Synthesis of supported palladium catalysts

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Abstract

The synthesis of supported palladium catalysts is reviewed with emphasis on a summary of the chemistry of catalyst synthesis, oxide and carbon support properties and case studies from the period 1990–2000. With oxide supports aqueous precursor solutions are often used. The charge of the complex in combination with the iso-electric point (IEP) of the support is an important property to consider during synthesis affecting both dispersion and distribution over large support bodies. With carbon supports direct reduction of palladium precursor may occur that leads to large metallic Pd particles. With the latter support lyophilicity can largely affect Pd emplacement. With oxide and carbon supports sol–gel, deposition–precipitation, deposition–reduction, ion-exchange and impregnation methods have been applied. In general it turns out that the thermal treatment often dominates the primary application of the Pd-precursor in establishing the ultimate metal dispersion. Thermal treatment in an inert atmosphere at temperatures not exceeding 773 K prior to reduction is beneficial for the Pd dispersion. Gas-phase reduction leads to smaller Pd particles than does liquid-phase reduction. In our opinion large progress can be made to develop highly loaded thermostable Pd catalysts by utilizing deposition–precipitation techniques in combination with anchoring sites on the support. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst synthesis; Palladium; Catalysts; Impregnation; Ion-exchange; Oxide supports; Carbon supports

1. Introduction

Solid supported catalysts are complex assemblies the preparation of which is a challenging task. Even when it is known which active sites and other features are needed to make a catalyst effective for a specific application, its preparation, generally from simple precursors, is complex and laborious. Already minor adjustments of the preparation conditions can significantly influence the delicate balance of conflicting demands: a high activity, a high selectivity and a long lifetime [1].

A high activity of a supported catalyst often calls for a large active surface area and, thus, for small particles, i.e. a high dispersion of the active phase. Because small particles, especially small metal particles, tend to sinter already at relatively low temperatures, these generally are applied onto a pre-existing support material which itself is thermally stable and maintains a high specific surface area up to high temperatures [2]. Suitable and frequently used support materials are alumina, silica and carbon, all being compounds with high melting and decomposition temperatures. With these supports other important (physical) features like texture (specific surface area, pore size distribution and pore volume), density and mechanical strength can be established.

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A complication is that catalyst particles must have a prescribed size and shape to be applicable in a specific reactor and/or to be removable from the liquid-phase by filtration or centrifugation. Due to this, a large specific surface area can only be attained when support bodies are highly porous, which might conflict with the desired thermal stability of the texture. Moreover, narrow and long pores might hinder transport of reactants and/or products which generally is undesirable. Furthermore, a high porosity might bring along a decreased mechanical strength causing the formation of fines and loss of (expensive) catalytic material.

With most catalyzed reactions the combined chemical properties of the active phase and the support bring about the catalytic functionality. But even when the support material only serves as a vehicle for keeping the catalytically active species separated, these species have to interact in some degree and in some way with the support. And due to this interaction, which nature is often still unknown, the catalytic performance strongly depends on a complex mix-up of contributions of the morphology and dispersion of the active particles and, with metal catalysts, with the electronic properties of the metal [3,4].

A survey of the literature learns that, although a growing number of contributions deal with supported palladium catalysts, not many focus on the preparation process itself. Generally, an earlier developed procedure is somewhat optimized, with the reaction to be catalyzed as the ultimate test. Studies on the various steps in a synthesis route, separately and in the sequence of the total procedure, are relatively scarce.

Here we survey the preparation of palladium catalysts supported on some oxidic and carbon materials. In this review we follow the general survey on supported catalyst preparation as earlier given by Augustine [5]. This enables us to confine mainly to contributions of the last decade. Furthermore, we will concentrate on those contributions which give experimental details on the preparation, hereby allowing scientific interpretation.

In Section 2 we deal with surface properties of oxidic and of carbon supports in relation to that of a number of precursor compounds important for mutual interaction, notably in the first step of most synthesis routes. In Section 3 first we review the state of the art with respect to the preparation of Pd catalysts on oxidic supports, mainly of Pd on silica and alumina,

then we focus on the synthesis of palladium on carbon supports. With some general remarks in Section 4 we conclude this review.

2. The chemistry of catalyst synthesis

Preparation of supported catalysts generally involves contacting a (porous) pre-shaped support with most often an aqueous solution of a suitable precursor of the active component which, in one of the subsequent preparation steps, is converted into the active component. Only when a sufficiently high interaction between the two exists at this stage of the procedure, ultimately the wished distribution and high dispersion of the active component can be achieved. With poor interactions notably during removal of the solvent, i.e. during drying, an unwanted re-distribution may occur leading to egg shells and broad particle size distributions of the active component [1]. The interaction between the solvated precursors and the support surface as modified by the solvent is generally of an electrostatic nature. First we will briefly deal with the solvated precursors. Next we will concentrate on the interaction between solvent and support surface and adsorption sites suitable for interaction with the precursors.

2.1. Precursor solutions

Solvation of metal cations in water leads to formation of partially covalent bonds between the central cation and the water ligands. Charge transfer from filled orbitals of the water ligands to the central metal ion raises the positive charge on the hydrogen atoms of the coordinated water molecules. This increases their acid character and promotes hydrolysis. In a general form the hydrolysis reaction is expressed by

$$x\text{M}^+ \text{ (aq)} + y\text{H}_2\text{O} \rightleftarrows \text{M}_x(\text{OH})_y \text{ (aq)}^{(xn-y)+}$$
$$+ y\text{H}^+ \ (K_{xy})$$
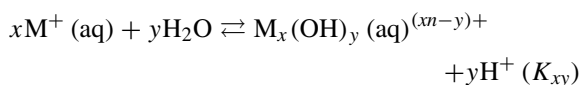
This reaction reflects that, depending on the nature of the cation, besides monomeric also oligonuclear species can be formed. With cations with a very high charge even proton abstraction from the hydroxide ligand may occur and oxo species are formed [6,7].

The Pd^{2+} ion favors the formation of square planar PdL_4 complexes and in water, with no other complexing ligands present, exclusively $Pd(H_2O)_4^{2+}$ exists in solutions with a pH < 1. For this ion a $pK_a = 2.3$ has been measured. At pH > 1 polynuclear palladium species are gradually formed as described by Bönneman et al. [8] for solutions of palladium nitrate. Didillon et al. [9] investigated the formation of colloidal PdO particles by hydrolysis of a palladium nitrate solution. At pH values of 2 and 2.8 they obtained particles of 1.8–1.9 nm. Neutralization of a basic solution of pH = 12 down to pH = 1.8 resulted in the same small particles of 1.7–1.8 nm. These findings are interesting for of the preparation of supported catalysts with well-defined palladium particle sizes.

In view of the (surface) chemistry of the oxidic and carbon supports cationic or anionic palladium precursor ions have to be available in a pH range of ∼3 to ∼9. The complex ion, $Pd(NH_3)_4^{2+}$, is stable in neutral and moderately basic environments and the ligands and possibly nitrate can simply be removed from the loaded support by heating. The most utilized negatively charged palladium complex ion is $PdCl_4^{2-}$, which is stable in neutral and acid solutions, provided the Cl/Pd ratio is high enough to avoid hydrolysis. Generally a solution of $PdCl_2$ in diluted chloric acid is used.

Many authors make use of neutral palladium complexes that interact, generally from non-polar environment, with specific surface sites of the supports. Most often the acetylacetonate complex of palladium, $Pd(C_5H_7O_2)_2$ or simply $Pd(acac)_2$, in inert solvents like benzene and toluene is used. Another precursor is $Pd(C_3H_5)_2$ dissolved in pentane. This allylic complex is highly reactive towards water and hydroxylated surfaces.

2.2. Oxidic supports

Surfaces of most oxides are hydroxylated or, in any case, become hydroxylated upon contact with liquid water or water vapor. The nature of the surface hydroxyl groups has been identified by IR spectroscopy. The OH stretch region of most oxides contains several bands corresponding to different types of surface groups [10,11]. Roughly these hydroxyl groups can be classified as acid, neutral and basic (Brønsted-sites). Besides, coordinatively unsaturated metal sites (CUS)
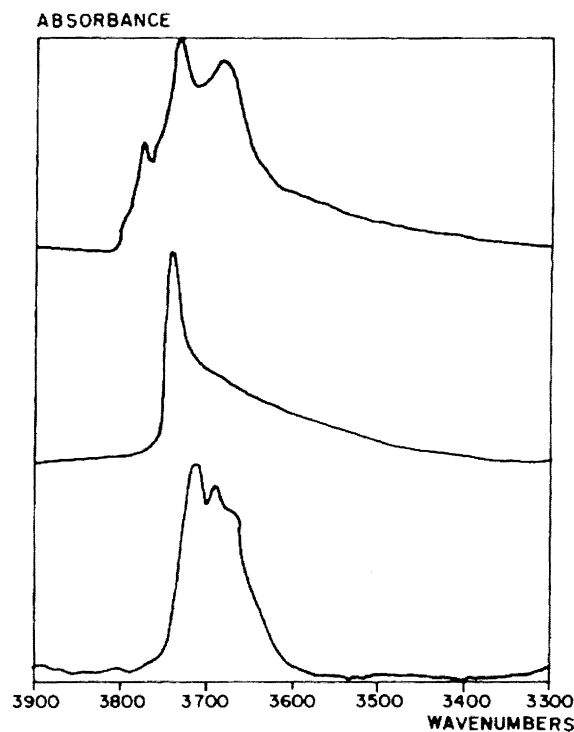

Fig. 1. IR-spectra (OH stretch region) of, from top to bottom, γ-Al_2O_3, SiO_2 and TiO_2. Reproduced with permission [1].

can be present which may act as Lewis-acid centers [1]. The lower the OH stretching frequency for a given support, the more its acidic character. With γ-alumina, as shown in Fig. 1, roughly three band systems are present that can be assigned to specific surface OH configurations. The high-frequency band is due to single bonded, basic hydroxyl groups, the other bands correspond to more acidic bridged hydroxyls. With silica the sharp band at $3740\,cm^{-1}$ is ascribed to isolated and presumably also to geminal hydroxyls, while the broader band at lower wave numbers is due to the presence of hydroxyl groups exhibiting hydrogen bonding [11].

Van Veen et al. [12] revealed that many $M(acac)_n$ complexes show a well defined reactivity towards the surface groups on γ-alumina. Acetylacetonate-complexes, stable in the presence of H^+ and OH^-, such as these of palladium, platinum and cobalt only react with the CUS sites, and thus, can be used to probe the nature of the oxidic support surface sites.

When dispersed in aqueous solutions the surface of particles of mineral amphoteric oxides such as silica and alumina becomes generally charged. Charging is due to de-protonation for neutral and positively charged surfaces by Eq. (1), and for neutral and negatively charged surfaces as described by Eq. (2) as

$$M\text{–}OH + H^+ \rightleftarrows M\text{–}OH_2{}^+ \tag{1}$$

$$M\text{–}OH \rightleftarrows M\text{–}O^- + H^+ \tag{2}$$
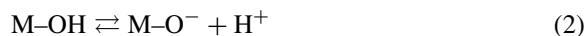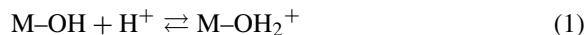
where M is Si, Al, Ti, etc.

