

# Poisoning and deactivation of palladium catalysts

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## Abstract

Some of the major causes for deactivation and premature degradation of palladium catalysts are briefly summarised. These include particle growth for various reasons, coke deposition and coke transformation, the influence of the support material on long term stability and modifications at the palladium surface itself such as valency changes or the formation of simple but stable molecular surface species. In addition, variations of physical properties as well as chemical poisoning, corrosion and leaching are discussed. In spite of the large body of literature concerning the common phenomenon catalyst deactivation specific information accessible for the various kinds of palladium catalysts being used worldwide is still quite limited. There is a serious need for future studies on properties of palladium-based catalytic systems regarding, for example, the interactions between carbon, hydrogen and supported palladium as a ternary system. Observations on different deactivation processes on Pd/SiO<sub>2</sub> catalysts occurring under industrial conditions are compiled. It was tried to roughly differentiate between different degrees of coking and coke transformation in mainly thermally or purely catalytically driven catalyst coking on the one hand and of moderate or enhanced corrosion phenomena or changes of the properties of the palladium itself on the other. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Uncontrolled and accidental poisoning or deactivation of palladium catalysts by various mechanisms can be a considerable financial burden in chemical industry and is still on focus of academic as well as technological research. Some typical large scale applications of palladium catalysts are their use in the hydrogenation of organic fine chemicals, aromatic hydrogenations,

petroleum refining, the selective hydrogenation of acetylene to ethylene, the production of acetaldehyde by oxidation of ethene, the production of vinyl-acetate and, to an increasing extent, the use in different kinds of automotive exhaust gas catalysts [1,2].

As a result of the great economic relevance of palladium-based catalysts in these and related fields of chemical technology many investigations have been performed to study the physico-chemical properties of these materials in more detail and to reveal the various reasons for loss of activity or selectivity under unfavourable or irregular operation conditions. A better understanding of deactivation processes is essential for improving and optimising

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process conditions, the catalysts themselves and for circumventing premature catalyst degradation in order to minimise additional costs.

Conversely, controlled poisoning of palladium-based catalytic systems can have a beneficial impact on performance. A prominent example is the use of lead compounds in the production of the Lindlar catalyst to improve and to fine-tune its properties such as the selectivity in the hydrogenation of  $C\equiv C$  to  $C=C$  bonds by blocking certain active sites [3,4].

In the present contribution, some of the most important reasons for the deactivation of palladium catalysts are sketched. A few examples and references were selected from the large body of existing literature on catalyst deactivation. They are focused predominantly on some recent and typical studies and observations including own work. A complete review addressing all different aspects of catalyst deactivation is beyond the scope of this short summary. Additional details and related references are accessible from authoritative surveys and proceedings (e.g. [5–7], and the literature cited therein).

## 2. Typical reasons for deactivation of palladium catalysts

### 2.1. Crystallite growth/sintering/agglomeration

Morphological changes of palladium entities due to particle growth by different processes including sintering and agglomeration [8–10] are a major cause for a decrease of activity down to uneconomic levels or even complete deactivation of palladium catalysts. It has been observed that under the influence of hydrogen particle growth of finely dispersed, unsupported palladium may occur even at temperatures as low as 330 K [11,12]. The various parameters governing particle growth phenomena have to be considered already during the first steps of the preparation of palladium catalysts. Unfavourable and undesired effects may be suppressed by means of adequate impregnation agents and procedures, by controlled temperature and by the use of suitable support materials [13].

An impact of the properties of the metal precursor as well as the support on the final palladium dispersion obtained under identical preparation conditions was observed [14].

Conditioning treatments of the support materials by purification and by surface modification are well established as useful procedures especially in the field of carbonaceous catalyst supports. Some examples are the treatments with oxidising agents such as hydrogen peroxide or by using acids to remove ashes and contaminants. For activated carbons or carbon blacks the cleaning and surface conditioning leads (e.g.) to the generation of surface functional groups and to an increasing accessibility of other relevant sites including aromatic/graphitic structures and sites with few vicinal hydrogen atoms down to non-conjugated double bonds or vinylic/allylic entities. This can be of paramount influence on the precious metal dispersion to be obtained in the final Pd/C catalyst which are used (e.g.) in hydrogenation reactions [15–18]. The fine structure of the carbon support materials [19,20], their purity, their surface chemistry and, therefore, the precious metal/support interactions have to be examined and optimised [15–18,20] to establish adequate preparation conditions to achieve the best performance possible for the given application of the palladium catalyst.

