Structure-Performance Relations in Chemo-Selective
Liquid Phase Hydrogenation over Supported Gold Catalysts

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Abstract

Bulk gold is the most inert metal. However, when finely dispersed on a support it is a very active and selective catalyst for many reactions including hydrogenation. The performance of a supported gold catalyst is strongly influenced by the size, structure, and oxidation state of the supported gold species, the support material, preparation method, and pretreatment conditions.

In this thesis, the influence of the gold oxidation state, particle size, support material, and pretreatment conditions on the performance of supported gold catalysts in high pressure liquid phase hydrogenation of nitro aromatic compounds was investigated in particular by means of in situ studies. Aim of the thesis was to establish structure performance relations of supported gold catalysts for hydrogenation reactions, to aid to the design of more active, selective, and stable catalysts.

X-ray absorption near edge structure (XANES) spectroscopy in high energy resolution fluorescence detection (HERFD) mode was used to determine the electronic properties of supported gold catalysts and their dynamic changes under liquid phase reaction conditions. X-ray absorption spectroscopy was combined with ATR-FTIR spectroscopy to simultaneously monitor the course of the reaction. Catalyst pretreatment and hydrogenation of nitro aromatic compounds was performed in a newly designed autoclave reactor that allows X-rays to access the reaction mixture.

The first step in the research was to show the feasibility of this in situ batch reactor cell. The reduction behaviour of Pt and Re in Pt-Re bimetallic catalysts in the liquid phase at 120 °C and a hydrogen pressure of 10 bars was investigated for two different oxide supports (Al₂O₃ and TiO₂) to elucidate their role in the reduction process. Pt-Re bimetallic catalysts are used in the selective hydrogenation of carboxylic acids and amides, and the reduction step is generally carried out prior to the reaction. Applying a time resolution of one spectrum per minute allowed us to follow changes in the oxidation state of Pt and Re with high sensitivity. We found that titania caused Pt to reduce more efficiently than alumina, whereas a higher fraction of Re was reduced on alumina. It appears that on titania part of the Re was not associated with Pt, which made it harder to reduce. Furthermore the experiments identified clear differences compared to gas phase reduction, which was more efficient.
Next, we investigated the electronic properties of gold supported on ceria during catalyst pretreatment and the liquid phase hydrogenation of nitrobenzene using the in situ cell. In gold catalysis the oxidation state(s) of the active gold species are a matter of debate. In hydrogenation, cationic and reduced gold have been suggested to be associated with high catalytic activity. However, there is a lack of in situ studies determining the oxidation state of gold under reaction conditions. To determine the influence of cationic and reduced gold species on the catalytic activity, as prepared Au/CeO₂ was subjected to different liquid phase pretreatments. Thus we were able to vary the degree of reduction and obtain catalysts with different fractions of Au³⁺ and Au⁰. In the hydrogenation of nitrobenzene we observed that Au/CeO₂ that was free of measurable cationic gold was more active than Au/CeO₂ containing significant amounts of cationic gold. Further, remaining Au³⁺ reduced under reaction conditions without affecting the reaction rate. In conclusion we found that the cationic gold that we detected did not contribute to catalytic activity.

Particle size and support effects were determined for the liquid phase hydrogenation of nitrobenzene over gold supported on alumina and titania by kinetic experiments, electron microscopy, and in situ HERFD XANES. Catalysts with different particle sizes were obtained after liquid phase reduction at different temperatures between 60 and 200 °C. Reduced gold was essential for the hydrogenation to proceed. In particular, when supported on alumina a strong particle size effect was observed. The catalytic activity correlated well with the amount of particles smaller than 2 nm. However, at all pretreatment temperatures Au/TiO₂ was much more active than Au/Al₂O₃, and the catalytic activity was much less dependent on the particle size. We ascribed this to the ability of titania to help dissociating hydrogen.

Another kind of particle size effect was observed for Au/TiO₂ catalysts. By means of high-resolution electron microscopy we observed that large Au particles (~8 nm) supported on titania, provided they were multiple-twinned, broke-up into small clusters between 2 and 3 nm under liquid phase hydrogenation conditions. Multiple-twinned Au particles were obtained after gas phase reduction of as-prepared Au/TiO₂ at elevated temperature. EXAFS confirmed that the multiple-twinned particles were agglomerates of smaller clusters. In contrast, calcination caused a strong interaction between Au and titania and the formation of mainly single crystalline Au particles between 4 and 5 nm, which were relatively stable in liquid phase hydrogenation. Reduction and calcination led to gold particles that were fundamentally different.
The gas phase hydrogenation of nitrobenzene over gold nanoparticles supported on titania and alumina was investigated by in situ infrared spectroscopy. While adsorption and reduction of nitrobenzene readily proceeded on both catalysts, repeated adsorption and reduction showed that nitrobenzene was not able to displace aniline from titania and that less and less nitrobenzene adsorbed in each cycle. The first adsorption was found to occur through hydrogen-bonding interactions with surface hydroxyl groups. In the presence of aniline, nitrobenzene adsorbed on other sites on titania, but still interacted with hydroxyl groups on alumina.
Zusammenfassung


HERFD XANES (high energy resolution fluorescence detected X-ray absorption near edge structure spectroscopy) wurde verwendet, um die elektronischen Eigenschaften heterogener Goldkatalysatoren und deren dynamische Veränderungen in der Flüssigphase unter Reaktionsbedingungen zu bestimmen. Röntgenabsorptionspektroskopie wurde mit ATR-FTIR (attenuated total reflectance-Fourier transform infrared) Spektroskopie kombiniert um gleichzeitig den Umsatz der Reaktion zu verfolgen. Katalysator-Vorbehandlung sowie die Hydrierung von Nitroaromaten wurde in einem neuen Autoklaven durchgeführt, der so adaptiert wurde, dass Röntgenstrahlen Zugang zur Reaktionsmischung haben.

Die Durchführbarkeit dieser Experimente wurde zu Beginn überprüft. Das Reduktionsverhalten von Platin und Rhenium in bimetallischen Pt-Re-Katalysatoren in der Flüssigphase bei 120 °C und 10 bar Wasserstoff wurde für die Trägermaterialien Al₂O₃ und TiO₂ untersucht, um deren Rolle im Reduktionsprozess aufzuklären. Bimetallische Pt-Re Katalysatoren werden bei der selektiven Hydrierung von Carbonsäuren und Amiden eingesetzt, und die Reduktion des Katalysators wird üblicherweise vor der Reaktion durchgeführt. Die Messung eines Spektrums pro Minute ermöglichte uns, die Veränderungen des Oxidationszustandes von Pt und Re mit hoher Empfindlichkeit zu detektieren. Wir fanden heraus, dass Pt auf TiO₂ effizienter reduziert wurde, als auf Al₂O₃, während ein höherer Anteil des Re auf Al₂O₃ reduzierte. Es scheint, dass auf TiO₂ ein Teil des Re nicht in Kontakt mit Pt war, was dessen Reduktion erschwerte.
Weiters wurden deutliche Unterschiede zur Gasphasenreduktion festgestellt, die effizienter war.


Ein weiterer Partikelgrößeneffekt wurde bei Au/TiO$_2$ Katalysatoren beobachtet. Mittels hochaufgelöster Elektronenmikroskopie beobachteten wir, dass große Goldpartikel (~8 nm) auf TiO$_2$, wenn sie polykristallin waren, unter Flüssigphasenhydrierungsbedingungen in kleine Partikel von ca. 2 bis 3 nm auseinanderbrachen. Polykristalline Au Partikel wurden durch Gasphasenreduktion

1. Introduction

1.1. Heterogenous catalysis

Catalysis has been successfully employed in the chemical industry for more than 100 years, it plays a key role in our society today, and it will become increasingly important in the future. More than 80 % of all chemicals are produced with the help of catalysts. Petrochemistry is driven by catalytic processes. Many organic intermediates used for the manufacture of pharmaceuticals, crop protecting agents, dyes, plastics, fibers, resins, and pigments can only be produced by catalytic methods. Catalysts are also important in environmental pollution control, as illustrated by the three way catalyst which effectively reduces emissions from car engines. The term “catalysis” has already been introduced by Berzelius in 1836 and the definition of Ostwald from 1895 that “a catalyst accelerates a chemical reaction without affecting the position of the equilibrium” still holds today. Generally catalysts are divided into two large groups: homogeneous catalysts and heterogeneous (solid-state) catalysts. In homogeneous catalysis the catalyst and the reactants are in the same phase. Homogeneous catalysts are usually coordination complexes or chemical compounds. In heterogeneous catalysis the reaction proceeds between several phases. Usually the catalysts are solids, and the reactants are gases and/or liquids. Heterogeneous catalysts are for example metals, oxides, zeolites, and sulphides. Either the bulk material is used, or the active material is finely dispersed on a support, such as silica, alumina, or carbon. The major advantage of heterogeneous catalysts is that they can be easily separated from the product. This can be done for example by filtration or directly such as in gas phase reactions in fixed bed reactors. The separation of homogeneous catalysts usually affords more complicated methods such as distillation, liquid-liquid extraction, or ion-exchange. Thus the majority of catalysts used in industry are heterogeneous with a market share of about 85 %. A heterogeneous catalytic reaction consists of three basic steps. In the first step, reactants adsorb on the catalyst surface, where intramolecular bonds are broken or weakened. In the second step, the adsorbed species react on the catalyst surface. In the third step, products desorb from the catalyst surface, thereby regenerating the active sites for the subsequent catalytic cycle. A catalyst renders an energetically favourable reaction pathway, in which the activation energies of all intermediate steps are low compared to the activation energy of the
uncatalyzed reaction. Apart from increasing the reaction rate, catalysts also affect the selectivity of chemical reactions. By applying different catalysts completely different products can be obtained from the same starting material. The main properties determining the performance of a catalyst are activity, selectivity and stability. Nowadays, as the efficient use of raw materials and energy becomes increasingly important, catalysts with high selectivity to the desired products are essential.\textsuperscript{1,2}

\subsection{1.2. Catalysis by gold}

\subsubsection{1.2.1. Properties of gold}

Gold is in Group 11 of the periodic table and has the atomic configuration [Xe]4f\textsuperscript{14}5d\textsuperscript{10}6s\textsuperscript{1}. Together with copper and silver it belongs to the group of “coinage metals”. Due to its beauty and durability, gold has been used in jewellery and coinage for centuries. It exhibits the highest malleability of all metals. Among all metals gold has the most positive redox potential (\(\varepsilon_0 = +1.5\) V forAu/Au\textsuperscript{3+}), the highest electronegativity of 2.4 according to Pauling, and its electron affinity is greater than that of oxygen. Oxidation states of Au are -1 (e. g. RbAu, CsAu), +1, +2, +3, and +5, with +1 and +3 being the most common.\textsuperscript{3}

\subsubsection{1.2.2. History of catalysis by gold}

Bulk gold is the most inert metal. However, when finely dispersed on a support, molecules such as hydrogen, oxygen, and carbon monoxide chemisorb on the surface, and it is highly active in many reactions.\textsuperscript{4} For a long time gold has been regarded as poorly active. This changed only in the 1970s, when Bond and Sermon,\textsuperscript{5,6} reported the hydrogenation of alkenes and alkynes over Au/SiO\textsubscript{2} at temperatures below 473 K, and Parrvano et al.\textsuperscript{7,8} reported hydrogen and oxygen transfer reactions over Au/Al\textsubscript{2}O\textsubscript{3} and Au/MgO catalysts. About 10 years later two very important findings were reported: Haruta et al.\textsuperscript{9,10} discovered that Au nanoparticles supported on metal oxides were the most active catalysts for CO oxidation, and that they were still active at temperatures as low as 200 K. At about the same time Hutchings predicted and confirmed experimentally that Au\textsuperscript{3+} was the most active catalyst for the hydrochlorination of acetylene.\textsuperscript{11} Since then interest and research in catalysis by gold has grown continuously.
1.2.3. Hydrogenation over supported gold catalysts

Gold catalyzes various hydrogenation reactions such as the hydrogenation of alkenes\textsuperscript{5,12-16} alkadienes,\textsuperscript{17-20} alkynes,\textsuperscript{21-24} $\alpha,\beta$-unsaturated carbonyl compounds,\textsuperscript{25-28} and nitro compounds.\textsuperscript{29-31} In contrast to traditional hydrogenation catalysts such as platinum, palladium or ruthenium, which require modification, it often shows remarkable selectivities when multiple functional groups are present. This makes gold a potential catalyst for the development of new, clean and sustainable production routes with minimal side product formation. Supported gold catalysts were very selective in purifying alkene streams, to prevent poisoning of the polymerization catalysts and ensure pure products.\textsuperscript{32} On the other hand, over the industrially-used palladium catalysts, oligomers are formed, that reduce lifetime.\textsuperscript{21} Selectivities up to 90% were obtained over gold for the selective hydrogenation of $\alpha,\beta$-unsaturated carbonyl compounds to the corresponding unsaturated alcohols, which are important intermediates in the production of fine chemicals and pharmaceuticals.\textsuperscript{26,28,33,34} Substituted aromatic amines, also important industrial intermediates, were selectively prepared from the corresponding nitro compounds with supported gold catalysts,\textsuperscript{29} whereas other catalytic systems exhibited major drawbacks such as by-product formation\textsuperscript{35-38} and limited reusability.\textsuperscript{39} Hydrogenation reactions over gold have in common that the hydrogen molecule must be dissociated before it reacts.

1.2.3.1. Interaction of gold and hydrogen

In hydrogenation reactions, chemisorption and dissociation of hydrogen are the essential initial steps. There are only a few studies that investigate the interaction of hydrogen with gold. On Au(110) (1 x 2) surfaces no hydrogen chemisorption was observed.\textsuperscript{40} Weak adsorption of a small amount of hydrogen was found on thin, unsintered gold films: At a pressure of 0.3 Pa and a temperature of 78 K, the hydrogen coverage was less than 0.015.\textsuperscript{41} Hydrogen desorbed at around 125 K. The hydrogen desorption activation energy was estimated to be around 12 kJ/mol. Low coordinated gold atoms on the film surface were suggested to act as adsorption sites. Lin and Vannice\textsuperscript{42} detected weak, reversible adsorption of hydrogen on 30 nm gold particles on TiO$_2$ at 300 and 473 K leading to a coverage of about 1% of the total amount of gold. As the hydrogen uptake was found to be greater at 473 K than at 300 K it was suggested that the adsorption of hydrogen is an activated process and very likely
associated with hydrogen dissociation. The chemisorption of hydrogen on $\text{Al}_2\text{O}_3$ supported gold particles with a mean cluster size of about 4 nm was examined by Jia and co-workers.\textsuperscript{43} They observed that about 14% of the surface atoms adsorbed hydrogen almost irreversible at 273 K. The hydrogen chemisorption properties of $\text{Au/Al}_2\text{O}_3$ and $\text{Au/SiO}_2$ catalysts were investigated by Bus et al.\textsuperscript{44} in a temperature range of 298 to 523 K. For the 1 to 1.5 nm supported gold clusters, H/M values (number of adsorbed hydrogen atoms per total number of metal atoms) of at least 0.1 and as high as 0.73 were determined. However only 10-30% of the total adsorbed hydrogen did not desorb while evacuating for 2 h at the analysis temperature. The shapes of the hydrogen adsorption isotherms indicated that hydrogen chemisorbs dissociatively. The hydrogen uptake increased or was constant with temperature. This was ascribed to the hydrogen chemisorption on gold being activated. The $\text{Au/Al}_2\text{O}_3$ catalyst with the smallest particle size of about 1 nm exhibited the highest hydrogen uptake per surface atom. At this size, most of the surface consists of atoms at corner and edge positions. Thus it was proposed that hydrogen atoms only adsorb at edges and corners of the gold particles. In summary, hydrogen chemisorbs on gold, though weakly and in small amounts. For both the hydrogen uptake and the strength of adsorption there is a clear particle size effect. With decreasing particle size, increasing amounts of hydrogen are chemisorbed and an increasing fraction is adsorbed strongly.

**1.2.3.2. H/D exchange over gold**

The simplest reaction involving hydrogen is the $\text{H}_2$-$\text{D}_2$ exchange reaction. Nieuwenhuys et al.\textsuperscript{45} demonstrated that $\text{Au/Al}_2\text{O}_3$ catalysts which had a gold particle size smaller than 3 nm catalyzed the hydrogen-deuterium exchange reaction even at room temperature. Bus et al.\textsuperscript{44} also proved that isotope exchange occurred over supported gold catalysts in a flow reactor. For $\text{Au/Al}_2\text{O}_3$ catalysts with particle sizes between 1 and 3 nm, the H/D ratio at the reactor exhaust increased with increasing temperature. The temperature dependence of the HD concentration was ascribed to two effects; the dissociation of hydrogen being activated on gold and increase of the rate constant for the recombination of hydrogen and deuterium atoms with increasing temperature. Bond et al.\textsuperscript{46} also found a strong particle size effect with the smaller particles being more reactive (vide infra). Boronat et al.\textsuperscript{47,48} investigated the nature of the adsorption sites of hydrogen on $\text{Au/TiO}_2$ catalysts with similar particle sizes of
about 3.3 nm. By IR spectroscopy of adsorbed CO, different gold surface sites were identified, which could be assigned via DFT calculations. These results were then correlated to those obtained from H/D exchange experiments, and it was confirmed that among the different gold surface sites only low coordinated gold atoms at corners and edges, not directly bonded to oxygen, were active for hydrogen dissociation. Recently, Fujitani et al.\textsuperscript{49,50} reported that the H\textsubscript{2} dissociation rate of small Au clusters (< 2nm) supported on TiO\textsubscript{2}(110) single crystals was a function of the number of Au atoms located at the perimeter of the particles. To confirm that the active sites for the dissociation of H\textsubscript{2} over Au/TiO\textsubscript{2} were located at the Au-Ti interface, catalysts, the authors performed H\textsubscript{2}-D\textsubscript{2} exchange experiments over TiO\textsub{x}/Au(111) model surfaces. The model catalysts were prepared by deposition of Ti on Au(111) via evaporation from a Ti rod, followed by annealing between 500 and 700 K at different oxygen pressures. Thus Ti oxides with different oxidation states formed on the Au(111) surface. H\textsubscript{2}-D\textsubscript{2} experiments were performed at 350-475 K. The HD formation rate increased linearly with the concentration of TiO\textsubscript{2}. No HD formed in the presence of reduced Ti, TiO, Ti\textsubscript{2}O\textsubscript{3}, and Ti\textsubscript{3}O\textsubscript{5}. TOF and activation energy for HD formation over TiO\textsubscript{2}/Au(111) agreed well with data reported for Au/TiO\textsubscript{2}(110) surfaces. Thus, the authors proposed that Au\textsuperscript{δ+}-O\textsuperscript{δ--}Ti sites, formed at the perimeter interface between Au and stochiometric TiO\textsubscript{2} were the active sites for the dissociation of H\textsubscript{2} on Au/TiO\textsubscript{2} catalysts.

1.2.3.3. The oxidation state of active gold species

With regard to heterogeneous catalysis by gold, there is no consensus on the oxidation state of the catalytically active species. In CO oxidation, which has been extensively studied, cationic,\textsuperscript{51-55} reduced,\textsuperscript{56-58} and negatively polarized\textsuperscript{59-62} gold species have been proposed to be catalytically active. Also in hydrogenation, which has been studied to a much lesser extend, the catalytically active Au species have been suggested to be cationic\textsuperscript{15,17-19,63,64} and reduced.\textsuperscript{20} In particular for hydrogenation reactions in situ studies, elucidating the oxidation state of gold under reaction conditions are rare.\textsuperscript{15,63,65}
1.2.3.4. Hydrogenation of nitro aromatic compounds

Substituted aromatic amines are important intermediates in chemical industry for the production of fine chemicals, pharmaceuticals, herbicides and polymers. In general, they are prepared via catalytic reduction of the corresponding nitro compounds. While simple nitro compounds are easily hydrogenated over a wide range of commercial catalysts, the selective hydrogenation of nitro groups in the presence of other reducible functional groups is a more difficult task. Aromatic amines containing double bonds can be produced by employing stoichiometric reducing agents such as sodium hydrosulfite, iron, tin, or zinc in ammonium hydroxide. These processes however produce large amounts of by-products. The reduction of nitro groups in the presence of olefinic groups can be also performed over homogeneous cobalt and ruthenium sulfide catalysts, but their application is limited, because of low yields and formation of sulfur containing by-products. Iron based homogeneous catalysts are selective for the reduction of nitroaromatics containing different functional groups such as 3-nitrochlorobenzene, 2-nitrotoluene, and 4-nitrobenzylnitrite, but exhibit drawbacks concerning recovery and re-use. Heterogeneous Pt catalysts modified by H3PO2 or Pb catalyze the chemoselective reduction of a variety of functionalized nitro aromatics. However V and Fe salts have to be added to avoid the accumulation of undesired hydroxylamine intermediates. Because of the complex composition of the system, hampering the control of the catalyst behavior, applications are limited. Corma et al. discovered that supported gold catalysts catalyzed the liquid phase hydrogenation of substituted nitro aromatics under mild conditions (100-120 °C, 9 bar H2 pressure). Over 1.5 wt % Au/TiO2 and 4.5 wt % Au/Fe2O3 with average particle sizes of 3.7 nm, nitroaromatics containing additional functional groups such as double bonds, carbonyl, amide or nitrile groups were converted to the corresponding amines with very high selectivities (> 95 %) at high conversion (> 95 %). Only for the reduction of 4-nitrobenzaldehyde a selectivity of 80 % at 100 % conversion was obtained for Au/Fe2O3. At the same time as Corma et al., Chen and coworkers reported that 1 wt % gold supported on silica, prepared by an in situ reduction method, with uniform particles of 7-9 nm, effectively catalyzed the selective reduction of various substituted aromatic nitro compounds, though at somewhat higher temperatures (120-140 °C) and H2 pressure (20-40 bar). In contrast, Au/SiO2 prepared by traditional impregnation was 5 times less active. Taking into account, that the
dissociation of hydrogen is rate determining, Corma et al. found an enhanced activity of 1 order of magnitude with bimetallic AuPt/TiO\textsubscript{2} catalysts with a Pt content of 0.01%, preserving high chemoselectivity (93%). Pt readily dissociates hydrogen, thus in the presence of Pt the amount of dissociated hydrogen on the surface was probably increased. Pt contents larger than 0.01% led to a further increase of activity but significant decrease of selectivity.\textsuperscript{71,72} Upon kinetic and IR measurements a reaction pathway for the hydrogenation of nitrobenzene over Au/TiO\textsubscript{2} was suggested.\textsuperscript{30} It was proposed that on Au/TiO\textsubscript{2} nitrobenzene first reacts to the intermediate phenylhydroxylamine both directly and via nitrosobenzene and is then further hydrogenated to aniline. Because of the gradual accumulation of phenylhydroxylamine on the catalyst surface it was suggested that its conversion to aniline was the rate determining step. Richner et al.\textsuperscript{73} studied the reaction mechanism of the liquid phase hydrogenation of nitrobenzene over Au/TiO\textsubscript{2} by in situ ATR-FTIR spectroscopy. Applying two independent ATR-FTIR probes they were able to simultaneously and in situ monitor both the liquid phase and the solid/liquid interface. The solid/liquid interface was monitored by immobilising a thin film of the catalyst of a few micrometers thickness on one of the ATR-FTIR probes dipping in the reaction mixture. Due to the porosity of the catalyst film both the solid/liquid interphase and the liquid phase were measured. The liquid phase was monitored by a second, uncoated ATR-FTIR probe, which was in direct contact with the reaction mixture. Thus, compounds adsorbed on the surface of the catalyst could be identified by the differences between the two spectra without calibration. The catalyst, 1.5 wt% Au/TiO\textsubscript{2} with a mean particle size of 3.8 nm was provided by the World Gold Council. The reactions were carried out at 120 °C and a hydrogen pressure of 10 bar. During the hydrogenation of nitrobenzene neither in the liquid phase nor at the solid/liquid interphase nitrosobenzene was detected. However, the accumulation of phenylhydroxylamine was detected at the solid-liquid interphase, and it was concluded that its hydrogenation to aniline was the slowest step in the overall reaction. The phenyl hydroxylamine coverage on the catalyst surface reached its maximum after around 30 min reaction time. Within this time the initial catalytic activity decreased from 5 mmol h\textsuperscript{-1} to a nearly constant value of 3 mmol h\textsuperscript{-1}. Hence it was concluded that the catalytic activity was hardly influenced by bulk concentrations of reactants, intermediates and products, and that common models such as Hougon-Watson/Langmuir Hinshelwood could not be applied. Additional experiments at
different hydrogen pressures up to 50 bar revealed a proportional increase of the initial reaction rates with increasing hydrogen pressure, indicating that the hydrogenation of nitrobenzene was first with regard to hydrogen pressure. The fact that no nitrosobenzene was detected suggests a very low concentration of nitrosobenzene on the catalyst surface. Thus the reduction of nitrosobenzene to phenylhydroxylamine is probably much faster than the initial reduction of nitrobenzene to nitrosobenzene. Makosch et al. found that over Au/CeO₂ the hydrogenation of nitrobenzene proceeded not only by the direct but by the condensation route. In the condensation route the intermediates nitrosobenzene and phenylhydroxylamine condensate to form azoxybenzene, which is reduced to azobenzene, and finally to aniline. Over Au/CeO₂ nitrosobenzene accumulated on the surface, because its conversion was rather low. In contrast, over Au/TiO₂ nitrosobenzene reduced very fast to phenylhydroxylamine. Additional nitrosobenzene formed via decomposition of phenylhydroxylamine, which was catalyzed by CeO₂. CeO₂ also catalyzed the condensation step. Thus the support directly governed the reaction mechanism. The interactions between reactants and catalyst in the chemoselective hydrogenation of nitrostyrene over Au/TiO₂ were studied combining kinetic measurements, in situ IR spectroscopy and realistic quantum chemical modeling. The high chemoselectivity was attributed to the higher intrinsic activity of gold for the hydrogenation of the NO₂ group than of the double bond and to the preferential adsorption of the NO₂ group, when both groups are present. On the basis of calculations, it was proposed, that nitrostyrene selectively adsorbs via the NO₂-group on two low coordinated Au atoms, at intervals of 2.6-2.7 Å to an oxygen atom of the support. The calculated energy for this adsorption mode was 15.4 kcal/mol.