The charged surface in combination with the charged layer around the particle is called the electrical double layer. The pH value at which the net surface charge is zero is referred to as the zero point of charge (ZPC) or often loosely the iso-electric point (IEP).

At pH values below its IEP an oxide particle tends to adsorb compensating anions like $PdCl_4{}^{2-}$. At pH values above its IEP, the surface becomes negatively charged and cations like $Pd(NH_3)_4{}^{2+}$ can be adsorbed [13].

From the above it follows that the pH of the solution determines the nature as well as the concentration of the charged surface sites and, thus, the counter ions that can be adsorbed. Therefore, it is important to know the evolution of the surface charge as a function of pH. In Table 1 a number of IEP values of support materials are given. It is important to realize that the actual

Table 1
Iso-electric points of various oxides[a]

Type	Oxide	IEP	Adsorption
Acidic	Sb_2O_3	<0.4	
	WO_3	<0.5	Cations
	SiO_2	1.0–2.0	
Amphoteric	MnO_2	3.9–4.5	Cations or anions
	SnO_2	~5.5	
	TiO_2	~6	
	$\gamma\text{-}Fe_2O_3$	6.5–6.9	
	ZrO_2	~6.7	
	CeO_2	~6.75	
	$\alpha,\gamma\text{-}Al_2O_3$	7.0–9.0	
Basic	Y_2O_3	~8.9	Anions
	$\alpha\text{-}Fe_2O_3$	8.4–9.0	
	ZnO	8.7–9.7	
	La_2O_3	~10.4	
	MgO	12.1–12.7	

[a] Adapted from [13].

IEP value of a support material can deviate somewhat from the values given in the table because of specific pre-treatments and the presence of contaminations. For example, Vordonis et al. revealed that the IEP and the concentration of the charged surface groups at each pH can be regulated by the temperature and by 'doping' the support with ions like Li^+, Na^+ and F^- [14].

Suspended in aqueous solutions basic OH groups will be involved primarily in reaction (1), acidic hydroxyls in reaction (2). Of the oxides of interest here, γ-alumina contains pre-dominantly basic hydroxyl groups, IEP $\approx$ 8. Silica is acidic, IEP $\approx$ 2. At pH values above the IEP the surface is negatively charged and will adsorb cations. Below the IEP the support surface will be positively charged and anionic species can adsorb [1,15]. As an example in Fig. 2 the extent of adsorption of $Pd(NH_3)_4{}^{2+}$ on silica as a function of the pH is shown as measured by Contescue et al. [16].

2.3. Carbon supports

2.3.1. Materials

In addition to oxide materials, carbon supports are very important in catalysis. Carbon materials are often used because of their high surface area and chemical inertness, in particular in strong basic and acid environments. For gas-phase applications its high thermal stability relating to the high melting point is of relevance. Especially, for the production of precious metal catalysts, carbon is a suitable support material due to the easy reclaim of the metal by burning off the carbon. The chemical inertness of carbon, however, can sometimes be a disadvantage. The low reactivity of the surface makes it difficult to deposit metals, therefore, pre-treatment of the carbon in oxidizing environment is generally used to introduce oxygen containing surface groups, thus, enhancing the interaction with the metal [1,17]. This will be discussed in more detail in Section 2.3.2.

Of the many types of carbons, activated carbon is still the one most commonly used as an absorbent and a catalyst support, because of its high surface area (500–1200 m^2/g) and low costs. It is produced by pyrolysis of natural or synthetic organic polymer materials. Mostly, natural materials like wood, coconut shells or fruit pits are used. The carbon material is activated by an air or steam treatment to increase the accessibility of the carbon surface. After activation the
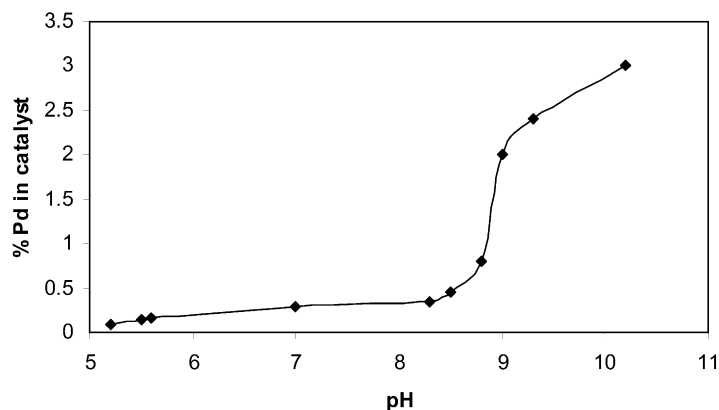
Fig. 2. Effect of impregnation pH on the extent of $Pd(NH_3)_4^{2+}$ adsorption on silica. Adapted from [16].

carbon still contains a large range of elements, such as hydrogen, oxygen and, important for catalysis, sulfur. The texture of activated carbon is extremely complex since it involves macropores, mesopores as well as micropores [1,5,17,18]. Fig. 3 shows an average structure of activated carbon, consisting of aromatic sheets and strips, with variable slits of molecular dimensions, these being the micropores [19]. Both during the emplacement of the active component and during
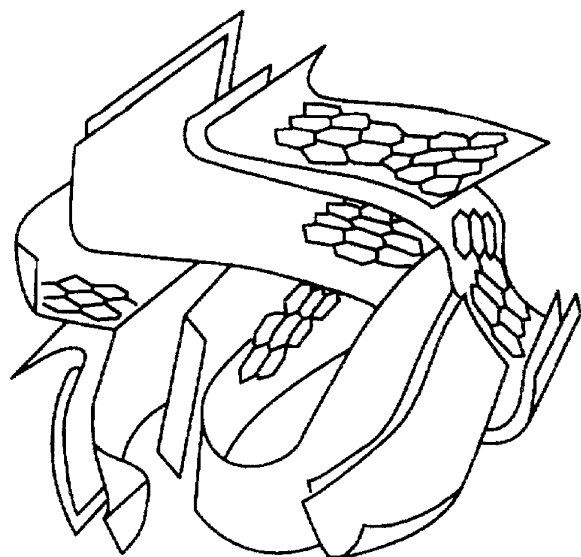
catalysis the complex texture results in poor control and reproducibility [1,17,18].

The carbon molecular sieves (CMS) are a special type of activated carbon. The slit-shaped and almost uniform micropores of these materials are used for separation of air and benzene from cyclohexane. An advantage of CMS as catalyst support over zeolites is that these can be prepared with larger pore volumes while the pore size can be easily adjusted. Another difference between CMS and zeolites is the geometry of the micropores: in zeolites the pores are channels and cavities whereas in CMS the pores are slit-shaped, which influences the accessibility [17,20].

Carbon blacks are carbonic products obtained by thermal decomposition or incomplete combustion of hydrocarbons. They are commercially available with a wide range of surface areas and porosities. Structures ranging from non-porous highly ordered and homogeneously graphitized carbon black to highly porous aggregates with surface areas up to $1500 \, m^2/g$ are available [1,17,21].

In contrast to activated carbon and carbon black, graphite is a highly crystalline material composed of stacked planes of aromatic rings $0.335 \, nm$ apart, see Fig. 4. It originates from high temperature treated carbon. The electronic character of the stacked aromatic systems makes it possible for definite atoms or molecules to slip between the layers, either accepting or donating electrons to bond with the carbon system, a process referred to as intercalation [1,5]. Except for this interplanar area, graphite particles are essentially non-porous, and thus, graphite is not commonly used
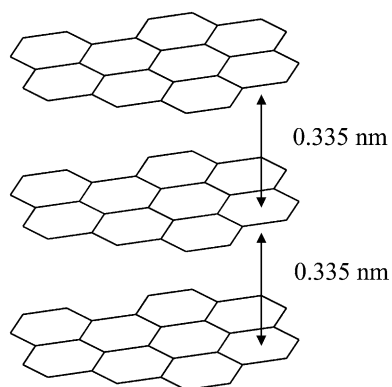

Fig. 3. Schematic representation of the structure of activated carbon. Reproduced with permission [19].

Fig. 4. Layer structure of graphite. Adapted from [5].

Fig. 5. Schematic view of parallel and fishbone carbon nanofibers. Redrawn from [22].

as a catalyst support. However, after an oxidation treatment the edges of the planes contain a.o. acidic functional groups which enable adsorption of the precursor of the active phase. These modified graphites can be used to adsorb cations from neutral and basic media.

Emerging carbon support materials are carbon nanofibers. These fibers with a diameter between 10–200 nm are grown from decomposition of carbon containing gases (e.g. CH_4, CO, C_2H_4) on small metal particles of similar sizes. Carbon atoms are generated on the free metal surface, diffuse through the particle and are converted into a graphite-based fiber by segregation. By proper choice of the synthesis conditions (temperature, gas and metal used) the morphology of the fiber can either be of the fishbone (exposed edge planes) or the parallel type (exposed basal planes), see Fig. 5. Potentially these materials have unique properties for use as a support. They have a high surface area (10–200 m^2/g) and do neither possess micropores nor impurities (such as sulfur or inorganic matter) [1,22,23]. A major disadvantage to the application of carbon nanofibers for catalytic purposes was their limited availability and high production costs. However, recently these drawbacks have been overcome due to the development of fluidized bed technology for large-scale production [23,24]. Lately de Jong and Geus have written an extensive review about the synthesis and applications of carbon nanofibers [23].