Regarding the stability of the palladium dispersion during reduction treatments the selection of suitable support materials is of great importance as well. Under a given set of conditions variations of precious metal dispersion and the loss of active area of a palladium catalyst with increasing temperature may be enhanced in the case of rather inert support materials compared to  $SiO_2$  or  $Al_2O_3$  [21,22]. This is also the case under the actual operation conditions of supported palladium catalysts: an influence of the support on the stability of particle size was observed. Pd/ $TiO_2$  catalysts showed sintering at 500°C under the influence of hydrogen whereas Pd/ $Al_2O_3$  catalysts were found to be more resistant under the same conditions [23]. The Pd-based catalysts were identified as the most efficient ones for the catalytic combustion of methane to carbon dioxide and water. Also in these applications it was found that the tendency to sintering and poisoning and the thermal stability is dependent on the support [24]. Considering the long term stability of the Pd-dispersion, again, interdependencies between support material and the resistance of the final Pd-catalysts against catalyst deactivation were also found for other support materials such as  $ZrO_2$ , MgO,  $SiO_2/AlPO_4$  [25,26] or for ternary systems [10].

Not only modification of the support but also of the precious metal component may be helpful: addition of (e.g.) Pt was shown to be effective in preventing catalyst deactivation by improving the heat resistance and the dispersion of supported oxidised palladium particles [27]. Here, finely dispersed Pt crystallites, tightly attached to the support surface, were found to serve as anchoring sites for Pd.

In the selective catalytic reduction of  $\text{NO}_x$  by methane on Pd/zeolite catalysts a pronounced loss of activity was observed depending on the presence of water vapour. Formation of palladium oxide was detected and it was concluded that the tendency towards Pd-agglomeration was promoted by water [28]. In addition to particle growth effects, valency changes between  $\text{PdO}_x$  and metallic Pd may simultaneously be of prominent relevance [29]. This illustrates that several positive or detrimental influences could act together and might affect the degree and the stability of the dispersion of palladium particles including changes of the chemical valency in oxidation of particle surfaces on the one hand or the formation of palladium hydride on the other (Section 2.2.2).

In addition to variations of the particle size a critical enhancement of the physical or chemical interactions between palladium and organic reactants, intermediates, by-products or degradation products, ending with significant catalyst coking, can be of importance. The influence of feed ratios during the operation of Pd/activated carbon catalysts that are deactivated by means of sintering or by coking has been revealed [30].

## 2.2. Influence of carbon deposition

### 2.2.1. Catalyst coking

Catalyst deactivation by coking is a very common problem of considerable industrial relevance [31].

Different species of coke and special grades of carbons may be deposited, transformed or generated which have to be identified in detail according to their individual impact on the catalytic activity for a given process [32–34]. Harmful, harmless, invisible and beneficial types of coke have to be considered and discriminated between as highlighted by Menon [35,36].

It is well known that the performance of palladium catalysts can be affected by the deposition of, or the mutual interactions with, carbonaceous species.

Reactivation for re-establishing the adequate catalyst performance can be straightforward and successful [37]. However, under certain conditions it is also possible that controlled regeneration treatments of deactivated, coked palladium catalysts on various supports by means of dioxygen or dihydrogen are not sufficient to regain the initial catalytic activity [38].

The nature of the carbonaceous deposits and the strength of their interactions with certain surface sites of palladium catalysts is crucial with respect to a detrimental impact on activity. A surface analytical study on the deactivation of Pd/SiO<sub>2</sub> hydrogenation catalysts after different times of smooth operation under industrial conditions showed that the degree of deactivation was not simply correlated with the degree of coverage of the supported palladium catalyst but with the morphology and contamination level of the deposited carbon and, additionally, the valency state of the precious metal [39]. The former finding is consistent with results from kinetic studies on Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> hydrogenation catalysts showing that coke formation on the active sites and coke formation on the support have to be considered separately [40]. Carbons of different morphology and aromaticity/graphiticity may show different interactions between the precious metal particles and the support material. The Figs. 1–4 show scanning electron micrographs of Pd/SiO<sub>2</sub> catalysts of different degree of deactivation which were used in the selective catalytic hydrogenation of acetylene to ethylene (see also Section 2.2.2 and [39]). They reveal distinct differences of the surface morphology and the microstructure of the carbon layers which were deposited under varying conditions.

Finally, it has been shown that palladium atoms of low co-ordination number are more resistant to deactivation by coking under reforming conditions. This has been studied on Pd/silica catalysts of varying dispersion [34,41].

