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Supercritical Fluids in Amination and Partial Oxidation Reactions

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presented by

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Summary

Supercritical (sc) fluids have several advantageous features that can be exploited in heterogeneous catalysis. Sc solvents can afford higher reaction rates by reducing or eliminating mass transfer resistances, prolonged catalyst lifetime, and through fine tuning of solvent properties by varying pressure and temperature the product distribution can be influenced. Sc solvents can efficiently substitute for organic solvents and offer easy separation of products and solvent. The opportunities are manyfold but in heterogeneous catalysis this potential has been recognized only recently. This thesis shows the application of sc fluids in three classes of reactions: amination of bifunctional alcohols in sc ammonia, epoxidation of propylene with in situ formed hydrogen peroxide, and partial oxidation of alcohols in sc carbon dioxide.

Amination of alcohols is a technically important process. Literature on the amination of bifunctional alcohols is scarce. Recently, the amination of diols in sc ammonia was shown in our laboratory to afford high yields to diamines. Sc ammonia suppressed the consecutive reactions of the more reactive product amines. Particularly high selectivities were achieved for cyclohexane-1,4-diol. It was not sure whether the high selectivity was due to the higher reactivity of the secondary hydroxyls or to the suppression of some side reactions. To better understand the reactivity of diols in sc ammonia, the amination of the secondary alcohols cyclohexane-1,3-diol and pentane-2,4-diol in sc ammonia in a continuous fixed bed reactor was studied. Application of sc ammonia as solvent and reactant suppressed the catalyst deactivation and improved the selectivities to aminoalcohol intermediates, whereas the selectivities to diamines remained poor (8–10%). The main reason for the poor diamine selectivity of 1,3-dihydroxy compounds is the hydrogen atom at the C-atom between the hydroxy bearing carbons. This hydrogen atom enables water elimination leading to undesired monofunctional products via an allylic alcohol intermediate. This contrasts the behavior of 1,4-dihydroxy compounds affording high aminol and diamine selectivities under similar conditions. Amination of bifunctional secondary alcohols with ammonia was found to be faster, but not more selective than that of primary diols.

Epoxidation of propylene still is an unsolved process for heterogeneous catalysis. Considerable effort has been made in the past decades to develop a heterogeneous catalytic process for the substitution of the conventional chlorohydrin and co-product routes, which are inefficient on an atomic basis. The one-pot epoxidation process with propylene, oxygen and hydrogen over a Pd-Pt/TS-1 catalyst, which combines *in situ* formation of hydrogen peroxide over the noble metals and epoxidation of propylene on TS-1, appeared to be a promising method: Recent studies reported relatively high selectivity to propylene oxide. Here this reaction was investigated, including the nature of side reactions, in a fixed bed reactor under high pressure conditions. The continuous operation allowed the study of catalyst deactivation and changes in product distribution with time-on-stream. The initial propylene oxide selectivity was very high, 99% at 3.5% conversion, but the catalyst deactivated rapidly with time-on-stream and successively the formation of methyl formate became the prevalent reaction. Using carbon dioxide, instead of nitrogen, had a beneficial effect on the formation of propylene oxide, and even higher yields were obtained when increasing the pressure from 50–120 bar (sc fluid phase). Thermal analysis (TA-MS and TA-FTIR) indicated that catalyst regeneration requires oxidation at elevated temperature; washing with an organic solvent is less efficient. The serious catalyst deactivation and the striking shift in the selectivity pattern of the catalyst is traced to competing alcohol oxidation on platinum and palladium. The formic acid formed catalyzes its own formation from methanol as well as several other side reactions.

Liquid phase noble metal catalyzed aerobic oxidation of alcohols is an environmentally attractive method, because it utilizes oxygen or air as oxidant. It is widely used for the oxidation of diols and polyols in aqueous medium. Drawbacks of the method are the frequently observed formation of hydrogen, relatively high catalyst-substrate ratios and rapid deactivation of the catalyst. The oxidation of non-polar alcohols in organic solvents is sometimes slow and the flammability of the solvent is an obstacle for any practical application. A feasible solution is the use of sc (dense) carbon dioxide as solvent, a cheap and non-flammable medium with fair and tunable solubility in particular for weakly polar water-insoluble alcohols.

The experiments were carried out in a continuous fixed bed reactor. Oxidation of water-insoluble alcohols in sc carbon dioxide over a Pd-Pt-Bi/C catalyst afforded high reaction rates and yields up to 98% to the corresponding ketones, aromatic and α,β-unsaturated aliphatic aldehydes. The reaction rates were higher compared to vapor phase oxidation and catalyst deactivation was not observed.

The oxidation of octan-1-ol and octan-2-ol to carbonyl compounds, representing the transformation of water-insoluble primary and secondary alcohols, was studied over 0.5 wt% Pd/alumina at 80–140 °C and 75–125 bar, to get a deeper insight into Pt metal catalyzed oxidation. In the oxidation of octan-2-ol the selectivity was excellent (>99.5%) and independent of conversion, whereas octanal oxidized readily to octanoic acid even at low conversion. No significant catalyst deactivation was observed and the rate in carbon dioxide was higher by a factor of up to 2–4, compared to the oxidation in nitrogen. The complex effects of pressure and oxygen concentration on the reaction rate have been interpreted by studying the phase behavior in a high pressure view cell under reaction conditions. Above 40 °C a carbon dioxide-rich liquid phase was in equilibrium with an alcohol-rich phase. Under reaction conditions a swelling of the alcohol-rich liquid phase with carbon dioxide was observed. This swelling is expected to increase the concentrations of carbon dioxide and oxygen in that phase and improve transport properties with respect to chemical reactions.

The oxidation of benzyl alcohol was chosen as a model reaction for the synthesis of (deactivated) aromatic aldehydes. High rate and good selectivity to benzaldehyde (93–97%) has been achieved with 0.5 wt% Pd/alumina or 0.5 wt% Pd/C, at around 100 °C and 100 bar, using only moderate excess of oxygen. The byproduct benzoic acid has an autocatalytic effect on the hydration of benzaldehyde with the co-product water, and the subsequent oxidative dehydrogenation leads to benzoic acid, and benzyl benzoate by esterification. Promotion of Pd by Pb improves the selectivity. No catalyst deactivation or metal leaching have been observed. The method provides reasonable yields at much lower temperature than that applied in conventional gas phase oxidation, showing a potential for the synthesis of thermolabile, water-insoluble aromatic aldehydes.

Zusammenfassung

Überkritische Fluide haben viele für die heterogene Katalyse nützliche Eigenschaften. Überkritische Lösungsmittel ermöglichen höhere Reaktionsgeschwindigkeiten und längere Katalysatorlebenszeiten, indem sie Stofftransportwiderstände reduzieren oder gar eliminieren. Ausserdem kann die Produktverteilung durch Einstellung der druck- und temperaturabhängigen Lösungsmitteleigenschaften beeinflusst werden. Überkritische Fluide können organische Lösungsmittel ersetzen und ermöglichen eine einfache Trennung von Produkten und Lösungsmittel. Die Möglichkeiten überkritischer Fluide sind vielfältig, deren Potential in heterogener Katalyse wurde aber erst kürzlich erkannt. In dieser Arbeit wurde die Anwendung überkritischer Fluide in drei Reaktionsklassen untersucht: Aminierung bifunktionaler Alkohole in überkritischem Ammoniak, Epoxidation von Propen mit *in situ* gebildetem Wasserstoffperoxid, und die partielle Oxidation von Alkoholen in überkritischem Kohlendioxid.

Die Aminierung von Alkoholen ist technisch gesehen ein wichtiger Prozess. Über die Aminierung bifunktionaler Alkohole gibt es bis heute nur wenig Literatur. Kürzlich wurde in unserem Laboratorium gezeigt, dass die Aminierung von Diolen in überkritischem Ammoniak hohe Ausbeuten an Diamin liefert. Überkritischer Ammoniak unterdrückt Folgereaktionen der reaktiveren aminierten Produkte. Besonders hohe Selektivitäten wurden mit Cyclohexan-1,4-diol erhalten. Es war dabei nicht sicher, ob die hohen Selektivitäten dank der höheren Reaktivitäten sekundärer Hydroxyle erhalten wurden, oder durch die Unterdrückung einiger Nebenreaktionen bedingt waren. Um die Reaktivität sekundärer Diole in überkritischem Ammoniak besser zu verstehen, wurde die Aminierung der sekundären Alkohole Cyclohexan-1,3-diol und Pentan-2,4-diol in einem kontinuierlichen Festbettreaktor untersucht. Überkritischer Ammoniak, eingesetzt sowohl als Lösungsmittel als auch als Reaktant, unterdrückte dabei die Deaktivierung des Katalysators und verbesserte die Selektivität zum Zwischenprodukt Aminoalkohol, wobei die Selektivität zum Diamin gering blieb (8–10%). Der

Hauptgrund für die geringe Diaminselektivität von 1,3-Dihydroxyverbindungen ist das H-Atom am C-Atom zwischen den beiden Hydroxyl bindenden C-Atomen, welches die Wasserabspaltung unter Bildung unerwünschter monofunktionaler Nebenprodukte über ein Allylalkohol Zwischenprodukt ermöglicht. Dieses Verhalten unterscheidet sich von jenem der 1,4-Dihydroxy Verbindungen, welche unter ähnlichen Bedingungen hohe Selektivitäten zum Aminol und zum Diamin zeigen. Die Aminierung bifunktionaler sekundärer Alkohole in Ammoniak war schneller, aber nicht selektiver als diejenige primärer Diole.

Die Epoxidation von Propen ist in der heterogenen Katalyse noch immer nicht zufriedenstellend gelöst. In den letzten Jahrzehnten wurde beträchtlicher Aufwand betrieben, um einen heterogen katalysierten Prozess als Ersatz für die herkömmlichen Chlorohydrin- und Co-Produkt-Routen zu entwickeln, welche auf atomarer Basis ineffizient sind. Die Epoxidation mit Propen, Sauerstoff und Wasserstoff über einem Pd-Pt/TS-1 Katalysator, eine Reaktion, welche die *in situ* Bildung von Wasserstoffperoxid über den Edelmetallen und die Epoxidation von Propen über TS-1 in einem einzigen Prozessschritt vereinigt, erschien als vielversprechende Methode. Neuere Studien berichteten über relativ hohe Selektivitäten zum Propenoxid. Diese Reaktion, sowie der Verlauf von Nebenreaktionen, wurde in einem Festbettreaktor unter Druck untersucht. Die kontinuierliche Reaktionsführung erlaubte es, die Deaktivierung des Katalysators und Änderungen in der Produkteverteilung im Verlauf der Reaktion zu verfolgen. Die Anfangsselektivität zu Propenoxid war sehr hoch, 99% bei 3.5% Umsatz, aber der Katalysator deaktivierte innerhalb kurzer Einsatzzeit und die Bildung von Ameisensäure-methylester entwickelte sich zur Hauptreaktion. Wenn statt Stickstoff Kohlendioxid benutzt wurde, bildete sich mehr Propenoxid; noch höhere Ausbeuten wurden erzielt, wenn der Druck von 50 auf 120 bar erhöht wurde (überkritische Phase). Thermische Analyse (TA-MS und TA-FTIR) ergab, dass zur oxidativen Regeneration des Katalysators hohe Temperaturen benötigt werden; Waschen mit einem organischen Lösungsmittel ist weniger effizient. Die einschneidende Deaktivierung des Katalysators und die erstaunliche Verschiebung der Selektivität des Katalysators kann mit der kompetitiven Oxidation von Alkohol über Platin und Palladium erklärt werden. Die so gebildete Ameisensäure katalysiert ihre eigene Bildung aus Methanol und verschiedene andere Nebenreaktionen.

Edelmetalle katalysierte aerobe Oxidation von Alkoholen in flüssiger Phase ist ökologisch und ökonomisch eine attraktive Methode, da als Oxidationsmittel Sauerstoff oder Luft verwendet wird. Die Methode ist weit verbreitet für die Oxidation von Diolen und Polyolen in Wasser. Nachteile sind die häufig beobachtete Bildung von Wasserstoff, relativ hohe Katalysator-Substrat Verhältnisse und die schnelle Deaktivierung des Katalysators. Die Oxidation von nicht-polaren Alkoholen in organischen Lösungsmitteln ist oft langsam und die Entflammbarkeit des Lösungsmittels ist ein Hindernis für jegliche praktische Anwendung. Als mögliche Lösung empfiehlt sich der Gebrauch von überkritischem (verdichtetem) Kohlendioxid als Lösungsmittel, ein billiges und nicht-entflammbares Medium mit guter und einstellbarer Löslichkeit, im Besonderen für leicht polare, wasserunlösliche Alkohole.

Die Experimente wurden in einem Festbettreaktor durchgeführt. Die Oxidation von nicht-wasserlöslichen Alkoholen in überkritischem Kohlendioxid über einem Pd-Pt-Bi/C Katalysator ergab hohe Reaktionsgeschwindigkeiten und Ausbeuten bis zu 98% zu den entsprechenden Ketonen, aromatischen und α,β-ungesättigten aliphatischen Aldehyden. Die Reaktionsgeschwindigkeiten waren höher als diejenigen der Oxidation in der Gasphase, und es wurde keine Deaktivierung des Katalysators beobachtet.

Die Oxidation von Octan-1-ol und Octan-2-ol zu Carbonyl Verbindungen, stellvertretend für die Umwandlung von nicht-wasserlöslichen primären und sekundären Alkoholen, wurde über 0.5 Gew% Pd/Alumina bei 80–140 °C und 75–125 bar untersucht, um einen tieferen Einblick in Pt Metall katalysierte Oxidation zu erhalten. In der Oxidation von Octan-2-ol war die Selektivität hervorragend (>99.5%) und unabhängig vom Umsatz, während Octanal bereits bei geringem Umsatz zu Octansäure weiteroxidierte. Es wurde keine bedeutende Deaktivierung des Katalysators beobachtet und die Reaktionsgeschwindigkeit in Kohlendioxid war um einen Faktor 2–4 höher als bei der Oxidation in Stickstoff. Die komplexen Auswirkungen von Druck und Sauerstoffkonzentration auf die Reaktionsgeschwindigkeit wurden interpretiert unter Einbezug des Phasenverhaltens, welches in einem Hochdruck-

Sichtzellen-Experiment unter Reaktionsbedingungen geprüft wurde. Bei Temperaturen über 40 °C war eine kohlendioxidreiche flüssige Phase im Gleichgewicht mit einer alkoholreichen Phase. Unter Reaktionsbedingungen wurde ein Anschwellen der alkoholreichen flüssigen Phase mit Kohlendioxid beobachtet. Die Ausdehnung dieser Phase wurde auf die Anreicherung mit Kohlendioxid und Sauerstoff zurückgeführt, was sich insbesondere auf den Sauerstofftransport auswirkt.

Die Oxidation von Benzylalkohol wurde als Beispiel für die Synthese von (deaktivierten) aromatischen Aldehyden gewählt. Hohe Reaktionsgeschwindigkeiten und gute Selektivitäten zu Benzaldehyd (93–97%) wurden mit 0.5 Gew% Pd/Alumina oder 0.5 Gew% Pd/C bei etwa 100 °C, 100 bar und einem geringen Überschuss an Sauerstoff erzielt. Das Nebenprodukt Benzoesäure hatte einen autokatalytischen Effekt auf die Hydration von Benzaldehyd mit dem Co-Produkt Wasser. Nachfolgende oxidative Dehydrierung des dehydratisierten Benzaldehyd führte zu Benzoesäure und nach Veresterung zu Benzoesäure-benzylester. Promotierung von Pd mit Pb steigerte die Selektivität. Weder Deaktivierung des Katalysators noch Korrosion der Metallkatalysatoren wurde beobachtet. Die Methode bietet ansprechende Ausbeuten bei niedrigeren Temperaturen als die herkömmliche Oxidation in der Gasphase, was ein interessantes Potential für die Synthese thermolabiler, wasserunlöslicher aromatischer Aldehyde darstellt.

Chapter 1

General Introduction

Research in supercritical (sc) fluid application is driven by the prospect of higher reaction performance, lower environmental impact and simplification of processes. In this thesis sc fluids are applied in three distinct heterogeneously catalyzed reactions: amination of alcohols, epoxidation of propylene and partial oxidation of alcohols.

1.1 Supercritical Fluids and Heterogeneous Catalysis

In this first chapter the properties of sc fluids and some important applications in heterogeneous catalysis are exposed. The literature review focuses on the developments in the past decade [1-12]. Chemical Reviews has recently devoted an entire volume to sc fluids [13].

1.1.1 Supercritical Fluids - Fundamentals

Discovery and Definition

Baron Charles Caignard de la Tour discovered in 1822 the existence of a critical point noting that the gas-liquid phase boundary disappeared when he heated certain materials in a closed container [6].

The sc point of a substance is determined experimentally by measuring the lowest point of pressure and temperature where liquid and gas phase merge upon heating. Other methods are also known in the literature [14-16]. An elegant method is based on the critical opalescence - a phenomenon occurring at the critical point [17].

In thermodynamics the critical point of a pure substance is defined by Equation 1[18].

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \tag{1}$$

A fluid is termed supercritical, when its temperature exceeds the critical temperature. In literature often also higher than critical pressure is assumed for sc fluids (Figure 1-1).

Properties typical for sc fluids are usually restricted to the region near the critical point (reduced temperature T_r = 1.0–1.1, reduced pressure p_r = 1–2). As an example, hydrogen (T_c = -240 °C, p_c = 12.3 bar) is usually considered a gas. Therefore also the density must be higher than the critical density [19].

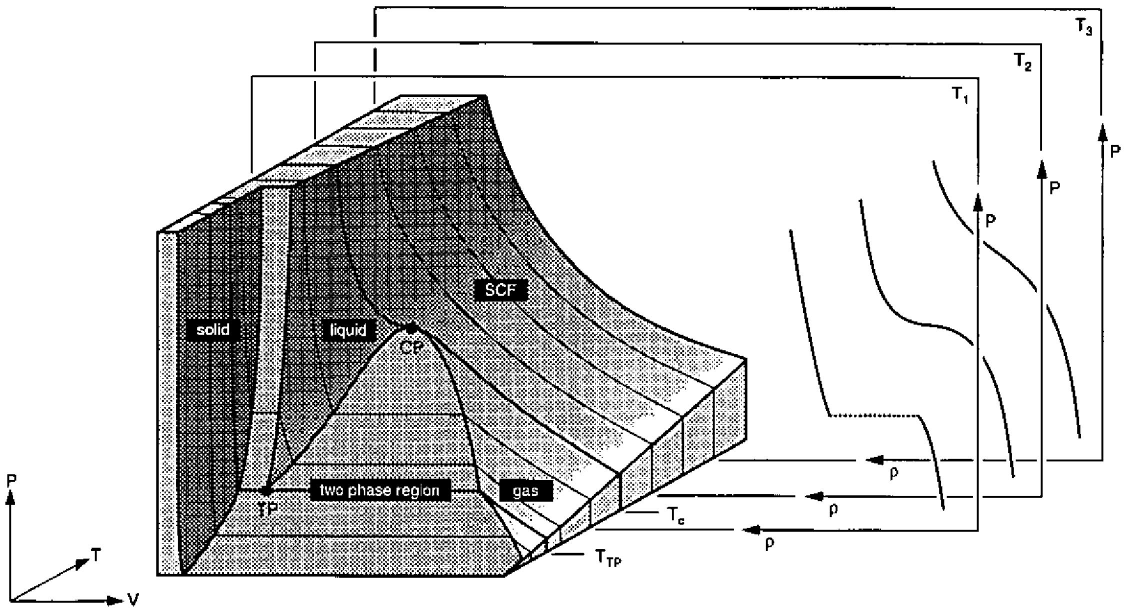


Fig. 1-1: Phase diagram of a pure compound showing domains where solid, liquid and gas (vapor), and sc fluid exist. TP triple point; CP critical point. Taken from Baiker [20].

Mixtures

Supercriticality is well-defined only for pure substances. However, all applications of sc fluids, and particularly chemical reactions, involve multi-component systems: solvent(s), reactant(s) and product(s). Multi-component systems cannot be described by the simple concept of a sc point. Immiscibility phenomena can still occur beyond the mixture's critical point ("retrograde condensation" [21, 22]). These systems are treated by concepts of fluid phase theory [23-25]. Van Konynenburg and Scott have set up a classification system [26, 27] for phase equilibria between multiple liquid and gas phases. The term "supercritical" is generally used in chemistry for two- and multi-component systems being beyond the critical parameters of the solvent or the mixture. For convenience, the term "supercritical" is used here for dense phases of components at temperatures exceeding its mixture critical point (irrespective of further liquid phases present). In contrast "subcritical" refers to the region below the critical point.

Properties of Supercritical Fluids

Tunability of the properties of a sc fluid is an important advantage over conventional solvents. Many of the physical properties of sc fluids, in particular the diffusivity, dynamic viscosity, thermal conductivity and heat capacity, are intermediate between those of a liquid and a gas [28-33] (Table 1-1), and can be tuned over a broad range by temperature and pressure: liquid-like dissolution power and gas-like mass transfer can be obtained [34, 35].

Critical properties are most pronounced in the immediate vicinity of the critical point of the fluid (near critical region). Further off the critical point the properties become either liquid- or gas-like [18]. In classical thermodynamics properties are proportional to the first and second derivatives of pressure, temperature and molar volume, which can be seen directly in the phase diagram. At the critical point a number of physical properties become zero (e.g. enthalpy of vaporization), others diverge (e.g. isothermal compressibility κ_T (Equation 2)). However, the isothermal compressibility (and other properties) do not become infinite at the critical point as suggested by classical thermodynamics. Density fluctuations and resulting effects, more thoroughly treated in statistical mechanics, have to be accounted for.

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \qquad (2)$$

Table 1-1 : Comparison of the magnitudes of physical properties of liquids, gases and sc fluids in the near critical region (data taken from Taylor [36] and Kerler [37])

physical quantity	gas (ambient)	sc fluid (T_c, P_c)	liquid (ambient)
density ρ ($kg\ m^{-3}$)	0.6–2	200–500	600–1600
dynamic viscosity η (mPa s)	0.01–0.3	0.01–0.03	0.2–3
kinematic viscosity ν^a ($10^6\ m^2\ s^{-1}$)	10–500	0.02–0.1	0.1–5
diffusion coefficient D ($10^6\ m^2\ s^{-1}$)	10–40	0.07	0.0002–0.002
thermal conductivity k ($W\ m^{-1}\ K^{-1}$)	0.01	0.01–0.1	0.01

[a] Kinematic viscosity was estimated from dynamic viscosity and density, $\nu = \eta/\rho$.

Since many physical properties of a fluid are density dependent, the properties of the fluid can be tuned by slight changes in pressure in the vicinity of the critical point.

The dynamic viscosity η of a sc fluid is comparable to the viscosity of a gas. However, the kinematic viscosity $\nu = \eta/\rho$ is very low in the critical region due to the high density of the fluid. Low viscosity causes high natural convection and strong buoyant effects in sc fluids [34, 38]. In consequence mass transfer resistances are relatively low and diffusivities are higher than in liquid phase.

The isobaric heat capacity diverges strongly around the critical point [39], whereas the isochoric heat capacity diverges only weakly [18]. Sc fluids thus combine relatively high heat capacity with enhanced heat transfer rates due to buoyancy [40].

An interesting phenomenon of sc fluids is clustering, also termed as local density enhancement or molecular charisma [3, 41-43]. Due to the larger free volume of sc fluids relative to liquids there is enough space for the molecules to move into energetically favoured positions. Solvent molecules gather around solute molecules and also solute molecules aggregate. Clustering is similar to cage formation that occurs in liquid phase chemistry. The phenomenon is particularly pronounced in dilute mixtures in the vicinity of the critical point [11, 12]. They can affect the outcome of chemical reactions.

In the immediate vicinity of the critical point the size of the fluid packets (or the range of those density fluctuations) becomes similar to the wavelength of visible light causing a phenomenon called critical opalescence [17].

Homogenization of the reaction mixture under sc conditions is another key advantage of sc fluids. Understanding the phase behavior, especially for multicomponent systems, is a demanding task [44-46] but crucial for reaction engineering. Most reactions involve a mixture of one or more solutes and a solvent. Additionally, in the course of a reaction the composition of the phase(s) change(s), either with time (batch reactor) or with location (fixed bed reactor). The solubility of the solutes in the solvent depends on the density of the solvent [47] which can be tuned through small changes in pressure, particularly in the vicinity of the critical point. Solubility of solid, liquid and gaseous solutes in sc solvents is commonly good [47, 48].

Solutes can sensitively modify the properties of fluids [35]. Often these effects are desired and cosolvents, also termed as entrainers, are added to the fluid, to enhance the solubility of solutes by orders of magnitude [35, 46, 49]. In contrast, antisolvents decrease the solubility of other solutes [50].

The particular behavior of sc fluids complicates modelling of fluids in the near critical region [51, 52]. Simple forms of equations of state fail to predict properly the fluids under high pressure [44, 53]. Multi-component mixtures are even more complex and often impossible to predict.

Carbon Dioxide

Carbon dioxide is the most widely used sc solvent. It is readily available and cheap. It is an ideal substitute for organic solvents with a polarity similar to $CHCl_3$, fluorinated hydrocarbons or fluoroether [54].

Modifiers such as ethanol increase the polarity of the solvent and extend its application range to polar substances. Use of micelles and surfactants with hydrophilic cores has also been proposed [55-57].

Mass transport properties of $scCO_2$ have been reviewed recently [58].

Water

Properties of scH_2O are striking [39, 59]. When water is heated to the critical point it expands by a factor of 3 and the extent of hydrogen bonds breaks down to a third [60]. The relative permittivity ε (dielectric constant) drops from 80 to 5 [39]. The ion-product constant K_w depends strongly on the temperature and pressure [11].

In the temperature range 200–350 °C most organic substances become soluble. In scH_2O even oxygen and to some extent ions are soluble. ScH_2O serves as a substitute for organic solvents as long as the organic solutes are thermally stable [61, 62]. Another limitation is corrosion by scH_2O. These restrictions can also be exploited (e.g. waste destruction).

Other Fluids

Water and carbon dioxide are the most frequently used sc solvents. Other solvents often are too expensive (e.g. Xe) or unstable under reaction conditions (e.g. ethene). Critical data of some other substances are collected in Table 1-2 and some of their applications have been reported in Møller [59].

1.1.2 Kinetic concepts

High pressure, and particularly sc conditions, influence chemical reactions in various ways. The effect of pressure on the equilibrium and on the rate of a chemical reaction [4, 12, 64] can be evaluated by Equation 3 and Equation 4, respectively.

$$\left(\frac{\partial}{\partial P}\ln K_x\right)_{T,x} = -\frac{\Delta V_r}{RT} \tag{3}$$

K_x is the equilibrium constant in molar fractions and ΔV_r is the molar reaction volume change.

$$\left(\frac{\partial}{\partial P}\ln k_x\right)_{T,x} = -\frac{\Delta V^{\ddagger}}{RT} \tag{4}$$

In transition state theory [65] the rate constant k_x depends on pressure proportionally to the change in activation volume $\Delta V^{\ddagger}$ (Equation 4). Equation 4

Table 1-2: Critical data (temperature, pressure, and density) of sc fluids used as solvents (data taken from ref [63].

solvent	T_c, °C	p_c, bar [a]	ρ_c, kg m^{-3} [b]
sulfur hexafluoride	45.5	37.7	735
nitrous oxide	36.4	72.55	452
water	373.9	220.6	322
ammonia	132.3	113.5	235
carbon dioxide	30.9	73.7	468
methanol	239.4	80.92	272
ethane	32.2	48.84	203
ethene	9.1	50.41	214
ethanol	240.7	61.37	276
propane	96.6	42.50	217
propylene	91.6	46.01	233
propan-1-ol	263.6	51.70	275
propan-2-ol	235.1	47.62	273
xenon	16.5	58.4	1110

[a] The number of digits given indicates the estimated accuracy of this quantity.

[b] Although values for the critical density are given to three decimal places, they cannot be assumed accurate to better than a few percent

assumes that the transition-state transmission coefficient is equal to unity and independent of pressure.

Typical values for $\Delta V^‡$ for high-pressure liquid-phase or gas-phase reactions are in the range –30 to 30 cm^3 mol^{-1}, depending on structure (bond formation or bond breaking in the formation of the activated complex) and solvation [4, 66]. Near the critical point values of $\Delta V^‡$ are in the order of magnitude of liters per mol owing to the large negative partial molar volumes of the reactants and transition states.

In heterogeneous catalysis reactants and products undergo several distinct physical and chemical processes in a particular sequence as illustrated in Figure 1-2. Each step of this sequence can be the overall rate limiting step. Elimination of interphases as well as enhanced mass and heat transfer in the sc media increase the rates of heterogeneously catalyzed reactions.

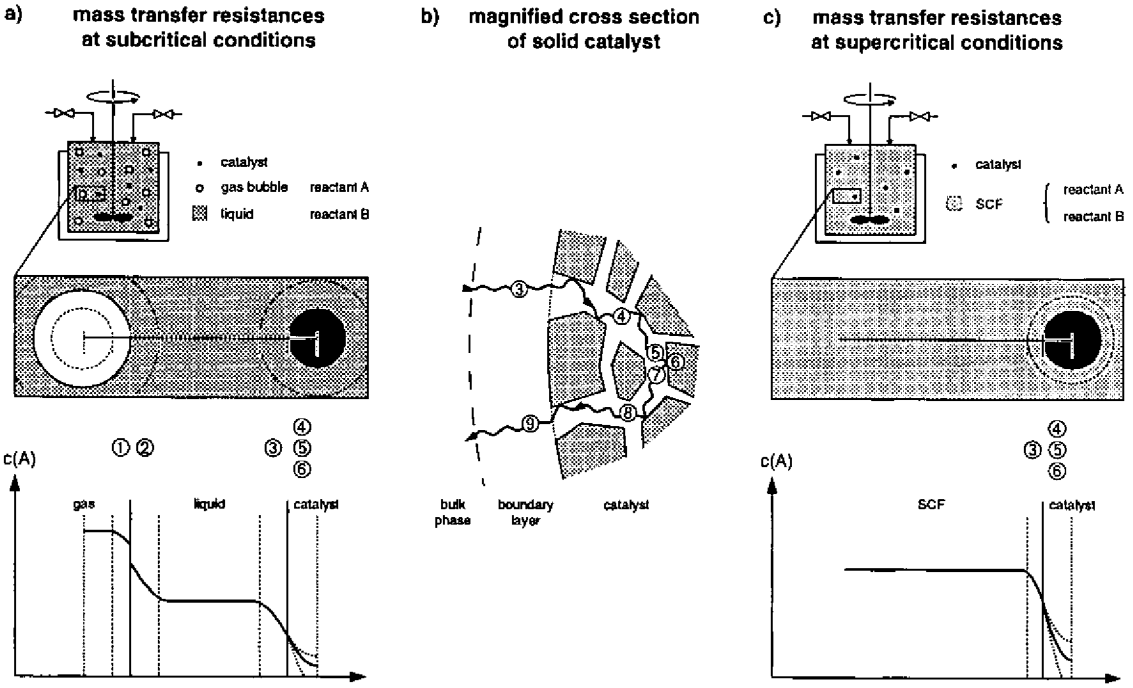


Fig. 1-2: Sequence of physical and chemical steps occurring in a heterogeneous catalytic gas/liquid reaction (slurry phase). Part a) shows a representative section of the reactor content consisting of a gas bubble and a solid catalyst particle and the corresponding mass-transfer boundary layers (resistances) at subcritical conditions. Part b) provides a magnified cross section of the catalyst particle. A representative concentration profile of reactant A is depicted on the bottom. The following physical and chemical steps occur in the reaction: (1) diffusion of gaseous reactant A from bulk gas phase to the gas/liquid interface; (2) absorption of A at the gas/liquid interface and ensuing diffusion to the liquid bulk phase; (3) diffusion of reactants from bulk liquid phase through stagnant fluid film surrounding the solid catalyst particle; (4) internal diffusion; (5) adsorption; (6) surface reaction; (7) desorption; (8) internal diffusion; (9) diffusion of products through boundary layer into bulk fluid. Part c) shows the corresponding situation at sc conditions: under sc conditions gas/liquid transfer resistance (steps 1 and 2) is eliminated and external fluid film diffusion resistance (step 3) is reduced due to lower viscosity of sc fluids. Taken from Baiker [20].