Corma et al. showed that supported gold catalysts were also capable to produce oximes via hydrogenation of α,β-unsaturated nitro compounds. Oximes are important intermediates in the synthesis of polymers, fungicides, biochemicals, or fragrances. For instance the preparation of cyclohexanone oxime is a key step in the nylon-6 production. Generally oximes are produced by condensation of carbonyl compounds with hydroxylamine, which has the disadvantage of both being toxic and unstable. Their synthesis via reduction of α,β-unsaturated nitrocompounds can usually only be accomplished using stoichiometric amounts of organic hydrogen donors, such as ammonium formate, decaborane, and formic acid. However over Au/TiO₂ trans-β-
nitrostyrene for instance was converted to the corresponding oxime at 90 °C and 10 bar hydrogen pressure within 2 hours with 97 % selectivity. Also with additional electron withdrawing groups such as methoxy or halogenes bound to the aromatic ring, or aliphatic unsaturated nitrocompounds such as 1-nitro-1-cyclohexene selectivities > 90 % at high conversion levels (> 90 %) were achieved.

With supported Au catalysts it was also possible to perform cascade reactions, i. e. coupling of the hydrogenation of the nitroaromatic compound with the consecutive reaction of the amine with carbonyl compounds, olefins or alkynes. Thus starting from nitrobenzene and benzaldehyde for instance N-benzylidenamine was formed with 93 % selectivity at 94 % conversion after two hours at 120 °C and 4 bar hydrogen pressure. If the imines were hydrogenated further, the corresponding secondary amines were formed. Grirrane et al. demonstrated that symmetric and asymmetric aromatic azo compounds could be directly synthesized from the respective nitro compounds via a two step-one pot reaction using Au/TiO₂. Au/TiO₂ was active and selective for both the hydrogenation of the nitro groups and the oxidation of the anilines to the azo compounds. In contrast, Au supported on carbon did not catalyze the oxidation of the anilines to the azo compounds. Au/CeO₂ was less active than Au/TiO₂ and exhibited a lower applicability.

Currently polyurethanes are produced on an industrial scale using the highly toxic phosgene as reactant. Juarez et al. recently reported a phosgene-free preparation of polyurethane precursors based on catalysis by gold. Likewise in a two step one-pot reaction polyurethane precursor carbamic acid, N,N'-(4-methyl-1,3-phenylene)bis-\(\text{C},\text{C}'\)-dimethyl ester was prepared starting from 2,4-dinitrotoluene using gold supported on nanocrystalline ceria. In the first reaction step 2,4-dinitrotoluene reduced to 2,4-diaminotoluene under hydrogen. In a second step 2,4-diaminotoluene reacted with dimethyl carbonate via an N-carbamoylation reaction to produce carbamic acid, N,N'-(4-methyl-1,3-phenylene)bis-\(\text{C},\text{C}'\)-dimethyl ester.

Yamane et al. showed that Au/Fe₂O₃ catalyzed the one pot synthesis of indoles starting from (2-nitroaryl) alkynes via successive hydrogenation and reductive amination, as well as aniline derivatives from nitroaromatics and aldehydes via hydrogenation of the nitroaromatic followed by reductive amination.

Beside batch liquid phase reactions, supported gold catalysts were also successfully employed in continuous gas phase hydrogenation of substituted aromatic nitro compounds such as p-chloro-nitrobenzene. P-chloroaniline is produced in large
quantities and serves as intermediate for the production of various fine chemicals such as pharmaceuticals and agrochemicals. For the synthesis typically Fe in acid media is used, which leads to the formation of 5-20 times more by-product (toxic Fe hydroxide sludge) than product and low overall yields. A more sustainable route is the batch liquid phase production over transition metal catalysts. Drawbacks arise from partial hydrogenolysis of the Cl-substituent, i.e. formation of aniline. Cardenas-Lizana et al. studied the influence of the support material on the activity of supported gold catalysts in the selective gas phase hydrogenation of p-chloro-nitrobenzene. Hence 1 mol % gold supported on different metal oxides such as Al₂O₃, TiO₂, Fe₂O₃ and CeO₂ were prepared by deposition precipitation and impregnation. Deposition precipitation led to particle sizes in the range of 1.5-2.8 nm, whereas upon impregnation larger particles of 3.5-9 nm were formed. For all catalyst irrespective of the support material 100 % selectivity towards p-chloro-aniline was achieved at 428 K and atmospheric hydrogen pressure. The catalytic activity increased with decreasing particle size with an optimum at about 3 nm. Catalysts with particle sizes ≤ 3.5 nm showed higher initial activities, but gradually deactivated with time on stream, whereas Au catalysts with lower dispersions exhibited no deactivation. The performance of 1.9 wt % Au/Al₂O₃ prepared by standard wetness impregnation, with a particle size range of 2-8 nm was further investigated by Cardenas-Lizanza et al. It exclusively reduced p-chloronitrobenzene to p-chloroaniline in a temperature range from 393-523 K, and up to 80 hours time on stream no catalyst deactivation was observed. Under similar reaction conditions, 6.8 wt % Pd/Al₂O₃ was much more active, but yielded solely nitrobenzene and aniline, which formed by composite hydrodechlorination and hydrogenation. It was expected that combining Au and Pd would produce a catalyst which was more active towards the formation of the desired p-chloroaniline. Thus a Au-Pd/Al₂O₃ catalyst prepared by contacting pre-reduced Pd/Al₂O₃ with HAuCl₄ with a molar ratio of Pd/Au of 10/1 was tested. However the incorporated Au had no effect, and the catalyst exhibited similar activity and selectivity as Pd/Al₂O₃. TPR and H₂ uptake measurements showed only marginal interaction between Au and Pd. Au/Al₂O₃ was further tested in the hydrogenation of a series of mono- and di-substituted nitroaromatics. The corresponding substituted amino compounds were formed with 100 % selectivity. Regarding the catalytic activity a substituent effect was observed. The reaction rate increased with increasing electron withdrawing ability of the substituents from nitrotoluene < nitrobenzene < chloronitrobenzene/bromonitro-
benzene < dichloronitrobenzene. In a continuative study the possible promoting effect of Pd on the activity of Au/Al₂O₃ in the gas phase hydrogenation of p-chloronitrobenzene at 373 K was assessed. Bimetallic Au-Pd/Al₂O₃ catalysts with molar Au/Pd ratios of 8, 20, and 88 were prepared by co-deposition precipitation with urea or coimpregnation. Catalyst characterization by TPR and DRIFTS using CO as a probe molecule suggested the formation of bimetallic particles and surface Au-Pd interactions. The catalytic activity of Au-Pd/Al₂O₃ with a molar ratio of Au/Pd of 20 was three times higher compared to Au/Al₂O₃, while 100 % selectivity to p-chloroaniline was retained. At higher Pd contents (Au/Pd = 8) the reaction rate further increased, however both p-chloronitroaniline and nitrobenzene formed, the latter due to Pd promoted hydrodechlorination. Au/Al₂O₃ was chosen to study the influence of the preparation method on the catalytic performance. The catalysts were either prepared by deposition precipitation with urea (Au-DPU) or impregnation (Au-IMP) followed by pretreatment in flowing H₂ at 573 K for 2.5 hours, which resulted in mean particle sizes of 3 nm (Au-DPU) and 4.5 nm (Au-IMP), respectively. The residual chlorine content was < 200 ppm after deposition precipitation and 9800 ppm after impregnation. Both catalysts were 100 % selective towards p-chloroaniline. Their catalytic activities however were significantly different. The rates per gold surface obtained from TEM were more than one order of magnitude higher for Au-DP (418 umol/(m² Au*h)) compared to Au-IMP (29 umol/(m² Au*h)). The lower activity of Au-IMP was attributed to a cooperative effect of larger Au particles being intrinsically less active, and the residual chlorines, being able to adsorb on metallic gold and suppress adsorption of reactants. In a further study, Cardenas-Lizanza et al. compared the performance of 1 mol% Au/TiO₂ and Au/Al₂O₃ also in the continuous gas-phase hydrogenation of p-chloronitrobenzene at 453 K. The particle sizes of both catalysts were in a range of 1-20 nm, with mean values of 6 nm in the case of Au/TiO₂, and 9 nm for Au/Al₂O₃. TPR of Au/Al₂O₃ and Au/TiO₂ delivered a H₂ consumption peak at 432 and 434 K respectively, which were attributed to the reduction of Au³⁺ to Au⁰. For Au/TiO₂ an additional shoulder at 457 K was observed, which was suggested to be due to reduction of Au species interacting more strongly with the support or a partial reduction of TiO₂. Both catalysts produced p-chloroaniline as sole product. Similarly, only o- and m-chloroaniline were generated from the corresponding chloronitrobenzene isomers. The specific reaction rates per Au surface area were up to 4 times higher for Au/TiO₂ compared to Au/Al₂O₃. Both catalysts were most reactive
towards the hydrogenation of o-chloronitrobenzene, followed by p- and m-
chloronitrobenzene. The higher activity for ortho and para isomers was suggested to be
caused by resonance stabilisation rather than steric effects. The highest rate obtained
for the o-isomer was explained by a more electrophilic N in the nitrogroup due to the
proximity with the Cl-substituent, which makes it more prone to nucleophilic attack.
The higher activity of Au/TiO$_2$ compared to Au/Al$_2$O$_3$ was ascribed to a combined
effect of a smaller average Au particle size, and a possible activation of the reactants
through interaction(s) with surface oxygen vacancies on the TiO$_2$ support.
Furthermore, the performance of Au/Al$_2$O$_3$ and Au-Ni/Al$_2$O$_3$ in the continuous
selective gas phase hydrogenation at 573 K of m-dinitrobenzene to m-nitroaniline,
which is a valuable intermediate in production of various fine chemicals, was
investigated by Cardenas-Lizanza et al.$^{85}$ Au-Ni/Al$_2$O$_3$ (1 mol % Au, 10 mol % Ni)
was prepared by impregnation of a prereduced Ni/Al$_2$O$_3$ catalyst with HAuCl$_4$,
followed by a heat treatment in flowing N$_2$ to 1273 K, to form the Au-Ni alloy. For
direct comparison, 1 mol % Au/Al$_2$O$_3$, which was also prepared via impregnation, was
subjected to the same treatment. Au-Ni alloy formation was confirmed by XRD,
diffusive reflectance UV-VIS, and HRTEM. Both catalysts presented discrete metal
particles with a broad size distribution of $<$5-200 nm and pseudo-spherical
morphology. Interestingly, Au/Al$_2$O$_3$ was nearly one order of magnitude more active
compared to the Au-Ni alloy catalyst and 100 % selective towards the formation of m-
nitroaniline, whereas Au-Ni/Al$_2$O$_3$ catalyzed both the partial and complete
hydrogenation of m-dinitrobenzene, with a shift towards complete hydrogenation at
increasing conversion levels. The authors provisionally attributed the difference in the
catalytic performance to differences in adsorption and activation of the reactants.
Cardenas-Lizanza et al.$^{86}$ further investigated the effects of the gold particle size as
well as the nature of the support (anatase vs. rutile) on the performance of Au/TiO$_2$
catalysts in the gas phase hydrogenation of m-dinitrobenzene at 473 K. Mixed
anatase/rutile catalysts with different mean particle sizes in a range of 3.4-10 nm were
obtained by varying the Au loading (0.1 and 1 mol %) and the reduction temperature
(603 - 1273 K). With increasing metal content and/or pretreatment temperature gold
particle sizes increased. When the same reduction temperature was applied, catalysts
with higher rutile content delivered broader Au particle size distributions and larger
mean values. For example after pretreatment of 0.1 wt % Au/TiO$_2$ containing 16 %
rutile a mean particle size of 3.4 nm was obtained, whereas 0.1 wt % Au/TiO$_2$
consisting of 100 % rutile delivered a mean particle size of 6.4 nm. It was suggested that this was due to a weaker interaction of gold with rutile than with anatase, inducing agglomeration of gold. A marked dependence of the specific activity was found for particle sizes < 5 nm, i.e. the rate increased with decreasing particle size, whereas the catalytic activity of Au/TiO₂ bearing particles > 5 nm was insensitive to particle size. The support composition (anatase/rutile) on the other hand, did not significantly influence the catalytic activity. Also the selectivity to the desired product m-nitroaniline was particle size dependent. Au/TiO₂ catalysts with an average particle size < 5 nm preferentially formed m-nitroaniline, while Au/TiO₂ with a mean particle size > 5 nm predominantly promoted the complete hydrogenation to m-PDM. Similarly to the catalytic activity, the nature of the support material did not affect the product distribution. The authors attributed the particle size effect on the catalytic performance to changes in the electronic structure of the supported Au nanoparticles, affecting the mechanism of adsorption and activation of m-dinitrobenzene. He et al. studied the selective liquid phase hydrogenation of chloronitroaromatics to the corresponding chloroanilines over Au/ZrO₂ catalysts. The as prepared catalyst contained particles between 2 and 5 nm with a mean particle size of 4 nm. XPS measurements identified both Au⁰ and Au⁺¹ species (ratio: ~7), whereas after calcination at 200 °C for 5 hours almost all gold was reduced. Both as prepared and calcined Au/ZrO₂ selectively (> 95 % at 100 % conversion) catalyzed the reduction of para- and o-chloronitrobenzene, and 2,5-dichloronitrobenzene to the respective chloroaniline derivatives. However, calcined Au/ZrO₂ was slightly more active than as prepared Au/ZrO₂ containing cationic gold. Thus the authors proposed that reduced Au species were the catalytically active sites for the hydrogenation of chloronitrobenzenes. In terms of recyclability the two catalysts exhibited remarkable differences. Reduced Au/ZrO₂ did not deactivate significantly. In the third reuse it still reached 86% conversion of p-chloronitrobenzene at 150 °C and 10 bar H₂ after 5 hours, compared to 100 % conversion when freshly used. In contrast, as prepared Au/ZrO₂ only achieved 49 % conversion when reused for the third time under similar conditions. Leaching of gold in as prepared Au/ZrO₂ was excluded, which could have been an explanation for the large loss of activity. However, as-prepared Au/ZrO₂ after reaction contained larger particles (mean diameter 7 nm) compared to an average particle size of 4 nm of the fresh catalyst. The higher activity of pretreated Au/ZrO₂ in recycling experiments was thus related to a higher stability of the pre-reduced nanoparticles towards sintering.
Catalyst stability and recyclability are important for both economic and environmental reasons. In this context, Ge et al.\textsuperscript{88} developed a stable and (magnetically) recyclable core-satellite nanocomposite catalyst via encapsulation of gold nanoparticles prior attached to silica cores in mesoporous silica shells. Magnetical recyclability was achieved by adding superparamagnetic \( \text{Fe}_3\text{O}_4 \) to the silica core colloids. The performance of the catalytic system was tested in the liquid phase hydrogenation of 4-nitrophenol with NaBH\(_4\) as hydrogen source. The catalyst retained its activity in six consecutive cycles. Dotzauer et al.\textsuperscript{89} investigated the catalytic activity of gold nanoparticle/polyelectrolyte film containing membranes in the reduction of nitroaromatic compounds by NaBH\(_4\). Different membrane types containing gold particles with an average size of 12 nm selectively catalyzed the reduction of the nitro groups in the presence of cyano-, chloro-, and styrenyl groups amongst others, maintaining their activity up to several hours time on stream. However, for some substrates, depending on the substituent(s) on the aromatic ring, beside the corresponding amino compounds also the respective nitroso compounds formed, and the product distribution could be tuned by varying the solution flux through the membrane. By increasing the flux, the ratio of aniline/nitroso compound decreased. For example, the hydrogenation of o-nitrotoluene at low flux produced 94 % o-aminotoluene, whereas at high flux only 34 % were formed. Shimizu and coworkers\textsuperscript{90} investigated the influence of particle size and nature of the support on the chemoselective hydrogenation of nitroaromatics over supported gold catalysts. The catalysts were prepared by a colloid deposition method. After calcination at 300 °C mean particle sizes in the range of 2-3 nm were obtained, irrespective of the support material (\( \text{Al}_2\text{O}_3, \text{SiO}_2, \text{MgO}, \text{montmorillonite, carbon} \)). \( \text{Au/Al}_2\text{O}_3 \) with larger particles was prepared by annealing of the as-prepared Au colloid mixture at 165 °C giving a mean particle size of 6 nm, or calcination of the as prepared catalyst at 1000 °C to deliver particles of 30 nm. EXAFS analysis confirmed that all supported gold species were in the metallic state. The hydrogenation of nitrostyrene, which was used as model reaction, was performed at 160 °C and 30 bar hydrogen. \( \text{Au/Al}_2\text{O}_3 \) with a mean particle size of 2.5 nm was both most active and selective among the catalyst tested with a selectivity to 4-aminostyrene of 89 % at 100 % conversion, achieving almost the performance of \( \text{Au/TiO}_2 \) provided by the WGC. To investigate the stability of the catalyst, it was recovered after reaction, washed and calcined at 400 °C. Upon reuse the catalyst exhibited only a slightly decreased activity and selectivity. For \( \text{Au/Al}_2\text{O}_3 \)
the scope of the reaction was tested using nitroaromatic compounds bearing alkene, carbonyl, amide and ester groups, and selectivities in the range of 78-99% were obtained. The activity of the Au nanoparticle supported on Al₂O₃ depended strongly on the particle size. The TOF per surface site increased with decreasing Au particle size and so did the rate of the OH/D₂ exchange reaction. Au nanoparticles of similar mean particle sizes were found to be most active when supported on an acid-base bifunctional support (Al₂O₃) rather than on a basic (MgO) or acidic (SiO₂) support. Thus the authors concluded that these surface acid base pair sites were required for the dissociation of hydrogen and proposed that the gold atoms at the metal-support interface were the catalytically active sites. The same authors also investigated the selective hydrogenation of nitrocyclohexane to cyclohexanone oxime over gold supported on Al₂O₃, MgO and SiO₂. Also for this reaction the catalytic performance depended strongly on the support material and the gold particle size. Au/Al₂O₃ with a mean particle size of 2.5 nm was the most efficient catalyst delivering 86% selectivity towards cyclohexanone oxime at 100 °C and 6 bar hydrogen. The authors suggested that acid-base pair Al⁺O⁻ sites were the adsorption sites for the nitro group and in cooperation with unsaturated Au atoms responsible for the dissociation of hydrogen. As supported Au catalysts are very active in the low temperature water gas shift reaction (180 °C-250 °C) Liu et al. investigated whether they were also active in the chemo selective hydrogenation of nitro aromatics with CO and H₂O as hydrogen source. 1.5 wt % Au/Fe(OH)₅ prepared by co-precipitation, followed by pretreatment in static air at 200 °C, 1.6 wt % Au/Fe₂O₃, produced via co-precipitation and subsequent pretreatment in static air at 500 °C, and 4.4 wt % Au/Fe₂O₃ provided by the World Gold Council were tested in the hydrogenation of various substituted nitro aromatic compounds in the presence of H₂O at 100-120 °C and 15 bar CO. XPS identified a mixture of Au⁺ and Au⁰ (Au⁺/Au⁰: 0.07) for Au/Fe(OH)₅ and solely metallic Au for the Au/Fe₂O₃ catalysts. Particle sizes obtained by TEM were 1.0-2.5 nm for Au/Fe(OH)₅, and 3-9 nm for Au/Fe₂O₃. Thus the pretreatment conditions significantly affected the Au oxidation state and particle size. In the hydrogenation of p-nitroacetophenone 1.5 wt % Au/Fe(OH)₅ containing the smallest Au particles was 4 times more active than 1.6 wt % Au/Fe₂O₃ and almost twice as active as 4.4 wt % Au/Fe₂O₃ (WGC). Analysis of the gas after reaction by GC revealed the formation of CO₂, but not of H₂. In the absence of nitro compounds, neither CO nor H₂ formed, suggesting that the water gas shift reaction did not occur under the applied reaction conditions.
conditions. The authors however speculated that the WGS shift reaction occurred, but that the atomic hydrogen formed immediately reacted with the nitro group without forming molecular H₂. In a related work He et al. studied the room temperature reduction of a wide range of nitro compounds with CO and H₂O as hydrogen source over Au supported on TiO₂, CeO₂ and Fe₂O₃. Both Au particle size and nature of the support strongly influenced the catalytic activity. At 25 °C and 1 atm of CO, Au/TiO₂ with the smallest mean particle size of the catalysts tested (1.9 nm) was the most active in the hydrogenation of nitrobenzene with a TOF of 33 h⁻¹, followed by Au/TiO₂ with a mean particle size of 3.5 nm (19 h⁻¹), Au/CeO₂ (5.9 h⁻¹) and Au/Fe₂O₃ with a mean particle size of 3.9 nm (0.9 h⁻¹). Au/TiO₂ (1.9 nm) exhibited > 95 % selectivity at 100 % conversion to the respective substituted amino compound regardless of the presence of electron-donor or –acceptor substituents. Furthermore, the catalytic activity increased remarkably when increasing the CO pressure from 1 to 5 atm, but leveled off at higher pressures. When H₂ was used instead of CO the hydrogenation reaction did not proceed. The authors suggested that transient Au-H species formed via reduction of H₂O by CO could be involved in the rate determining step of the reaction.

In summary, compared to other catalytic systems gold catalysts have the big advantage of being very selective in hydrogenating the nitro group without the addition of any promoters and in the presence of a broad range of other reducible functional groups. Clearly the particle size influences the activity, which increases with decreasing particle size in particular for particles below 5 nm. On the other hand, the influence of the support is not clear. The gas phase hydrogenation of p-chloronitrobenzene did not seem to be affected by the support material. On the other hand the liquid phase hydrogenation of 4-nitrobenzaldehyde was nearly 100 % selective over Au/TiO₂, whereas over Au/Fe₂O₃ 20% hydroxylamines were formed. The addition of very small amounts of Pd or Pt, which readily dissociate hydrogen, to supported Au catalysts significantly, enhances their activity, while preserving high chemoselectivity. Regarding the reaction mechanism it was confirmed that over Au/TiO₂ nitrobenzene reacts via the direct route to phenylhydroxyamine, which reacts further to aniline before desorbing from the catalyst surface. With respect to the nature of the catalytically active sites, the most common proposal is that the hydrogenation of nitro compounds takes place at low coordinated Au atoms at the metal support interface. Finally, due to gold’s unique properties, the hydrogenation of nitro compounds can be coupled with other transformations such as oxidation, N-carbamoylation and reductive
amination which allows the production of valuable industrial materials such as azo compounds, polyurethane precursors, or indoles directly from the respective nitro compounds in a two step one pot process.
1.3. Scope of the thesis

This dissertation aims at establishing structure-performance relations in the hydrogenation of nitro aromatic compounds over oxide supported gold nanoparticles, to enable the design of more active, selective and stable gold catalysts. This thesis comprises eight chapters. The current chapter gives an introduction into catalysis by gold, with the main focus lying on hydrogenation. The interaction of gold and hydrogen is described and the literature on hydrogenation of nitro aromatic compounds over supported gold catalysts is reviewed. Chapter two describes the methods and techniques used in this work, including the experimental details. It covers catalyst preparation, kinetic experiments, and the applied ex situ and in situ catalyst characterization techniques such as X-ray absorption spectroscopy, electron microscopy, and elemental analysis. Chapter three describes the successful application of a newly constructed autoclave reactor for in situ determination of the oxidation state of supported metals in the liquid phase under pressure by means HERFD XAS. The feasibility of the setup was confirmed by monitoring the reduction behaviour of Pt and Re in bimetallic Pt-Re catalysts. This cell was designed and constructed with another Ph.D student, Martin Makosch. In chapter four the in situ cell was used to determine the oxidation state of gold in Au/CeO2 catalysts and its dynamic changes during catalyst pretreatment and liquid phase hydrogenation of nitrobenzene. HERFD XAS was combined with online ATR-FTIR spectroscopy to simultaneously monitor the course of the reaction. Chapter five describes particle size and support effects in the liquid phase hydrogenation of nitrobenzene over gold supported on alumina and titania. In chapter six the redispersion of multiple-twinned gold particles in the liquid phase is described. Chapter seven presents an in situ IR study about gas phase adsorption and hydrogenation of nitrobenzene on gold supported on alumina and titania. Chapter eight includes the general conclusion and outlook.
References

   14581–14587.


2. Methods

2.1. Catalyst preparation

There are many methods of preparation of supported Au catalysts, the most important being deposition precipitation, coprecipitation, impregnation, and gas- and liquid-phase grafting. Commercial Au catalysts are prepared by deposition precipitation (DP), because it is easiest to handle. The only disadvantage of DP is that it cannot be used for activated carbon and metal oxides with an isoelectric point (IEP) smaller than 5, such as SiO$_2$ (IEP=2).\textsuperscript{1} In this work gold supported on TiO$_2$, CeO$_2$, and Al$_2$O$_3$ were prepared by DP with urea (DPU).\textsuperscript{2} In contrast to DP with NaOH, which was developed by Haruta,\textsuperscript{3} all gold in solution is deposited on the support, which results in a good control of the gold loading, in particular at higher loadings. Tetrachloroauric acid (HAuCl$_4$) is used as Au precursor and the synthesis is performed at 80 °C. In the first step of DPU hydroxochloro gold complexes, formed in water trough hydrolysis, adsorb on the metal oxide support. In the second step, these complexes adsorb in such manner that one Au(III) is coordinated by one urea molecule.\textsuperscript{4,5}

The following support materials were used: TiO$_2$ (Aeroxide P25, Acros Organics) TiO$_2$ (Hombikat UV 100, Sachtleben Chemie GmbH), CeO$_2$ (99.9 %, ABCR Chemicals), and Al$_2$O$_3$ (Aluminiumoxid C, Degussa). Prior to the synthesis, the ceria was calcined at 500 °C for 5 hours to remove any residual chlorides. To prepare a supported Au catalyst with a Au loading of 0.7 wt %, 0.086 mg of chloroauric acid (HAuCl$_4$, 49 wt% Au, ABCR-Chemicals) was dissolved in deionized water (600 mL). The support material (6.0 g), and urea (1.8 g; puriss p.a. ≥99.5%, Riedel-de Haën) were added with continuous stirring. The mixture was heated to 80 °C and stirred for 16 h in a closed Teflon vessel. After cooling to RT, the solid product was obtained after filtration and washed five times with deionized water to remove residual chloride ions. To confirm the removal of chloride, AgNO$_3$ solution (1M) was added to the filtrate. Precipitation of AgCl was not observed. The product was dried at RT under vacuum in the dark for 48 h.

