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Applied Catalysis A: General 173 (1998) 259–271



# Carbons as supports for industrial precious metal catalysts

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## Abstract

This review deals with the use of activated carbon, carbon black and graphite as well as graphitised materials as support material for the manufacture of commercially available precious metal powder catalysts. The manufacture of these carbons is described briefly, together with their most important chemical and physical properties that are tightly related to catalyst manufacture and use of such catalysts. The main industrial applications of carbon supported precious metal catalysts are also reviewed. Most of these applications make use of powder based catalysts and involve the hydrogenation of an organic substrate molecule. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Carbon; Catalyst support; Properties of carbon; Precious metal catalysts; Catalyst manufacture; Industrial application; Hydrogenation; Fuel cell

## 1. Introduction

Catalysis is of vital importance to today's fine chemical industry. There are only a small number of chemical processes that are still conducted without the addition of a catalyst [1,2].

Supported catalysts are of special interest, for they allow for the fine dispersion and stabilisation of small metallic particles. They provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal, even when the latter is ground to a fine powder. For example, fractions exposed close to 100% are available for platinum on carbon catalysts.

In the fine chemical industry catalysts based on precious metals on activated carbon supports are fre-

quently used, because such systems exhibit interesting features with regard to their application. Activated carbons are stable in both acidic and basic media, which is not true for alumina or silica. Alumina as well as silica are dissolved at high pHs and the former is also attacked at very low pHs [3,4].

A very important point for the economic use of precious metal catalysts, especially highly loaded ones, is recovery, refining and recycling of the metal. This procedure is simplified by the use of carbon as support, for this material can be burnt off, leading to highly concentrated ashes that permit an economical recovery of the precious metal [5,6]. This technology is also very effective from an ecological standpoint, for it does not produce large amounts of solid waste that need to be landfilled.

Precious metal on carbon catalysts are mainly used in liquid phase hydrogenation, dehydrogenation or oxidation reactions in the fine chemicals area. Often,

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these processes are conducted in stirred tank batch reactors, so the catalysts are finely divided solids to ensure easy suspension in the reaction medium (precious metal powder catalysts). Extruded or granulated carbon supports are used to meet the demand for fixed bed catalysts in the production of bulk chemicals.

With respect to the fine chemicals business, powder precious metal catalysts are the most frequently used catalysts. About 30% of the catalysts in this sector are supported palladium catalysts, most of them being used for hydrogenation reactions, e.g. the synthesis of amines from nitro compounds or the saturation of carbon–carbon and carbon–heteroatom multiple bonds.

To date, three forms of carbon are used as supports for precious metal catalyst manufacture to provide optimum properties and performance in the multitude of different applications exercised by the chemical industry. The most important carbon support material is activated carbon, followed by carbon black and graphite or graphitised materials [7,8]. However, compared to the main stream applications of these carbons such as water and gas treatment, rubber production or refractories, their use as catalyst supports is almost negligible [9].

Numerous publications have been written about carbon and its use as an adsorbent, catalyst support or catalyst in its own right. Production of carbon materials, their properties and their use in catalyst manufacture will be described in the following sections from an industrial point of view. Emphasis is given to the catalyst manufacture process and the applications of carbon supported precious metal catalysts.

## 2. Manufacture of carbon supports

### 2.1. Activated carbon

There is exhaustive literature, e.g. [7,9–11], dealing with manufacture of activated carbons, so only a brief review of the most important steps is given here.

Currently, activated carbon is manufactured from suitable precursors in two ways: chemical activation and physical activation. Hereby, the rudimentary pore structure of the precursor material is developed by controlled carbon burn-off and mainly the tarry and

non-graphitic carbon material is gasified, leaving behind a porous network of highly disordered graphitic material bearing surface oxide groups.

Chemically activated carbons are manufactured by the simultaneous carbonisation and activation of the raw material at 600–800°C. The activating agent for this process, e.g.  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$ , is incorporated into the raw material before heating starts. In this way, particularly wood-based activated carbons are made from sawdust.

Physically or so-called steam activated carbons are manufactured from a precarbonised material which is obtained by thermal decomposition of a carbonaceous precursor at 600–800°C in the absence or under controlled admission of air [12]. The activation step is usually performed in the presence of steam and/or  $\text{CO}_2$  at 800–1100°C.

Wood, coal, lignite, coconut shell and peat are the most important raw materials for the production of activated carbons, although other materials such as fruit pits, synthetic polymers or petroleum processing residues can also be used. The final products show different properties, e.g. pore structure and surface area, depending on the nature of the precursor, the nature of the activating agent and the conditions of the activation process.

Washing steps with pure water or mineral acids may be included into the process for the activated carbon manufacture to diminish the ash content. Such a washing step may prove very important when the activated carbon is to be used as catalyst support, for it removes potential catalyst poisons [13] and pore plugging materials. Furthermore, a high ash content may disturb the recovery and the refining of the precious metal from the spent catalyst [5,6].

