CHAPTER 1

PREPARATION OF SUPPORTED METAL CATALYSTS

Guido Mul¹ and Jacob A. Moulijn²

¹Photocatalytic Synthesis Group, IMPACT Institute, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

²Reactor and Catalysis Engineering Group, Delft ChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

1.1 Introduction

In the chemical industry, the majority of the reactions take place at the surfaces of heterogeneous catalysts. The efficiency of a heterogeneous catalytic process is thus largely determined by the quality of the catalysts used, i.e. the exposed surface area of active phase and the stability. It is instructive to show the correlation between the exposed (specific) surface area, and the particle size of the catalytic material. Let us suppose that the active phase (density $\rho$ in kg/m$^3$) consists of uniform spherical particles. The specific area can be calculated as follows:

Volume of one particle, $V = \frac{1}{6} \pi d^3$ (m$^3$)
Weight of one particle, $W = \frac{1}{6} \rho \pi d^3$ (kg)
Surface area of one particle, $S_p = \pi d^2$ (m$^2$)
Specific surface area, $S_A = \frac{S_p}{W} = \frac{\pi d^2}{(\rho \frac{1}{6} \pi d^3)} = \frac{6}{\rho d}$ (m$^2$/kg)

Figure 1.1 shows a plot of this calculation. As an example, nickel has been chosen. It is obvious that only at low values of the particle sizes
(1–10 nm) are reasonable surface areas obtained. It is impossible to apply such small particles in reactors, and therefore support bodies are applied. Catalyst supports are in general porous materials, to allow a high loading of highly dispersed metal particles, whereas the particles of the active phase need to be synthesized in such a way that they are as small as possible.

Despite the observations made above, many authors of papers in catalysis journals seem to ignore the importance of the preparation procedure used for the eventual catalytic results they obtain. The procedure used is usually described in very general terms, and often conditions are used that appear to have no fundamental reasoning, e.g. the used catalyst precursor, calcination conditions, pH of precursor solution (often not mentioned), temperature of solutions, etc. Fortunately, other researchers take the preparation of catalysts seriously and many publications and textbooks exist that discuss the preparation of catalysts on a scientific basis.\textsuperscript{1} Of particular note is

![Figure 1.1 Specific surface area as a function of crystalline size of Ni (\(\rho = 8900 \text{ kg/m}^3\)).](image)
the group of Geus (and continued in the group of de Jong) at the Utrecht University in The Netherlands,\textsuperscript{1,2} where years of research on the preparation of catalysts has lead to a more scientific basis for catalyst preparation.

Several procedures exist in order to attach the active phase to the support, i.e. to prepare supported catalysts. In the catalyst manufacturing industry, impregnation is usually employed, for practical and economic reasons. Impregnation allows the use of pre-shaped or structured supports. Preparation of catalysts starting from these commercially available supports is attractive because a support with optimal properties can be selected.

From a chemical point of view impregnation and precipitation represent two extreme cases:

- Impregnation is often related to ion-exchange, where the interaction with the support is dominant;
- Precipitation in principle is a crystallization process and can occur in the bulk of the liquid or on a relatively inert surface. Here, particles of active phase can be kept small because the support particles act as crystallization nuclei for the active phase precursor.

In this chapter the most common techniques for preparation of supported metal catalysts will be discussed, including impregnation, co-precipitation, homogeneous deposition precipitation, and precipitation at constant pH. In addition, recently introduced novel technologies involving organic functionalization of supports in combination with deposition of surfactant functionalized metal particles,\textsuperscript{3} as well as photodeposition, usually applied in the rapidly emerging field of photocatalysis,\textsuperscript{4,5} will be discussed. In principle, these techniques can all be used to attach the active phase to supports, some preferably in the form of a powder, others in the form of a pre-shaped body. First, a general description of the techniques will be presented. Then, the techniques are illustrated by specific examples of the preparation of metallic catalysts. In view of the expertise of the authors of this chapter, Pt, Au, and Ag as the active metal phases will be emphasized. The last two examples are focused on the
production of propene oxide and, as a consequence, they refer to an unresolved research issue. Furthermore, for Au catalysis we have included potential applications in photocatalytic conversions.6

1.2 General Description of Preparation Methods

1.2.1 Impregnation

Impregnation is a preparation technique in which a solution of the precursor of the active phase is brought into contact with the support. Two methodologies exist. In dry impregnation, also referred to as “pore volume impregnation”, just enough liquid (solution of the precursors) is used to fill the pore volume of the support. In wet impregnation the support is dipped into an excess quantity of solution containing the precursor(s) of the active phase. Wet impregnation is sometimes also called impregnation in excess of solution (IES).7 In dry impregnation the solubility of the catalyst precursors and the pore volume of the support determine the maximum loading available each time of impregnation. If a high loading is needed, successive impregnations (and heat treatments) may be necessary. When several precursors are present simultaneously in the impregnating solution the impregnation is called “co-impregnation”. In the first step of impregnation three processes occur:

• transport of solute to the pore system of the support bodies;
• diffusion of solute within the pore system;
• uptake of solute by the pore wall.

In the case of wet impregnation, a fourth process is operative, viz. transport of solute to the outer particle surface. Depending on the process conditions, different profiles of the active phase over the support body will be obtained. For instance, depending on the pH, the interaction with the support can be strong or weak, and even repulsion can exist.

Soluble catalyst precursors are fixed to the support either by reaction, exchange with surface OH groups, and/or by adsorption.
In the former case, the concentration (density) of surface OH groups, which depend on the pre-treatment of the support, is crucial. In the latter case, the surface charge plays an important role. At a pH value of the so-called Point of Zero Charge (PZC) the surface is electrically neutral. At pH values above PZC, the surface is negatively charged, while at pH values below PZC the surface is positively charged (see Figs. 1.2 and 1.3).

For silica this can be illustrated as follows. At pH = 3 the surface is neutral. In a mildly basic environment H$^+$ is removed, and, as a result, the surface is negatively charged. In an acid environment the surface will become protonated. If it is intended to deposit anions onto the carrier surface, the preparation should proceed at pH values below the PZC, whereas if cations are to be deposited, a pH value above that of the PZC is preferred (Fig. 1.2). Table 1.1 gives PZC values for alumina, silica, and a mixture of alumina and silica.

It should be mentioned that the exact PZC values not only depend on the chemical nature of the carrier, but also on its history and the method by which it was prepared. Of course, for the solid
At improper pH values (e.g. pH > 12 for alumina), the carrier itself may be dissolved. It is illustrative to compare the adsorption of \([\text{Pt(NH}_3\text{)}_4]^{2+}\) cations on alumina and silica and experimental results are shown in Fig. 1.4.