2.2. Catalyst pretreatment

After preparation, the supported Au species are mainly in the 3+ oxidation state. Thus, prior to catalytic experiments the as prepared catalysts are usually pretreated to form
metallic Au clusters. Oxidic Au reduces in oxidizing, reducing, and inert atmospheres.\textsuperscript{2,4} The temperature, at which full reduction in a certain atmosphere is reached, is mainly governed by the support material. Pretreatment can be performed in the gas- or in the liquid phase. The gas (mixture), heating rate, set temperature, and dwell time, and, if performed in the liquid phase, the gas pressure and the kind of solvent determine the oxidation state and cluster size distribution after pretreatment.

In chapter four as prepared Au/CeO\textsubscript{2} was pretreated in toluene, that is, in the solvent of the subsequent reaction at 10 bar H\textsubscript{2}. Both pretreatment and the subsequent liquid phase hydrogenation were performed in a newly constructed in situ cell, which is described in section 2.3.2. Toluene (25 ml), was added to as prepared Au/CeO\textsubscript{2} (0.30 g). Residual air was removed by flushing the autoclave three times with H\textsubscript{2}. After setting the pressure to 10 bar H\textsubscript{2}, the suspension was heated with continuous stirring (1500 rpm) at 4 °C min\textsuperscript{-1} to the desired pretreatment temperature (60 or 100 °C), and this temperature was maintained for 30 min. After cooling down to 60 °C, the hydrogenation experiment was started by adding the substrate (vide infra).

Au/Al\textsubscript{2}O\textsubscript{3} and Au/TiO\textsubscript{2} catalysts, which were investigated in chapter five, were also pretreated under H\textsubscript{2} in the liquid phase. Pretreatment and catalytic tests were performed in stainless steel autoclaves, which are described section 2.3.1. The catalyst (50 mg) and toluene (25 mL) were put into the autoclave, purged three times with H\textsubscript{2}, and pressurized with H\textsubscript{2} to 10 bars. The mixture was heated under stirring (500 rpm) to the desired pretreatment temperature (60, 100, 150 or 200 °C) and kept at this temperature for 30 min. After cooling to about 40 °C, the hydrogenation experiment was started (vide infra).

In chapter six the influence of difference pretreatment conditions on the catalytic performance and the structure of supported Au particles was investigated. As-prepared Au/TiO\textsubscript{2} was reduced in a flow of 5 % H\textsubscript{2}/He (100 ml/min) at room temperature for 45 min, and at different temperatures (40, 60, 80, 100, 150, 200, 300 °C) for 20 minutes with a heating rate of 2 °C/min, followed by cooling down to room temperature under the same conditions. Alternatively as-prepared Au/TiO\textsubscript{2} was calcined in flowing air (100 ml/min) at 300, 400 and 500 °C with a heating rate of 2 °C/min and a dwell time of 30 min followed by cooling down to room temperature under the same stream.
Catalyst pretreatment was performed only shortly before kinetic experiments, and until their use the pretreated catalysts were stored in the freezer at -18 °C under exclusion of light.

2.3. Kinetic experiments

2.3.1. High pressure liquid phase hydrogenation

The high pressure liquid-phase hydrogenation of nitrobenzene, 4-nitrobenzaldehyde, benzaldehyde, and nitrosobenzene was performed in stainless steel autoclaves with a volume of 50 ml from Premex Reactor AG (Lengnau, Switzerland), which were equipped with a gas in- and outlet, a sample port, a thermocouple, external heating and readout for temperature and pressure. Stirring was performed with a magnetic stirrer. Usually 0.05 - 0.30 g substrate, 0.05 - 0.30 g catalyst, 25 g solvent (THF or toluene), and 0.14 ml mesitylene as internal standard were used. Before the reaction was started, residual air was removed by flushing the reactor three times with hydrogen to 10 bars while stirring followed by venting. Then the autoclave was pressurized with hydrogen to 10 bars and heated to the reaction temperature of 100 °C without stirring. When 100 °C were reached, stirring was started and the reaction time was set to zero. Samples of about 1 ml were withdrawn by means of a sample tube at room temperature, at reaction time 0, after 10, 30, 60, 120, 180, and 240 min. If necessary, the reaction was continued overnight until full conversion was reached. The samples were filtered to remove residual catalyst material. The concentration of reactants and products was quantified by gas chromatography on an Agilent 7820A gas chromatograph equipped with a HP5-MS column. The column was initially held at 80 °C for 2 min and then heated to 300 °C with a rate of 20 °C per minute. The main product of the reduction of 4-nitrobenzaldehyde – 4-aminobenzaldehyde is not stable, because the aldehyde- and the amino-group react via condensation to imines, which can reduce further. These products could not be detected directly by GC because they were too heavy to be brought into the gas phase. They were found after reaction in the form of an orange solid sticking to the wall of the autoclave. Their amount was determined via the carbon balance.
2.3.2. In situ high pressure liquid phase hydrogenation

In situ high pressure liquid phase hydrogenation experiments at the synchrotron were performed in a newly constructed in situ cell.\textsuperscript{6,*} The cell was an autoclave reactor which was modified to perform high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) of the catalyst in the reaction mixture and to monitor simultaneously the reaction by means of attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy with a probe dipped into the slurry.\textsuperscript{7,8} Figure 1 shows a schematic drawing of the setup.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{HERFD_XAS_ATR_FTIR_cell.png}
\caption{Schematic drawing of the HERFD XAS/ATR-FTIR cell. Outer view of the cell (a), vertical cut view of the cell (b), detail drawing of the cell parts (c).\textsuperscript{6}}
\end{figure}

The autoclave had a volume of 50 ml and consisted of a polyethetherketon (PEEK) inlet with a thickness of 1.5 mm, which was encased by a stainless steel container. A window cut into the steel allowed X-rays to access and exit the inner part of the autoclave through the PEEK. The autoclave was equipped with a gas in- and outlet, a thermocouple, a mechanical stirrer, external heating, and readout for temperature and pressure. The conversion of nitrobenzene was monitored in situ by means of an ATR-FTIR system (Mettler Toledo) with a DiComp optical fiber immersion probe attached to a ReactIR 45 spectrometer. One spectrum per minute (average of 16 scans) was recorded, with a resolution of 2 cm$^{-1}$ in the range 750 to 2000 cm$^{-1}$. Background spectra of the catalyst suspension were collected in toluene at respective temperatures.

\textsuperscript{*} in collaboration with Martin Makosch.
Hydrogenation of nitrobenzene was performed directly after liquid phase pretreatment of the as-prepared catalyst, which is described in section 2.2. Between 0.30 and 0.21 g nitrobenzene were added to the freshly pretreated catalyst (0.30 g) suspended in toluene (25 ml). After purging with H₂ three times, the autoclave was pressurized with 10 bars H₂, and heated with continuous stirring (1500 rpm) at 4 °C min⁻¹ to the desired reaction temperature (100 °C or 60 °C).

2.3.3. Determination of conversion, rate, selectivity, and carbon balance

The conversion (X), rate, and selectivity (S) were calculated using the following formulas:

\[
X(t) = \frac{\text{mol(total)}(t) - \text{mol(substrate)}(t)}{\text{mol(total)}(t)} \times 100\%
\]

\[
\text{rate} = -\frac{d(\text{mol(reactant)})}{dt} \times \text{g(metal)}
\]

\[
S(\text{product}A)(t) = \frac{\text{mol(product}A)(t)}{\text{mol(all products})(t)} \times 100\%
\]

The carbon balance was determined using the following formula:

\[
\text{Cbalance}(t) = \frac{\text{mol(substrate)}(t) + \text{mol(all products)}(t)}{\text{mol(substrate)}(RT)} \times 100\%
\]

*RT: room temperature*

2.4. Scanning transmission electron microscopy

To determine Au particle size distributions and the morphology of Au particles scanning transmission electron microscopy (STEM) was used. In STEM a small, convergent beam is scanned over a defined area of the sample. At each spot the selected detector records the transmitted or scattered electrons for image formation. In STEM three types of detectors, the bright field (BF), the annular dark field (ADF), and
the high angular dark field (HAADF) detectors are used. The BF detector records the intensity of the direct beam. The ADF detector detects scattered electrons, which are diffracted in crystalline areas and incoherent Rutherford scattering, which is scattering to high angles. The HAADF detector records mainly Rutherford scattering.\textsuperscript{9}

Electron microscopy measurements were performed on a HD2700CS (Hitachi, aberration-corrected dedicated scanning transmission electron microscope (STEM), cold FEG, 200 kV) or a Tecnai F30 ST (FEI, FEG, 300 kV). The high-resolution capability of HD2700CS (shown to be better than 0.1 nm) is due to a probe corrector (CEOS) that is incorporated in the microscope column between the condenser lens and the probe-forming objective lens so that a beam diameter of ca. 0.1 nm can be achieved.\textsuperscript{10} A special bright field setting allows one to record highly-resolved phase-contrast STEM (PC-STEM) images (similar to HRTEM) without delocalization artifacts. With high-angle annular dark field detectors (HAADF) attached to both microscopes, the intensity of incoherently scattered electrons is measured leading to images dominated by atomic number (Z) contrast.\textsuperscript{11} In such images, the Au particles appear as bright patches. For the (scanning) transmission electron microscopy (STEM) investigations, the catalyst material was dispersed in ethanol and a few drops of the suspension were deposited onto a perforated carbon foil supported on a copper grid. Usually 300 particles were counted in the HAADF-STEM images to determine the particle size distributions.

2.5. Elemental analysis

The Au content of the supported Au catalysts (Au/TiO\textsubscript{2}, Au/Al\textsubscript{2}O\textsubscript{3}, and Au/CeO\textsubscript{2}) was determined by means of atomic absorption spectroscopy (AAS). The Ti content of Au/TiO\textsubscript{2} catalysts was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). AAS is based on the absorption of radiation energy by free atoms. Radiation sources are usually hollow cathode lamps, which are made of or contain the element under investigation, and emit the characteristic spectrum of this element. According to Lambert-Beer's law the absorption of the incident radiation is proportional to the concentration of the element in the sample. ICP-OES is based on the spontaneous emission of radiation by free atoms or ions, when excited by thermal or electric energy. In ICP-OES excited atoms and ions are produced by means of the
inductively coupled plasma. The intensity of the emission is proportional to the concentration of the element in the sample.\textsuperscript{12}

The AAS measurements were performed using a Varian SpectrAA 220 FS spectrometer and the ICP-OES measurements were conducted using a Varian VISTA PRO AX spectrometer. Sample preparation was performed via microwave assisted digestion by adding 1 ml of nitric acid, 2 ml of hydrofluoric acid and 3 ml of hydrochloric acid to 40 mg of catalyst for determining the Au content, and 10 mg of catalyst for determining the Ti content. The amount of Au and Ti in the samples was quantified by measuring calibration curves.

2.6. Infrared spectroscopy

The gas phase adsorption and hydrogenation of nitrobenzene on Au/TiO\textsubscript{2} and Au/Al\textsubscript{2}O\textsubscript{3} catalysts were investigated in situ by infrared spectroscopy in transmission mode (chapter seven). Infrared spectroscopy is a very important technique in heterogeneous catalysis. It allows studying the interaction between adsorbed molecules and the catalyst surface. Thus one gains a better insight in the structure of the surface and the surface chemistry of the catalyst.\textsuperscript{13} The infrared (IR) region of the electromagnetic spectrum lies between the ultraviolet-visible (UV-VIS) and the microwave region and comprises the wavenumbers in the range of 14300 to 10 cm\textsuperscript{-1}. Generally the IR region is divided into three parts, the near IR (14300- 4000 cm\textsuperscript{-1}), the mid-IR (4000-400 cm\textsuperscript{-1}), and the far IR (400-10 cm\textsuperscript{-1}) region. In infrared spectroscopy mainly the mid-IR region is used. The absorption of infrared radiation of a molecule is based on its transition between energy levels of molecular vibration. A molecule absorbs infrared light, when the electric dipole moment of the molecule changes according to a molecular vibration. Most of the chemical compounds fulfill this prerequisite. Each compound has a characteristic absorption spectrum, which allows its identification and quantification.\textsuperscript{14} In addition, changes in molecular vibrations are induced by the surrounding environment. Therefore, as mentioned above, the surface of a catalyst can be studied by means of IR spectroscopy of adsorbed molecules. Quantitative measurements are based on Lambert-Beer's law. The absorbance (A) is directly proportional to the concentration (c) of a light absorbing species in solution and the path length (d) of the light.
Lambert-Beer's law is additive and therefore applicable for mixtures in solution. Today, most of the IR spectrometers are Fourier-transform IR spectrometers, which possess high sensitivity and resolution, and allow fast recording of spectra.\textsuperscript{15}

In chapter four the conversion of nitrobenzene in the liquid phase was monitored online by attenuated total reflectance-fourier transform infrared (ATR-FTIR) spectroscopy with an immersion probe dipping in the reaction mixture. The experimental details are described in section 2.3.2. ATR-IR spectroscopy enables investigating solid, liquid and gaseous samples directly without preparation. The sample is in direct contact with the ATR crystal, which is made of a material with a high refractive index such as germanium or zinc selenide. The IR beam is passed through the crystal via total reflection and in doing so it also penetrates a few micrometers into the sample. This results in an attenuation of the evanescent wave in dependence of the material under investigation.

In chapter seven, the adsorption and hydrogenation of nitrobenzene was studied in situ by IR spectroscopy in transmission mode. The as-prepared catalysts were pressed into self-supporting pellets and placed in the heatable sample holder of a transmission IR cell.\textsuperscript{16} The cell had four gas inlets, which were used to introduce helium, helium saturated with nitrobenzene, and hydrogen respectively, and for the exhaust. Gas flows were adjusted by mass flow controllers. Transmission infrared measurements were performed on a Biorad FTS 3000 Excalibur Fourier transform infrared spectrometer with a resolution of 4 cm\textsuperscript{-1} using a mercury cadmium telluride (MCT) detector. The as prepared catalyst pellet was heated to 100 °C in a helium flow of 160 mL/min and kept under these conditions for 60 min. Then H\textsubscript{2} (180 ml/min) was introduced for 45 min at 100 °C to reduce the catalyst. After flushing with helium for 30 min, the sample was allowed to cool down to room temperature under the helium flow. At room temperature a spectrum for use as background was recorded. Next, nitrobenzene was adsorbed on the catalyst until a constant signal was obtained. To remove nitrobenzene from the gas phase, the cell was flushed with helium and then heated to 100 °C. Nitrobenzene was reduced in a flow of H\textsubscript{2} (20 ml/min). For recycling experiments,
helium saturated with nitrobenzene was again introduced for 30 min followed by reduction in flowing H₂. Four recycling experiments were performed.

2.7. X-ray absorption spectroscopy (XAS)

XAS is a very powerful method to determine electronic and structural properties of catalysts. A main advantage compared to other techniques is that it can be applied in situ under reaction conditions. Another advantage is that no long-range order of the material is required as it is the case for methods such as XRD. Hence the material under investigation can be amorphous, liquid, or gaseous.¹⁷,¹⁸ Time resolved studies allow investigating dynamic changes of catalysts under pretreatment and reaction conditions. When X-ray radiation hits matter the incident intensity will be reduced according to the absorption properties of the material being irradiated.

The decrease in intensity dI of a monochromatic X-ray beam passing through a material of the length dx is given by

\[
dI = \mu(E)I dx
\]  \hspace{1cm} (1)

with \(\mu(E)\) being the linear absorption coefficient, which is a function of the photon energy. Integration of equation 1 over the whole path length through the material yields Lambert Beer's law:

\[
I = I_0 \exp(-\mu(E)x)
\]  \hspace{1cm} (2)

In an X-ray absorption spectrum the intensity is smoothly declining with increasing energy. When the energy of the incident X-ray beam is larger than the binding energy of a bound electron, this electron is excited to the continuum by the photo-electric effect, and the intensity of the absorption increases sharply. This sharp rise is called the absorption edge. At the absorption edge, the kinetic energy \(E_{\text{kin}}\) of the electron equals \(E_0\), which is the binding energy or “inner potential”. If the energy of the incoming X-ray beam is larger than \(E_0\), the kinetic energy of the photoelectron is given by

\[
E_{\text{kin}} = h \nu - E_0
\]  \hspace{1cm} (3)
As the electrons in each element have characteristic binding energies ($E_0$), XAS is an element-specific method. The absorption edge is called K edge, when core electrons are excited from the 1s core level. When core electrons are excited from the 2s, 2p$_{1/2}$, and 2p$_{3/2}$ core levels respectively, the absorption edges are called L$_1$, L$_2$, and L$_3$ edges. The K and L$_1$ edges probe the p density of states (DOS), whereas the L$_2$ and L$_3$ edges probe mainly the d DOS and the s DOS to a much lesser extent. In this work the Au L$_3$ edge is exploited to investigate the electronic and geometric properties of supported Au catalysts. The outgoing photo-electron can also be described as a spherical electronic wave. The wavelength $\lambda$ is given by $\lambda = \frac{2\pi}{k}$, with $k$ being the photo-electron wave vector. Its energy is proportional to the square root of the kinetic energy of the photo-electron:

$$k = \left[ \frac{8\pi^2 m}{h^2} \left( h\nu - E_0 \right) \right]^{1/2}$$

(4)

with $m$ the mass of the electron, and $h$ Planck's constant.

The outgoing electronic wave moves away concentrically from the absorbing atom. When encountering neighbouring atoms it scatters off hence forming a backscattered wave. The outgoing and backscattered waves show constructive and destructive interferences, and thus the final state is given by their sum:

$$\Psi_{\text{Final}} = \Psi_{\text{Outgoing}} + \Psi_{\text{Backscattered}}$$

(5)

Fermi's Golden Rule describes that the probability of photoelectric absorption ($P$) is directly proportional to the X-ray absorption coefficient $\mu(E)$:

$$\mu \propto P = \frac{2\pi^2 e^2}{\hbar c^2 m} \left| \langle \Psi_{\text{final}} | E \cdot r | \Psi_{\text{initial}} \rangle \right|^2 \rho(E_f)$$

(6)

Here $\omega$ is the angular frequency, $e$ the electron charge, $\Psi_{\text{final}}$ the final state wave function (equation 5), $\Psi_{\text{initial}}$ the initial wave function of the bound electron, $E$ the electric field polarization vector, $r$ the position vector of the scatterer with respect to
the absorber atom, and \( \rho(E_f) \) the density of allowed states at the final energy \( E_f \). The electric field polarization vector and the position vector define, if the transition is dipole allowed or not. The photoelectric absorption probability \( P \) is proportional to the final state \( \Psi_{\text{final}} \), which is a function of two interfering waves. Thus \( P \) is not a smooth function but exhibits maxima and minima, which are called EXAFS-wiggles. Figure 1 shows an XAS spectrum of Au foil recorded at the Au L\(_3\) edge. The normalized absorption coefficient is plotted against the energy of the X-rays.

![Figure 1. Au L\(_3\) edge spectrum of gold foil.](image)

A spectrum consists of three areas:

(i) The pre-edge region

(ii) The X-ray absorption near edge structure (XANES) region, which starts at the absorption edge.

(iii) The extended X-ray absorption fine-structure (EXAFS) region, which starts about 50 eV above the absorption edge.

The X-ray absorption coefficient \( \mu(E) \) is defined as

\[
\mu(k) = \mu_0(k)(1 + \chi(k))
\]  

(7)
with \( \mu_0 \) the atomic background, describing the X-ray absorption of the free atom, and \( \chi(k) \) the EXAFS function, which describes the oscillatory part of the absorption.

\[
\mu(k) = \mu_0(k) \{1 + \chi(k)\} \tag{8}
\]

Since the oscillatory part is a result of the interference between the outgoing and backscattered waves, \( \chi(k) \) provides geometric information about the local environment of the absorbing atom. This is due to the fact that the kind (\( Z \)) and number (\( N \)) of neighbouring atoms, their distance (\( R \)) and (static and thermal) disorder (\( \sigma \)) are responsible for the shape (phase and amplitude) of the backscattered wave. All these parameters are described mathematically in the EXAFS equation \( \chi(k) \) and can be determined by careful analysis. The EXAFS equation \( \chi(k) \) in the single scattering approximation, which is valid at about 50 eV above the absorption edge can be used for most experiments. This approximation assumes that the electron scatters only once before its return to the absorbing atom. \( \chi(k) \) is given by

\[
\chi(k) = \sum_{j=1}^{J} A_j(k) \sin(2kR_j + \varphi_j(k)) \tag{9}
\]

Neighbouring atoms are grouped in coordination shells. A coordination shell comprises \( N \) atoms of the same element at about the same distance \( R_j \) from the absorber atom. \( J \) refers to \( j^{th} \) coordination shell. \( A_j(k) \) is the backscattering amplitude and \( \varphi_j(k) \) the phase-shift experienced by the photo-electron in the scattering process. That \( \chi(k) \) is given by the sum over all coordination shells underlines the fact that X-ray absorption is a bulk method. All atoms of the absorbing element are probed equally. \( A_j(k) \) and \( \varphi_j(k) \) are functions of the photoelectron wave vector \( k \) (equation 4) The phase shift \( \varphi_j(k) \) is characteristic for each pair of absorber and scatterer atom and is tabulated or can be calculated.

The backscattering amplitude \( A_j(k) \) is defined as product of three terms:

\[
A_j(k) = \frac{S_0^e e^{-2R_j/\lambda}}{kR_j^2} \times e^{-2\sigma_j^2 k^2} \times N_j F_j(k) \tag{10}
\]
The first term describes the attenuation of the signal, the second the disorder of the investigated material, and the third term describes the scattering power of shell \( j \). \( S_0^2 \) is the amplitude reduction factor, which accounts for the incomplete transfer of the energy of the photons to the photoelectron due to shake-up/shake-off processes and many body effects in the absorbing atom. Usually \( S_0^2 \) values are in the range of 0.75 and 0.95 [9]. The exponential term including the mean free path \( \lambda \), which is defined as \( \lambda = \frac{2\pi}{k} \), considers the finite lifetime of the excited state. The term \( \frac{1}{R^2} \) considers the loss of intensity of the photoelectron due to the spherical character of the wave. The second term contains the Debye-Waller factor, \( \sigma_j^2 \) and describes the variation in \( R_j \) due to structural disorder in the material and thermal motion, i.e. the static and thermal disorder. The scattering power is described by the third term. It is a function of the number \( (N_j) \) of neighbouring atoms in the \( j^{\text{th}} \) shell and the scattering power \( F_j(k) \) of the neighbouring atom \( j \), which is characteristic for each element. The different dependencies of the terms in equation 10 on \( k \) help discriminating them during analysis. In fact photoelectrons are scattered off electrons of neighbouring atoms. Scattering is most efficient, when the kinetic energy of the outgoing photoelectron has about the same value as the orbital energy of the electrons in the neighbouring atoms. Thus, outgoing electrons with a low kinetic energy are effectively scattered off light neighbouring atoms, whereas outgoing electrons with a high kinetic energy are most effectively scattered off heavy neighbouring atoms. To gain information about the local geometry around the absorbing atom the EXAFS spectra need to be analyzed. For data analysis many different programs are available. In this work the Athena and Artemis software packages were used. An EXAFS data analysis starts with the substraction of the monotonically decreasing background. Then the edge position \( E_0 \) and the atomic background are determined. In the next step the atomic background is subtracted and the spectrum is normalized. Finally the EXAFS data is fitted using references to obtain the above described parameters.

In chapter seven, XAS measurements at the Au L\(_3\) edge were performed at the SuperXAS beamline at the Swiss Light Source (SLS at Paul Scherrer Institute, Villigen, Switzerland) in transmission mode by measuring the intensity of the beam before and after the sample by ionization chambers. The Swiss Light Source has a ring
energy of 2.4 GeV, a ring current of 400 mA, a magnetic field of 2.9 T, and is operated in the “top-up” injection mode. The incident energy was focused with two mirrors and monochromatized using a double crystal monochromator equipped with a pair of Si (111) crystals. About 30 mg of catalyst were used for the preparation of self supporting pellets with a diameter of 5 mm in order to obtain optimal transmission properties. The pellets were placed in a sample holder and measured at room temperature. One spectrum per sample was recorded in the energy range of 11.8 to 13.0 keV with a scan time of 45 min. The EXAFS data were analyzed using Athena and Artemis software packages. The first shell was fitted in R space (1.5 < R < 3.5 Å) after Fourier transformation (3 < k < 13 Å⁻¹) using a k weighting of 2. Average cluster sizes were determined from the coordination numbers using established methods and assuming spherical particles.¹⁹

2.7.1. X-ray absorption near edge structure (XANES) spectroscopy

The XANES part of an XAS spectrum gives information about the oxidation state and the local geometry of the absorbing atom. It reflects the empty density of states (DOS) of the electronic transition.¹⁸ In this work the Au L₃ edge was investigated. The intensity of the whiteline, corresponds to the number of holes in the 5d band. Bulk gold exhibits a small whiteline because some orbitals are pushed above the Fermi level due the hybridization of s, p, and d orbitals. The electron configuration of bulk gold is [Xe]4f⁴5d¹⁰⁶s¹⁺ₓ and not [Xe]4f⁴5d¹⁰⁶s¹, which would be the ideal configuration. Small Au clusters on the other hand exhibit a slightly weaker whiteline intensity, because their bands are narrower, which results in less hybridization.²⁰-²³ If Au is in a positive valence state, such as in Au₂O₃ or HAuCl₄, more states in the 5d band are empty, and the XANES spectrum exhibits an intense whiteline. Thus the intensity of the whiteline can be used to study the oxidation state.

2.7.2. High-energy fluorescence detected X-ray absorption spectroscopy (HERFD XAS)

In this work XANES spectra were measured in the high-energy-fluorescence detection (HERFD) mode, which gives much better resolution of the spectra with sharper features than is possible with standard detection methods.²⁴-²⁸ In general fluorescence detection is applied for diluted samples or in cases, when the sample cannot be
prepared thin enough to provide sufficient transmission. For conventional detection methods the energy resolution is restricted by the life-time broadening of the core-hole. In HERFD this limitation is avoided by detecting a fluorescence decay channel with a longer core-hole life time. This leads to less broadening according to Heisenberg's indetermination principle ($\Delta E \sim h/\Delta t$). Thus, spectra with higher energy resolution and sharper features can be obtained, which is illustrated in Figure 3. It shows a XANES spectrum of Au foil, which was recorded both in normal transmission mode and by HERFD.