### 2.2.2. Interactions between carbon, hydrogen and palladium

Investigating and interpreting certain types of catalyst deactivation and coking mechanisms as governed by the mutual interactions between hydrogen, carbon and palladium it is helpful to consider the situation from the point of view of binary (Pd/H, Pd/C) as well as of ternary systems (Pd/H/C).

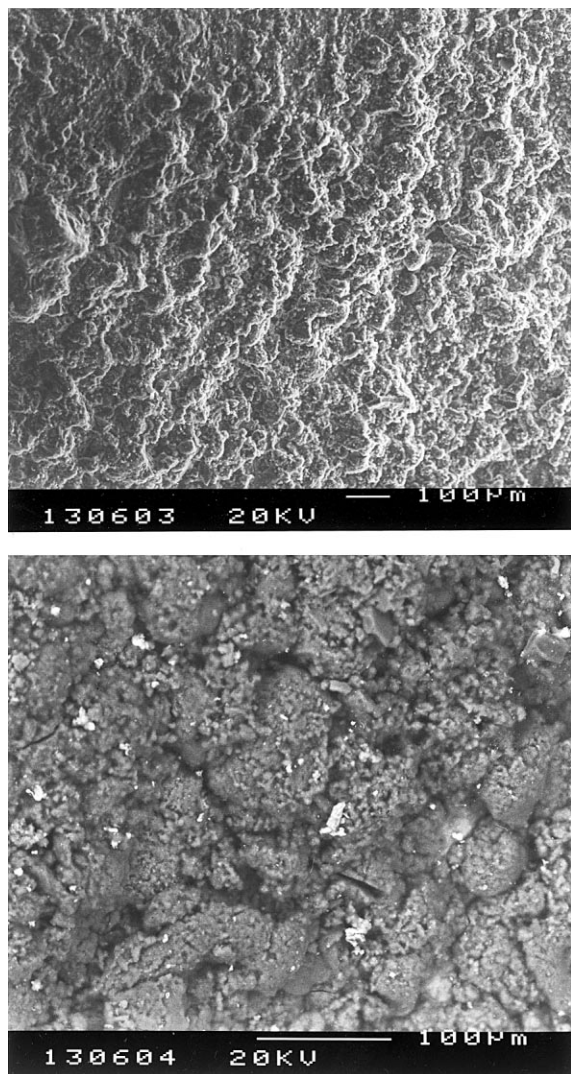


Fig. 1. Scanning electron micrographs of carbon deposits on Pd/SiO<sub>2</sub> catalysts of different degree of deactivation, deposited at  $T < 200^{\circ}\text{C}$  during the selective catalytic hydrogenation of acetylene to ethylene. Coarse, amorphous carbons and contaminants.

The ability of palladium to absorb large quantities of protons after dissociative adsorption of hydrogen molecules is well known [42] and has been investigated in detail ([43,44], and literature cited therein). The dissolved protons are situated in octahedral sites of the fcc Pd lattice [45]. The mechanical and electronic properties of the precious metal are strongly affected by the lattice expansion during the formation

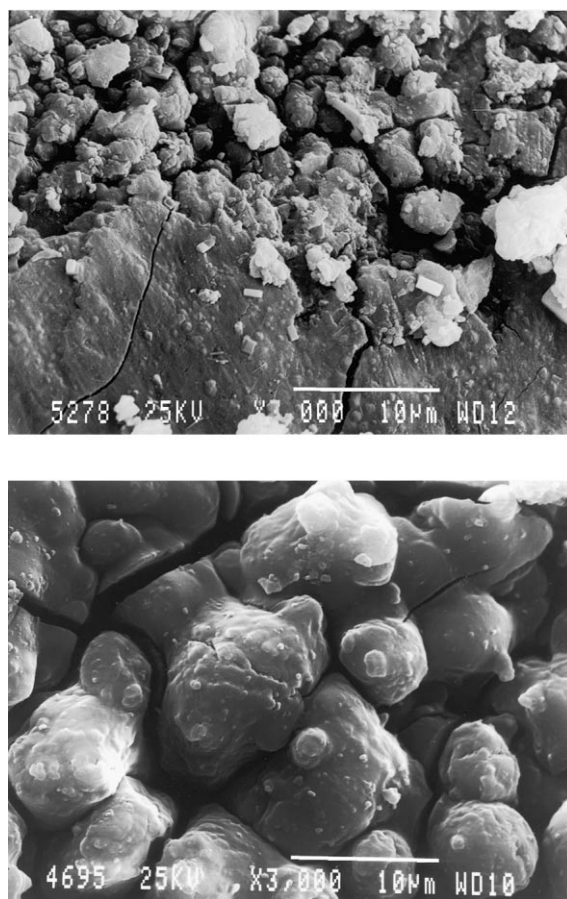


Fig. 2. Transition region between an closed layer and a mechanically damaged region of CVD-carbon of enhanced dimension.

of palladium hydride from the dilute  $\alpha$ -phase (low hydrogen concentrations) over the pressure plateau region of the  $\alpha/\beta$ -phase transition up to the fully loaded  $\beta$ -phase [43,44].