These data show that silica adsorbs the Pt-ions much better than alumina. The explanation is as follows. The Pt is introduced as a positive ion, and the charge of silica and alumina will be different: silica has a negative charge already at pH 6 (PZC of silica is about 3), while the alumina surface at this pH is still positively charged. With an increasing pH the amount of Pt precursor adsorbed on silica increases: the surface contains more and more negative sites for Pt attachment. For alumina, Pt containing cations only start to adsorb...
on the surface at pH > 8, while the amount is much less than on silica. Apparently, with silica, a good catalyst can be prepared with [Pt(NH₃)₄]²⁺, while with alumina this appears less feasible. If PtCl₆⁻ had been chosen as the Pt complex, results would have been the other way round. In conclusion, if ion-exchange phenomena dominate the preparation process, [Pt(NH₃)₄]²⁺ is preferred for the preparation of Pt/SiO₂ catalysts and PtCl₆⁻ for alumina-based catalysts. It should be mentioned that the presence of Cl⁻ ions in catalyst formulations is usually undesirable, because it induces metal particle sintering upon calcination, and in several cases poisoning of the catalyst. Extensive washing procedures are needed, which will be further addressed in the case study on the preparation of Au catalysts.

1.2.1.1 Impregnation profiles on pre-shaped catalyst support bodies

For impregnated catalysts a completely uniform profile of the active material over the pre-shaped support particle is not always the optimal profile. It is possible to generate profiles on purpose, and in this way to improve the catalyst performance in specific reactions. Figure 1.5 shows four major types of active-phase distribution in catalyst spheres. The grey regions represent the areas impregnated with the active phase. Type a is a uniform catalyst while the others have a non-uniform active-phase distribution. They are sometimes referred to as “egg-shell”, “egg-white” and “egg-yolk” catalysts, respectively. The optimal profile is determined, among other things, by the reaction kinetics and the mode of catalyst poisoning. For example, an egg-shell catalyst is favorable in the case of a reaction with a positive reaction order, whereas an egg-yolk catalyst is the best choice for reactions with negative orders. When pore-mouth poisoning is dominant it might be attractive to locate the active sites in the interior of the catalyst particles. Another factor is attrition. If attrition is important and if the active phase is expensive (e.g. in the case of precious metals), it might be preferable to place the active phase in the interior of the catalyst particles.

Achieving these distributions can best be discussed by analysis of a practical example. Consider the processes occurring during wet
impregnation of alumina using a solution of $\text{H}_2\text{PtCl}_6$. As previously discussed, the alumina surface interacts with $\text{H}_2\text{PtCl}_6$ by adsorption of $\text{PtCl}_6^{2-}$:

$$\begin{align*}
2 \text{Al(OH)}_2^+ + \text{PtCl}_6^{2-} & \rightarrow \left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Pt} \\
\text{Cl} \\
\text{O} \\
\text{Al} \\
\text{Al}
\end{array} \right]^{4+} + 2 \text{HCl}
\end{align*} \quad (1.1)
$$

The number of surface sites limits the amount of Pt complexes that can be adsorbed. Typically, Pt-$\gamma$-alumina catalysts contain up to 1 wt% Pt. Adsorption is a fast process and in general an egg-shell catalyst will be formed. The addition of a second component to the impregnating solution allows fine-tuning of the catalyst. This is illustrated in Fig. 1.6.
Impregnation of \( \text{H}_2\text{PtCl}_6 \) was carried out in the presence of citric acid, which adsorbs more strongly than \( \text{H}_2\text{PtCl}_6 \) (and HCl). Without the presence of citric acid, an egg-shell type of profile for Pt is obtained (Fig. 1.6(a)). When some citric acid is present, this will be adsorbed on the outer layers of the support body, and the Pt ions will adsorb in a ring at the inside (Fig. 1.6(b)). Higher citric acid concentrations will eventually lead to distribution c. The interaction and profiles obtained using the citrate method, have recently been investigated in detail using magnetic resonance imaging, including spatial distributions within a catalyst support body and the evolution of these distributions in time.\(^9\)

1.2.1.2 Drying

The drying step, which follows the impregnation step, also affects the distribution of the active phase. In drying, the solution in the pores will become oversaturated and precipitation takes place. Because of the large surface area, and associated here with the large number of nuclei, a high dispersion can be realized. In principle, rapid evaporation is favorable because it causes rapid super-saturation, and associated with that, a high dispersion. However, if fast drying is achieved by rapid heating of the wet support bodies, boiling phenomena might result in an inhomogeneous distribution. On the other hand, slow drying in combination with well-crystallizing precursor salts, will yield an egg-shell distribution. This is the result of the crystals formed initially at the pore mouths of the support, initiating migration of the impregnation liquid to the outer surface of the support by capillary forces. It has been shown for various catalysts that the use of less well-crystallizing salts gives a more homogeneous distribution of the active phase over the support body.\(^{10}\) Also the viscosity of the solution plays a role: at higher viscosity the flow rates toward the pore mouth are reduced and a more homogeneous profile results. A related problem arises from the range of pore sizes of the supports. The biggest pores will first empty themselves, the solution accumulating in the smaller pores. A loss of dispersion is the result. Thus, drying is a very critical step and may well determine the quality of the catalyst. Drying in a microwave or freeze-drying is applied occasionally...
because these methods usually lead to more uniform distribution of
the active phase over the particle, or a structured reactor, as will be
discussed in the following section.

1.2.1.3 Preparation of structured catalysts (monoliths)

Recently, the use of monolith reactors also in multiphase applica-
tions has received much attention.11–13 They exhibit high rates and
high selectivity due to the short diffusion paths. They show interest-
ing hydrodynamic behavior. For instance, under industrial
conditions, the flow rates are too high to operate a packed bed
counter-currently, but in a structured reactor, tailored design is pos-
sible that allows counter-current operation. It is remarkable that for
multiphase applications, so-called Taylor flow (the liquid/gas system
flows as a train of liquid slugs separated by gas bubbles with a size
exceeding the diameter of the channels) is the normal regime.11–13
An attractive characteristic of this regime is the very high mass trans-
fer from the gas bubble to the liquid.

Synthesis of catalytic monoliths is far from straightforward.
Nijhuis et al.14 have provided an overview of preparation procedures
for catalytic monoliths. Obtaining a homogeneous metal distribution
is often troublesome. Vergunst14,15 has shown that an appropriate
drying method is crucial in this respect. Monolith catalysts were pre-
pared by wet impregnation of an alumina-washcoated cordierite
monolith with a solution of Ni(NO₃)₂·6H₂O. This was achieved by plac-
ing the monolith in the impregnation solution for 1 h. Subsequently,
the channels were dried. Figure 1.7 shows a schematic representa-
tion of the impregnation profiles obtained after drying by different
methods, viz. using stationary air in an oven (a), flowing air (up
flow) (b), a microwave (c), or freeze-drying ((d) and (e)).

The drying method had a profound effect on the impregnation
profile. Conventional drying (in an oven with stationary air) pro-
duced an increased Ni concentration near the entrance and
exit of the monolith. Drying in flowing air shows accumulation of
Ni at the point of first contact between gas and solid (the top of
the monolith). The reason for these non-uniform profiles is that
during drying, the liquid present in the interior of the monolith migrates outward due to evaporation of the liquid at the external surface. If the Ni has little or no interaction with the support, it will move with the liquid to the exterior, where the liquid evaporates and the Ni precipitates. Microwave drying yields a rather uniform distribution because heat is supplied throughout the support and therefore evaporation of the liquid occurs more homogeneously. The effect of freeze-drying is that the liquid is prevented from flowing to the external surface of the support, thereby also yielding a much more homogeneous distribution of Ni throughout the support. Another method of obtaining a uniform metal profile in the case of monoliths is deposition precipitation, which will be discussed next.