![Figure 3. XANES spectra of Au foil, recorded in transmission mode (solid line) and by HERFD (dashed line).](image)

The transmission spectrum exhibits a small whiteline, whereas in the HERFD spectrum the intensity of the whiteline is significantly higher. In addition, also all other features are much more distinct. Another advantage of HERFD XAS is that it is an element specific detection method. This allows recording spectra in ranges, which are not accessible by conventional detection, because undesired edges of other elements interfere. HERFD is also applicable for the elements in the fifth row of the periodic table, because due to the delocalization of the 5d electrons, final state effects are insignificant. On the other hand, spectra of 3d transition metal complexes should be analyzed carefully, because here final state effects can be strong.\textsuperscript{28}

In chapter 4, Au L\textsubscript{3} HERFD spectra were continuously collected during pretreatment of supported gold catalysts in the liquid phase and during liquid phase hydrogenation.
The time resolution was one spectrum per minute. The experiments were performed at the XAS-XES beamline ID26 of the European Synchrotron Radiation Facility, Grenoble, France, which is operated at an energy of 6.0 GeV and a ring current of 50–90 mA. The measurements were conducted by using the third harmonic of two U35 undulators. The incident energy was monochromatized through a pair of Si(111) single crystals. Three Pd/Cr mirrors at 2.5 mrad relative to the incident beam suppressed higher harmonics. The X-ray beam was 0.3 mm wide and 1 mm high, with a total flux of $5 \cdot 10^{12}$ photons s$^{-1}$. HERFD was performed with a horizontal plane Rowland circle spectrometer in combination with an avalanche photodiode (Perkin-Elmer). The spectrometer was tuned to the Au La1 fluorescence line (9713 eV) through four Ge(660) crystals. A total resolution of 2.1 eV was obtained. The raw HERFD XAS spectra were treated with the Athena software. After background subtraction the raw data were normalized in the range between 11.98 and 12 keV. The spectra were smoothed by the Savitzky-Golay method. Assuming that the cationic Au was in the 3+ oxidation state, the fraction of cationic and reduced gold in the samples was determined from linear combinations of the spectra of Au$_2$O$_3$ and gold foil. Exposure of the slurry to X-rays in the absence of hydrogen did not cause any changes to the spectra, which indicates that reduction of the gold precursor, and thus beam damage, did not occur.
References


3. In situ determination of the oxidation state of supported metals in the liquid phase

3.1. Introduction

To improve the performance of catalysts, structure-performance relations need to be known. They can only be determined by applying in situ characterization techniques. While for gas phase reactions various in situ cells exist, there are only a few reports about in situ setups for liquid phase reactions. In this work, the feasibility of a newly constructed in situ cell, designed to study heterogeneous catalysts in the liquid phase by means of X-ray absorption spectroscopy was evaluated. The reduction behaviour of Pt and Re in Pt-Re bimetallic catalysts in the liquid phase at 120 °C and a hydrogen pressure of 10 bars was investigated by simultaneous recording of X-ray absorption near edge structure (XANES) spectra at the Pt and Re L₃ edges in fluorescence mode. The homemade cell consisted of a stainless steel autoclave reactor with an opening (cut window) and a PEEK inlet, allowing the X-rays to penetrate the reaction mixture. Pt-Re catalysts are commonly used in the production of high octane gasoline blends from catalytic reforming of naphtha. However, their application to fine chemicals production was only reported recently by Manyar et al., who reported that a Pt-Re catalyst could selectively hydrogenate carboxylic acids to alcohols and amides in liquid phase under relatively mild conditions when compared to the commercial systems. The catalytic performance of Pt-Re bimetallic catalysts in the aforementioned hydrogenations was found to be linked to the interaction between metals, support, and solvent used. By means of ex situ gas phase characterization, Manyar et al. suggested that the difference in activity was due to the metal support interaction which lead to differences in the overall oxidation state of the metals. However, the metal oxidation state prior and during reaction remains unknown, which can only be unveiled if the reduction step is followed by in situ characterization. Herein, we report the in situ recording of the reduction of a Pt-Re catalyst, generally carried out before reaction, in liquid phase 10-20 bar hydrogen, on one hand and in the gas phase with 1 bar on the other hand. This is the first study, to our knowledge, that in situ determined differences in the extent of metal reduction depending on the media. Two solvents (THF and hexane) and two oxide supports (Al₂O₃ and TiO₂) were investigated to elucidate their role on the oxidation state of the metals.
3.2. Introduction

Alumina (γ type, Ketjen Catalysts) and titania (P90, Nippon Aerosil) were used as received. Platinum nitrate (assay 15.14%) and perrhenic acid (assay 39.4%) solutions were supplied by Johnson Matthey. 4 %Pt-4%Re/Al₂O₃ and 4 %Pt-4%Re/Al₂O₃ were prepared by sequential incipient wetness impregnation. Pt was deposited first. Platinum nitrate solution, diluted with doubly distilled deionised water (18 MΩ) to yield a volume equal to the pore volume of the respective support was added to the support in three portions under stirring. After drying at 120 °C for 12 hours and calcination at 500 °C for 4 hours, the process was repeated for Re.

Liquid phase reductions were performed using 300 mg of catalyst, 25 ml of solvent (THF or hexane) and 10 bar H₂ pressure in an autoclave reactor modified to achieve access of X-rays to the inner part of the reactor. Pt and Re L₃ edges were monitored within a single measurement. The Re L₃ edge was recorded in normal fluorescence with a KETEK detector and the Pt L₃ edge was monitored using HERFD (High Energy Resolution Fluorescence Detection) recently introduced to the SuperXAS beamline of the Swiss Light Source (SLS). Gas phase reduction was monitored with the same X-ray emission spectrometer and performed in a 3 mm OD and 100 μm thin quartz tube loaded with about 20 mg of catalyst over which a flow of 10 mL/min of pure hydrogen was passed through. In both cases, the heating rate was 20 °C/min up to 120 °C. Spectra of reference compounds were measured prior to the in situ experiments. For Pt, monometallic catalyst reduced in situ at 300 °C was used as reference for metal part and catalyst after calcination for oxidic part. For Re, calcined catalyst was used as reference for oxidic part whereas catalyst reduced in situ at 600 °C was used as metal reference.

3.3. Results and discussion

A representative spectrum of Pt L₃ edge HERFD recorded in situ during liquid phase reduction is depicted in Figure 1. After 15 min, the white line of Pt had visibly reduced in intensity and shifted by ca. 1 eV to lower energies, demonstrating reduction.
Figure 1. Pt L$_3$ edge HERFD-XANES spectra of 4%Pt-4%Re/Al$_2$O$_3$ recorded in situ in THF and 10 bar of pure H$_2$ at 120 °C. (●) Start of reduction and (■) after 15 min. Insert shows first derivative.

The final oxidation state of the metals was obtained within the first 15 min (Fig. 2), revealing the celerity of the reduction procedure both in gas and liquid phase.

Figure 2. Evolution of Pt L$_3$ edge HERFD-XANES spectra as a function of time of 4%Pt-4%Re/Al$_2$O$_3$ collected in THF with 10 bar of pure H$_2$ at 120 °C. (■) 15 min; (●) 30 min and (▲) 60 min.
Due to the good spectra quality, peak deconvolution was possible using linear combination of standard spectra to obtain the fraction of metallic to oxidic species at different stages of the pre-treatment. The process is depicted in Figures 3 and 4 for the Pt and Re L₃ edges, respectively, and summarized in Tables 1 and 2. The influence of oxidic platinum (PtOₓ) corresponds to the sum of PtO and PtO₂ contributions and ReₓOₓ to the sum of all oxidic rhenium species, namely ReO₂ and Re₂O₇. Deconvolution were performed using the reference spectra, with an uncertainty better than ± 5%.

**Figure 3.** Pt L₃ edge HERFD-XANES spectrum of 4%Pt-4%Re/Al₂O₃ after reduction in hexane 10 bar of pure H₂ at 120 °C. (●) original data; ( —— ) overall fitting; (———) Pt metal reference and ( — ) PtOₓ reference.

**Figure 4.** Re L₃ edge HERFD-XANES spectrum of 4%Pt-4%Re/Al₂O₃ after reduction in hexane 10 bar of pure H₂ at 120 °C. (●) original data; ( —— ) overall fitting; (———) Re metal reference and ( — ) ReₓOₓ reference.
Table 1. Summary of the Pt L3 edge HERFD-XANES deconvolutions.

<table>
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<th>Sample</th>
<th>Treatment</th>
<th>PtOx (%)</th>
<th>Pt₀ (%)</th>
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<td>100</td>
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<tr>
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<td>Calcination</td>
<td>100</td>
<td>--</td>
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<tr>
<td>4%Pt-4%Re/TiO₂</td>
<td>Gas phase reduction</td>
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<td>100</td>
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Table 2. Summary of the Re L3 edge XANES deconvolutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Re₂Oₓ (%)</th>
<th>Re₀ (%)</th>
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</tbody>
</table>

To compare the effectiveness of gas respective to liquid phase reduction, 4%Pt-4%Re/Al₂O₃ sample was reduced for 1 h in both mediums. Gas phase reduction reduces Pt more efficiently than liquid phase reduction since it completely reduces Pt to its metallic state, which contrasts to the 80% reduction performed in liquid phase. This contrasting result clearly elucidates the relevance of in situ characterization. Changing the solvent from hexane to THF caused a small decrease of the amount of reduced Pt. Catalysts performed selective hydrogenations better in non-polar solvents like hexane or dodecane. With respect to Re, the same extent of reduction was observed for liquid and gas phase reduction. Gas phase reduced rhenium completely and liquid phase to 95%. In this case solvent had no influence on the amount of Re reduced. Reduction of rhenium oxides to metallic in a monometallic catalyst is only possible at high temperatures, which suggests that the reduction of rhenium is due
to hydrogen spillover from platinum, suggesting close contact of the metals. The accurate particle size distribution is hard to measure with conventional transmission electron microscopy, because of the proximity of the atomic numbers of Pt and Re. CO pulse chemisorption, yielded Pt particles sizes smaller than 10 nm for both catalysts, which means that a significant amount of atoms are present at the surface and thus may be exposed to interactions resulting in different degrees of reduction depending on the conditions used. Since catalysts performed better when supported on titania,\textsuperscript{14} it is important to compare the reduction of the metals with both supports in the same solvent. Results showed that Pt reduced by an extra 21\% when supported on TiO$_2$, which might affect the catalytic performance. In contrast, rhenium was found to be harder to reduce on titania compared with alumina. A number of explanations may be proposed including the possibility that some of the Re is not in contact with Pt making it harder to reduce. Also, the, strong metal support interaction between Re and TiO$_2$ might play a role.

3.4. Conclusions

In conclusion, this study corroborates the current idea that in situ spectroscopy offers more reliable information about the catalyst structure. Liquid phase reduction is less efficient than gas phase at least when Pt is concerned. The solvent has a small but measurable contribution to the amount of metallic phase after reduction, which might be in some cases sufficient to explain differences of catalytic performance. Titania as a support caused Pt to reduce more efficiently than alumina. Titania seems to have a fraction of Re not associated to Pt which is different from alumina. The study, demonstrates the possibility to evaluate active species oxidation state in autoclave reactors commonly used by fine chemical industry. The experiments identified clear differences in catalyst structure within a gas phase reactor compared to a liquid phase one.
References

4. The dynamic structure of gold supported on ceria, in the liquid-phase hydrogenation of nitrobenzene*

4.1. Introduction

Bulk gold is the most inert metal. However, when finely dispersed on a support, it is a very active catalyst in many reactions, and molecules such as hydrogen, oxygen, and carbon monoxide chemisorb on the surface of the gold. Examples of such reactions are CO oxidation, the water gas shift reaction, selective alcohol oxidation, the hydrochlorination of ethyne, the epoxidation of propene, and hydrogenation reactions including the hydrogenation of alkenes, alkadienes, alkynes, α,β-unsaturated carbonyl compounds, and nitro compounds. A unique property of gold is its high chemo-selectivity due to preferential adsorption of oxygen-containing groups, in contrast to conventional hydrogenation catalysts such as palladium, platinum, and ruthenium, which must be modified. Gold is, therefore, a promising catalyst for the development of new, clean, and sustainable industrial processes with a minimal formation of side products. Although many studies aim to describe the catalytically active sites, there is disagreement about the nature of catalytically active sites in heterogeneous gold catalysis. Various suggestions have been made to explain the catalytic activity of supported gold catalysts, for example the size, structure, and morphology of the supported gold species, the interface between gold particles and the support, and the oxidation state(s) of gold in the catalysts. In particular, the oxidation state of the active gold species is still unclear. The catalytically active gold species in the well-studied CO oxidation have been proposed to be cationic, fully reduced, and negatively polarized gold. Aberration-corrected scanning transmission electron microscopy revealed that gold bilayer clusters, approximately 0.5 nm and containing about 10 gold atoms on FeOx supports, are highly active in CO oxidation. Cationic gold has been proposed to be essential for reaching high catalytic activity in the water gas shift reaction over gold supported on nano-crystalline La-doped CeO2. Although hydrogenation has not been studied to the same degree as oxidation, there is still no consensus with regard to the oxidation state of the active

* This work was performed in collaboration with another Ph.D. student, Martin Makosch.
gold species. Cationic\textsuperscript{16-20, 45} and reduced\textsuperscript{21} gold have been associated with high catalytic activity. In conclusion, the nature of the active species in heterogeneous catalysis by gold is still unclear. In particular, in hydrogenation reactions in situ studies\textsuperscript{16,17,46} determining the oxidation state of gold during operation are seldom. The aim of our work was to study in situ the electronic properties of a supported gold catalyst (Au/CeO\textsubscript{2}) in a liquid-phase hydrogenation reaction, namely the hydrogenation of nitrobenzene to form aniline. This reaction has been studied extensively, both mechanistically and kinetically, and is applied in large scale industrial processes to produce 90 to 95\% of the world’s production of aniline.\textsuperscript{47} Corma et al.\textsuperscript{30} recently discovered that supported gold catalysts catalyze the liquid-phase hydrogenation of aromatic nitro compounds under mild conditions (100-120 °C, 10 bar H\textsubscript{2}). Using a newly constructed in situ cell, we recorded simultaneously and in situ high resolution XANES (X-ray absorption near edge structure) spectra of the at the Au L\textsubscript{3} edge in fluorescence mode of the catalyst in the reaction mixture and monitored the reaction by ATR-FTIR (attenuated total reflectance-Fourier transform infrared) spectroscopy with a probe dipped into the slurry.\textsuperscript{48,49} The cell is an autoclave reactor modified to achieve access of the X-rays to the inner part of the reactor.\textsuperscript{50} X-ray absorption spectroscopy (XAS) is a very powerful technique to determine the structural and electronic properties of catalysts under reaction conditions.\textsuperscript{51} The X-ray absorption near-edge structure part of an XAS spectrum gives information about the oxidation state and the local geometry of the absorbing atom. It reflects the empty density of state (DOS) of the electronic transition.\textsuperscript{52} XANES spectra were measured in high-energy-fluorescence detection (HERFD) mode, which gives much better resolution of the spectra with sharper features than is possible with standard detection methods.\textsuperscript{46,53-56} ATR-FTIR spectroscopy is a reliable technique for monitoring online reactions.\textsuperscript{57-59} Molecular vibrations that lead to changes in the molecule’s dipole momentum, induced by MID infrared radiation (4,000-400 cm\textsuperscript{-1}), enable the identification and quantification of most of the organic compounds. Thus, we determined the electronic properties of gold supported on ceria and the changes it undergoes under different pretreatment and reaction conditions and, at the same time, monitored the course of the reaction.
4.2. Experimental Section

Au/CeO$_2$ was prepared by deposition precipitation with urea. First, though, CeO$_2$ (99.9 %, ABCR-Chemicals) was calcined at 500 °C for 5 h to remove any residual nitrates. To prepare 0.8 wt % Au/CeO$_2$, HAuCl$_4$$\cdot$H$_2$O (0.085 g; Au: 49 %, 99.9 % metal basis, ABCR-Chemicals) was dissolved in deionized H$_2$O (500 ml). CeO$_2$ (5.0 g) and urea (1.5 g; puriss. p. a. ≥ 99.5 %, Riedel-de Haën) were added while stirring. The mixture was heated to 80 °C and stirred for 16 h in a closed teflon vessel. After cooling to room temperature, the solid product was obtained after filtration and washed five times with deionized water to remove residual chloride ions. To verify the removal of chloride 1 M AgNO$_3$ solution was added to the filtrate. Precipitation of AgCl was not observed. The product was dried at room temperature under vacuum in the dark for 48 h. The gold loading of the catalyst was determined by AAS on a Varian SpectrAA 220 FS spectrometer after dissolving an aliquot of the sample in a mixture of HCl/HNO$_3$/HF.

Pretreatment of the catalyst and the hydrogenation of nitrobenzene were carried out in a newly constructed autoclave reactor that enables X-rays to penetrate the reaction mixture. Pretreatment of the catalyst was performed in toluene, i.e. in the solvent of the subsequent reaction, at a hydrogen pressure of 10 bar. Au/CeO$_2$ (0.30 g) as prepared was added to 25 ml toluene, and residual air was removed by flushing the autoclave three times with H$_2$. After changing the pressure to 10 bar H$_2$, the suspension was heated while stirring (1,500 rpm) at 4 °C/min to the desired pretreatment temperature (60 or 100 °C) and kept at this temperature for 30 min. After pretreatment, the mixture was left to cool to 60 °C, and 2.13 g nitrobenzene were added. After purging with H$_2$ three times, the autoclave was pressurized with 10 bar H$_2$ and heated (4 °C/min) while stirring at 1,500 rpm to the reaction temperature of 100 °C. The start of heating was set as reaction time zero. Alternatively, in one experiment, the reaction was performed at 60 °C. The conversion of nitrobenzene was monitored in situ by an ATR-FTIR system (Mettler Toledo) with a DiComp optical fiber immersion probe attached to a ReactIR 45 spectrometer. One spectrum per minute (average of 16 scans) was recorded with a resolution of 2 cm$^{-1}$ in the range 750 to 2,000 cm$^{-1}$. Background spectra were collected of the suspension of the catalyst in toluene at the respective temperatures.

HERFD spectra at the Au L$_3$ edge were continuously collected during pretreatment of the catalyst and during hydrogenation of nitrobenzene with a time resolution of one
scan per minute. The experiments were performed at the XAS-XES beamline ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, which is operated at an energy of 6.0 GeV and a ring current of 50 to 90 mA. The measurements were carried out using the third harmonic of two u35 undulators. The incident energy was monochromatized by a pair of Si(111) single crystals. Three Pd/Cr mirrors at 2.5 mrad relative to the incident beam suppressed higher harmonics. The size of the X-ray beam was 0.3 mm wide and 1 mm high, with a total flux of $5 \times 10^{12}$ photons s$^{-1}$. High energy resolution fluorescence detection was achieved by a horizontal-plane Rowland circle spectrometer in combination with an avalanche photodiode (APD, Perkin Elmer). The spectrometer was tuned to the Au L$_\alpha_1$ fluorescence line (9713 eV) by four Ge (660) crystals. A total resolution of 2.1 eV was obtained.

4.3. Results

Figure 1 shows the evolution of Au L$_3$ HERFD spectra of Au/CeO$_2$ measured in situ during reduction to 60 °C (a) and 100 °C (b). In both cases, the spectra during the first 10 minutes were measured at room temperature before introducing H$_2$. These spectra show an intense first feature, the whiteline. Its intensity corresponds to the number of holes in the 5-d band and its high intensity is typical of gold in the 3+ oxidation state. The subsequent spectra were taken while heating at 4 °C/min at 10 bar hydrogen. In both experiments, the intensity of the whiteline decreased fast and features appeared at 11.93, 11.95, and 11.97 keV, typical of metallic gold; thus, Au$^{3+}$ species reduced to Au$^0$. In the case of reduction at 60 °C, the whiteline decreased gradually during heating (10 min) and continued to decrease at a slightly slower rate at a constant temperature of 60 °C for 30 min. Reduction was incomplete (vide infra). During heating to 100 °C, the reduction of the whiteline was complete at about 90 °C.
Figure 1. Au L$_3$ HERFD spectra of as prepared 0.78 wt% Au/CeO$_2$, recorded during pretreatment in toluene at 10 bar H$_2$ and 100 °C (a) and 60 °C (b). The time resolution was one spectrum per minute. Spectra within the first 10 min were measured at room temperature before introducing H$_2$.

Figure 2 shows the Au L$_3$ HERFD spectra after pretreatment at 60 and 100 °C and that of gold foil. The spectrum after pretreatment at 100 °C resembles that of the gold foil, with the exception of a slightly weaker whiteline intensity, indicative of small clusters.$^{60, 61}$ There was no evidence of cationic gold. Au/CeO$_2$ pretreated at 60 °C shows a higher whiteline intensity than that of gold foil and a lower intensity between 11.925 and 11.935 keV, indicating that a fraction of the gold species was cationic. Assuming that the cationic gold was in the 3+ oxidation state, the fraction of cationic and reduced gold was determined from linear combinations of the spectrum of Au$_2$O$_3$ and Au foil, yielding 28 % Au$^{3+}$ and 72 % Au$^0$.
Figure 2. Au L₃ HERFD spectra of Au/CeO₂ after pretreatment at 60 and 100 °C and of gold foil.

Table 1. Fraction of Au³⁺ and Au⁰ in Au/CeO₂ after pretreatment and during hydrogenation of nitrobenzene and reaction rates for hydrogenation at 100 °C after pretreatment of Au/CeO₂ at 60 and 100 °C.

<table>
<thead>
<tr>
<th>Pretreatment temp./°C</th>
<th>Reaction temp./°C</th>
<th>Reaction time/min</th>
<th>Au⁰/%</th>
<th>Au₂O₃/%</th>
<th>Reaction rate /mmol/(gAu*s)</th>
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a: Rate between 0 and 10 min. b: Rate between 10 and 30 min.

Table 1 gives the Au³⁺ and Au⁰ fractions in Au/CeO₂ after the respective pretreatment and under the applied hydrogenation conditions after different reaction times. The initial catalytic activity and after 10 min reaction time are given for reaction at 100 °C over Au/CeO₂ pretreated at 60 and 100 °C.

Hydrogenation of nitrobenzene was performed right after the respective pretreatment, and Au L₃ HERFD spectra were recorded in situ throughout the whole reaction. Figure
Figure 3 shows Au L₃ HERFD spectra after pretreatment at 100 °C and after 10, 30, and 60 min reaction at 100 °C. It shows that gold is fully reduced at the beginning of the reaction, i.e. after pretreatment at 100 °C, and remained in the reduced state throughout the reaction.

Figure 3. Au L₃ HERFD spectra of Au/CeO₂ after pretreatment at 100 °C and during hydrogenation of nitrobenzene at 100 °C after 10, 30, and 60 min reaction time.

Figure 4 shows Au L₃ HERFD spectra measured during the first 10 min of the hydrogenation of nitrobenzene at 100 °C after pretreatment of Au/CeO₂ at 60 °C. Under reaction conditions, the intensity of the whiteline decreased rapidly. Starting from 28 % Au³⁺ after pretreatment, the Au³⁺ fraction decreased to 15 % after 3 min and 9 % after 6 min. After 10 min the spectra matched that of gold foil, and cationic gold was not detected. Thus, Au³⁺ converted to Au⁰ under the reaction conditions.

Figure 4. Au L₃ HERFD spectra of Au/CeO₂ after pretreatment at 60 °C and during hydrogenation of nitrobenzene at 100 °C after 3, 6, and 10 min reaction.
Figure 5 presents Au L$_3$ HERFD spectra after pretreatment of Au/CeO$_2$ at 60 °C and during hydrogenation of nitrobenzene at 60 °C. At a reaction temperature of 60 °C the intensity of the whiteline also decreased continuously as the reaction proceeded, though at a slower rate than during hydrogenation at 100 °C. Starting from 24 % Au$^{3+}$ after pretreatment, the Au$^{3+}$ fraction was 20 % after 10 min and 10 % after 30 min of reaction. After 60 min the reduction was complete and the spectra resembled that of the foil.

Figure 5. Au L$_3$ HERFD spectra of Au/CeO$_2$ after pretreatment at 60 °C during hydrogenation of nitrobenzene at 60 °C after 10, 30, and 60 min reaction, and of gold foil.

Figure 6 shows the conversion of nitrobenzene at 100 °C after pretreatment at 60 and 100 °C as determined from the intensity of the infrared band of the asymmetric stretching of the nitro group at 1,530 cm$^{-1}$. The corresponding fractions of Au$^{3+}$ are plotted against the reaction time.
Figure 6. Hydrogenation of nitrobenzene at 100 °C and 10 bar H₂ after pretreatment of Au/CeO₂ at 60 °C (red triangles) and 100 °C (black squares) given by the decreasing amount of nitrobenzene in the reaction. The corresponding fractions of Au³⁺ (yellow triangles for Au/CeO₂ pretreated at 60 °C and black crossed squares for Au/CeO₂ pretreated at 100 °C) are plotted against the reaction time. For both pretreatments two straight lines between 0-10 min and 10-30 min respectively represent the conversion of nitrobenzene over time.

The conversion curves after each of the pretreatments can be divided into two more or less linear segments, between 0 and 10 min and 10 and 30 min reaction time respectively. The initial activity (0-10 min) of the catalyst pretreated at 100 °C, at which cationic gold was not detected, was higher (0.19 mmol/(gAu*s)) than that of the catalyst reduced at 60 °C, which contained significant amounts of cationic gold (0.14 mmol/(gAu*s)). Thus, it is clear that the cationic gold present after treatment at 60 °C does not lead to high catalytic activity. After around 10 min the activity of Au/CeO₂, pretreated at 60 °C, decreased to 40 % of its initial activity resulting in 0.06 mmol/(gAu*s). At the same time the reduction of Au³⁺ was complete. However, the catalytic activity of the fully reduced Au/CeO₂ after pretreatment at 100 °C showed exactly the same behavior and also decreased to 40 % after around 10 min resulting in 0.08 mmol/(gAu*s). Thus, there is no correlation between catalytic activity and the amount of cationic gold; the decrease in activity is the same, irrespective of whether the sample contains measurable amounts of cationic gold.