2.3.2. Surface chemistry

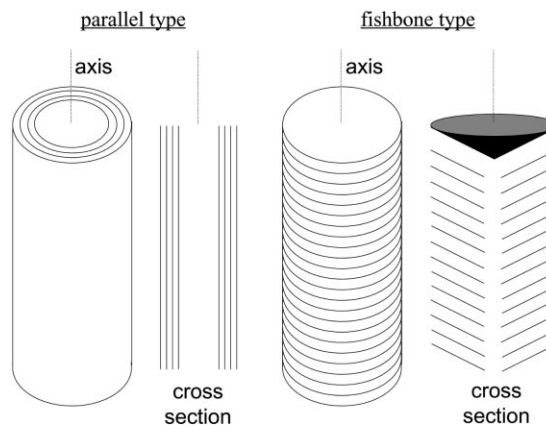Oxygen containing surface groups are by far the most important groups influencing the surface charac-

teristics and adsorption behavior of activated carbon. On activated carbon these groups are always present. Their amount is highly dependent on the way of preparation. They are formed not only by reaction with oxygen, but they also result from reaction with other oxidizing gases (ozone or carbon dioxide) and solutions containing nitric acid, hydrogen peroxide or hypochlorite. The precise nature of carbon–oxygen structures is not entirely established, but the results of many studies using FTIR, Boehm-titrations and TPD demonstrate that several types of surface-oxygen groups can be distinguished [17,18,25], as shown in Fig. 6. Treatment of carbon does not only introduce oxygen groups, but can also affect the carbon bulk chemistry. Darmstadt et al. reported that when
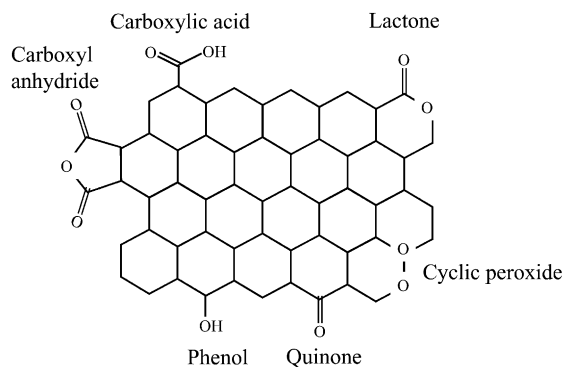

Fig. 6. Different types of oxygen containing surface groups on activated carbon. Adapted from [27].
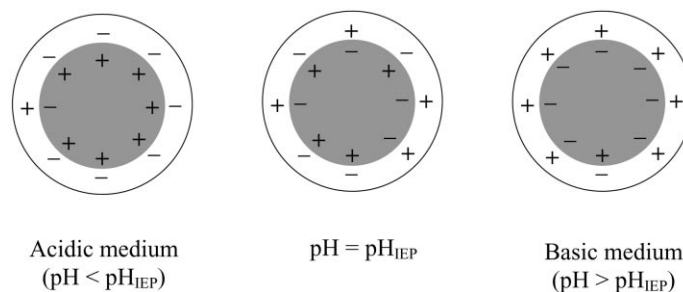
Fig. 7. Schematic representation of the amphoteric character of carbon. Adapted from [17].

catalytically grown carbon nanofibers are treated in nitric acid (373 K, 12 h) pores are formed and the ordering of the graphitic structure decreases [26]. Carbon nanofibers have small diameters (10–200 nm), so a treatment of 12 h induces severe modifications. When the treatment is confined to 1–2 h the carbon bulk properties are not affected [22].

The oxygen containing surface groups can be divided in acidic, neutral and basic. This implies that the carbon surface may have different amounts and types of oxygen surface groups and, consequently, both negatively and positively charged surface sites exist in aqueous solution, depending on the pH. At pH > IEP the carbon surface, covered by deprotonated acidic groups, will attract cations from solution; at pH < IEP it will attract anions [13,17]. This is illustrated in Fig. 7. When preparing a supported catalyst, one needs not only physically accessible sites but also chemical reactivity toward the metal precursor. The electrostatic repulsion between the charged surface and the ionic catalyst precursor may be stronger than the non-specific dispersion forces of attraction. This results in a loss of catalyst dispersion. The catalyst dispersion is optimal when the entire carbon surface is accessible, i.e. when there is electrostatic attraction between the positively charged surface (below pH_{IEP}) and the catalyst precursor anions or vice versa [17].

Carboxyl, quinone and lactone groups are acidic. Because of their negative charge they enhance the interaction between the carbon surface and a positively charged metal precursor. Furthermore, they decrease the hydrophobicity of the carbon, thus, making the surface more accessible for the aqueous solution of the metal precursor [17,27–29]. Suh et al. have proven for Pd on activated carbon that the metal dispersion

increases with increasing amounts of surface oxygen groups [30]. Phenols, carbonyls and ethers are weakly acidic to neutral. Prado-Burguete et al. found that these oxygen groups increase the interaction of the metal precursor or the metal particle with the support, thus, minimizing sintering [29]. Carbons heated in oxygen always contain basic next to acidic sites. When a carbon surface is freed from all surface groups by heating to ca. 1273 K in vacuum or in an inert atmosphere and subsequently comes into contact with oxygen after cooling, acidic sites appear to be destroyed and only basic surface oxides are formed. Boehm et al. concluded that basic surface groups are localized at the same edges as acidic groups, but their quantity is lower. The basicity is explained in terms of the π-sites of the carbon basal plane interacting with water, as shown in the reaction below.

$$C_\pi + 2H_2O \rightarrow C_\pi H_3O^+ + OH^-$$

Increase of the amount of basic sites on the basal plane surface will both enhance the electrostatic attraction with the metal anion complex (e.g. $C_\pi H_3O^+$–$PdCl_4^{2-}$) and diminish the repulsion (e.g. COO^-–$PdCl_4^{2-}$), thus, increasing the dispersion [17,18,25,31–33]. Leon y Leon et al., for example, described the basicity of carbon in terms of pyrone-type structures: where two non-neighboring oxygen atoms constitute one basic site. These two atoms are proposed to be located in two different rings of a graphitic layer, so as to favor resonance-stabilization of the positive charge [31].

Nitrogen is not always present on carbons, but it can be introduced. Ammonia is often used for the preparation of these nitrogen-containing carbons. Although characterization of the nitrogen groups is
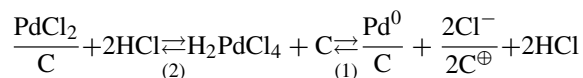
difficult because oxygen and nitrogen functional groups in IR coincide, it is assumed that amides, imides and lactams are created around 473 K in flowing NH$_3$. At higher temperatures in an inert atmosphere these nitrogen-containing groups convert to pyridines and pyrroles [17,18,32].

2.3.3. Precursor-surface interaction

From this last paragraph it is clear that the oxygen surface groups play a very important role in the dispersion of the active phase. The exact nature of the interaction between the palladium precursor and the oxygen groups is not fully clear, however. In order to gain more information on the fundamental interactions between palladium (precursor) and carbon Mojet et al. [34] have done an XAFS study of a palladium catalyst on carbon fiber support. This study showed that no oxygen is present in the first coordination shell of palladium after ion-exchange of [Pd(NH$_3$)$_4$](NO$_3$)$_2$. Secondly, the XAFS data pointed to an strong metal–carbon interaction before and after reduction, responsible for anchoring of the metal particles to the carbon surface after reduction. Although a direct Pd/O contribution could not be detected, oxygen might be situated at a slightly longer distance. Probably the carboxylic groups on the surface and the π-system of the support stabilize the well-dispersed precursor complex. This work will be discussed in more detail in Section 3.2.4. Also Ryndin et al. did not find indications for interaction between Pd(II) ions

and oxygen-containing surface groups [35], which is to be expected because the metal precursor they used (PdCl$_4^{2-}$) was negatively charged as were the oxygen surface groups. These findings necessitate to further investigate the precise role and interaction of the oxygen groups with the metal-precursors.

Simonov et al. have done extensive research on the chemical processes which occur when H$_2$PdCl$_4$ from aqueous solution is adsorbed on the surface of graphite-like carbon materials [36,37]. They found that adsorption proceeds through two competitive pathways: reduction to form metallic Pd particles (process 1) and formation of π-complexes of PdCl$_2$ with C=C fragments of the carbon matrix (process 2):

$$\frac{PdCl_2}{C} + 2HCl \underset{(2)}{\rightleftarrows} H_2PdCl_4 + C \underset{(1)}{\rightleftarrows} \frac{Pd^0}{C} + \frac{2Cl^-}{2C^\oplus} + 2HCl$$

The first process is localized near the exterior surface of the carbon particles. Reduction of palladium is due to the high reducing power and the conductivity of graphitic carbon. Because no evolution of carbon oxides is observed upon reduction of palladium, carbon oxidation is excluded as electron source. Simonov et al. state that Pd(II) ions are discharged by the "electron gas" of carbon accompanied by adsorption of Cl$^-$ ions. C$^\oplus$ is a positively charged "hole" which appears at the carbon surface when Pd(II) is reduced. The Cl$^-$ anions compensate the charge through the formation of an electric double layer on the carbon surface. This
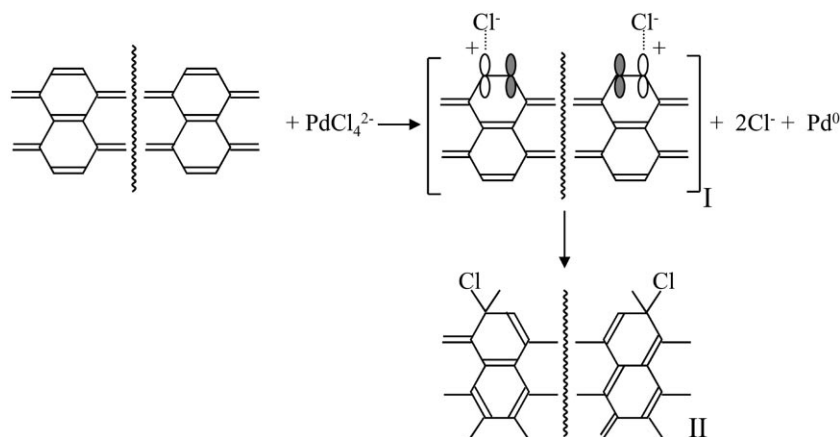

Fig. 8. Scheme representing the adsorption of Cl$^-$ anions to compensate the number of electrons consumed from the carbon to reduce palladium [36].

is illustrated in Fig. 8 [36]. The spontaneous reduction of H_2PdCl_4 results in Pd^0 particles of a broad size range of 6–100 nm [36,37].

Process (2) takes place on the entire surface of the support and results in a uniform distribution of adsorbed $PdCl_2$ (1.6–1.8 nm). An XPS study on H_2PdCl_4 adsorption on oxidized carbons revealed that Pd(II) complexes with oxygen containing groups are not formed. $PdCl_2$ is adsorbed on the carbon surface to form π-complexes with the C=C fragments of the carbon network. On the carbon surface at least three types of adsorption occur: weak (A_1, basal plane), strong (A_2, edge plane) and very strong or irreversible (A_3, micropores), as shown in Fig. 9. When carbon is treated to increase the amount of oxygen surface groups, A_2 and A_3 sites disappear. During drying Pd(II) compounds migrate along the surface to form small clusters. The centers of agglomeration are the surface steps, due to the high adsorption potential of these regions [35,37,38]. This is schematically represented in Fig. 10.