1.1.3 Opportunities of Supercritical Fluid Application

Sc fluids were first applied in physical processes such as the extraction of coffeine from green coffee in carbon dioxide. Other processes followed and are now well established [36, 67, 68]: production of fine powders, waste treatment, etc. Many chemical reactions have been performed in sc fluids, including inorganic, organic, heterogeneously and homogeneously catalyzed, biochemical, electrochemical, photochemical, thermal and sonochemical reactions.

In the past few years sc fluid applications have experienced growing interest. Impetus derives from the many opportunities of sc fluids in reaction engineering and processing and from increased environmental awareness. These opportunities are summarized below.

Effect of Pressure on Rate

The rate of reaction increases in high density operation relative to gas phase operation. The rate constant will also increase depending on the activation volume of the reaction.

Control of Selectivity

Control of solvent properties by temperature and pressure as well as clustering offer the possibility to improve the selectivity of a reaction. Additionally cosolvents can alter rates through specific interactions, and the presence of different phases and relative solubility of solutes therein offer even more opportunities to tune reactions.

Enhanced Mass and Heat Transfer

Homogenization of the reaction mixture accompanied by superior mass and heat transfer can reduce or even eliminate mass transfer resistances in heterogeneous catalysis. Increased heat transfer also implies that highly exothermic reactions, such as oxidations, where temperature control is essential for selectivity and product stability, are predestinated for sc fluid operation.

Catalyst Lifetime and Regeneration

Studies have shown that the catalyst lifetime under sc conditions can be increased relative to operation in the gas phase [69, 70]. Under high pressure conditions precursors of carbonaceous deposits on the catalyst surface, which otherwise cause catalyst deactivation, can be solvated in the dense medium and extracted from the catalyst surface. It has also been demonstrated that spent catalyst can be regenerated by extraction of deposits in $scCO_2$ [71].

The sc fluid condenses inside the catalyst pores, offering enhanced solubility but lower diffusivities within the pores of the catalyst relative to the gas phase [72, 73].

Facilitated Separation

Downstream processing with sc fluids is straightforward: solvent and products separate simply by pressure release. Work-up unit operations such as rectification are not necessary. In more intricate cases products and solvent are separated by adding an antisolvent or by selectively precipitating solutes of the reaction mixture.

The benefits in costs of separation are partially withdrawn by the more expensive operation of the high pressure reactor.

Process Intensification

Higher reaction rates and simple product workup intensify the process: smaller reactors, less space and less capital is required for equal performance [74, 75].

Safety and Environment

Substitution of organic solvents by sc fluids such as carbon dioxide and water results in more environmentally benign processes. The downside is that high-pressure equipment demands special safety precautions.

1.1.4 Literature Survey of Heterogeneous Catalytic Reactions in Supercritical Fluids

Almost until the last decade only very few applications of sc fluids in heterogeneous catalysis have been developed.

Table 1-3 provides a comprehensive summary of heterogeneously catalyzed reactions performed under sc conditions. Sc water oxidation [7, 76] as well as several classical industrial processes such as ethylene polymerization [77], ammonia synthesis and methanol synthesis have been omitted intentionally. Some of these processes are performed at conditions far above the critical point and thus they do not exploit the critical phenomena. Processes reported until 1997 have been reviewed by Baiker [20]. New entries in this table are discussed below.

Alkylation

Parsons and co-workers [78] investigated a series of Heck palladium-coupling reactions in superheated (260 °C) and scH_2O. The catalytic performance of Pd complexes was compared to a heterogeneous 30% Pd/C catalyst. The heterogeneous catalyst was slightly less active. The reactions behaved similarly to those in traditional organic solvents. Bases were added for the removal of the acid generated during reaction. Under sc conditions, addition of these bases did not sufficiently suppress hydrogenation and hydrogenolysis side reactions and the reaction was more sensitive to steric effects and to the structure of the alkene.

Poliakoff and co-workers [79] developed a method for the continuous formation of a series of ethers, acetals and ketals over the solid acid catalysts Deloxan ASP and Amberlyst 15 in sc fluids. Etherification in $scCO_2$ was more selective than in sc propane, probably due to higher solubility of the ether in $scCO_2$ and to separation of the poorly soluble co-product water. Its separation hindered rehydration of products and drove this equilibrium reaction towards products. The authors suggested that the nonpolar solvents used may promote the reaction by increasing the interaction among the polar species (alcohols, reaction intermediates and the catalyst surface).

Amination

Fischer studied the amination of various diols by ammonia under sc conditions [80-84]. See chapter 1.2.3 on page 26 for a more detailed discussion of the results.

Cracking

The former study of *n*-heptane cracking [85] was enriched with an investigation of Norpar 12 hydrocarbon fuel cracking over different zeolites [86-88]. It was found that operation under sc conditions is superior to gas phase operation because of enhanced cracking rates and higher catalyst lifetime. The liquid-like density in the catalyst pore facilitated the *in situ* extraction and continuous removal of coke precursors that are responsible for catalyst deactivation.

Disproportionation

Parsons and co-workers [89] used the disproportionation of cyclohexene to benzene, cyclohexane and hydrogen over Pt in scH_2O to demonstrate the potential of *in situ* fiber-optic Raman spectroscopy - a powerful method for near-real-time measurement of reaction rates. Water is well suited as solvent for Raman spectroscopy, because it has only a low intensity spectrum. At 200 bar and 375 °C equilibrium conversion was attained within a few minutes.

Esterification

Vieville *et al.* had previously studied esterification of oleic acid and methanol in scCO_2 [90, 91]. Recently, the use of scCO_2 as a reaction medium and as a source of carbonate for the carbonation of glycerol to glycerol carbonate was examined [92]. Ethylene carbonate was a necessary coreactant to start the reaction. Among the various catalysts tested, Amberlyst A26, zeolite 13X and Purosiv zeolite gave the best yields to glycerol carbonate.

Fischer-Tropsch Synthesis

In previous work [93-98] Fujimoto and co-workers found that sc conditions were optimal for Fischer-Tropsch synthesis because heat transfer and removal of waxy products from the catalyst surface was more efficient than in gas phase, and diffusivity and reaction rates were higher than in liquid phase. Moreover, the selectivity to olefin was much higher under sc conditions compared to liquid and gas phase operation. In recently published work [99, 100] the effect of addition of 1-tetradecene, a chain initiator, on product distribution was examined. 1-tetradecene promoted formation of hydrocarbons larger than C_{14} and inhibited formation of C_1-C_{13} hydrocarbons.

Following the development of an efficient on-line GC method for analysis of C_1–C_{30} products of Fischer-Tropsch synthesis [101], Bochniak and Subramaniam [102] studied the Fischer-Tropsch reaction in near-critical *n*-hexane. Tuning the pressure over the range 1.2–2.4 P_c the syngas conversion could be tripled and the product selectivity was optimized. The effectiveness of the catalyst increased with pressure. The liquid-like properties of *n*-hexane at high pressure allowed extraction of heavier hydrocarbons from the catalyst pores.

Ermakova *et al.* [103] studied the Fischer-Tropsch synthesis over a precipitated iron catalyst at 6–21 bar and 250–350 °C. Under sc conditions the reaction rate and yield of the desired olefin fraction (C_5–C_{11}) was higher than those of a reference process carried out in the absence of a solvent. *N*-hexane (80 mol% in reaction mixture) was optimum, supposingly because the critical point of this reaction mixture corresponded to the reaction temperature and pressure. A kinetic model was derived from the experimental data, which can serve as a basis for the design of a chemical reactor and process scale-up.

Hydrogenation

About half of the double bonds of fatty acids of vegetable oil have to be hydrogenated to attain the melting point and the oxygen stability required for margarine and shortening. Sc conditions can capitalize on this transformation: the reactants then form a homogeneous phase, thus eliminate gas/liquid mass transfer, resulting in much higher hydrogenation rate. Another advantage is the significantly reduced *cis-trans* isomerization of double bonds, a prerequisite for edible oils.

Härröd and Møller formerly elaborated a hydrogenation method for fatty acids [104, 105] and now applied it successfully to the full and partial hydrogenation of fatty acid methyl esters (FAME) in sc propane [106, 107]. Under the best conditions the reaction was 500 times faster than traditional batch hydrogenation. Higher lipid solubility could be attained by keeping the level of hydrogen (antisolvent) low [106]. Rapid deactivation of the catalyst was observed during hydrogenation of methylated rapseed oil, whereas with methylated sunflower oil a catalyst lifetime similar to those in industrial processes was achieved. Formation of aldehyde and fatty alcohol, and over-hydrogenation to hydrocarbon, occurred along with main reactions of FAME hydrogenation (C=C bond hydrogenation).

Andersson *et al.* [108] developed a two-step procedure sequence, coupling enzymatic synthesis of fatty acid methyl esters in $scCO_2$ and their hydrogenation to fatty alcohols over commercial hydrogenation catalysts in either $scCO_2$ or sc propane. Yields to fatty alcohols were highest in sc propane, but significant amounts of *n*-alkane by-product formed, while virtually no alkanes were produced in $scCO_2$.

A patent to Hoffmann-La Roche [109] claims a process for the continuous hydrogenation of organic compounds over amorphous metal alloy catalysts. The process is performed using a solvent under conditions above its critical point. The method is particularly suited for the selective hydrogenation of alkynes (e.g. dehydroisophytol) to alkenes (i.e. isophytol) in CO_2 over $Pd_{81}Si_{19}$. This catalyst is claimed to exhibit high activity under the conditions applied, good thermal conductivity and, unexpectedly for a glassy metal catalyst, no brittling under the influence of hydrogen.

Bertucco *et al.* [110, 111] previously studied the catalytic hydrogenation of the double bonds of an unsaturated ketone in $scCO_2$. Later [112, 113] they showed that three phases (liquid-liquid-catalyst) were present in the reactor owing to the large hydrogen concentration. High yield in saturated ketone was obtained in $scCO_2$, a medium with fair solubility for hydrogen and the liquid reactant. Kinetic data obtained on a gradientless internal-recycle reactor were fit to kinetic models in order to simulate the performance of a semi-industrial trickle-bed reactor.

Arai and co-workers [114-117] were searching ways to transform heavy crude oil to lighter liquids. They investigated the denitrogenation of coal tar pitch over a NiMo-Al_2O_3 catalyst in a mixture of toluene and tetralin [114, 115]. Nitrogen was selectively removed under the hydrogenating atmosphere. The reaction proceeded faster under sc conditions than in the liquid phase due to higher diffusivity and less coke deposition on the catalyst. In a subsequent study hydrodesulfurization of dibenzothiophene to biphenyl and cyclohexylbenzene was studied [116] over the same catalyst. In scH_2O the reaction mixture formed a homogeneous phase. The reducing agent either was hydrogen or it formed *in situ* via water-gas-shift reaction from CO or via formic acid. Introduction of CO was most effective. In their latest study [117] hydrogenation of hydrocarbons through partial oxidation of other hydrocarbons was studied in scH_2O. Partial oxidation with oxygen produces carbon monoxide which in turn produces the active hydrogenating species via water-gas shift reaction. This method is interesting, because it does not demand costly hydrogen or carbon monoxide for reduction.

Heterogeneous catalytic synthesis of N,N-dimethylformamide and methylformamide from CO_2 and NH_3 was developed by Kröcher *et al.* [118-123]. This method turned out to be very powerful: with the best catalyst, a Ru containing silica hybrid gel catalyst, the turnover frequencies of the best hitherto known homogeneous catalysts were exceeded. It was shown recently [124, 125] that the reaction mixture was not homogeneous, but mass transport limitations appeared to be absent under the conditions applied.

Isomerization

Subramaniam and co-workers studied the isomerization of hex-1-ene for over a decade [70, 126-137]. This reaction is well suited for fundamental studies on sc fluids in heterogeneous catalysis, because the reactants and the main products have similar critical parameters. The thorough study of this reaction resulted in a highly optimized process. Near critical conditions were found to be superior to both sub- and sc conditions, because they afforded an optimum combination of transport and solvent properties, thereby maximizing isomerization rate and catalyst lifetime. Recently the authors [138, 139] focused on the reduction of hexene oligomer formation by deaeration of the feed, by mitigation of peroxide impurities and by passivation of the reactor surface by silicosteel coating. The reduction of these prolific "coke" precursors resulted in constant catalyst activity and it permitted a reliable study of the isomerization kinetics. The effective diffusivity of hexene in the catalyst pores was determined and the effectiveness of the catalyst was assessed.

Oxidation

Partial oxidation under sc conditions has long been neglected, but it became the target of many investigations in the past two years.

Oxidation of isobutane to isobutanol (ROH) was investigated by Fujimoto and co-workers [94, 140]. In a recent paper [141] the initial stage of the reaction was examined: di-*tert*-butyl peroxide (ROOR) formed with a selectivity of 30% at short time-on-stream. This provided further evidence for the peroxy radical mechanism of this reaction. ROOR decomposed to ROH by abstracting a hydrogen radical from isobutane.

Leitner and co-worker [142] presented the oxidation of olefins in $scCO_2$ with oxygen in the presence of aldehydes as sacrificial co-oxidants. No catalyst was required, but the reaction was promoted by the stainless steel of the reactor wall. Presumably the stainless steel initiated the radical reaction, via formation of acylperoxy radicals from the aldehyde and oxygen. The oxidation stopped immediately upon addition of a radical scavenger. The higher reaction rates in $scCO_2$ than in toluene were explained by the good miscibility of oxygen with sc fluids.

Akgerman and co-worker [143] aimed at the total oxidation of ethanol and acetaldehyde over Pt/TiO_2 in $scCO_2$ in a fixed bed reactor. At 90 bar and 150–300 °C complete combustion of ethanol dominated, but the intermediates acetaldehyde (up to 30% yield) and traces of CO also formed. The Langmuir-Hinshelwood type mechanism for direct oxidation of ethanol to CO_2 with dehydrogenation of an ethoxy intermediate as rate-controlling step in the oxidation of ethanol to acetaldehyde predicted the experimental data very accurately.

Willey and co-worker [144, 145] studied the continuous partial and total oxidation of methanol in sub- and $scCO_2$ (at around 90 bar) over iron oxide based aerogels. Product distribution depended strongly on the reaction temperature in the range 200–300 °C and on the catalyst composition: pure iron oxide aerogel favored dimethyl ether formation, 20% iron in molybdenum oxide resulted in dominantly formaldehyde, and low levels of well dispersed iron oxide in silica favored methyl formate production.

Rayner and co-workers [146] investigated the diastereoselective sulfoxidation of chiral sulfides with *tert*-butyl hydroperoxide. In conventional solvents and in $scCO_2$ Amberlyst 15 was particularly effective for oxidation of sulfides derived from methionine and cysteine. In $scCO_2$ diastereoselectivity depended dramatically on pressure (Figure 1-3), whereas no diastereoselectivity could be observed in conventional solvents. The selectivity rose to a maximum of over 95% diastereomeric excess at 180 bar.

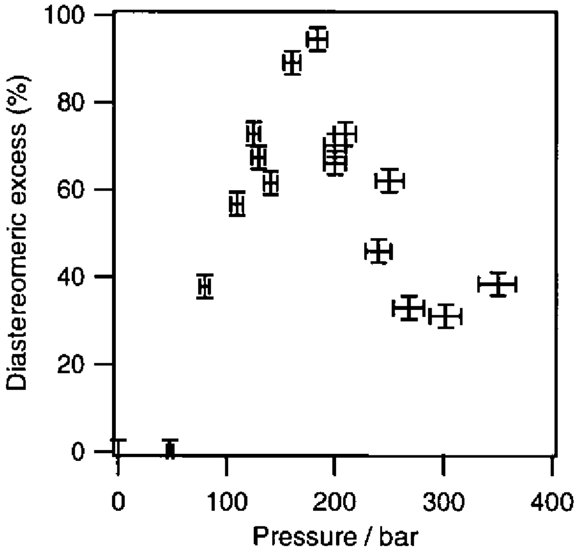


Fig. 1-3: Variation of diastereoselectivity with pressure for oxidation of Cbz-CysS-MeOMe. Adapted from Oakes *et al.* [146].

Parsons and co-worker [147] studied the dehydrogenation and oxidation of cyclohexane, cyclohexene and cyclohexanol over PtO_2 and 10% Pt/C in scH_2O. The amount and number of reaction products (e.g. benzene, cyclohexanone and phenol) depended on the temperature and the presence of acid (HCl) or base (NH_4OH) additives. The selectivities reported are low, nevertheless it is concluded that the targeted transformations in scH_2O are attainable.

Abraham and co-workers [148, 149] investigated the partial oxidation of methane to methanol over Cr_2O_3 in scH_2O. A relatively high selectivity to methanol (40%) at a conversion of 10% was achieved. The reaction proceeded about half as fast in scH_2O than in the gas phase. Besides methanol, formic acid, acetic acid, ethyl alcohol, acetone and carbon dioxide formed. The oxygen balance revealed a much higher oxygen level in the product stream than in the feed, suggesting that the solvent water was involved in the mechanism. The stability of the catalyst proved to be insufficient in a subsequent study [150], as chromium slowly depleted from the catalyst bed.

Martin and Kerler [16, 37, 151] investigated the partial oxidation of propane to oxygenates (acetone, acroleine, acrylic acid) in $scCO_2$ in a batch reactor. Among the various catalysts tested cobalt oxide on silica afforded the highest total oxygenate selectivity (59% at 12% conversion). $ScCO_2$ exhibited optimum mass transfer rates (gas-like) and solvent power (liquid-like). At the transition from sub- to sc conditions consecutive reactions of oxygenates on the catalyst surface were considerably reduced and the propane conversion and oxygenate selectivity rose significantly (Figure 1-4)[151]. The phase behavior of binary mixtures of propane and carbon dioxide were examined in the vicinity of their critical point [16] using the opalescence effect.

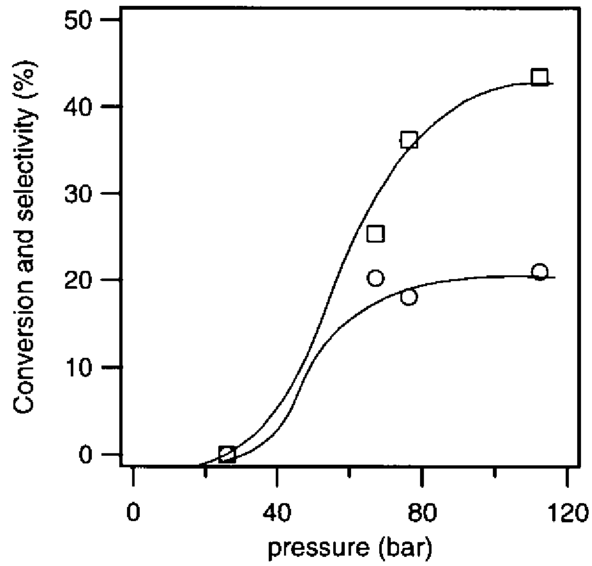


Fig. 1-4: Propane conversion ○ and selectivity □ to oxygenates. Conditions: 2.4 wt% Co_3O_4/SiO_2, propane:air:CO_2 = 1:5–7:100–124, 280 °C. Taken from Martin *et al.* [151].

Hydroformylation

In the past two years three research groups published their results on hydroformylation over supported and insoluble rhodium complexes in $scCO_2$.

Abraham and co-workers [152, 153] developed a process based on carbon-supported rhodium-phosphine complexes to transform propylene to butanal by H_2 and CO. The reaction, however, was not selective (only 1.5% selectivity to butanal). Elucidation of the reaction mechanism and identification of intermediates may provide a basis for future improvements in selectivity. It was hoped that sc fluids allow the substitution of organic solvents currently used in the oxo-process and product separation would be facilitated. Also higher reaction rates were expected in homogeneous phase operation.

Cole-Hamilton and co-workers reported the hydroformylation of hex-1-ene [154, 155] and of methanol [156]. Hydroformylation of hex-1-ene was carried out in $scCO_2$ over *in situ* prepared, liquid, but CO_2-insoluble, rhodium phosphine and phosphite catalyst [154, 155]. They assumed that the excess ligands, which dissolve the rhodium complex, act as a solvent in which the catalytic reaction takes place. The catalyst was easily separated from the products and could be reused several times. In the second study methanol was carbonylated to acetic acid over a polyvinylpyrrolidone-supported rhodium catalyst [156]. $ScCO_2$ helped overcome the problems of liquid phase reactions (catalyst leaching) and gas phase reactions (low methanol through-put). Rates up to ca. 50% of those in liquid phase homogeneous reactions were attained.

Poliakoff, van Leeuwen and co-workers [157] studied the continuous selective hydroformylation of higher olefins in $scCO_2$. The reactions were performed with a mixture containing CO_2 (120 bar), syngas (50 bar) and oct-1-ene at 80 °C over a rhodium complex immobilized on silica. The hydroformylation was over three times faster than the batch reaction in toluene but only half as fast as the homogeneous analogue under comparable condition. Enhanced mass transport in $scCO_2$ was assumed to play a crucial role. The catalytic performance remained stable over several days.

Oligomerization

Ethylene polymerization with sc fluids is a well-known industrial process [77]. These reactions have intentionally been omitted from this review. One example of oligomerization is included because it uses a concept similar to those described above.

Fujimoto and co-workers [158] performed ethylene oligomerization to C_4–C_9 on H-ZSM-5 zeolite. In sc *n*-pentane, ethylene oligomerization was faster and the catalyst lifetime was greatly extended in comparison to gas-liquid phase operation. Sc *n*-pentane extracted medium-molecular-weight oligomers *in situ* from the catalyst. The regeneration of the spent catalyst, however, did not restore the full original activity, due to the limited affinity of *n*-pentane to catalyst poison and difficult pore diffusion of high-molecular-weight polymers.

Table 1-3: Overview of heterogeneously catalyzed reactions under sc conditions. (Sheet 1 of 3)

Reaction/Reactant	Catalyst	Solvent	T / °C	P / bar	r [a]	S [b]	a [c]	Reference
A Alkylation								
benzene and ethylene	Y-type zeolites		250–285	70–80	↗	↗	↗	[159, 160]
isopentane and isobutene	Y-type zeolite	isopentane	50–200	35–46	↗		↗	[161-163]
isobutane and isobutene	Y-type zeolite	isobutane	50–140	35–50	↗		↗	[161-163]
but-1-ene and isobutane	HY-type zeolite, sulfated zirconia	CO_2	50–140	34.5–155.1			↗	[164]
mesitylene, anisol and propylene	polysyloxane (amino-polysiloxane)-supported solid acid	propylene	160–180	220	↗			[165]
alkenes and arenes	Pt/C	H_2O	400			↘		[147]
mesitylene, anisol and propan-2-ol	amino-polysiloxane-supported solid acid	CO_2	200–300	150–220	↗			[165]
alcohol to acetal, ketal and ether	amino-polysiloxane, ion exchange resin	CO_2, propane	100–200	60–200	↗		↗	[79]
B Amination								
3-aminopropan-1-ol, cyclohexane-1,3-diol, cyclohexane-1,4-diol, propanediols, pentane-2,4-diol	Co-Fe	NH_3	195	50–135		↗		[80, 82-84, 166]
C Cracking								
heptane, petroleum	promoted HY-type zeolite	heptane	325	34	↗		↗	[85-88]
D Disproportionation								
toluene to p-xylene and benzene	zeolite ZSM-5		320–325	33.6–56		↗	↗	[167]
1,4-diisopropylbenzene to cumene and 1,3,5-triisopropylbenzene	zeolite 13 NaHX	benzene, *n*-pentane	260	200			↗	[2, 168-170]
cyclohexene to benzene, cyclohexane and hydrogen	Pt	H_2O	375	200				[89]
ethylbenzene to benzene and diethylbenzene	zeolites (HY, H-ZSM-5, H-mordenite)	butane, pentane	300–400 >550	50			↗	[168, 171, 172]
E Esterification								
oleic acid and methanol	macroporous ion-exchange resin	CO_2	40–68	9.5–13				[90, 91]
glycerol and CO_2	ion exchange resin, zeolites	CO_2	40–70	100–130				[92]
F Fischer-Tropsch Synthesis								
CO and H_2 to liquid hydrocarbons	Ru/Al_2O_3, Co/SiO_2, Fe	*n*-hexane	240	45	↘ [e]	[d]	↗	[94, 97, 98, 173]
CO and H_2 to liquid hydrocarbons with addition of 1-olefins to produce wax	$Co-La/SiO_2$, Ru/Al_2O_3	*n*-pentane	210–240	45	↘ [e]	↗	↗	[95, 96, 99, 100, 173]
CO and H_2 to liquid hydrocarbons	$Fe-Cu-K/SiO_2$	propane	250	55		↗		[174, 175]
CO and H_2 to liquid hydrocarbons	Fe	*n*-hexane	240	35–70		↗		[101, 102]
CO and H_2 to liquid hydrocarbons	Fe		250–350	6–100				[103]

Table 1-3: Overview of heterogeneously catalyzed reactions under sc conditions. (Sheet 2 of 3)

Reaction/Reactant	Catalyst	Solvent	T / °C	P / bar	r[a]	S[b]	a[c]	Reference
G Hydrogenation								
fats, oils and fatty acid methyl esters	Pd/C, Pd on amino-polysiloxane	propane	50–150	70–120	↗	↗		[104-107]
fats and oils	Pd or Pt on amino-polysiloxane	CO_2	60–160	80–160	↗	↗		[176-178]
fatty acid methyl esters	Cu-chromite, and Cr-free catalyst T-4489	CO_2, propane	210–250	150–250				[108]
acetophenone	Pd/amino-polysiloxane	CO_2	90–300	1.20	↗	↗		[179]
cyclohexene	Pd/amino-polysiloxane, Pt/amino-polysiloxane	CO_2, propane	40–320	0.60–1.20	↗			[179]
1,2-(methylenedioxy)-4-nitrobenzene	Pd/amino-polysiloxane	CO_2	90	1.40	↗			[179]
m-cresol, benzaldehyde, propionaldehyde, acetophenone, cyclohexanone, cyclohexanole, furan, nitrobenzene, N-benzylidene-methylamine, butan-2-one oxime, oct-1-yne, oct-1-ene, cyclohexene, isophorone	various noble metal catalysts on amino-polysiloxane	CO_2, propylene						[165]
ethyl pyruvate to (*R*)-ethyl lactate	Pt/Al_2O_3 and cinchonidine as modifier	ethane, propane	40–100	70–250	↗	↗		[180, 181]
triple bond of propagylic alcohol, phenylacetlyene	$Pd_{81}Si_{19}$	CO_2	50–180	50–200	↗			[109]
double bond of unsaturated ketone	Pd/Al_2O_3	CO_2	150–250	120–250	↗			[110-113]
hydrogenation of hydrocarbons through partial oxidation and water-gas-shift	$NiMo\text{-}Al_2O_3$	H_2O	400	270				[117]
hydrodesulfurization of dibenzothiphene	$NiMo\text{-}Al_2O_3$	H_2O	400	300				[116]
denitrogenation of coal tar pitch	$NiMo\text{-}Al_2O_3$	toluene/tetraline mixture	380–450	70–200	↗		↗	[114, 115]
dimethylamine, CO_2 and H_2 to dimethylformamide	sol-gel $RuCl_2X_2$, X = $PMe_2(CH_2)_2Si(OEt)_3$	CO_2						[118-125]
H Isomerization								
hex-1-ene to hex-2-ene (cis/trans) and hex-3-ene	$\gamma\text{-}Al_2O_3$/Al-metal shell catalyst		220–250	50–800	↗	↗ [f]	↗	[2, 69, 169, 170]
hex-1-ene	Pt/Al_2O_3	CO_2 and cosolvents *n*-pentane, *n*-hexane	235–310	35–180	↗	↗ [f]	↗	[70, 126-139]
hex-1-ene to olefinic oligomers	Pt/Al_2O_3		281	277				[130]
xylene isomerization to p-xylene	solid acid, various molecular sieves		320	32	↗		↗	[182]
I Oxidation[g]								
toluene to benzaldehyde	Co/Al_2O_3	CO_2	130–230	80				[183]
propylene to propylene glycol	$CaI_2/CuI/Cu_2O$ on MgO or alumina		70–400	> 70	↘	↗		[184, 185]
isobutane to *tert*-butyl alcohol	$SiO_2\text{-}TiO_2$, Pd/C		153	44–54	↗		↗	[94, 140, 141]
cis-cyclooctene, cyclohexene, oct-1-ene, *trans*-hex-3-ene, isophorone, (*R*)-(+)-limonene	initiation by stainless steel-reactor wall	CO_2	55	190	↗			[142]
ethanol to acetaldehyde	Pt/TiO_2	CO_2	150–300	89.6				[143]

Table 1-3: Overview of heterogeneously catalyzed reactions under sc conditions. (Sheet 3 of 3)

Reaction/Reactant	Catalyst	Solvent	T / °C	P / bar	r [a]	S [b]	a [c]	Reference
methanol to dimethyl ether, methyl formate, formaldehyde	iron oxide on silica, molybdenum oxide aerogels	CO_2	200-350	90				[144, 145]
chiral sulfides to sulfoxides (diastereoselective)	ion exchange resin	CO_2	40	100–120		↗		[146]
alcohols to aldehydes, ketones and carboxylic acids	Pd/alumina, Pt/alumina, Pd/carbon, Pd-Pt/carbon, Pd-Pt-Bi/carbon	CO_2	60–140	60–140	↗			[186-188]
propylene to propylene oxide	Pd-Pt/TS-1	CO_2	43	50–120	↗			[189]
cyclohexane, cyclohexene, cyclohexanol	PtO_2, Pt/C	H_2O	375					[147]
methane to methanol	Cr_2O_3	H_2O	400–475	114–439	↘[e]	↗		[148, 149]
propane to acetone	Co_3O_4/SiO_2	CO_2	240–300	20-120	↗	↗		[37, 151]
K Hydroformylation								
propylene to butanal	supported metal-phosphine ligands, Rh/C	CO_2						[152, 153]
hex-1-ene, non-1-ene	insoluble Rh (II) phosphite and phosphine	CO_2	100	42–246	↗	↗		[154, 155]
methanol to methyl ethanoate and ethanoic acid	Rh/polyvinylpyrrolidone	CO_2	150	200	↗		↗	[156]
oct-1-ene	Rh-complex on silica	CO_2	70–90	170–180	↗		↗	[157]
L Oligomerization								
ethylene	H-ZSM-5 zeolite	*n*-pentane	300	55	↗		↗	[158]

[a] change of reaction rate in the sc region with respect to subcritical conditions (↗ increase, ↘ decrease)

[b] change of selectivity in the sc region with respect to subcritical conditions (↗ increase, ↘ decrease)

[c] change of catalyst lifetime in the sc region with respect to subcritical conditions (↗ increase, ↘ decrease)

[d] higher olefin content

[e] vs. gas

[f] changes *cis/trans*, double bond and side reactions

[g] Total oxidation in scH_2O (SCWO) has intentionally been omitted since it has been reviewed recently by Ding *et al.* [7].

1.2 Amination of Diols

1.2.1 Introduction

Reactions in which an amino group is inserted into an organic molecule are generally termed amination. Here we focus on heterogeneously catalyzed amination of alcohols, i.e. the reaction of a primary or secondary alcohol with ammonia or an amine to the corresponding primary, secondary and tertiary amine.

The amination of alcohols has been described already by Sabatier and Mailhe at the beginning of this century. Nowadays amination of alcohols is a well established process for the manufacture of a variety of aliphatic and aromatic amines. The industrial importance is indicated by the immense number of patents. Many reviews can be found in the open literature [190, 191].

1.2.2 Methods for the Preparation of Amines from Alcohols

Two main classes of catalysts are used for the amination of aliphatic alcohols: metal catalysts offering hydrogenation-dehydrogenation activity and solid acids catalyzing dehydration. A third class, phosphate catalysts, catalyzes amination via a "phosphate ester" mechanism, but is not discussed here.