4.4. Discussion

As shown by the intensive whiteline in the Au L₃ HERFD, as prepared Au/CeO₂ mainly contained gold in the 3+ oxidation state. During pretreatment at 100 °C, the
reduction of Au\(^{3+}\) was fast and complete. Pretreatment at 60 °C led to slower reduction and, after pretreatment, about 25 to 30 % cationic gold was left. The liquid phase hydrogenation of nitrobenzene was performed at 100 °C and 10 bar \(\text{H}_2\), which are mild conditions, as commonly reported in the literature for such catalytic systems.\(^{30}\) The catalyst without measurable amounts of cationic gold was more active than the catalyst containing cationic gold. Thus, the observed cationic gold does not show high catalytic activity. Moreover, the fraction of cationic gold present in Au/CeO\(_2\) pretreated at 60 °C was not maintained under reaction conditions; it converted to Au\(^0\), and after 10 min reduction was complete. At the same time the activity of this catalyst decreased by 60 %. However, Au/CeO\(_2\), pretreated at 100 °C, was fully reduced from the beginning and showed exactly the same deactivation behavior. After about 10 min the catalytic activity decreased by 60 %. Thus, the decrease in catalytic activity is not related to the reduction of cationic gold, which is probably due to poisoning of the catalyst surface by reaction intermediates/and or deposition of carbonaceous species.\(^{49}\) After both pretreatments, the reaction eventually proceeded without detectable amounts of cationic gold. The above results were supported by an additional experiment. The hydrogenation of nitrobenzene over Au/CeO\(_2\), pretreated at 60 °C, was performed at 60 instead of 100 °C. Reduction of Au\(^{3+}\) also occurred under these conditions but was slower than under the reaction conditions at 100 °C. Significant amounts of Au\(^{3+}\) were present for at least 30 min. The conversion of nitrobenzene was low but constant during this period, although the fraction of Au\(^{3+}\) decreased from 25 to 10 %. Thus, varying amounts of Au\(^{3+}\) did not influence the catalytic activity. If undetected cationic gold were responsible for the catalytic reaction, then it would have been located at an undetectable site and would have been very stable to maintain its oxidation state. We estimate that about 1 % of cationic gold can be detected by HERFD.

For hydrogenation reactions over supported gold catalysts it has been suggested that cationic and reduced gold can be highly active. Our results are in good agreement to those of Hensen et al.,\(^{21}\) who studied the structure and oxidation state of gold supported on ceria in the selective gas phase hydrogenation of 1,3-butadiene by XAS. They found that the catalytic activity of 0.08 wt % Au/CeO\(_2\) obtained after leaching by NaCN, which comprised solely isolated Au\(^{3+}\) increased strongly with the reduction temperature i.e. the amount of reduced gold. They further observed an increasing catalytic activity of the as prepared non pre-reduced catalyst with time on stream, which was ascribed to a slow reduction of Au\(^{3+}\) under reaction conditions. Thus, they
also observed changes of the catalyst structure under reaction conditions. Cationic gold prepared by deposition precipitation is inactive in hydrogenation of nitrobenzene and 1,3-butadiene. Our results contrast with those of Guzman and Gates,\textsuperscript{16,17} who concluded that mononuclear Au(III) species supported on MgO were the catalytically active species in the hydrogenation of ethylene. A cationic gold complex (Au(CH\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})) was deposited on MgO. EXAFS spectroscopy under working conditions did not show Au-Au contributions, however the XANES spectra exhibit a decrease in the white line intensity during the first 30 min of the reaction. The authors attribute this decrease to changes in site symmetry of the mononuclear gold species rather than changes in the oxidation state of gold, such as partial reduction. Homogeneous cationic complexes of gold are active catalysts.\textsuperscript{62} This suggests that cationic gold, in a heterogeneous catalyst might be active when prepared from an appropriate cationic gold complex. However, many homogeneous reactions proceed with both Au(I) and Au(III) pre-catalysts, and the oxidation state of the active species has not yet been identified.\textsuperscript{62} Zhang et al.\textsuperscript{18} investigated the nature of the active gold species in the hydrogenation of 1,3-butadiene over Au/ZrO\textsubscript{2} catalysts by preparing catalysts with different fractions of Au\textsuperscript{3+}. They concluded that site isolated Au\textsuperscript{3+} ions, which they observed in Au/ZrO\textsubscript{2} catalysts with loadings lower than 0.1 wt% were the active sites for the hydrogenation of 1,3-butadiene. However, the catalysts were only characterized prior to the reaction (TPR and XPS) but neither during nor after the reaction. They further varied the calcination temperature of a 0.8 wt % Au/ZrO\textsubscript{2} catalyst in a range between 473-773 K to obtain catalysts with different ratios of Au\textsuperscript{3+}/Au\textsuperscript{0}, whereat the fraction of cationic gold decreased with increasing calcination temperature, and so did the catalytic activity. The decrease in catalytic activity was attributed to the decrease of the fraction of cationic gold. However simultaneously with increasing calcination temperature the mean particle size increased significantly from 4 nm at a calcination temperature of 473 K, to 7 nm at 573 K, and 12 nm at 773 K. Thus the decrease in activity might as well be a result of the increasing particle sizes.

With regard to the activation of hydrogen on supported gold catalysts, several studies suggested that the presence of metallic gold particles is essential. Mohr et al.\textsuperscript{63,64} identified the edges of single crystalline cubocatahedral Au nanoparticles with a mean diameter of 9 nm supported on ZnO as active sites for the selective hydrogenation of the CO group of acrolein to allyl alcohol. Via selective decoration of the Au faces by indium leaving the edges uncovered, an increased selectivity to the desired allyl
alcohol was observed. Bus et al. investigated the interaction of hydrogen with Au/Al₂O₃ and Au/SiO₂ catalysts combining X-ray absorption spectroscopy, hydrogen chemisorption, and H/D exchange experiments. They found that with decreasing particle size, increasing amounts of hydrogen were chemisorbed and an increasing fraction adsorbed strongly. The Au/Al₂O₃ catalyst with the smallest particle size of about 1 nm exhibited the highest hydrogen uptake per surface atom. At this size, most of the surface consists of atoms at corner and edge positions. Thus it was proposed that hydrogen atoms only adsorb at edges and corners of the gold particles. Additional H/D exchange experiments showed that hydrogen adsorbed dissociatively on gold and that the adsorption was activated. By combining isotopic H/D exchange experiments with IR and DFT results, Boronat et al. demonstrated that among the different gold sites identified, only low coordinated, neutral gold atoms, located at corner or edge positions of Au/TiO₂ catalysts were able to dissociate H₂. Fujitani et al. studied the H₂-D₂ exchange reaction over Au/TiO₂ (110) surfaces with different gold particle sizes. With decreasing gold particle size the rate of HD formation increased. For particle sizes below 2 nm a marked increase in activity was observed. However, the apparent activation energies for the H₂-D₂ exchange reaction were almost identical for all Au/TiO₂ (110) model catalysts regardless of the differences in the gold particle sizes. Thus the authors concluded that the nature of the active sites for the dissociation of H₂ over Au/TiO₂ (110) were the same irrespective of the size of the gold particles and proposed that the gold atoms at the metal-support interface were the catalytically active sites. Shimizu and coworkers investigated the influence of particle size and nature of the support on the chemoselective hydrogenation of nitroaromatics over supported gold catalysts. Regarding the Au particle size they observed an increasing activity for the OH/D₂ exchange reaction with decreasing particle size. Au nanoparticles of similar mean particle sizes were found to be most active when supported on an acid-base bifunctional support (Al₂O₃) rather than on a basic (MgO) or acidic (SiO₂) support. Thus the authors concluded that these surface acid base pair sites were required for the dissociation of hydrogen and proposed that the gold atoms at the metal-support interface were the catalytically active sites.

We determined in situ the oxidation state of gold in our highly responsive catalysts and simultaneously monitored the conversion of nitrobenzene. In our system we observed that, when cationic gold remained after pretreatment, it was reduced under the reaction conditions. We found no evidence that the detected cationic gold contributed to
catalytic activity. On the contrary, the fully reduced catalyst was more active than the partially oxidized catalyst.

4.5. Conclusions

In situ HERFD XANES spectroscopy at the Au L\textsubscript{3} edge during catalyst pretreatment and the liquid phase hydrogenation of nitrobenzene revealed large changes in the oxidation state of gold in Au/CeO\textsubscript{2} catalysts. Ex situ characterization is not quantitative for the structure under catalytic conditions. Liquid-phase pretreatment of as prepared Au/CeO\textsubscript{2} at 100 °C led to complete reduction of the gold species, whereas pretreatment at 60 °C resulted in the incomplete reduction of the gold species. Reduced Au/CeO\textsubscript{2} was more active in the liquid-phase hydrogenation of nitrobenzene at 100 °C than cationic gold containing Au/CeO\textsubscript{2}. When cationic gold was present at the beginning of the reaction it reduced under the reaction conditions, which was accompanied by loss of 60 % activity. However, deactivation is not related to the amount of cationic gold, because Au/CeO\textsubscript{2} that was fully reduced at the beginning of the reaction became deactivated in the same manner, probably because of blocking of the active surface. We did not find that cationic gold prepared by deposition precipitation on ceria is related to catalytic activity.
References


5. Particle size and support effects in hydrogenation over supported gold catalysts

5.1. Introduction

Gold nanoparticles on metal oxide supports are very selective catalysts in a variety of applications.1 Two key parameters for the activity of gold catalysts are the particle size and the support. The strong size dependence of activity for gold is perhaps best illustrated by the fact that bulk gold is mostly inert.2 Nanoscopic gold particles supported on metal oxides however, introduced to catalysis by Haruta and coworkers,3 are active in a variety of reactions, such as low temperature CO oxidation, hydrogenation, and the water-gas shift reaction.1

The relationship between particle size and activity has been intensely investigated both theoretically and experimentally.4-14 While most authors consider a particle size of less than about 2 nm to be crucial for activity, there is no consensus on the reason for this effect. Some argue that increased numbers of low-coordinated gold atoms are necessary,6,7,14 others suggest electronic effects based on particle size or combinations of the two.5,9,10,12,13 Most work relating catalytic activity to particle size in catalysis by gold was done for CO oxidation. When comparing particle size and activity, especially for experimental work rather than simulations, not only the average particle size, but the complete particle size distribution must be considered. Bond argued that for catalysts with a broad distribution of particle sizes, the lower end of the particle size distribution contributes most to the activity, and that looking only at average particle sizes is misleading.12 Bus et al. showed that gold particles with particle sizes of 2 nm and less are particularly active in the hydrogenation of cinnamaldehyde.9 Haruta and coworkers found a similar particle size effect in HD-exchange reactions on gold particles supported on titania and attributed this effect to the perimeter size of the particles.11 Nakamura et al. showed that titanium supported on gold is not active in HD-exchange. If it is oxidized to TiO2 however, the system becomes active.15 This shows that the interface of metallic gold and titatium oxide is crucial for activity. Corma and coworkers used DFT calculations and infrared spectroscopy to show that hydrogen is activated on neutral gold atoms with low coordination numbers.16,17 A much investigated hydrogenation reaction over supported gold catalysts is the reduction of nitroaromatic compounds to the corresponding anilines.18-23 As aromatic
amines with other reducible functionalities such as double bonds are key intermediates in a variety of applications, an efficient and selective method for the reduction of substituted nitroaromatic compounds is of considerable importance. The rate limiting step in the hydrogenation of nitrobenzene over gold supported on titania is the dissociation of hydrogen. This reaction can therefore be used to study the effect of particle size and support on the activation of hydrogen in an industrially relevant reaction.

This work determines the effect of particle size and support on the hydrogenation of nitroaromatic compounds catalysed by supported gold nanoparticles. We compare kinetic data, high energy resolution fluorescence detected X-ray absorption (HERFD XAS) measurements and particle size distributions obtained by TEM for gold on alumina respectively titania. By detecting a fluorescence line with an instrumental energy bandwidth on the order of the core hole lifetime broadening HERFD XAS spectra are obtained with a good signal to background ratio and with line-sharpened absorption features.

5.2. Experimental

Catalyst preparation: The catalysts were prepared by deposition-precipitation with urea. 0.086 mg of chloroauric acid (HAuCl₄, 49 wt% Au, ABCR-Chemicals) and 1.8 g of urea (puriss., Riedel-de Haën) were added to a suspension of 6 g of the support material (TiO₂: Hombikat UV 100, Sachtleben Chemie GmbH; Al₂O₃: Aluminiumoxid C, Degussa) in deionized water (600 mL). This suspension was stirred at 80°C for 16 h and then filtered. The solids were washed with deionized water until the resulting filtrate was free of chloride (as tested by addition of silver nitrate). They were then dried under vacuum for 72 hours, collected in a vial and stored in the freezer at -18 °C under exclusion of light.

Atomic Absorption Spectroscopy: Samples for AAS were prepared by microwave assisted digestion. 1 mL of nitric acid, 2 mL of hydrofluoric acid and 3 mL of hydrochloric acid were added to 40 mg of catalyst. The mixture was heated to 160 °C during 20 minutes and kept at that temperature for another 30 minutes while stirring in the microwave oven. AAS measurements were performed on a Varian SpectrAA 200 FS spectrometer with a C₂H₂/Air burner. The Au-content was quantified by calibration with a standard solution (gold solution, 1000 ppm in 1 M hydrochloric acid, Fisher-Scientific). All samples were measured three times.
<table>
<thead>
<tr>
<th>Sample name</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂</td>
<td>Au/TiO₂ as prepared</td>
</tr>
<tr>
<td>Au/Al₂O₃</td>
<td>Au/Al₂O₃ as prepared</td>
</tr>
<tr>
<td>Au/TiO₂-100</td>
<td>Au/TiO₂ reduced at 100 °C, 30 min, 10 bar and after catalytic use at 100 °C</td>
</tr>
<tr>
<td>Au/Al₂O₃-60</td>
<td>Au/Al₂O₃ reduced at 60 °C, 30 min, 10 bar and after catalytic use at 100 °C</td>
</tr>
<tr>
<td>Au/Al₂O₃-100</td>
<td>Au/Al₂O₃ reduced at 100 °C, 30 min, 10 bar and after catalytic use at 100 °C</td>
</tr>
<tr>
<td>Au/Al₂O₃-150</td>
<td>Au/Al₂O₃ reduced at 150 °C, 30 min, 10 bar and after catalytic use at 100 °C</td>
</tr>
<tr>
<td>Au/Al₂O₃-200</td>
<td>Au/Al₂O₃ reduced at 200 °C, 30 min, 10 bar and after catalytic use at 100 °C</td>
</tr>
<tr>
<td>Au/Al₂O₃-aniline</td>
<td>Au/Al₂O₃ reduced at 100 °C, 30 min, 10 bar and after catalytic use at 100 °C with 5x excess aniline</td>
</tr>
<tr>
<td>Au/TiO₂-rec</td>
<td>Au/TiO₂ reduced at 100 °C, 30 min, 10 bar and after catalytic use at 100 °C for three cycles</td>
</tr>
</tbody>
</table>

Transmission Electron Microscopy: Samples for TEM were prepared by filtration of the reaction mixture, washing with toluene and subsequent collection of the solids. TEM measurements were made on a HD2700CS (Hitachi, aberration-corrected dedicated STEM, cold FEG, 200 kV) and a Tecnai F30 ST (FEI, FEG, 300 kV).

Catalytic experiments: Catalytic experiments were performed in 50 mL stainless steel autoclaves from Premex Reactor AG (Lengnau, Switzerland). Magnetic stirring at 500 rpm was used. The catalyst (50 mg) and toluene (25 mL) were put into the autoclave, purged three times with hydrogen, pressurized with hydrogen to 10 bar, and heated to the desired pretreatment temperature (60 °C, 100 °C, 150 °C, respectively 200 °C). The suspension was then stirred at that temperature for 30 minutes. After cooling, a solution of nitrobenzene toluene (5 mL) was added, the suspension again put under a hydrogen pressure of 10 bar, heated to 100 °C and left to react under stirring at 500 rpm. Samples for GC were typically taken before heating, when the desired reaction
temperature was reached, after 10, 30, and 60 minutes and then every hour. Aniline poisoning experiments were performed by adding a threefold respectively fivefold molar excess of aniline together with the nitrobenzene and internal standard. Recycling experiments were performed by running the reaction with 100 mg of catalyst for 90 minutes, cooling down, adding new nitrobenzene (200 mg per cycle for Au/TiO₂, 50 mg per cycle for Au/Al₂O₃) in toluene (5 mL) and heating up again after pressurizing. Three such cycles were performed in each experiment. Samples were taken after heating up, after 10 minutes and after 90 minutes in each cycle. One mL of each sample and 20 µL mesitylene were mixed to produce the GC sample. Quantification by gas chromatography (GC) was carried out on an Agilent 7820 A chromatograph with a HP 5 ms column. The column was first kept at 80 °C for two minutes, and then heated to 300 °C at a rate of 20 °C per minute. An FID detector was employed.

XAS Measurements: All in situ HERFD XANES measurements were performed in a setup recently described in.³² Reduction experiments were performed in toluene. For each experiment, 300 mg of the “as prepared” catalyst was put into the reactor in 25 g of solvent. After that, the reactor was flushed three times with 10 bars hydrogen and finally pressurized to 10 bars hydrogen. Subsequently, the mixture was heated (4 K min⁻¹) to the corresponding temperature (60 °C, 100 °C, 150°C, respectively 200 °C) under mechanical stirring at 1500 rpm. As soon as the heating was started, HERFD XAS scans were recorded with a time interval of 1 min. The hydrogenation of nitrobenzene was performed in toluene. For that, 300 mg nitrobenzene were added to the reaction mixture of freshly reduced catalyst at 60 °C. After that, the cell was closed, flushed three times with 10 bars hydrogen, and finally pressurized to 10 bars hydrogen. Subsequently the mixture was heated (4 K min⁻¹) to reaction temperature (100 °C). As soon as heating was started, HERFD XAS spectra were recorded for 50 min with a time interval of 1 min. All experiments were recorded at beamline ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The ring operated in uniform mode at a ring current of 200 mA. Three u35 undulators using the third harmonic were employed for the HERFD XAS measurements. The incident energy was monochromatized by a pair of Si(111) crystals. Three Pd/Cr mirrors positioned at 2.5 mrad relative to the incident beam were used to suppress higher harmonics and focus the beam on the sample with a size of 600 µm horizontal and 200 µm vertical. The estimated flux was 8x10¹³ photons s⁻¹. HERFD spectra were measured by using a vertical-plane Rowland circle X-ray emission spectrometer in
combination with an avalanche photodiode (APD, Perkin Elmer). The scattering angle in the horizontal plane was ~130°. The spectrometer was tuned to the Au L\textsubscript{\alpha} fluorescence line (9713 eV) using the [660] reflection of four spherically bent Ge crystals. A total resolution of 2.1 eV was obtained. The raw HERFD XAS spectra were treated with the Athena software. After background subtraction the raw data were normalized in the range between 11.98 and 12 keV. The spectra were smoothed by the Savitzky-Golay method. Due to the good spectra quality, it was possible to obtain the fraction of oxidic to metallic gold at different stages of the pre-treatment and reaction using linear combinations of the initial spectra and fully reduced spectra of the catalyst. The results were smoothed by adjacent averaging. Exposure of the slurry to X-rays in the absence of hydrogen did not cause any changes to the spectra, which indicates that reduction of the gold precursor, and thus beam damage, did not occur.

5.3. Results

The gold content by mass of the catalysts as determined by atomic absorption spectroscopy was 0.74±14% for Au/TiO\textsubscript{2} and 0.69±9% for Au/Al\textsubscript{2}O\textsubscript{3}. Figure 1 illustrates two typical micrographs. The small bright dots represent the metal particles which were up to 8 nm in diameter for Au/Al\textsubscript{2}O\textsubscript{3}-100 (Figure 1A) and up to 26 nm in diameter for Au/Al\textsubscript{2}O\textsubscript{3}-200 (Figure 1B). Especially Au/Al\textsubscript{2}O\textsubscript{3}-200 showed a large particle size distribution.

![Figure 1. TEM images of Au/Al\textsubscript{2}O\textsubscript{3}-100 (A) and Au/Al\textsubscript{2}O\textsubscript{3}-200 (B).](Image)
Figures 2A and 2B show the particle size distributions for Au/TiO₂ and Au/Al₂O₃. Average particle size for Au/TiO₂ was 2.3 nm and for Au/Al₂O₃ 1.6 nm. Most of the particles in Au/TiO₂ had particle sizes below 4 nm, with only a small fraction between 4 and 8 nm. The fractions below 2 nm and from 2 nm to 4 nm were roughly equal. For Au/Al₂O₃, hardly any particles larger than 4 nm were observed.
Figure 2. Particle size distributions for all catalysts (A) Au/TiO$_2$; (B) Au/Al$_2$O$_3$; (C) Au/TiO$_2$-100; (D) Au/Al$_2$O$_3$-60; (E) Au/Al$_2$O$_3$-100; (F) Au/Al$_2$O$_3$-150; (G) Au/Al$_2$O$_3$-200; (H) Au/Al$_2$O$_3$-aniline; (I) Au/TiO$_2$-rec; (J) Au/Al$_2$O$_3$-rec.
For Au/TiO$_2$-100, there was an increase in average particle size from 2.1 nm to 3.6 nm (Figure 2C), but a significant fraction under 2 nm remained. Most of the particles were in the range between 2 nm and 4 nm and there were no particles larger than 12 nm. Figures 2D to 2G show the particle size distributions for Au/Al$_2$O$_3$-60, Au/Al$_2$O$_3$-100, Au/Al$_2$O$_3$-150, and Au/Al$_2$O$_3$-200. The fraction from 2 nm to 4 nm was the dominant fraction in all cases, but otherwise there was considerable variation. The fraction of particles under 2 nm was 7% for pretreatment at 60 °C, 15% for pretreatment at 100 °C, 28% for pretreatment at 150 °C and 0.7% for pretreatment at 200 °C. Figure 2H shows the particle size distribution of Au/Al$_2$O$_3$ after reaction in which the fivefold excess of aniline was present in the reaction mixture. The average particle size increased from 1.6 nm to 7.1 nm and the fraction of particles smaller than 2 nm decreased from 83% to 1.4 %. This indicates that adding aniline had caused sintering. Figures 2I and 2J show the particle size distributions of Au/TiO$_2$-rec and Au/Al$_2$O$_3$-rec. Again, average particle size was increased and the quantity of particles with a particle size of less than 2 nm decreased to 1.3% in TiO$_2$-rec and to 2.5% in Au/Al$_2$O$_3$-rec. This shows that recycling of the catalyst leads to sintering.

Figure 3A shows catalytic data for the reduction of nitrobenzene by Au/TiO$_2$ after various pretreatments. There was no large effect of pretreatment temperature on the activity; all showed a rapid decrease of nitrobenzene. Full conversion was achieved within two hours in all cases. Figure 3B shows kinetic data for the reduction of nitrobenzene over alumina-supported gold. In all cases, the catalyst was not only considerably less active than gold supported on titania, but there was also a significant effect of the pretreatment temperature on catalytic activity. Both pretreatment at 60° C and at 200 °C gave drastically reduced activity of the catalyst compared to the optimum activity achieved for pretreatment at 150 °C. This is the catalyst with the largest fraction of particles below 2 nm. The catalyst pretreated at 60 °C showed hardly any activity in the first 10 minutes of reaction, but became active later on, though at moderate rate. The catalyst pretreated at 200 °C showed low activity during the whole reaction time.
Figure 3. Nitrobenzene consumption in the reduction of nitrobenzene catalyzed by
titania-supported Au (A) and alumina-supported Au (B) for pretreatment temperature
of 60 °C (■), 100 °C (●), 150 °C (▲) and 200 °C (▼).

Figure 4 shows the Au L₃ HERFD XAS spectra of Au/Al₂O₃ during heating and
reduction at different temperatures. The first intense feature in the spectrum, the
whiteline, corresponds to the electronic transition from the core state (2p) to the lowest
unoccupied state.³³ Because we excite the L₃ edge, the d DOS is probed. The intensity
of the whiteline increases with the number of holes in the 5d-band,⁸ and thus the gold
oxidation state. The starting spectrum showed a large whiteline, typical of Au³⁺. For
pretreatment at 60 °C (Figure 4A) the whiteline at ~ 11.92 keV decreased only slightly
during the pretreatment and remained at more than 80% of its original intensity,
indicating only partial reduction. At 100 °C (Figure 4B) the whiteline intensity
diminished rapidly and was characteristic for metallic gold in nanoparticles after 30
minutes. Peaks at ~11.93 keV, ~11. 95 keV and ~11.97 keV appeared, which are
indicative of gold-gold scattering, and thus particle formation. For hydrogen treatment
at 150 °C (Figure 4C) and 200 °C (Figure 4D), the reduction proceeded much faster.
The whiteline reached its final intensity within 10 minutes from the beginning of the
heating.
Figure 4. Au L$_3$ HERFD XAS spectra of Au/Al$_2$O$_3$ recorded during heat up and reduction under 10 bar of hydrogen at 60 °C (A), 100 °C (B), 150 °C (C) and 200 °C (D). The autoclave was heated during the first 20 minutes.
Figure 5 shows the change of the amount of cationic gold during pretreatment at different temperatures. Pretreatment at 60 °C only resulted in a slight reduction of the amount of cationic gold in the catalyst. Pretreatment at a 100 °C led to full reduction in 25 min. Reduction proceeded considerably faster at 150 °C and 200 °C, with full reduction in about 10 minutes. The initial onset of the reduction in the first few minutes was due to the heating of the reaction mixture.

![Figure 5](image)

**Figure 5.** Amount of cationic gold as a determined by linear fitting taking the first spectrum of the catalyst and the spectrum of gold foil as references during reduction under 10 bar of hydrogen at 60 °C (■), 100 °C (●), 150 °C (▲) and 200 °C (▼).

Figure 6 shows the Au L₃ HERFD XAS spectra of Au/Al₂O₃ during reaction at 100 °C after pretreatment at 60 °C. The whiteline decreased quickly after reaching 100 °C. After fifteen minutes the catalyst was fully reduced, as indicated by the complete loss of the whiteline and by the appearance of peaks at ~11.93 keV, ~11.95 keV and ~11.97 keV.

![Figure 6](image)

**Figure 6.** Au L₃ HERFD XAS spectra of Au/Al₂O₃ recorded during reaction at 100 °C under 10 bar of hydrogen after pretreatment at 60 °C.
Catalytic experiments (not shown) for the reduction of nitrobenzene in the presence of excess amounts of aniline showed that the activity of Au/TiO$_2$-100 was not affected by adding up to fivefold excess of aniline to the reaction mixture. The activity of Au/Al$_2$O$_3$-100 however was reduced by the fivefold excess of aniline, though not by the threefold excess.