1.2.1.4 **Homogeneous deposition precipitation via pH increase**\(^{1,16,17}\)

As previously discussed, as a result of the use of impregnation techniques, the active phase of the catalyst can be located at the outside of the particles leading to relatively large crystallites. Furthermore, the combination of high loading and high dispersion is difficult to obtain when impregnation is used, and usually the impregnation procedure has to be repeated to achieve a well-dispersed catalyst with a high loading. An alternative method called “homogeneous deposition precipitation” (HDP)\(^{1,16,17}\) can be used to obtain uniform
catalysts. In HDP the support is introduced in the precipitation vessel as a powder. Figure 1.8 illustrates a laboratory unit for the preparation of catalysts by HDP. The pH is slowly increased by injection of a basic NaOH or NH₃ solution in the precipitation vessel. Alternatively, urea can be added to the solution. If the mixture is heated slowly, at 363 K urea starts to decompose:

\[
\text{CO(NH}_2\text{)}_2 + 3 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{NH}_4^+ + 2 \text{OH}^-.
\]  \hspace{1cm} (1.2)

Due to this reaction the pH slowly increases.

In the HDP procedure, the desired metal ion deposits in the form of the hydroxide. To obtain a homogeneous distribution, nucleation of the hydroxide must occur uniformly on the surface of the support particles, and not in the bulk solution. To prevent the latter, the suspension must be vigorously stirred and the pH must be adjusted slowly. The large surface of the support particles favors uniform nucleation of a large number of nuclei, and as a consequence, the crystallites formed are very small. With this procedure, highly dispersed catalysts can be prepared with a high metal loading. In Fig. 1.8, a pH curve as a function of base injection is shown. Typically, the maximum in the pH at around 40 min as a function of the amount
of base injected, is indicative of a low interaction between the precipitating compound and the support, and usually indicates that poor catalysts with a low dispersion will be obtained. The explanation is as follows. The pH rises into the super-saturation region of the hydroxide of the desired metal ion. Once the first nuclei have been formed, rapid growth of these first nuclei occurs, consuming large amounts of OH\(^{−}\) ions, causing the pH to drop (the injected amount of base per time cannot compensate for the OH\(^{−}\) consumption). At some point (around 50 min) a steady state is reached in which the OH\(^{−}\) consumption and injection rate are again in equilibrium. On the other hand a smooth rise of the precipitation curve is expected if a strong interaction between the precipitating precursor and the support particles exists, since then metal hydroxide concentration does not enter the super-saturation region, thus preventing the high precipitation rates. In conclusion, monitoring of the pH during the precipitation process yields valuable information on whether highly dispersed catalysts will be obtained or not, especially if precipitation curves both with and without supports can be compared.

1.2.1.5 (Co)precipitation at constant pH

This preparation technique is related to homogeneous deposition precipitation, but here the base and the precursor solution are injected simultaneously to the suspension of the catalyst support at a fixed pH. In this way, the interaction of the precipitating compound with the support can be optimized, while at the same time the crystallization of unwanted compounds, such as large crystallites of basic copper nitrate in the case of copper catalysts, can be prevented.\(^{18,19}\)

Precipitation at constant pH (Fig. 1.9) is also a prerequisite in order to co-precipitate two catalyst components at the same time. This is illustrated for example by the preparation of Pd/La catalysts for methanol decomposition.\(^{20}\) The preparation procedure and the La\(_2\)O\(_3\)/Pd weight ratio of these Pd/La\(_2\)O\(_3\)/SiO\(_2\) catalysts (5 wt% Pd) were found to be important for high catalytic activities in methanol decomposition. If the precipitation procedure leads to La\(_2\)O\(_3\) deposition in the final step, which is the result of the HDP method,
coverage of Pd particles by La$_2$O$_3$ patches occurs, which negatively affects the activity. Co-precipitation of La in Pd at fixed pH was found to lead to an optimized interaction of Pd with La$_2$O$_3$ and thus to an optimized use of expensive Pd.

Co-precipitation is also applied in the synthesis of hydrotalcite-like precursors (HTlcs) for catalysts e.g. based on Cu-Zn-Al$^{21}$, or Co-Al catalysts$^{22,23}$ Synthetic HTlcs, with a general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{m-}]_{x/m} \cdot nH_2O$, are hydrated hydroxycarbonates of a random lamellar structure. These materials can be visualized as brucite-type octahedral layers, in which $M^{3+}$ cations partially substitute for $M^{2+}$ cations ($x = M^{3+}/M^{2+}+M^{3+}$). The cations are located in the center of the octahedron formed by six hydroxyl groups. The metal-octahedra share edges to form two-dimensional infinite sheets, similar to brucite (Mg(OH)$_2$). The brucite-like layers can stack to build a tridimensional network and are linked by various chemical interactions (mainly hydrogen bonding) between the sheets. The positive charge resulting from this substitution is balanced by anions (often carbonate) together with water molecules arranged in interlayers.
Supported Metals in Catalysis

Alternating with the octahedral sheets. The structure, as outlined above, is further illustrated in Fig. 1.10. Hydrotalcite-like compounds (HTlc) have attracted much attention in recent years as catalyst precursors and catalyst support. This is due to (i) their ability to accommodate a large variety of bivalent and trivalent cations, (ii) the homogeneous mixture of the cations on an atomic scale, and (iii) the formation of thermostable mixed oxides, often denoted as ex-HTlc, with high surface area upon decomposition. The first two properties are a result of the precursor while the last property appears to be related to the decomposition mechanism. The transitions in the structural properties of Co-based hydrotalcites upon high temperature treatments have been extensively studied in our group. In the first decomposition step, water is removed from the structure. This transition is followed by dehydroxylation and decarbonation, as well as carbonate reorganization in the interlayer. Thermal treatment in air finally leads to a solid solution of cobalt spinels (Co(Co,Al)O). Mixtures of CoO and CoAlO are formed upon treatment in inert.

Many papers dealing with applications, and variations in synthesis parameters of hydrotalcite-like compounds can be found in the open.

Figure 1.10 Schematic illustration of the structure of hydrotalcite-like compounds.
literature, but it is beyond the scope of this chapter to present an overview here. On concluding this paragraph, it should be mentioned that hydrotalcite-like compounds are often used as catalyst precursors in the catalyst industry, because of the properties stated above.

1.2.1.6 Synthesis by using organic functionalization

A commonly known disadvantage of the use of homogeneous catalysts and enzymes in the chemicals industry is the difficulty of separating the active catalyst and the product (often also dissolved in the liquid phase). One of the most commonly proposed solutions to overcome this problem is to immobilize the organo-metallic catalyst or enzyme on an inert support, such as silica. It is not within the scope of the present chapter to discuss immobilization extensively. However, it should be mentioned that the immobilization techniques used by the metal-organic community has inspired the use of metal complexes for preparation of heterogeneous catalyst synthesis, in particular to prepare alloys. Examples include the synthesis of Au catalysts, and mixed Au-Pt catalysts. Van Gorp prepared combinations of Rh and Cu and Pd and Cu catalysts using organo-metallic compounds. Complexes containing two metals in a fixed ratio, such as \((\text{p-tolyl})_4 \text{Cu}_2\text{Rh}_2\) were used. The advantage of this complex is that it decomposes readily at mild temperatures into the mixed metallic particles, eliminating the necessity of a high temperature hydrogen reduction, which might cause sintering of the small metal particles.