Activated carbons are produced as powders or granules, the former being obtained by grinding of the latter. In addition, formed activated carbons are produced by extrusion of precarbonised material followed by further carbonisation and, finally activation. Thus, many different forms of activated carbon are available.

In 1994, about 313 000 metric tons of activated carbon were consumed in the western world [14], but less than 1% of this material was used as catalyst support. Consequently, activated carbon is usually not specifically made for use in catalyst production. As a result intensive quality control of a given carbon is

carried out by the catalyst manufacturer to ensure a constant quality of the catalysts.

## 2.2. Carbon black

Carbon blacks are manufactured by the pyrolysis of hydrocarbons such as natural gas or oil fractions from petroleum processing [9]. Due to the nature of the starting materials, the ash content of carbon black is very low, frequently well below 1 wt%.

The most important production process is the furnace black process in which the starting material is fed to a furnace and burned with a limited supply of air at about 1400°C. Cracking and polymerisation of hydrocarbon molecules followed by dehydrogenation of the polymer species leads to spherical turbostratic carbon particles.

Immediately behind the reaction zone, the gas stream is quenched with a water spray to 200–250°C. At this temperature, further reaction of the carbon black with oxidising components of the furnace gases, e.g. steam or CO<sub>2</sub>, is suppressed. Some oxidation, however, occurs and leads to the formation of surface oxide groups.

The consumption of carbon black in the western world was about 3 360 000 metric tons in 1994 [15], but hardly any of this material is currently used as catalyst support. For special applications such as catalyst manufacture, the more expensive acetylene black is used. Due to the special manufacturing conditions at high temperatures (> 2500°C) partial graphitisation occurs in this material.

## 2.3. Graphite and graphitised material

Hardly anything of the vast amount of natural graphite mined all over the world or manufactured by man is currently used as catalyst support [16]. This is particularly due to the low surface area of only 10–50 m<sup>2</sup>/g graphite. Nevertheless, for some applications such graphite is indeed used as support material.

However, high surface area graphite (HSAG) is available from graphitised material by a special grinding process. Surface areas of 100–300 m<sup>2</sup>/g make this graphite an interesting support material for precious metal catalysts [17–20].

Another support material of interest to catalyst manufactures is graphitised carbon black. This high

surface material is obtained by recrystallisation of the spherical carbon black particles at 2500–3000°C. The partially crystallised material possesses well-ordered domains. The degree of graphitisation is determined by the process temperature.

## 3. Chemical and physical properties and carbon supports

### 3.1. Activated carbon

The primary role of the support is to finely disperse and stabilise small metallic particles and thus provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal even when the latter is ground to a fine powder. Thus, the most important parameters for the catalyst manufacturer and the user of a catalyst are the porosity and the pore size distribution of the activated carbon as well as its surface area. Additional important parameters are the particle size distribution of a powder or granulate, the attrition resistance and the ash content. Formed activated carbons must also exhibit a sufficient high crush strength. Together with the surface chemistry of the activated carbon, these factors strongly influence the performance of the finished catalyst. With activated carbons these parameters can be varied over a wide range and adapted to the requirements of the application in question [21].

The morphology of an activated carbon powder as observed by electron microscopy is largely determined by the raw material that has been used for the manufacture of the carbon. Characteristic differences of wood, peat and coconut shell based activated carbons are easily recognised, for the nature of the starting material is directly reflected in the final product (cf. Fig. 1).

Furthermore, the nature of the raw material also influences the filtration behaviour of an activated carbon. This is shown in Table 1. Another parameter that influences the filterability of an activated carbon is its particle size distribution. The two distribution curves shown in Fig. 2 are closely related to the filtration characteristics of the two samples: sample A, represented by the broader curve, needs more time to filter than sample A' that has no fine particles, even if the median particle size and other parameters of the two carbons are almost the same.

