shifts towards higher values (Figure 8.3.b). There is a loss of pore volume after steaming (-34%), which is only half of that of silica (Figure 8.2.b).

Table 8.3 Textural features.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>(S_{BET}) (m².g⁻¹)</th>
<th>Pore volume (mL.g⁻¹)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(\gamma)-alumina</td>
<td>235</td>
<td>0.52</td>
<td>7.3</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td>550</td>
<td>0.84</td>
<td>6.4</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>180</td>
<td>0.39</td>
<td>7.0</td>
</tr>
<tr>
<td>(28)</td>
<td>SA(12/steam)</td>
<td>170</td>
<td>0.44</td>
<td>8.1</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>400</td>
<td>0.64</td>
<td>6.0</td>
</tr>
<tr>
<td>(29)</td>
<td>AS(15/steam)</td>
<td>170</td>
<td>0.42</td>
<td>8.8</td>
</tr>
</tbody>
</table>
8.2.2 NMR

Figure 8.4 gives the $^{29}$Si CP-MAS NMR spectra of SA(12/anh) and SA(12/steam). Except the noisier signal of SA(12/steam) that comes from a smaller acquisition time, the resonances show great similarity. It means that steaming does not lead to agglomeration of the dimeric silicon species that populate the surface of SA(12/anh). The $^{27}$Al NMR spectra are the same before and after steaming (not shown here).

Figure 8.5 gives the $^{27}$Al NMR spectra of AS(15/anh) and AS(15/steam). The three main peaks at around 0 ppm, 30 ppm and 60 ppm correspond to six-, five- and four-coordinated aluminium species (Chapter 4). The steaming leads to a greater number of five-coordinated species while the number of four- and six-coordinated species decreases. The $^{29}$Si NMR spectra are similar before and after steaming (not shown here).
8.2.3 CO adsorption followed by infrared spectroscopy

8.2.3.1 Infrared spectra of the OH stretching region

Figure 8.6 gives the impact of steaming on the OH stretching region of alumina and Si/Al$_2$O$_3$ (left panel). The ascription of each band to a local OH structure is based on the DFT calculations of Digne et al.$^{[34]}$ The grafting of silicon species on alumina in anhydrous
Effect of steaming

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conditions (entry 3) causes the disappearance of the OH bands characteristic of the (100) surface \(3770 \text{ cm}^{-1}\) and (110) surface \(3793 \text{ cm}^{-1}\) of alumina, the attenuation of the band at 3730 cm\(^{-1}\), and the appearance of silanol species \(3744 \text{ cm}^{-1}\). The band at 3590-600 cm\(^{-1}\) is attenuated and a broad signal, due to the interaction of AlOH and SiOH species, appears at around 3610 cm\(^{-1}\). After steaming, SA(12/steam) (entry 28) shows a peak at 3790 cm\(^{-1}\) which was no longer visible on SA(12/anhydrous). Apart from this peak the rest of the spectra, especially the presence of silanol groups \(3744 \text{ cm}^{-1}\) and a shoulder at 3730 cm\(^{-1}\), is similar to that of SA(12/anhydrous).

On Al/SiO\(_2\) (right panel), the grafting of aluminium species in anhydrous conditions causes the disruption of the interaction between silanol groups on silica, characterized by a low-wavenumber tail between 3400 cm\(^{-1}\) and 3700 cm\(^{-1}\). The spectra before and after steaming of AS(15/anhydrous) are very similar and dominated by the isolated silanol band at 3745 cm\(^{-1}\), but AS(15/anhydrous) shows a small bump at around 3600 cm\(^{-1}\) that is no longer visible on AS(15/steam) after steaming.