Simonov et al. summarize in their review the factors determining the ratio $PdCl_2/Pd^0$ in adsorbed compounds: the chemical nature of the support surface, its textural characteristics and grain sizes and the conditions for the deposition of palladium compounds (especially pH and composition of the gas-phase) [37]. These variables will be discussed further in Section 3.2.4.
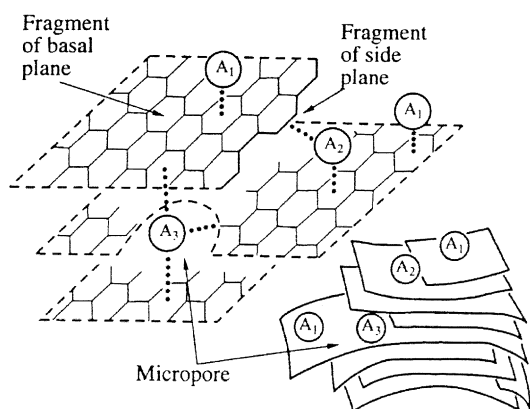

Fig. 9. Probable positions of the irreversible (A_3), strong (A_2) and weak (A_1) adsorption of H_2PdCl_4 on the surface of carbon. Reproduced with permission [37].
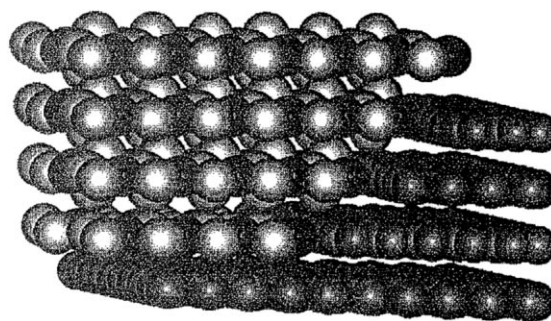

Fig. 10. $PdCl_2$ agglomeration on carbon surface steps. Reproduced with permission [38].

3. Catalyst synthesis — case studies

In our survey of the literature we will use the classification as given by Augustine [5] and other authors in the field [39,40]. This classification is mainly based on the nature of the first step in the procedure in which the active component(s) and the support are combined. Unfortunately, although this seems straightforward, it sometimes appeared difficult to label unambiguously a number of synthesis descriptions as given in the literature.

3.1. Oxide-supported catalysts

3.1.1. Co-precipitation

In the first step of the co-precipitation procedure a compound is formed which is the precursor for both the active component and the support. Using sol–gel, Lopez et al. prepared Pd/SiO_2 catalysts by heating a mixture of an aqueous alcoholic solution of tetraethoxysilane, and an aqueous solution of $PdCl_2$ or $Pd(NH_3)_4Cl_2$ in ammonia [41,42]. The palladium–silica precipitate was extensively dried at 70–100°C for 12 h and calcined for 4 h at 450°C. Subsequent reduction at 450°C for 4 h resulted with loadings below 0.5 wt.% in a high dispersion of Pd on silica with a high surface area of around 800 m^2/g. TEM and chemisorption characterization demonstrated the presence of a narrow size distribution of particles smaller than 1 nm. At higher loadings particle sizes became comparable with these obtained with the impregnation technique.

Zou and Gonzalez investigated the thermal stability of silica-supported Pd catalysts prepared by the sol–gel

method [43]. They mainly used mixtures of Pd(acac)$_2$ and tetraethoxysilane in ethanol, sec-butanol or acetone. By fine-tuning of the reaction conditions, the relative amounts of reactants and the nature of the solvent they succeeded in the production of a catalyst with coinciding average particle sizes and average pore diameters which suppresses sintering of palladium up to 650°C. With TEM and H$_2$ chemisorption Pd particles of 2.4–3 nm were shown to be present (BET surface 650 m^2). In oxygen the Pd particles appeared to be stable, but in hydrogen sintering occurred at 650°C, probably due to a mechanism in which Pd hydride is involved.

Kim et al. [44] used the sol–gel technique for the synthesis of Pd/Al$_2$O$_3$ three-way catalysts and studied the influence of the pH on the features of the ultimate catalysts. They stirred a mixture of a basic (ammonia) or acidified (nitric acid) aqueous solution of aluminum isopropoxide and a Pd(acac)$_2$ solution in acetone for 5 h at 50°C. After drying at ambient temperature for 24 h and calcination at 500°C for 24 h the catalysts were reduced. Differences were found in the reducibility of the two samples. The catalyst prepared at the highest pH needed the highest reduction temperature, i.e. 300°C. NMR measurements indicated that the palladium ions preferentially and strongly interact with tetrahedrally coordinated aluminum ions, present in basic environments. This catalyst showed also the highest Pd dispersion, the most homogeneous Pd distribution and the highest BET surface. These findings underline the conclusions of Lecloux and Pirard [45] that the sol–gel process applied to catalyst syntheses, requires particular well-defined conditions for controlling the morphology of the resulting solids.

With a somewhat modified approach Schneider et al. [46] produced highly porous palladium–titania aerogels. They re-dispersed pre-formed titania gels and added different Pd precursor solutions before drying, under supercritical conditions. Best results were obtained with palladium acetate, although also with this precursor rather large Pd particles were obtained, at least 20 nm, depending on calcination and reduction temperature.

A general procedure for the production of highly loaded palladium catalysts via co-precipitation was presented by Fujitani et al. [47]. They prepared a precipitate by addition of an aqueous solution of Na$_2$CO$_3$ to a solution containing a palladium and a nitrate precursor of the support metal, in this case gallium. After aging at 70°C for 1 h and thorough washing the residue was dried overnight in static air at 110°C, calcined at 350°C for 2 h. and reduced at 250°C. Unfortunately, no further specification of the palladium dispersion was given.

3.1.2. Deposition–precipitation

For a general introduction of this synthesis technique we refer to Geus and co-workers [2,48] and de Jong [49]. Deposition–precipitation can be used to produce catalysts with a variety of supports. Augustine et al. prepared, e.g. 1% Pd/MgO by addition of an aqueous solution of Pd(NO$_3$)$_2$ to a stirred slurry of the support in an aqueous solution of NaOH [50]. After washing the residue was dried overnight at 110°C and reduced in hydrogen. Up to 400°C the palladium dispersion (40%) was found to be independent of the reduction temperature. With CeO$_2$ as the support material Shen et al. demonstrated using XPS [51], EXAFS [52] and chemisorption measurements [53] that the above procedure leads to the presence of a rather high surface concentration of Pd^{2+} ions, even after reduction at 500°C. Obviously, the high pH values applied give rise to a strong interaction of the metal ions with the surface. Interestingly, the catalysts prepared with PdCl$_2$ as the precursor show a significant higher ion-concentration than the catalysts prepared from the nitrate salt.

3.1.3. Deposition–reduction

In the deposition–reduction technique one starts with a suspension of the support material in a solution of the active metal. By introduction of a soluble reducing agent, the metal is directly applied onto the support [54,55]. This procedure is especially suitable for the production of noble metal catalysts because of their favorable reduction potentials. Fogassy et al. deposited palladium up to a loading of 10% directly on silica, alumina and carbon black by addition of sodium formate, the reducing agent, to a boiling suspension of the supports in a solution of K$_2$PdCl$_4$ at a pH value of 10–11. Unfortunately, no specifications of the obtained catalysts were presented [56].

An interesting procedure, called "controlled colloidal synthesis", has been developed by Beck et al. [57]. They effected this control by restricting the

localization of the reduction of the palladium precursor to a well-designed solid/liquid interfacial layer on a silica support. They postulated that by using a proper binary liquid system for the suspension of the support, good separation can be achieved between the adsorption layer and the liquid-phase for one of the two components. If one of the reaction partners is soluble only in one component, or this component itself is the reducing agent, the reduction is localized. As a binary mixture they used ethanol/toluene (6/94), ethanol also being the reducing agent. The support was silica and Pd/acetate (in toluene) was the precursor. Although the mean Pd dispersions and particle sizes did not differ appreciably from these achieved via the normal impregnation route, TEM results revealed sharper size-distributions. Furthermore, it appeared that the reduction is a rather slow process. Due to this, the mean particle size could be readily controlled by varying the reduction time, 6 nm after 1.5 h and 26 nm after 12 h as determined with CO adsorption.

A similar but less controllable procedure was used by Farrauto et al. [58]. These authors obtained 4 wt.% palladium on zirconia, titania, ceria and alumina catalysts by dry impregnation of these supports with a solution of $Pd(NO_3)_2$ followed by the addition of hydrazine to form metallic palladium. Bond and Rawle [59] used the same reduction method for the production of 4–5 wt.% Pd/SiO_2 catalysts using H_2PdCl_4 and $Pd(NO_3)_2$ as the palladium precursors. With the nitrate precursor a dispersion of 13% was obtained, with the chloride in acid environment a dispersion of only 5%. A last example of fixation by reduction has been given by Ilinitch et al. [60]. For the production of γ-Al_2O_3 supported Pd and Pd/Cu catalysts as well as membranes loaded with these metals, they used sodium borohydride ($NaBH_4$) as the reducing agent at room temperature.

3.1.4. Photo-deposition

Recently, an example of the photo-deposition procedure has been given by Amalric-Popescu and Boszon-Venduraz, who deposited metallic Pd particles onto SnO_2 by irradiating a suspension of this support in a aqueous solution of $Pd(NO_3)_2$ [61]. Rather large particles (4.5 nm) were formed as determined by these authors from XRD-line broadening. With silica and alumina supports this route is not accessible.

3.1.5. Impregnation/ion-exchange

In most scientific studies wet or dry impregnation or ion-exchange is used for the production of supported Pd catalysts. For a detailed description of these techniques we refer to Augustine [5] and Schwartz [39].

Sivaraj et al. [62] prepared a series of Pd catalysts on alumina supports obtained by calcining aluminum hydroxide at different temperatures prior to $Pd(NH_3)_4^{2+}$ and/or $PdCl_4^{2-}$ exchange. With acid-base titrations they found that the IEP value shifted from 7.6 after calcination at 400°C to 8.7 after treatment at 900°C. Connected with this and perhaps even more important is the observed decrease of the exchange-site concentration from 6.3 to 3.0 sites/nm^2. Cordi and Falconer pre-calcined their alumina support samples at 600°C before loading them by dry impregnation with an aqueous solution of $PdCl_2$, to dehydrate the alumina support and to oxidize contaminants on the surface [63]. Zou and Gonzalez [64] treated their silica support with diluted nitric acid in order to remove traces of alkali metal ions. The importance of such a treatment especially in scientific research is blatantly revealed by Prins and co-workers [65,66] who demonstrated that the impurities commonly found in commercial silicas are sometimes effective promoters, in their case, for the synthesis of methanol from syngas over Pd/SiO_2 catalysts. Other authors aim at the formation of a specific phase before applying palladium species. An example for this is the formation of δ-Al_2O_3 from a commercial γ-Al_2O_3 material by calcination at 1000°C for 6 h [67]. Similar pre-treatments might also be important in view of the (temperature) conditions chosen for the catalytic process under study. We have found that, generally, in preparations via ion-exchange with non-aqueous precursor solutions pre-calcination is executed. The importance thereof has been demonstrated by Van Veen et al.: with $Pd(acac)_2$ as the precursor the rate of exchange with dehydroxylated surfaces is substantially higher than with hydroxylated surfaces [12]. With γ-Al_2O_3 extrudates the obtained catalysts showed an egg-shell distributions, while with the hydroxylated support an even distribution was obtained.