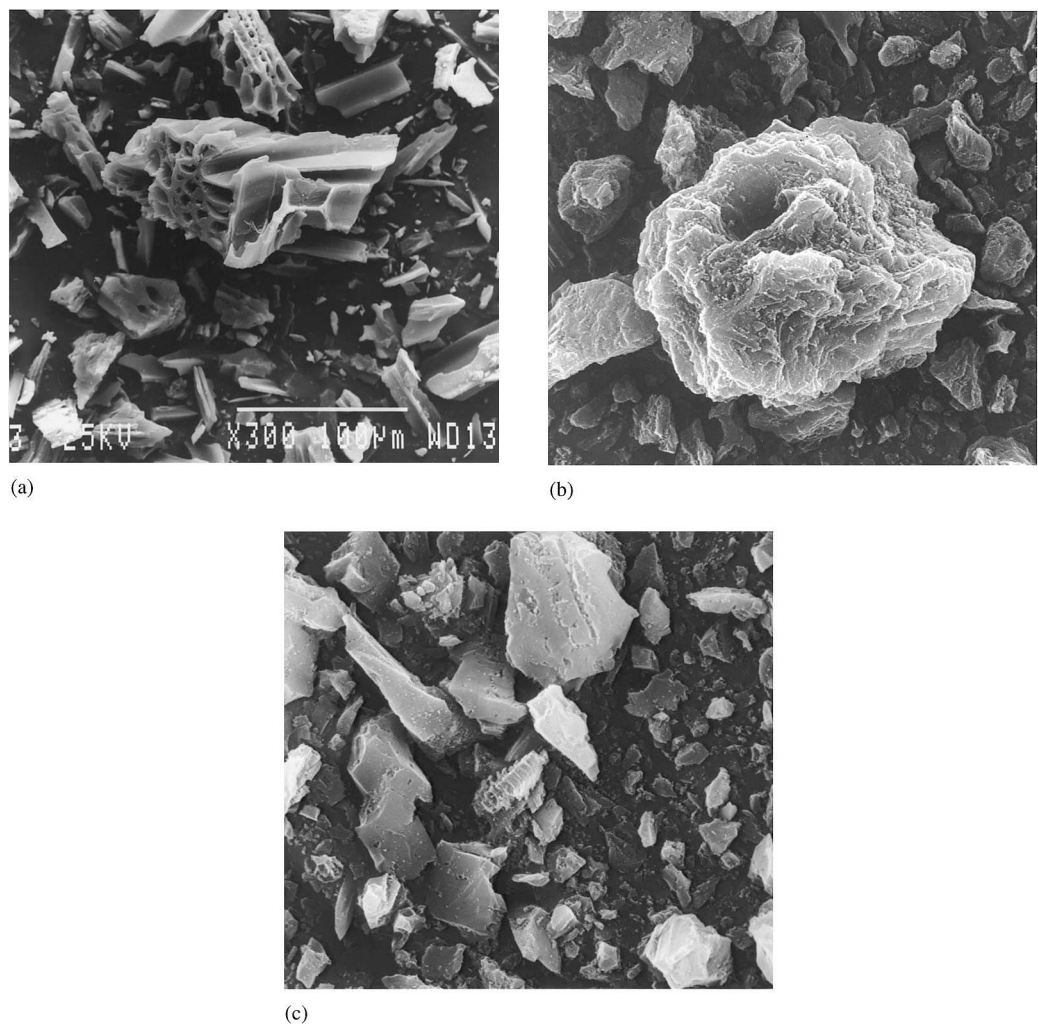


Fig. 1. SEM images of wood (A), peat (B) and coconut shell (C) based activated carbons; magnification is 450:1 (A) and 1000:1 (B, C), respectively.

Table 1  
Selected properties and filtration behaviour of different activated carbons

Sample	Raw material	Median particle size [μm]	Relative filtration time
A	Wood	24	1.0
A'	Wood	23	0.6
B	Peat	20	2.7
C	Coconut shell	28	6.6

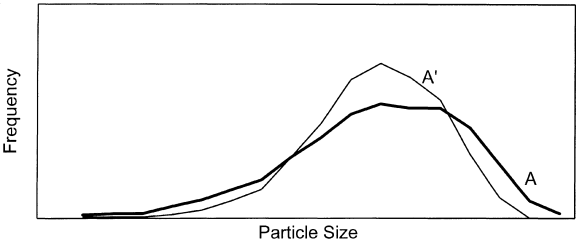


Fig. 2. Particle size distribution curves for samples A and A'.

To maintain a constant particle size distribution during the handling of an activated carbon and the use of the catalyst made thereof, the attrition resistance has to be as high as possible. Otherwise, a large fraction of extremely fine particles is generated, especially when the catalyst is recycled and used several times, and severe filtration problems may occur.

The particle size distribution also plays an important role with respect to the catalytic performance. An increase in the geometric surface area of the solid with decreasing particle size leads to higher catalytic activity. Thus, a compromise for the particle size has to be found to optimise activity and filterability.

Activated carbons with specific pore volumes well above 1.5 ml/g are commercially available, although most of the material used for catalyst manufacture typically possesses specific pore volumes of about 0.9–1.3 ml/g [7,8,10]. The pore size distribution plays an important role, for it not only determines the surface area available for the deposition of highly dispersed, catalytically active precious metal crystallites, but also controls the access of substrate molecules to these supported metallic particles. Highly porous materials provide easy access of the reactants to the catalytically active sites and thus exhibit higher activity. On the other hand, they are sensitive to poisoning, as catalyst poisons easily penetrate the pore system and reach the metal particles. However, in some cases this phenomenon is exploited to remove undesired by-products from a reaction mixture, e.g. in decolourisation.

Thus, the pore structure of an activated carbon support has to be a compromise, balancing the fraction

of micro-, meso- and macropores to a reaction-dependent optimum. The pore structure, and hence the activity of the corresponding catalyst, can be roughly tuned by the choice of the raw material (cf. Fig. 3; Samples A–C). Fine tuning of the porous structure can be achieved by varying the degree of activation of the carbon [22] (cf. Fig. 3; Samples D–G).

The specific surface area of a solid is closely related to its pore structure. Activated carbons used for catalyst manufacture usually have specific surface areas of 800–1200 m<sup>2</sup>/g, depending on the degree of activation.