Metal Catalysts - Dehydrogenation Mechanism

The most suitable metal catalysts for amination of aliphatic alcohols are supported Cu and the Group VIII transition metal catalysts Ni, Fe, Co and Pd. Reactions are typically performed at 50–300 bar and 180–250 °C. Relatively high catalyst: alcohol ratios are required (5–30 wt% for batch operation), except for Pd.

Amination on metals is suggested to proceed via dehydrogenation. The main steps of this reaction series are (Figure 1-5):

1. Dehydrogenation of the alcohol to an adsorbed carbonyl intermediate.
2. Condensation of the intermediate with either ammonia, a primary or secondary amine via a carbinolamine adduct to form an imine or enamine type intermediate.
3. Hydrogenation of the intermediate to the product amine.

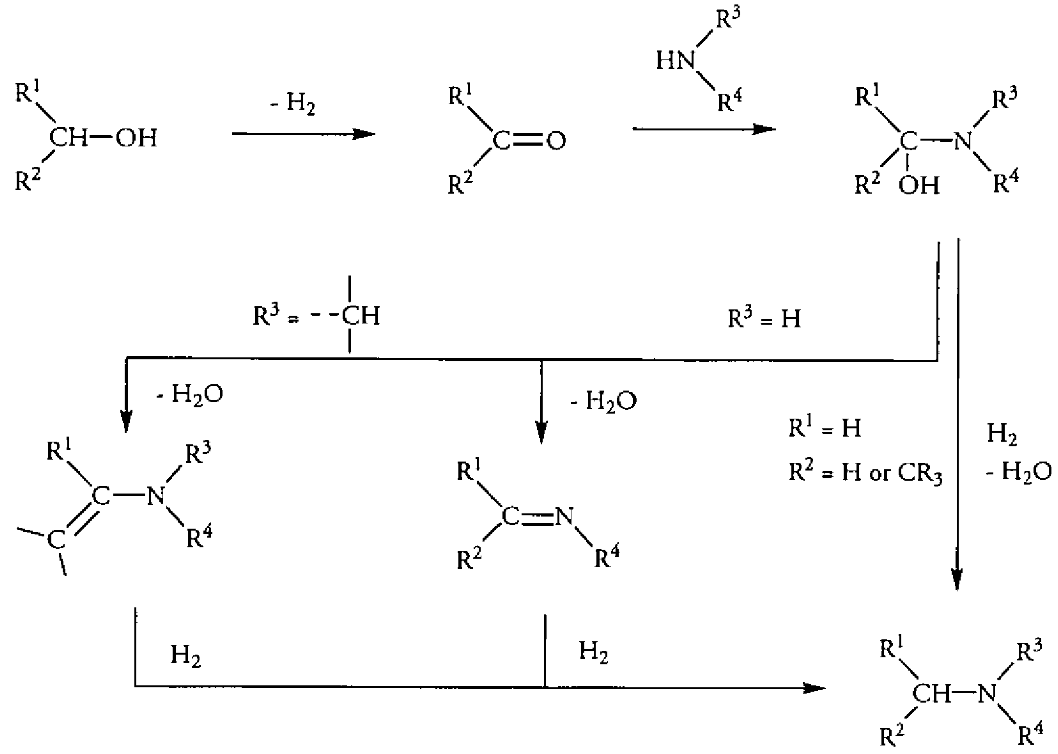


Fig. 1-5: Amination of alcohols via dehydrogenation.

In the case of monofunctional aliphatic alcohols the rate limiting step of this mechanism was demonstrated to be the abstraction of the α-hydrogen.

Hydrogen is not present in the overall chemical balance of the reaction but plays an important role in the reaction: in presence of hydrogen predominantly saturated amines form, whereas imines, enamines and nitriles are favored in the absence of hydrogen, especially at higher temperatures. Hydrogen also suppresses the disproportionation of reactant and product amines and it prevents catalyst deactivation by incorporation of nitrogen and/or carbon into the metal lattice. In absence of hydrogen adsorbed amines often undergo C-N bond cleavage and subsequently form surface nitrides, carbides or carbonaceous deposits.

Other side reactions include the condensation and decarbonylation of intermediate carbonyl compounds. Also hydrocracking and hydrogenolysis of the amines can become significant at higher temperatures when Group VIII metal catalysts are used, but with Cu C-C bond cleavage is not significant. With bifunctional alcohols the condensation and disproportionation reactions can result in polyamines of various lengths. Various heterocyclic products may also form in side reactions, depending on the distance between the two functional groups.

Carbonyl compounds, i.e. the intermediates after the first step in the amination of alcohols, can also be aminated over metal catalysts. Their reaction occurs at lower temperature and affords high selectivity. This reaction is usually termed reductive alkylation in the literature, as in this case stoichiometric amounts of hydrogen is required for the synthesis of saturated amines.

Solid Acid Catalysts - Dehydration Mechanism

Various oxides and zeolites are used as catalysts for the amination of typically small chain alcohols. These reactions proceed via acid-catalyzed dehydration of the alcohol to the corresponding alkene and subsequent amination with the reactant amine or ammonia according to the Markownikow orientation rule (Figure 1-6). Ammonia and amines are suggested to adsorb as ammonium species on Brønsted acid sites. Adsorption of amine is much stronger than that of ammonia. Proper strength of acid sites is crucial for high activity and selectivity.

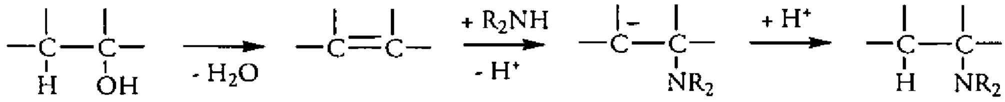


Fig. 1-6: Amination of alcohols via dehydration mechanism.

Reaction temperatures required (250–450 °C) are considerably higher than those of metal-catalyzed amination. In zeolites the channel size can sterically hinder the formation of bulky products, which can lead to a favored product distribution.

Alkenes are intermediates in the amination via dehydration. Their amination over metals generally fails due to nitrile formation and alkene polymerization. In contrast, acidic zeolites afford excellent selectivities by Markovnikov addition. Alkenes adsorb through a π-complex with the surface OH groups.

1.2.3 Amination of Bi- and Polyfunctional Alcohols

Only little has been reported in the early literature about the amination of bifunctional and polyfunctional alcohols. Its investigation, however, is meaningful: nowadays diamines are manufactured by amination of the corresponding chlorides - a method with several severe drawbacks: hydrogen chloride is corrosive and its neutralization produces stoichiometric amounts of sodium chloride.

Amination of bi- and polyfunctional alcohols has been reviewed recently by Fischer et al. [191]. The reactions discussed are the formation of ethylene diamine from ethanolamine and ethylene glycol (see also [192]), amination of ethylene glycol with amines, amination of higher aliphatic diols, amination of polyoxyalkylene diols and triols with ammonia, synthesis of polyalkylene polyamines and amination of sugars. It has been concluded that amination of di- and polyfunctional alcohols can be performed under conditions similar to those applied in the amination of simple aliphatic alcohols. However, amination of bi- and polyfunctional alcohols is much more complex because numerous side reactions can interfere. Optimization of the yield by varying the reaction parameters and the catalyst is much more demanding than in the case of amination of monofunctional alcohols.

Fischer reported many details of the synthesis of primary amines from aliphatic diols with ammonia over an unsupported Co based catalyst and over Ni on silica [80-84]. The effect of pressure (50–150 bar), temperature (135–235 °C), contact time and reactant ratio on the product distribution were studied. Reactions were run in ammonia (critical parameters of NH_3: 114.8 bar, 132.4 °C) as solvent and reactant.

Catalyst screening revealed that only Co-, Ni- and Cu-based catalysts were useful for the amination of propane-1,3-diol (Figure 1-7) [80]. In a more profound study of Co catalyzed amination Fischer found that the best catalyst, 95 wt% Co-5 wt% Fe, contained only very weak acidic sites, which are unable to chemisorb ammonia. Absence of strong acidic and basic sites is crucial to avoid acid-base catalyzed side reactions such as retro-aldol reaction, hydrogenolysis, alkylation, disproportionation, dimerization and oligomerization. Addition of Fe to the Co catalyst was required to retain the active but metastable β-Co phase and to suppress its transformation to the thermodynamically stable α-Co phase. The effect of temperature (150–210 °C), pressure (50–150 bar) and contact time were investigated. Astonishingly, the selectivity to the amino alcohol intermediate and the desired diamine rose dramatically in the transition from sub- to supercritical conditions. At best, 32% diamine yield and 8% intermediate amino alcohol at almost complete conversion was obtained. The existence of a single (sc) phase eliminates the interphase mass transfer resistance. It is suggested that sc conditions increase the surface concentration of NH_3, favoring the desired amination reaction and suppressing the side reactions. The Co-Fe catalyst did not deactivate significantly within the first ten days of use.

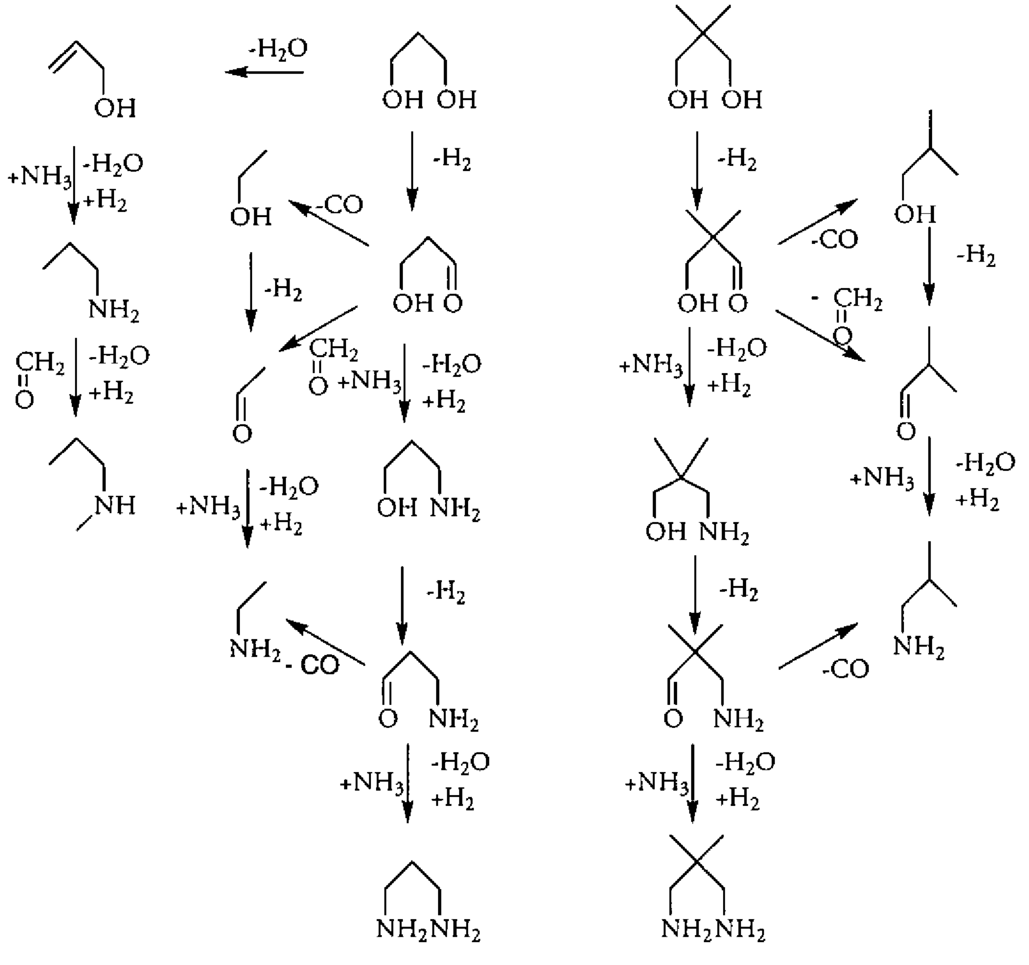


Fig. 1-7: Proposed reaction scheme for the amination of propane-1,3-diol and 2,2-dimethylpropane-1,3-diol.

Generally a high ammonia:alcohol ratio (here: 20) has to be used to compensate the higher reactivity of intermediate and product amines compared to ammonia and to obtain good selectivities in primary amines. Use of excess ammonia successfully suppressed oligomerization.

Application of $scNH_3$ afforded significantly higher selectivity to primary diamines in the amination of propane-1,3-diol and 2,2-dimethylpropane-1,3-diol (Figure 1-7). Selectivity to amines increased with increasing pressure by a factor of 4 to 18 in the near critical region of ammonia. This improvement was attributed to the higher surface concentration of ammonia and to suppression of degradation reactions. This effect can also be interpreted as selective poisoning of the metal catalyst.

Amination over a commercially available nickel catalyst was also studied and the reactivity of the structurally related 2,2-dimethylpropane-1,3-diol, 2-methylpropane-1,3-diol and propane-1,3-diol was compared (Figure 1-7) [83]. The aim was the elucidation of the relationship between the structure of the reactant diol and the diamine selectivity. Reactions were performed at 135 bar and 180–235 °C. A strong dependence of amination selectivity on the diol structure was revealed: Under best conditions 2,2-dimethylpropane-1,3-diol yielded 53% of the corresponding diamine and 5% amino alcohol intermediate. In contrast, both 2-methylpropane-1,3-diol and propane-1,3-diol afforded low diamine and amino alcohol yields owing to poor selectivities. Direct elimination of water, which is not possible with 2,2-dimethylpropane-1,3-diol due to a missing hydrogen at the C2 position, was regarded to cause the difference.

The effect of pressure on the amination of propane-1,3-diol and 3-aminopropan-1-ol over the Co-Fe catalyst, and that of 2,2-dimethylpropane-1,3-diol over the Ni catalyst, to the corresponding diamines was thoroughly investigated [82]. In both cases a dramatic increase in diamine selectivity was observed at the transition of sub- to supercritical conditions. This behavior was explained by mass transfer and coverages of adsorbed surface species: At medium pressures (<90 bar) the reaction mixture consists of two phases: a liquid phase, rich in the organic reagents, and a gas phase containing mostly ammonia. Besides, under sc conditions the reaction mixture forms a homogeneous phase: mass transfer resistances at the interphases are eliminated and the reaction proceeds faster. Under sc conditions the surface concentration of NH_3

is expected to increase. High ammonia coverage favors the amination and suppresses degradation by hydrogenolysis and dimerization.

Amination of cyclohexane-1,4-diol was studied over the Co-Fe bimetallic catalyst [84]. A high yield of 67% for diamine was obtained at 195 °C and 135 bar. If the unreacted diol and the amino alcohol were recycled, the efficiency of this method would even be higher and the amount of by-products would be reduced to ca. 3%. Compared to the amination of propane-1,3-diols, retro-formylation is not possible with the ketone (secondary alcohol), and elimination of water is unlikely because of the cyclic strain.

1.3 Epoxidation of Propylene

1.3.1 Introduction

Propylene oxide is a commodity chemical which is used as an intermediate for the production of polymers (polyurethanes, polyesters), oxygenated solvents (propylene glycol ethers) and industrial fluids (monopropylene glycol and polyglycols). Its annual worldwide production capacity in 1991 was $3.9 \cdot 10^6$ t [193].

1.3.2 Manufacture of Propylene Oxide

Propylene oxide is produced by selective epoxidation of propylene. Industrial production of propylene oxide is shared equally by the chlorohydrin route and the hydroperoxide route [194].

An extensive research has been devoted to the development of a one-pot, direct and selective oxidation process with air. Various methods have been proposed, but they are still far from commercialisation.

Conventional Industrial Processes

The synthesis of propylene oxide via the chlorohydrin route was first described by Wurtz in 1859 (Figure 1-8) [195]. In this reaction the alkene reacts with hypochlorous acid (HOCl) to produce chlorohydrin. The hypochlorous acid is produced *in situ* by an equilibrium reaction with water and chlorine. The chlorohydrin is dehydrochlorinated to the epoxide using aqueous calcium hydroxide. Because of the disposal problem (chlorinated by-products and stoichiometric amounts of brine) no new chlorohydrin plants are built [193].

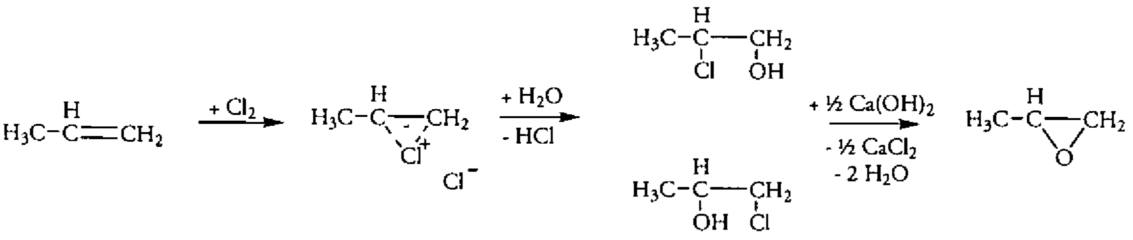


Fig. 1-8: Chlorohydrin route to propylene oxide.

The hydroperoxide route is a two stage process [193]: In the first step an organic peroxide is formed (usually from isobutane or ethylbenzene), and in the second step propylene reacts with the peroxide to form propylene oxide. The drawback of this method is the stoichiometric formation of co-product alcohol.

Direct Oxidation

Around 1940 a process for the direct epoxidation of ethylene was developed [195]. 90% selectivity was achieved over 10 wt% Ag/α-Al_2O_3 at 230 °C and 30 bar. The conversion was kept below 10% to prevent oxidative decomposition.

This method takes advantage of the particular activation of oxygen over Ag [196]. Ag provides four different adsorption modes for oxygen: molecular adsorption, incorporation into the Ag lattice (subsurface), nucleophilic atomic and electrophilic atomic oxygen. These four modes have specific reactivities towards epoxidation.

Nucleophilic atomic oxygen dominates at low oxygen coverage. It deprotonates acidic organic molecules, resulting first in a strong adsorption and ultimately in decomposition of the organic molecule.

At higher oxygen coverage, the lattice of Ag saturates. Surface oxygen becomes polarizable and adopts electrophilic nature. Electrophilic atomic oxygen interacts with the π-electrons of ethylene, ensuing in epoxidation.

Unfortunately, propylene oxide yields are very low by this method. Nucleophilic atomic oxygen easily deprotonates propylene to the stabilized allyl structure, i.e. the first step towards decomposition. On the other hand propylene polarized by electrophilic atomic oxygen decomposes easily via abstraction of the γ-hydrogen.

Recently, ARCO Chemical Technology [197, 198] has patented a method for the catalytic gas-phase epoxidation with molecular oxygen over Ag supported on carbonates and titanates. The best selectivity to propylene oxide was 56% at a conversion of 7%. Even this system still does not meet the requirements of a commercial process and no successful direct oxidation route to propylene oxide has been found to date.

Other Processes

A variety of other processes have been proposed, but none of them is a real alternative to existing processes. Propositions include the epoxidation using molten salts [199, 200], use of nitrous oxide as oxidant as well as photochemical, electrochemical, biocatalytic and non-catalytic processes [195].

A promising route has been proposed recently by Haruta and co-workers [201, 202]. In this method propylene is epoxidized with hydrogen (sacrificial reducing agent) and oxygen over a Au/TiO_2 catalyst at 30–120 °C. High selectivities (>90%) were obtained, but conversions, as reported in the open literature, are still below 5%. The method suffers from low hydrogen efficiency and the catalyst deactivates by oligomer formation and site blocking. The same authors have patented an improved method affording a propylene oxide yield of 9.6% [203].

1.3.3 The Hydroperoxo Route

Homogeneous To Heterogenous Catalysis

Alkenes can efficiently be epoxidized with inorganic peracids, produced from hydrogen peroxide with metal oxides [204]. Later organic peroxides replaced inorganic peroxides as epoxidizing agents saving the expensive production of hydrogen peroxide. In the Halcon process, for instance, propylene was epoxidized with alkyl hydroperoxides in the presence of soluble metal compounds as catalysts [205]. The alkyl hydroperoxides were produced by autooxidation of isobutane and ethylbenzene.

In the late sixties Shell developed a heterogeneous titania/silica catalyst for the epoxidation of olefins with alkyl hydroperoxides [206] (Figure 1-9). This catalyst had the advantage of being completely insoluble in the reaction medium, which made it eminently suitable for continuous operation. In addition, higher selectivities (94% at 96% ethylbenzene hydroperoxide conversion) were achieved than with the hitherto used homogeneous catalytic system (90% at 92% conversion).

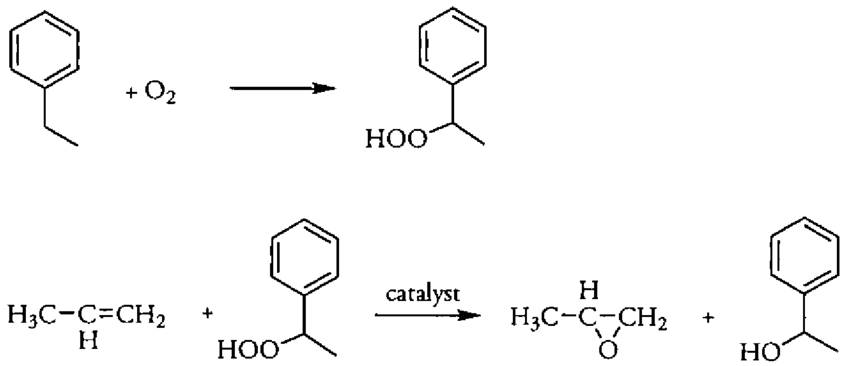


Fig. 1-9: Hydroperoxide route to propylene oxide: Auto-oxidation of ethylbenzene to the hydroperoxide (above) and its use in catalytic epoxidation (below).

Organic Peroxides To Hydrogen Peroxide

The TiO_2-SiO_2 catalyst developed by Shell only operates with organic peroxides and therefore significant amounts of co-products are formed. The use of hydrogen peroxides as oxidant is preferred, because then water is the only co-product. The cheap aqueous hydrogen peroxide cannot be used with the Shell catalyst, because water retards the reaction and because the epoxide formed readily decomposes on the catalyst to the corresponding glycol. To attain high yield with hydrogen peroxide, apolar solvents have to be applied and the water formed has to be removed continuously during reaction by azeotropic distillation.

The invention of titanium silicalite TS-1 by Enichem in 1983 offered new opportunities for propylene epoxidation [207-210]. TS-1 is a crystalline zeolite with MFI lattice in which some Si atoms have been substituted isomorphously by Ti ($xTiO_2.(1-x)SiO_2$, $0<x<0.04$) [211]. The degree of substitution is limited to prevent extra-framework TiO_2. TS-1 is prepared via hydrolysis of a mixture of alkoxides of Ti and Si in an alkali-free solution with tetrapropyl ammonium hydroxide, distillation of the alcohols and crystallization of the resulting gel at 175 °C.

TS-1 has exceptional catalytic properties. The surface of TS-1 is hydrophobic and the small diameter of the pores induces some reactant shape selectivity. Ti occupies tetrahedral positions, but interaction with the solvent and peroxide molecules leads to octahedral coordination. The adsorption of molecules on Ti leads to higher coordination of Ti. Ti^{IV} can coordinate hydrogen peroxide either by formation of a titanium peroxo complex, or by bonding the hydroperoxo species end-on [207]. Hydrogen peroxide coordinated on Ti yields electrophilic oxygen that can attack the double bond π-electrons of propylene.

TS-1 does not catalyze olefin epoxidation with organic hydroperoxides due to steric reasons, but epoxidation with hydrogen peroxide performs well [207]. Side reactions include hydrolysis to glycols, C=C bond cleavage and ether formation. The reaction is performed in polar solvents such as methanol, methyl acetate, acetonitrile and *tert*-butyl alcohol. Ethanol is not suitable because it is slowly oxidized. Methanol assumably participates in the reaction mechanism via coordination to Ti, a feature that only protic solvents possess (Figure 1-10).

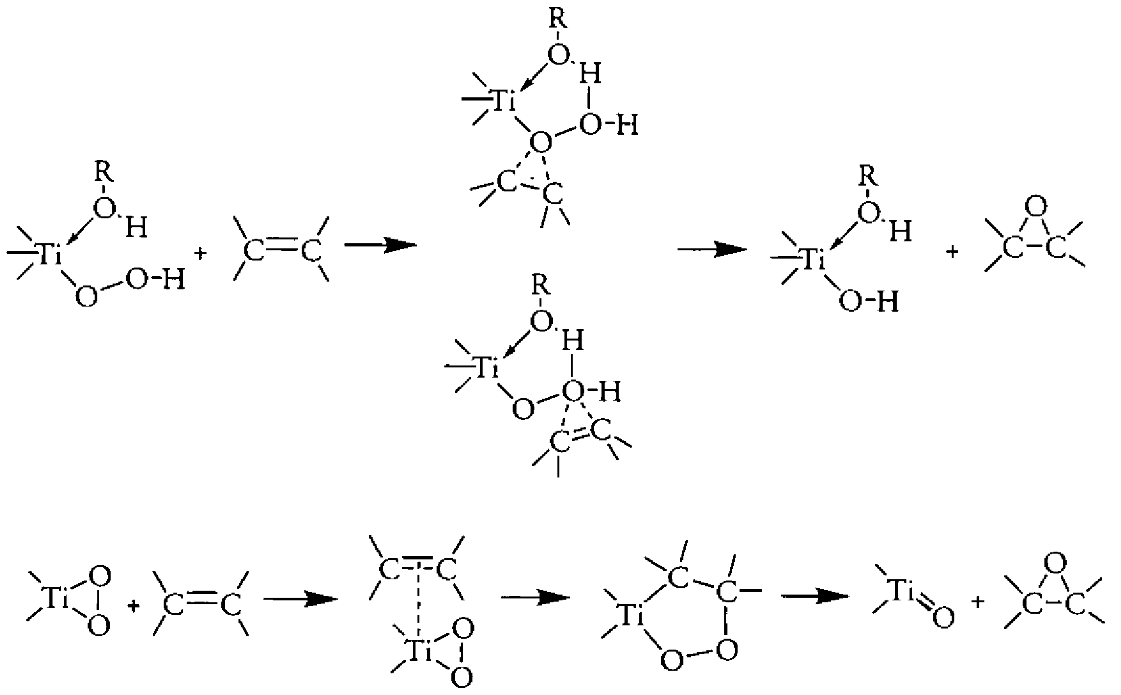


Fig. 1-10: Possible mechanisms proposed for the epoxidation of propylene with end-on hydrogen peroxide and methanol assistance (above) and with side-bonded hydrogen peroxide (below). Adapted from Notari [207].

Enichem has developed a two-stage process for propylene epoxidation: first hydrogen peroxide is produced by alkylantraquinones via hydrogenation over Pd followed by oxidation with oxygen. Then the olefin is epoxidized over TS-1 [194, 212-214]. The production of hydrogen peroxide uses two solvents: an organic solvent and a water/methanol mixture.

Ex Situ to in Situ Hydrogen Peroxide

Hydrogen peroxide shipping is a cost factor and somewhat hazardous [194, 212]. Safe handling is critical because in presence of metals in basic conditions, hydrogen peroxide readily decomposes to water and oxygen. Further development of the epoxidation process is directed to the substitution of hydrogen peroxide by its *in situ* formation from hydrogen and oxygen [194, 212].

One first approach for the *in situ* formation of hydrogen peroxide makes use of the conventional anthraquinone process for the production of hydrogen peroxide, which can be integrated into a one-pot process with the epoxidation of propylene. This method has been investigated by Enichem and a propylene oxide yield of 78% has been achieved [194, 212, 215]. A second concept is based on the oxidation of propylene by a hydrogen-oxygen gas mixture over a precious metal containing titanium silicalite. Hydrogen peroxide is directly synthesized from hydrogen and oxygen at the precious metal sites of the bifunctional catalyst and consumed as an oxidant for epoxidation at the Ti-sites.

Such a one-pot process integrating hydrogen peroxide formation and epoxidation was recently patented by Tosoh Corp, Japan [216-218]. Propylene was epoxidized with *in situ* formed hydrogen peroxide from hydrogen and oxygen over a catalyst with group VIII metals (such as Pd, Pt) on titanium silicalite at 10–35 °C. Similarly, BASF has patented [219-221] a method for the production of propylene oxide over titanium and vanadium silicalite-supported platinum metal catalyst. A selectivity to propylene oxide of 92.3% was attained at 1.8% conversion.

In the open literature, Hölderich and co-workers have reported the epoxidation of propylene over Pd-Pt/TS-1 with hydrogen and oxygen in a methanol-water mixture (3:1) [222-225]. At best, 11.6% propylene oxide yield with 46% selectivity has been achieved with 1 wt% Pd - 0.02 wt% Pt/TS-1 in the semicontinuously operated process.

Development of processes via the hydroperoxide route requires further considerable improvements and the flammability of oxygen-hydrogen mixtures represents a critical point in any industrial application.

1.4 Partial Oxidation of Alcohols

1.4.1 Introduction

Aldehydes, ketones and carboxylic acids play an important role in fine chemistry. For their synthesis from alcohols traditional synthetic organic chemistry employs a variety of oxidants such as the oxides of chromium, manganese, selenium or lead [226]. These stoichiometric reactions produce aqueous solutions of inorganic salts which are environmentally hazardous. For industrial application nonpolluting oxidants such as oxygen or peroxides [227] are preferable. Nitrous oxide and ozone are also considered as prospective oxidants [228, 229].

Direct heterogeneous oxidation with oxygen is the simplest imaginable alternative, because oxygen is readily available and often even air can be used.

1.4.2 Classes of Partial Oxidation

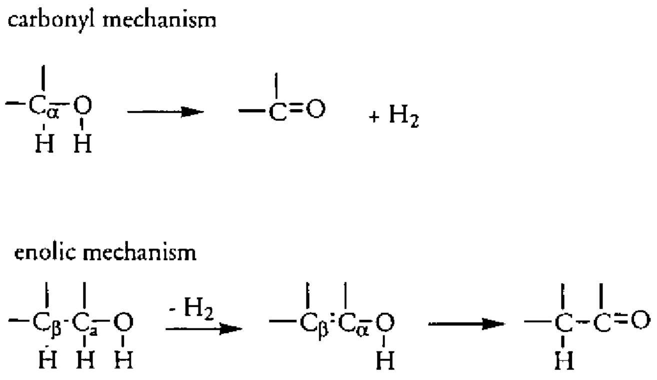
Three types of partial oxidation are distinguished: dehydrogenation [230, 231], oxidation and oxidative dehydrogenation [226].

Dehydrogenation

Dehydrogenation is an endothermic reaction. Conversion is often limited by thermodynamic equilibrium. Hence high reaction temperatures are advantageous. The number of molecules increases in the reaction, calling for low partial reactant pressures. The reaction is usually carried out at atmospheric pressure and 250–400 °C to reach acceptable conversions.

Metals (Cu, Ag) and mainly metal oxides are used as catalyst. Most oxide catalysts and supports for metallic catalysts also catalyze dehydration and on some oxides, such as alumina, dehydration even predominates. Addition of small amounts of strong basic oxide, such as sodium, poisons acidic centers, suppresses dehydration activity and increases dehydrogenation selectivity.

In most cases the reaction rate can be described by the Langmuir-Hinshelwood rate expression. Two different mechanisms have been suggested for the dehydrogenation of alcohols: the "carbonyl" mechanism and the "enolic" mechanism (Figure 1-11).


carbonyl mechanism

enolic mechanism

Fig. 1-11: "Carbonyl" mechanism and "enolic" mechanism

In the carbonyl mechanism the hydrogens from the carbonyl group and from the α-carbon atom are split, either simultaneously or in two steps. Over oxide catalysts the alcohol first adsorbs dissociatively with the formation of a surface alkoxide and an adsorbed hydrogen atom. In the next, rate-limiting step, the α-hydrogen is abstracted, which forms a hydrogen molecule with an adsorbed hydrogen. The formed aldehyde or ketone remains adsorbed either through its C=O group or enolic group -C=C-O-. In the enolic mechanism the β-hydrogen of the adsorbed surface alkoxide is split and an alkenol intermediate is formed. This mechanism is not applicable to metals.