Palladium has been revealed to be also able to incorporate carbon and is, indeed, catalytically active in the transformation of amorphous carbon into aromatic/graphitic carbon. The contribution of transformed carbons to the cumulated amount of coke can be enhanced if additional contaminants (Ni, Fe, etc.) are present. Furthermore, the speed of coke deposition and of coke transformation may increase with increasing amounts of such contaminants. Several authors have shown it to be adequate to regard these specific properties of palladium under two different aspects:

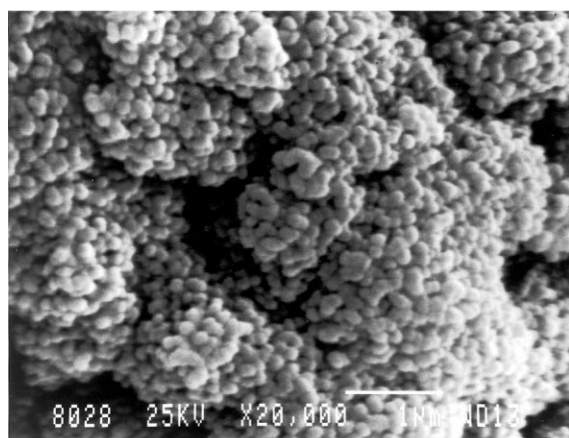
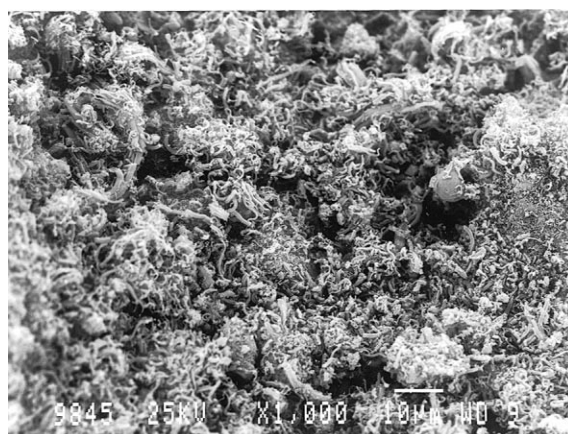
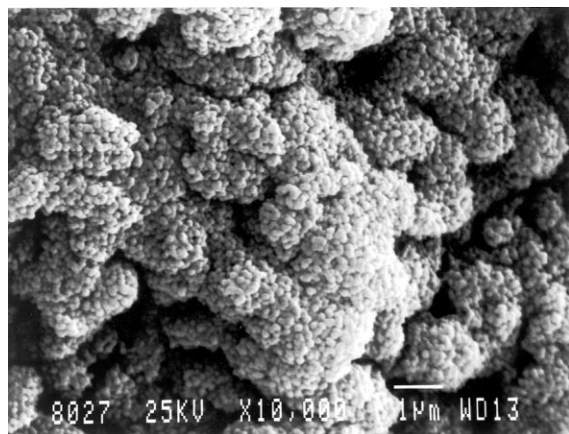


Fig. 3. Polymer-like carbon (from [39]).

Fig. 4. Carbon filaments and amorphous carbon. (from [39]).

1. The impact of a solution/precipitation mechanism in the incorporation and the transformation of carbonaceous deposits in catalyst coking.
2. The impact of incorporated carbon on interstitial sites on the hydrogen storage properties and on the formation of the hydride phases of palladium.