The surface chemistry of an activated carbon particularly influences the catalyst manufacture and the performance of a catalyst [23,24]. Most of the chemical properties arise from the incorporation of oxygen into the carbon surface during manufacture of the support.

The functionalities present on the carbon surface in the form of surface oxides (e.g. carboxylic groups, phenolic groups, lactonic groups, etheric groups) are responsible both for the acid/base and the redox properties of the activated carbon [21]. These surface groups act as nucleation centres for the generation of highly dispersed metallic crystallites. Depending on which type of surface functional group is involved in the metal deposition on the carbon surface, two mechanisms play a role: adsorption of ionic species at acidic and basic sites or deposition of metallic species by a redox reaction with the carbon. For the first mechanism, the point of zero charge of the activated carbon is of major importance [25,26]. Mixtures of the two mechanisms are possible.

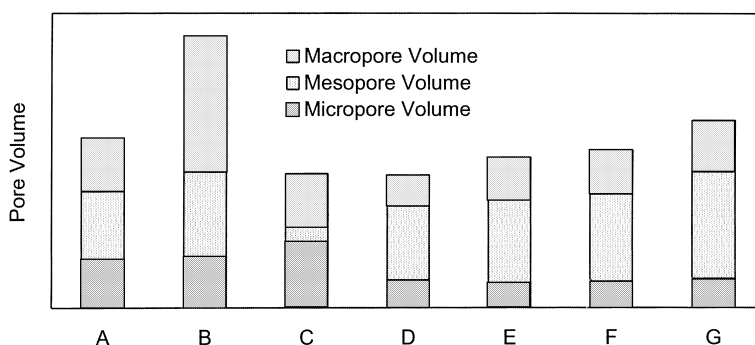


Fig. 3. Pore volume distribution and BET surface area of wood (A), peat (B) and coconut shell (C) based activated carbons and of wood based activated carbons with varying degrees of activation (D–G), respectively.

Furthermore, the surface functionalities are assumed to stabilise the metallic crystallites under sintering conditions.

Other heteroelements such as hydrogen or nitrogen also play an important role with regard to the surface chemistry of activated carbons. The unambiguous identification of surface heteroelement species is a delicate art and requires much experience [10,23,24]. This is partly due to the presence of inorganic impurities, e.g. calcium, potassium, alumina, silica, sulphur and iron and other heavy metals, that may change the acid/base or redox properties of the activated carbon. Sample history also plays an important role, for slow oxidation of the carbon occurs over prolonged times at ambient temperature.

The principles as discussed heretofore for activated carbon powders are essentially the same for granulated and extruded activated carbons. However, the requirements concerning the mechanical strength and attrition resistance are even higher for the latter. When these supports are used for the manufacture of catalysts with egg-shell type macroscopic metal distribution, slight attrition immediately leads to losses in the active component and consequently catalytic activity. To provide such a high attrition resistance, predominantly activated carbons from coconut shell are used.

### 3.2. Carbon black, graphite and graphitised material

At first glance, carbon blacks and graphite materials on the one side and activated carbons on the other side are very similar, even if one has to take care not to confuse them [8]. However, three major differences exist between activated carbon and the other carbons.

First, compared to activated carbon, the latter only possess limited specific surface area in the range of 100–1500 m<sup>2</sup>/g in the case of furnace carbon blacks and 60–300 m<sup>2</sup>/g in the case of HSAG and acetylene blacks. Second, the pore structures of carbon black and graphite, respectively, are very different from those of activated carbon. In both materials, the porosity is built up from three-dimensional agglomeration of very small (5–100 nm), non-porous primary particles into branched chains and clusters, which is not the case of activated carbon [7,9]. Third, graphite materials consist of more or less crystallised particles, which is also true for acetylene black due to the special manufacturing conditions.

Surface functionalities of carbon black are principally the same as in activated carbon [23,24]. The oxygen content as surface oxidic groups of a carbon black may be much higher than in activated carbon, up to 15 wt%. In graphite, due to the high temperature treatment, surface oxide groups only play a minor role and the material is hydrophobic.

## 4. Industrial manufacture of carbon supported precious metal catalysts

### 4.1. General remarks

Generally, three main aspects determine the catalytic performance of a precious metal catalyst on a given support: the macroscopic distribution of the metal in the individual support particles, the microscopic distribution of the metal crystallites on the support surface and the oxidation state of the metal species on the support surface. The microscopic distribution of the metal crystallites is referred to as dispersion or fraction exposed. Control over these factors to tune the catalyst performance is accomplished industrially with metal loadings up to 40 wt%.

Concerning the macroscopic distribution of the precious metal on a carbon support, two major types exist: uniform and egg-shell distribution. Mixed types between these extreme situations are possible. The distribution profile is determined by the preparation method and further treatment of the catalyst. Which type of metal location is chosen for a catalyst depends on the specific requirements of an application and shall be discussed later (cf. Section 5).