Oxidation

Oxidation is carried out with an excess of air or oxygen at 350–450 °C. This method is used for the production of formaldehyde over an $Fe_2O_3.MoO_3$ catalyst.

Oxidative Dehydrogenation

In oxidative dehydrogenation the alcohol is dehydrogenated to the aldehyde or ketone and simultaneously the hydrogen formed is oxidized to water. The overall reaction is exothermic. Oxidative dehydrogenation is the most important process for the production of aldehydes from alcohols.

1.4.3 Oxidative Dehydrogenation

The oxidative dehydrogenation is an irreversible process and therefore the choice of the reaction temperature is governed by catalyst activity and selectivity. Strict temperature control is essential to avoid total combustion.

The most important side reactions are the formation of carboxylic acids, oxidative degradation of the carbon chain to lower aldehydes, and total oxidation of the organic products and reactants to carbon dioxide and water.

For the oxidative dehydrogenation of alcohols either oxides, often combinations of oxides such as $Fe_2O_3.MoO_3$, or metals, mainly Ag and Pt metals are used.

Metal-Oxide Catalysts

On oxide-based catalysts in the gas phase the generally accepted reaction mechanism is the Mars-van Krevelen mechanism [232]. It proceeds in four steps:

1. Adsorption of the alcohol on the oxidized catalyst surface, either bound by the OH group or as an alkoxy.
2. Dehydrogenation of the adsorbed alcohol.
3. Desorption of the aldehyde or ketone, eventually incorporation of (lattice) oxygen and desorption of carboxylic acid.
4. Reoxidation of the reduced catalyst surface by oxygen from the gas phase. The oxygen is incorporated into the lattice of the catalyst.

Metal Catalysts

Metal catalyzed oxidative dehydrogenation of alcohols are performed in the liquid and in the gas phase.

In the gas phase mostly Ag and Cu based catalysts are used. The most important applications is the BASF formaldehyde process and the production of acetaldehyde, glyoxal and acetone. These reactions are performed at atmospheric pressure and 600–730 °C.

1.4.4 Liquid Phase Metal Catalyzed Oxidative Dehydrogenation

Introduction

In the liquid phase mainly Pt and Pd based catalysts are applied with oxygen or air as oxidant. Liquid phase dehydrogenation allows lower reaction temperatures compared to gas phase processes. It is therefore an attractive method for the oxidation of temperature sensitive alcohols. Reactions are usually carried out in batch reactors, at atmospheric pressure and 20–80 °C [233].

The partial oxidation of alcohols was first reported by Döbereiner [234] in 1845, who observed the Pt catalyzed conversion of methanol and ethanol via aldehyde and carboxylic acid to carbon dioxide. In 1855 Strecker reported the partial oxidation of cinnamyl alcohol [235]. The method has been elaborated over the years and it has found some applications mainly in carbohydrate chemistry.

Mechanism

Liquid phase reactions are considerably more difficult to investigate than gas-phase reactions. Consequently, less is known about the reaction mechanism in solution. The mostly accepted mechanism involves the following steps:

1. Adsorption of the alcohol on a reduced surface site (e.g. Pt^0). Alcohol does not adsorb on oxidized surface sites (i.e. Pt^{n+}).

2. Dehydrogenation of the alcohol on the catalyst surface, forming a carbonyl and adsorbed hydrogen (i.e. reduction of other surface sites).

3. Oxidation of the adsorbed hydrogen by oxygen (i.e. oxidation of the surface) by oxygen.

4. Desorption of the products carbonyl compound and water.

There is no agreement in the literature whether the oxidative dehydrogenation in the liquid phase proceeds via adsorbed alkoxy species or whether the abstraction of hydrogen is oxygen assisted or not. It is evident that the nature and the coverage of adsorbed species depend upon many factors such as pH, oxygen availability, alcohol concentration and the chemical nature and oxidation state of the metal.

It is very difficult to describe the kinetics of the reaction [236]. In many cases the rate of oxidation was described by Equation 5, where Θ_i is the surface coverage of the oxidizing species and the organic adsorbate [237]. The mechanism requires the presence of two surface sites (reduced Pt^0 and oxidized Pt^{n+}). Equation 5 implies that there is an optimum of oxygen and alcohol coverage of the catalyst surface, and a too high oxygen coverage ("over-oxidation") results in deactivation.

$$\text{rate of oxidation} = k\, \Theta_{Ox}^{\ m}\, \Theta_{organic}^{\ n} \tag{5}$$

The nature of adsorbates and the reaction pathways have been reviewed recently [238]. *In situ* EXAFS studies of Pt-O bonds under reaction conditions are expected to provide even more insight [239]. The reaction can also be described by electrochemical concepts: each platinum metal particle functions as an electrochemical cell [240].

Side Reactions

In liquid phase oxidation high selectivities (90–99%) can be attained [237]. However primary alcohols usually produce carboxylic acids in a consecutive reaction. In the presence of water geminal diols form by hydration of the carbonyl compounds. Acids form much faster via dehydrogenation of geminal diols than via direct oxygen insertion (Figure 1-12) [237]. High aldehyde selectivities are obtained only if the primary hydroxyl group is located next to an aromatic ring or a C=C double bond in the α-position, thereby stabilizing the aldehyde. Oxidation obeys the order of reactivity aldehydes > primary hydroxyl > secondary hydroxyl.

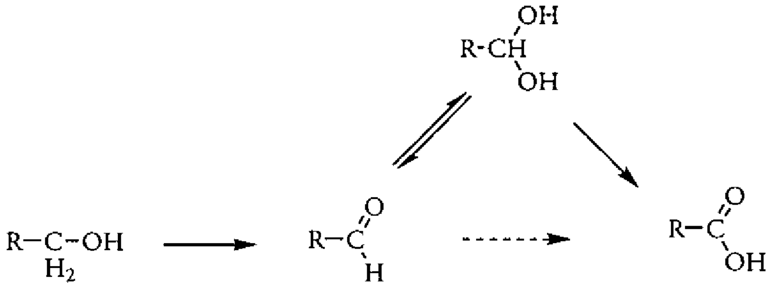


Fig. 1-12: Oxidation of a primary alcohol.

Ether and ester formation are typical side reactions in non-aqueous solvents. In some instances alkenes and hydrogen formed under reaction conditions. The latter poses a potential danger as hydrogen forms explosive mixtures with air [236].

Pt also activates C-H bonds (hydrocarbon reforming catalyst). Therefore Pt may be used only under mild conditions, i.e. in liquid phase.

Modifiers and Promoters

The major drawbacks of this method are the rather high catalyst-alcohol ratios (20–50 wt%) and the rapid deactivation of the catalyst. Addition of modifiers and promoters increases the performance of the catalyst and improved selectivities, rates and catalyst lifetime are obtained.

Typically π-electron metal promoters such as Bi, Pb and Sn are added to the catalyst [233, 237, 240]. Little is known about their participation in the mechanism. Nevertheless, many speculative models can be found in literature, and geometric blocking, reduction of the size of the active site ("ensemble effect", reducing C-C bond cleavage on the big active sites), creation of a new active center for oxygen adsorption (bifunctional catalysis), complex formation and corrosion prevention have been suggested. Unfortunately, these (non-noble) promoters easily leach out under acidic and oxidizing conditions.

Some amines were also shown to improve the selectivity and rates in partial oxidation of L-sorbose [241].

Deactivation

Little is known about the causes of deactivation on metallic Pd and Pt. Deactivation is a complex phenomenon which depends on many factors such as the nature of the catalyst, the solvent and the reaction conditions [233, 242]. Deactivation occurs by poisoning of the metal surface and by corrosion of the noble metal and the promoters [233, 243]. Also irreversible deactivation of the catalyst by restructuring and leaching, and by crystallite growth (Ostwald ripening) has been reported [236].

Poisoning by strongly adsorbed organic products and CO usually is reversible. CO can be removed by oxidation with oxygen and carboxylic acids are removed at higher pH by deprotonation.

"Oxygen poisoning" ("over-oxidation") is a decrease in catalytic activity when too much oxygen is adsorbed and dehydrogenation is hindered (Equation 5) [233, 243, 244]. There is a balance between over-oxidation of the surface and over-oxidation of the molecule leading to degradation [242]. Over-oxidation may also lead to metal corrosion.

Regeneration of the catalyst involves washing, treatment with hydrogen and oxygen, and combinations thereof.

Recently, gold catalysts were shown to have very high stability and little sensitivity to over-oxidation and self-poisoning, along with higher selectivity in the partial oxidation of diols than that of Pd or Pt [245, 246].

Solvents

Partial oxidation has been performed in many different solvent systems. Water is almost exclusively used, for safety reasons. Water is especially suitable for the transformation of carbohydrates. Oxygen solubility in water is low

(12.6 mmol l^{-1} at 25 °C) [229] which conditions also help to minimize over-oxidation of Pt and Pd. Note that liquid phase oxidations are often mass transport limited [236], which is advantageous to minimize over-oxidation. Organic solvents offer tenfold higher oxygen solubility and are suitable for the oxidation of apolar alcohols.

Other systems proposed include the creation of an aqueous emulsion with apolar alcohols by vigorous stirring, use of surfactants to solubilize apolar alcohols in water [247], multiphase systems with organic and aqueous phases [248], and sc fluids.

Heyns [249, 250], Sneeden *et al.* [251], Karrer [252], and Dalton [253] have investigated the oxidation of various alcohols (including steroids) over Pt and Pt/C in aqueous and organic solvents (*n*-heptane, acetic acid, benzene, dioxane, ethyl acetate). Oxidation of non-polar, water insoluble alcohols proceeds well in organic solvents. Organic solvents reduce the formation of acid via hydration of the aldehyde. Unfortunately, their application is limited because organic solvents are flammable under oxidative conditions.

Akihisa and Sakamaki [254, 255] have studied the oxidation of cholesterol to the corresponding ketone over prereduced Pt in ethyl acetate and *tert*-butyl alcohol. The reaction was performed at ambient pressure and also at 20–25 bar oxygen. It is clear that such harsh conditions are restricted to the laboratory.

In organic solvents the reaction must be run at low concentrations of alcohol (<10%) to avoid clumping of the catalyst by the water produced. Higher aldehyde selectivity can be obtained when the co-product water is removed continuously by azeotropic distillation [256].

Only a few processes in sc fluids have been established for the oxidation of alcohols (methanol [144, 145], ethanol [143]) ("Oxidation" on page 16), and none of them is designed for the partial oxidation of alcohols over noble metals.

Fulton *et al.* [257] have studied the solubility of alcohols in $scCO_2$ at 200–400 bar and 40 °C. Alcohol aggregates in $scCO_2$ via intermolecular hydrogen bonds.

1.5 Scope of the Thesis

The scope of this thesis was to extend the application range of sc fluids in heterogeneous catalysis. Intrigued by the striking opportunities for sc fluids in reaction engineering, three classes of reactions have been chosen for investigation: amination of alcohols, epoxidation of propylene and partial oxidation of alcohols.

Amination of bifunctional alcohols in ammonia has been shown in our laboratory to be an efficient method for the one-pot synthesis of diamines. From those previous results it was not clear whether the higher reactivity of secondary hydroxyl groups or their position (1,4) caused the excellent diamine selectivity in amination of cyclohexane-1,4-diol. My study assessed the amination of pentane-2,4-diol and cyclohexane-1,3-diol, which reactants possess secondary hydroxyl groups in β-positions.

Until very recently partial oxidation in sc fluids was barely investigated. Sc fluids, however, meet particularly well the requirements of oxidations [258]: heat removal is more efficient compared to gas phase operation and mass transfer resistances are reduced compared to the liquid phase. Two substantially different and technically important partial oxidation reactions have been selected for a detailed investigation of the potential of sc fluids.

Among the various propositions found in literature for epoxidation of propylene, epoxidation with *in situ* generated hydrogen peroxide is a promising method. Our aim was to study the time-on-stream behavior of this reaction in the continuous high-pressure fixed-bed reactor. The effect of diluants CO_2 and N_2 on the reaction were compared and the effect of $scCO_2$ was investigated.

The partial oxidation of non-polar alcohols has been chosen as a third model reaction. The feasibility of this process in $scCO_2$ instead of the conventional organic solvents was studied. We were particularly interested in the interplay of kinetics and the phases present under reaction conditions.

Chapter 2

Experimental

This chapter describes the experimental setup used and reports general features concerning the analysis methods. Specific descriptions of the experiments are given in the pertinent chapters.

2.1 Catalytic Reactions

2.1.1 Amination

Amination of alcohols was performed on the same system as previously used by Fischer [81] (Figure 2-1). This apparatus consists of four units: dosing of the gases (hydrogen and nitrogen) and liquids (ammonia and alcohol), the reactor and the separation unit for the separation of liquid and gases.

The system included both a main and a secondary gas feed section. The main gas feed section allowed accurate control of the hydrogen flow rate in the range 0–16 Nl h^{-1}. It consisted of a bulkhead union to refill the connecting line from a hydrogen cylinder, a stainless steel stop valve, a 7 μm stainless steel filter, a manometer (0–250 bar) with insulating valve to measure the pressure upstream of the flow meter and a high pressure mass flow controller to adjust the hydrogen flow rate. The second gas feed section was used for nitrogen. It comprised a 1/8" bulkhead union to refill the unit from a gas cylinder, a stainless steel stop valve and a check valve (1 psi).

Alcohol and pressurized liquid ammonia were pumped by two separate syringe pumps (ISCO 500D) to the reactor. The pump has a capacity of 507 ml, and provides a flow rate of 1.0–170 ml min^{-1} at a maximum pressure of 259 bar.

The reactor was a high pressure tube (Inconel®-718) of 38 ml volume manufactured by the in-house engineers. The maximal working pressure of the reactor was 200 bar at 300 °C. The reactor was protected against overpressure by a nickel rupture disc with 200 bar release pressure. A more detailed description of the reactor including the layout is given in Fischer [81]. The temperature in the reaction zone was measured by a thermocouple located in the center of the tube. The reactor heating was regulated by a PID cascade controller. The heating system also comprised a preheater upstream of the reactor. The reaction mixture passed through the reactor in a down flow fashion. The catalyst was situated in the center of the reactor and the remaining free volume was filled with glass pellets.

The reactor was connected to a cooler section, a 100 cm long 1/8" tube attached to the inlet of the separator.

Product separation was carried out in a 0.36 ml high pressure gas/liquid separator with a maximum operating pressure of 200 bar, maximum operating temperature of 50 °C and a total capacity of 35 ml.

The gas outlet line included a 7 μm filter, and a manual back pressure regulator (Tescom, 4000 psi). This back pressure regulator set the total pressure in the system. The liquid outlet contained a 15 μm filter, a stop valve and a needle valve. The liquid phase was collected manually from the needle valve for analysis by GC.

2.1.2 Epoxidation of Propylene

For the epoxidation of propylene (Figure 2-2) and the partial oxidation of alcohols (Figure 2-3) another high-pressure system was set up. The reactor design and its heating was the same as in the amination. The peripheral system was modularly designed.

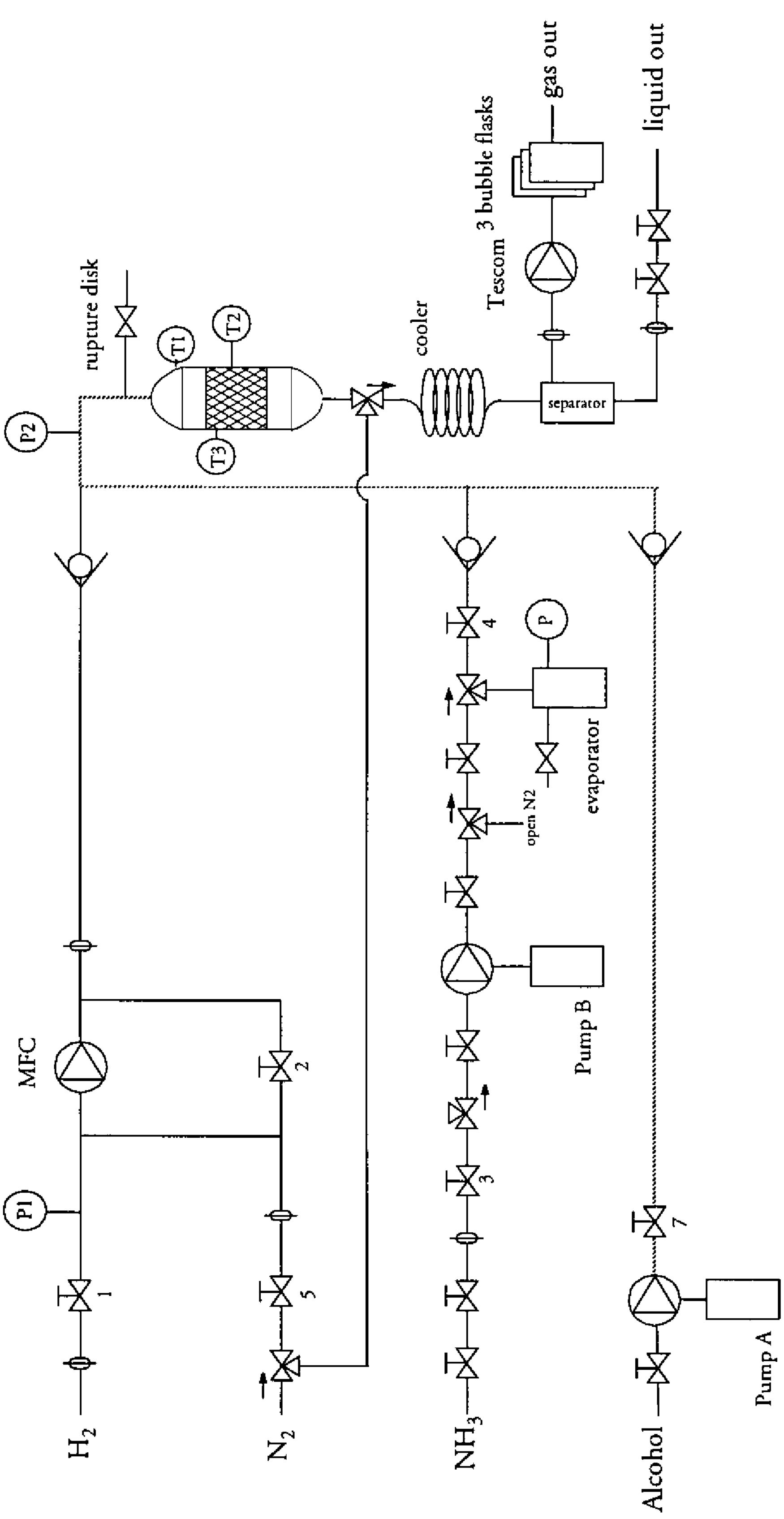


Fig. 2-1: Flow scheme for the amination

In the epoxidation of propylene up to five separate reaction feed streams and one stream for the inertization by nitrogen were used. Carbon dioxide and propylene were pressurized by two compressors (PM101, NWA, D-Lörrach). To alleviate the pressure fluctuations of the compressors, the feed streams were partially depressurized to a set feed pressure. Propylene was then dosed at constant flowrate by a Gilson M305 piston pump with 5SC pump head (range of flowrates 0.010–5 ml min^{-1}). Carbon dioxide could be substituted by nitrogen (max. 200 bar, from the cylinder).

The methanol-water mixture was dosed by another Gilson M305 piston pump equipped with a 10SC pump head (flowrate range 0.050–10 ml min^{-1}).

Hydrogen was pressurized by a compressor (CU 105, NWA). Hydrogen and oxygen (max. 200 bar, from the cylinder) were fed to the reactor by 6-port-valves dosing 0.05 ml pulses at constant frequency from the high pressure feed side to the reactor.

Oxygen and carbon dioxide (or nitrogen) feed were premixed on one side, and the other feed streams on the other side. Only thereafter the actual reaction mixture was formed.

The pressures upstream and downstream of the reactor were monitored and adjusted with a CO_2/N_2 pressure regulator in front of the reactor.

The product stream was depressurized in two stages (PE103, NWA). The two valves of the PE103 module also served as flow regulator. The liquid effluent could be sampled or collected in a bottle. The flowrate of the gas was measured with a flowmeter. The gas was optionally analyzed on-line by GC and vented off.

For safety reasons several precautionary measures were taken: the system was equipped with two flame backstrike valves before mixing the two reactant streams. The system was set to shut down automatically in case of large pressure fluctuations in the reactor (usually ± 3 bar). Fluctuations could be caused by thermal runaway of the reaction (sudden pressure and temperature rise), by irregularities in the dosing of the feed or in the separation and venting of the products, or even by blocking of the catalyst bed. This automatic shutdown prevented possible damage to the system and it also avoided kinetic measurements under non-stable conditions. The system was placed behind a metal shield to protect the operator in case of an explosion.

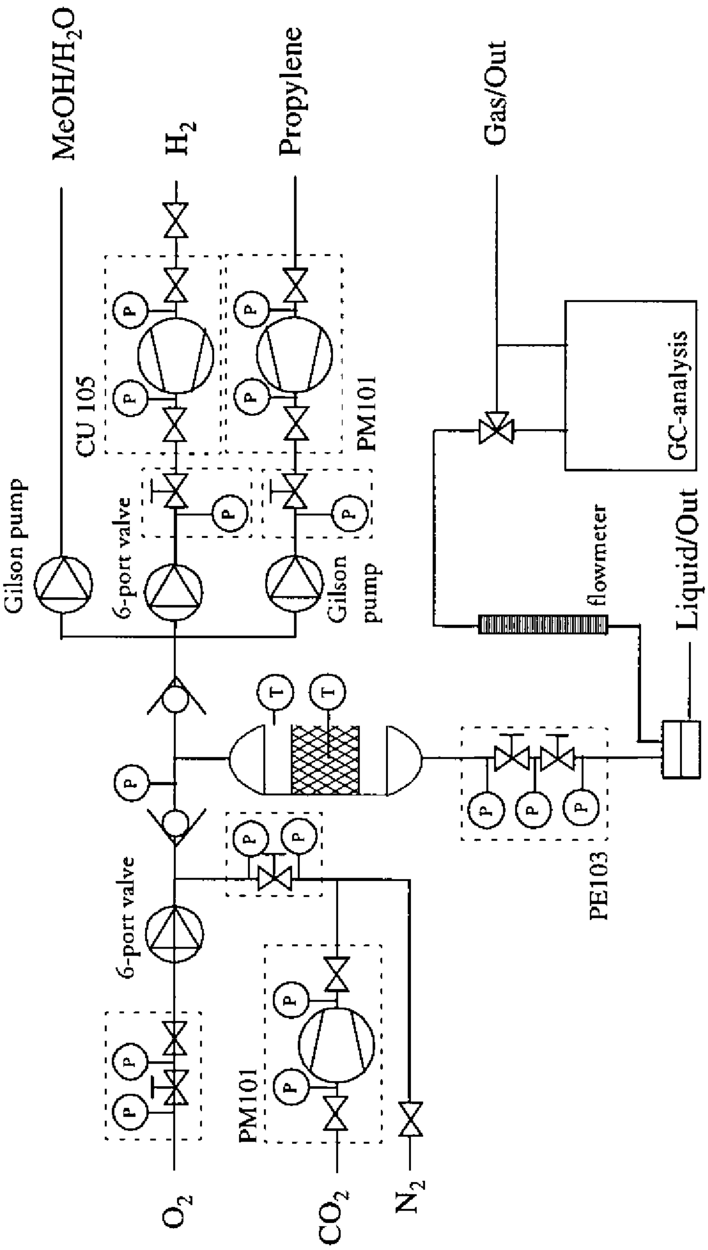


Fig. 2-2: System for the epoxidation of propylene

2.1.3 Partial Oxidation of Alcohols

For the partial oxidation of alcohols the system previously employed for propylene epoxidation was simplified (Figure 2-3). Liquid samples were collected and analyzed by GC.

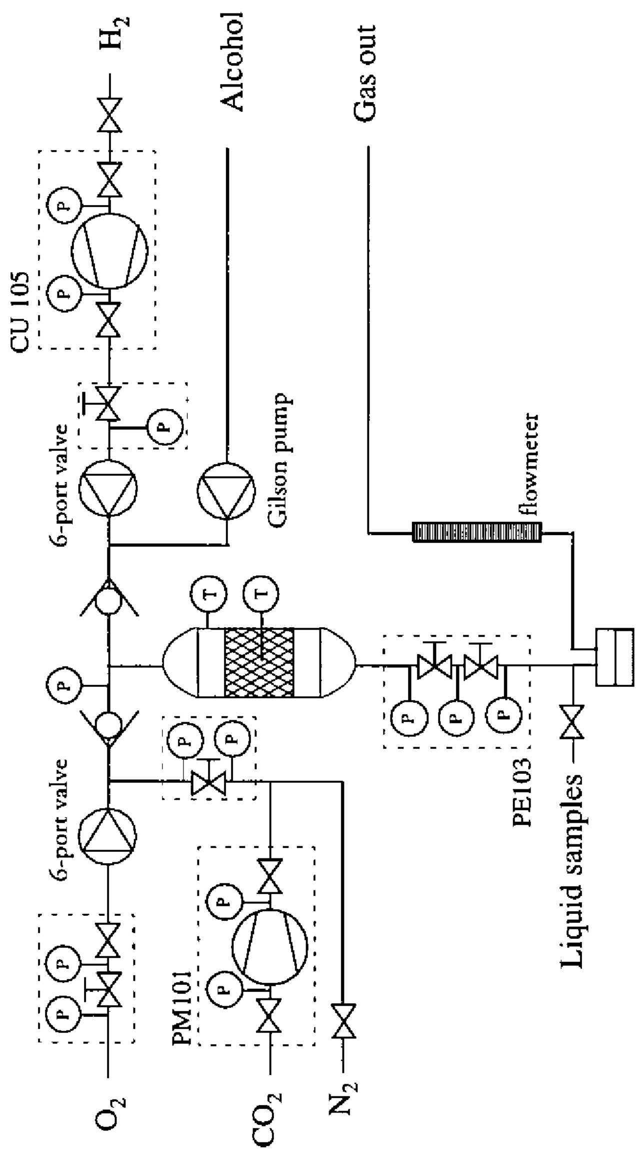


Fig. 2-3: System for the partial oxidation of alcohols

2.2 Analysis

The catalysts were characterized by chemisorption, physisorption, TA-MS, TA-FTIR, TEM and XRD.

For the qualitative and quantitative analysis of the reaction products GC-MS and GC were used. The temperature profiles and corresponding retention times of components detected in the GC analysis are given in Table 2-1.

2.2.1 Amination

Sampling and analysis were performed analogous to the method described by Fischer [81]. The same analytical equipment was used: a HP 5890 gas chromatograph equipped with an autosampler (HP 7673A), an integrator (HP 3369) and a FID detector.

A sample amount of 0.5 µl was injected into the purged packed injector at 150 °C. A HP-1701 capillary column (length 30 m, inner diameter 0.53 mm, film thickness 1.0 µm, 1.5 ml min^{-1} He) was used to separate the components.

2.2.2 Epoxidation of Propylene

Liquid and gaseous products formed in the reaction. The gaseous effluent of the reaction was analyzed on-line on a HP 5890 gas chromatograph. Samples of 1 ml were injected into the HP SPB-1 fused silica capillary column (60 m). The separated components were detected with a TCD detector (200 °C).

Products in the liquid phase were identified by GC-MS and by GC with authentic samples. Samples (0.1 µl) of the liquid product were injected manually (150 °C) into the GC.

2.2.3 Partial Oxidation of Alcohols

Liquid samples were collected, diluted with propanol and analyzed by GC. The HP 5890 gas chromatograph was equipped with a cool on-column injector to prevent further reactions in the injector. An amount of 0.5 µl was injected into the HP-FFAP column (length 30 m, inner diameter 0.53 mm, film thickness 1.0 μm, 20 kPa He). The separated components were detected with a FID detector.

The reliability of the analysis was verified with an internal standard (pentadecane/undecane).

Table 2-1: Temperature profiles and retention times of the GC method used.

Reaction	Reactant	Temperature Profile	Compound	Retention time (min)
Amination	Cyclohexane-1,3-diol	80 °C, 10 min;	1,3-diaminocyclohexane	21.2
		10 °C min^{-1} to 140 °C;	3-aminocyclohexanol	24.2
		140 °C, 15 min;	cyclohexane-1,3-diol	28.5
		10 °C min^{-1} to 250 °C;		
		250 °C, 15 min.		
	Pentane-2,4-diol	80 °C, 10 min;	2,4-diaminopentane	14.6
		10 °C min^{-1} to 140 °C;	4-amino-2-pentanol	19.1
		140 °C, 15 min;	pentane-2,4-diol	23.5
		10 °C min^{-1} to 250 °C;		
		250 °C, 15 min.		
Epoxidation	Propylene	40 °C, 2.7 min;	Carbon dioxide	4.8
		20 °C min^{-1} to 100 °C;	Water	5.4
		100 °C, 5 min;	Propylene	5.6
		20 °C min^{-1} to 110 °C;	Methanol	7.0
		110 °C, 10 min;	Methyl Formate	8.6
		20 °C min^{-1} to 180 °C.	Acrolein	11.0
			Propylene Oxide	12.2

Table 2-1 : Temperature profiles and retention times of the GC method used.

Reaction	Reactant	Temperature Profile	Compound	Retention time (min)
Partial Oxidation	Octan-2-ol	50 °C; 5 °C min^{-1} to 115 °C; 40 °C min^{-1} to 230 °C; 230 °C, 2 min.	Octan-2-one Octan-2-ol	8.5 11.9
	1-Phenylethanol	50 °C; 5 °C min^{-1} to 115 °C; 40 °C min^{-1} to 230 °C; 230 °C, 2 min.	Acetophenone 1-Phenylethanol	15.3 16.6
	Octan-1-ol	50 °C; 5 °C min^{-1} to 115 °C; 115 °C, 5 min; 40 °C min^{-1} to 230 °C; 230 °C, 10 min.	Octanal Octan-1-ol Octanoic acid Octyl octanoate	8.4 14.5 17.7 23.0
	Benzyl alcohol	50 °C; 5 °C min^{-1} to 115 °C; 115 °C, 5 min; 40 °C min^{-1} to 230 °C; 230 °C, 10 min.	Benzaldehyde Benzyl alcohol Benzoic acid Benzyl benzoate	14.2 16.9 20.8 23.6
	p-Anisyl alcohol	50 °C; 5 °C min^{-1} to 115 °C; 40 °C min^{-1} to 230 °C; 230 °C, 2 min.	p-Anisaldehyde p-Anisyl alcohol	18.0 19.4
	Cinnamyl alcohol	50 °C; 5 °C min^{-1} to 115 °C; 115 °C, 5 min; 40 °C min^{-1} to 230 °C; 230 °C, 10 min.	Cinnamaldeyde Cinnamyl alcohol	18.1 19.4

Chapter 3

Amination Reactions

Cobalt-Catalyzed Amination of Cyclohexane-1,3-diol and Pentane-2,4-diol in Supercritical Ammonia

3.1 Abstract

The one-step procedure of amination of bifunctional secondary alcohols to diamines was investigated in a continuous fixed bed reactor. Application of $scNH_3$ as solvent and reactant suppressed the catalyst deactivation and improved the selectivities to aminoalcohol intermediates, whereas the selectivities to diamines remained poor (8–10%). The main reason for the poor diamine selectivity of 1,3-dihydroxy compounds is the hydrogen atom at the C-atom between the hydroxy bearing carbons. This hydrogen atom enables water elimination leading to undesired monofunctional products via allylic alcohol intermediate. This contrasts the behaviour of 1,4-dihydroxy compounds affording high aminol and diamine selectivities under similar conditions. Amination of bifunctional secondary alcohols with ammonia was found to be faster, but not more selective than that of primary diols.

3.2 Introduction

Heterogeneously catalyzed amination of alcohols is an economically important pathway for the manufacture of various aliphatic and aromatic amines [190, 191, 259-262] (Figure 3-1). However, yields and selectivities are rather low in the synthesis of aliphatic diamines from the corresponding diols and ammonia, and only alternative routes are applied for the production of these important intermediates.