![Figure 7. Nitrobenzene conversion during recycling for Au/TiO$_2$ (■) and Au/Al$_2$O$_3$ (●). Pretreatment and hydrogenation were carried out at 100 °C under 10 bars of hydrogen.](image)

Figure 7 shows the evolution of the amount of nitrobenzene after addition of extra nitrobenzene at 90 and 180 minutes over Au/TiO$_2$ and Au/Al$_2$O$_3$. Both catalysts showed reduced activity with each subsequent addition of nitrobenzene. For a reaction order of zero in nitrobenzene, the amount of substance consumed in a given interval is proportional to the rate.\textsuperscript{23,25} This assumption is reasonable in this case given the linear behavior observed previously (Figure 3). For Au/TiO$_2$, 1.45 mmol of nitrobenzene were consumed in the first cycle, 1.24 mmol in the second cycle and 0.9 mmol in the third cycle. For Au/Al$_2$O$_3$, 0.37 mmol were consumed in the first cycle, 0.21 mmol in the second cycle and 0.14 mmol in the third cycle. This reduction in activity which cannot be caused by accumulation of product, as greater amounts of aniline had no effect on catalytic activity. Poisoning by an intermediate, e.g. the intermediate nitroso species\textsuperscript{23} or particle sintering therefore are the likely cause of the lower activity.
5.4. Discussion

Au/TiO\textsubscript{2} was the more active catalyst for the hydrogenation of nitrobenzene. It was also less susceptible to loss of activity under different pretreatment conditions and with excess aniline. In contrast, the activity of Au/Al\textsubscript{2}O\textsubscript{3} was strongly dependent on pretreatment temperature. Both low and high pretreatment temperatures reduced its activity, which we attribute to particle size (vide infra). Hydrogen treatment of gold precursors on alumina at 60 °C leads to incomplete reduction. However gold rapidly reduces under reaction conditions, leading to large particles, which do not contribute to activity. The low initial conversion for Au/Al\textsubscript{2}O\textsubscript{3} pretreated at 60 °C suggests that catalysts rich in cationic gold are not particularly active and that reduction of the catalyst is essential.\textsuperscript{22} This is in agreement with theoretical work showing that positively charged gold atoms do not activate hydrogen.\textsuperscript{16} It also matches similar observations for the same reaction over gold supported on ceria, where cationic gold was shown to not participate in the reaction.\textsuperscript{32} Recycling had a strong negative effect on the activity of both catalysts. This is due to sintering of the smallest particles.

Table 2. Average particle sizes, percentages of particles under 2 nm and reaction rates for the first 30 min. on Au/Al\textsubscript{2}O\textsubscript{3} for different pretreatment temperatures.

<table>
<thead>
<tr>
<th>Pretreatment temperature / °C</th>
<th>Average particles size after reaction / nm</th>
<th>Percentage of particles under 2 nm after reaction / %</th>
<th>Rate based on conversion in the first 30 min / mol g\textsubscript{Au}^{-1}h\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>4.1</td>
<td>7</td>
<td>0.44</td>
</tr>
<tr>
<td>100</td>
<td>2.9</td>
<td>15</td>
<td>0.96</td>
</tr>
<tr>
<td>150</td>
<td>2.5</td>
<td>28</td>
<td>1.40</td>
</tr>
<tr>
<td>200</td>
<td>5.9</td>
<td>0.7</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The activity of Au/Al\textsubscript{2}O\textsubscript{3} correlated with the fraction of particles with a particle size under 2 nm that were measured after the corresponding reaction (Table 2). This correlation is in agreement with Bond’s theory that only particles with particle sizes below a certain limit contribute to the activity of the catalyst.\textsuperscript{12,13} It also matches previous observations that particles with particle size of less than 2 nm are particularly active in the reduction in various other reactions.\textsuperscript{9,11,34} Zanella and coworkers found that small particles are very active in the hydrogenation of crotonaldehyde.\textsuperscript{34} Bus et al. observed a similar trend for hydrogenation of cinnamaldehyde.\textsuperscript{9} Fujitani et al. also found such a particle size dependence for activity in H/D-exchange.\textsuperscript{11} These size effects have been attributed to a variety of properties that change with size; Bond
however correctly points out, that a correlation of size and activity is not sufficient to assign that size dependence to any particular cause.\textsuperscript{13} Hydrogen adsorption on Au/Al\textsubscript{2}O\textsubscript{3} is activated.\textsuperscript{35} As hydrogen splitting is the rate limiting step in the reaction,\textsuperscript{25} any effect of the support on the intrinsic activity of the catalyst could reflect the ability of the support to aid in the activation of hydrogen. Studies by Haruta\textsuperscript{11} and Corma\textsuperscript{20} show that the gold support interface plays a crucial role in the hydrogenation process. Similar effects of the interface between gold particle and support have been reported for gold on titanium carbide\textsuperscript{36} and gold on iridium.\textsuperscript{37} Corma and coworkers found by inelastic neutron scattering that gold particles supported on ceria split hydrogen heterogeneously, with the formation of a gold hydride species and bridging hydroxyl groups on the support.\textsuperscript{38} Collins et al. found evidence for hydrogen spillover for gold supported on ceria-zirconia with the hydrogen found in bridging hydroxyl groups; they also proposed that CO and hydrogen are activated on the same sites on gold.\textsuperscript{39} Panayotov and Yates investigated hydrogen activation on Au/TiO\textsubscript{2} and also found spillover of hydrogen to form bridging hydroxyl groups.\textsuperscript{40} They proposed a mechanism based on spillover of atomic hydrogen with the formation of a bridging hydroxyl and the electron going to a shallow trap state of titania. Recent work showed that the atomic hydrogen then diffuses into the titania lattice, protonating the semiconductor and donating an electron.\textsuperscript{41} Fujitani and coworkers showed that TiO\textsubscript{x} supported on gold is able to split hydrogen.\textsuperscript{11,15} They found that completely oxidized titanium is necessary to catalyze HD exchange. This is further evidence for the importance of the metal oxide support in hydrogenation reactions over gold. Molina et al. found by DFT calculations on small planar gold clusters that hydrogen adsorbs preferentially in the plane of the cluster, and that a hydride species is formed.\textsuperscript{42} For a heterolytic splitting mechanism, assuming that the activation barrier towards adsorption of hydrogen and the stability of the resulting hydride are relatively similar between different supports, the differences in intrinsic activity can be explained by the ability of the support to stabilize the protons produced in the reaction. Lavalley reviewed methods to probe basicity with probe molecules,\textsuperscript{43} and found that titania has stronger basic sites than alumina when probed with halogenated alcohols. As these are protic acids, the results should give a reasonable approximation of the affinity towards protons. Using the method of decomposition of methylbutynol introduced by Lauron-Pernot et al.,\textsuperscript{44} Zaki and coworkers also found stronger basic surface sites for titania than alumina.\textsuperscript{45} For a homogeneous splitting
mechanism with formation of shallow trapped states, basicity of the support is still important, as the metaloxide is protonated. There is also an additional factor, which is the ability of the support to accommodate the resulting electrons. An irreducible support like alumina is less able (if at all) to do this compared to a reducible support like titania. Activity thus not only depends on particle size, it also varies with the support, which plays a role in homolytic or heterolytic hydrogen activation with spillover. In all, we attribute the greater intrinsic activity of Au/TiO₂ to the ability of the metal-support interface to help split hydrogen and the hydrogen to spill over to the support and form hydroxyl and reduce the support. If activity occurs on or near the metal support interface, the particle size also reflects its length.

5.5. Conclusion

Hydrogenation of nitrobenzene over supported gold shows large particle size and support effects. On Au/Al₂O₃, the activity relates to the fraction of gold particles smaller than 2 nm. Highly uncoordinated gold atoms are required to split hydrogen. Gold on titania showed much less dependence on particle size, which we ascribe to the ability of the support to help dissociate hydrogen. This leads to catalysts which are much more active. Reduced gold is essential for the hydrogenation to occur.
References


6. Particle size effect in gold catalysis: redispersion of gold multiple-twinned particles during liquid phase hydrogenation

6.1. Introduction

Redispersion of supported metal particles is a highly interesting topic, in particular because it is the reverse process of sintering, which is a main course of catalyst deactivation.\textsuperscript{1-7} Deactivation through sintering can be restored via redispersion of the supported metal particles applying appropriate conditions.\textsuperscript{2-6} Redispersion consists of complex physical and chemical processes,\textsuperscript{8} and is a strong function of temperature, atmosphere, time and support. In addition it is strongly influenced by the selection of the metal, its loading, and/or promoters, as well as catalyst preparation.\textsuperscript{1,9-11} Redispersion has been reported and investigated for supported metals such as Pt,\textsuperscript{3,5,12-18} Pd,\textsuperscript{6,19-21} Rh,\textsuperscript{22-27} Co,\textsuperscript{28-31} Ni,\textsuperscript{32-34} and Ag.\textsuperscript{35,36} The mechanisms differ strongly in dependence of the metal, the support, their interaction, and the applied conditions. Supported platinum catalysts, used in naphta reforming, disperse in oxidizing conditions in the presence of chlorine at temperatures of about 823 K which is called oxychlorination. Surface-mobile [Pt\textsuperscript{IV}O\textsubscript{x}Cl\textsubscript{y}] surface complexes are formed.\textsuperscript{5,12} Rh supported on $\gamma$-Al\textsubscript{2}O\textsubscript{3} on the other hand redispersed upon adsorption of CO at room temperature via disruption of the metallic crystallites and ultimately formation of isolated Rh-geminal dicarbonyl species, in which the oxidation state of Rh was +1. CO desorption changed the oxidation state of Rh to 0 again and the metal clusters rearranged.\textsuperscript{22,25} Often redispersion of supported metal catalysts was achieved via oxidation and reduction treatments, mostly at elevated temperature.\textsuperscript{18,23,26,28,31-33,35} The redispersion of supported Co nanoparticles, which is a key step in Fischer Tropsch catalyst regeneration occurs via formation of hollow oxide shells under oxidizing conditions due to the Kirkendall effect, and break up of the latter under reducing conditions to multiple metallic particles.\textsuperscript{28,31,37} In contrast, Ag/SnO\textsubscript{2} redispersion was produced by treatment in H\textsubscript{2}, which led to the formation of large (20 nm) particles of Ag\textsubscript{3}Sn, which then redispersed to small Ag particles by oxidation.\textsuperscript{35} While for the above-mentioned metals redispersion has been studied and successfully applied for catalyst regeneration for many years there are only a few, very recent studies reporting
the redispersion of supported gold particles. For gold supported on ceria and europium-doped ceria, it was reported that the increase in the concentration of oxygen vacancies in the presence of CO or hydrogen at 300 °C changed the gold crystallite size by breaking off and migration of gold nanoparticles towards the oxygen vacancies on the support. The catalytic activity of Au/CeO₂(Eu) in CO oxidation significantly increased after pretreatment under reducing conditions. Deng et al. reported that a redispersion of gold in Au/CeO₂ catalysts, used in the low temperature water gas shift reaction at 100 or 200 °C, was possible through treatment in oxygen at 400 °C, which at the same time let to a complete recovery of the initial catalytic activity. Goguet et al. found that the strong increase in the catalytic activity of Au/C catalysts during the carbonylation of methanol in the presence of MeI was due to a transformation of the initial Au particles (>10 nm) to gold dimers and trimers. MeI played a key role in the redispersion process. Prasad et al. reported the conversion of polydisperse gold colloids with particle sizes up to a few hundred nanometers to nearly monodisperse particles between 5 and 9 nm by adding surface-active ligands such as thiols, amines, silanes and phosphines.

We herein report the redispersion of Au/TiO₂ catalysts during the high pressure liquid phase hydrogenation of nitroaromatic compounds. Gold catalyzes various hydrogenation reaction among them hydrogenation of alkenes, alkadiens, alkynes, α,β-unsaturated carbonyl compounds, and nitro compounds. The size of supported Au clusters dramatically affects the catalytic activity. While bulk gold is catalytically inactive, the high activity of Au nanoclusters was attributed to the increased proportion of low coordinated Au sites, electronic effects, and the involvement of the metal-support interface in the activation of reactants. Numerous studies observed a significant increase of the catalytic activity for particles smaller than 3 nm. In this size range the particles lose their metallic character. The d-band gets narrower and shifts closer to the Fermi level, resulting in an increased reactivity to adsorb reactants. However, particle size alone is no guarantee for high activity. Additionally, an efficient corporation with the support is required. To date the influence of the support is not very well understood. However, in particular in hydrogenation of nitroaromatic compounds the use of TiO₂ very often led to significantly higher activity and selectivity compared to other metal oxide supports. Corma et al. have shown that Au/TiO₂ selectively reduced the nitro group in the presence of various reducible functional groups such as double bonds,
carbonyl, amide or nitrile groups under mild conditions (100-120 °C, 10 bar H₂). The redispersion of Au/TiO₂ during the liquid phase hydrogenation of 4-nitrobenzaldehyde, nitrobenzene and nitrosobenzene was determined by electron microscopy and EXAFS. The most direct methods, TEM and STEM, provide real images of the particles, which is important to get an impression of the homogeneity of a sample resulting evaluation of hundreds of particles. EXAFS on the other hand is a bulk technique, which provides averaged particle sizes from a relatively large volume.

6.2. Experimental

6.2.1. Catalyst preparation and pretreatment

Au/TiO₂ was prepared through deposition precipitation with urea. For the preparation of 0.7 wt % Au/TiO₂ 0.086 g of HAuCl₄·H₂O (49 wt% Au, ABCR-Chemicals) were dissolved in 600 ml deionized H₂O. Then 6.0 g of TiO₂ (Aeroxide P25, Acros Organics) and 1.8 g urea (puriss., Riedel-de Haën) were added while stirring. The mixture was heated to 80 °C and stirred for 16 hours in a closed Teflon vessel. After cooling down to room temperature, the solid product was gathered through filtration and washed 5 times with deionized water to remove residual chloride ions. To confirm the removal of chloride, AgNO₃ solution (1M) was added to the filtrate. Precipitation of AgCl was not observed. The yellowish product was dried at room temperature under vacuum in the dark for 48 h. The resulting catalyst was referred to as “as-prepared”. If it was not directly used after synthesis, it was stored in the freezer (-18 °C) under exclusion of light. With the aim to achieve different gold particle sizes and to investigate the influence of different pretreatment conditions, as-prepared Au/TiO₂ was reduced in a flow of 5 % H₂/He (100 ml/min) at room temperature for 45 min, and at different temperatures (40, 60, 80, 100, 150, 200, 300 °C) for 20 minutes with a heating rate of 2 °C/min, followed by cooling down to room temperature under the same conditions. Alternatively as-prepared Au/TiO₂ was calcined in flowing air (100 ml/min) at 300, 400 and 500 °C with a heating rate of 2 °C/min and a dwell time of 30 min followed by cooling down to room temperature under the same stream. Catalyst pretreatment was performed only shortly before kinetic experiments, and until their use the pretreated catalysts were stored in the freezer at -18 °C under exclusion of light.
6.2.2. Kinetic experiments

The liquid-phase hydrogenation of 4-nitrobenzaldehyde, nitrobenzene, nitrosobenzene, and benzaldehyde was performed in stainless steel autoclaves with a volume of 50 ml from Premex Reactor AG (Lengnau, Switzerland), which were equipped with a gas in-and outlet, a sample port, a thermocouple, external heating and readout for temperature and pressure. Stirring was performed with a magnetic stirrer. To perform a kinetic experiment, the catalyst, the substrate, THF or toluene as solvent, and mesitylene as internal standard were placed in the reactor. Usually 0.06 g catalyst, 0.06 g substrate, 25 g solvent and 0.14 ml internal standard were used. In general samples of around 1 ml were taken at room temperature 0, 10, 30, 60, 120, 180 and 240 min by means of a sample tube. After filtration to remove residual catalyst, the concentration of reactants and products was quantified by gas chromatography on an Agilent 7820A gas chromatograph equipped with a HP5-MS column. The column was initially held at 80 °C for 2 min and then heated to 300 °C with a rate of 20 °C per minute. If necessary the reaction was continued overnight until full conversion was reached. Before the reaction was started, residual air was removed by flushing the reactor three times with hydrogen to 10 bars while stirring followed by venting. Then the autoclave was pressurized with hydrogen to 10 bars and heated to the reaction temperature of 100 °C without stirring. When 100 °C were reached, stirring was started and the reaction time was set to zero. The main product of the reduction of 4-nitrobenzaldehyde – 4-aminobenzaldehyde is not stable, because the aldehyde- and the amino-group react via condensation to imines, which can reduce further. These products could not be detected directly by GC because they were too heavy to be brought into the gas phase. They were found after reaction in form of an orange solid sticking to the wall of the autoclave. Their amount was determined via the carbon balance.

6.2.3. Catalyst characterization

The Au content of Au/TiO₂, as determined by means of AAS using a Varian SpectrAA 220 FS spectrometer was 0.78 wt %. The Ti content of Au/TiO₂ was determined by ICP-OES using a Varian VISTA PRO AX spectrometer. Sample preparation was performed via microwave assisted digestion by adding 1 ml of nitric acid, 2 ml of
hydrofluoric acid and 3 ml of hydrochloric acid to 40 mg of catalyst for determining the Au content, and 10 mg of catalyst for determining the Ti content. Electron microscopy measurements of Au/TiO$_2$ catalysts after pretreatment and after reaction were performed on a HD2700CS (Hitachi, aberration-corrected dedicated scanning transmission electron microscope (STEM), cold FEG, 200 kV) or a Tecnai F30 ST (FEI, FEG, 300 kV). The high-resolution capability of HD2700CS (shown to be better than 0.1 nm) is due to a probe corrector (CEOS) that is incorporated in the microscope column between the condenser lens and the probe-forming objective lens so that a beam diameter of ca. 0.1 nm can be achieved.\textsuperscript{79} A special bright field setting allows one to record highly-resolved phase-contrast STEM (PC-STEM) images (similar to HRTEM) without delocalization artifacts. With high-angle annular dark field detectors (HAADF) attached to both microscopes, the intensity of incoherently scattered electrons is measured leading to images dominated by atomic number (Z) contrast.\textsuperscript{80} In such images, the Au particles appear as bright patches. The catalysts after reaction were recovered by filtration of the reaction mixture and washing with THF for several times followed by drying at room temperature under vacuum. For the (scanning) transmission electron microscopy (STEM) investigation, the catalyst material was dispersed in ethanol and a few drops of the suspension were deposited onto a perforated carbon foil supported on a copper grid. Usually 300 particles were counted in the HAADF-STEM images to determine the particle size distributions. For Au/TiO$_2$ pretreated in H$_2$ between 60 and 300 °C, all measured particles (about 100) were taken into account. XAS measurements at the Au L$_3$ edge were performed at the SuperXAS beamline at the Swiss Light Source (SLS at Paul Scherrer Institute, Villigen, Switzerland) in transmission mode by measuring the intensity of the beam before and after the sample by ionization chambers. The Swiss Light Source has a ring energy of 2.4 GeV, a ring current of 400 mA, a magnetic field of 2.9 T, and is operated in the “top-up” injection mode. The incident energy was focused with two mirrors and monochromatized using a double crystal monochromator equipped with a pair of Si (111) crystals. About 30 mg of catalyst were used for the preparation of self supporting pellets with a diameter of 5 mm in order to obtain optimal transmission properties. The pellets were placed in a sample holder and measured at room temperature. One spectrum per sample was recorded in the energy range of 11.8 to 13.0 keV with a scan time of 45 min. The EXAFS data were analyzed using the Athena and Artemis software packages. The first
shell was fitted in R space (1.5 < R < 3.5 Å) after Fourier transformation (3 < k < 13 Å⁻¹) using a k weighting of 2. Average cluster sizes were determined from the coordination numbers using established methods and assuming spherical particles. 81

6.3. Results

Figure 1 shows representative HAADF-STEM micrographs and the corresponding particle size distributions of Au/TiO₂ as prepared, after pretreatment in H₂ at room temperature, 40, 60, 80, 100, 200, and 300 °C, and after calcination in air at 300 and 500 °C. Representative HAADF-STEM micrographs and particle size distributions of the catalysts after their use in the reaction are also presented in the figure. Table 1 summarizes the catalytic activity and selectivity in liquid phase hydrogenation of 4-nitrobenzaldehyde and the averaged Au particle sizes determined by HAADF-STEM.

All results in Figure 1 and Table 1 were obtained from the same batch of Au/TiO₂ and each experiment was repeated twice, except for the recycling experiments. The bright dots in the HAADF-STEM micrographs correspond to the Au particles (Z contrast). As prepared Au/TiO₂ (Figure 1-a, Table entry 1) contained the smallest Au clusters with a mean size of 0.8 nm and a narrow size distribution. The Au clusters were evenly distributed on the support. Au/TiO₂ pretreated in H₂ at RT (Figure 1-b, Table 1 entry 2) and 40 °C (Figure 1-c, Table 1 entry 4) exhibited slightly larger particles of around 1.4 nm and 1.1 nm respectively, which were also uniformly dispersed and narrowly distributed. Pretreatment in H₂ between 60 and 300 °C led to the formation of large clusters heterogeneously spread on the support, presumably formed after reduction of the precursor. Pretreatment in H₂ between 60 and 100 °C gave Au clusters of around 8 nm with a broad distribution. Pretreatment in H₂ at 200 °C yielded even larger particles of around 10 nm, which were also broadly distributed. Pretreatment in H₂ at 300 °C resulted in particles of around 8 nm. Upon pretreatment in air between 300 and 500 °C, Au clusters with sizes between 4 and 5 nm formed, which were rather homogeneously distributed on the support. Thus, depending on the pretreatment conditions, widely varying particle sizes and distributions can be obtained in agreement with the general literature. Pretreatment in H₂ at RT and 60 °C, and calcination at 300 °C generated the most active catalysts, exhibiting a rate of 0.11 mmol/(gₐu*s) at 50 % conversion. For these two catalysts, the three kinetic measurements gave rather similar results, as indicated by standard deviations of 0.03 and 0.04. On the other hand for Au/TiO₂
pretreated at RT the rates scattered strongly, resulting in a standard deviation of 0.08, which was probably due to incomplete reduction during pretreatment. This was indicated by the color of the catalyst after pretreatment, which was yellowish, similar to as prepared Au/TiO₂, whereas fully reduced Au/TiO₂ is usually purple. The partially oxidic catalyst then reduced further under reaction conditions, which occurs in an uncontrolled thus non-reproducible manner. Pretreatment in H₂ between 80 and 300 °C resulted in quite similar catalytic activities in the range of 0.08 - 0.10 mmol/(gₐu*s) at 50 % conversion. Au/TiO₂ calcined at 400 and 500 °C was less active with rates of 0.07 and 0.06 mmol/(gₐu*s), respectively. The least active catalyst, Au/TiO₂ pretreated in H₂ at 40 °C with a rate of 0.05 mmol/(gₐu*s), was about half as active as the most active ones. Also this catalyst was yellowish in color after pretreatment. This is most probably the reason for the low activity, because we recently found for gold supported on ceria⁸² and alumina⁸³ that catalysts which contained cationic gold were less active than when fully reduced, and that cationic gold did not contribute to the catalytic activity. Among the calcined samples the catalytic activity decreased with increasing calcination temperature and particle size. For pretreatment in H₂ the optimum temperature was 60 °C. Taking into account the large differences in the initial particle sizes ranging from 1 to 10 nm, the differences in the catalytic activity were relatively small. Also, the selectivity to the desired product 4-aminobenzaldehyde was comparable for all catalysts being around 75 % at full conversion.