Figure 8.6 Infrared spectra of the OH stretching region of alumina, SA(12/anhydrous), SA(12/steam) (left), and silica, AS(15/anhydrous), AS(15/steam) (right). Numbers in brackets correspond to entries in Table 3.1.
8.2.3.2 Infrared spectra of the CO stretching region upon CO adsorption

Figure 8.7 gives the evolution of the CO stretching region (between 2100 cm\(^{-1}\) and 2250 cm\(^{-1}\)) (left panel) and OH stretching region (right panel) of Si/Al\(_2\)O\(_3\) materials after progressive coverage of the surface with CO. The CO region for alumina (entry 1) is characterized by two main peaks at around 2175-2215 cm\(^{-1}\) and 2160 cm\(^{-1}\) corresponding to CO adsorption on weak/medium LAS and weak OH groups, respectively. CO adsorption on these OH groups leads to negative bands in the OH region: These weak OH groups are mainly Al(VI)-OH of the (100) surface (3770 cm\(^{-1}\)) and Al(V)-OH of the (110) surface (3730 cm\(^{-1}\)). The grafting of silicon species on SA(12/anh) (entry 3) causes the appearance of strong Lewis acid sites (2230 cm\(^{-1}\)) and the decrease of the number of weak/medium Lewis acid sites. Silanol groups appear, as indicated by a new band at around 2135 cm\(^{-1}\) corresponding to CO physisorption on silanols. The peak corresponding to CO adsorption on OH groups in the CO region is due to the co-adsorption of CO on silanols (3745 cm\(^{-1}\)) and Al(V)-OH of the (110) surface (3730 cm\(^{-1}\)). The Al(VI-OH) of the (100) surface do no longer adsorb CO as they were grafted by silicon species during synthesis. The appearance of a band of perturbed

![Figure 8.7](image_url)
OH at low wavenumber (ca. 3400 cm\(^{-1}\)) proves the existence of BAS. The spectra of SA(12/steam) (entry 28) (both CO and OH region) are similar to those of SA(12/anh); the band of weak/medium LAS is slightly more intense. Table 8.4 gives the integration of the bands corresponding to LAS, normalized by the weight of the wafer and the surface area of the sample. The number of weak/medium LAS decreases sharply upon grafting of silicon species (SA(12/anh)) on alumina. After steaming (SA(12/steam)), the number of both weak/medium and strong LAS increases: There are twice as many strong LAS as there were before steaming. In accord with our previous observations on Si/Al\(_2\)O\(_3\) materials, there is no specific peak corresponding to adsorption on BAS on SA(12/anh), but nor is there any after steaming on SA(12/steam).

**Table 8.4** Number of sites probed by CO (a.u. isosurface).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample name</th>
<th>BAS</th>
<th>LAS</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>γ-alumina</td>
<td></td>
<td>0</td>
<td>1465</td>
</tr>
<tr>
<td>(15)</td>
<td>Silica</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td></td>
<td>39</td>
<td>374</td>
</tr>
<tr>
<td>(28)</td>
<td>SA(12/steam)</td>
<td></td>
<td>82</td>
<td>629</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>520</td>
<td>38</td>
<td>98</td>
</tr>
<tr>
<td>(29)</td>
<td>AS(15/steam)</td>
<td></td>
<td>71</td>
<td>65</td>
</tr>
</tbody>
</table>

[a] no specific peak corresponding to adsorption on BAS.

Figure 8.8 gives the CO stretching region (left panel) and OH stretching region (right panel) of Al/SiO\(_2\) materials upon CO adsorption. The CO region of silica (entry 15) is characterized by two peaks at 2156 cm\(^{-1}\) and 2138 cm\(^{-1}\), corresponding to adsorption on weak OH groups, i.e. silanols interacting with each other, and physisorption on silanols, respectively. The perturbed OH band shifts from 3745 cm\(^{-1}\) to 3600 cm\(^{-1}\) (weak OH groups) and 3660 cm\(^{-1}\) (physisorption). The presence of BAS on AS(15/anh) (entry 19) causes a large shift of the OH band from 3640 cm\(^{-1}\) (Chapter 7) to ca. 3400-3500 cm\(^{-1}\), and the presence of a specific peak in the CO region at 2178 cm\(^{-1}\). Strong LAS are also visible in the CO region (2230 cm\(^{-1}\)). After steaming, the OH and CO regions of AS(15/steam) (entry 29) look like those of silica: There is nearly no peak for BAS in the CO region nor perturbed OH band for BAS in the OH region. However, strong LAS and weak/medium LAS are detected in the CO region. Despite the less intense peak, the number of strong LAS per surface unit (Table 8.4) is greater for AS(15/steam) than for AS(15/anh) due to a lower surface area, and the number of weak/medium LAS is lower, so that the total number of LAS per surface unit does not change after steaming.
8.3 Discussion