Also pre-functionalization of the support has been applied e.g. in the synthesis of SiO\(_2\) supported Pt catalysts with well defined particle size distributions. Pt nanoparticles with an average size of similar to 3 nm were successfully immobilized on the surface of SiO\(_2\) and functionalized with –NH\(_2\) and –SH groups through chemical reduction process using polyvinylpyrrolidone as a stabilizer and different reducing agents.

On concluding this paragraph on immobilization, it should be stated that it is seldom applied in the catalyst industry, because of the high price of the chemicals required, and, if applicable, the air sensitivity of the organo-metallic complexes.
1.2.1.7 *Photodeposition of metals on semiconductor supports*\(^4,5,29\)

When a semiconductor absorbs UV/Vis light of energy greater than the so-called band gap between the highest energy level of the valence band and lowest level of the conduction band, a transition in the electronic state occurs. Both photo-excited electrons and holes are formed. For crystalline semiconductor particles, the transition of an electron from the valence band to the conduction band is followed by migration of photo-excited electrons and holes to the surface. The “holes” are capable of oxidizing a substrate by accepting an electron, and “electrons” able to reduce a (second) substrate. If this substrate is a metal ion, deposition, referred to as photodeposition, can be induced.\(^30\) This has been mainly applied for TiO\(_2\) supported metal particles and for applications in photocatalysis.\(^31\) For example, for Au deposition, in practice a suspension of TiO\(_2\) in AuCl\(_4^-\) is exposed to UV light. A hole scavenger, such as methanol, also needs to be present to prevent accumulation of positive charges during the photodeposition procedure.\(^32\) Figure 1.11 demonstrates the principle of the procedure. Interestingly, when the synthesis of Au nanoparticles is analyzed by UV-Vis probes *in situ*, the deposition

![Figure 1.11](image-url)

*Figure 1.11* Principle of photodeposition of Au particles on the surface of TiO\(_2\) crystals. Oxidation of methanol is required to prevent charge accumulation.
of the particles can be followed by the growth of the surface plasmon band at approximately 540 nm. The obtained particles sizes are in the order of approximately 20 nm, using this methodology, which is still rather large for various applications in heterogeneous catalysis.

A recent example of an advanced form of this methodology is provided by Zhang and coworkers for Ag deposition. Under ambient light illumination, silver nanoparticles on a TiO$_2$ support were synthesized by a triblock copolymer induced reduction of Ag(NH$_3$)$_2^+$ ions in ethanol. Conventional chemical reducing agents, thermal treatment, and radiation sources are no longer necessary in this novel approach. This novel ambient light route has been successfully applied to deposit silver nanoclusters on TiO$_2$ of about 2 nm in size, strongly anchored to the TiO$_2$ particles with high dispersion. The obtained catalysts were highly active in various photocatalytic applications. The scale of the procedure requires development of photo reactors, while these are usually not available in catalyst manufacturing facilities.

1.2.1.8 Calcination procedures

All of the above-described techniques produce a dried solid catalyst, which is usually further treated at elevated temperature in static or flowing air, which is referred to as calcination. It was already discussed that drying is a crucial step in the impregnation preparation procedure, and recent studies have demonstrated that calcination conditions will also largely determine the eventual size distribution of the obtained metal nanoparticles. This will be further addressed in the following case studies.

1.3 Case Studies

In the following, three examples of the effect of the preparation of metal catalysts on the performance in the desired reactions will be discussed. In the first example the very important effect of heat treatment after the impregnation procedure is illustrated by a study on the redox activity of Pt(O) catalysts as a function of heat treatment and particle size.
In the second example we will focus on preparation methodologies for gold catalysts, and the effect on the performance of gold in selective epoxidation of propene to PO (see reaction scheme in Fig. 1.12).

The commonly proposed mechanism for the reaction is that hydrogen and oxygen recombine on the catalyst surface to yield a peroxy intermediate, which subsequently reacts with propene to yield PO and water.\textsuperscript{34,35} Recently, evidence for the formation of this peroxide intermediate was provided,\textsuperscript{36,37} suggesting alternative mechanisms are less likely.

In the final example, we will continue with the subject of selective oxidation of propene to PO, but this time using advanced CaCO\textsubscript{3} supported Ag catalysts. The focus is directed towards a novel synthesis procedure, in which La incorporation is shown to have a significant effect on the alkali content of the catalyst and thus on the resulting catalyst performance. Although much less significant as the case for the Au catalysts, recent new information on the role of the support and the preparation procedures has appeared in the open literature, and this is briefly addressed.\textsuperscript{38–41}

1.3.1 Impregnation: preparation of Pt catalysts, the effect of the pre-treatment conditions

Although Pt catalysts have been and are used extensively in various processes, such as hydrogenation/dehydrogenation, and are usually...
prepared by impregnation, the procedure is often described in very limited detail. In Section 1.2 various aspects of the preparation of Pt catalysts by impregnation have already been discussed (use of precursors, co-adsorbents, and effect of PZC of the supports). It was mentioned that drying needs to be well controlled in order to obtain a high dispersion. Another experimental condition of great importance is the heating rate chosen for the pre-treatment of the catalyst system. In a paper by the group of de Jong, it was reported that a low heating rate (0.2 K/min) is essential in order to obtain small Pt clusters of 13–20 atoms (Pt < 1.1 nm), in the case of zeolite-Y supported catalysts. The beneficial effect of low heating rates is explained by the slow desorption of water and ammonia (in cases where [Pt(NH₃)₄]²⁺ was used as the precursor) from the zeolite in combination with stabilization of the Pt particles by the cavity walls. A higher heating rate of 1 K/min resulted in a bi-model distribution, in which 5 wt% of the Pt was present as particles of 4–9 nm, and 95% as particles of 1–1.2 nm. The importance of these findings can be illustrated by work done in our own group on the behavior of Pt-based catalysts in reduction/oxidation cycles, which is of relevance to NOx decomposition in lean-burn applications.

We have applied our Multi-Track reactor, an advanced TAP-like reactor system, to evaluate the number of redox-active Pt surface sites (Ptₘₜₖₐₜ redox) on Pt/Al₂O₃ catalysts as a function of Pt dispersion. The number of Ptₘₜₖₐₜ redox sites was compared with the total number of Ptₘₜₖₐₜ sites determined by conventional volumetric CO chemisorption.

1.3.1.1 Procedures

A detailed description of the catalyst preparation and the Multi-Track set-up can be found elsewhere. Before performing titration experiments in Multi-Track, the catalyst (1 wt% Pt on Alumina) was subjected to two different pre-treatments:

Pre-treatment procedure M1. After inserting the fresh catalyst into the vacuum system, it was heated up to 573 K at 10 K/min⁻¹. The catalyst
was stabilized for 2 h. This treatment leads to catalyst M1 and was intended to preserve the structure fresh catalyst as much as possible.