The microscopic distribution of the precious metal crystallites on the carbon support surface often should be as high as possible. However, for several applications it is not very high dispersion that is looked for, but a controlled, narrow crystallite size distribution to optimise the exposed metal surface area. This is because extremely dispersed metal crystallites do not necessarily exhibit high activity in a specific reaction. Control over the crystallite size distribution may be achieved by both the pretreatment of the carbon support under oxidising conditions [27,28] and the technique of precious metal deposition on the support.

The oxidation state of the metal crystallites also exerts an important influence on the performance of a given catalyst. For some application, the use of oxidic catalysts that are reduced in situ gives a higher performance than a prereduced catalyst.

#### 4.2. Preparation techniques

The preparation methods [29,30] for activated carbon, carbon black and graphite supported precious metal catalysts are essentially the same and will thus be discussed at the same time.

There are three main preparation techniques that are used today for catalyst manufacture: ionic adsorption, colloid deposition and electroless plating. Of course, mixtures of these methods are also possible. For example, carbon supports very often have a more negative redox potential than a given species to be deposited which may lead to simultaneous adsorption and reduction processes. These methods are applicable for the manufacture on a scale varying from grams to metric tons per day. However, due to their complex nature, much work is necessary to successfully manufacture commercial quantities of carbon supported precious metal catalysts having the improved performance of a laboratory sample.

Adsorption of ionic species such as  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ,  $[\text{PtCl}_6]^{2-}$ ,  $[\text{Pd}(\text{OH})_4]^{2-}$  onto the carbon support occurs via the functional groups on the surface. By this mechanism, uniformly impregnated catalysts are available for an equilibrium between adsorbed and free ions exists and diffusion into the core of each individual support particle can occur.

The other extreme, egg-shell impregnation, is achieved by deposition of a preformed or in situ generated precious metal colloid. These colloid particles readily adsorb on the external surface of the support particles and in their macropores. The size of the colloid particles controls their penetration into the pore system. Due to the size of the colloid particles, the accessibility of the inner pore system is only very limited, which leads to egg-shell distribution of the metal.

Electroless plating may already occur when the first metal ions reach a virgin support surface and come into contact with redox active sites. In this way, nucleation centres are generated. Further deposition of metal atoms on these metal clusters or crystallites

by a redox mechanism can be achieved by adding a reducing agent to the reaction mixture. This method is also very effective for the site selective deposition of a second metal on preformed metal crystallites, e.g. platinum crystallites. Thus, well-defined bimetallic and promoted catalysts are readily available [31].

Many carbon supported precious metal catalysts are manufactured in a reduced form and are ready-for-use. A final reduction step is included in the preparation process. To reduce precious metal powder catalysts, the reducing agent is added to the catalyst slurry directly after the impregnation step. Reducing agents such as hydrogen, formaldehyde, hydrazine, sodium formate or sodium borohydride are frequently used.

An important point with respect to reduced catalyst types is that the reduction of the metal is not quantitative and a small fraction of oxidic species always remains on the carbon support. On the other hand, due to the redox activity of the carbon, a considerable fraction of the metal loading in oxidic catalyst types is reduced to the metallic state [32]. To illustrate this, the TPR curves of a reduced and an oxidic catalyst are shown in Fig. 4). The degree of reduction for the former is only 75%, whereas it is about 45% for the latter.

When graphite or graphitised materials are used as supports, they often require a pretreatment under oxidising conditions to generate surface functionalities as anchoring sites for ionic species to be adsorbed from solution and finally to fix the metal crystallites [33–35]. Without such a pretreatment, the dispersion of the supported metallic phase may be low at industrially interesting metal loadings.

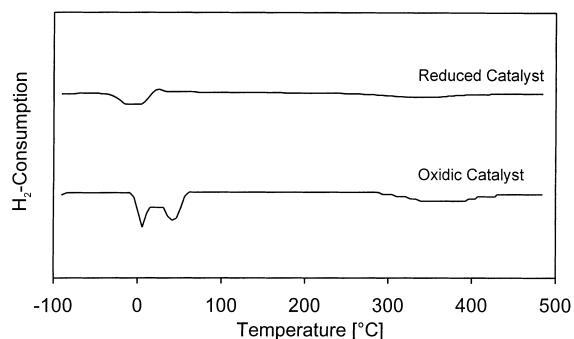


Fig. 4. TPR curves of a reduced and an oxidic palladium and carbon catalyst.

Fixed bed catalysts on carbon supports are mostly manufactured by pore volume impregnation (incipient wetness impregnation), and not in slurry phase as for powder catalysts. For this reason, a one pot preparation of a catalyst is not possible. The preparation procedure has to be divided into single steps if the support has to be contacted with more than one reagent. Usually, these steps are separated by a drying step. For example, reduction is always a single step and often gaseous hydrogen is used to carry it out. Nevertheless, the basic impregnation mechanisms are essentially the same as described for powder precious metal catalysts.

## 5. Major applications for carbon supported precious metal catalysts

### 5.1. General remarks

When choosing a catalyst for a given chemical process one always has to consider several, sometimes contradictory, parameters at the same time. For example, finely divided powders are easy to suspend in a liquid reaction medium, giving rise to a high external surface, low diffusion distances in the porous structure of each individual particle and consequently low mass transfer limitations. On the other hand, suspensions of such fine powders may prove to be very difficult to filtrate from the product solution, leading to time consuming separation steps.