8.3.1 The effect of steaming on Si/Al₂O₃ materials

The consequences of steaming on the textural features of Si/Al₂O₃ are limited (Table 8.3, Figures 8.2.a and 8.3.a). The porosity of alumina is maintained, but the distribution of silicon species inside the pores is modified. Other studies had even demonstrated the beneficial effect of silica-coated alumina, where surface silica species protect the alumina core from sintering by limiting the diffusion of aluminium species, especially at moderate silica loading (between 10 wt.% and 20 wt.% SiO₂). NMR results (Figure 8.4) confirm that the structure of the deposit is not deeply changed, nor that of the support.

The values of the turnover frequency (TOF) of the BAS for m-xylene isomerization obtained on Si/Al₂O₃ (1.4×10⁻³ s⁻¹site⁻¹) and Al/SiO₂ materials (4.3×10⁻⁴ s⁻¹site⁻¹) enable the calculation of the number of BAS (Table 8.5, col.5). On Si/Al₂O₃, the number of BAS slightly decreases after steaming, and the percentage of BAS of the total ethanol dehydration sites decreases (col. 6). The percentage of free (100) surface of the alumina support (col. 8) is calculated as the difference between the number of BAS and ethanol dehydration sites, it
shows that the (100) surface has been slightly uncovered during steaming, whereas the overall alumina surface is more covered (col. 7).

Steaming on Si/Al$_2$O$_3$ leads to a rearrangement of the silica surface: The greater number of weak/medium LAS (Table 8.4), many of which are located on the (100) surface, is associated to a higher percentage of free (100) surface of SA(12/steam) (Table 8.5, col. 8). Moreover, the ethanol dehydration peak has a slightly higher temperature after steaming (Figure 8.1), which indicates that a lower percentage of the ethanol dehydration sites are BAS. This is consistent with the results shown in Table 8.5, col. 6.

We proposed in Chapter 5 a model for the BAS in Si/Al$_2$O$_3$ consisting of a silanol attached to the Al(V)-OH of the (110) surface of γ-alumina (3730 cm$^{-1}$ in IR) and interacting with a tri-coordinated aluminium of the same surface (originally Al(IV)-OH, 3790 cm$^{-1}$ in IR). In certain conditions (e.g. grafting of the BAS), the interaction does no longer exist and the isolated aluminium atom form a strong LAS. In the present study, the number of strong LAS increases (Table 8.4); in IR a band at 3790 cm$^{-1}$ appears in the OH region, while the band at 3730 cm$^{-1}$ remains visible. Thus, steaming causes a loss of BAS by disrupting the interaction between the silanol and the tri-coordinated aluminium, leading to more strong LAS or Al(IV)-OH species on the (110) surface.