**Pre-treatment procedure M2.** After inserting the reactor into the vacuum system it was heated up to 773 K (10 K/min). Subsequently, the catalyst was subjected to H\textsubscript{2} pulses (10\textsuperscript{17} molecules per pulse, 1 pulse/sec) for 1 h. Then, the reactor was cooled to 573 K, and stabilized for 2 h. This treatment results in catalyst M2 and was meant to induce sintering of Pt particles in order to study the influence of the particle size on redox behavior by comparing catalysts M1 and M2.

Following these pre-treatments, titration experiments were performed at temperatures between 473 K and 573 K. Pure hydrogen (10\textsuperscript{17} molecules per pulse) was used to reduce the Pt catalyst. The catalyst is denoted as “completely reduced” when the area under the hydrogen-signal was constant. Pulses of 20 vol.% O\textsubscript{2} in Ar (10\textsuperscript{17} molecules per pulse) were used to re-oxidize the reduced catalyst. The catalyst is denoted “completely oxidized” when the area under the succeeding oxygen-signals is constant.

Figure 1.13 shows a typical result of a titration experiment, and indicates the high sensitivity of the Multi-Track system (responses of one single pulse were detected and calculated to construct the curves shown in Fig. 1.13).

From the area under the curves, the total hydrogen needed for reduction of the Pt surface can be calculated. A remarkable difference in the amount of hydrogen needed to reduce the surface of catalysts M1 and M2 can be observed. By repeating the H\textsubscript{2}/O\textsubscript{2} reduction/oxidation cycles, it was confirmed that the hydrogen uptake values were reproducible within ±10%. After the Multi-Track titration experiments, the dispersion of the catalyst was determined in a separate set-up by conventional CO chemisorption. The Pt dispersion as derived from the CO chemisorption experiments was decreased from 0.73 for catalyst M1 to 0.47 for catalyst M2, indicating that the pre-treatment procedure M2 indeed induced sintering of Pt. For catalyst M2, the number of chemisorption sites as determined by CO chemisorption, and the number of surface sites participating in
the H₂/O₂ cycles in the Multi-Track experiments (Pt₄₅ redox) are in good agreement. On sample M1, however, only 10% of the Pt₄₅ sites as determined from CO chemisorption appear to be involved in the redox cycles.

The discrepancy between the CO chemisorption experiment and the Multi-Track experiment for catalyst M1, can be explained by the large difference in applied H₂ partial pressure in the Multi-Track experiment and in pre-conditioning the catalyst before CO chemisorption. During the H₂ titration procedure in the Multi-Track reactor the partial pressure of hydrogen is extremely low, at least eight orders of magnitude lower than the H₂ partial pressure in the pre-treatment for the CO chemisorption experiment (typically performed with pure H₂, at 553 K, for 2 h). Under Multi-Track conditions, 90% of the surface sites in catalyst M1 are apparently not affected by hydrogen, while these sites are reduced in the hydrogen pre-treatment of the CO chemisorption experiments.

Figure 1.13  Reduction by a train of hydrogen pulses of previously O₂-oxidized Pt catalysts. For pre-treatment conditions of catalysts M1 and M2 see text above.
Interestingly, the Multi-Track results appeared very representative for the behavior of the catalysts under realistic deNOx conditions, showing a significant increase in performance after sintering, in agreement with the higher reducibility of catalyst M2 in Multi-Track conditions. Several authors have noticed an influence of the Pt dispersion on the performance of Pt-group catalysts in HC-SCR.\textsuperscript{44,45} Burch \textit{et al.}\textsuperscript{45} presented an apparent hyperbolic relation between dispersion of the fresh catalyst and turnover frequency (TOF) in HC-SCR over Pt/Al\textsubscript{2}O\textsubscript{3} and Pt/SiO\textsubscript{2} catalysts. Catalysts with a large Pt particle size exhibit a higher TOF than those with small size. It was further shown by various research groups that highly dispersed Pt catalysts undergo sintering in HC-SCR, which is proposed to be an NO induced process.\textsuperscript{45–47} It should be mentioned that a particle size dependency on activity of Pt catalysts has not only been observed in reactions involving the reduction of NO,\textsuperscript{48} but also in many other oxidation reactions. The rates of the oxidation of propene,\textsuperscript{49} methane,\textsuperscript{44,50–52} benzene,\textsuperscript{53,54} and other hydrocarbons,\textsuperscript{54} are all increased as a function of increasing Pt particle size, which we suggest, based on our Multi-Track data, is the result of a higher reducibility of the Pt sites involved in the reactions.

In summary, for Pt catalysts prepared by impregnation, various preparation variables can be changed (as indicated in the paragraph discussing impregnation techniques in general), but the most important factor for the eventual particle size/performance of these catalysts is the heat treatment. Heating rate and temperature of pre-conditioning of the Pt catalysts are crucial.

1.3.2 Precipitation vs. impregnation by ion-exchange: Au precursors and the effect of the method of preparation and selected support on performance in selective epoxidation of propene over Au/TiO\textsubscript{2} catalysts

Au catalysts have received considerable attention recently because of the extraordinary performance in the low temperature oxidation of CO\textsuperscript{55} and high selectivities of over \textit{99\%} in the direct epoxidation of propylene in the presence of hydrogen. Besides the extraordinary
performance in oxidation of CO and propene, Au catalysts have also been reported to be very effective in promoting photocatalysis.\textsuperscript{6,32,56} The preparation procedure was found crucial, in particular in relation to the effect on the OH population of the applied TiO$_2$ support. In photocatalysis, these OH-groups are essential for activity, in particular for conversion in organic phases. Hugon and coworkers have recently given an overview of impregnation procedures that might lead to improved catalysts.\textsuperscript{7} Here, we will further focus on the effect of preparation on the performance in epoxidation reactions.

The first reports of Haruta and coworkers have initiated many ongoing academic studies that focus on the mechanism of the reactions (CO oxidation and propene epoxidation) and the effect of the Au particle size on the activity and selectivity in propene epoxidation, e.g. Refs. 37, 57–63. A peroxide-like intermediate is proposed to selectively react with propylene to yield PO.\textsuperscript{37} This was previously illustrated in Fig. 1.12. Industrial interest has also been significant, as patents have appeared recently on improvements of the Au/TiO$_2$ system, which mainly claim promoters of the catalytic system to reduce hydrogen consumption. The most recent breakthrough was reported by the Haruta group, applying mesoporous structures and methylation of support groups.\textsuperscript{60,61} This improvement of the catalyst system enhanced the PO yield to about 10%.

As stated, to obtain Au particles with a high selectivity, and stability, the preparation procedure and support appear to be of crucial importance. Furthermore, the morphology and composition of the support appear also of crucial importance, as is illustrated by the following.

\subsection{Experimental}

To evaluate the role of the support, the following catalysts were prepared.\textsuperscript{64} Degussa P25 (80\% anatase, 50 m$^2$/g), was applied as the TiO$_2$ support for the 1 wt\% Au-catalysts. TS-1 was synthesized either using tetraethyl orthosilicate (TEOS), TPA-OH (tetra-propylammonium hydroxyde, Aldrich) and TBOT (tetrabutylorthotitanate) (Catalyst TS-1a), or SiO$_2$ particles (Degussa Aerosil) rather than...
TEOS, keeping the other ingredients and procedures similar (Catalyst TS-1b). An extensive description of the preparation of the TS-1 supports can be found elsewhere.