Recent studies of our group [80, 83, 84, 263] have shown that $scNH_3$ can advantageously be used as a solvent and reactant in the amination of simple alkanediols to diamines. The amination selectivity increases remarkably in the narrow pressure range of subcritical-supercritical transition of the medium. The selectivity improvement is attributed to the higher concentration of ammonia on the catalyst surface which favors the amination with ammonia and suppresses undesired elimination and dimerization type side reactions. For the amination of a series of diols unsupported Co stabilized with 5 wt% Fe was found to be an efficient catalyst.

These studies indicated that the structure of diol is crucial for obtaining good yield. Substitution of the H atoms at the α-C atom by methyl groups in propane-1,3-diol increases the diamine yield because elimination of water affording a reactive allylic alcohol intermediate becomes impossible [80, 263].

The highest yield (67%) was achieved in the amination of cyclohexane-1,4-diol to 1,4-diaminocyclohexane in $scNH_3$, and the amount of by-products (beside the useful aminoalcohol intermediate) was less than 5% [84]. It is not clear yet whether the outstanding amination selectivity has to be attributed to (i) the change from 1,3- to 1,4 positions of the OH functions which allows only the formation of the homoallylic alcohol by-product, or (ii) the higher reactivity of secondary alcohols in amination reactions compared to that of primary alcohols [264, 265]. In order to clarify the role of reactant structure, we extended our studies to the amination of cyclohexane-1,3-diol and pentane-2,4-diol in $scNH_3$, using the same Co-Fe catalyst [84] and similar reaction conditions.

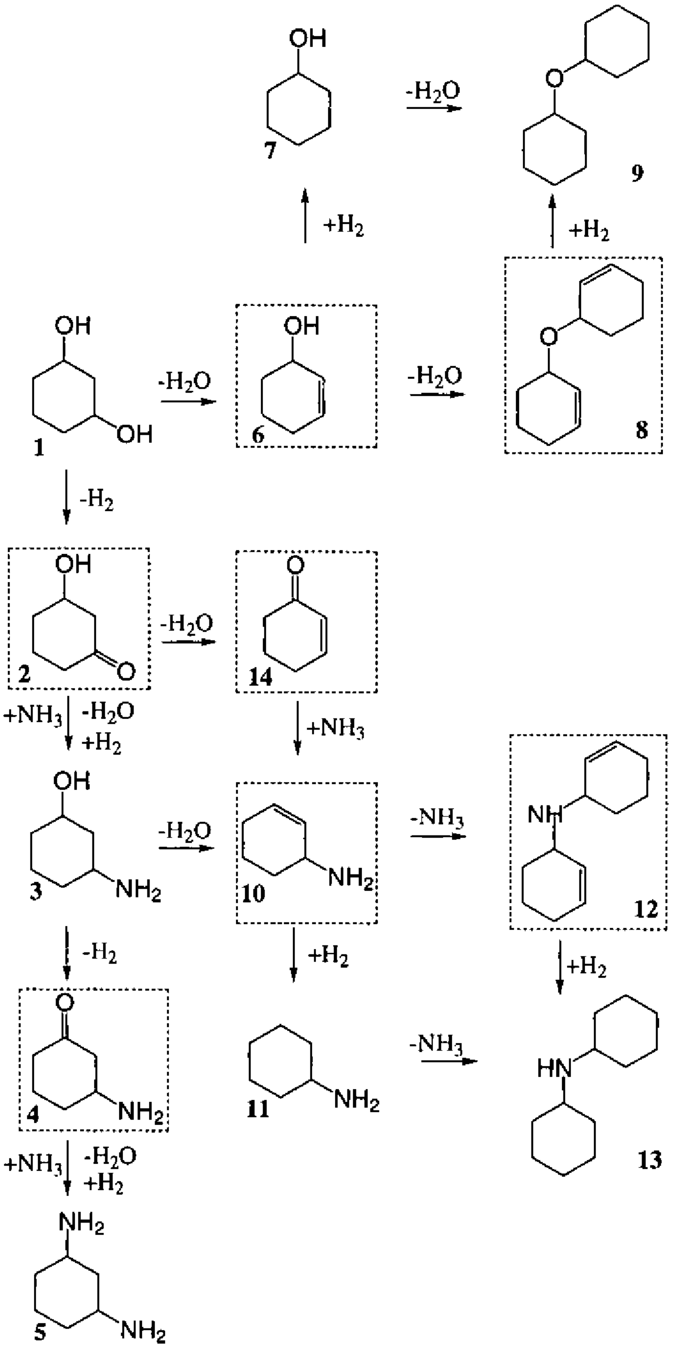


Fig. 3-1: Amination of cyclohexane-1,3-diol to 1,3-cyclohexyldiamine via 3-aminocyclohexanol. Intermediates in dashed boxes were not identified.

3.3 Experimental

Cyclohexane-1,3-diol (98%, Aldrich), pentane-2,4-diol (99%, Fluka), ammonia (99.998%, Pan-Gas), hydrogen (99.999%, Pan-Gas) and nitrogen (99.995%, Pan-Gas) were used without further purification.

The Co-Fe catalyst was prepared by coprecipitation [80]. Aqueous solutions of cobalt nitrate and iron nitrate, and ammonium carbonate were mixed at room temperature and the pH was set to 7. The precipitate was filtered off, washed carefully with water, dried at 120 °C in vacuum and calcined at 400 °C for 4 h. Before the experiments, the catalyst was activated in the reactor in hydrogen (30 ml min^{-1}) for 4 h at 330 °C. Characterization of the catalyst by N_2-physisorption, XRD, XPS, TPR, ICP-AES, NH_3-chemisorption and DRIFT spectroscopic measurements is described elsewhere [80].

Amination experiments were carried out isothermally in a tubular flow reactor with an inner diameter of 13 mm and 38 ml volume. The reactor was loaded with crushed and sieved catalyst particles of 150 to 400 µm. The solution of cyclohexane-1,3-diol in ammonia, or liquid ammonia and pentane-2,4-diol were dosed to the reactor by ISCO D500 syringe pumps. The pressure in the reaction system was set by a TESCOM back pressure regulator. Details of the reaction conditions are indicated in the Figure captions. The liquid product was separated from the gas and analyzed by an HP5890 gas chromatograph (HP 1701 column, FID-Detector). The products were identified by GC-MS analysis.

3.4 Results

Preliminary experiments indicated that even a rather high ammonia:alcohol molar ratio of 30–60 could not eliminate dimerization and oligomerization of the intermediate and product amines. Hydrogen in low concentration (NH_3:H_2 60:1) was applied to prevent the undesired dehydrogenation reactions (formation of nitriles and carbonaceous deposit). A comparatively short contact time (5.55 g h mol^{-1}) was chosen in order to reduce the contribution of consecutive side reactions.

The reactant diols and the product amines are highly soluble in liquid ammonia at room temperature. It was shown for propane-1,3-diol [80] that the dilute reaction mixture formed a homogeneous fluid at or above the critical pressure (114.8 bar) and temperature (132.4 °C) of ammonia.

Amination of pentane-2,4-diol was carried out in the temperature range 165–210 °C and pressure range 53–142 bar. Selectivities to diamine were around 10% at best (see Table 3-1) but these values decreased further after 3–4 h time-on-stream. GC analysis indicated the formation of numerous high molecular weight by-products. It is likely that the unstable performance of the Co-Fe catalyst is due to oligomer formation and site blocking. For comparison, no catalyst deactivation was observed with the same catalyst even after several days in the amination of propane-1,3-diol under otherwise similar conditions [80].

Table 3-1: Amination of various dihydroxy compounds: the best selectivities achieved at medium conversions under different conditions. (Molar ratio in the feed: diol:H_2:NH_3 1:2:60)

reactant diol	catalyst	τ [a]	p (bar)	T (°C)	Conv. (%)	S_{aminol} (%)	$S_{diamine}$ (%)	S_{sum} (%) [b]
pentane-2,4-diol	Co-Fe	11.1	135	180	53	31	10	41
pentane-2,4-diol	Co-Fe	11.1	135	186	85	13	9	22
cyclohexane-1,3-diol	Co-Fe	5.55	135	170	56	39	8	47
cyclohexane-1,3-diol	Co-Fe	5.55	106	170	21	12	4	16
cyclohexane-1,3-diol	Co-Fe	5.55	53	170	79	16	5	17
propane-1,3-diol [c]	Ni	11.1	135	189	59	-	-	26
propane-1,3-diol [d]	Co-Fe	16.6	135	195	84	30	18	48
2,2-dimethylpropane-1,3-diol [c]	Ni	11.1	135	195	40	32	53	85
2,2-dimethylpropane-1,3-diol [c]	Ni	11.1	135	210	75	7	70	77
cyclohexane-1,4-diol [e]	Co-Fe	11.1	135	165	76	42	55	97

[a] space time (g h mol^{-1})

[b] cumulative selectivity

[c] from Ref [83]

[d] from Ref [263]

[e] from Ref [84]

When the amination of cyclohexane-1,3-diol was carried out at 135 bar and in the temperature range 170–200 °C, lower temperatures led to lower diol conversion, higher aminol selectivity and less by-products. Accordingly, catalyst stability and the influence of pressure was investigated at 170 °C. As it is illustrated in Figure 3-2, the performance of the 95 wt% Co - 5 wt% Fe catalyst varied significantly with the total pressure. At medium pressures (e.g. 53 bar, Figure 3-2a), in the presence of liquid and gas (vapor) phases, the catalyst deactivated rapidly and steady state conditions could not be reached within 8 h. Besides, the amination selectivity was poor, at best (3.5 h) only 16% to the aminoalcohol intermediate and 5% to diamine (Table 3-1). Working in scNH$_3$ (e.g. at 135 bar, Figure 3-2b) the performance of the bimetallic catalyst stabilized within a few hours and the selectivity to aminol increased above 30% (Table 3-1).

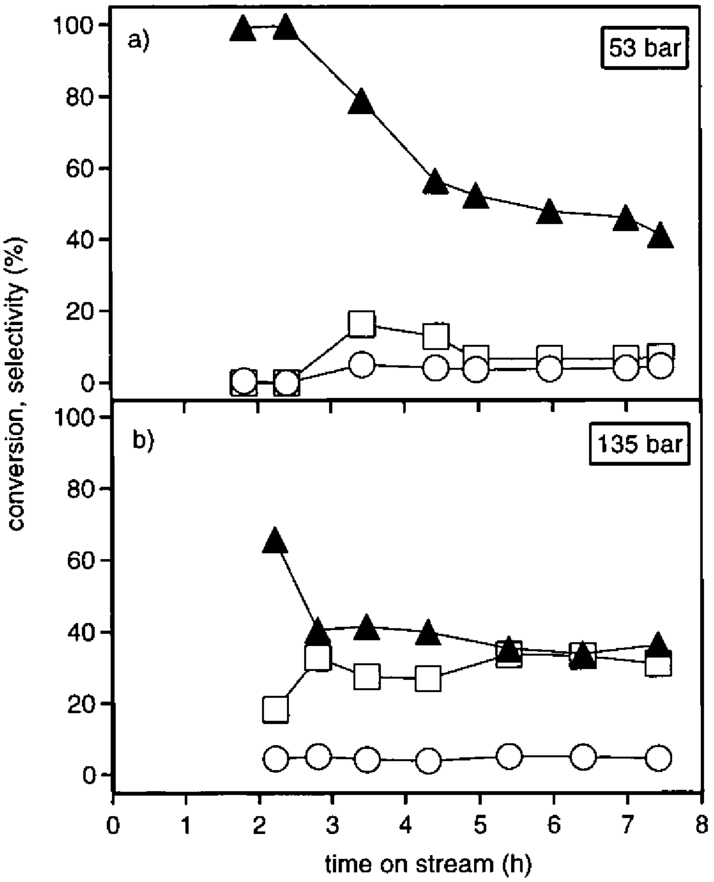


Fig. 3-2: Effect of pressure and time-on-stream on the performance of a 95 wt% Co - 5 wt% Fe catalyst in the amination of cyclohexane-1,3-diol. Conditions: 53 bar (a) or 135 bar (b), 170 °C, space time 5.55 g h mol^{-1}, molar ratio of alcohol:H$_2$:NH$_3$ 1:2:60. ▲ conversion, □ selectivity to aminol, ○ selectivity to diamine

Figure 3-1 lists some products of the amination of cyclohexane-1,3-diol identified by GC-MS. The middle pathway represents the target reaction from the diol (**1**) via the aminol (**3**) to the diamine (**5**). The intermediate carbonyl compounds (**2** and **4**) formed by dehydrogenation could not be detected, but it is assumed that their formation represents the rate determining steps [190, 266]. Major side reactions are the dehydration of **1** to an allylic alcohol **6** or the trimer **14**. The reactive allylic alcohol is rapidly transferred to cyclohexanol (**7**) and an ether (**8**, **9**) via dehydration. Similarly, the key intermediate aminoalcohol (**3**) can afford cyclohexyl- and dicyclohexylamine (**11**, **12**, **13**) by dehydration and hydrogenation reactions. The selectivities to the undesired products **7** and **11** were considerably (by 60 rel.%) smaller under sc conditions (135 bar) than at medium pressure (53 bar). Note that dimerization and oligomerization of the bifunctional reactant and products **1** - **5** are not shown in Figure 3-1.

3.5 Discussion

The diamine selectivities obtained in the amination of pentane-2,4-diol and cyclohexane-1,3-diol are very low. This observation corroborates the former reports that direct amination of diols to diamines is difficult and stepwise amination is more promising [267-269].

Higher pressures are favorable for the amination of cyclohexane-1,3-diol (Figure 3-2). The cumulative selectivity to aminol and diamine is higher, and stabilization of the catalyst is achieved more readily, likely due to suppressed blocking of active sites by oligomers. At pressures far below the critical pressure ($P_c(NH_3)$ = 113.5 bar) the reaction mixture consists of two phases: a liquid phase rich in non-volatile alkanediol and products, and a gas phase containing predominantly ammonia and hydrogen. $ScNH_3$ is an excellent solvent for amines and alcohols due to extended hydrogen bonding [270]. In the near critical and sc region the reaction mixture forms a single homogeneous phase with significantly enhanced mass transport due to the elimination of phase transfer resistance, and to the higher diffusion coefficients and lower viscosity, compared to the situation in the liquid phase. Chemical equilibria and kinetics may also change substantially with pressure, but this effect on every particular reaction is very complex [12, 18, 20, 64].

We assume that the concentration of ammonia at the catalyst surface in presence of the homogeneous sc phase is higher than at subcritical conditions, which favors the desired reactions **1** → **5** and suppresses oligomerization and elimination (degradation) type side reactions (Figure 3-1).

The best cumulative selectivities to aminol and diamine, achieved in the amination of the secondary alcohols pentane-2,4-diol and cyclohexane-1,3-diol, are 41 and 47%, respectively. When neglecting the poor stability of Co-Fe catalyst in the former reaction, this selectivity range is comparable to the best value (48%) achieved in the amination of the primary alcohol propane-1,3-diol, under similar conditions (Table 3-1). The secondary alcohols are significantly more reactive, as indicated by the lower reaction temperature required to achieve comparable conversions. However, this structural difference favors the side reactions even more and the final diamine selectivities are only 8–10%, about half of that achieved in the amination of propane-1,3-diol (18%). Consequently, the outstanding selectivities obtained in the amination of cyclohexane-1,4-diol (Table 3-1) should be attributed to the 1,4-position of the OH groups, rather than the higher reactivity of secondary alcohols.

3.6 Conclusions

Direct amination of pentane-2,4-diol and cyclohexane-1,3-diol over a 95% Co - 5% Fe catalyst revealed that applying $scNH_3$ as solvent and reactant can minimize catalyst deactivation by suppressing dimerization and oligomerization type side reactions, and improve significantly the selectivity to the intermediate aminoalcohol. A comparison of the amination of various linear and cyclic, primary and secondary dihydroxy compounds in $scNH_3$ [80, 82-84] suggests that good diamine selectivities can be obtained in one step procedure only, when the formation of a reactive allylic alcohol by-product by elimination of water is unfavorable or even impossible.

Chapter 4

Continuous Epoxidation of Propylene with Oxygen and Hydrogen on a Pd-Pt/TS-1 Catalyst

4.1 Abstract

Propylene epoxidation over a Pd-Pt/TS-1 catalyst with *in situ* formed hydrogen peroxide was carried out in a fixed bed reactor under high pressure conditions. The continuous operation allowed the study of catalyst deactivation and changes in product distribution with time-on-stream. The initial propylene oxide selectivity was very high, 99% at 3.5% conversion, but the catalyst deactivated rapidly with time-on-stream and successively the formation of methyl formate became the prevalent reaction. Using carbon dioxide, instead of nitrogen, had a beneficial effect on the formation of propylene oxide, and even higher yields were obtained when increasing the pressure from 50–120 bar (sc fluid phase). Thermal analysis (TA-MS and TA-FTIR) indicated that catalyst regeneration requires oxidation at elevated temperature; washing with an organic solvent is less efficient. The serious catalyst deactivation and the striking shift in the selectivity pattern of the catalyst is traced to competing alcohol oxidation on platinum metal.

4.2 Introduction

A considerable effort has been made in the past decades to develop heterogeneous catalytic processes for the economic production of propylene oxide from propylene [193, 212]. The two main commercial epoxidation routes are the chlorohydrin and the hydroperoxide processes, both in the liquid phase. Examples on oxidation with hydroperoxides include the Halcon-ARCO and Shell processes using organic hydroperoxides [205, 206], and the Enichem technology based on TS-1 and hydrogen peroxide [208-210]. For the latter process the best selectivity to propylene oxide (97% at 90% hydrogen peroxide conversion) was achieved by Clerici *et al.* after hydrophobization of the Ti-substituted molecular sieve [210].

Direct oxidation in the gas phase with molecular oxygen is catalyzed by silver supported on carbonates and titanates (ARCO Chemical Technology [197, 198]), and gold on titania [201, 271-275]. The latter catalyst is highly selective (>99%) and up to 9.6% yield to propylene oxide has been attained [203].

Epoxidation of propylene by Pd-Pt/TS-1 is a particularly interesting approach as the *in situ* formation of hydrogen peroxide from a mixture of oxygen and hydrogen over the noble metals and epoxidation of propylene by TS-1 are combined in the same catalyst [207, 212, 216-220, 222, 224, 225]. In a comparative study TS-1 alone afforded 39% propylene oxide yield (based on propylene) using hydrogen peroxide as oxidant, while no epoxidation occurred when a mixture of hydrogen and oxygen was employed [224]. With 1 wt% Pd - 0.1 wt% Pt/TS-1 and a hydrogen/oxygen mixture 5.3% yield has been obtained under the same conditions.

During reaction hydrogen peroxide, formed on the surface of the noble metal, has to diffuse to the isolated Ti sites in the TS-1 matrix. Obviously, proper design and synthesis of the multicomponent catalyst is crucial for efficient cooperation between the redox metal sites and the Lewis acidic Ti sites. A previous study [225] has shown that catalyst preparation by simple impregnation of TS-1 and autoreduction of the $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$ precursors in nitrogen at 150 °C is a suitable technique. Reduction with hydrogen or calcination at higher temperatures are detrimental leading to agglomeration of Pd on the external surface of TS-1. At best, 11.7% propylene oxide yield with 46% selectivity has been achieved with a 1 wt% Pd - 0.02 wt% Pt/TS-1 catalyst [225]. When the autoclave was operated semi-continuously, the propylene oxide selectivity increased up to 60% due to the lower propylene concentration in the reactor and the suppressed formation of propane [223].

The propylene conversion could be further improved by addition of NaBr or polyfluorinated hydrocarbons in small amounts, but the selectivity was barely influenced. Interestingly, higher amount of polyfluorinated hydrocarbons had the opposite effect and decreased the propylene oxide yield.

The aim of our work was to study the epoxidation of propylene and the nature of side reactions in a continuous fixed bed reactor under high pressure conditions. The catalyst chosen corresponds to the best performing material from Hölderich *et al.* [224, 225], and the feed stream composition was set to mimic the initial composition in their batch experiments.

4.3 Experimental

4.3.1 Materials

The catalyst 1 wt% Pt - 0.02 wt% Pd/TS-1 was prepared according to a former procedure [224, 225]. 4 g TS-1 (National Chemical Laboratory, Pune, India, calcined, Si/Ti: 40) was suspended in 16 ml distilled water. The aqueous solutions (1 ml) of the proper amounts of $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$ (both from Alfa Aesar) were added and the slurry was stirred at 50 °C for one day. The solvent was then evaporated at 50 °C in vacuum and the catalyst dried at 60 °C for one day. Prior to use the catalyst was autoreduced in argon at 150 °C for 2 h.

Propylene (99.8%), hydrogen (99.999%), oxygen (99.95%), carbon dioxide (99.5%), methanol (99.8%) and deionized water were used without further purification.

4.3.2 Catalytic Epoxidation

Epoxidation experiments were carried out isothermally in a tubular flow reactor with an inner diameter of 13 mm and 38 ml volume. Methanol and water (3:1 by weight) were dosed by a Gilson 305 piston pump. Propylene was compressed to 30 bar and fed to the system by a pump. Hydrogen and oxygen were supplied to the reactor using a 6 port valve dosing 0.05 ml pulses at high pressure and constant frequency. The constant pressure in the system was maintained by a back-pressure regulator with nitrogen. The total gas flow was controlled at the vent.

The feed composition was chosen to be outside the flammable (and explosive) range. The reactor system (Figure 4-1) was specially designed for safety precautions (robust design, mixing of reactants in correct order, flame stop valves, pressure switch-off, on-line analysis for monitoring). Carbon dioxide was used as co-solvent for high pressure experiments due to its high heat capacity and relative inertness.

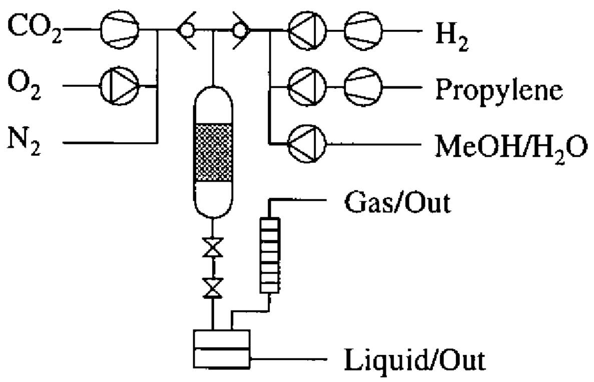


Fig. 4-1: Apparatus and experimental setup

Standard reaction conditions were 50 bar, 43 °C, and a flow consisting of nitrogen (33.3 mol%), methanol (23 mol%), propylene (18.7 mol%), water (13.2 mol%), oxygen (7.2 mol%), and hydrogen (4.6 mol%). In some experiments nitrogen was replaced by carbon dioxide but otherwise the feed composition remained the same. In all experiments 3.8 g catalyst was used, corresponding to a space time of 3.09 g h mol^{-1}.

The gaseous products were separated from the liquid product and analysed on-line by an HP 5890 gas chromatograph (HP SPB-1 fused silica capillary column, TCD detector). All products have been calibrated using mixtures with known composition. The products in the liquid phase were identified by GC-MS, and by GC with authentic samples. Propylene oxide yield was calculated based on the propylene mass flow rate. A black precipitate was found in the liquid product after starting the feed, likely due to wash-out of the finest catalyst particles.

4.3.3 Thermal Analysis

One part of the spent catalyst was refluxed in methanol at 80 °C for 3 h and filtered off. This washed spent catalyst and the untreated spent catalyst were analyzed by the coupled thermoanalytical method (TA-MS), using a Netzsch STA 409 thermonalyzer connected by a heated steel capillary with a quadrupol mass spectrometer (Balzers, QMG 420). The samples were heated in 20 vol% O_2 - 80 vol% He mixture. The system was equipped with a gas pulse device (Netzsch) that enables the injection of a controlled amount of the gas into the carrier gas stream which is necessary for the quantification of the mass spectrometric signals. Details of this procedure have been published elsewhere [276, 277].

The evolution of methyl formate by-product was additionally investigated by a TA-FTIR system (Netzsch STA 449 connected by heated capillary to a spectroscope (VECTOR 22, Bruker Optik). In both measurements the heating rate was 10 °C min^{-1}.

4.4 Results

4.4.1 Catalytic Experiments

At first the catalyst stability was studied under standard reaction conditions. The catalyst was active and highly selective at the beginning of the reaction but its performance decreased monotonously with time-on-stream (Figure 4-2). After each period of time-on-stream (ca. 8 h per day) the feed was stopped, and the catalyst was flushed with nitrogen. At the onset of the reaction the propylene oxide yield was 3.5% with a selectivity higher than 99%. The yield decreased monotonously with time-on-stream and more by-products formed. The major by-product, detected by GC analysis, was methyl formate. A possible oxidation-esterification route from methanol to methyl formate is shown in Figure 4-4. At the beginning (<3 h) the ester formed only in traces, but its amount increased steadily till it became the main product and after 35 h propylene oxide was barely detectable (Figure 4-3). Acetone, acrolein, acrylic acid and monomethylated glycols have been identified as further by-products originating from propylene (Figure 4-5). Their time-resolved formation showed a picture similar to that of methyl formate. For example, acrolein was formed only in traces at the beginning, but its selectivity based on propylene attained 20% after 20 h time-on-stream (not shown). Some of these products dimerize and oligomerize easily on the acid sites of the catalyst. During operation the liquid downstream had usually a yellow to brown colour indicating some oligomer formation.

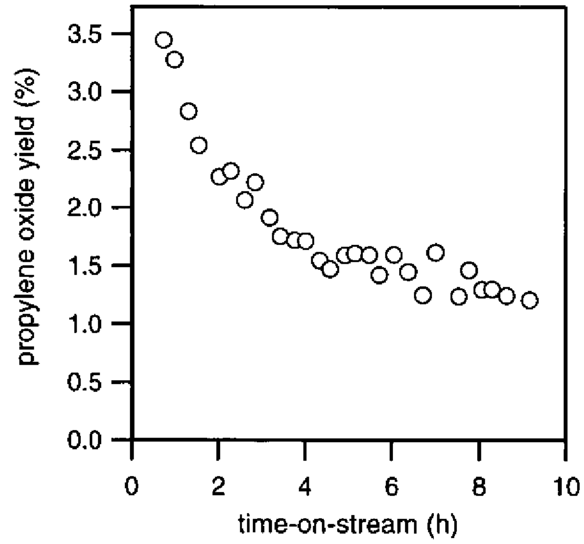


Fig. 4-2: Propylene oxide yield as a function of time-on-stream (standard conditions, first day)

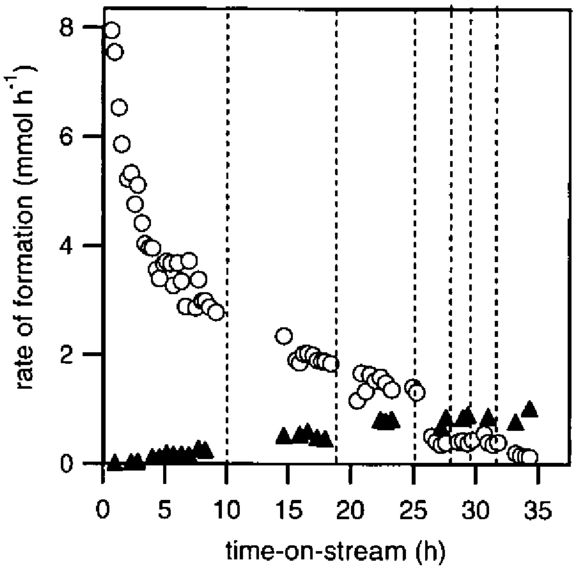
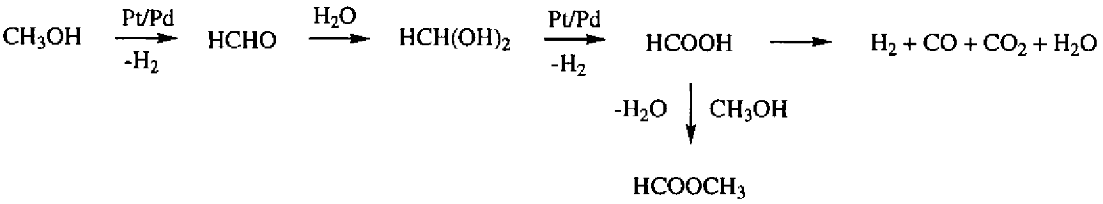


Fig. 4-3: Long term behaviour of the catalyst, illustrated by the rate of formation of propylene oxide (O) and methyl formate (▲) (standard conditions). Dashed lines indicate breaking of operation (overnight periods).



$$\begin{array}{ccccccccc} \mathrm{CH_3OH} & \xrightarrow[-\mathrm{H_2}]{\mathrm{Pt/Pd}} & \mathrm{HCHO} & \xrightarrow{\mathrm{H_2O}} & \mathrm{HCH(OH)_2} & \xrightarrow[-\mathrm{H_2}]{\mathrm{Pt/Pd}} & \mathrm{HCOOH} & \longrightarrow & \mathrm{H_2 + CO + CO_2 + H_2O} \\ &&&&&& {\scriptstyle -\mathrm{H_2O}}\big\downarrow{\scriptstyle \mathrm{CH_3OH}} && \\ &&&&&& \mathrm{HCOOCH_3} && \end{array}$$

Fig. 4-4: A conceivable reaction scheme for methanol oxidation

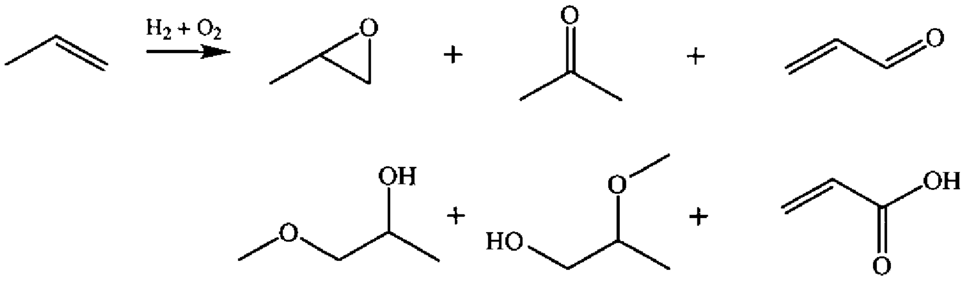


Fig. 4-5: Products of propylene oxidation detected by GC-MS

The influence of some reaction parameters has been studied on the partially deactivated catalyst. The most interesting observation is that the yield of propylene oxide depends on the diluent nitrogen or carbon dioxide (Table 4-1). The propylene oxide yield increased significantly after switching from nitrogen to carbon dioxide and the opposite effect was observed when switching back to nitrogen. Increasing the total pressure in the system in the presence of carbon dioxide from 50 to 120 bar also increased the propylene oxide yield by around 20 rel.% (not shown). Unfortunately, these observations are only qualitative as the continuous catalyst deactivation hindered any quantitative analysis.

Table 4-1: Effect of changing the diluent gas on the rate of formation (mmol h^{-1}) of some major products. Note that the continuous catalyst deactivation (Figure 4-3) also contributed to the observed changes.

Time-on-stream (h)	Diluent gas	Propylene oxide	Methyl formate	Acrolein	Acetone
7 - 8	nitrogen	2.8	0.2	0	0.03
13 - 15	carbon dioxide	3.5	0.5	0.06	0.09
17 - 18	nitrogen	2.0	0.5	0.09	0.07
30 - 32	nitrogen	0.5	0.9	0.3	0.1

An increase in temperature from 43–63 °C in carbon dioxide at 120 bar lowered the propylene oxide yield to one half and enhanced the amount of methyl formate. This result confirms the earlier observation by Laufer *et al.* [222] that higher reaction temperatures are detrimental to the epoxidation reaction, likely due to enhanced decomposition of hydrogen peroxide.