### Table 8.5 Comparison of the density of m-xylene conversion sites and ethanol conversion sites and the percentage of surface aluminium species; percentage of free (100) surface of alumina in Si/Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>EtOH dehydration sites (nm$^2$)</th>
<th>TOF ($\times 10^{-3}$ s$^{-1}$ site$^{-1}$)</th>
<th>BAS (nm$^2$)$^a$</th>
<th>Percentage of BAS in EtOH dehyd. sites (%)</th>
<th>Percentage of surface aluminium species (%)</th>
<th>Percentage of free surface (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)</td>
<td>SA(12/anh)</td>
<td>0.23</td>
<td>1.4</td>
<td>0.11</td>
<td>47</td>
<td>57</td>
<td>14</td>
</tr>
<tr>
<td>(28)</td>
<td>SA(12/steam)</td>
<td>0.22</td>
<td>1.4</td>
<td>0.09</td>
<td>40</td>
<td>43</td>
<td>16</td>
</tr>
<tr>
<td>(19)</td>
<td>AS(15/anh)</td>
<td>0.45</td>
<td>0.43</td>
<td>0.39</td>
<td>100</td>
<td>56</td>
<td>-</td>
</tr>
<tr>
<td>(29)</td>
<td>AS(15/steam)</td>
<td>0.10</td>
<td>0.96</td>
<td>0.10</td>
<td>100</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

### 8.3.2 The effect of steaming on Al/SiO$_2$ materials

The presence of aluminium species on silica does not prevent the silica structure from undergoing deep changes during steaming, as indicated by the variations observed on textural features (Table 8.3, Figures 8.2.b and 8.3.b). $^{27}$Al NMR spectra (Figure 8.5) indicate the higher concentration of five-coordinated aluminium after steaming, which according to our observations$^{[12]}$ (Chapter 4) are associated to species connecting isolated species. Thus, steaming causes the agglomeration of surface species that were initially dispersed. However, according to Sato et al., the effect of steaming on silica could have been worse without aluminium species, with a high number of silica particles agglomerating and higher impact on
the pore diameter and surface area, since the diffusion of silica surface species is not inhibited.\textsuperscript{[5]}

The IR and IR-CO results show that the surface of AS(15/steam) is similar to that of a partially dehydroxylated silica surface, although some Lewis acid sites are detected (Figures 8.6 and 8.8); BAS are no longer visible. It means that, aside from the sintering effect on the silica support, steaming causes the agglomeration of the well-dispersed surface aluminium species, whereas the total number of LAS per surface unit is retained (Table 8.4). As a consequence, the number of BAS probed by ethanol dehydration (Table 8.1) strongly decreases after steaming, as well as the conversion rates for \( m \)-xylene isomerization (Table 8.2). This confirms that BAS in Al/SiO\(_2\) materials are associated to well-dispersed aluminium species. Assuming that all the ethanol is dehydrated on BAS, the TOF for \( m \)-xylene isomerization is calculated (Table 8.5, col. 4). The TOF increases after steaming, but the uncertainty on the calculation is high due to the low amount of ethanol dehydrated and conversion values of \( m \)-xylene.

8.4 Conclusion

Steaming does not lead to the same effect on Si/Al\(_2\)O\(_3\) and Al/SiO\(_2\) samples. The protective effect of the silicon species that cover the alumina surface in Si/Al\(_2\)O\(_3\) materials limits the diffusion of aluminium species. Nonetheless, part of the surface silicon species are redistributed on the alumina facets, according to a mechanism that is still unclear, but leading to a greater coverage of the global alumina surface. The structure of the BAS, in agreement with our previous assumptions, is disrupted due to steaming, and their number decreases.

On Al/SiO\(_2\), the structure of the alumina deposit is altered in such a way that it cannot prevent the silica structure itself from sintering. LAS, which global number is stable after steaming, are associated to clusters of aluminium species, while BAS are lost due to the agglomeration of dispersed aluminium species.
Concluding remarks and Outlooks

This thesis aimed at rationalizing the question of the nature of Brønsted acid sites on amorphous aluminosilicates (ASAs). A set of model ASAs were synthesized by grafting to represent the diversity of ASAs stemming from a large number of synthesis techniques. The structural characterization of deposited elements on the grafted ASAs (Si/Al$_2$O$_3$ and Al/SiO$_2$) enabled the accurate description of the surface structure and distribution of silicon and aluminium species, and gave hints on the deposition process of molecular precursors depending on the synthesis conditions.