AuCl$_3$ was used as the Au source. Incipient wetness impregnation was performed by adding the AuCl$_3$ solution to the appropriate amount of TiO$_2$ support, followed by drying at 375 K (5 K/min), and calcination at 673 K (5 K/min) for 1 h. In a homogeneous deposition precipitation method (method HDP-I), a gradual increase of the pH of an AuCl$_3$/TiO$_2$ suspension (acidified to pH 3, and a TiO$_2$ amount of 100 g/L) was brought about by injection of a diluted NH$_4$OH solution. In a pH-static precipitation method (method HDP-II), a solution of AuCl$_3$ was injected at pH 10 (made basic through NH$_4$OH) into the TiO$_2$ suspension (100 g/L). After precipitation, the catalysts were filtered, dried at 375 K in static air (5 K/min) and calcined at 673 K (5 K/min) for 1 h, again in static air. A more detailed description of the preparation can be found in Xue et al.$^{48}$

1.3.2.2 Impregnation vs. precipitation

Catalysts prepared by impregnation were found to be completely inactive in the epoxidation reaction of propene.$^{65}$ Figure 1.14 shows a SEM

![Image](b1215_Chapter-01.qxd_11/28/2011_5:02_PM_Page_25)

**Figure 1.14** Representative micrographs of the Au/TiO$_2$ catalysts prepared by impregnation (SEM micrograph, Fig. 1.14(a)) and precipitation (HDP-II, TEM micrograph, Fig. 1.14(b)).
picture of an impregnated Au catalyst on TiO$_2$, and a TEM picture of a precipitated catalyst using method HDP-II (same TiO$_2$ support). A ready explanation for the inactivity of the catalysts prepared by the impregnation method is found in the large Au particle diameter, which exceeds 100 nm, and can even be observed by SEM. This gold particle size is very large compared to that of the precipitated catalyst, which can only be observed using TEM. From Fig. 1.13, the Au size for the precipitated catalyst is estimated at 3–10 nm, and particles are homogeneously dispersed throughout the catalyst sample.

1.3.2.3 Precipitation conditions

Catalysts prepared by method HDP-I, with an Au loading of 1 wt% or 3 wt%, showed a very high activity for hydrogenation of propylene to propane at 323 K, in agreement with data provided by Haruta. Minor amounts of acetone were also produced. Catalytic activity for the formation of PO from propylene was not found. Haruta reports that the Au particle size strongly affects the reactivity and selectivity in the oxidation of propylene in the presence of hydrogen. Only when the Au particles exceed 2 nm, and are smaller than 10 nm, is the desired conversion to PO achieved. Apparently, catalysts prepared by method HDP-I had particle sizes below 2 nm, independent of the TiO$_2$ support used, or the speed of base addition. This explains why mainly products of hydrogenation, rather than epoxidation, were obtained. The minor amounts of acetone were most likely formed by reaction of propane and oxygen.

Generally, catalysts prepared by method HDP-II with a TiO$_2$ “concentration” of 50 g/L (or below), were not catalytically active in the oxidation of propylene below 373 K. This suggests that insufficient nucleation sites were available for the genesis of a highly dispersed system. In agreement with this tentative conclusion, upon calcination Au particles were sintered to sizes larger than 10 nm, thus explaining the low activity (confirmed by TEM analysis, not shown).

When a specific concentration of 100 g/L TiO$_2$ (anatase) was applied, selective catalysts were formed. Apparently, this support
density is high enough to achieve sufficient interaction between the precipitating Au and the support. This resulted in the particle size distribution shown in Fig. 1.13(b), which appears to induce selective propene epoxidation. Using a feed of 10% propylene, 10% H₂ and 10% O₂ in He with a flow rate of 50 ml/min at 353 K, a propylene conversion of 0.7% was achieved using 250 mg catalyst. The selectivity to PO was 99%. The hydrogen efficiency amounted to an approximate 23%, the other product of hydrogen consumption being water. Some other factors were also investigated. Lowering the pH of the precipitation suspension resulted in a catalyst with a reduced performance. Increasing the Au loading from 1 to 3 wt%, yielded catalysts with significantly decreased activity. In both cases larger Au particles were obtained, explaining the decreased performance.

1.3.2.4 Support effects

Many researchers have observed that the Au/TiO₂ catalysts rapidly deactivated, typically within one hour. Deactivation can be prevented, if the TiO₂ is supported on SiO₂, or if TS-1 is used as the support. However, if a silicalite-derived material containing Ti (TS-1) is used as the support material, the preparation method of the support itself appeared to also largely affect the activity. A combined SEM and TEM study was conducted to analyze the various catalysts and to obtain insight into the reasons for the low activity in propylene epoxidation of some catalysts, and the high activity and selectivity of others.

Two synthesis methods were applied to prepare the TS-1 supports (TS-1a and TS-1b). It was found that, after deposition of Au by precipitation method HDP-II, TS-1a was a good catalyst, whereas catalyst TS-1b was totally inactive. In Figs. 1.15(a) and (b), TEM pictures of the Au-TS-1 samples are shown. The morphology of the two samples is quite different. TS-1a consisted of very small crystallites (10 nm), agglomerated to form 150 nm particles, whereas TS-1b consisted of 35 µm crystals. The size of the gold particles in the TS-1a sample with the small crystallites, was estimated to be 3–15 nm, which is not significantly smaller than those observed on the edges
of the large TS-1b crystals. However, Titanium is an essential factor in the activity of dispersed gold catalysts in the epoxidation of propylene. It was therefore hypothesized that, since the Au particles were all located on the outside of the crystals, the Ti-phase is located in the interior of the support containing the large crystals.

Essentially the gold particles only “see” silica moieties, and do not interact with the Ti-phase present. This hypothesis, however, could not be verified experimentally.

Concluding, this example is probably the best to show the dramatic difference between an impregnation procedure, homogeneous deposition precipitation (HDP), and precipitation at constant pH. Impregnated catalysts are usually inactive, HDP leads to very small particles with hydrogenation activity, whereas the use of precipitation at constant pH yields highly selective epoxidation catalysts. Furthermore, the morphology of the TS-1 support was shown to play an important role in obtaining active catalysts. Recently various alternative procedures as compared to the ones described above are available, of which optimized impregnation,\(^7\) use of ligand protected particles,\(^6\) and photodeposition\(^3,32\) appear quite promising.
1.3.3 Co-precipitation: preparation of advanced CaCO₃ supported Ag catalysts

1.3.3.1 Introduction

Direct oxidation of propylene to propylene oxide (PO) with high selectivity and activity is yet to be achieved in heterogeneous catalysis, as was already indicated in the description on the preparation of the Au catalysts. Obviously, the most attractive reaction is the direct oxidation with oxygen, rather than using the previously discussed mixture of oxygen and hydrogen:

\[ \text{H}_2\text{C} = \text{CH}_2\text{CH}_3 \quad \xrightarrow{k_1} \quad \text{CO}_2 + \text{H}_2\text{O} \quad \xrightarrow{k_3} \quad \text{H}_2\text{C} \rightarrow \text{CH}_2\text{CH}_3 \quad \xrightarrow{k_2} \]

Although epoxidation of ethylene with O₂ over Ag catalysts has been industrially applied for many years, the catalysts used for this process typically show poor selectivity in the epoxidation reaction of propylene, yielding mainly CO₂ and water.

