

Bimetallic palladium catalysts: influence of the co-metal on the catalyst performance

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Abstract

An overview about the effect of co-metal on the performance of Pd in bimetallic catalysts is presented. In the first part, the promotion of monometallic catalysts by addition of a second metal is described from a general point of view in terms of: (i) electronic effects; (ii) geometric effects; (iii) the occurrence of mixed sites; and (iv) the disappearance of the β -PdH phase. The second part presents the main methods to prepare bimetallic catalysts through the unselective and selective depositions of the co-metal precursor and the use of heterobinuclear complexes. The influence of preparation methods on the chemical state and the spatial distribution of both components are highlighted. In the last part, a short overview is given about the influence of co-metal addition on some important reactions in which Pd is the reference active phase: (i) selective hydrogenation of highly unsaturated aliphatic hydrocarbons; (ii) hydrogenation of aromatics or hydrodearomatisation; (iii) hydrogenation of nitrogen-containing compounds; (iv) reactions involving CO; and (v) hydrodechlorination. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The first clear realization that chemical reaction between two gaseous reactants can occur at a metal surface, without the latter being chemically unchanged, is due to Humphrey Davy in 1817 (see [1,2] for a brief historical survey). In experiments for the development of miner's safety-lamp, Davy observed that a Pt wire remained hot without flame in the presence of coal-gas and air. Davy deduced that the coal-gas and air combined without flame when in contact with the hot Pt surface. Only Pt and Pd wires were effective.

This is probably the first report of a catalytic activity on a Pd surface. A second breakthrough by the end of the 19th and early 20th centuries was the extensive Sabatier's works on hydrogenation of several organic and inorganic substrates on a wide variety of powdered metal catalysts among them Pd. The benefit brought by "alloying" two active metals, or an inactive with an active one, was early recognized, and systematic studies were carried out between the first and the second world wars. From the first finding about stabilization of Pt gauzes in the NH₃ oxidation by adding Pd, some of the best achievements in catalysis by alloying metals can be found in the refining industry with the very classical reforming Pt-based catalysts promoted by Ir, Re, Ge, Sn, ... and selective hydrogenations in petrochemistry with promotion of Pd with Sn, Au, Cu, Pb, ...

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At the beginning, the behavior of alloys catalysts was interpreted by both the electronic theory of catalysis and the Rigid Band Theory (RBT) of alloys. The former stated that molecules are activated during the adsorption process by either releasing or accepting one electron, whilst the latter postulated that the number of d-band holes could be decreased by alloying a metal containing more valence electrons, from an electron transfer. Actually, the interpretation of the alloying effect has been found much more complicated later, though this initial concept remained still ever stimulating.

It is first necessary to precise what we are meaning when using the terminology of “alloy”. Taking the proposition of Ponc and Bond [1], we will adopt this term to describe “. . . any metallic system containing two or more components, irrespective of their intimacy of mixing or the precise manner in which their atoms are disposed . . .”. On that account, alloys can be formed from a metal and a clearly non-metal, i.e. Pd and B or Si, or two metals forming a continuous series of solid solutions over the whole concentration range, i.e. PdAg. This definition of “alloys” catalysts being settled, the alloying effect, promotion of the catalytic properties of one metal by addition of a second component, enters in the general frame of the “structure-activity” relationships.

It was shown that a large number of reactions exists for which the rate per unit of catalyst area depends on the superficial structure of a catalyst with a given chemical composition. This general concept of “structure-sensitivity” was particularly fruitful in the field of catalysis by metals. Depending on whether the turnover frequency (TOF), or rate per unit surface area or per accessible metal atom, is affected or not by the metallic structure the reactions have been called “facile” or “demanding” [3], or later on by the terms structure-insensitive or structure-sensitive [4]. The first to recognize this concept was Taylor in 1925 [5] who said: “. . . the amount of surface which is catalytically active is determined by the reaction catalyzed. There will be all extremes between the case in which all the atoms in the surface are active and that in which relatively few are so active. . .”.