Due to the relevance of these processes in large scale applications (e.g. in the selective catalytic hydrogenation of acetylene to ethylene) this is outlined here in some more detail:

1. Ni and Fe were concluded to be far more efficient in the graphitisation of amorphous carbon deposits than is Pd. This may be the reason that the formation of graphite-like carbons and of filamentous

carbon by catalytically driven coke transformation can be observed at the surface of Pd catalysts to an increasing extent when Fe, Ni (or Co) particles are present, predominantly in the reduced state [39,46–49]. However, the formation of filamentous carbon recently was also observed on supported palladium (Pd/CeO<sub>2</sub>) and especially on palladium black [50]. Under the influence of metallic contamination changes between thermally to catalytically driven coking processes occur and the internal structure of the deposited carbon may be transformed to various sp<sup>2</sup>/sp<sup>3</sup> compositions and hydrogen contents [39,51]. This is of relevance for the strength of the adhesion of carbons to the catalyst surface and the feasibility of reactivation

treatments. Furthermore, interdependencies between catalyst selectivity in acetylene hydrogenation, coke formation rate and the surface coverage with hydrogen were observed for Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts [52].

2. The capability of Pd to incorporate carbon entities during the hydrogenation of acetylene was reported [53]. It was also revealed that a metastable Pd–C phase can be formed by acetylene or ethylene together with the formation of a carbonaceous overlayer. As a consequence of the incorporation of carbon, inhibition of the formation of  $\beta$ -palladium hydride may occur [54,55]. This work on the impact of interstitial carbon on the properties of the ternary Pd/H/C system has been extended to supported catalysts such as Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/C [56,57].

For Pd/C catalysts different situations during deactivation under the influence of carbon were found and discussed by Krishnankutty and Vannice [57]:

1. Carbon overlayers on Pd particles.
2. Partial carbon overlayers and bulk carbide.
3. Partial carbon overlayer no bulk carbide.
4. No carbon overlayer but interstitial carbon.

Again, a decreased ability of palladium containing carbon to form  $\beta$ -phase Pd-hydride was reported resulting in a lowered chemisorption activity.

Finally, with respect to the chemical and mechanical properties of cokes the activity of Pd in cyclotrimerisation reactions of acetylene to benzene-like entities has to be considered [58]. This may also be of some relevance during deposition, formation or transformation of coke and regarding the importance of acetylene fragments or acetylene-like intermediates in the formation of carbons and in radicalic addition processes [59,60].

Under industrial operation conditions it may be difficult to clearly discriminate between the impact of sintering, coking, inorganic poisons and corrosion products and finally of gaseous components and intermediates. Nevertheless, Fig. 5 compiles some of the simultaneous or alternative processes which were observed with more or less pronounced specific predominance on Pd/SiO<sub>2</sub> catalysts after different irregular operation conditions during the selective catalytic hydrogenation of acetylene to ethylene in the

HCl recycle gas stream of the vinyl chloride process [39,51] (Fig. 5).

These various processes include:

- Chemical vapour deposition of a well-defined species of pure carbon (deposition of “CVD-coke”, precursor: mainly acetylene plus by-products from dimerisation and cracking reactions).
- Formation or transformation of carbon to sp<sup>2</sup> type entities which are chemically bound to a polymer-like matrix; (sp<sup>2</sup>/sp<sup>3</sup>-intranetwork vibrations as well as graphite modes were observed for this kind of coke demonstrating the close interactions between these different entities [51]); the catalytic influence of additional metallic contaminants from the reactor material is of importance for the transformation processes.
- Moderate corrosion: formation of an iron compound with *one* molecule of complexed water: [Fe(H<sub>2</sub>O)Cl<sub>5</sub>]<sup>2-</sup>.
- Enhanced corrosion: deposition of inorganic corrosion products (Fe, Ni, Cr, etc.).
- Accidental valency changes of the supported palladium: formation of palladium oxides or oxy-chlorides during corrosion under the access of traces of humidity and air [39].

These findings illustrate, that even on palladium catalysts from large scale applications and even for the case of strongly contaminated material of complicated composition the actual reasons for premature deactivation under specific plant and process conditions can be worked out in more detail. This is of beneficial impact on future optimisations.

### 2.2.3. Formation of stable molecular surface species

When studying palladium/carbon interactions mostly coke species of extended molecular size and interstitial carbon species or carbides were highlighted due their striking appearance (Section 2.2.2). Recent neutron spectroscopic studies revealed an additional property of palladium in the context of an unusual kind of catalyst deactivation which occurred during hydrogenation reactions [61–63]. In that case the typical effects of sintering (Section 2.1), coking (Sections 2.2.1 and 2.2.2) or poisoning (Section 2.4) were missing. Monitoring the properties of the deactivated palladium catalysts as a function of time of operation revealed that the amount of polyaromatic