Uniformly impregnated catalysts are preferentially used when no mass transfer limitations during the catalytic reaction are expected. Sintering of the metal crystallites is minimised with this catalyst type [36], because high local concentrations of metal are avoided when usual catalyst loadings of about 5 wt% are used. In egg-shell type catalysts, the precious metal is located in the outer periphery of the support particles. Such a distribution is useful when diffusional restrictions inside the pore structure of the support occur. On the other hand, poisoning of such a catalyst may be rapid, for the accessibility of the active metal surface is good for both the substrate and the poison.

Table 2 summarises the main reactions that are currently conducted on an industrial scale with the aid of carbon supported precious metal catalysts (from [37–39]). The large majority of these reactions are hydrogenation reactions (see also in [7,8]). The appli-

cation of precious metal catalysts on carbon supports is now illustrated in the following sections. For this purpose, some special chemical reactions that are interesting from an industrial point of view were selected.

### 5.2. Selected processes with activated carbon supported precious metal powder catalysts

#### 5.2.1. Hydrogenation of halogenated nitroaromatic compounds

Halogen substituted aromatic amines are widely used for the production of pharmaceutical and agrochemical substances. Industrially, they are mainly produced from the corresponding nitro compounds by hydrogenation. This reaction often is accompanied by simultaneous dehalogenation that decreases the yield of the desired product and causes corrosion problems due to the formation of halogen acids.

To keep halogen elimination as low as possible, various types of catalysts have been developed and applied in industrial processes. Currently, partially poisoned supported platinum catalysts on activated carbon are used to enhance the selectivity.

Although some of these modifications keep halogen elimination below 0.1%, other by-products, e.g. azo or azoxy compounds, are formed. These compounds represent a severe problem, especially in the case of dihalogenated substrates.

Recently, a new modified carbon supported iridium based catalyst has been developed for the selective reduction of halogenated aromatic nitro compounds [40]. This new multimetallic catalyst contains iridium and promoters such as manganese, iron, cobalt, nickel, copper or ruthenium. With this commercial iridium catalyst, halogenated nitroaromatic compounds are hydrogenated with excellent selectivity.

Thus, the new multimetallic iridium catalyst is an interesting alternative to the conventional platinum catalysts, in addition, since the formation of toxic by-products is almost completely suppressed. Post-treatment of the product to remove undesired by-products is no longer necessary with this catalyst.

#### 5.2.2. Hydrogenation of nitro compounds

The hydrogenation of nitro compounds to the corresponding amines is a very important reaction, as



Table 2

Main application fields for carbon supported precious metal powder catalysts

Reaction	Metal catalyst				
	Pd	Pt	Ir	Ru	Rh
Monoolefins to alkanes	•	•		•	•
Diolefins to monoolefins	•				
Cyclohexene to cyclohexane	•	•			•
Acetylenes and <i>cis</i> -Olefins	• <sup>a</sup>				
Acetylenes to alkanes	•				
Aromatic ring hydrogenation	•	•		•	•
Pyridine ring hydrogenation	•			•	•
Aliphatic aldehydes to alcohols		•		•	
Aromatic aldehydes to alcohols	•	•			
Aliphatic ketone to alcohols				•	
Aromatic ketones to alcohols	•	•			
Aliphatic nitro compounds to primary amines	•	•			•
Aromatic nitro compounds to anilines	•	•			
Nitrosoaromatic compounds to anilines	•	•			
Hydrazones to hydrazines	•	•			
Imines to amines	•	•			
Aromatic nitro compound to <i>para</i> -aminophenols		•			
Halogenated aromatic nitro compounds to halogenated Anilines		• <sup>a</sup>	•		
Aliphatic nitriles to primary amines	•	•			•
Aliphatic nitriles to secondary amines	•				•
Aliphatic nitriles to tertiary amines	•	•			
Aromatic nitriles to primary amines	•	•			
Aromatic nitriles to secondary amines		•			•
Aromatic nitriles to tertiary amines	•	•			
Reductive akylation	•	•			
Reductive amination	•	•			
Disproportionation	•				
Hydrodehalogenation	•	•			
Oxidation of alcohols	•	•			
Dehydrohalogenation	•	•			
Rosenmund reaction	•				
Debenzylation	•				
Carbon–oxygen cleavage	•	•			
Carbon–nitrogen cleavage	•	•			
Hydroxylamine synthesis	•	•			
Decarbonylation	•				
Fat and fatty acid hardening	•				
Carboxylic acid compounds to alcohols	•			•	
Electrocatalysts for fuel cell applications			•		

<sup>a</sup> Partially poisoned.

these chemicals are used as basic raw materials for urethanes, rubber chemicals, dyes and pharmaceuticals. Depending on the reaction conditions and the catalyst, the reaction may be directed towards a specific product [38,39,41].