It was found that when the hydroxyl density of the support is higher than the 3.5 nm$^{-2}$, the maximum yield of grafting is reached because of the size of the precursor molecule (Chapter 4). Under aqueous conditions, the partial hydrolysis of the alkoxy moieties gives better access to the surface and re-activate the deposited species, which enables unlimited grafting. The use of other precursors with different functionalization, or several precursors at once or step-by-step, could generate different structures of deposit, hence different acidic properties.

The characterization of Si/Al$_2$O$_3$ and Al/SiO$_2$ materials by ethanol adsorption and dehydration followed by thermogravimetry enabled a better comprehension of the surface structure and reactivity (Chapters 5-8). The relation between acidity and surface functionalization was demonstrated. A detailed study of the infrared spectra of the OH stretching region at different stages of grafting showed that the grafting of silicon species on γ-alumina was selective to its facets (Chapter 5); it led to the formation of Brønsted acid sites when silicon species were grafted on the (110) surface. The optimization of the distribution of facets could be a solution to enhance the Brønsted acidity of Si/Al$_2$O$_3$. Since commercial ASA prepared by other means has revealed to closely resemble Si/Al$_2$O$_3$ materials (Chapter 7), the research on model Si/Al$_2$O$_3$ obtained by grafting could also beneficial for industrial catalysts.
The presence of water (four equivalents per precursor molecule) enabled the grafting of large amounts of silicon at once without grafting the Brønsted acid sites, as observed when repeating anhydrous grafting or grafting under CVD conditions. There may be an optimum concentration of silicon species and water/precursor ratio to access the highest density of Brønsted sites on the (110) surface of γ-alumina.

Associated to the characterization of acidity, the characterization of surface structure yielded the nature, structure, number, and strength of Brønsted acid sites. CO adsorption followed by infrared spectroscopy turned out to be the best technique to discriminate between the different nature and strength of acid sites. Since the ethanol adsorption and dehydration followed by thermogravimetry yielded the number of active sites, a systemic comparison of ASAs by the two means should enable to precisely determine the absorption factors in CO-infrared for each type of acid site and allow their quantification.

It was proved that some Brønsted acid sites are specific to ASAs and weaker than those of zeolites (Chapter 6); their number decreases when increasing the activation temperature (Chapter 7). The question as to the role of the coordination number of aluminium atoms that form a BAS is still pending; we showed that on Al/SiO₂ materials this coordination does not change upon adsorption of a reactant, however this may not be the case on Si/Al₂O₃, for which such a characterization is more difficult.

A lot remains to understand on the role of post-treatments such as steaming (Chapter 8). The nature of the support and its stability could be made to be reactive towards steaming, to induce the redistribution of both support species and surface species in Si/Al₂O₃ materials. The grafting on boehmite, for example, could be studied. Conversely, the steaming of Al/SiO₂ materials is much more challenging since the aluminium species readily agglomerate and do not prevent the silica support from sintering.
References


159, 317.


49, 7776.


[77] Bourdillon, G., PhD, Université de Poitiers, **1985**.


List of Publications

1. *Synthesis of amorphous aluminosilicates by grafting: Tuning the building and final structure of the deposit by selecting the appropriate synthesis conditions*  
   **Chapter 4**

2. *Quantification of Brønsted acid sites of grafted amorphous silica-alumina compounds and their turnover frequency in m-xylene isomerization*  
   **Chapter 5**

3. *Creation of Brønsted acidity by grafting aluminium isopropoxide on silica under controlled conditions: Determination of the number of Brønsted sites and their turnover frequency for m-xylene isomerization*  
   **Chapter 6**

4. *The variety of Brønsted acid sites in amorphous aluminosilicates and zeolites*  
   **Chapter 7**
Conferences

1. Swiss Chemical Society, Fall Meeting, 2012, Zürich, **Poster Presentation**

2. XI$^{\text{th}}$ Europacat, Lyon, 2013, **Poster-Oral Presentation**
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