It was attempted to regenerate the spent catalyst *in situ*, but the initial activity of the catalyst could not be restored. In one case the catalyst was heated to 150 °C for 2 h under nitrogen. In another attempt the catalyst was flushed with a stream of 5% oxygen in nitrogen at 150 °C for 2 h. Considerable amounts of carbon dioxide and methyl formate were detected in the effluent stream, but the reactivation failed.

4.4.2 Thermal Analysis

The main (volatile) species, detected by MS and FTIR during TPO of spent and washed catalyst samples, were water, carbon dioxide, methanol and methyl formate. The results in Figure 4-6 illustrate that evolution of carbon dioxide (m/z = 44) from the spent catalyst occurred in several steps. The first peak, centred at 87 °C, is followed by a broad signal between 125–190 °C and a strong peak at 211 °C. Further evolution of carbon dioxide is represented by a very broad signal spread in the range 250–620 °C. After washing the catalyst with methanol, carbon dioxide evolved in two steps: the first, very strong peak at 92 °C is followed by a broad signal in the range 150–600 °C.

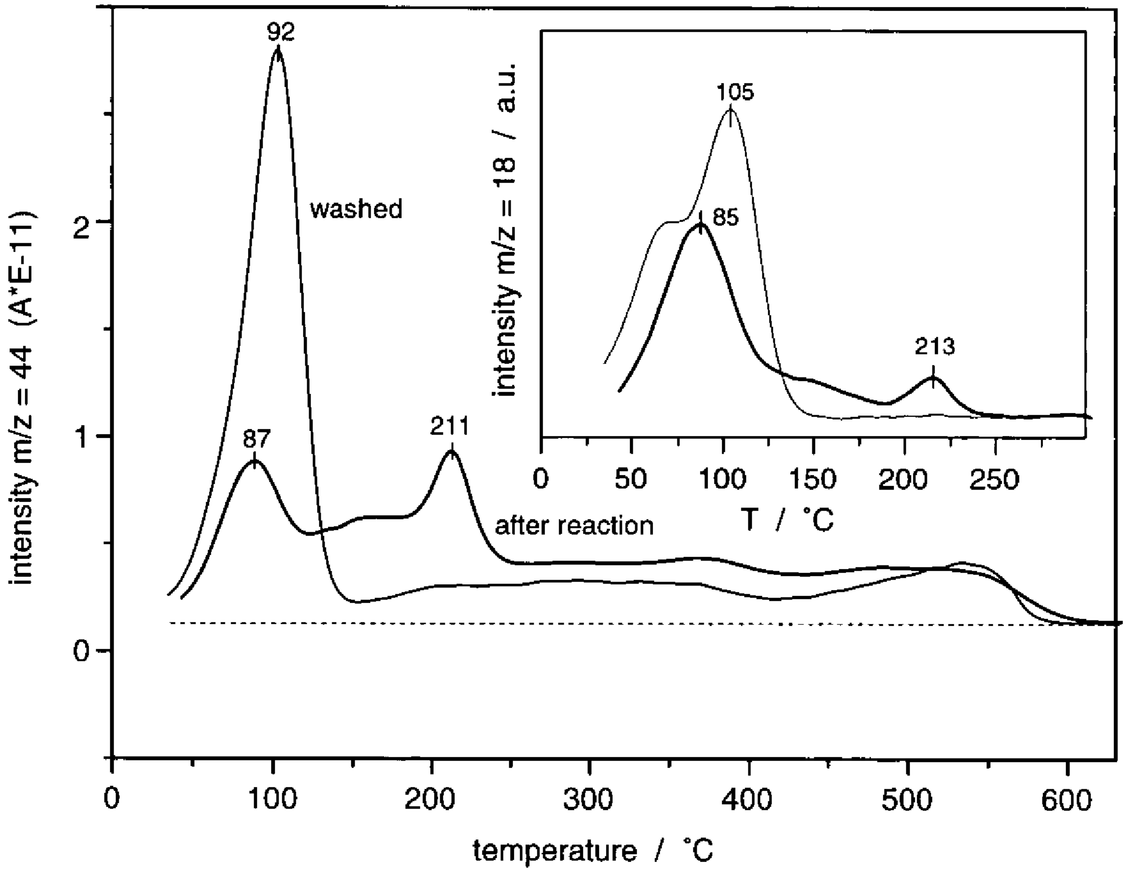


Fig. 4-6: Temperature programmed oxidation of the spent catalyst. Full picture: Evolution of CO_2 (m/z = 44) from the spent catalyst (bold) and from the spent catalyst washed with methanol. Inset: evolution of water (m/z = 18) in the low temperature range of the experiment.

The mass spectrometric signals of water (m/z = 18) are displayed in the inset of Figure 4-6. The majority of water is removed during the first step centered at 85 °C. The second broad signal in the range 125–190 °C is followed by a distinct peak at 213 °C. After washing the spent catalyst with hot methanol, desorption of water is finished below 150 °C.

There are two origins of carbon dioxide evolution during TPO measurements. Desorption of adsorbed species, together with adsorbed water, occurs up to ca. 150 °C. At higher temperatures, carbon dioxide is mainly formed as a product of the oxidation of organic residue. The amounts of both kinds of carbon dioxide are given in Table 4-2.

Table 4-2: Amount of CO_2 (in wt.% related to the catalyst) in spent and washed catalysts as determined by temperature programmed oxidation experiments.

sample	adsorbed CO_2	CO_2 from combustion
spent catalyst	0.9	2.1
washed catalyst	2.7	1.1

The results in Figure 4-6 and Table 4-2 can be interpreted as follows. Washing of the spent catalyst with refluxing methanol led to the partial removal of non-volatile organic residue. The amount of carbon dioxide evolved at higher temperatures decreased considerably after washing. Washing removed also the organic species resulting in the evolution of carbon dioxide from the spent catalyst in the range 125–250 °C (Figure 4-6). These region of easily oxidizable species in the spent catalyst should include the evolution of carbon dioxide originating from decomposition of formic acid (Figure 4-4). During refluxing the spent catalyst with methanol, formic acid is transformed to methyl formate. Methyl formate (m/z = 60) was difficult to detect by MS in the spent catalyst but its evolution from the washed catalyst at low temperatures was clearly observable (not shown). Partial removal of the high molecular weight organic residue from the catalyst pores during washing with methanol lead to increased adsorption of carbon dioxide and water during exposure to air (Table 4-2), which is a frequently observed phenomenon with microporous materials.

Evolution of volatile compounds from the catalysts during TPD in nitrogen is illustrated in Figure 4-7. The two FTIR spectra in the lower part of Figure 4-7 were measured at about 110 °C in order to minimize the influence of water. A comparison with the reference spectra in gas-phase indicates the desorption of two main organic compounds: methanol and methyl formate.

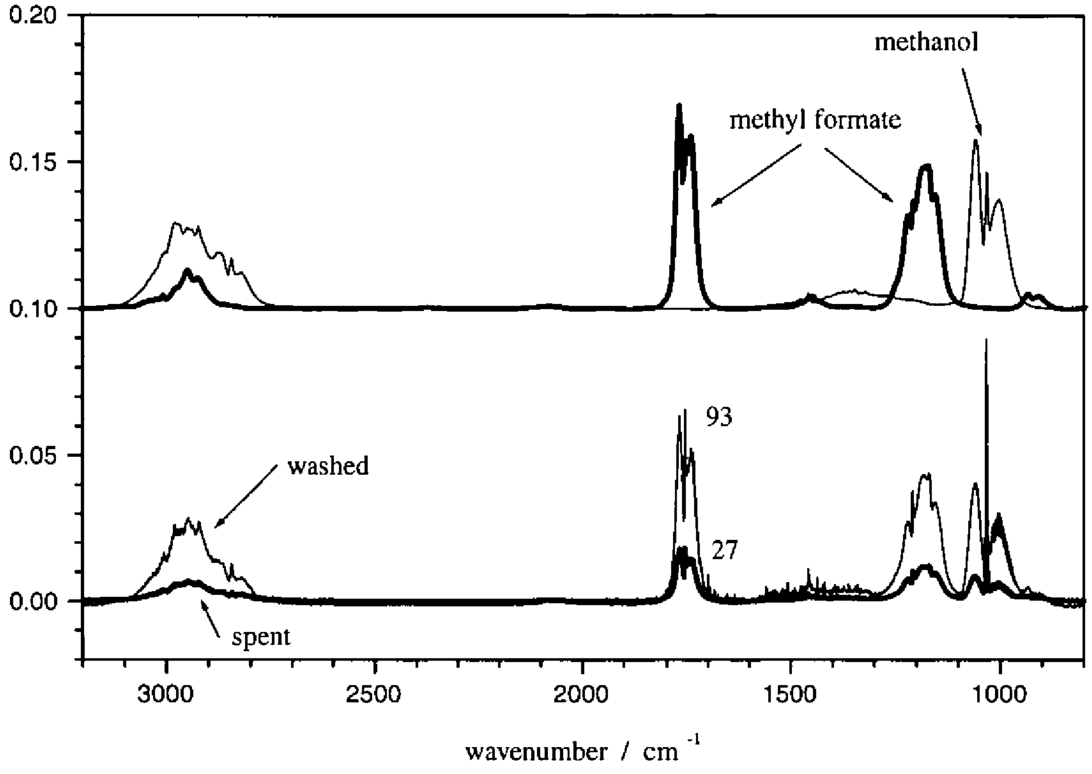


Fig. 4-7: Upper part: FTIR gas-phase spectra of methanol and methyl formate (bold). Lower part: FTIR gas phase spectra of spent (bold) and washed catalysts at 110 °C during heating in nitrogen.

Quantification of the spectra in the range 1700–1800 cm^{-1} revealed a remarkably higher evolution of methyl formate from the washed sample then the unwashed spent catalyst (by a factor of ca. 3.5).

4.5 Discussion

4.5.1 Nature of Catalyst Deactivation

Epoxidation of propylene with a mixture of hydrogen and oxygen in a continuous fixed bed reactor demonstrated that the Pd-Pt/TS-1 catalysts lost its epoxidation activity within 35 h on stream (Figure 4-2 and Figure 4-3). During this period not only the reaction rate decreased monotonously but also the selectivity pattern changed strikingly. The selectivity to epoxide decreased and successively methyl formate became the major species, at least among the volatile products. Non-volatile products (presumably oligomers) could not be analyzed by GC but their presence was clearly indicated by thermal analysis of spent and washed catalysts, and by darkening of the colour of the effluent with time-on-stream. The activity of the catalyst could not be recovered by heating in air or nitrogen at 150 °C. Thermal analysis demonstrated that washing the spent catalyst with refluxing methanol could not completely remove the organic residue and their oxidative removal required elevated temperatures (Figure 4-6). This observation confirms the formation of high molecular weight non-volatile oligomers, as all the volatile products identified by GC and GC-MS (Figure 4-4 and Figure 4-5) are well soluble in methanol.

Most of the by-products, shown in Figure 4-5, are assumed to form from propylene oxide by acid-catalyzed rearrangement (acetone, acrolein) or acid-catalyzed nucleophylic addition of methanol (1-methoxypropan-2-ol and 2-methoxypropan-1-ol). Further oxidation of acrolein on Pd or Pt yields acrylic acid. Some of these species are prone to dimerize and oligomerize in the presence of an acid catalyst. The strong Lewis acidity of isolated Ti-sites in TS-1 is well known and the acidity of the peroxo complex is even higher [207]. But it is also known that in the presence of an olefin reactant epoxidation is usually favored by TS-1 compared to the other acid-catalyzed reactions including epoxide rearrangements.

The key question is, why shifts the selectivity of Pd-Pt/TS-1 catalyst with time-on-stream from propylene epoxidation to other undesired acid-catalyzed reactions? The steadily increasing formation of methyl formate provides the answer to this dilemma (Figure 4-3). A unique property of platinum metals is that they can activate molecular oxygen, hydrogen and alcohols under very mild conditions. This is the basis of the well known aerobic oxidation of alcohols [237]. Facile oxidation of methanol, being present in excess, yields formaldehyde (Figure 4-5). Oxidation of aldehydes is slow, but hydration with water provides the geminal glycol which is readily oxidized (via oxidative dehydrogenation) to formic acid. Hydration of aldehydes is acid-base catalyzed [278] and the product formic acid can accelerate this process. In an equilibrium reaction formic acid can produce methyl formate, or decompose to carbon oxides, hydrogen and water. The decomposition is catalyzed by Pt and Pd. Formic acid is the strongest acid in the system (pK_a 3.77 [279]), which seems to be responsible for the acid-catalyzed side reactions, including oligomerization. The high molecular weight by-products migrate slowly and can block the narrow channels of TS-1. Blocking of the channels hinders the diffusion of propylene and H_2O_2 (from the noble metal surface to the Ti-sites), leading to suppressed epoxidation rate.

Coming back to some other by-products originating from propylene (acetone, acrolein), their formation by direct (allylic) oxidation of propylene on palladium is unlikely. Under the conditions applied palladium is very selective to the oxidation of alcohols and aldehydes. For example, unsaturated alcohols can be oxidised to unsaturated carbonyl compounds without attacking the C=C double bond [247].

Summarizing this working hypothesis, formation of formic acid on Pt and Pd is an autocatalytic process, and this by-product seems to be responsible for acceleration of other undesired acid-catalyzed reactions and suppression of propylene oxide formation. This detrimental process could be alleviated by replacing methanol with another suitable organic cosolvent such as acetone, acetonitrile or methyl acetate [209]. Unfortunately, these solvents are not recommended for propylene epoxidation with hydrogen peroxide due to safety reasons or too low reaction rates [210]. A more appropriate approach could be the improvement of the Pd-Pt/TS-1 catalyst by selective poisoning to suppress methanol oxidation. A third possibility, neutralization of the acid formed in side reactions, is a demanding task as too high base concentration can deactivate TS-1 [207].

4.5.2 Epoxidation in Supercritical Carbon Dioxide

At 50 bar the feed most likely consists of three fluid phases: gas (nitrogen, oxygen, hydrogen, propylene), polar liquid (methanol, water) and apolar liquid (propylene). When nitrogen is replaced by carbon dioxide at the same pressure, the amount of apolar liquid phase is expected to increase. It is not clear yet what is the nature of this "solvent effect": whether the remarkable enhancement in propylene oxide formation (Table 4-1) should be attributed to a change in the phase composition in the feed or rather to some specific interaction involving carbon dioxide (e.g. diminishing the rate of methanol oxidation). For comparison, the presence of a considerable amount of apolar solvent (polyfluorinated hydrocarbon) decreased the epoxide yield over a similar catalyst [223].

Increasing the total pressure to 120 bar, carbon dioxide (T_c = 30.9 °C, P_c = 73.8 bar) forms an apolar sc phase that can dissolve oxygen, hydrogen and propylene. It is assumed that under these conditions only two phases are present: the apolar sc phase and the polar liquid phase. We propose that the observed small but significant increase in propylene oxide yield by 20 relative % should be attributed to the facilitated mass transport resulting in higher concentrations of the reactants at the active sites.

4.6 Conclusions

Epoxidation of propylene with noble metal-promoted TS-1 and a hydrogen/oxygen mixture has been carried out in a continuous high pressure reactor. On the basis of the time-resolved changes in the product distribution, and thermal analysis of the spent catalyst, we propose that formation of formic acid from methanol co-solvent is the key for understanding the remarkable catalyst deactivation. This strongly acidic species catalyzes the formation of several by-products and also its formation from methanol. Reactivation of the catalyst requires an oxidative treatment at elevated temperatures but treatments at high temper-

Chapter 5

Partial Oxidation of Alcohols in Supercritical Carbon Dioxide

5.1 Abstract

Oxidation of water-insoluble alcohols in $scCO_2$ over a Pd-Pt-Bi/C catalyst in a continuous fixed bed reactor affords high reaction rates and yields up to 98% to the corresponding ketones, aromatic and α,β-unsaturated aliphatic aldehydes, without the risk of using a flammable organic solvent.

5.2 Introduction

Partial oxidation of alcohols over supported platinum metal catalysts is an attractive, environmentally friendly process: air or oxygen can be used as oxidant in aqueous medium under mild conditions. The method has been widely used for the transformation of polyols and carbohydrates [280, 281]. Primary and secondary alcohols are readily oxidized to carboxylic acids and ketones, respectively, but partial oxidation of primary alcohols to aldehydes is limited to aromatic and α,β-unsaturated aliphatic alcohols where hydration and further dehydrogenation of the intermediate aldehyde is minor [237, 247]. Drawbacks of the method are the frequently observed catalyst deactivation necessitating high catalyst-substrate ratio (20–50 wt%) [233, 237], and the explosion risk in case of readily dehydrogenating substrates [236]. Oxidation of water-insoluble alcohols is rather slow in organic solvents [282] and because of safety reasons the process is unattractive even on a laboratory scale [233].

To overcome these restrictions, the organic solvent can be replaced by $scCO_2$ [283, 284] i.e. CO_2 under conditions above its critical temperature ($T_c = 31.1$ °C) and pressure ($p_c = 73.8$ bar). $ScCO_2$ has a number of distinct advantages over conventional organic liquid solvents, among which adjustable solvent strength and favorable transport properties are probably the most important. This medium is especially attractive for the oxidation of weakly polar, water-insoluble alcohols, due to the low polarity of $scCO_2$. Besides, CO_2 is relatively inert, non-flammable under oxidizing conditions, and has a high heat capacity - an important feature for exothermic reactions. Products and solvent can easily be separated by releasing the pressure of the reaction mixture.

There are only two examples on the partial oxidation of alcohols with a solid catalyst in $scCO_2$ reported in the literature. Oxidation of methanol on iron oxide containing aerogels [145], and ethanol on Pt/TiO_2 [143] to the corresponding aldehyde affords moderate yields (15–30 %) compared to the conventional gas phase oxidation of small chain aliphatic alcohols [231]. Here we show that oxidation in $scCO_2$ is an excellent alternative to liquid phase reactions in organic solvents, affording the conversion of water-insoluble alcohols to (deactivated) carbonyl compounds at high rate and selectivity.

The experiments have been performed in a high-pressure continuous fixed bed reactor over a promoted noble metal catalyst (4 wt% Pd - 1 wt% Pt - 5 wt% Bi/C). It has been shown before that Bi or Pb promotion can remarkably enhance the performance of Pt and Pd [243, 285-287]. For the study of the influence of reaction parameters, the conditions were chosen to achieve conversions in the range 2–10% in order to minimize the temperature gradients in the catalyst bed. In some cases the contact time and temperature were increased to achieve high conversions, though optimization of the reaction conditions was not attempted. These results, illustrating the potential of the method in the synthesis of activated and non-activated aldehydes and ketones, are collected in Table 5-1.

Table 5-1: Selected examples on the partial oxidation of primary and secondary alcohols to carbonyl compounds in $scCO_2$. Catalyst: 4 wt% Pd - 1 wt% Pt - 5 wt% Bi/C (3 g), W/F = 0.61–1.63 g h mol^{-1}.

Alcohol	Oxygen [mol%]	Alcohol [mol%]	Butanone co-solvent [mol%]	p [bar]	T [°C]	Residence time [s]	Yield [%]	Sel. [%]
octan-2-ol	4	2	-	110	140	17	68	> 99.5
1-phenylethanol	2.7	2.7	5.3	110	140	13	95	> 99.5
1-phenylethanol	5.3	2.7	5.3	110	140	13	98	99
octan-1-ol	6	3	-	120	110	9.5	18	34
octan-1-ol	2.5	5	-	95	80	25	11	82
benzyl alcohol	2.5	5	-	95	80	13	26	99
benzyl alcohol	2	2	-	120	100	9.5	65	78
p-anisyl alcohol	2	2	4	120	110	9.5	70	87
cinnamyl alcohol	4	2	4	120	110	9.5	78	98
cinnamyl alcohol	4	2	8	120	110	9.5	61	96

5.3 Experimental

The reactions have been performed in a tubular flow reactor with an inner diameter of 13 mm and 38 ml volume. The alcohols were dosed by a Gilson 305 piston pump. Oxygen was supplied to the reactor using a six-port valve dosing 0.05 ml pulses at high pressure and constant frequency. The constant pressure in the system was maintained by a pressure regulator with carbon dioxide. The total gas flow was controlled at the vent. The 4 wt% Pd - 1 wt% Pt - 5 wt% Bi/C catalyst (CEF 196 RA/W, Degussa, BET surface area 930 $m^2 g^{-1}$) was reduced *in situ* in hydrogen at 100 °C for 2 h prior to the kinetic measurements. For the parameter study the feed flow consisted of 5 mol% alcohol, 2.5 mol% oxygen and 92.5 mol% CO_2. 2 g catalyst was used, corresponding to a space-time related quantity W/F = 0.81 g h mol^{-1} (W = catalyst weight, F = molar feed rate). The liquid products were separated from carbon dioxide and identified by GC and GC-MS. Yield and selectivities were determined by GC analysis using the internal standard method.

5.4 Results and Discussion

Octan-2-ol has been converted to octan-2-one with higher than 99.5% selectivity even at around 70 % conversion. Only traces of oct-2-ene (by dehydration) and oct-4-ene (by dehydration and subsequent double bond migration) have been formed. The yield (68 %) could be further increased by applying higher amount of catalyst or lower mass flow rate. The parameter study indicated that the octan-2-one yield increased exponentially with increasing temperature and approximately linearly with contact time. A bell-shaped curve was found for the effect of oxygen concentration in the feed (Figure 5-1). The maximum in yield is attributed to the so-called over-oxidation of the catalyst, a phenomenon commonly observed with platinum metal catalysts [233, 236, 237]. The rate of oxidative dehydrogenation of alcohols is considerably higher on the reduced metal surface than on the oxygen-covered metal. Though oxygen is necessary to shift the alcohol-carbonyl compound equilibrium by oxidizing the hydrogen abstracted from the substrate, too high surface oxygen coverage reduces the overall reaction rate. An additional effect is the decreasing density of $scCO_2$ with increasing oxygen concentration, which may reduce the solubility of reactant and product. Changes in density of $scCO_2$ can explain also the influence of total pressure in the reactor. At constant temperature the yield reached a maximum at 110–120 bar.

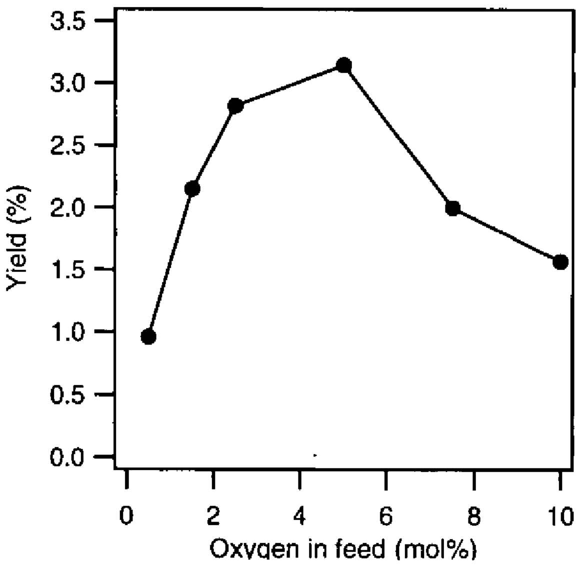


Fig. 5-1: Effect of oxygen concentration in the feed on the yield to octan-2-one. Conditions: 100 °C, 95 bar, 2 g catalyst, W/F = 0.81 g h mol^{-1}, 5 mol% octan-2-ol, rest O_2 and CO_2.

Oxidation of octan-2-ol was relatively slow compared to the conversion of other secondary alcohols, such as 1-phenylethanol (Table 5-1). The transformation of 1-phenyl ethanol to acetophenone was nearly quantitative. Only traces of di-(1-phenylethyl)-ether were detected. The selectivity decreased to 99% at high temperature and high oxygen excess due to some product degradation. In these reactions the solid substrate was dissolved in butanone for feeding, because the reactor tubes and valves were not heatable. Comparative experiments with octan-2-one indicated that the yield decreased with increasing amount of this co-solvent suggesting that its amount should be kept at low level (Figure 5-2). The change in reaction rate may be connected to H-bonding between the substrate and co-solvent. Formation of H-bonded species (clusters) can change the phase behavior in $scCO_2$.

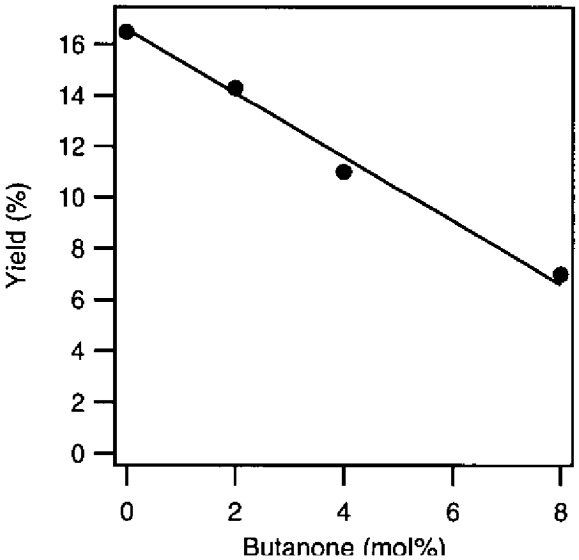


Fig. 5-2: Dependence of octan-2-one yield on butanone concentration in the feed. Conditions: 120 °C, 120 bar, 2 g catalyst, W/F = 0.61 g h mol^{-1}, 2 mol% octan-2-ol, 4 mol% O_2, rest CO_2.

Transformation of primary alcohols to aldehydes under similar conditions was fast but non-selective (Table 5-1). For example, octan-1-ol was oxidized to a mixture of octanal, octanoic acid and octyl octanoate. Oct-2-enal and dioctyl ether were produced in traces. Transient experiments indicated that the acid-catalyzed side reactions (ester and ether formation) were accelerated by the product octanoic acid. In general, the selectivity to octanal decreased rapidly with increasing conversion, especially at high temperature. Relatively good selectivity could be achieved by working at 60–80 °C and high contact time (Table 5-1). Still, the aldehyde yield was always less than 20 %. For comparison, partial oxidation of primary aliphatic alcohols, such as dodecanol to dodecanal, is also non-selective in aqueous medium [247], due to the high reactivity of aliphatic aldehydes for hydration and subsequent rapid dehydrogenation. Remarkably better selectivities can be achieved when the product aldehyde is stabilized by an aromatic ring or a C=C double bond. Benzyl alcohol was oxidized to benzaldehyde, benzoic acid and benzyl benzoate. Dibenzyl ether formed in traces. Higher than 99 % selectivity for benzaldehyde was obtained at 60–80 °C (Table 5-1). At 100 °C or higher the selectivity dropped below 80 %. Clearly, good yield can be achieved only at moderate temperature and longer contact time (higher amount of catalyst and/or lower mass flow rate). Oxidation of p-anisyl alcohol to p-anisaldehyde afforded even better yields, presumably due to the electron-releasing methoxy group in para position (Table 5-1).

The highest aldehyde yield with high selectivity was obtained in the oxidation of the α,β-unsaturated alkylaromatic alcohol, cinnamyl alcohol. The negative impact of the co-solvent, used for dosing the solid substrate, is confirmed by the last two entries in Table 5-1. The aldehyde yield dropped from 78% to 61% when the alcohol was diluted with double amount of butanone. Again, dosing of melted substrate can eliminate this complication.

5.5 Conclusion

From the results presented we can conclude that the aerobic oxidation of alcohols to carbonyl compounds in $scCO_2$ is a good alternative to the well-known aqueous phase oxidation on supported platinum metal catalysts. The present method has obvious advantages for the transformation of water-insoluble alcohols, avoiding the application of flammable organic solvents. Aqueous phase oxidations are typically performed at 40–90 °C for 3–10 h reaction time [233, 236, 237, 247, 281]. In the present study only 10–25 s residence time was necessary to achieve 65–98 % yields to ketones, aromatic and α,β-unsaturated aldehydes. The yields and selectivities may be further improved by applying longer residence times at relatively low temperature, and by direct dosing of melted substrates (without co-solvent). No catalyst deactivation or metal leaching was observed with time-on-stream. Generally, steady-state conditions were reached within 2–3 h. Limitation of the method is similar to that of the aqueous phase oxidation on platinum metal catalysts, namely that primary aliphatic aldehydes cannot be synthesized with good selectivity.

Chapter 6

Palladium-Catalyzed Oxidation of Octyl Alcohols in Supercritical Carbon Dioxide

6.1 Abstract

Noble metal catalyzed aerobic oxidation of alcohols to carbonyl compounds or carboxylic acids is an efficient method, but the frequently observed catalyst deactivation, and flammability of organic solvents in case of water-insoluble alcohols, limit the application range. We applied supercritical (sc, dense) carbon dioxide as solvent, a cheap and non-flammable medium with fair and tunable solubility in particular for weakly polar water-insoluble alcohols. The experiments were carried out in a continuous fixed bed reactor, over 0.5 wt% Pd/alumina, at 80–140 °C and 75–125 bar. A comparative study of oxidation of octan-1-ol and octan-2-ol to carbonyl compounds, chosen as model reactions, demonstrated that the method is well-suited for the partial oxidation of secondary alcohols with molecular oxygen, whereas for primary alcohols the selectivity is low. In the oxidation of octan-2-ol the selectivity was excellent (>99.5%) and independent of conversion. No significant catalyst deactivation was observed and the rate in CO_2 was higher by a factor of up to 2–4, compared to the oxidation in nitrogen. The complex effects of pressure and oxygen concentration on the reaction rate have been interpreted by studying the phase behavior in a high pressure view cell under reaction conditions.

6.2 Introduction

The Pt-catalyzed oxidation of cinnamyl alcohol to cinnamaldehyde by oxygen was discovered by Strecker in 1855 [235]. Nowadays supported noble metal catalysts in aqueous medium are widely used for the oxidation of water-soluble alcohols and polyols (carbohydrates) in the synthesis of specialty and fine chemicals possessing carbonyl or carboxylic groups [230, 233, 236, 237, 281]. The method is attractive from both economic and environmental points of view: molecular oxygen is a cheap and readily available oxidant and water is the co-product. Oxidations are typically performed with 5–10 wt% Pt or Pd supported on carbon or alumina, in the temperature range 40–90 °C. Batch reaction time is usually 3–10 h. Catalyst deactivation is frequently observed and a relatively high catalyst/reactant mass ratio (0.2–0.5) is necessary even after promotion by lead or bismuth [233, 247].

Undesired formation of hydrogen by fast dehydrogenation of some alcohols and carbohydrates [236] is a major obstacle for safe operation. The explosion risk is even higher when flammable organic solvents (e.g. heptane [249]) are used for water-insoluble alcohols. Good knowledge of the reaction and strict control of the reaction conditions (oxygen concentration, temperature, heat and mass transport) is necessary, even when working in a laboratory reactor.

An alternative solution may be to carry out the reaction in sc carbon dioxide ($scCO_2$; $T_c = 30.9$ °C, $p_c = 73.8$ bar). $ScCO_2$ has several distinct advantages over conventional liquid solvents. Its solvent strength can be tuned by varying the density (pressure). This medium is especially suited for weakly polar, water-insoluble alcohols due to its low polarity. CO_2 is relatively inert, non-flammable, and it has a comparatively high heat capacity - an important feature for exothermic reactions. $ScCO_2$ is a fairly good solvent for many organic reactants and oxygen, and transport limitations typical for liquid solvents may completely vanish due to the high (gas-like) diffusivities. Products and solvent separate simply by releasing the pressure after reaction.

Sc solvents have found numerous applications in heterogeneous [5, 12, 20] and homogeneous catalysis [62, 288], but reports on partial oxidation in sc fluids are scarce. Oxidation of sc isobutane with air has gained importance because of the use of its oxidation products *tert*-butyl hydroperoxide and *tert*-butyl alcohol in the manufacture of propylene oxide and methyl *tert*-butyl ether, respectively [94, 140, 141, 289, 290]. $ScCO_2$ was used as solvent in the conversion of toluene to benzaldehyde over CoO [183], and for the transformation of propylene to propylene glycol over copper iodide and copper oxide [184]. Other interesting applications are the partial oxidation of cumene [291] and olefins [142], catalyzed by the steel reactor wall.