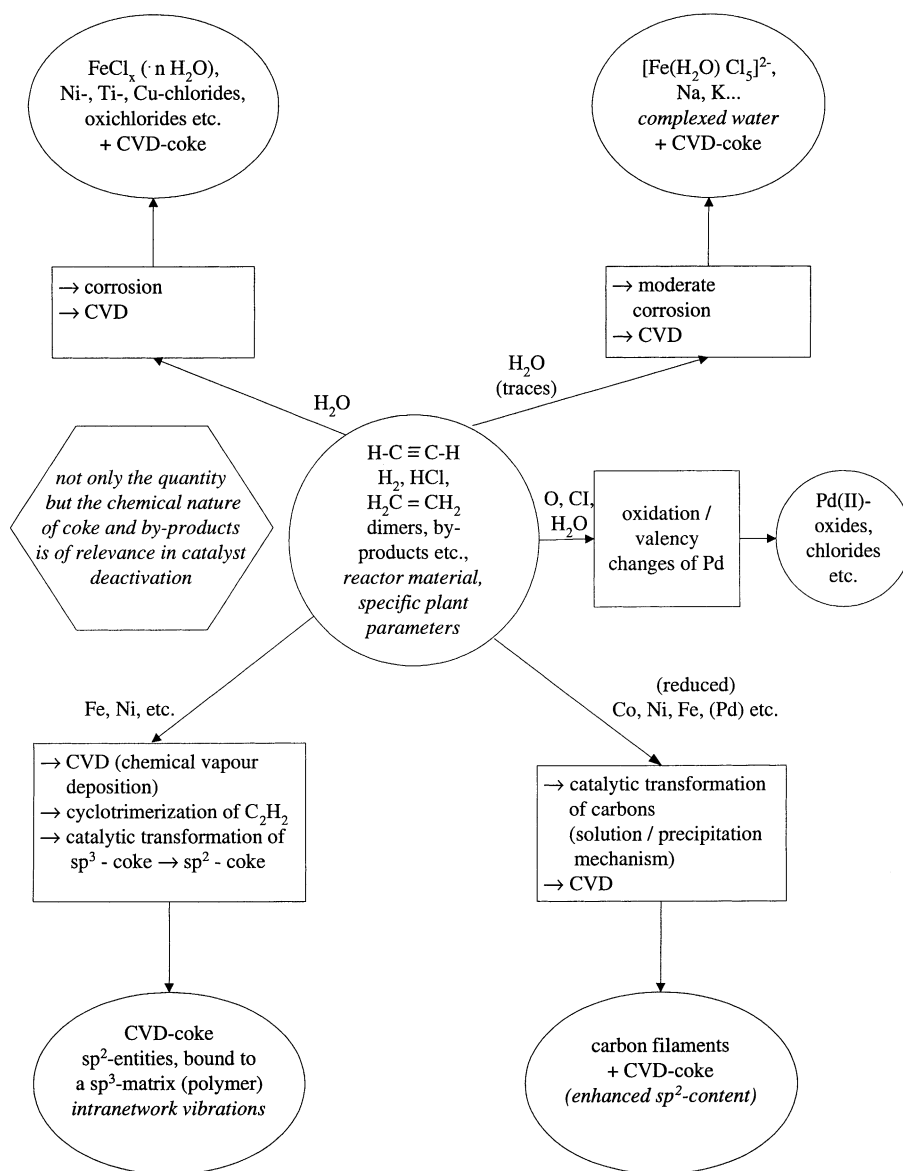


Fig. 5. Schematic representation of different processes observed under various irregular operation conditions during the selective catalytic hydrogenation of acetylene to ethylene in the vinyl chloride process. Catalyst: Pd/SiO<sub>2</sub>. Compiled from [39,51,62].

carbonaceous deposits which were strongly attached to the catalyst surfaces — surprisingly — were not of direct influence on hydrogen storage and release nor on the catalytic activity. Again (Section 2.2.1), there was no simple correlation between the total amount of carbon and the catalytic activity but there was with the specific nature of the carbonaceous species

present. Very simple molecular structures appeared at the catalyst surfaces which finally could unambiguously be identified as CH<sub>3</sub> groups chemically bound to the palladium surface in a C<sub>3v</sub> site. The normalised intensities of the Pd-CH<sub>3</sub> surface species showed an exact correlation with the degree of catalyst deactivation. In this case the ability to form palladium

Table 1  
Summary of Section 2.2: interactions between palladium/hydrogen/carbon

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Dissociative adsorption of hydrogen, H-absorption as interstitial protons.
Formation of $\alpha$ - and $\beta$ -palladium hydride, pressure plateau of the $\alpha/\beta$ -phase transition.
Deposition of cokes of different $sp^2/sp^3$ character and adhesion properties.
Incorporation of carbon — interstitial carbon — (carbides).
Influence of incorporated carbon on the formation of $\beta$ -palladium-hydride.
Catalytic transformation of amorphous carbon into aromatic/graphitic carbon (solution/precipitation mechanism; Pd less active than Co, Ni, Fe, etc.).
Catalytic growth of filamentous carbon (Pd less active than Co, Ni, Fe, etc.).
Cyclotrimerisation of acetylene to benzene-like entities.
Formation of stable molecular surface species ( $CH_3$ -Pd).
Low co-ordinated Pd may be more resistant to deactivation by coking.