The low selectivity of these catalysts in the oxidation of propylene is often explained by the difference in mechanism for the formation of PO from propene and EO from ethane.\(^{67}\) In both cases, the reaction involves the interaction of the alkene with an oxygen radical on the Ag surface, yielding an epoxide intermediate.\(^{58}\) In the case of propene, abstraction of a hydrogen atom of the CH₃ group of the epoxide precursor by reaction with a neighboring oxygen radical on the Ag surface results in the formation of CO₂, rather than PO (reaction pathway k2 is preferred in the above propene epoxidation scheme). Due to the absence of the specific hydrogen (CH₃ group) in the ethylene molecule, high selectivities can be obtained for ethylene.

The selectivity of Ag-based catalysts in propylene oxidation is expected to improve by the preparation of Ag sites without destructive
neighboring oxygen radicals. The formation of these isolated Ag sites might be approached by preparation of very small Ag particles. This might be achieved using catalysts based on zeolites and mesoporous materials,\textsuperscript{69,70} sol-gel preparation methods\textsuperscript{71,72} or alloying of Ag with e.g. Au.\textsuperscript{18} Unfortunately, none of these methods has appeared to be successful in significantly improving PO selectivity in propylene epoxidation. Another approach is based on poisoning of a specific amount of Ag sites with either an alkali metal,\textsuperscript{73-75} or gas phase additives, such as NO or alkyl halides,\textsuperscript{73,76} which has been successfully used in improving the selectivity of ethylene epoxidation catalysts. Recently the particular use of an alkali carbonate to support the Ag particles in combination with these “poisoning” promoters has been claimed in a Canadian patent by Union Carbide (1,282,772 (1991)). This catalyst does not necessarily contain $\alpha$-alumina, commonly used in selective ethylene epoxidation catalysts. Besides the alkaline earth metal carbonate (Mg, Sr, Ca, Ba) as the support material, another novel aspect is the specific use of KNO$_3$, in combination with NO/NO$_2$ as gas phase additives, to enhance the selectivity for the desired products in alkene epoxidation reactions. Again, poisoning of a specific amount of Ag sites seems to be the reason for the high selectivity of these Ag-based catalysts.

As many as ten patents have been assigned to ARCO Chemical, all describing improvements of the Union Carbide Patent for the epoxidation of propylene. Selectivities as high as 50\% have been claimed, in the range of 2–5\% conversion, based on a 10\% propylene and 5\% oxygen feed. Various modifications have been claimed of which the most important one is that also silver catalysts supported on other alkaline earth metal compounds than carbonates are active,\textsuperscript{38,41} such as calcium titanate, tribasic calcium phosphate, calcium molybdate, or calcium fluoride, as well as the magnesium and strontium analogues. Such supports provide significantly higher selectivity to the desired epoxide than would be expected from the performance of related materials. Selectivities are lower than those reported in the original Union Carbide patent.

The specific method of preparation of the Ag catalysts is usually impregnation of the carbonate by a solution containing silver ions
and organic complexing agents, such as ethylene diamine, oxalic acid, and ethanol amine. The patent discloses the formation of a slurry, which is spread on a flat surface and roasted to remove organic precursors and reduce the silver. The potassium nitrate is added by impregnation after reduction of the silver precursor to the metallic state, but may also be included in the silver precursor solution. The procedure is rather tedious and involves two different impregnation steps. Recently we have developed precipitation methods (US patent 6,392,066) to obtain active catalysts based on the compositions claimed in the Union Carbide and Arco patents. We have found that the inclusion of lanthanum nitrate, or other rare earth metal nitrates, in the precipitation solution is essential in order to obtain active alkaline earth metal carbonate supported silver catalysts by this preparation procedure. Furthermore, the inclusion of promoting amounts of Cl$^-$ and K$^+$ or Na$^+$ in the precipitation solution significantly enhances the selectivity in propylene oxidation.

1.3.3.2 Precipitation of carbonate supports: experimental

Precipitated catalysts were prepared by a HDP procedure. Base injection into a precursor solution was performed using the equipment described in Fig. 1.8. The base used consisted of a solution of 60 g/L K$_2$CO$_3$, which was injected under vigorous stirring at 5 ml/min in to a 250 ml solution of precursor. A reference catalyst was prepared by using only 5 g Ca(NO$_3$)$_2$.4H$_2$O and 2.5 g AgNO$_3$. The pH changed as a function of the amount of base solution injected and the amount of remaining Ag$^+$ and Ca$^{2+}$ present in the solution. When the precipitation rate equals the rate of base (carbonate) injection, the pH attains a constant value (see Section 1.2). AgCO$_3$ is precipitated before CaCO$_3$ at pH 7, followed by CaCO$_3$ initiating at pH 8.5 and continuing at a steady state level at a pH of 7.5.

The procedure including structural promoters (rare earth metal nitrates), was conducted as follows. A 4 g/L KOH and 46 g/L K$_2$CO$_3$ containing base solution was injected at 5 ml/min into a HNO$_3$ acidified catalyst precursor solution (pH 3) of 2.5 g AgNO$_3$, 5 g
Ca(NO$_3$)$_2$·4H$_2$O, and 1 g La(NO$_3$)$_3$·6 H$_2$O. The precipitation was completed in 50 min and injection of the basic solution was ended at a final pH of 10. Please note that we also changed the composition of the base solution by adding KOH to the K$_2$CO$_3$ solution.

The precipitates were filtered (not washed), dried, and calcined at 600 K (heating rate 10 K/min) for only ten minutes, sufficient to reduce the Ag precursor without decomposition of the nitrates incorporated into the catalyst. A yellowish/brown catalyst was obtained.

1.3.3.3 Results and discussion

An overview of the effect of the precipitation variables on morphology, chemical composition and performance in selective propene oxidation is given in Table 1.1. The precipitated catalysts without La addition to the solution showed a much lower selectivity than the selectivity of the catalysts prepared by impregnation reported in the Arco patents, which is 40–50% in comparable experimental conditions. At most, a selectivity of 8% was obtained, at 6% propene conversion (see Table 1.2) for these precipitated catalysts.