It is of major importance that hydrogen starving conditions do not occur during reduction of nitro compounds with palladium on activated carbon [42]. If this happens, the metal may rapidly be leached from the support, depending on the complex formation

ability of the amine product. This is observed for oxidic as well as for reduced catalysts, but oxidic types are much more prone to metal leaching than reduced ones. Uniformly impregnated catalysts are also more likely to lose a part of the precious metal loading by leaching than egg-shell catalysts. With activated carbon supported platinum catalysts, this problem may also occur, but in general it is less severe.

The leaching of precious metal can be minimised by either improving the availability of hydrogen in the liquid reaction medium or by optimising the “catalyst side” of the process. The former can be achieved by using a special reactor design, e.g. a loop reactor, using a special stirrer or increasing the hydrogen partial pressure in the reactor. Hereby, the transfer of gaseous hydrogen into the liquid phase is improved. Coming from the “catalyst side” of the process, two approaches are possible: use less catalyst for the reaction or decrease the precious metal loading of the catalyst, e.g. 3 wt% instead of 5 wt%.

All of the actions described above lead to a higher availability of hydrogen at the catalytically active metal particles on the carbon support. Thus, stabilisation of the metal in its hydridic form is achieved and leaching is avoided.

Preparation of aniline from nitrobenzene is readily accomplished with activated carbon supported palladium catalysts in excellent yield. In the presence of a partially poisoned platinum on carbon catalyst, however, phenylhydroxylamine is formed. When dilute aqueous sulfuric acid is present, *para*-aminophenol can be synthesised over the platinum catalysts on activated carbon. This reaction proceeds via the hydroxylamine by acid catalysed Bamberger rearrangement [43].

### 5.2.3. Fatty acid hardening

Unsaturated free fatty acids are an environmentally friendly feedstock for the production of oleochemical intermediates that are mainly required in the detergent industry. One important reaction is the complete hardening of unsaturated natural fatty acids by hydrogenation [44,45]. Another reaction is the selective hydrogenation of unsaturated fatty acids to a specified iodine number.

Currently, nickel on kieselguhr is used as a catalyst for this reaction, but environmental problems as well as problems with the catalyst performance itself con-

tinue to increase the pressure on this type of catalyst. Nickel catalysts rapidly deactivate due to the formation of nickel soaps, the hydrogenated product has to be purified carefully to remove all residual nickel and finally the spent nickel catalyst has to be disposed or given away to be used elsewhere, e.g. in the metallurgical industry to recover the nickel metal.

Supported palladium catalysts on activated carbon overcome the main disadvantages of the nickel catalysts. With recently developed fixed bed catalysts it is possible to run the free fatty acids hardening reaction as a continuous process with much higher space-time yields than in the current batch process.

The poisoning of the catalyst by sulphur containing compounds in the starting material has to be prevented by suitable process design and application of optimum reaction conditions.

## 5.3. Selected processes with carbon black supported precious metal powder catalysts

### 5.3.1. Hydrogenation of dinitrotoluene

The polyurethane intermediate toluenediamine is produced from the dinitro compound using an iron promoted acetylene black supported palladium catalyst [46]. By adding iron to the catalyst, tar formation is strongly reduced. Alternative catalysts such as activated nickel or nickel on silica can also be used. This hydrogenation is not as easy as it is for nitrobenzene. To achieve complete conversion, the reaction has to be run for a certain time after apparent completion to ensure total conversion.

### 5.3.2. Electrocatalysts for fuel cell applications

Electrochemical fuel cells convert the chemical energy of a fuel directly into electric power employing a catalytic process. Fuels for this kind of power generation, such as hydrogen or methane, are oxidised at the anode of the fuel cell, while oxygen is simultaneously reduced at the cathode. The only off-gas product of a hydrogen fed fuel cell is water vapour. Coupling of the two half cells then allows for the clean production of electric power, as the emission of greenhouse gases and other pollutants is reduced compared to conventional techniques.

The catalysts applied in low temperature fuel cell technology, e.g. phosphoric acid fuel cells (PAFC) and proton exchange membrane fuel cells (PEMFC),