When the palladium precursor is applied by ion-exchange and/or wet impregnation it has to be taken into account, that the rate of its extraction from the solution is controlled by the limited rate of

adsorption and often, with macroscopic porous support bodies, by pore diffusion. Unfortunately, in most descriptions information concerning the period of interaction is lacking. One of the exceptions is the work of Neyertz and Volpe who measured the removal of Pd(acac)$_2$ from γ-Al$_2$O$_3$/toluene suspensions under well defined conditions [68]. At room temperature, equilibration of precalcined support samples of 0.5 g in an excess of a 0.03 mol/l solution of Pd(acac)$_2$ in toluene, lasted about 80 min.

An example of a nice prescription for the preparation of Pd/SiO$_2$ catalysts (∼1.5 wt.%) using ion-exchange in aqueous solutions is given by Zou and Gonzalez [64]. They applied an interaction period with Pd(NH$_3$)$_4^{2+}$ of 12 h, keeping the suspension with the pre-calcined silica support (Cab-O-Sil, M-5, surface area 200 m^2/g) at a pH value of 9 to maximize the 'metal-support' interaction. After heat-treatment in inert gas and reduction at 400°C they obtained dispersions as high as 70%. A suitable exchange procedure, as mentioned above, involves the interaction of Pd(acac)$_2$ or similar complexes dissolved in, e.g. benzene or toluene with alumina supports. Most of the authors follow the procedure as earlier presented by Boitiaux et al. [69] and used in the studies of Van Veen et al. [11,12].

After ion-exchange the loaded samples can be separated from the excess liquid-phase by filtration or centrifugation. Zou and Gonzalez [64] filtered their suspension and washed the residue in order to remove the weakly adsorbed precursor. Goetz et al. [70] and Pisanu and Gigola [71] in their ion-exchange synthesis of various Pd/α-Al$_2$O$_3$ catalysts (0.09, 0.2 and 0.3 wt.%) dried unwashed samples. Only at 0.09 wt.% loading high palladium dispersions of about 50% were obtained after reduction in hydrogen at 300°C. Notably, Venezia et al. underline the importance of the washing step in avoiding the formation of large palladium particles in the final reduction step due to the presence of an excess of the palladium precursor [72].

After wet impregnation, despite the sometimes high Pd-loadings, the solvent is removed by evaporation at room temperature or at higher temperatures, whether or not under decreased pressure, leaving all of the components in the dried precursor and taking the risk of formation of undesired egg-shell distributions of the active phase [73,74]. The drying procedure can severely influence the ultimate distribution of the active component, especially with macroscopic, porous support bodies [75]. When all or part of the impregnated precursor is only weakly interacting with the pore walls, outward transport of the palladium precursor is hardly avoidable. Some authors chose for a slow drying procedure. Most of the solvent is removed under decreased pressure at room temperature after which the sample is further treated in a stove at enhanced temperatures. Most authors dried their samples "overnight" in static air at a temperature between 80 and 120°C without further explanation of the chosen conditions. It is beyond the scope of this review to further discuss the process of drying. Here we confine to the statement that focussed on the drying of supported palladium catalyst precursors no scientific study has been published up to now.

In a next step of the synthesis procedure the dried precursor generally is heat treated in air (calcination) or in an inert gas before, in the final step, palladium is converted into the metallic state, almost always in a flow of hydrogen. In many papers this heat treatment step, as well as the subsequent reduction step, are better documented than the foregoing steps. By using different treatment conditions, i.e. durance and temperature, a number of authors used one of these steps to obtain palladium catalysts with different particle sizes and dispersions in order to measure the influence of these parameters on the selectivity and activity of a defined hydrogenation reaction. Zou and Gonzalez [64] studied the heat treatment variables which affect the chemistry associated with the preparation of Pd/SiO$_2$ catalysts via dry impregnation under optimized conditions with Pd(NH$_3$)$_4$(NO$_3$)$_2$ as the precursor and Cab-O-Sil, M-5, (SA 200 m^2/g) as the support. All heat treatments were followed by the same reduction procedure at 400°C. They found that heat treatment in hydrogen up to 400°C without pre-treatment in oxygen resulted in poor dispersions of 10–20%, as measured with H$_2$ and CO chemisorption as well as with TEM, probably due to hydride formation. Pre-treatment in oxygen at 100, 200 and 300°C led to substantially higher dispersion of around 40% for all temperatures. Pre-treatment in argon or helium resulted in the highest dispersions of about 70%. Oxidation of the reduced catalysts at 300°C and re-reduction at 400°C did not change the original palladium dispersion.

Łomot et al. demonstrated that the palladium dispersion strongly depends on the loading. With exactly

the same pre-treatment in oxygen at 300°C and reduction in hydrogen at 300°C their 1.45 wt.% Pd/γ-Al$_2$O$_3$ catalyst showed a dispersion of 62% while with the 0.39 wt.% loaded catalyst a dispersion of 91% was measured with CO chemisorption [76]. They furthermore speculated that at reduction temperatures as high as 600°C Pd/Al species are formed in the metal support interface, which highly influences the catalytic properties in the reforming of, e.g. *n*-hexane and its branched isomers. Burch and Urbano found with their 4 wt.% loaded alumina catalysts, manufactured using the incipient wetness technique with Pd(NO$_3$)$_2$ as the precursor salt, that the atmosphere and durance of the pre-treatment hardly influence the resulting dispersions (around 20%) when the subsequent reduction is executed at 500°C [77]. Obviously, this reduction temperature is such high that possible differences introduced in the pre-treatment step became leveled out.

It is generally accepted that with pre-treatments in oxygen containing atmospheres the temperature has to be chosen below the decomposition temperature of the formed palladium oxide phase to avoid sintering due to the weaker interaction of the metallic particles with the support. A convincing example of the dependence of the ultimate Pd dispersion on the calcination temperature has been presented by Papaefthimiou et al. [78]. They calcined a series of samples of a 0.3 wt.% loaded Pd/γ-Al$_2$0$_3$ catalyst subsequently at temperatures in the range of 500–800°C with steps of 50°C and found a fall of the dispersion from 100% with the lowest temperature to only 4% after treatment at 800°C. The most severe decrease was observed going from 750 to 800°C probably due to thermal decomposition of formed PdO at this high temperature.

The decomposition temperature, however, is found to depend on the nature of the support material as demonstrated by Farrauto et al. [58]. Using thermal gravimetric measurements they found with their 4 wt.% Pd catalysts, prepared using reduction precipitation and precalcination in air at 500°C, the highest decomposition temperature with PdO/Al$_2$O$_3$ (810°C) and the lowest with PdO/ZrO$_2$ (682°C). XRD line-broadening results showed that the decomposition was accompanied by sintering. An interesting observation has been reported by Cordi et al. A 3 wt.% Pd/Al$_2$O$_3$ catalyst, reduced at 300°C exhibited re-dispersion of the metal during a subsequent treatment in helium at 500°C [63].

Also the nature of the palladium precursor influences the ultimate dispersion, as has been demonstrated by Seone et al. [79]. After calcination in a stream of air at 350°C and reduction in hydrogen at 250°C, their 0.3 wt.% Pd/α-Al$_2$O$_3$ ex-nitrate catalyst exhibited a dispersion of ~22% while the 0.3 wt.% ex-chloride catalyst only showed a dispersion of around 8%. This low value turned out to be hardly depending on the reduction temperature.

Earlier we reported the work of Didillon et al. [9] concerning the formation of palladium oxide colloidal particles from acidic palladium nitrate solutions by adding an alkaline solution. Authors demonstrated that using the dry impregnation technique, the colloidal suspensions containing PdO particles of 1.8–1.9 nm can be used for the production of catalysts with well defined palladium dispersions. After drying, reduction was performed at 150°C. Although authors did not observe significant sintering at this temperature no information is available concerning the resistance towards sintering of such systems at higher temperatures. Nevertheless, the above procedure may be interesting especially when very well defined palladium dispersions are desired.

Above survey demonstrates that many factors influence the ultimate dispersion of a given catalyst system. With high loadings it is always difficult to attain and maintain high dispersions because it is impossible to bind all the precursor molecules strongly and well dispersed to the support. Of course, the 'critical' loading up to which sintering readily can be suppressed will depend on the nature, the structure and the pre-treatment of the support and as well as on the nature of the precursor and the used procedure and conditions used to apply the precursor onto the support.

3.2. Carbon-supported catalysts

3.2.1. Deposition–precipitation

Jin et al. [80] have deposited palladium (5 wt.%) on pitch-based activated carbon fibers. The fibers had been activated by a treatment in 70% nitric acid at 353 K for 3 h to introduce oxidic surface groups. The Pd/C catalysts were prepared by alkaline hydrolysis of palladiumchloride to deposit Pd(OH)$_2$ followed by liquid-phase reduction using formaldehyde as reducing agent. The metal dispersion, thus, obtained ranged from 55 to 77%. Also Farkas et al. [81] deposited

Table 2
Effect of support activation and reduction procedure on Pd dispersion[a]

Support	S_{BET} (m^2 g^{-1})[b]	Dispersion Pd (%, H$_2$ chemisorption)	
		Reduction H$_2$	Reduction HCOONa
Activated carbon HCl	1000	48	10
Activated carbon O$_2$/N$_2$	1130	41	20
Activated carbon HNO$_3$	910	50	20
Graphite	8.4	48	20
Carbon black	36	43	10

[a] Adapted from [81].

[b] As reported. For microporous supports, however, S_{BET} is only a relative measure and has no physical meaning.

palladium on carbon using deposition precipitation. Instead of carbon fibers they used graphite, carbon black and activated carbon pre-treated with HCl, O$_2$/N$_2$ or HNO$_3$. The palladium precursor, K$_2$PdCl$_4$, was added to an aqueous suspension of the support and the pH of the solution was adjusted to 10–11 by addition of a KOH-solution. Precipitated Pd(OH)$_2$ was reduced by HCOONa or H$_2$. The effects of the type of support, pre-treatment and the reduction procedure on the Pd dispersion are presented in Table 2. From the table it can be concluded that reduction by hydrogen results in a much higher dispersion than reduction by HCOONa. With only the dispersion data available it is not possible to determine whether a broad or small particle size distribution was present.

3.2.2. Deposition–reduction

Another method to apply palladium on carbon is deposition–reduction. Hoogenraad et al. [82] used this method to deposit palladium on parallel carbon nanofibers (surface area = 230 m^2/g). Their method consists of four steps: pre-treatment of the fibers in boiling 65% nitric acid (10–30 min), suspension of the treated nanofibers in water and subsequently addition of an aqueous solution of (Pd(NH$_3$)$_4$Cl$_2$). Finally, a formaldehyde solution was injected to reduce the palladium ions. The precipitation and reduction of palladium was performed under a nitrogen atmosphere. After reduction the suspension was filtered and dried in an inert atmosphere at room temperature. Additional drying of the loaded carbon nanofibers involved heating, still in inert atmosphere, in 12 h up to 353 K and cooling. This procedure of slow heating was chosen to avoid sintering. The resulting (2.5 wt.%) Pd/C catalysts were characterized with TEM and

XRD. In the fresh catalyst no palladium species on the carbon nanofibers were perceptible. Only after reduction in hydrogen at 523 K palladium particles with a mean size of 4 nm could be observed. The size of the particles increased during prolonged reduction due to sintering. When air had not been excluded during preparation and drying the extent of sintering turned out to be larger. Probably, in the presence of oxygen the palladium particles became re-oxidized, which enhanced their mobility and sintering. Another parameter studied by Hoogenraad et al. was the effect of the pre-treatment of the carbon nanofibers. It was found that when the carbon fibers had not been pre-treated in nitric acid hardly any palladium was deposited onto the fibers. Pre-treatment of the support for only 10 min in HNO$_3$ appeared to be sufficient to obtain the maximal ($\sim$2.5–3 wt.%) Pd loading. The surface oxygen groups, thus, created either anchor the palladium precursor directly to the surface or make the hydrophobic fibers more accessible for the aqueous precursor.