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hydrides was not hampered significantly and no indications for the predominance of interstitial carbon or carbides were obtained. This may be the reason that no deceleration of the hydrogen uptake by strongly adherent polyaromatic coke or by the simple Pd-CH<sub>3</sub> compound occurred. The catalyst surface was modified by strongly bound  $sp^3$  entities which presumably changed the surface polarity and accessibility for the adsorption of  $sp^2$  type aromatic reactants. In this case, variations of the adsorption properties but not of the absorption properties of palladium were of relevance and loss of activity was caused by the presence of large quantities of a simple but stable organometallic surface compound. The stability of the CH<sub>3</sub>-Pd species may be understood regarding recent investigations by Schulz and co-workers on Fe- and Co-based catalytic systems [64].

For clarity, the different points addressed in Section 2.2 are summarised in Table 1.

### 2.3. Physical properties

An important parameter for long term performance can be the mechanical stability of the support material. Enhanced mechanical abrasion of the catalytically active species from the support or insufficient interaction between precious metal crystallites and the support under given process conditions may lead to a loss of active species or to undesirable debris of (e.g.) oxide particles or carbonaceous entities. Hence, the corresponding mechanical requirements for the catalyst have to be precisely determined, adjusted and optimised for the individual application or process conditions.

Furthermore, it is well known that the mechanical properties of palladium change periodically during hydrogenation of the element from low concentrations ( $\alpha$ -hydride phase) over the  $\alpha/\beta$ -phase transition to the fully loaded  $\beta$ -hydride-phase. This is observed for bulk as well as for finely divided palladium. The  $\alpha$ -phase material is still quite hard, whereas under certain conditions the  $\beta$ -phase hydride can appear as a soft material which may tend to form agglomerates. Enhanced mechanical stress or cold working applied to palladium hydrides may cause enhanced defect density such as dislocations in the bulk material. This can result in pronounced hysteresis effects of the hydrogen adsorption/desorption isotherms or the kinetics of hydrogen storage and release ([43,44] and literature cited therein) by originating trap sites for hydrogen (see e.g. [65]). Such effects may be of concern in applications where the reversible hydrogen storage inside the material is suspected to be of some relevance in the technical application or for the occurrence of particle growth (Section 2.1). In spite of the possibility that there could be stronger forces tending to remove deformation damage from bulk palladium or from larger particles compared to the very finely dispersed species there may still be some future benefit in studying the consequences of changing micromechanical properties due to hydrogenation and oxidation for the case of supported palladium.

### 2.4. Poisoning

In addition to the effects of catalyst coking (Section 2.2.1) the deposition and accumulation of excessive amounts of metallic species, debris, inorganic oxides,



contaminants and corrosion products can have an impact on the persistence of the catalytic activity of palladium catalysts. In addition to a purely physical shielding of the active surface area, the chemical effects of poisoning, selective poisoning, alloying or various other phenomena have to be considered.

For the case of palladium the influence of carbon monoxide is well known to modify the adsorption properties and catalytic surface conditions [66]. Prominent properties are the stacking efficiency and the interactions between CO molecules and certain surface sites of palladium ([66,67], and literature cited therein). Therefore, in many applications such as hydrogenation reactions the purity of educt streams with respect to (e.g.) CO has to be monitored.

On the other hand selective poisoning of palladium to fine tune selectivity is a well established procedure in catalyst preparation and catalyst operation [3,4]. When poisoning by heavy metals such as lead in the well-known Lindlar catalyst is used to do so, the term promotion is frequently employed, whereas regarding the introduction of poisonous compounds such as amines to the catalyst operating in the reaction mixture, usually the terms modification or regulation are employed [68].