To modify the morphology of the catalyst system, lanthanum was added to the precipitation solution. As indicated in Table 1.2, this induces K incorporation in the catalyst formulation, whereas the morphology of the silver particles was also affected. However, a high selectivity was still not obtained. Changing the base composition from a K$_2$CO$_3$ solution to a mixed KOH/K$_2$CO$_3$ solution, did not effect the performance either, although the cubic crystals of CaCO$_3$ were better defined, and the Ag particles were somewhat sintered compared to the preparation using the K$_2$CO$_3$ solution without KOH. High selectivities were obtained by using a combination of the KOH/K$_2$CO$_3$ basic solution and La in the precursor solution. A selectivity of 31% to PO was obtained, which is close to the performance of the Arco catalysts. Variation of the amount of La affects the obtained selectivity; 7 wt% La gave the best selectivity. Addition of La also slightly enhanced the activity of the catalyst.
The catalysts prepared with La surprisingly contained a higher amount of K than those prepared without La. We suggest that La enhances potassium uptake as the catalyst forms, because part of the La precipitates as a mixed potassium lanthanum carbonate, i.e. $\text{KLa(CO}_3\text{)}_2$. A similar compound has been reported for sodium in the literature. A second important observation is that the presence of both La and K in the catalyst does not necessarily induce a high selectivity, unless KOH is also employed in the basic $\text{K}_2\text{CO}_3$ solution. Omission of KOH from the basic solution results in a similar chemical composition (compare cases two and four in Table 1.2) but a much less selective catalyst. This is most likely a consequence of the precipitation procedure itself. Without KOH in the base, a step-wise precipitation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sel.</th>
<th>XRD</th>
<th>SEM</th>
<th>K</th>
<th>La</th>
<th>Ca*</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>8</td>
<td>Ag CaCO$_3$</td>
<td>$\text{CaCO}_3$: Cubes and spheres</td>
<td>0.07</td>
<td>—</td>
<td>64.5</td>
<td>48</td>
</tr>
<tr>
<td>Adding La</td>
<td>11</td>
<td>Ag LaO$_2$CaO$_3$ CaCO$_3$</td>
<td>$\text{CaCO}_3$: Cubes—less defined, bigger</td>
<td>0.38</td>
<td>8.2</td>
<td>54.7</td>
<td>41.3</td>
</tr>
<tr>
<td>Adding KOH</td>
<td>9</td>
<td>Ag CaCO$_3$</td>
<td>$\text{CaCO}_3$: Cubes—very well defined</td>
<td>0.07</td>
<td>—</td>
<td>64.5</td>
<td>45</td>
</tr>
<tr>
<td>KOH and La</td>
<td>31</td>
<td>Ag CaCO$_3$</td>
<td>$\text{CaCO}_3$: Cubes—less defined, bigger</td>
<td>0.33</td>
<td>8.2</td>
<td>52</td>
<td>40.2</td>
</tr>
</tbody>
</table>

* Percentage given as weight percent CaCO$_3$. The composition usually adds up to 108–112%. This indicates that part of the Ca in the precursor solution precipitated as Ca(OH)$_2$, and is converted to CaO, rather than CaCO$_3$, upon calcination.

Preparation of Supported Metal Catalysts
occurs, in which La (and K) is entirely precipitated first, followed by Ag (as the carbonate), and Ca (as the carbonate). With addition of KOH, a simultaneous precipitation of La (and K) and Ag occurs (indicated by the beige coloring of the precipitate), apparently increasing the interaction between the La (and K) and the Ag. This hypothesis is corroborated by EDAX analysis, which shows that La was always associated with Ag in the catalytic composition if a KOH/K₂CO₃ base composition had been used. Furthermore, SEM analysis showed that only the combination of the two modifications (OH⁻ addition to the base and the presence of La in the precipitation mixture), causes a unique weblike structure of the silver particles, supported by CaCO₃ crystallites that did not show a high degree of ordering. Relatively large CaCO₃ clusters formed, that had a less-defined cubic structure than observed in the catalysts prepared without La. These results suggest that a more amorphous structure of CaCO₃ leads to higher PO selectivity. The weblike structure of silver in the La-containing catalysts might provide increased surface area for increased activity and an open pore structure of the active sites for increased selectivity.

As a final note on preparation of these advanced catalysts, it should be mentioned that replacing Ca with Ba, and adding Cl to the preparation mixture yields the best catalyst obtained to date. The Ba-containing catalyst shows initial selectivities of up to 58% towards PO. Unfortunately, the selectivity decreased with time on stream and reached a steady state level of about 45% at 3% conversion at 235°C after 3 h. It should be noted that the 45% selectivity found for the Ba-containing catalyst is higher than obtained for the impregnated catalyst. Besides the addition of Cl to the catalyst, the synergy between BaCO₃, Ag and La(OH)CO₃ also seems to be even better than the synergy between CaCO₃, Ag and La(OH)CO₃.

1.3.3.4 Understanding of the function of the components in the catalytic formulation

Recently progress has been made to optimize the composition of the Ag catalyst. A crucial factor of the incorporation of the K or Na in the catalyst formulation is the effect of this promoter on the particle
size of the Ag clusters. Lambert and coworkers\textsuperscript{41} have indicated that an optimized particle size of Ag is in the order of 20–40 nm. These particles are significantly bigger than previously indicated for Au catalysts, and were obtained by applying the impregnation procedures indicated in the patent literature. Also the group of Oyama\textsuperscript{38} has demonstrated and confirmed the high performance of these catalyst formulations based on silver, and also indicated that not only the particle size, but also the Ag morphology changes as a function of the preparation conditions. More rough and less well structured Ag particles have been found as a result of a ball milling procedure, which in combination with particle sizes in the order of 400–700 nm provided the most effective catalysts. Also the positive effect of NaCl on the catalyst performance was confirmed.\textsuperscript{38} These authors propose that NaCl not only helped increase the dispersion of the silver on the CaCO\textsubscript{3} support, but also probably increased the quantity of electrophilic oxygen species favorable for epoxidation.

Very recent literature indicates that Ag clusters of only several tens of atoms, also yield exceptionally high selectivities in epoxidation of alkenes, other than ethane.\textsuperscript{78} The preparation of these clusters is currently only possible in very small quantities, and upscaling of the vacuum methodologies is very necessary.\textsuperscript{79} Perhaps also atomic layer deposition, recently applied successfully,\textsuperscript{80–82} could provide for a solution, in particular if this becomes feasible in a continuous mode of operation.

1.4 General Conclusions on the Preparation of Metal Catalysts

In this chapter, an overview has been presented on the common techniques for the preparation of catalysts in the laboratory. It was by no means meant as being a complete guide to the preparation of metal catalysts, but the authors hope to have given some basic principles, as well as some case studies that provide some new and useful information to the reader, especially those interested in the preparation of Pt, Au and Ag catalysts. Of the preparation techniques mentioned, impregnation is often the easiest to apply, but in the
example of the Au catalysts it was shown that only by precipitation of the precursor at fixed pH were selective catalysts obtained. In the case of the advanced Ag catalysts, the used preparation procedure in the literature (impregnation with organic precursors) could be simplified by precipitation, using promoters that steer the precipitation sequence and capture alkali ions from the solution, incorporating these in the catalysts. We hope to have shown using the example of the Pt catalysts that not only do the conditions for the impregnation or precipitation itself (such as pH of solutions, suspension densities, rate of base addition, stirring of the suspension etc.) have a profound effect on the behavior and structure of the catalysts eventually obtained, but also the applied drying procedures and, even more importantly, the heat treatment. It is the hope of the authors that future publications in the catalysis literature will pay more attention to the preparation procedure used, to allow a better comparison of catalysts in different laboratories, and to obtain improved catalysts for the desired applications.

References