Heal and Mkayula [83] used deposition–reduction for the preparation of (5 wt.%) palladium on activated carbon catalysts. In a suspension of activated carbon they reduced an aqueous solution of Na$_2$PdCl$_4$ with sodium hypophosphite or with formaldehyde. The activated carbon samples were pre-treated in several ways: oxidation in air (burn-off), with nitric acid or with furfuryl alcohol to block the micropores. Sodium hypophosphite resulted in smaller particles than formaldehyde. Burn-off (15–25%) had a positive influence on the palladium dispersion, probably caused by an increase of the surface heterogeneity. Nitric acid treatment resulted in larger Pd particles and preferential blocking of carbon micropores by

furfuryl alcohol had no effect. They found that the deposition–reduction technique yields catalysts with metal particles located mainly in the wider pores. Apparently, the liquid-phase reduction is so fast that penetration into the smaller pores is not possible.

Yang et al. [84] applied deposition–reduction with a $Pd(NO_3)_2$ precursor, but they used an alternative procedure for the activation of the support. Instead of creating oxygen surface groups on the surface with an acid treatment, they pre-adsorbed halogen ions. First activated carbon was immersed in a halide solution (NaCl, KBr, NaI) and halogen ions were adsorbed on the carbon for at least 10 h. After separation of the supernatant liquor a $Pd(NO_3)_2$ solution was added. After the precipitation or complexation of the Pd^{2+} ions with the halogen ions for some hours the mixture was reduced with hydrazine. They compared the, thus, obtained results with these obtained with non-pre-adsorbed supports. The pre-adsorption of different halogen ions on the carbon resulted in significant changes in the ultimate Pd^0 particle size distribution. When using Cl^- pre-adsorption some of the Pd particles grew much larger than without pre-adsorption, whereas Br^- ions resulted in smaller and more uniform particles. With I^- the Pd particle size is greatly reduced (2–6 nm) and a very uniform particle size distribution is obtained. Yang et al. concluded that functional ion pre-adsorption on a support is an efficient method for the preparation of highly dispersed Pd/C catalysts. Its most important advantage might be that functional ions or groups can be selected based on the interaction between metal precursors and functional ions. This is not possible when an oxidative pre-treatment is used.

3.2.3. Impregnation and drying

Gurrath et al. [85] have closely investigated the preparation of palladium on activated carbon catalysts using incipient wetness impregnation. These carbons (produced from peat, coconut shell and pyrolyzed hydrocarbons) were subjected to treatment with oxygen, hydrogen, chlorine or ammonia at elevated temperatures to get catalyst supports differing in pore structure and surface properties. Palladium was deposited from anionic (H_2PdCl_4 in water), neutral ($Pd(OAc)_2$ in acetone), and cationic ($[Pd(NH_3)_4](NO_3)_2$) complexes, to study the difference in interaction. These complexes were introduced into the pores of the supports by

incipient wetness impregnation, with the Pd concentration of the solutions adjusted to get a metal loading of 100 µmol/g of support. Samples with supported Pd complexes were dried in an oven at 380 K followed by outgassing in vacuum at the same temperature. Subsequently, the samples were reduced in pure hydrogen heating to the final temperature at a rate of 20 K/min.

As expected, treatment with oxygen resulted in supports with a significant larger number of acidic groups at the expense of basic groups. The pre-treatment in chlorine, hydrogen and ammonia led to the opposite effect. These treatments used caused only small changes of the porous structure of the carbons. However, the results of CO chemisorption measurements proved to be strongly dependent on the reduction temperature. Fig. 11a shows with H_2PdCl_4 as the precursor a relatively small amount of CO uptake after H_2 reduction at room temperature. However, catalysts prepared from the tetramine complex and reduced at room temperature showed a larger uptake of CO (see Fig. 11b). With both catalysts always a strong decrease in the palladium dispersion was observed upon reduction above 420 K, due to sintering of the metal.

In comparison to the reduction temperature, the nature of the palladium precursor compound and the pre-treatment of the carbon support had a smaller effect on the ultimate metal dispersion. This is rather unexpected, because when looking at the work of Brunelle [13], it is found that the final dispersion of the metal is determined amongst other things by the repulsion and attraction between charged supports and anionic, neutral and cationic metal precursors.

The use of the tetramine complex tends to result in the poorest dispersions (2–31%). Gurrath et al. [85] ascribe this observation to the direct reduction with hydrogen of the adsorbed $[Pd(NH_3)_4]^{2+}$ complex. A mobile $[Pd(NH_3)_2H_2]$ species is formed, which leads to easy agglomeration. When the Pd complex is first thermally decomposed under helium, higher dispersions are obtained. No general trends for Pd dispersion as a function of the pre-treatment procedure could be detected, partially due to overlapping effects of the nature of the Pd precursor. Several possible explanations have been cited for the limited effects of the carbon surface groups on the dispersion of the catalysts studied in this work. Thermal decomposition of surface groups is not a valid explanation, since this process occurs only above 470 K.
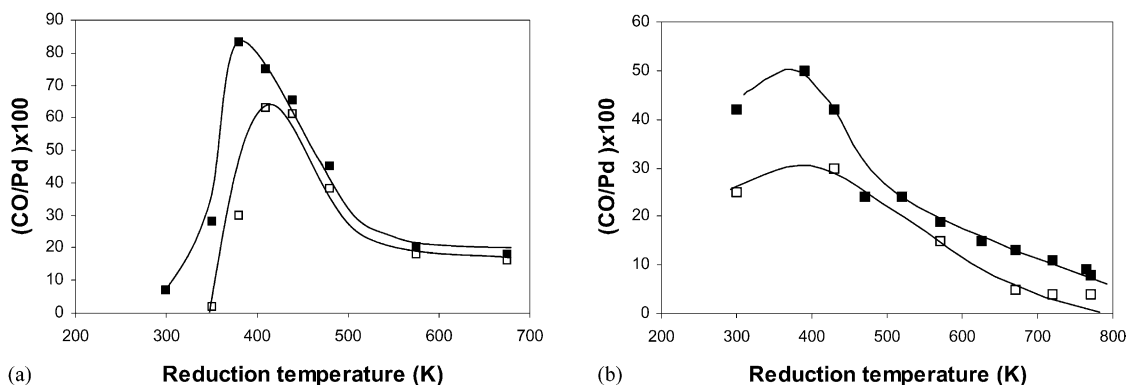
Fig. 11. Dispersion values (CO/Pd) as a function of the reduction temperature (treatment with H_2 for 1 h): (a) for H_2PdCl_4 on Anthralur-HT; (b) $[Pd(NH_3)_4](NO_3)_2$ on Norit-ox. The metal loadings were 50 μmol/g (open symbols) and 200 μmol/g (filled symbols). Redrawn from [85].

However, some compensating phenomena can occur. Two examples will be given here. The first one refers to the surface sites capable of anchoring metal complexes and stabilizing the supported metal against sintering. If for instance carboxylic surface groups are destroyed by heat treatment under ammonia, the Pd complex may be adsorbed by ligand exchange with the newly created N-containing groups on the modified surface. As a consequence, the Pd dispersion can be the same. Secondly, catalysts pass through several stages during the preparation and the surface groupings act in co-operation with other factors. A positive and a negative influence of the carbon treatment in one stage might be compensated in subsequent steps. Another important influence is the presence of micropores in activated carbons. Gurrath et al. found that narrow pores are not easily accessible to more bulky molecules, implying that part of the support is lost for metal emplacement. The small and planar molecules of $PdCl_4^{2-}$ complexes can penetrate deeper into smaller pores than the more bulky $[Pd(NH_3)_4](NO_3)_2$ and trimeric $[Pd(OAc)_2]_3$ precursors.

Krishnankutty et al. [86–88] investigated the effect of the nature of the Pd precursor and carbon pre-treatment in the preparation of Pd/C catalysts by incipient wetness impregnation as well. Carbon black was given a high temperature pre-treatment under flowing H_2 (C-HTT-H_2) or Ar (C-HTT-Ar) for 16 h at 1223 K to remove sulfur and oxygen from the surface. A pre-treated C-HNO$_3$ sample was prepared by boiling a portion of the C-HTT-Ar sample in 15.8 M

HNO$_3$ for 6 h. An incipient wetness method under nitrogen was exploited to prepare 3 wt.% Pd/C catalysts. Pd(acac)$_2$ dissolved in dried THF to produce Cl-free catalysts and PdCl$_2$ dissolved in water were used as precursors. After the high temperature treatment of the support sulfur has been removed from the surface, so the carbon surface could not have been contaminated with sulfur. After reduction the observed Pd lattice expansion, suppressed hydrogen chemisorption and decreased hydride formation pointed to the presence of interstitial carbon and carbon that covers the Pd surface. Carbon from the Pd(acac)$_2$ precursor was found to contaminate both the bulk and the surface of Pd crystallites in Pd/C catalysts during a standard hydrogen reduction at 573 K. This carbon could be removed by calcination in oxygen. Krishnankutty et al. proposed, as shown in Fig. 12, a model in which a Pd/C catalyst could contain a mixture of particles of type A–D with various extents of carbon coverage [88]. The observed phenomena during dispersion measurements in this study can be explained by Pd particles of type C (partial carbon overlayer and bulk carbide). Therefore, when determining with chemisorption the dispersion of Pd/C catalysts prepared with Pd(acac)$_2$ it is of great importance to subtly remove carbon of the surface of the palladium particles.