There are only a few examples on the partial oxidation of alcohols in $scCO_2$. In the oxidation of methanol over iron oxide based aerogels the temperature and catalyst loading were the crucial parameters governing the selectivities to formaldehyde, methyl formate and dimethyl ether [144, 145]. At temperatures above 200 °C total oxidation dominated. Compared to conventional gas phase oxidation, application of $scCO_2$ provided a 3–5 fold increase in the rate of partial oxidation, and the onset of total oxidation shifted to higher temperatures. Ethanol oxidation over Pt/TiO_2 was carried out at 90 bar in the temperature range 150–300 °C [143]. Interestingly, the rate of partial oxidation to acetaldehyde was independent of O_2 concentration, though high O_2 concentration favored the consecutive reactions to CO and CO_2.

We have recently reported that $scCO_2$ is an excellent solvent for the partial oxidation of higher molecular weight, water-insoluble alcohols with oxygen [187]. The aim of the present work is to get a deeper insight into the Pt-metal catalyzed oxidation reaction by combining the catalytic study with phase behavior measurements in a high pressure view cell. The catalytic experiments have been carried out in a continuous fixed bed reactor. Partial oxidation of octan-1-ol and octan-2-ol has been chosen as model reactions, representing the transformation of water-insoluble primary and secondary alcohols. Octanols and octanals are major components of synthetic citrus oils in perfumery [292].

6.3 Experimental

6.3.1 Catalytic Tests

The reactions were performed isothermally in a tubular flow reactor with an inner diameter of 13 mm and 38 ml volume. The reactor set-up has been published recently [189]. Temperature was measured in the catalyst bed by a thermocouple well placed in the center of the bed. Octan-1-ol and octan-2-ol were dosed by a Gilson 305 piston pump. Oxygen was supplied to the reactor using a six-port valve dosing 0.05 ml pulses at high pressure and constant frequency. The constant pressure in the system was maintained by a pressure regulator with CO_2 or nitrogen. The total gas flow was controlled at the vent. Standard conditions for the parameter study were 95 bar, 120 °C and the feed flow consisted of 5 mol% octan-2-ol, 2.5 mol% oxygen and 92.5 mol% carbon dioxide. This molar composition remained the same at all different pressures. 5 g of catalyst was used, corresponding to a catalyst bed length of 5 cm. The space time related quantity W/F was 1.02 g h mol^{-1} (W = weight of catalyst, F = molar feed rate). Glass beads (2 mm diameter, bed lenght of 5 cm) were filled above the catalyst bed. The catalyst was a 0.5% Pd/alumina (Engelhard N° 4586, cylindric tablets with 3.2 mm height and diameter; egg-shell type, BET surface: 96 m^2 g^{-1}, metal dispersion: 0.29 determined by hydrogen chemisorption). The catalyst was reduced *in situ* in hydrogen at 100 °C for 2 h prior to use, and its performance usually reached steady-state within 2 h time-on-stream. Under the conditions applied in this study catalyst deactivation was minor. For the parameter study conversion was kept below 10% to minimize temperature gradients in the catalyst bed.

The liquid products were separated from CO_2 and analyzed by GC (HP-FFAP column) and identified by GC-MS. The selectivity and yield take into account all products formed.

6.3.2 Phase behavior

The phase behavior of the system under reaction conditions was investigated in a computer controlled high pressure view cell, equipped with on-line digital video imaging and recording. The magnetically stirred cell consisted of a horizontal cylinder equipped with a sapphire window covering the entire diameter and an opposite, horizontally moving piston equipped with another sapphire window for illumination of the system. This setup allowed the observation of even minor volumes of gaseous and liquid phases. The basic setup of the video imaging is described in detail elsewhere [15].

Due to limitations of the view cell in handling oxygen, the phase behavior experiments were carried out with a mixture of air and nitrogen instead of oxygen. Oxygen and nitrogen are similar in polarity and molecular mass, and the critical points of both gases (O_2: -119 °C, 50 bar; N_2: -147 °C, 34 bar) are far from that of CO_2 (31 °C, 74 bar). We therefore assume that dilute mixtures of oxygen or nitrogen in CO_2 behave similarly. 5 mol% octan-2-ol, 2.5 mol% of O_2-N_2 mixture (30% air, 70% N_2) and 92.5 mol% carbon dioxide were supplied to the view cell. Changes in the phase behavior, induced by variation of temperature and pressure, were monitored.

6.4 Results

6.4.1 Oxidation of Octan-2-ol

Preliminary screening of various supported Pt, Ru and Pd catalysts revealed that 0.5 wt% Pd/alumina afforded the best activity combined with good stability. Accordingly, all experiments discussed below were carried out with this catalyst.

Oxidation of octan-2-ol yielded almost exclusively octan-2-one (Figure 6-1). Even at high temperatures (140 °C) and high conversion the side-products oct-2-ene and oct-4-ene formed only in traces. Formation of olefins is attributed to dehydration of octan-2-ol at the acidic sites of the alumina support, and to subsequent isomerisation on Pd. No oxidative product degradation and acid formation were observed.

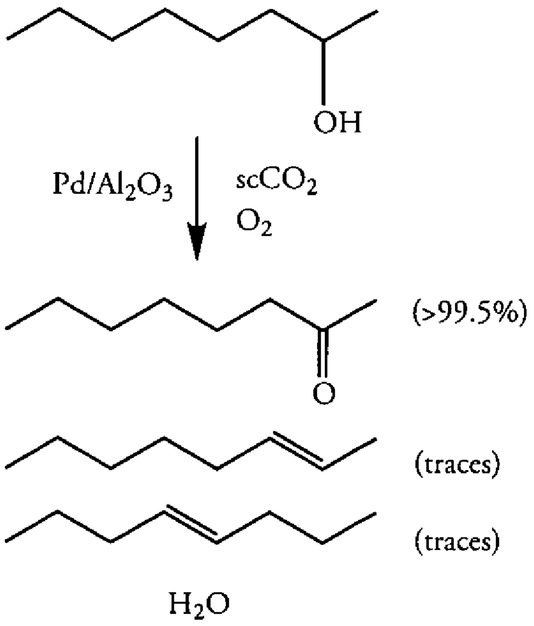


Fig. 6-1: Products formed in the oxidation of octan-2-ol.

The octan-2-one yield went up exponentially by increasing the temperature (Figure 6-2) and varied almost linearly with the space time related parameter W/F (Figure 6-3).

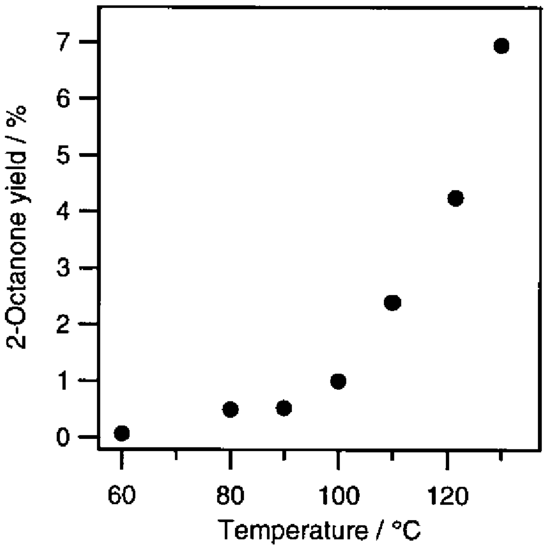


Fig. 6-2: Effect of temperature on the yield to octan-2-one. Conditions: 95 bar, 5 g 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}, 5 mol% octan-2-ol, 2.5 mol% O_2, 92.5 mol% CO_2.

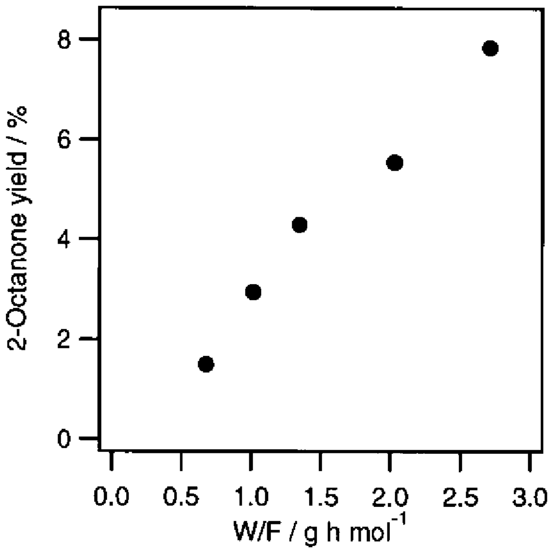


Fig. 6-3: Effect of space time related parameter W/F on the yield to octan-2-one. Conditions: 120 °C, 95 bar, 5 g 0.5% Pd/alumina, 5 mol% octan-2-ol, 2.5 mol% O_2, 92.5 mol% CO_2.

The effect of pressure on the octan-2-one yield was rather complex and strongly depended on the set of other parameters (Figure 6-4). Under standard conditions, at 120 °C, the yield showed a maximum at around 100–110 bar (curve a). The maximum was less pronounced when the temperature was lowered to 100 °C (curve b). When the reaction was carried out at 120 °C with double the amount of oxygen in the feed, the yield rose monotonously with increasing pressure with only a weak "shoulder" at around 100 bar (curve c). The latter experiment was repeated at half space time (W/F = 0.51 g h mol^{-1}) and a similar linear dependence was found though the yields were lower.

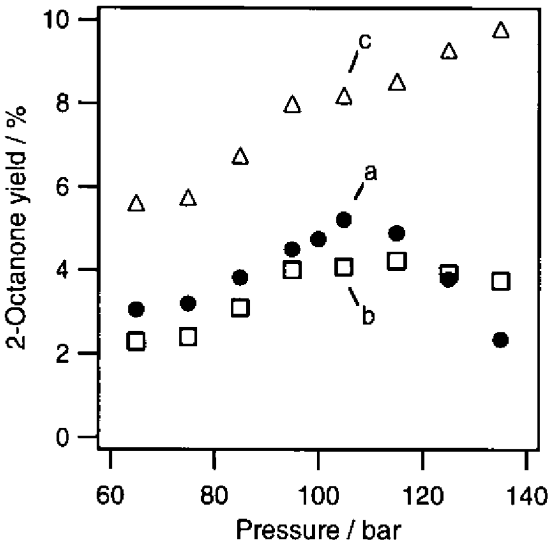


Fig. 6-4: Dependence of octan-2-one yield on the total pressure. (a) ● 120 °C, W/F = 1.02 g h mol^{-1}, 2.5 mol% O_2, (b) □ 100 °C, 2.03 g h mol^{-1}, 2.5 mol% O_2, (c) △ 120 °C, 1.02 g h mol^{-1}, 5.0 mol% O_2. Other conditions: 5 g 0.5% Pd/alumina, 5 mol% octan-2-ol, rest CO_2.

Variation of oxygen concentration in the feed resulted in a bell-shaped curve of the octan-2-one yield, as shown in Figure 6-5. The maximum at 7.5–10 mol% oxygen corresponds to a 200–300 mol% excess related to the stoichiometric ratio (octanol + ½ O_2). Interestingly, at low oxygen concentration the ketone yield dropped to zero and the reaction did not proceed by anaerobic dehydrogenation at 120 °C. It has been shown earlier that the best catalysts for anaerobic dehydrogenation of octan-2-ol are Raney Ni [230] and copper chromite [293], and the necessary reaction temperatures are considerably higher (174 and 300 °C, respectively).

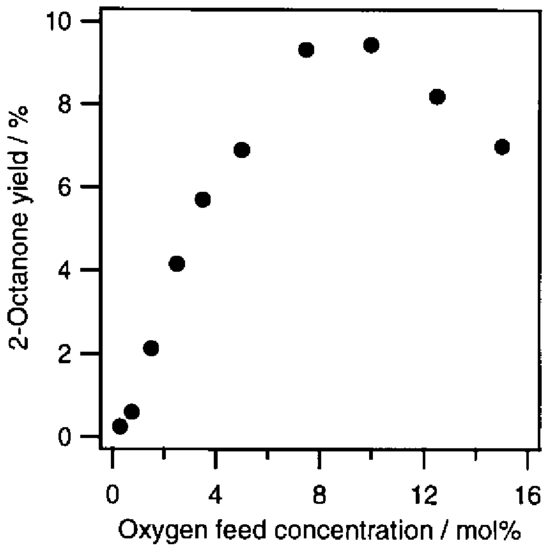


Fig. 6-5: Dependence of octan-2-one yield on oxygen concentration in the feed. Conditions: 120 °C, 95 bar, 5 g 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}, 5 mol% octan-2-ol, rest O_2 and CO_2.

When CO_2 was replaced by nitrogen, the octan-2-one yield dropped by a factor of 2 to 4. In nitrogen no optimum pressure was found and the yield increased steadily with increasing total pressure. Some examples are listed in Table 6-1 to illustrate the solvent effect of dense CO_2.

Table 6-1: Oxidation of octan-2-ol in nitrogen or carbon dioxide. Conditions: 5 g 0.5 wt% Pd/alumina, 5 mol% octan-2-ol, 2.5 mol% O_2, 92.5 mol% CO_2

Solvent (Diluent)	p bar	T °C	W/F g h mol^{-1}	Conv. %
Nitrogen	85	100	2.03	1.5
Carbon dioxide	85	100	2.03	3.1
Nitrogen	95	120	1.02	1.2
Carbon dioxide	95	120	1.02	4.3

Variation of the reaction parameters revealed that the octan-2-one yield could be increased without any loss in selectivity. For example, 46% yield was obtained at 140 °C by applying a relatively high space time (W/F) (Table 6-2).

However, under these conditions there was a significant temperature gradient (10 °C) in the catalyst bed. The only limit to further increasing the yield of the strongly exothermic reaction was the insufficient rate of heat transport in the reactor set-up used.

Table 6-2: Some examples of the oxidation of octan-2-ol at higher conversion. Conditions: 5 g 0.5 wt% Pd/alumina, solvent $scCO_2$

Octan-2-ol mol%	Oxygen mol%	p bar	T °C	W/F g h mol^{-1}	Conv. %	Sel. %
6	3	110	140	2.71	46	>99.5
6	3	110	140	1.02	21	>99.5
10	2.5	95	120	1.02	11.6	>99.5

6.4.2 Oxidation of Octan-1-ol

Oxidation of octan-1-ol resulted in a mixture of octanal, octanoic acid and octyl octanoate as major products (Figure 6-6). Traces of octyl ether were also found among the products. A parameter study revealed that reasonably good octanal selectivity can be achieved only at low conversions (Table 6-3). The influence of reaction conditions on the rate and octanal selectivity is illustrated by two typical examples in Figure 6-7 and Figure 6-8. Increasing the temperature from 80 to 140 °C reduced the octanal selectivity to about one-half, though the octan-1-ol conversion was only 12% at 140 °C (Figure 6-7). Above 120 °C the major product was the acid, not the aldehyde. Similar, but less pronounced effects on the conversion rate and selectivity were observed, when the space time or the oxygen concentration in the feed were increased (not shown here). The only exception was the variation of the total pressure in the system (Figure 6-8). Though the alcohol conversion increased with increasing pressure, the aldehyde selectivity slightly increased.

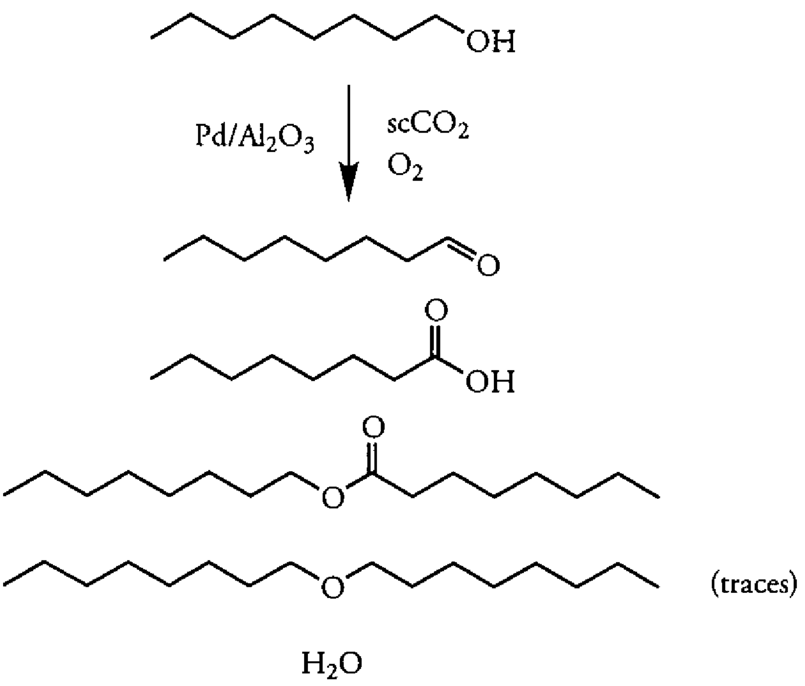


Fig. 6-6: Products formed in the oxidation of octan-1-ol.

Table 6-3: Oxidation of octan-1-ol to octanal. Conditions: 5 g 0.5 wt% Pd/alumina, 3 mol% octan-1-ol, 6 mol% O_2, 91 mol% CO_2, 110 bar

T °C	W/F g h mol^{-1}	Conv. %	Sel. %
80	1.02	3.3	73
140	1.02	10.5	38
140	2.71	22.0	27

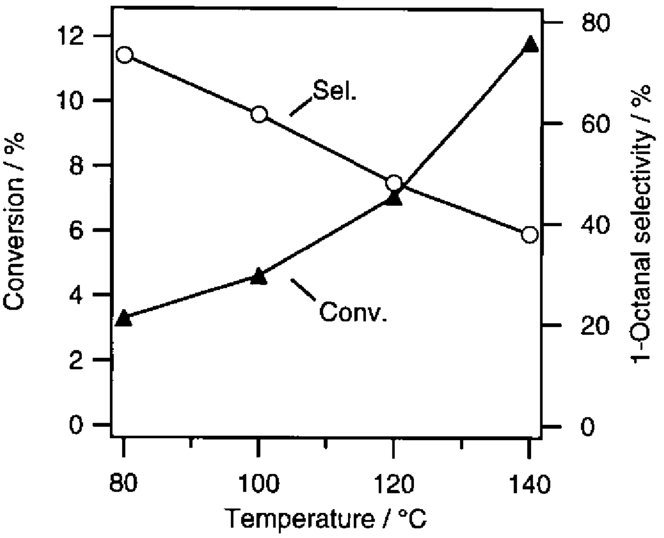


Fig. 6-7: Influence of temperature on octan-1-ol conversion and octanal selectivity. Conditions: 110 bar, 6 mol% O_2, 3 mol% octan-1-ol, 91 mol% CO_2, 5 g 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}.

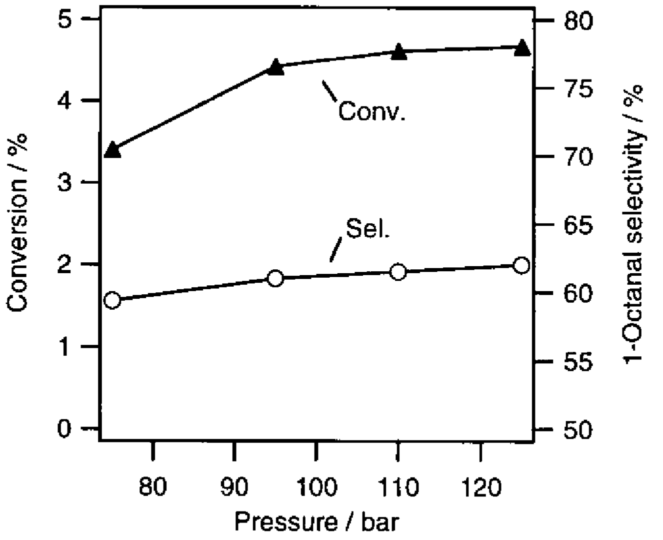


Fig. 6-8: Dependence of octan-1-ol conversion and octanal selectivity on the total pressure. Conditions: 100 °C, 6 mol% O_2, 3 mol% octan-1-ol, 91 mol% CO_2, 5 g 0.5% Pd/alumina, W/F = 1.02 g h mol^{-1}.

It seems that in this reaction the selectivity to the aldehyde intermediate is primarily determined by the alcohol conversion. This correlation is illustrated in Figure 6-9 by all data obtained in a broad range of reaction conditions. The dashed hyperbolic curve reflects the limited potential of the catalyst (Pd/alumina) and solvent ($scCO_2$) for the partial oxidation of octan-1-ol.

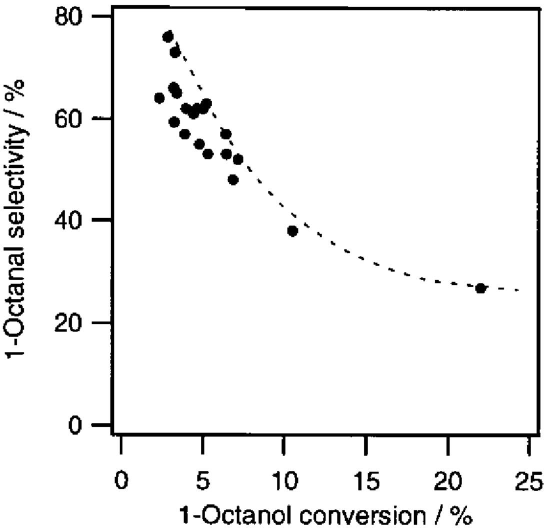


Fig. 6-9: Dependence of octanal selectivity on octan-1-ol conversion. Conditions: 80–140 °C, 75–125 bar, 5 g 0.5% Pd/alumina, W/F = 0.68–2.71 g h mol^{-1}, 3–10 mol% octan-1-ol, 1.5–10 mol% O_2, rest CO_2.

6.4.3 Phase behavior

The phase behavior of the system under reaction conditions was investigated in a magnetically stirred high pressure view cell. Measurements were carried out along the bubble-point phase boundary of the gas-liquid equilibrium in the temperature region of the catalytic experiments. Figure 6-10 shows typical interlaced video images in the view cell under reaction conditions: a small alcohol-rich liquid phase at the bottom of the reactor is topped by a CO_2-rich sc phase.

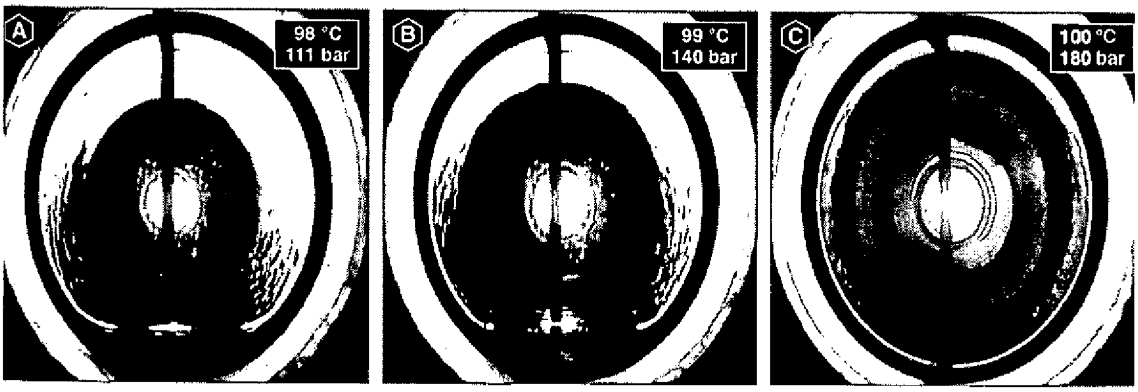


Fig. 6-10: Interlaced video images of the view cell under reaction conditions (5 mol% octan-2-ol, 2.5 mol% O_2-N_2 mixture, 92.5 mol% CO_2), showing a two-phase equilibrium of a liquid octan-2-ol-rich phase and a "sc" CO_2-rich phase at 100 °C. The amount of liquid phase decreases with increasing pressure. The vertical line is the thermocouple and at the bottom of the reactor the liquid phase is clearly visible. The round bright spot at the opposite end of the cell is the sapphire window used for illumination. In the middle of the reactor at the bottom lies the magnetic stirrer.

The results of the phase behavior experiments are shown in Figure 6-11. The phase behavior of the reaction system under conditions of the oxidation reaction was found to be parallel to that of the octanol - CO_2 system [294]. This binary mixture shows a type II behavior [22], according to the classification of Scott and van Konynenburg [295]. That is, the liquid-liquid immiscibility is limited to low temperatures, not interfering with the gas-liquid critical line of the mixture. Addition of 2.5 mol% nitrogen-oxygen mixture to the octanol - CO_2 system resulted in a shift of the gas-liquid phase boundary to higher pressures by about 20 bar.

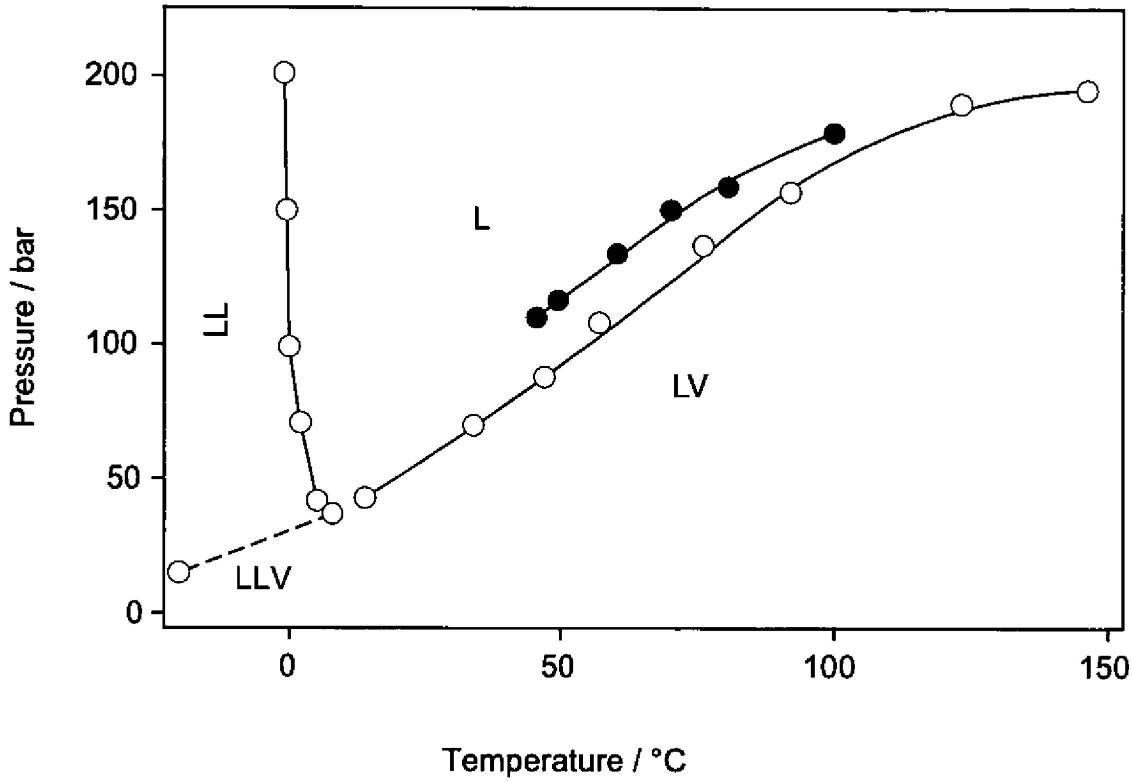


Fig. 6-11: Isoplethic bubble-point gas-liquid phase boundary of the ternary mixture CO_2/octan-2-ol/air (●)compared with the isoplethic phase boundaries of the CO_2/octan-2-ol binary mixture (○) (6.3 mol% octan-2-ol in CO_2, data taken from Ref. [294]). L: one liquid region; LL: two partially miscible liquid phases; LV: liquid-vapor coexistence region; LLV: line of coexistence of two partially miscible liquid phases with a common vapor phase. Note that the region of liquid-vapor coexistence is limited by the dew-point gas-liquid phase-boundary at low pressures (not drawn).

6.5 Discussion

6.5.1 Oxidation of Alcohols in $scCO_2$ - Scope and Limitation

The model studies with octan-1-ol and octan-2-ol demonstrate that the Pd-catalyzed aerobic oxidation in $scCO_2$ is limited to the transformation of secondary alcohols to ketones. This type of reaction is fast and highly selective. For example, 46% octan-2-one yield was obtained at only 40 s residence time and the selectivity was almost 100% (Table 6-2). No catalyst deactivation or metal leaching was observed over a time-on-stream period of 110 h. Optimization of the reaction conditions and catalyst has not been attempted yet, still, the studies indicate that the selectivity to ketone is very high and independent of alcohol conversion. A comparison with the literature data in Table 6-4 indicates that the selectivity in $scCO_2$ is outstanding.

Table 6-4: Oxidation of octyl alcohols to carbonyl compounds (octanal, octan-2-one and octan-3-one) at atmospheric pressure

Alcohol	Oxidant	T °C	Catalyst	Solvent	Operation	React. time /h	Yield %	Sel. %	Ref.
octan-1-ol	air	340	Au	-	continuous	-	83	92	[296]
octan-1-ol	no [a]	265-300	Cu/MgO	-	continuous	-	58	99	[297]
octan-1-ol	oxygen	20	Pt	ethyl acetate	batch	20	21	-	[251]
octan-1-ol	no [a]	250-300	CuO	-	continuous	-	98	-	[298]
octan-1-ol	no [a]	450	Cu-Zn-Bi	-	continuous	-	94	95	[299]
octan-2-ol	no [a]	300-325	Cu chromite	no solvent	batch	3.8	37	-	[293]
octan-2-ol	oxygen	20	Pt	*n*-heptane	batch	96	80	92	[249]
octan-2-ol	oxygen	60	Ru-Co-hydrotalcite	toluene	batch	2	97	97	[300]
octan-3-ol	no [a]	174	Raney Ni	no solvent	batch	15	83	92	[230]

[a] dehydrogenation without oxidant

Unfortunately, no fair comparison of the reaction rates is possible due to the strikingly different reaction conditions applied (temperature, reactor operation mode). On the basis of the comparative experiments in nitrogen and CO_2 (Table 6-1) we can conclude that dense CO_2 has a remarkable positive solvent effect on the oxidation rate.

Aerobic oxidation of primary alcohols to aldehydes in $scCO_2$ is non-selective. At low conversion the aldehyde is the major product, but with increasing conversion the corresponding acid and ester (formed from the reactant and product) become the dominant products (Figure 6-7 and 7; Table 6-3). Interestingly, a similar behavior was observed in the Pt-catalyzed aerobic oxidation of 1-dodecanol in water [237, 247]. The initial high selectivity to aldehyde was diminished with increasing conversion due to rapid hydration of the aldehyde, followed by dehydrogenation of the geminal diol to the corresponding carboxylic acid. The similar selectivity patterns obtained in the oxidation of primary aliphatic alcohols in water and in $scCO_2$ indicate that - at least in this respect - the solvent has no significant influence on the reactions occurring on the metal surface. Apparently, the presence of co-product water on the metal surface is sufficient for the rapid hydration of aldehyde intermediate, as shown in Figure 6-12. Water regenerates after dehydrogenation to acid, and ester formation with the reactant alcohol increases further the amount of water on the catalyst surface available for hydration. Note that deactivated carbonyl compounds, e.g. aromatic aldehydes and particularly ketones, hydrate only to a negligible extent.