Sulphur plays an important role in changing the catalytic properties of palladium catalysts [69,70]. In the catalytic combustion of methane to carbon dioxide and water and in oxidation reactions in the exhaust of lean-burn natural gas engines sulphur is identified as being a critical contaminant [71]. Partial deactivation of palladium was observed from sulphur-containing gases [70,72]. Studies on SO<sub>2</sub>/Pd interactions on three-way catalysts showed that the poisoning of the Pd component was partly irreversible due to direct interactions between Pd and SO<sub>2</sub> [73]. An additional impact of the presence of water was believed to be competitive action between water and SO<sub>2</sub> which was dependent on temperature [71].

In hydrogenation reactions, the presence of H<sub>2</sub>S can also have a detrimental impact [74]. However, for the conversion of butadiene on Pd/SiO<sub>2</sub> it was shown that a pronounced temperature dependence exists for deactivation and reactivation procedures, allowing to achieve an enhancement of selectivity to butenes [75]. This finding illustrates a delicate balance of harmful and helpful interactions between sulphur and catalysts [75,76]. Palladium catalysts may also be pre-sulfided

to enhance their selectivity in reductive alkylation reactions [77].

Hydrogen treatment of sulphur-poisoned supported Pd-complex catalysts used in selective hydrogenation of styrene to ethylbenzene was shown to be able to partially eliminate the sulfur compound [78]. Furthermore, Pd–Pt bimetallic interactions were observed to be effective to improve resistance to irreversible sulfur adsorption and sulfur-induced coke formation during isomerisation of *n*-hexane [79].

Again, it is evident that various reasons and critical conditions for distinct poisoning have to be identified in detail and simultaneously considered to adjust adequate activity and useful selectivity of the palladium catalysts [10,29].

### 2.5. Leaching

Especially in slurry-phase hydrogenation reactions the loss of precious metal by formation of soluble complex compounds may occur. To prevent this, it is of major importance to avoid hydrogen starving conditions and to keep the palladium crystallites in a well-reduced, metallic state [80].

Nitro compounds are well-known agents to mobilise Pd or Pt by oxidising the metals easily which are then complexed with product amine and lost in the bulk liquid. In addition to this loss of precious metal from the support causing severe catalyst deactivation, product contamination and expensive removal of the contaminant from the product add to the additional costs of such a process.

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 stirring device or increasing the hydrogen partial pressure in the reactor. Hereby, the transfer of gaseous hydrogen into the liquid phase is improved. For modifying or adapting the “catalyst side” of the process two approaches are possible: to use smaller quantities of catalyst for the reaction or to decrease the precious metal loading of the catalyst (e.g. 3 wt.% of precious metal instead of 5 wt.%) [18]. All these actions lead to a higher availability of hydrogen at the catalytically active metal particles on (e.g.) a carbon support. Thus, stabilisation of the metal in its metallic

or hydridic form is achieved and leaching is avoided sustaining the catalytic activity of the supported palladium.

### 3. Conclusions

A short summary of some of the major causes of deactivation and premature degradation of palladium catalysts was given. Prominent features as highlighted and categorized in the recent literature were particle growth for various reasons, coke deposition and coke transformation, the influence of the support material on long term stability, modification at the palladium surface itself including valency changes or the formation of simple but stable organometallic surface species and the variations of physical properties as well as chemical poisoning, corrosion or leaching.

However, in spite of the large existing body of literature concerning catalyst deactivation as a common phenomenon in academic research and industrial technology, specific information accessible for the various kinds of palladium catalysts being used worldwide is still quite limited. There appears to be a serious need for future studies on properties of palladium-based catalytic systems regarding, for example, the interactions between carbon, hydrogen and supported palladium as a ternary system. Furthermore, the interdependencies between dynamic variations of the microstructure of supported particles of palladium and the catalytic activity in (e.g.) oxidation reactions are of paramount interest [81].

In industrial applications it may be difficult to strictly and definitely differentiate between certain simple reasons for deactivation. The conditions for the occurrence of purely thermally or purely catalytically driven catalyst coking on the one hand and of moderate or enhanced corrosion phenomena or changes of the properties of the palladium itself on the other have to be studied in much deeper detail under different operation conditions for the specific industrial process. However, it seems encouraging to observe surprisingly well-defined species such as CVD-coke or stable methyl groups on deactivated palladium catalysts from large scale technical operation. Furthermore, it seems possible to roughly discriminate between different deactivation phenomena which may

occur during the selective catalytic hydrogenation of acetylene under more or less irregular conditions.

This underlines the benefits of translating and utilizing results from academic studies on deactivation and poisoning under controlled laboratory conditions and from surface science work onto the level of large scale technical applications and vice versa.

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