Au/TiO₂ as prepared

![Image of Au/TiO₂ as prepared]
Au/TiO₂ (H₂, RT) before reaction  after reaction  after recycling experiment

Au/TiO₂ (H₂, 40) before reaction  after reaction
Au/TiO₂ (H₂, 60) before reaction  after reaction

Au/TiO₂ (H₂, 80) before reaction  after reaction  after recycling experiment
Au/TiO$_2$ (H$_2$, 100) before reaction after reaction

Au/TiO$_2$ (H$_2$, 200) before reaction after reaction
Au/TiO₂ (H₂, 300) before reaction  after reaction  after recycling experiment

Au/TiO₂ (air, 300) before reaction  after reaction
Figure 1. Representative HAADF-STEM micrographs and particle size distributions of as prepared Au/TiO₂, and of differently pretreated Au/TiO₂ before and after reaction, in the liquid phase hydrogenation of 4-nitrobenzaldehyde to 4-aminobenzaldehyde at 100 °C and 10 bar H₂. For Au/TiO₂ pretreated in H₂ at room temperature, 80 °C and 300 °C, TEM micrographs and particle size distributions after recycling experiments are given.
Table 1. Particle size before and after reaction and catalytic activity and selectivity of differently pretreated Au/TiO$_2$, in the liquid phase hydrogenation of 4-nitrobenzaldehyde to 4-aminobenzaldehyde at 100 °C and 10 bar H$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pretreatment temperature / °C</th>
<th>Pretreatment gas</th>
<th>Rate at 50 % conversion /mmol/(g$_{Au}$*s)</th>
<th>Selectivity at 100 % conversion /%</th>
<th>HAADF-STEM mean particle size before reaction /nm</th>
<th>HAADF-STEM mean particle size after reaction /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>as prepared</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.8 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>H$_2$</td>
<td>0.11 ± 0.08</td>
<td>80</td>
<td>1.4 ± 0.3</td>
<td>2.1 ± 0.8</td>
</tr>
<tr>
<td>3$^a$</td>
<td></td>
<td></td>
<td>0.05</td>
<td>76</td>
<td>2.1 ± 0.8</td>
<td>3.0 ± 1.4</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>H$_2$</td>
<td>0.05 ± 0.01</td>
<td>70</td>
<td>1.1 ± 0.2</td>
<td>2.7 ± 0.6</td>
</tr>
<tr>
<td>5$^a$</td>
<td></td>
<td></td>
<td>0.11 ± 0.03</td>
<td>75</td>
<td>8.2 ± 3.2</td>
<td>3.0 ± 1.2</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>H$_2$</td>
<td>0.08 ± 0.02</td>
<td>55</td>
<td>7.6 ± 2.9</td>
<td>3.0 ± 1.7</td>
</tr>
<tr>
<td>7$^a$</td>
<td></td>
<td></td>
<td>0.04</td>
<td>75</td>
<td>3.0 ± 1.7</td>
<td>2.7 ± 1.5</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>H$_2$</td>
<td>0.08 ± 0.02</td>
<td>75</td>
<td>8.1 ± 2.7</td>
<td>3.0 ± 1.5</td>
</tr>
<tr>
<td>9</td>
<td>150</td>
<td>H$_2$</td>
<td>0.10 ± 0.02</td>
<td>75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>H$_2$</td>
<td>0.09 ± 0.03</td>
<td>75</td>
<td>9.5 ± 4.1</td>
<td>2.5 ± 1.2</td>
</tr>
<tr>
<td>11</td>
<td>300</td>
<td>H$_2$</td>
<td>0.08 ± 0.03</td>
<td>67</td>
<td>8.2 ± 3.8</td>
<td>2.8 ± 1.2</td>
</tr>
<tr>
<td>12$^a$</td>
<td></td>
<td></td>
<td>0.04</td>
<td>15</td>
<td>2.8 ± 1.2</td>
<td>3.5 ± 1.4</td>
</tr>
<tr>
<td>13</td>
<td>300</td>
<td>Air</td>
<td>0.11 ± 0.04</td>
<td>75</td>
<td>3.7 ± 1.0</td>
<td>4.4 ± 3.7</td>
</tr>
<tr>
<td>14</td>
<td>400</td>
<td>Air</td>
<td>0.07 ± 0.01</td>
<td>70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>500</td>
<td>air</td>
<td>0.06 ± 0.01</td>
<td>70</td>
<td>4.8 ± 1.2</td>
<td>4.7 ± 1.2</td>
</tr>
</tbody>
</table>

$^a$: Recycling experiment: After the reaction the used catalyst was filtered, washed several times with THF, dried at room temperature and then reused in the recycling experiment. Except for the recycling experiments, all reactions were performed three times each and the average results are given.
To determine whether the average particle size and size distribution changed under reaction conditions, the catalysts after reaction were subjected to HAADF-STEM measurements (Figure 1, Table 1). The Au clusters of Au/TiO2 calcined at 500 °C after reaction (Figure 1-j, Table 1 entry 15) were, like the Au particles after pretreatment, rather homogeneously distributed on the support, with an average particle size of 4.7 nm compared to 4.8 nm after pretreatment. Both before and after reaction we did not observe Au clusters with sizes below 2 nm. The fraction of Au particles between 2 and 4 nm was 28 % after reaction compared to 23 % before reaction. Both before and after reaction the majority of the particles, namely 59 % was in the size range of 4-6 nm. Thus, the particle size distribution of Au clusters in Au/TiO2 calcined at 500 °C hardly changed under the applied reaction conditions. Figure 1-i shows representative HAADF-STEM micrographs and the particle size distribution of Au/TiO2 calcined at 300 °C before and after reaction. Before reaction 2 % of the Au clusters were below 2 nm, whereas after reaction no particles below 2 nm were observed. The fraction of particles between 2 and 4 nm decreased from 65 % to 58 % due to formation of larger clusters. Thus Au particles in Au/TiO2 calcined at 300 °C slightly sintered during reaction. Figure 1-b presents HAADF-STEM micrographs and particle size distributions of Au/TiO2 pretreated in H2 at room temperature before and after reaction. During reaction the fraction of particles with sizes below 2 nm, from 97 % to 50 %. At the same time the fraction of particles in the size range of 2 to 4 nm increased from 3 % to 44 %. After reaction, 6 % of the Au clusters were larger than 4 nm, whereas before reaction no particles larger than 3 nm were observed. The average Au particle size (Table 1 entry 2) increased from 1.4 nm to 2.1 nm. Sintering of Au clusters also occurred for Au/TiO2 pretreated in H2 at 40 °C. HAADF-STEM micrographs and particle size distributions before and after reaction are shown in Figure 1-c. After pretreatment all observed Au particles had a size of 2 nm or smaller, while after reaction only 20 % were in this size range. The majority of the particles, 72 % was between 2 and 4 nm, and 8 % larger clusters formed. During reaction the mean particle size increased from 1.1 nm to 2.7 nm (Table 1 entry 4). Au/TiO2 pretreated in H2 between 60 and 300 °C significantly changed under reaction conditions. The HAADF-STEM micrographs after reaction show a large number of small particles, in contrast to the large particles before reaction. Figure 1-d shows HAADF-STEM micrographs and the particle size distribution of Au/TiO2 after pretreatment in H2 at 60 °C and after hydrogenation of 4-nitrobenzaldehyde. After pretreatment no particles
smaller than 2 nm were observed. 2 % of the Au clusters were between 2 and 4 nm, 22
% had sizes between 4 and 6 nm, 36 % were in the size range of 6 to 8 nm, and 40 %
were larger than 8 nm. In contrast after reaction, 11 % of the Au particles were 2 nm or
smaller, the majority of 77 % was in the size range of 2 to 4 nm, and 10 % exhibited
sizes between 4 and 6 nm. The average Au particle size decreased from 8.2 nm before
reaction to 3.0 nm after reaction. Similar results were obtained for Au/TiO₂ pretreated
in H₂ at 80 °C. The mean Au particle size decreased during reaction from 7.6 nm to 3.0
nm. After reaction 30 % of the particles were 2 nm or smaller, 47 % were between 2
and 4 nm, and 18 % between 4 and 6 nm. In contrast before reaction, we did not
observe particles smaller than 2 nm, 3 % had sizes between 2 and 4 nm, and 29 % were
between 4 and 6 nm. Nearly 70 % of the particles were larger than 6 nm. Au/TiO₂
pretreated in H₂ at 100, 200, and 300 °C gave comparable results. After pretreatment
we did not observe particles below 2 nm and less than 10 % were in the size range of 2
to 4 nm. More than 90 % of the particles were larger than 4 nm. In contrast, after
reaction between 80 and 90 % of the particles were smaller than 4 nm. After reaction,
the fraction of particles smaller than 2 nm was 27 % for pretreatment at 100 °C, 36 %
for pretreatment at 200 °C, and 19 % for pretreatment at 300 °C. During reaction the
average Au particle size decreased from 8.1 nm to 3.0 nm for Au/TiO₂ pretreated at
100 °C, from 9.5 nm to 2.5 nm for Au/TiO₂ pretreated at 200 °C, and from 8.2 nm to
2.8 nm for the catalyst pretreated at 300 °C. Thus, Au particles supported on TiO₂ after
pretreatment in H₂ between 60 and 300 °C redispersed under the applied reaction
conditions. These results were reproduced with two new batches of Au/TiO₂ for two
different pretreatment conditions (reduction in H₂ at 80 and 300 °C).
To determine whether the small particles possibly formed because of leaching of Au
and redeposition during reaction we determined the Au and Ti contents of some of the
catalysts before and after reaction by AAS and ICP-OES. We found that leaching of
around 8 % of Au occurred. If leaching would be the reason for the formation of small
particles, the gold content should have decreased to a much larger extent. Hot filtration
experiments are in line with the results from elemental analysis. We found 20 %
conversion in 17 hours of 4-nitrobenzaldehyde after hot filtration compared to 6 %
conversion in the blank experiments and full conversion in the respective catalytic
experiments, indicating that there is activity, be it very low, of the liquid phase.
Figure 2 shows the conversion and selectivity plot of the liquid phase hydrogenation of
4-nitrobenzaldehyde over Au/TiO₂ pretreated in H₂ at 80 °C. Beside the main product
4-aminobenzaldehyde, significant amounts of oligomeric and polymeric compounds formed due to the well known condensation of primary amines and aldehydes to imines. These products could not be detected directly by gas chromatography but were determined via the carbon balance (Figure 2-b). Further, small amounts of 4-aminotoluene and 4-aminobenzylalcohol (each < 5%) were detected by gas chromatography. Within 300 minutes, 4-nitrobenzaldehyde fully converted.

![Conversion and selectivity plot](image)

**Figure 2.** Conversion- (a) and selectivity plot (b) for the hydrogenation of 4-nitrobenzaldehyde with Au/TiO₂ reduced in 5% H₂/He at 80 °C, (□) 4-nitrobenzaldehyde, (○) 4-aminobenzaldehyde, (▲) 4-aminotoluene, (■) 4-aminobenzylalcohol, (●) condensation products, (▼) C-balance; (0.4 mmol substrate, 10 bar H₂, 100 °C).

Some catalysts, namely Au/TiO₂ pretreated in H₂ at RT, 80 °C, and 300 °C were reused in the hydrogenation of 4-nitrobenzaldehyde. The recycled catalysts, gathered through filtration followed by washing with THF, and drying were only half as active as the fresh ones. Figure 3 shows the conversion and selectivity plot for the hydrogenation of 4-nitrobenzaldehyde over recycled Au/TiO₂, initially reduced in H₂.
at 80 °C. The selectivity to 4-aminobenzaldehyde at full conversion was slightly higher with the recycled catalyst than with the fresh one due to less formation of condensation products. Like the fresh sample also the recycled catalyst produced only low amounts (<5 %) of the secondary products 4-aminotoluene and 4-aminobenzylalcohol.

Figure 3. Conversion- (a) and selectivity plot (b) for the hydrogenation of 4-nitrobenzaldehyde with recycled Au/TiO$_2$ (previously reduced in 5 % H$_2$/He at 80 °C) (□) 4-nitrobenzaldehyde, (○) 4-aminobenzaldehyde, (▲) 4-aminotoluene, (●) condensation products, (▼) C-balance; (0.4 mmol substrate, 10 bar H$_2$, 100 °C).

Figure 1-e shows a representative HAADF-STEM micrograph and the particle size distribution of Au/TiO$_2$ pretreated in H$_2$ at 80 °C after the recycling experiment. After reuse 42 % of the particles were smaller than 2 nm, compared to 30 % before recycling. At the same time, the fraction of particles between 2 and 4 nm slightly decreased from 47 % to 39 %, and the fraction of particles with sizes between 4 and 6 nm decreased from 18 % to 13 %. The average Au particle size slightly decreased from 3.0 nm to 2.7 nm (Table 1 entry 10). Recycling of Au/TiO$_2$ pretreated in H$_2$ at room temperature (Figure 1-a, Table 1 entry 3) decreased the fraction of Au particles smaller
than 2 nm from 50 % to 20 % and led to an increase of particles between 2 and 4 nm from 44 % to 61 %. The fraction of particles between 4 and 6 nm increased from 6 % to 15 %. After recycling the average Au particle size was 3.0 nm, compared to 2.1 nm before reaction. Figure 1-h shows a TEM micrograph and the particle size distribution of Au/TiO₂ pretreated in H₂ at 300 °C after reuse in the hydrogenation of 4-nitrobenzaldehyde. During the recycling experiment the fraction of particles smaller than 2 nm decreased from 19 to 7 %. The fraction of particles between 2 and 4 nm stayed the same and was 64 % after recycling, whereas the percentage of particles with sizes between 4 and 6 nm increased from 13 % to 23 %. The average Au particle increased from 2.8 nm to 3.5 nm (Table 1 entry 12). Au particles in Au/TiO₂ pretreated in H₂ at room temperature and 300 °C slightly sintered upon reuse. However, no sintering occurred for Au/TiO₂ pretreated in H₂ at 80 °C. As the catalytic activity of all these samples decreased by half upon reuse, sintering cannot be the cause of the deactivation. The decrease in catalytic activity is probably due to poisoning of the catalyst surface by reaction intermediates and/or deposition of carbonaceous species. To corroborate the results obtained from HAADF-STEM, we performed EXAFS measurements at the Au L₃ edge of Au/TiO₂ before and after reaction. For these experiments a new batch of Au/TiO₂ was used. Figure 4 presents the XANES spectra of Au/TiO₂ after pretreatment in H₂ at 80 °C and after hydrogenation of 4-nitrobenzaldehyde, and of Au foil. The main features in the spectrum after pretreatment and after reaction matched that of the Au foil, thus the Au clusters were fully reduced.

Figure 4. XANES spectra at the Au L₃ edge of Au/TiO₂ pretreated in H₂ at 80 °C (blue) and after hydrogenation of 4-nitrobenzaldehyde at 100 °C and 10 bar H₂ (red), and of Au foil (green).
Figure 5. EXAFS functions (a) and corresponding Fourier transforms (b) of Au/TiO\textsubscript{2} after pretreatment in H\textsubscript{2} at 80 °C (blue), after hydrogenation of 4-nitrobenzaldehyde at 100 °C and 10 bar H\textsubscript{2} (red) and of gold foil (green).

Figure 5 shows the EXAFS functions (a) and Fourier transforms (b). The quality of the EXAFS data was good up to at least 12 Å\textsuperscript{-1}. The amplitude of the oscillations and thus the intensity of the Fourier transforms were highest for Au foil, followed by Au/TiO\textsubscript{2} after pretreatment, and Au/TiO\textsubscript{2} after reaction, directly indicating that there are differences in structure. The intensity of the EXAFS oscillations is directly proportional to the averaged number of scattering atoms surrounding the central atom, and hence the average cluster size. The data of Au/TiO\textsubscript{2} after pretreatment and after reaction were fitted to Au-Au coordination numbers of 9.3 and 8.0 respectively (Table 2). Table 2 presents the mean particle size of the catalyst before and after reaction as determined from the EXAFS coordination number assuming spherical particles.\textsuperscript{81} For comparison the HAADF-STEM mean particle sizes are also given. The EXAFS mean particle sizes before and after reaction were 2.1 and 1.4 nm, respectively. Though the
trend is the same, these results largely deviate from the HAADF-STEM mean particle sizes of 7.1 and 2.5 nm.

Table 2. Coordination numbers of Au/TiO$_2$ pretreated in H$_2$ at 80 °C before and after hydrogenation of 4-nitrobenzaldehyde at 100 °C and 10 bar H$_2$, and corresponding average Au particle sizes determined by EXAFS and HAADF-STEM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>EXAFS mean particle size / nm$^a$</th>
<th>TEM mean particle size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO$_2$, before reaction</td>
<td>9.3</td>
<td>2.1</td>
<td>7.1 ± 3.6</td>
</tr>
<tr>
<td>Au/TiO$_2$, after reaction</td>
<td>8</td>
<td>1.4</td>
<td>2.5 ± 0.8</td>
</tr>
</tbody>
</table>

$^a$: EXAFS mean particle size$^{81}$ determined assuming spherical particles.

An explanation for the smaller particle sizes obtained by EXAFS could be that the large particles that we see in HAADF-STEM are not single crystal particles but aggregates of smaller clusters.

Figure 6 shows zoomed phase-contrast (PC) STEM micrographs of Au particles supported on TiO$_2$ after pretreatment in H$_2$ at 300 °C. The sizes of the particles were between 9 and 13 nm. The particles were not single crystals but multiply-twinned with clearly visible grain boundaries.$^{85-87}$ In each particle, crystalline segments of different shapes are joined in different ways. Likely, the EXAFS data probe the size of the individual grains. The structure of the small particles obtained after reaction dynamically changed under the electron beam, and therefore we could not determine their structure. This behavior has also been observed by Iijima et al.$^{88}$ and was recently reported by Zhang et al.$^{89}$ for Au particles of 3 nm supported on carbon.
Figure 6. PC-STEM micrographs of Au clusters supported on TiO$_2$ after pretreatment in H$_2$ at 300 °C.

Figure 7 shows representative PC-STEM micrographs of Au particles supported on TiO$_2$ after calcination at 500 °C with sizes between 5 and 10 nm. In contrast to the Au clusters after pretreatment in H$_2$, most of the Au particles were single crystals (figure 7-a, b, c), only some (figure 7-d) were multiple twins.
To determine if redispersion of gold might be restricted to 4-nitrobenzaldehyde to occur or is more universal another batch of Au/TiO₂ was tested in the hydrogenation of nitrobenzene, nitrosobenzene, and benzaldehyde. The catalyst was pretreated in H₂ at 80 °C. Table 3 presents the conversion of the substrates and the corresponding mean particle sizes of Au/TiO₂ after a reaction time of 240 min at 100 °C and 10 bar H₂. The mean particle size of Au/TiO₂ after pretreatment was 10.5 nm with a broad size distribution. After 240 min, the conversion of nitrobenzene was 96 %. With nitrosobenzene, which is a reactive intermediate in the reduction of nitrobenzene to aniline, full conversion was reached. The Au particle sizes after reaction of both substrates were narrowly distributed around 2.5 nm. Thus, redispersion occurred also in the presence of nitrobenzene and nitrosobenzene. On the other hand, only 15 % of benzaldehyde converted under the applied conditions. The Au particle size only slightly decreased to around 7 nm. This suggests that the nitro-group, reaction intermediates, and/or aniline might play an active role in the redispersion of gold during reaction.
Table 3. Mean particle sizes of Au/TiO$_2$ after 240 min hydrogenation of nitrobenzene, nitrosobenzene and benzaldehyde respectively at 100 °C and 10 bar H$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conversion / %</th>
<th>Mean particle size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au/TiO$_2$ (H80)$^a$</td>
<td>-</td>
<td>10.5 ± 5.2</td>
</tr>
<tr>
<td>2</td>
<td>nitrobenzene</td>
<td>96</td>
<td>2.5 ± 0.8</td>
</tr>
<tr>
<td>3</td>
<td>nitrosobenzene</td>
<td>100</td>
<td>2.5 ± 0.9</td>
</tr>
<tr>
<td>4</td>
<td>benzaldehyde</td>
<td>15</td>
<td>7.0 ± 3.2</td>
</tr>
</tbody>
</table>

$a$: This catalyst was used for all three experiments. The reaction time for all substrates was 240 min.

To investigate at what point in the reaction the redispersion took place, the hydrogenation of nitrobenzene over Au/TiO$_2$ pretreated in H$_2$ at 80 °C was stopped at different conversion levels and the particle sizes were determined. Figure 6 shows the mean particle size plotted against the conversion level. The error bars correspond to the standard deviation of the mean particle size. After pretreatment the mean Au particle size was 10.5 nm. After 2 min of reaction, i.e. while heating in H$_2$ to the desired reaction temperature of 100 °C it was 7.4 nm. Virtually no conversion of nitrobenzene was detected by GC. After 5 min, the reaction temperature of 100 °C was reached. The conversion of nitrobenzene was 7 % and the mean Au particle size 3.6 nm. After 15 min at a conversion level of 16 % the mean Au cluster size was 3.4 nm. After 40 % conversion (30 min) the mean Au particle size was 2.9 nm. With increasing conversion and decreasing mean particle size, the size distributions became narrower, as illustrated by the decreasing standard deviations. In summary, redispersion occurred fast at the beginning of the reaction at conversion levels < 10 %.
Further, we wanted to determine, if redispersion occurred only in the presence of reactants and/or intermediates or also in pure solvents. We were also interested in the influence of gas atmosphere and temperature. Therefore, another batch of Au/TiO$_2$ pretreated in H$_2$ at 80 °C was subjected to different reaction conditions and times, and subsequently the Au particle sizes were determined by TEM (Table 4). Two different solvents, THF and toluene were tested at two different temperatures (25 and 100 °C), in two different gas atmospheres (10 bar H$_2$ and 7 bar He). All experiments were stopped after 2 and 30 min respectively to be able to observe time dependent changes to a certain extent. Both solvents yielded similar results, therefore only those of THF are presented in Table 4. In H$_2$ atmosphere Au particles redispersed both at RT and 100 °C. Thus in H$_2$ redispersion was independent of temperature in the temperature range investigated. In He, Au supported on TiO$_2$ redispersed at 100 °C but not at RT indicating that under inert gas redispersion was temperature dependent. The mean Au particle size under H$_2$ at 100 °C was 3 nm after 2 min and 7 nm after 30 min. Thus redispersion was followed by sintering. These results show the dynamic changes of the catalyst under varying conditions.
Table 4. Mean particle sizes of Au/TiO$_2$ pretreated in H$_2$ at 80 °C after subjection to different reaction conditions.

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>reactant</th>
<th>gas (p)</th>
<th>T / °C</th>
<th>mean p. size after 2 min / nm</th>
<th>mean p. size after 30 min / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.2$^a$ ± 4.7</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>-</td>
<td>H$_2$ (10)</td>
<td>100</td>
<td>3.4 ± 1.1</td>
<td>7.4 ± 2.7</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>-</td>
<td>H$_2$ (10)</td>
<td>25</td>
<td>3.9 ± 1.5</td>
<td>3.0 ± 1.2</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>-</td>
<td>He (7)</td>
<td>100</td>
<td>2.9 ± 1.1</td>
<td>3.4 ± 1.0</td>
</tr>
<tr>
<td>6</td>
<td>THF</td>
<td>-</td>
<td>He (7)</td>
<td>25</td>
<td>10.3 ± 6.6</td>
<td>12.6 ± 8.4</td>
</tr>
</tbody>
</table>

a: Mean particle size of Au/TiO$_2$ after pretreatment in flowing H$_2$ at 80 °C. This catalyst was used for all experiments described in this table.

6.4. Discussion

Upon pretreatment of as prepared Au/TiO$_2$ in flowing H$_2$ between 60 and 300 °C large Au clusters with mean sizes of 8 to 10 nm and broad size distributions formed. The Au clusters were fully reduced as determined by EXAFS measurements of Au/TiO$_2$ after pretreatment at 80 °C and after reaction, and in situ EXAFS measurements of Bus et al.\textsuperscript{90} who found a complete reduction of Au species supported on titania at 60 °C under the same conditions. Most probably the large clusters formed after reduction of the Au precursor due to the elevated temperature. It was found that pretreatment of Au/TiO$_2$ in H$_2$ at RT for 45 min afforded fully reduced Au clusters of about 1.5 nm.\textsuperscript{90} Possibly, H$_2$O formed during the reduction of the Au precursor facilitated the formation of large particles, because UHV studies about the nucleation of Au clusters on mildly hydroxylated and slightly reduced TiO$_2$(110) surfaces showed that water binds to oxygen vacancy centers, which otherwise act as nucleation sites for Au.\textsuperscript{91,92} We observed for all samples pretreated in H$_2$ between 60 and 300 °C that the large particles broke up into small clusters of about 2-3 nm in the liquid phase during hydrogenation of 4-nitrobenzaldehyde, nitrobenzene, and nitrosobenzene at 100 °C.
and 10 bar H₂, but also in pure solvents such as THF and toluene in the presence of H₂ at room temperature and 100 °C, and in an inert gas atmosphere only at the elevated temperature of 100 °C. Thus, the large Au clusters broke apart under reducing conditions. Significant amounts of particles below 2 nm formed, which are regarded as highly active, whereas after pretreatment the catalysts did not contain particles smaller than 2 nm. Leaching as reason for the formation of small particles was excluded. We observed leaching of Au of about 8 %, but this is by far not enough to generate the observed small particles. For the hydrogenation of 4-nitrobenzaldehyde the redispersion was a function of the conversion level; we observed the largest decrease of the mean Au particle size from 10.5 to 3.6 nm at the beginning of the reaction at conversion levels below 10 %. During further conversion of 4-nitrobenzaldehyde the mean Au particle size decreased more slowly until 3 nm were reached. At the same time the particle size distribution continuously became narrower. A break-up of Au particles that were unsupported was reported by Prasad et al. 43 who found that polydisperse Au colloids up to several hundred nanometers in size broke apart to particles narrowly distributed between 5 and 9 nm upon addition of surface-active ligands such as thiols, amines, silanes, and phosphines. These and our results suggest that different substrates influence the dynamic changes occurring in the liquid phase in different ways and that a complex interplay between sintering and redispersion occurs. It seems that the interaction of 4-nitrobenzaldehyde and benzaldehyde with the catalyst surface might hamper or slow down the break-up of Au clusters. This observation is supported by Marks, who noted in his review 93 about experimental studies of small particle structures, that both temperature and chemisorption are important, but that to date their influence is not understood. In contrast to the reduced samples, Au clusters in calcined Au/TiO₂ with the majority of the particles in the size range between 2 to 8 nm did not break apart under the applied reaction conditions. On the contrary, the particle size distribution of Au/TiO₂ calcined at 500 °C hardly changed during hydrogenation and Au clusters in Au/TiO₂ after calcination at 300 °C slightly sintered under reaction conditions. Thus, in the liquid state, reduced and calcined Au/TiO₂ exhibit quite different behaviours. While the particle size in the calcined samples was rather stable, the reduced catalysts were dynamically changing. Phase-contrast STEM micrographs of large Au clusters of both reduced and calcined Au/TiO₂ revealed that their structures differed significantly from each other. After pretreatment in H₂ at elevated temperature, the Au clusters were polycrystalline, with a so-called multiple
twin morphology, while the calcined catalysts mainly contained Au single crystals. Multiple-twinned particles (MTPs) are widespread among transition metals with face-centred-cubic crystal lattices. Known for 50 years, they have been studied extensively. MTPs are composed of slightly distorted tetrahedral segments joined along twin boundaries forming a five-fold symmetry axis. There are two basic forms - decahedral particles built up of five, and icosahedral particles comprising 20 tetrahedral subunits. However, tetrahedral segments joined in this way do not fully fill the space. The resulting solid angle deficiency is compensated by a disclination resulting in an inhomogeneous strain throughout the whole particle. Very often, various more complicated shapes, constructed of MTPs as basic units with unknown internal structures are observed. The so-called polyparticles often represent the majority of the particles in a sample and are formed under non-equilibrium synthesis conditions. It seems that MTPs keep their integrity within such particles. The stability of polyparticles remains unclear. It was suggested that they are unstable intermediates trapped in place during cooling with not enough energy left to form a more favourable structure. On the other hand it was proposed that their structures coincide with local minima in energy. Our EXAFS results suggest that the large clusters after pretreatment in H₂ are agglomerates of smaller particles, because the coordination number identified particle sizes of 2.1 nm before reaction and 1.4 nm after reaction. This suggests that the large particles directly after reduction are actually aggregates of smaller clusters. The support material is responsible for the shape of the particles. On weakly interacting supports such as carbon, MTPs are formed preferentially, which are also formed in inert atmospheres such as argon. On the other hand, single crystals form on strongly interacting supports such as MgO, because the strong interaction forces the clusters to maximize their common surface with the support. Beside the electronic properties of the support, surface hydroxyl groups, and/or defects, and with it the stoichiometry of the metal oxide surface play a key role in the stabilization of nanoparticles. Au/TiO₂ is a typical representative for the complex interactions between Au and the support. In general, the interaction between Au and TiO₂ is weak, resulting in the formation of MTPs, however calcination in air strongly increases the interaction, and consequently fcc single crystals are formed. Haruta noted that the strong contact of Au particles with TiO₂ upon calcination is essential for the high catalytic activity in CO oxidation, because the metal support interface is thought to be the active site for the reaction.
hand, results of Claus et al.\textsuperscript{105} suggest that pretreatment in H\textsubscript{2}, which leads to a partial reduction of the surface of reducible metal oxides such as TiO\textsubscript{2},\textsuperscript{106,107} decreases the interaction of Au with the support. They found that an increase of the reduction time from 3 to 18 hours at 300 °C of Au/ZrO\textsubscript{2} increased the amount of MTPs by a factor of two. Ab initio simulations of the diffusion of atomic gold clusters on rutile TiO\textsubscript{2}(110) showed that on the stochiometric surface the mobility of the Au clusters was low, whereas on the reduced surface Au clusters moved fast between minima in the oxygen vacancy site.\textsuperscript{108} Iijima et al.\textsuperscript{88} reported dynamic changes Au clusters of around 2 nm in size supported on spherical silicon particles in the electron beam, illustrating their instability. In less than 0.1 seconds the Au clusters randomly changed their structure from single crystals to icosahedral and decahedral structures and vice versa. Recently it was observed that the structure of raft like Au particles smaller than 2 nm supported on nanostructured carbon dynamically changed their shape under the electron beam like an anchored droplet of a liquid.\textsuperscript{89} This behavior increased the availability of low-coordinated Au atoms, which are essential for catalytic activity. While these authors observe dynamic transformations of the structure of supported Au particles under electron beam irradiation, we observe in the liquid phase even the break-up of Au particles. Based on our findings we propose that the different behaviour of Au/TiO\textsubscript{2} after calcination and reduction is a result of the different strength of interaction between the Au particles and the support and with it entailed the different Au cluster morphologies. Calcination led to a strong interaction between Au and TiO\textsubscript{2} and the formation of Au single crystals, which were relatively stable under reaction conditions.