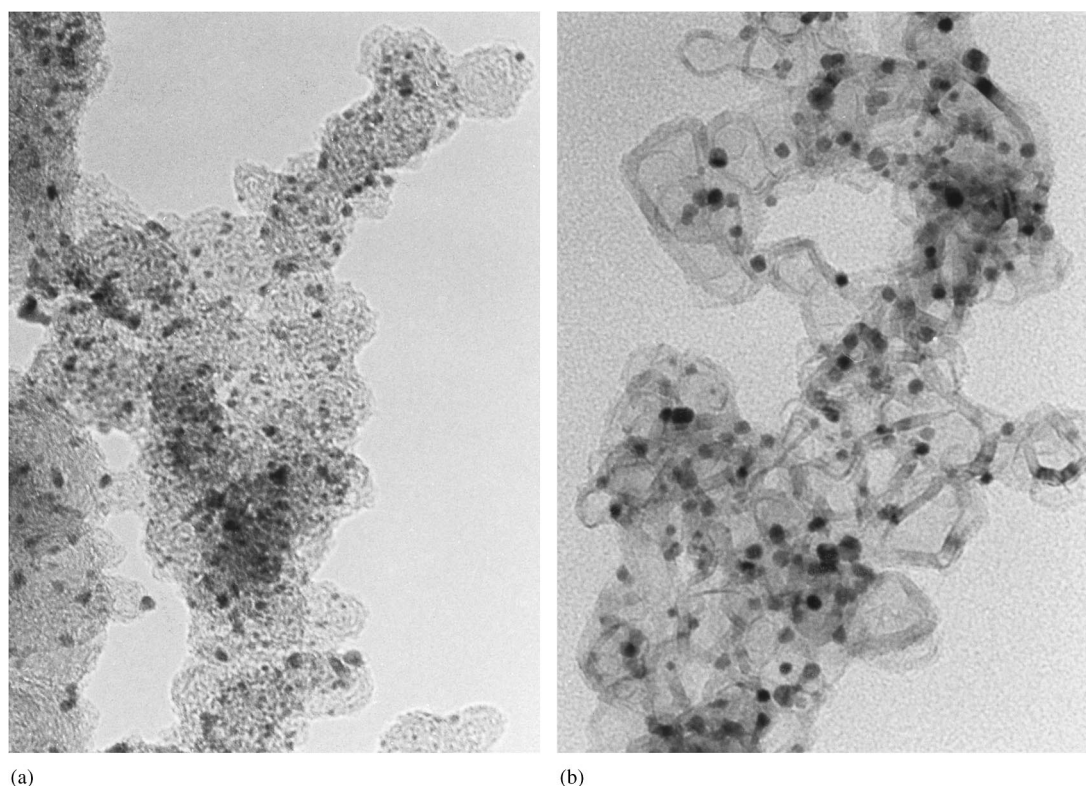


Fig. 5. TEM images of an anode catalyst with 10 wt% platinum on carbon black (A) and a cathode catalyst with 10 wt% platinum/chromium/cobalt on graphitised carbon black (B); magnification is 1 000 000 : 1 (A) and 700 000 : 1 (B), respectively.

are precious metal catalysts supported on carbon black [47,48].

Depending on the electrode and the fuel cell technology, the properties of the carbon black used for the manufacture of the electrocatalyst have to meet particular requirements [49].

Highly dispersed platinum on carbon black is frequently used as the anode catalyst in PAFC systems (cf. Fig. 5, A). Furnace blacks with hydrophilic character of the carbon surface are preferred.

The cathode catalyst for the reduction of oxygen may be manufactured from graphitised carbon black supported, finely divided PtCrCo (cf. Fig. 5, B) or other Pt alloys.

For this catalyst more severe requirements have to be met to achieve the required long-term stability of 40 000–60 000 h. Due to the presence of oxygen, support corrosion may occur. Furthermore, the water generated in the reaction on the cathode side has to be rapidly removed from the electrode. Both the kinetic

stabilisation of the support towards corrosion and the easy water removal by hydrophobisation of the carbon surface can be achieved by using partially graphitised carbon blacks or acetylene blacks [50,51].

Platinum on carbon black is also the most frequently used catalyst to build up the anode and the cathode side in PEMFC. The use of such catalysts with highly dispersed platinum crystallites has allowed for considerable progress in this technology. Metal loadings of 10–40 wt% are applied. For the anode side, carbon black supported platinum/ruthenium is preferably used, when an enhanced CO tolerance is required.

#### 5.4. Selected processes with graphite supported precious metal powder catalysts

As already mentioned earlier, examples of the industrial application of graphite supported precious metal catalysts in the chemical industry are rare. One process that makes use of such a catalyst is the

synthesis of hydroxylamine from nitrogen monoxide in the presence of hydrogen in dilute mineral acid. In this case, the catalytically active metal is platinum [52].

## 6. Outlook and future trends

In the near future, the use of carbon blacks and related materials as catalyst supports for precious metals may increase, due to the rapidly advancing development of fuel cells. PAFC as well as PEMFC systems represent an environmentally friendly technology and are believed to be close to commercialisation.

In addition, the use of the new carbon materials as industrial catalyst supports may develop rapidly with new interesting carbon materials emerging and becoming available on a commercial scale at reasonable prices. Some examples are activated carbon cloth, activated carbon spheres, carbon fibrils and the fullerene family (buckyballs and nanotubes). Nevertheless, a lot of research is still necessary to get these supports into new products.

A third very important point is the continuation of research to achieve a better basic understanding of the carbon support material and the catalysts made thereof. The impact of the chemical and physical properties of the carbon on the catalyst preparation and the catalytic performance are not yet sufficiently understood, even if good progress has been made in the past. However, this is a primordial prerequisite to really control catalyst manufacture and to design catalysts with specifically tailor-made performance by purposeful selection of an appropriate support and manufacture procedure. Highly selective reactions over, eventually chirally modified, precious metal catalysts on carbon supports are more and more important issues with regard to production economics and environmental protection legislation.

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