Fairly narrow Pd particle size distributions were obtained with all catalysts obtained from Pd(acac)$_2$ after reduction at 573 K, irrespective of carbon pre-treatment. Pd/C-AS, Pd/C-HTT-H_2
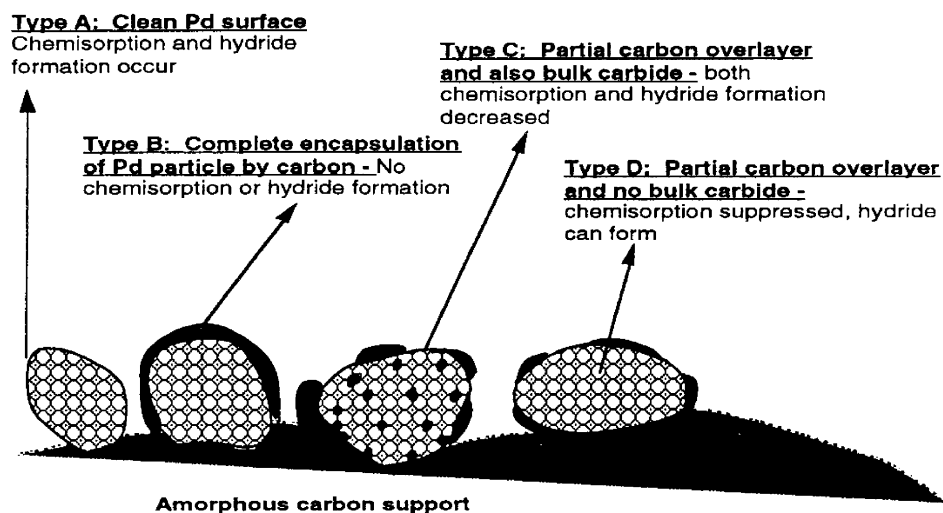
Fig. 12. Palladium particles with various extents of carbon surface coverage and/or bulk carbide. Reproduced with permission [88].

and Pd/C-HTT-Ar have similar Pd particle sizes, 3.5–4.3 nm, but Pd/C-HNO$_3$ showed a slightly larger size, 6.3 nm. This small increase, probably due to the lower surface area of the C-HNO$_3$ support, shows that small Pd particles are not preferentially stabilized by the oxygen groups of the support. Because the precursor is a neutral species an advantageous interaction between the precursor and the negatively charged support is not expected. Broader particle size distributions were obtained with the PdCl$_2$ precursor and even large Pd particles up to 45 nm were observed.

This can be ascribed to sintering of Pd particles from PdCl$_2$ at higher temperatures.

A substantial amount of research has been devoted to the palladium chloride precursor with incipient wetness impregnation. The work of Gurrath and Krishnankutty was already described, and below the most important results of other authors using PdCl$_2$ ([38,89–93] a.o.) are summarized. Moroz et al. [38] extended the work of Simonov et al. (see Section 3.2.4) using incipient wetness impregnation on carbon black. As has already been shown in Table 3

Table 3
Factors determining the PdCl$_2$:Pd^0 ratio in adsorbed compounds[a]

PdCl$_2$ high	Pd^0 high
1. Powdered carbon support	1. Granulated support
2. Low temperature	2. High temperature
3. The presence of ligands that decrease the $E^0_{Pd^{2+}/Pd}$ value (excess HCl)	3. Absence of ligands that decrease $E^0_{Pd^{2+}/Pd}$ value in the H$_2$PdCl$_4$ solution
4. The presence of electrolytes with lyophilic anions (SO$_4{}^{2-}$)	4. The presence of electrolytes with surface active anions (ClO$_4{}^-$)
5. The presence of additional oxidants (O$_2$, H$_2$O$_2$)	5. No other oxidants (inert)
6. Fast penetration of Pd(II) ions into the pores of carbon (high concentration H$_2$PdCl$_4$, incipient wetness impregnation or adsorption from solution under vigorous stirring)	6. Slow penetration of Pd(II) ions into the carbon pores (low concentration H$_2$PdCl$_4$ and excess solvent)
7. High coverage of the carbon surface by palladium compounds	7. Low coverage of the carbon surface by palladium compounds
8. Low electric capacity of the double electrical layer (DEL) of carbons (low surface area of carbon support or oxidized surface)	8. High electrical capacity of carbon DEL (large surface area carbon support, no oxidation of carbon support)

[a] Adapted from [37].

incipient wetness impregnation of H_2PdCl_4 on carbon results in a high $PdCl_2/Pd^0$ ratio. After drying 60% of the original amount of $PdCl_2$ is present in the form of small, highly dispersed clusters (<1.8 nm in size). XRD RED (radial electronic density distribution) analysis show a Pd/C distance. This is due to the earlier mentioned preference of the $PdCl_2$ clusters to coordinate near carbon surface steps.

A special carbon support material was used by Teunissen [90]. She used magnetic graphite-coated nickel–iron alloy particles (average size 25 nm) as catalyst support; the magnetic properties of these particles allow fast and simple catalyst recovery from liquid media. After incipient wetness impregnation with H_2PdCl_4, electron probe analysis showed a homogeneous distribution of palladium chloride over the sample. HRTEM images of the reduced (Pd on C/NiFe) catalyst displayed the presence of palladium particles of 3–4 nm. It turned out that no activation of the carbon coating was necessary to anchor the palladium complexes.

An important topic when using impregnation is the distribution of the active component over the macroscopic support bodies. Four major types of distributions are shown in Fig. 13. Each of these distributions have advantages and disadvantages. If a reaction is transfer limited, an "egg-shell" catalyst, having the active component on the outer surface of the support would be the most efficient. If no transfer limitations are present a uniform distribution is preferred. "Egg-white" and "egg-yolk" types are desirable if the reaction medium contains a catalyst poison. The exterior of the support can absorb the poison and the catalyst remains active for a longer time [1,5]. Bianchi et al. [94,95] have reported a special way of preparing an egg-white (5 wt.%) Pd/C catalyst. They used activated carbon and impregnated with H_2PdCl_4. During the adsorption process, 15 min, the vessel

was sonificated. Subsequently, the samples were reduced by addition of Na-formiate at 353 K. The counter-diffusion between impregnate and reducing agent brought about the egg-white distribution.

It is not possible to extensively review all precursors. Therefore, a short description of the most frequently applied palladium precursor complexes next to H_2PdCl_4 and the resulting catalysts will be given below. Hermans et al. [96] synthesized palladium based carboxylate-type compounds for the impregnation of active carbon. The selected compounds correspond to the general formula $Pd(O_2CR)_2$, $Pd(O_2CR)_2L_2$ or $Pd(O_2CR)_2L'$, with $R = CH_3$, C_2H_5 or C_6H_5, $L =$ pyridine or diethylamine, and $L' = 2,2'$-bipyridine or 1,10-phenanthroline. Pd/C catalysts (5 wt.%) were prepared by impregnation from solutions of these complexes in water, benzene or acetone, followed by drying and thermal activation under nitrogen. After activation only metallic palladium was detected, indicating that degradation of these complexes results in complete reduction of the metal. All catalysts prepared in benzene were found to have a high Pd dispersion, whereas impregnation with water or acetone as the solvent resulted in poorly dispersed catalysts. This is probably due to the influence of the solvent on the advantageous interaction between the (non-polar) support and the precursor solvent. Probably this interaction with acetone and water can be improved by creating additional oxygen surface groups on the support, which make the support more hydrophilic. Also the palladium/ligand ratio of the polydentate complexes appears to play an important role in the preparation of the catalysts, since these complexes can have a monomeric as well as a trimeric structure. The presence of monomeric structures results in higher dispersions than when trimeric species are present.

Other palladium precursors used are allylic Pd complexes $(C_3H_5PdC_5H_5)$ [35], palladium acetetate $(Pd(Oac)_2)$ [28], palladium acetylacetonate $(Pd(acac)_2)$ [97] and palladium polynuclear hydroxy complexes $(Pd(OH)_n)$ [37]. All of the above precursors give monomodal 1–2 nm Pd particles except the $Pd(acac)_2$ precursor, with which the catalyst is pyrolysed at high temperatures (873–1673 K) probably causing strong sintering. It is difficult to compare these methods because there is much variation in the preparation procedure (drying, calcination, and reduction).
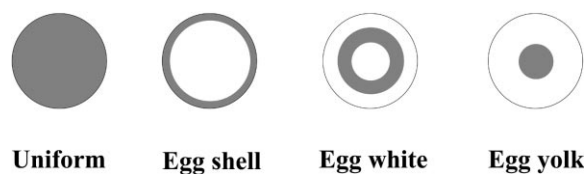

Uniform   Egg shell   Egg white   Egg yolk

Fig. 13. Distributions of active phase over support bodies. Adapted from [1].

3.2.4. Adsorption/Ion-exchange

The precursor that is most often employed for the preparation of Pd/C catalysts, using adsorption is H_2PdCl_4 ($PdCl_2$ in HCl). Simonov et al. have extensively studied the interaction of H_2PdCl_4 with different types of carbon supports and the parameters influencing the palladium dispersion [35–37,98–100]. The four key steps involved in the synthesis of Pd/C catalysts using adsorption are impregnation, washing, drying and reduction. Please note that a detailed description of the chemistry of the interaction of Pd and carbon is found in Section 2.3.3.

Simonov et al. carried out an adsorption of H_2PdCl_4 from an aqueous 0.01 M solution at 298 K in a controlled atmosphere (He, air or O_2) [36]. Adsorption on the powdered support was performed in a static reactor under strong stirring of the suspension or on the granulated support through circulative impregnation. After adsorption (1–3 h) the carbon was filtered, washed and dried in vacuum at 323 K. The Pd content of the samples was 2.0 wt.%. A Sibunit carbon support (graphite-like, $500\,m^2/g$) [101,102], pre-treated by boiling for 3 h in water or in an aqueous mixture of 15% HCl and 5% HF, was used. The palladium was deposited in two ways both resulting in large, non-uniform (6–100 nm) metallic Pd particles assembled on the external surface and small (1–3 nm) uniform $PdCl_2$ clusters evenly distributed over the surface [36]. The factors influencing the $PdCl_{2(s)}/Pd^0_{(s)}$ ratio are summarized in Table 3.

Besides the above-mentioned influences on the $Pd/PdCl_2$ ratio, the dispersion of the metallic palladium was found to be determined by at least three factors: support particle size, preliminary washing of the support with acid and the composition of the gas atmosphere. The average size of the metal particles formed increased with increasing carbon particle size, due to a relative decrease of external surface. Obviously, the concentration of sites for formation of metal nuclei decreased when the oxygen partial pressure in the gas atmosphere increased. Thus, oxygen not only reduces the quantity of metal phase formed, but inhibits the formation of Pd^0 crystallization sites as well. Initial ash removal from the support by acid washing enlarged the Pd particles too due to a decreased amount of nucleation sites. XRD and HRTEM results show also that the metallic Pd particles are spherical and that their average size was about 1.5–2

times larger than their crystallite size which shows a polycrystallinity of the particles [36].

The drying procedure has a significant influence on the features of the Pd/C catalysts as well. Fast drying by heating with solvent evaporation causes a small increase in the amount of Pd^0, due to the thermal decomposition of $PdCl_2$ complexes. Slow drying by storing impregnated carbon in air for a long time, however, decreases the amount of Pd^0, because metal particles dissolve under the action of O_2 and HCl. During drying Pd(II) compounds migrate over the carbon surface to the micropores and most disordered regions on the surface, and interact with each other resulting in agglomeration. The centers of agglomeration of $PdCl_2$, the surface steps that interact with the $(PdCl_2)_n$ clusters both chemically with π-bonds and epitaxially, are shown in Fig. 10. Another consequence of the removal of the solvent is the coverage of the surface of some Pd^0 and Pd(II) particles by fragments of the carbon framework. This effect is caused by "graphitization" of carbon around crystallites and is amplified by the ability of palladium to interact epitaxially with carbon networks [37].