On the other hand the weak interaction between Au and the support after pretreatment in H\textsubscript{2} probably played an important role in the redispersion of the apparently rather unstable agglomerates. It is likely that the support surface and thus its interaction with the Au particles changed as the catalysts were subjected to the various pretreatment and reaction conditions. This could lead to the break-up of the particles. It is possible that, as has been reported for Au/CeO\textsubscript{2}\textsuperscript{38} and Au/Ce(Eu)O\textsubscript{2}\textsuperscript{39} catalysts, additional oxygen vacancies form under reaction conditions, which act as preferential anchor sites for Au and caused the redispersion. Chen et al.\textsuperscript{109} reported even the complete wetting of a highly reduced titania surface by Au (mono) and bilayer structures. In contrast, the redispersion of Au supported on carbon during the carbonylation of methanol, in the presence of MeI,\textsuperscript{41,42} probably occurred via atomic abstraction and redeposition of Au by the latter, as indicated by the formation of gold dimers and
trimers starting from particles larger than 10 nm. While we observed redispersion under reducing conditions, Deng et al.\textsuperscript{40} observed redispersion of Au in Au/CeO\textsubscript{2} catalysts after calcination in oxygen at 400 °C.

In summary, by the applied reaction conditions we were able to break up large Au particles and form active small clusters. This study illustrates the complex interaction of Au particles with TiO\textsubscript{2} and their dynamic changes under varying conditions. This behaviour is quite general.

6.5. Conclusions

Electron microscopy and EXAFS measurements at the Au L\textsubscript{3} edge revealed dynamic changes in the dispersion of Au clusters in Au/TiO\textsubscript{2} catalysts in the liquid phase under reducing conditions in dependence of the applied gas phase pretreatment of the catalyst. Large, polycrystalline Au particles with mean sizes of around 9 nm formed during reduction in H\textsubscript{2} between 60 and 300 °C, pointing to the weak interaction of Au and the support. EXAFS measurements indicated that the Au particles observed by electron microscopy could be aggregates of smaller clusters. In contrast, calcination between 300 and 500 °C built up a strong interaction between Au and TiO\textsubscript{2}, which mainly led to the formation Au single crystals with averages sizes between 4 and 5 nm. The multiple-twinned Au particles after the reductive pretreatment were not stable under reaction conditions, but broke apart and formed significant amounts of Au clusters with sizes below 2 nm. No redispersion was observed for calcined Au/TiO\textsubscript{2}. Due to the strong metal-support interaction the large single crystal Au particles in these catalysts were rather stable under reaction conditions.
References


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7. **In situ infrared spectroscopy on the gas phase hydrogenation of nitrobenzene**

7.1. **Introduction**

Gold nanoparticles supported on metal oxides are active in numerous reactions.\(^1\) The activity of the gold depends on a variety of parameters, such as particle size\(^2,3\) support\(^4\) and method of preparation.\(^5\) Corma and coworkers reported that supported gold catalysts hydrogenate nitroaromatic compounds with great selectivity.\(^6\) The activity and selectivity of the reaction was attributed to interactions of the gold nanoparticles with the titania support, in particular the preferential adsorption through the nitro group on titania.\(^7\)

Infrared spectroscopy is one of the most used methods for investigating catalysts. It enables observing species adsorbed on catalyst surfaces. The spectra provide insight into the state of the surface and the mode of adsorption of the adsorbate.\(^8\) Adsorption and detection of probe molecules is a widely used method to gain insight into the structure of a catalytic surface, in particular for probe molecules, such as carbon monoxide, that exhibit backbonding.\(^9\) Adsorption of probe molecules can also be used to determine the acidity and basicity of surface sites.\(^10\) Vimont et al. argue, that due to the changes induced in the surface by adsorption of probe molecules, the best conditions for spectroscopic investigations are reaction conditions themselves and the best probe is the reactant.\(^11\)

The hydrogenation of nitroaromatics has been studied with infrared spectroscopy over a variety of catalytic systems such as palladium on carbon,\(^12\) nickel on titanium oxide in supercritical carbon dioxide\(^13\) and silver on aluminum oxide.\(^14\) Corma and coworkers used infrared spectroscopy in combination with theoretical calculations to show that nitrobenzene adsorbs preferentially through the nitro group on gold supported on titania.\(^7\) Richner et al. used attenuated total reflection IR methods to investigate the liquid phase hydrogenation of nitrobenzene over gold on titania and various reaction intermediates.\(^15\)

This study describes the adsorption behavior of nitrobenzene on supported gold catalysts. In situ infrared spectroscopy is used to detect adsorption of nitrobenzene and its reduction on a catalyst. Repeated cycles of adsorption of substrate and reduction are
employed to gain insight into the behavior of the catalyst under repeated use and how
new reactant is adsorbed in the presence of product.

7.2. Experimental
Synthesis by deposition precipitation with urea\textsuperscript{5} and characterization of the catalysts by
AAS and TEM were previously described.\textsuperscript{16} The catalyst powders were pressed into
pellets and mounted in a transmission IR cell\textsuperscript{17} with a heatable sample holder. The cell
had multiple gas inlets that were used to admit helium, hydrogen, and helium saturated
with nitrobenzene, respectively, as well as for exhaust. Gas flow was controlled by
mass flow controllers. Transmission infrared measurements were performed on a
Biorad FTS 3000 Excalibur Fourier transform infrared spectrometer with a resolution
of 4 cm\textsuperscript{-1}.

The sample was heated to 100 °C in a helium flow of 160 mL/min, kept under these
conditions for 60 min, then reduced at the same temperature in a hydrogen flow of 180
ml/min for 45 min and again flushed with helium for 30 min. The sample was allowed
to cool to room temperature in a flow of helium and a spectrum was taken for use as
background. Nitrobenzene was adsorbed on the catalyst until a constant signal was
reached; the cell was again flushed with helium to remove nitrobenzene from the gas
phase and then the sample was heated to 100 °C. The nitrobenzene was then reduced in
a hydrogen flow of 20 mL/min. For recycling experiments, helium saturated with
nitrobenzene was then again admitted for 30 min and the adsorbed nitrobenzene was
subsequently reduced in a hydrogen flow. This cycle of adsorption and reaction was
repeated four times.

7.3. Results
Figure 1 shows the spectra of Au/TiO\textsubscript{2} and Au/Al\textsubscript{2}O\textsubscript{3} after adsorption of nitrobenzene.
There were significant changes in the OH region between 4000 cm\textsuperscript{-1} and 3000 cm\textsuperscript{-1}.
The band at 3675 cm\textsuperscript{-1} in titania decreased, as did the band at 3750 cm\textsuperscript{-1} in alumina.
Increasing bands were observed at 3600 cm\textsuperscript{-1} and 3650 cm\textsuperscript{-1}, respectively, assigned to
nitrobenzene hydrogen bonded to bridging OH groups. Two main bands of
nitrobenzene were observed at 1530 cm\textsuperscript{-1} and 1350 cm\textsuperscript{-1}, assigned to the asymmetric
and symmetric C-NO\textsubscript{2} stretch in nitrobenzene, respectively. Several weak sidebands
are also observed at 1620 cm\textsuperscript{-1}, 1608 cm\textsuperscript{-1}, 1580 cm\textsuperscript{-1}, 1480 cm\textsuperscript{-1} and 1315 cm\textsuperscript{-1} (see
Table 1). These features match those reported in the literature for nitrobenzene adsorbed on the catalyst. \(^7,15\)

![Absorbance vs Wavenumber](image)

**Figure 1.** IR spectrum of Au/TiO\(_2\) (red) and Au/Al\(_2\)O\(_3\) (black) after adsorption of nitrobenzene to a constant signal and subsequent purging with helium at room temperature.
Table 1. IR bands and assignments.

<table>
<thead>
<tr>
<th>Band</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3750 cm⁻¹</td>
<td>Weak</td>
<td>$\nu$OH on Al₂O₃</td>
<td>18</td>
</tr>
<tr>
<td>3675 cm⁻¹</td>
<td>Medium</td>
<td>$\nu$OH on TiO₂</td>
<td>19</td>
</tr>
<tr>
<td>1625 cm⁻¹</td>
<td>medium</td>
<td>NH₂ bend aniline</td>
<td>20</td>
</tr>
<tr>
<td>1620 cm⁻¹</td>
<td>Weak</td>
<td>$\gamma$CH + $\nu$CN nitrobenzene</td>
<td>21</td>
</tr>
<tr>
<td>1608 cm⁻¹</td>
<td>Weak</td>
<td>A1 $\alpha$CCC + B1 $\alpha$CCC nitrobenzene</td>
<td>21</td>
</tr>
<tr>
<td>1600 cm⁻¹</td>
<td>Strong</td>
<td>Ring stretch aniline</td>
<td>20</td>
</tr>
<tr>
<td>1585 cm⁻¹</td>
<td>Medium</td>
<td>NH₂ bend aniline</td>
<td>22</td>
</tr>
<tr>
<td>1580 cm⁻¹</td>
<td>Weak</td>
<td>$\nu$CC nitrobenzene</td>
<td>21</td>
</tr>
<tr>
<td>1530 cm⁻¹</td>
<td>Strong</td>
<td>$\nu$C-NO₂ (as) nitrobenzene</td>
<td>21</td>
</tr>
<tr>
<td>1500 cm⁻¹</td>
<td>Strong</td>
<td>Ring stretch aniline</td>
<td>20</td>
</tr>
<tr>
<td>1480 cm⁻¹</td>
<td>Weak</td>
<td>$\nu$CC nitrobenzene</td>
<td>21</td>
</tr>
<tr>
<td>1470 cm⁻¹</td>
<td>Weak</td>
<td>Ring stretch $a''$ aniline</td>
<td>20</td>
</tr>
<tr>
<td>1350 cm⁻¹</td>
<td>Strong</td>
<td>$\nu$C-NO₂ (s) nitrobenzene</td>
<td>21</td>
</tr>
<tr>
<td>1315 cm⁻¹</td>
<td>Weak</td>
<td>$\gamma$CC+$\alpha$CCC nitrobenzene</td>
<td>21</td>
</tr>
</tbody>
</table>
Figure 2. IR spectra of Au/TiO$_2$ (A) and Au/Al$_2$O$_3$ (B) taken after adsorption of nitrobenzene, purging with helium and heating to 100 °C (black) and during the subsequent reduction in a flow of H$_2$ after 1 min (red) and after 4 min (blue).

After introducing hydrogen, nitrobenzene was quickly reduced to aniline over both catalysts, as shown by the disappearance of the characteristic nitrobenzene bands at 1530 cm$^{-1}$ and 1350 cm$^{-1}$ and the appearance of aniline bands at 1600 cm$^{-1}$ and 1500 cm$^{-1}$ (Figure 2). A similar reaction did not occur on the pure supports without gold nanoparticles (spectra not shown). The ring stretch band at 1600 cm$^{-1}$ was more intense than the ring stretch band at 1500 cm$^{-1}$ on Au/TiO$_2$. The opposite was observed on
Au/Al₂O₃. Aniline on Au/TiO₂ also showed a strong sideband at 1585 cm⁻¹ that was not present on Au/Al₂O₃. Au/Al₂O₃ showed a sideband at 1625 cm⁻¹.

Figure 3. Recycling on Au/TiO₂: IR spectra of Au/TiO₂ taken after adsorption of nitrobenzene for 30 min. in the first (black), second (red), third (blue), fourth (green), and fifth (yellow) cycle.

Figure 3 shows the IR spectra after the adsorption step of nitrobenzene on Au/TiO₂ in the five subsequent cycles of adsorption and reduction. The amount of adsorbed nitrobenzene decreased with each cycle, as can be seen by the decreasing intensity of the characteristic bands at 1530 cm⁻¹ and 1350 cm⁻¹. After the first admittance of hydrogen and subsequent second addition of nitrobenzene, aniline was observed by bands at 1600 cm⁻¹ and 1500 cm⁻¹. Aniline is thus not completely displaced by
nitrobenzene. The amount of aniline increased in the first two cycles and reached a maximum after the third cycle. In the surface hydroxyl region, the negative absorbance band at 3675 cm⁻¹ decreased up to the third cycle, whereas the feature at 3600 cm⁻¹ increased for two cycles and decreased afterwards.

Figure 4. Recycling on Au/Al₂O₃: IR spectra of Au/Al₂O₃ taken after adsorption of nitrobenzene for 30 min. in the first (black), second (red), third (blue), fourth (green), and fifth (yellow) cycle.

In the case of Au/Al₂O₃, the amount of adsorbed nitrobenzene was constant in each subsequent cycle. After each cycle, more aniline was observed (band at 1500 cm⁻¹).
The negative absorbance band at 3740 cm\(^{-1}\) increased with each cycle. The band at 3650 cm\(^{-1}\), was constant from the second cycle on.

Figure 5 shows the IR spectra during adsorption of nitrobenzene on Au/TiO\(_2\) (A, C) and on Au/Al\(_2\)O\(_3\) (B, D) in the fifth cycle. During the adsorption, a gradual increase of the bands of nitrobenzene over time (30 minutes) was observed. However, there were no changes in the surface hydroxyl region (Figure 5A) of titania. On Au/Al\(_2\)O\(_3\), the amount of adsorbed aniline slightly decreased during the adsorption of nitrobenzene. The band at 3750 remained constant, whereas the band at 3650 increased slightly (Figure 5B).

![Figure 5. IR spectra of Au/TiO\(_2\) (A, C) and Au/Al\(_2\)O\(_3\) (B, D) during adsorption the 5th cycle after 0 min (red), 10 min (blue), 20 min (red), and 30 min (black).](image)

During the subsequent reduction (Figure 6), the bands of nitrobenzene decreased virtually completely within one minute. The intensity of the bands of aniline remained constant on titania, suggesting it had already reached maximum coverage. On alumina, the amount of aniline increased to level observed before adsorption.
Figure 6. IR spectra of Au/TiO$_2$ (A) and Au/Al$_2$O$_3$ (B) before (red) and during reduction of nitrobenzene in the 5th cycle at 1 min (black), 4 min (black) and 7 min (green).

7.4. Discussion

7.4.1. Adsorption

The spectra of adsorbed nitrobenzene on the catalysts match those found in the literature.$^7$,$^{23}$ Adsorption of nitrobenzene also introduced changes in the OH region on both Au/TiO$_2$ and Au/Al$_2$O$_3$. The decreasing band at 3675 cm$^{-1}$ in titania has been assigned to surface hydroxyls in a bridging conformation.$^{19}$ The band at 3750 cm$^{-1}$ in alumina has also been assigned to surface hydroxyls, although the exact nature of that hydroxyl is controversial.$^{18}$ The increasing bands at 3600 cm$^{-1}$ and 3650 cm$^{-1}$,
respectively, are assigned to OH groups with a hydrogen bridge bond to the nitro group of nitrobenzene. A similar shift of hydroxyl bands upon adsorption of CO on Au/TiO₂ was observed by Boronat et al. 24 The shifts observed on titania match those found by Ahmad et al. for the adsorption of nitrotoluene. 25 These results are consistent with adsorption through hydrogen-bonding interactions as proposed by Busca. 26 In addition to adsorption through surface hydroxyl groups, adsorption on Lewis acid sites of the support as discussed by Boronat et al. 7 is also possible. The relative importance of each site mostly depends on the extent of hydroxylation of the surface.

7.4.2. Reduction

After introduction of hydrogen, all nitrobenzene on both catalysts was rapidly converted into aniline. The presence of gold was essential to activate hydrogen, as on the pure support materials, no reduction occurred. The infrared spectra of adsorbed nitrobenzene as well as the correlation of the behavior of OH stretch bands and characteristic nitrobenzene respectively aniline signals suggest that surface hydroxyls play a role in the adsorption of nitrobenzene on these metal oxide supports. Surface hydroxyls are present on metal oxides and their removal, if possible, requires harsh conditions. 18,27 It can thus be assumed that a supported gold catalyst at high temperatures under vacuum is hydroxylated to a great extent. These observations do not contradict Corma’s finding that the active site is nitrobenzene adsorbed through lowly coordinated gold atoms at the metal support interface.7 Only a relatively low amount of such a species would exist on the catalyst at any moment, whereas IR measurements would mostly show the majority of nitrobenzene molecules adsorbed elsewhere on the support. The fast reduction of all adsorbed nitrobenzene however suggests a high mobility of nitrobenzene or hydrogen (via spillover) on to the surface, even though it is unlikely that the spillover hydrogen reduces the nitrobenzene in both cases.

The work of Katritzky et al. showed that the intensity of infrared bands of substituted aromatics is dependent on the electronic effects of their substituent. 28,29 Tanaka and Ogasawara used this correlation in the investigation of aniline adsorbed on alumina and suggested that the band at 1600 cm⁻¹ decreases when the lone pair of the amino group interacts strongly. 22 The stronger relative intensity of the band at 1500 cm⁻¹ for aniline on Au/TiO₂ thus indicates stronger adsorption. Further evidence for stronger
adsorption is found in the position of the NH₂ bending vibration, which is found near its gas phase position of 1620 cm⁻¹ on alumina²⁰, but shifted to lower wavenumbers on titania.

7.4.3. Recycling

Recycling on Au/TiO₂ and Au/Al₂O₃ led to different results. Whereas the amount of adsorbed nitrobenzene decreased with each cycle on Au/TiO₂ and the amount of aniline reached a maximum after the third cycle, the amount of adsorbed nitrobenzene was almost constant on Au/Al₂O₃ and the amount of aniline did not reach a clear maximum. Adsorption of nitrobenzene in the presence of aniline is also dependent on the support. On Au/TiO₂ the aniline signal did not decrease during the adsorption of nitrobenzene. This suggests that nitrobenzene is not able to displace aniline on Au/TiO₂ and that it adsorbs on a different site. During the subsequent reduction, the amount of aniline was also constant, suggesting that the excess aniline desorbs into the gas phase. On Au/Al₂O₃, there is small loss of aniline during adsorption of nitrobenzene, suggesting that there is, at least partly, competition for the same sites. This is confirmed by the spectra of the surface hydroxyl region of the catalysts during adsorption of nitrobenzene in the presence of aniline. No changes are observed on Au/TiO₂. This shows, that on titania, nitrobenzene is not able to displace aniline from surface hydroxyl groups, and thus interacts with other surface sites, such as Lewis acid sites. On Au/Al₂O₃, the band at 3750 cm⁻¹ is constant, whereas the band at 3650 cm⁻¹ increases. This shows that nitrobenzene can still interact with surface hydroxyl groups of alumina in the presence of aniline, and thus suggests at least partial competition for the same site and displacement of aniline by nitrobenzene.

The different behavior of the supports can be explained by interactions with acidic surface hydroxyl groups, as aniline is a considerably stronger base than nitrobenzene. In case of desorption, the different behavior on the two catalysts is explained by the availability of adsorption site on titania. Aniline is adsorbed interactions with surface hydroxyl groups on the support, and can thus desorb easier from a more weakly interacting support (like alumina) than a more strongly interacting one (like titania). This result is in agreement with the strength of interaction derived from the relative intensity of aniline bands (vide supra).
Another possible mode for the adsorption is through Lewis acid sites on the surface. While differentiation of the two types of interaction from IR spectra is not straightforward, the correlation of the behavior of the hydroxyl bands with the presence of aniline and nitrobenzene on the catalyst suggest that surface hydroxyls play an important role in the adsorption of aniline. Busca showed that alumina has stronger (but less) Lewis acid sites than titania. Adsorption through Lewis acid sites would therefore be inconsistent with our observation that aniline is more strongly adsorbed on titania, even though we cannot exclude that. Table 2 summarizes the results.

Table 2. Adsorption sites for aniline and nitrobenzene at different stages of recycling.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Au/TiO₂</th>
<th>Au/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>Surface hydroxyl</td>
<td>Non-protic sites</td>
</tr>
<tr>
<td>First adsorption</td>
<td>nitrobenzene</td>
<td>nitrobenzene</td>
</tr>
<tr>
<td>First reduction</td>
<td>aniline</td>
<td>aniline</td>
</tr>
<tr>
<td>Later adsorptions</td>
<td>aniline</td>
<td>nitrobenzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.5. Conclusions

Supported gold catalysts are active in the gas phase hydrogenation of nitrobenzene. The product aniline adsorbs more strongly on titania than on alumina. Adsorption occurs through hydrogen-bonding interactions with surface hydroxyl groups on the metal oxide or through other (e.g. Lewis acid) surface sites. In the presence of aniline, nitrobenzene does not interact with surface hydroxyl groups on titania, but does so on alumina. The strong adsorption of aniline limits the adsorption of new nitrobenzene on the catalyst and may thus adversely affect the activity of the titania supported catalyst in continued use.
References

8. General conclusions and outlook

The aim of this doctoral research was to establish structure performance relations in hydrogenation over supported gold catalysts.

We designed and constructed a new cell for in situ HERFD XAS measurements of supported metal catalysts in the liquid phase. Gas phase reduction revealed different degrees of metal reduction compared to reduction in the liquid phase. From here on, we always reduced the catalysts in situ in the liquid phase.

By means of in situ HERFD XAS combined with online ATR-FTIR spectroscopy we found that cationic gold did not contribute to the catalytic activity in liquid phase hydrogenation of nitrobenzene. Any cationic gold remaining after pretreatment reduced under reaction conditions without affecting the rate, probably because of uncontrolled reduction leading to large particles. For the hydrogenation of nitro aromatic compounds, supported gold catalysts should therefore be fully reduced prior to the reaction by appropriate pretreatments. The oxidation state of the active gold species should be determined for hydrogenation of other functional groups.

Particle size and support effects in the liquid phase hydrogenation of nitrobenzene over Au/TiO$_2$ and Au/Al$_2$O$_3$ were investigated by means of kinetic measurements, electron microscopy, and HERFD XAS. For Au/Al$_2$O$_3$ the catalytic activity increased with the fraction of particles smaller than 2 nm. This was ascribed to their high fraction of low-coordinated gold atoms, which are the active sites for hydrogen dissociation. Au/TiO$_2$ was found to be much more active than the most active Au/Al$_2$O$_3$ catalyst. Furthermore, the influence of the particle size was less pronounced, and it was more stable in aniline poisoning and recycling experiments. The high intrinsic activity of Au/TiO$_2$ was ascribed to the ability of titania to help splitting hydrogen at the metal-support interphase. The investigation of other reducible supports able to help dissociate hydrogen might be of interest. Particle size and support effects should be investigated systematically for the hydrogenation of other reducible functional groups under similar conditions to be able to directly compare the results and to allow conclusions to be drawn about catalytic properties. Both catalysts were found to deactivate significantly.
during recycling due to sintering of small particles and blocking of active surface sites by deposition of carbonaceous species. Thus sintering needs to be prevented. This could be achieved for example by doping of the metal oxide support with another oxide that helps stabilizing small Au particles. Carbonaceous deposits need to be prevented or removed. Before re-use carbonaceous species should be removed by suitable treatments, for example by burning them off.

Redispersion of Au particles supported on TiO₂ under liquid phase hydrogenation conditions was established. Au particles broke apart into small clusters provided they were multiple twinned. EXAFS confirmed that the multiple twinned particles were agglomerates of smaller clusters. The formation of multiple twinned particles, which occurred during gas phase pretreatment of as prepared Au/TiO₂ at elevated temperature and their instability under reaction conditions was ascribed to a weak interaction of Au with the support. We found that calcination led to the formation of fundamentally different gold particles, namely Au single crystals, which were rather stable during reaction.

The gas phase adsorption and hydrogenation of nitrobenzene on Au/TiO₂ and Au/Al₂O₃ was investigated by in situ IR spectroscopy. We found that the hydrogenation of nitrobenzene proceeded readily on both catalysts. Nitrobenzene and aniline adsorbed on the metal oxide surfaces via hydrogen bonding with hydroxyl-groups or through other sites such Lewis acid sites. Aniline adsorbed more strongly on titania than on alumina. Recycling experiments showed that when new nitrobenzene was admitted to titania, on which aniline was adsorbed, nitrobenzene adsorbed on different sites. This resulted in less nitrobenzene adsorption with every subsequent cycle. On alumina the interaction with aniline was weaker and nitrobenzene was able to replace it. Both nitrobenzene and aniline adsorbed on the same sites. These data directly point to the influence of the support on the catalytic activity. It is these kind of measurements that will contribute to complete understanding of structure-performance relations.
Publications and presentations

Publications


U. Hartfelder, C. Kartusch, M. Makosch, M. Rovezzi, J. Sá, J. A. van Bokhoven, “Particle size and support effects in hydrogenation over supported gold catalysts“, manuscript in preparation.

**Presentations**

**Oral**


“In situ determination of the oxidation state of gold supported on ceria in the liquid phase hydrogenation of nitrobenzene“ C. Kartusch, M. Makosch, J. Sá, J. A. van Bokhoven, EuropaCat X, Glasgow, Scotland, August 28 – September 2, 2011

**Poster**


“Synthesis and characterization of well-defined mesoporous oxidic catalyst supports“ C. Kartusch, J. A. van Bokhoven, Austrian Chemistry Days, Vienna, Austria, August 24-27, 2009


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