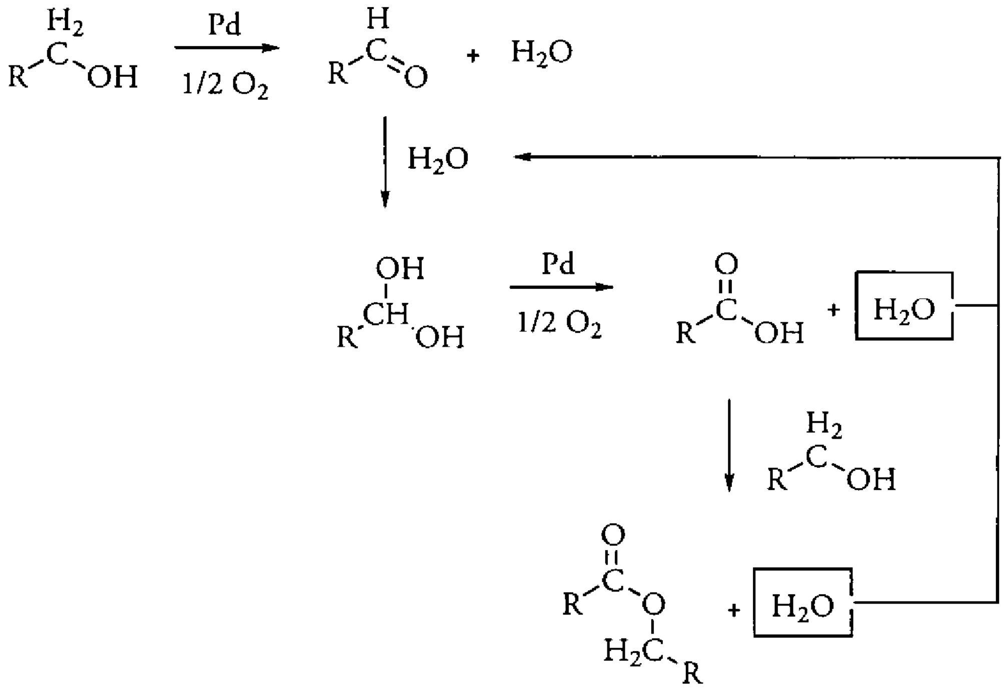


Fig. 6-12: Formation of acid and ester byproducts during oxidation of octan-1-ol.

Table 6-4 lists the characteristic features of various heterogeneous octanol oxidations with oxygen reported in the literature. The data show that the highest yields (up to 98%) to octanal could be achieved by copper-catalyzed anaerobic dehydrogenation at elevated temperatures [298]. Under these conditions water is absent and further oxidation is minor.

6.5.2 Oxidation of Octan-2-ol - Role of Phase Composition and Over-Oxidation of Pd

For the interpretation of the rate of octan-2-ol oxidation, two important points have to be discussed: the role of density and phase composition of the reaction mixture, and the effect of surface oxygen concentration.

The phase behavior studies have revealed that the reaction mixture consists of two phases over the whole temperature and pressure range investigated: a octan-2-ol-rich liquid phase and a CO_2-rich sc phase. Changes in the composition of these phases can be interpreted as follows:

(i) The solubility of octan-2-ol in CO_2 depends on the density of the mixture [47]. Because at standard reaction conditions (120 °C and 95 bar) the density of CO_2 (0.16 g ml^{-1}) is three times lower than the critical density of CO_2 (0.47 g ml^{-1}), the alcohol solubility is relatively low, which explains the presence of a octan-2-ol-rich liquid phase in the whole range of conditions applied. Parallel to the effect of temperature and pressure on the density of the CO_2-rich phase, the solubility of octan-2-ol increases with increasing total pressure and decreasing temperature. Isobaric addition of oxygen results in a decrease of density of the CO_2-rich phase, and thus diminishes the solubility of octan-2-ol.

(ii) The solubility of oxygen in the octanol-rich phase increases with increasing total pressure and oxygen partial pressure, and with decreasing temperature.

The phase behavior of the ternary system containing oxygen (nitrogen) shows a similar characteristic along the isoplethic gas/liquid bubble-point phase boundary compared to the binary system octan-2-ol:CO_2. Addition of oxygen (and nitrogen) results in a shift of the mentioned line to higher pressures. The change of composition of the two phases influences the reaction. Increasing oxygen concentration in the liquid phase leads to higher surface oxygen coverage and thus higher rates (yields). These effects can be clearly observed when increasing the total pressure (Figure 6-4) or the oxygen feed concentration at constant pressure (Figure 6-5), but only at low values up to the maxima. The combination of these two effects indicates that it is the liquid phase which is in contact with the catalyst and controls the reaction over the metal surface.

The decline of octan-2-one yield at high oxygen concentrations in the feed (Figure 6-5) is attributed mainly to "over-oxidation" of the metal surface. Over-oxidation is a thoroughly investigated phenomenon in the aerobic oxidation of alcohols over platinum metal catalysts [236, 244, 280, 301]. The basis of this unusual behavior is that the activity of the reduced metal for alcohol oxidation is remarkably higher than that of the oxygen-covered surface. Though oxygen is necessary for the reaction, too high oxygen coverage leads to a drop in the number of reduced surface metal sites available for alcohol adsorption and oxidation, and thus lowers the reaction rate. The correlation presented in Figure 6-5 may formally be described by the following rate Equation 6, where Θ_i represent corresponding surface coverages [237]:

$$r = k \cdot (\Theta_{\mathrm{oxygen}})^m \cdot (\Theta_{\mathrm{alcohol}})^n \qquad (6)$$

Note that changing only one parameter at a time (pressure or oxygen concentration) still does not allow a clear separation of the effects of phase composition and surface oxygen concentration, due to the mutual dependence of the parameters varied. Increasing the total pressure at constant oxygen feed concentration enhances oxygen solubility in the alcohol-rich phase which is in contact with the catalyst surface, and this change can also lead to too high surface oxygen coverage and thus over-oxidation (Figure 6-4). The strikingly different effects of increasing total pressure on the octanone yield when the set of other parameters was varied are also attributed to strong interactions between the parameters, i.e. their complex influence on the density and solubilizing power of the liquid phase, and on the oxygen coverage on Pd.

6.6 Conclusions

Partial oxidation of secondary alcohols to ketones in $scCO_2$ with molecular oxygen has distinct advantages compared to conventional processes. The selectivity of the reaction in dense CO_2 is outstanding, and the rate of conversion is remarkably higher than that of vapor phase oxidation under similar conditions, in the presence of a nitrogen diluent. Beside the higher rate, the absence of any significant catalyst deactivation is also attributed to the presence of $scCO_2$ as solvent. Furthermore, application of the non-flammable CO_2 is safer and provides easier product separation compared to liquid phase oxidations in organic solvents.

Our study also demonstrates that interpretation of the catalytic performance in dense (sc) CO_2 requires a careful analysis of the phase behavior of the system under reaction conditions, a matter which is often ignored in the pertinent literature.

Chapter 7

Continuous Oxidation of Benzyl Alcohol in Supercritical Carbon Dioxide

7.1 Abstract

Supercritical (sc, dense) carbon dioxide has been applied as solvent for the partial oxidation of benzyl alcohol with molecular oxygen in a fixed-bed reactor. High rate and good selectivity to benzaldehyde (93–97%) has been achieved with 0.5 wt% Pd/alumina or 0.5 wt% Pd/C, at around 100 °C and 100 bar, using only moderate excess of oxygen. The byproduct benzoic acid has an autocatalytic effect on the hydration of benzaldehyde, and the subsequent oxidative dehydrogenation leads to benzoic acid, and benzyl benzoate by esterification. Promotion of Pd by Pb improves the selectivity. No catalyst deactivation or metal leaching have been observed. The method provides reasonable yields at much lower temperature than that applied in conventional gas phase oxidation, showing a potential for the synthesis of thermolabile, water-insoluble aromatic aldehydes.

7.2 Introduction

Aerobic oxidation of alcohols to carbonyl compounds or carboxylic acids over Pt metals or Au has been thoroughly investigated in the past decades [233, 236, 237, 281, 302]. The reactions are generally carried out batchwise below 100 °C. The mild conditions and the aqueous medium are particularly well suited for the transformation of polyols and carbohydrates. Oxidation of water-insoluble alcohols may be carried out in the presence of a detergent [247], which additive, however, raises difficulties during work-up. Application of an organic solvent has also been proposed [249] but the explosion risk may hinder any practical application.

We have recently reported the application of $scCO_2$ (T_c = 31.1 °C, p_c = 73.8 bar) as a substitute for organic solvents in liquid phase oxidation of alcohols [187]. Dense, $scCO_2$ has a fair and tunable solubility for weakly polar, water-insoluble alcohols as well as for oxygen. It is a relatively inert and nonflammable solvent with high heat capacity. Despite of these and some other advantages, the potential of $scCO_2$ as solvent in partial oxidations is barely explored [5, 12, 20, 62, 288]. Partial oxidation of ethanol [143] in $scCO_2$ over Pt/TiO_2, as an alternative to gas phase oxidation, has already been attempted though the selectivity to acetaldehyde did not exceed 30%. We have also found that the Pt-metal catalyzed aerobic oxidation of primary alcohols to (activated) aldehydes in $scCO_2$ is non-selective, similarly to the oxidation in aqueous phase [187].

Here we report the oxidation of an aromatic alcohol with molecular oxygen in $scCO_2$ in a continuous fixed-bed reactor. The oxidation of benzyl alcohol to benzaldehyde has been chosen as a model reaction for the synthesis of (deactivated) aromatic aldehydes important in the field of fine and specialty chemicals.

7.3 Methods

The reactions have been performed isothermally in a tubular down-stream flow reactor with an inner diameter of 13 mm and 38 ml volume. Benzyl alcohol was dosed by a Gilson 305 piston pump. Oxygen was supplied to the reactor using a six-port valve dosing 0.05 ml pulses at high pressure and constant frequency. The constant pressure in the system was maintained by a pressure regulator with CO_2. The total gas flow was controlled at the vent.

The various supported Pd, Pt and Ru catalysts and their characteristics are listed in Table 7-1. The reactions under standard conditions have been carried out with 5 g 0.5 wt% Pd/alumina (Engelhard 4586; cylindrical, 3.2 mm length and diameter), corresponding to a catalyst bed length of 5 cm and a space time related quantity W/F of 1.02 g h mol^{-1}, where W is catalyst weight and F the total molar flowrate. Glass beads (0.2 cm, 5 cm bed length) have been placed above the catalyst. The catalyst was reduced *in situ* by hydrogen at 100 °C for 2 h prior to the measurements. Standard conditions for the parameter study were 95 bar, 80 °C and the feed flow consisted of 5 mol% benzyl alcohol, 2.5 mol% oxygen and 92.5 mol% CO_2. This molar composition remained the same at all pressures. The liquid products were separated from CO_2 and analyzed by GC and GC-MS.

Table 7-1: Comparison of structural and catalytic properties Pd, Pt and Ru catalysts (D = metal dispersion, S_{BET} = surface area). Conditions: 5 g catalyst, standard conditions

Catalyst	S_{BET} m^{2}g^{-1}	D %	Conv. %	$S_{ald.}$ %	S_{acid} %	S_{ester} %
0.5 wt% Pd/alumina, Engelhard 5077	89	24 [a]	13.5	95.6	0.1	4.8
0.5 wt% Pd/alumina, Engelhard 4586	96	29 [a]	8.6	93.0	1.5	5.5
0.5 wt% Pd/alumina, 0.05 wt% Pb promoted	-	-	7.9	95.5	0.7	3.8
0.5 wt% Pd/carbon, Engelhard 5156	1220	17 [b]	7.4	97.1	0.3	2.6
0.5 wt% Pt/alumina, Engelhard 1679	81	36 [a]	0.3	100 [c]	-	-
0.5 wt% Pt/alumina, Aldrich 20,601-6	103	43 [a]	0.4	100 [c]	-	-
0.5 wt% Ru/alumina, Engelhard 4871	96	7 [a]	0.4	100 [c]	-	-

[a] determined by H_2-chemisorption

[b] determined by XRD line broadening

[c] aldehyde is the only detectable product at this low conversion

Promotion of the 0.5 wt% Pd/alumina catalyst by lead was carried out by impregnation with an aqueous lead acetate solution, resulting in 0.05 wt% Pb content after drying in *vacuo* at room temperature and *in situ* reduction with gaseous H_2.

BET surface areas (S_{BET}) were obtained by physisorption of N_2 at 77 K using a Micromeritics ASAP 2000 instrument. Prior to measurement, the samples were outgassed to 0.1 Pa at 150 °C. Metal dispersion was determined by hydrogen chemisorption at 35 °C on a Micromeritics ASAP 2010C instrument. The samples were prereduced in H_2 at 350 °C and then evacuated at 0.1 Pa. The metal dispersion of a 0.5 wt% Pd/C (Engelhard 5156) was determined from X-ray line-broadening on a D-5000 Siemens diffractometer.

7.4 Results and Discussion

7.4.1 General Features

Oxidation of benzyl alcohol over the 0.5 wt% Pd/alumina catalyst afforded benzaldehyde as the major product with over 90% selectivity. Conversion and selectivities reached steady-state within 3 h time-on-stream as illustrated in Figure 7-1. The two byproducts benzoic acid and benzyl benzoate formed by further oxidation, and subsequent esterification with the reactant alcohol, respectively (Figure 7-2). It is assumed that direct oxidation of the relatively stable (deactivated) benzaldehyde is slow and barely contributes to the formation of benzoic acid. The main route is the acid (or base) catalyzed hydration with the co-product water, followed by the oxidative dehydrogenation of the hydrate [303]. The autocatalytic effect of the byproduct benzoic acid (pK_a = 4.2) resulted in a loss of the overall selectivity with time-on-stream as seen in Figure 7-1.

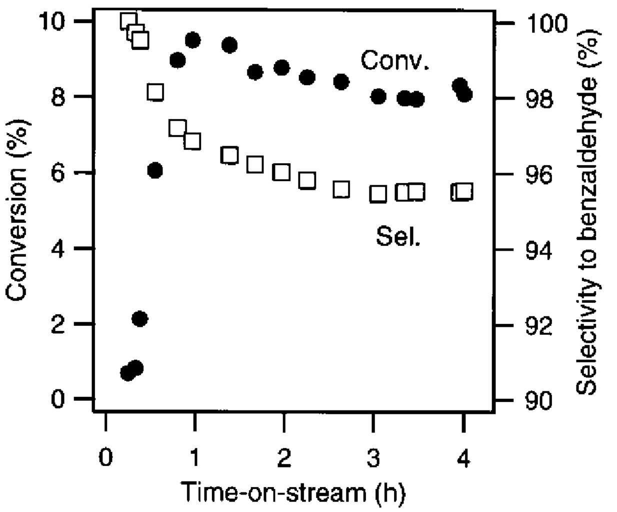


Fig. 7-1: Initial transient behavior during oxidation of benzyl alcohol; 5 g 0.5 wt% Pd/alumina promoted by 0.05 wt% Pb, otherwise standard conditions.

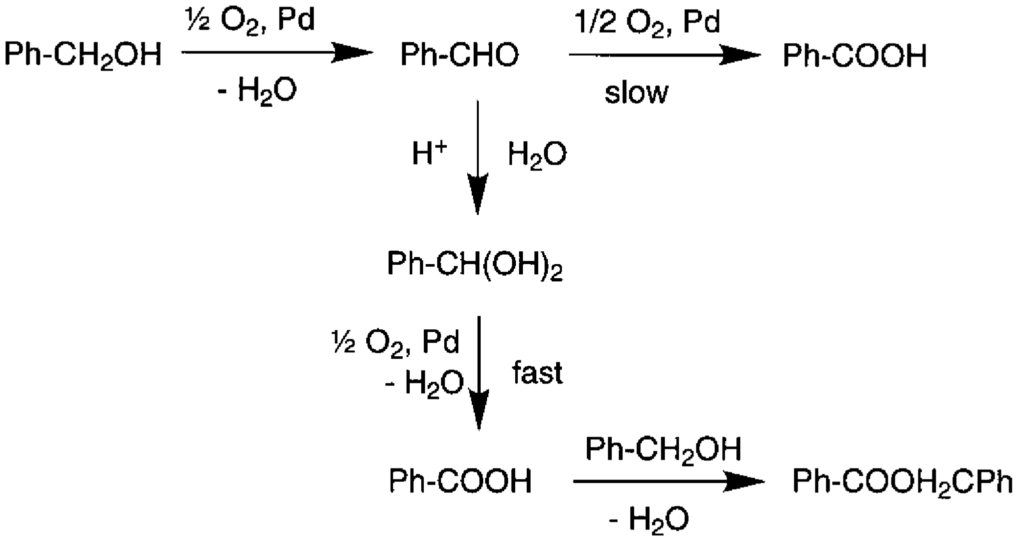


Fig. 7-2: Products formed in the oxidation of benzyl alcohol.

The Pt- or Pd-catalyzed aerobic oxidation of alcohols in aqueous medium is frequently accompanied by catalyst deactivation, and even leaching of the active component may be important [233, 236, 237, 281]. Working in $scCO_2$ we did not observe any significant deactivation or metal leaching. For example, the performance of the 0.5 wt% Pd/alumina catalyst was monitored for a period of 75 h time-on-stream (net working time). The parameters were varied in a broad range and the catalyst performance was tested repeatedly at 60 °C, 95 bar and W/F = 1.02 g h mol^{-1}. Under these conditions the conversion of benzyl alcohol remained in the range 4.8 ± 0.4% and no loss of activity was observed.

7.4.2 Influence of Reaction Parameters

The influence of some reaction parameters was investigated at relatively low conversions in order to minimize the temperature gradient in the catalyst bed. Raising temperature increased the conversion but lowered the aldehyde selectivity (Figure 7-3). Further oxidation was especially important at temperatures above 100 °C. For example, 35% conversion was obtained at 130 °C under otherwise standard conditions, and the selectivities to aldehyde, acid and ester were 87.6%, 2.4% and 10%, respectively

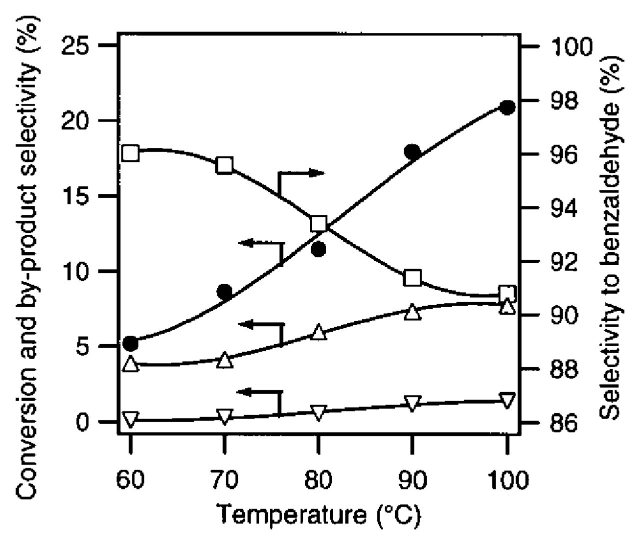


Fig. 7-3: Effect of temperature on the reaction rate and product distribution; conversion (●), selectivities to aldehyde (□), acid (▽), and ester (△); standard conditions.

The conversion of benzyl alcohol was linearly dependent on the space time related quantity W/F and the influence of this parameter on aldehyde selectivity was minor (Figure 7-4).

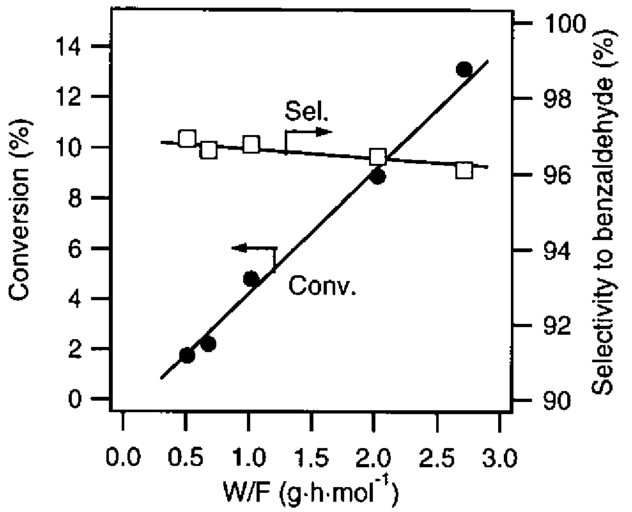


Fig. 7-4: Conversion and benzaldehyde selectivity as a function of the space time related parameter W/F; 60 °C, otherwise standard conditions.

The effect of oxygen concentration in the feed on the reaction rate is characterized by saturation-type curves (Figure 7-5). At low oxygen concentration the rate drops to zero, indicating that the contribution of anaerobic oxidation of benzyl alcohol is negligible at this temperature. For comparison, dehydrogenation of benzyl alcohol over CuO required at least 250 °C to achieve good yields to benzaldehyde [298]. The decrease of benzaldehyde selectivity with increasing amount of oxygen in the feed was pronounced only at temperatures around 80 °C or higher. No catalyst over-oxidation (i.e. a drop in rate due to too high oxygen coverage on the metal surface [280, 301]) was observed even at 7.5% O_2 in the feed, corresponding to 300% of the stoichiometric ratio for quantitative transformation of benzyl alcohol to benzaldehyde. The likely explanation is the facile oxidation of benzyl alcohol, and the absence of strongly adsorbing byproducts. As concerns the latter point, the good solubilizing power of $scCO_2$ may be crucial in removing byproducts from the metal surface.

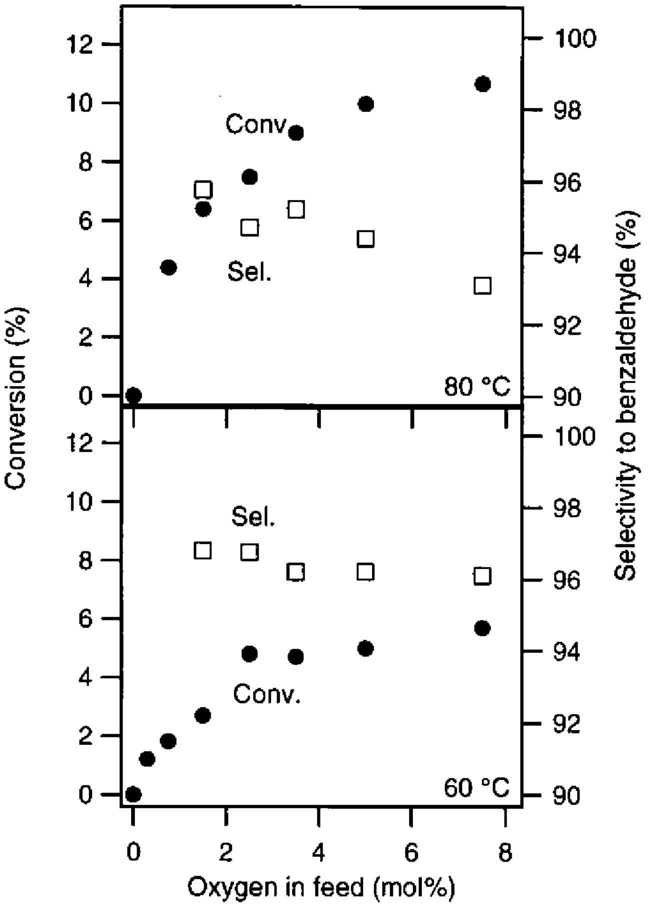


Fig. 7-5: Effect of oxygen concentration in the feed. Top: at 80 °C, bottom: at 60 °C; otherwise standard conditions.

The influence of total pressure on the rate and selectivity of oxidation is rather complex and strongly depends on the set of other parameters, such as the temperature (Figure 7-6). The highest conversion was achieved at 100–115 bar and the aldehyde selectivity was either constant or even increased with raising pressure. An explanation of these effects would require the knowledge of the phase behavior under reaction conditions but no data are available in the literature on the CO_2 - O_2 - benzyl alcohol - benzaldehyde system.

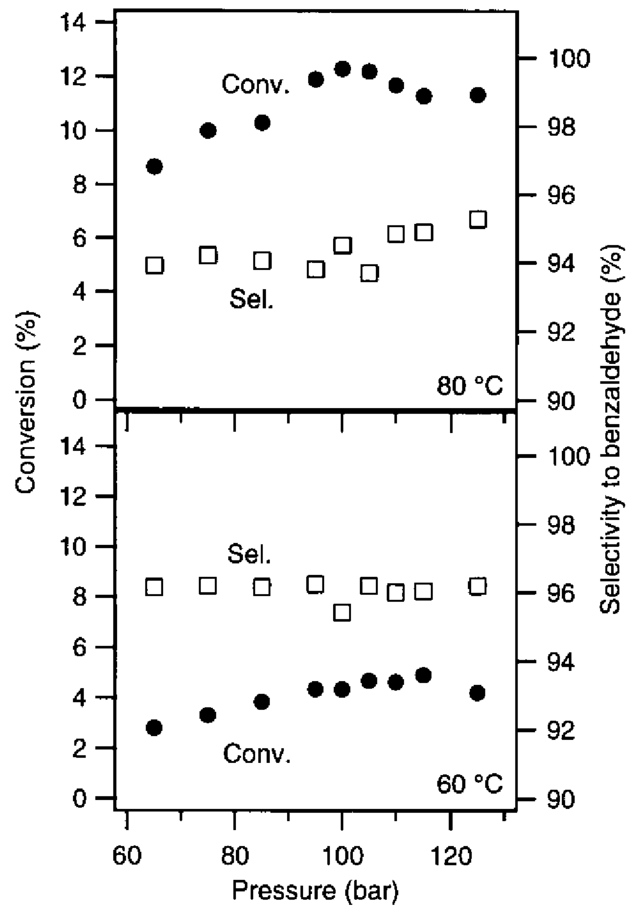


Fig. 7-6: Influence of total pressure on the catalyst performance. Top: at 80 °C, bottom: at 60 °C; otherwise standard conditions.

7.4.3 Comparison of Pt Group Metal Catalysts and the Influence of Promotion

A comparison of some supported Pd, Pt and Ru catalysts revealed that Pd is far the best catalyst for benzyl alcohol oxidation in $scCO_2$ (Table 7-1). The nature of support (alumina or carbon) and the Pd dispersion (17–29%) are of secondary importance: the aldehyde selectivity was always in the range 93–97% and the highest difference in conversion was less than a factor of 2.

It was attempted to improve the performance of palladium by promotion with lead. When using a 0.05 wt% Pb - 0.5 wt% Pd/alumina catalyst the selectivity to byproducts decreased from 7 to 4.5%, with only a small drop in activity (Table 7-1). The assumption that 1 adsorbed Pb atom occupies 2 surface Pd atoms [304], and all promoter atoms are located on the Pd surface, leads to an upper limit of 27% surface coverage of Pd by the lead promoter.

We have carried out some non-isothermal experiments involving a significant temperature gradient in the catalyst bed. These experiments confirmed that conversion of benzyl alcohol can be increased without any loss in aldehyde selectivity. For example, 96% benzaldehyde selectivity was achieved at 56% conversion with the 0.5 wt% Pd/alumina catalyst at around 100–120 °C (other conditions: 120 bar, W/F = 3.79 g h mol^{-1},10 mol% O_2, 5 mol% alcohol). The limit to further increasing the conversion in this highly exothermic reaction was the insufficient rate of heat transport in the reactor used.

To our knowledge, continuous vapour phase oxidation of benzyl alcohol on a broad range of different catalysts afforded at best 96% selectivity to benzaldehyde. Perovskite oxides [305-307] and Au [296] provided this selectivity at 48–50% conversion, at atmospheric pressure and ca. 350-450 °C. Obviously, the Pd-catalyzed oxidation in $scCO_2$, at high pressure but relatively low temperature, has a potential in the synthesis of non-volatile or thermally labile aromatic aldehydes important in fine chemistry. The major advantage of oxidation in dense CO_2, compared to liquid phase oxidation in acetic acid [251] or *n*-heptane [249], is the elimination of the explosion risk.

7.5 Conclusions

We have shown that only Pd has good activity and selectivity in the aerobic oxidation of benzyl alcohol to benzaldehyde in $scCO_2$. A 0.5 wt% Pd/alumina catalyst has been stable without any sign of metal leaching or deactivation within 75 h time-on-stream. Though the conditions have not yet been optimized, the method offers clear advantages compared to liquid phase, or high temperature gas phase, oxidation processes in the synthesis of aromatic aldehydes.

Chapter 8

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Final Remarks

Sc fluids are a real alternative for conventional organic solvents and afford improved reaction performance in the three heterogeneously catalyzed systems studied.

Amination of diols in $scNH_3$ is an efficient method for the production of diamines though the yield is strongly controlled by the chemical structure of the reactant. High selectivities of diamines with the functional groups in α- and γ-positions can only be obtained if dehydration is not possible. $ScNH_3$ suppresses dimerization and oligomerization type side reactions and reduces mass transfer resistances within the heterogeneous catalytic system. The potential of the method has not been investigated yet in the simpler amination of monofunctional alcohols and in the amination of the more reactive carbonyl compounds (reductive alkylation). The efficiency of the system which requires quite long times to reach steady-state conditions and allows only a few measurements per day could be increased. A further improvement is expected by optimizing the catalyst composition and the preparation procedure.

Continuous epoxidation of propylene with *in situ* generated hydrogen peroxide has revealed the selective deactivation of the catalyst and the accompanying shift in activity from olefin epoxidation to alcohol oxidation. Reaction rates are higher in presence of $scCO_2$ than with nitrogen as diluant, probably due to the reduction of mass transfer resistances. The initial epoxide selectivity is excellent, but the catalyst is not stable. The presence of hydrogen and oxygen in the reaction mixture is a severe restriction to any practical application. The prospective of this widely investigated method is, therefore, questionable. Many other promising processes for this very important reaction are currently under investigation. Among them, the gold catalyzed epoxidation in the gas phase has been improved steadily. That method is limited by the deactivation of the catalyst by formation of carbonaceous deposits. Sc fluids have the potential to solubilize and extract (*in situ*) the coke precursors. The low reaction temperature (40 °C) of this method would be ideal for $scCO_2$: At this low temperature,

$scCO_2$ is very dense and it solubilizes high quantities of the non-polar propylene and the gases hydrogen and oxygen.

Platinum metal catalyzed aerobic oxidation of alcohols in $scCO_2$ is an efficient method for water-insoluble non-polar alcohols. Ketones and deactivated aldehydes can be prepared with high yield and selectivity. The reaction rate is higher than in vapor phase oxidation and the catalyst exhibits better stability. Various reaction parameters have been studied though the reaction has not been optimized yet. Reasonable catalytic activity already at low temperature (30–40 °C) would allow higher concentrations of alcohols and oxygen in $scCO_2$, and - approaching the critical point of CO_2 - tunability would become a valuable instrument. It is hoped that future development of more efficient noble metal based bimetallic catalysts can afford high oxidation rates at close to ambient temperature, and helps utilize the advantages of $scCO_2$ as a solvent.

List of Publications

The pertinent chapters which are the source of the publications are given in brackets.

Publications

Cobalt-Catalyzed Amination of 1,3-Cyclohexanediol and 2,4-Pentanediol in Supercritical Ammonia, Jenzer G, Mallat T, Baiker A, Catal. Lett. 61: (3-4) 111-114 (1999) (Chapter 3)

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Partial Oxidation of Alcohols in Supercritical Carbon Dioxide, G. Jenzer, D. Sueur, T. Mallat and A. Baiker, Chem. Commun. (2000) 2247. (Chapter 5)

Palladium-Catalyzed Oxidation of Octyl Alcohols in "Supercritical" Carbon Dioxide, T. Mallat, G. Jenzer, M. Schneider, R. Wandeler and A. Baiker, J. Catal. (in press). (Chapter 6)

Continuous Oxidation of Benzyl Alcohol in "Supercritical" Carbon Dioxide, G. Jenzer, T. Mallat and A. Baiker, Catal. Lett. (in press). (Chapter 7)

Selective C-and O-Methylation of Catechol in Gas Phase over Modified γ-Aluminas, L. Kiwi-Minsker, G. Jenzer, L. Pliasova, A. Renken, Stud. Surf. Sci. Catal. 121: 159-164 (1999).

Conference Contributions

Continuous Oxidation of Alcohols to Carbonyl Compounds in Supercritical Carbon Dioxide, T. Mallat, G. Jenzer, M. Schneider, R. Wandeler and A.

Baiker, 5th European Congress on Catalysis, Limerick September (2001), planned.

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Gas-Phase Methylation of Catechol over Modified γ-Aluminas, L. Kiwi-Minsker, G. Jenzer, R. Doepper, A. Renken, EuropaCat-3, Krakow September (1997), Vol 2, 771.

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