According to Simonov et al. the origin of metal particles in the final Pd/C catalyst may be dual: some are formed at the initial stage during impregnation of carbon with H_2PdCl_4 (primary Pd^0, 6–100 nm) and other particles appear only when $PdCl_2$ reacts with a reducing agent (secondary Pd^0) [37]. Reduction with hydrogen at 523 K does not change the size distribution of primary Pd^0. Highly dispersed (1–5 nm) particles of secondary Pd^0 are formed during reduction of the surface π-complexes and $(PdCl_2)_n$ clusters. Oxygen-containing surface groups do not affect the ability of Pd^0 particles to sinter, apparently because these groups decompose or reduce under these reduction conditions (H_2, 523 K) in the presence of Pd. The average size of the secondary Pd^0 particles strongly depends on the presence of strong adsorption sites on the support (A_2, edge sites) and on the interaction of catalyst precursor and support. Due to the co-existence of two routes for the formation of Pd^0 particles a bimodal size distribution of the Pd/C catalyst is observed [37]. Benedetti et al. [103] confirmed this bimodal size distribution using a comparable preparation method. For the optimization of high dispersions it is very important to choose conditions that lower the amount of primary Pd^0 and enlarge the amount of secondary Pd^0.

Fenelonov et al. [100] extended the research on Pd/C catalysts with another carbon support, namely with carbon nanofibers. Because of the similar electronic properties of graphitic Sibunit material and graphitic carbon nanofibers it can be assumed that the same process take place when H_2PdCl_4 is adsorbed. The only major difference between the two types of carbon support is the absence of A3 absorption sites, because of the absence of micropores in carbon nanofibers. Fenelov concluded that carbon nanofibers are capable of stabilizing the finely dispersed Pd phase, due to a stronger interaction between catalyst precursor and the fiber support.

Also other authors dealt with H_2PdCl_4 adsorption on carbon supports ([83,103,104] a.o). Albers et al. [104] prepared Pd catalysts (5 wt.%) on activated carbon and carbon black. The supports were used in their original state as well as after HCl-treatment to reduce the ash and impurity content. It appeared that the acid treatment of the support enhanced the Pd dispersion and narrows the Pd particle size distribution.

In the literature on the preparation of palladium on carbon catalysts only cation exchange is described on negatively charged (oxygen containing surface groups) carbon supports. We found no literature on anion exchange on basic (positive) carbon supports.

The most widely applied cationic precursors are the palladium amine complexes. They are used in two forms, the $[Pd(NH_3)_4](NO_3)_2$ [22,34,90,105,106] and the $[Pd(NH_3)_4]Cl_2$ complex [22,83,105,107].

In our group extensive investigations have been carried out on the preparation of palladium on carbon nanofiber catalysts using ion-exchange [22,34,105]. Hoogenraad et al. utilized for their study carbon nanofibers of the parallel type (surface area $225\,m^2/g$) grown out of an iron on alumina catalyst. The fibers were activated by treating them in boiling concentrated nitric acid (10–120 min). Subsequently, the fibers were washed with water and dried for 1 h in air at 393 K. A weighted amount of the activated and dried support was suspended in water, the pH of which had been adjusted to a value of 5–6. Then an aqueous solution of a palladium-precursor $(Pd(NH_3)_4(NO_3)_2,$ $Pd(NH_3)_4Cl_2$ or $H_2PdCl_4)$ was injected under stirring. After this procedure the suspension was filtered and dried for 12 h at 353 K in air or in a nitrogen atmosphere. From thermogravimetric measurements the amount of carbon–oxygen sites was found to increase linearly with pre-treatment times up to 120 min. Nevertheless, activation for 10 min appeared to be sufficient to get a maximum loading. Prolonged activation turned out to increase the
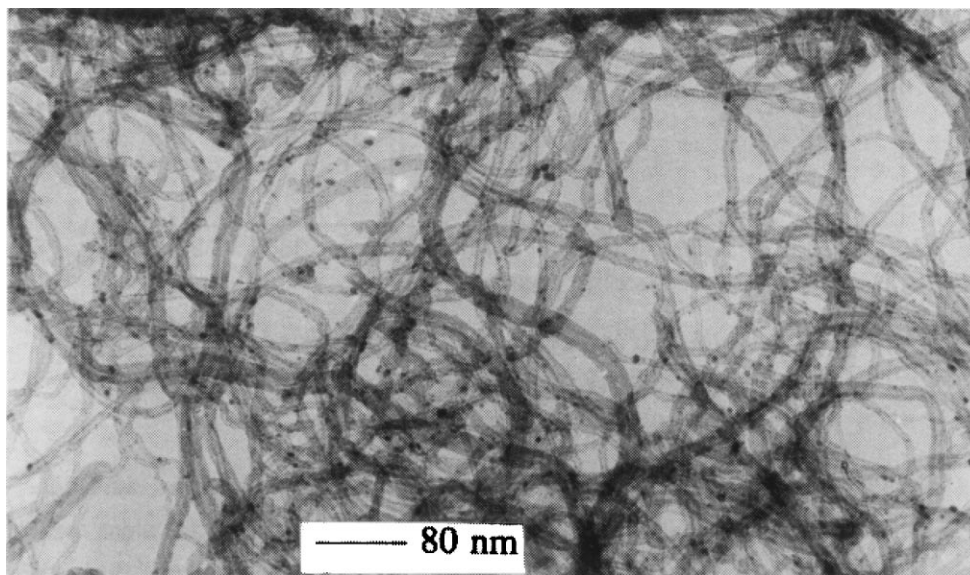

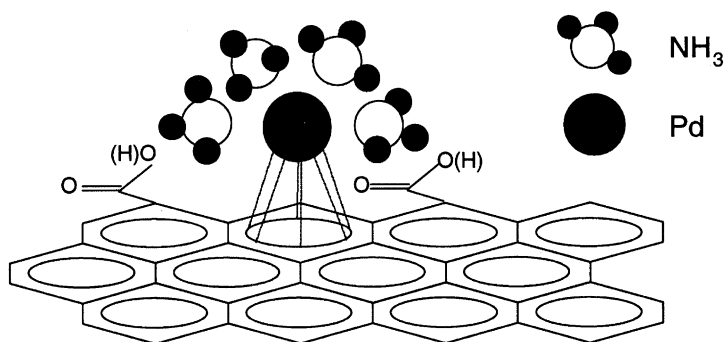Fig. 14. TEM micrograph of reduced palladium on carbon fibers [22].

Fig. 15. Schematic representation of the interaction of a palladium tetrammine complex with a parallel carbon fiber surface (dried catalyst) [22].

number of surface groups but not the final loading. The IEP of the treated carbon nanofibers was measured to be 2.3. The cationic palladium amine ($Pd(NH_3)_4^{2+}$) complexes should interact favorably with the support. The authors found that with non-pre-treated fibers no palladium could be adsorbed onto the surface of the nanofibers. Palladium chloride resulted in the precipitation of large particles (50–100 nm) of $Pd(OH)_2$ separate from to the support. Apparently, at a pH of around 5.5, which was adjusted by addition of a small amount of sodium hydroxide, the Cl/Pd ratio was too low to avoid hydrolysis. With the palladium amine precursors no nucleation of insoluble palladium species in the bulk of the solution was observed. TEM pictures and XRD patterns of dried samples did not show the presence of palladium particles, however, after reduction at 523 K for 2 h in hydrogen some sintering led to the formation of still very small palladium particles of 1–1.5 nm in diameter (3 wt.%), as can be derived from Fig. 14. Similar results were obtained using either $Pd(NH_3)_4(NO_3)_2$ or $Pd(NH_3)_4Cl_2$. When filtering and drying is executed in air instead of in inert gas, much larger particles (30–50 nm) were found. In air, decomposition of the amine complexes proceeded at lower temperatures, resulting in mobile palladium species that coalesce. Hoogenraad and Mojet [22,34,105] tried to gain information on the nature of the interaction of ionic palladium complexes and palladium metal atoms with the fiber surfaces using in situ EXAFS. With the dried sample no Pd/O distances were found. They found a Pd/C coordination number of six. Their conclusion was that the palladium

ions interact directly with the graphitic surface of the fibers. Nevertheless, oxygen surface groups must participate in these interactions, since without these groups adsorption of palladium on the surface does not take place. A schematic representation of the interaction involving oxidic surface groups is shown in Fig. 15. After reduction the Pd/Pd coordination number is eight. This number correlates with a particle size of 1–1.5 nm, in accordance with the TEM observations.

Summarizing, the most important factor when using ion-exchange for the deposition of palladium on carbon is a large amount of ion-exchangeable sites on the carbon surface [22,83,106].

4. Conclusions

- The synthesis of supported palladium catalysts has been reviewed involving the chemistry of catalyst synthesis, relevant support properties and case studies for oxide-supported and carbon-supported catalysts.
- Aqueous Pd-precursor solutions may consist of $Pd(OH)_4^{2+}$ at pH < 1 while colloidal PdO is formed at higher pH. In catalyst synthesis ligand-stabilized precursors are used in particular $Pd(NH_3)_4^{2+}$ and $PdCl_4^{2-}$. With non-aqueous precursor solutions $Pd(acac)_2$ is often applied.
- The precursor-support interaction during synthesis is advantageously rationalized by considering for oxides the IEP in combination with the precursor

ion charge. Silica and alumina are at present the most important supports for Pd catalysts.

- With carbon supports it turns out that additionally one has to consider the direct reduction of the Pd-precursor by the carbon support which gives rise to large Pd particles. Furthermore, the lyophilicity of carbon may affect catalyst synthesis. Activated carbon is extensively used while carbon nanofibers show great potential related to tailoring of surface properties, accessibility and mechanical strength.

- For oxide-supported Pd catalysts sol–gel techniques have been used giving rise to Pd particles of 1 nm at low loading. Ion-exchange and impregnation are most often used. In general, careful washing following adsorption is beneficial for dispersion as well as is calcination prior to reduction.

- For carbon supported catalysts is has been found that the thermal pre-treatment often is the dominant factor in determining the Pd dispersion. Thermal treatment in an inert atmosphere prior to reduction is essential in obtaining high Pd dispersion.

- From this literature review some general rules for the thermal pre-treatment of Pd catalyst precursors can be derived. High Pd dispersions call for decomposition of the precursor in an inert atmosphere. The reduction temperature should not exceed 423 K. Gas-phase reduction leads to higher dispersions than does liquid-phase reduction.

- The challenge to develop supported Pd catalysts that display a high dispersion at low loading even following high pre-treatment temperatures has hardly been addressed up till now. We feel that deposition–precipitation techniques in combination with anchoring sited on the support could be beneficially explored in this respect [108].

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