Generally speaking, superficial metallic structure refers to the coordination number between the active metal atoms which can be modified [1]: (i) by exposing

different crystallographic planes at the surface and making them imperfect by means of steps and kinks; (ii) by varying particle size in the critical range between 1 and 5 nm; (iii) by alloying the active metal with a second component; or (iv) by induction of a strong metal-support interaction with some supports. Each of these situations has been the subject of reviews, in particular the alloying effect in catalysis [6]. Albeit this separation seems somehow arbitrary, and could be criticized, there is more or less a general agreement to explain these structure-activity relationships with the help of geometric and electronic effects (*vide infra*).

In any case, understanding the alloying effect would require the best possible knowledge for the following points: (i) what is the chemical state of the two components? (ii) are the two elements intimately interacting in the same aggregates or not? (iii) does surface segregation of one component occur? (iv) are the two elements randomly distributed in the surface layer or not? The first and second points mainly address to the method used for preparing the catalysts and will be discussed in more details later (*vide infra*). The third question to be asked concerns the surface composition in bimetallic particles. The occurrence of segregation to the surface of one component of an alloy is now well established, as well as its influence on the catalytic properties (see [1]). Finally, on small particles (1–2 nm), surface atoms tend to represent the majority of the atoms of the particle and the surface enrichment loses meaning. Nevertheless, on these small aggregates the surface contains sites of different topologies: low index planes, kinks, edges, corners, etc. The distribution of the different components of the bimetallic particles could be ordered, and one component would occupy sites of a given topology preferentially [7–10].

It will be the aim of this review to look at the effect of the presence of a second component in Pd-based heterogeneous catalysts at the light of the above considerations. Alterations of the catalytic properties of Pd will be discussed in the frame of electronic and geometric effects, with respect to the different methods by which the alloy catalysts could be prepared. Some examples will be chosen to highlight these behaviors. This review will be restricted to Pd-based catalysts operating in a reductive atmosphere.

2. Electronic and geometric effects in catalysis by metals

As mentioned above, the structure-activity relationships are often explained on the basis of electronic and/or geometric effects. However, geometric and electronic influences cannot often be separated as independent parameters. For instance, increasing the size of metallic particles results in an electron bandwidth increase and a decrease of binding energies of core electron, but the nature of the exposed planes and the topology of the surface sites change as well. Nowadays, the debate between the electronic and geometric factors is only seen of historical interest in catalysis.

Moreover, we have to take care of a simple view of a geometric basis for explaining structure-sensitivity. There is the possibility, under high temperature conditions, or very reactive atmospheres, that surface mobility smoothes out geometric and structural features on small particles. This concept of flexible surface, mainly revealed by Somorjai [11], as well as the correlation between reactivity and restructuring ability appears extremely puzzling, though fruitful. This is particularly true with reactants induced segregation.

This phenomenon of surface layer reconstructing is not only restricted to high temperature treatment in reactive atmosphere but can also occur under mild conditions in reactions carried out in the liquid phase. By measurement of the catalysts potential [12], Bodnar et al. [13] have shown that metal promoters, deposited as Ge^{4+} , Pb^{2+} , Cu^{2+} and Sn^{2+} on the surface layer of Pd particles, can be found as bulk metal, adatoms or remain as ions after reduction in liquid phase. The prevailing phase depends on the reaction conditions and the substrate to be hydrogenated. As an example, Ge in Ge-promoted Pd/C will remain the same after the pre-reduction and hydrogenation of cinnamyl alcohol, mainly as Ge^0 , whilst it will transform into GeO_2 , and then be leached to the solution, upon hydrogenation of nitrobenzene.

2.1. Electronic effect in catalysis by alloys

To be short, the key point in this model lies in the interaction between the d-band orbitals of the surface sites with the molecular orbitals of reactants and products. Historically, the premises of this concept were

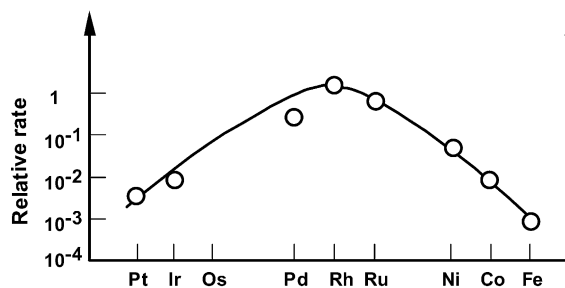


Fig. 1. Rate for C_2H_4 hydrogenation on some metal wires relative to Rh [15].

suggested by Sabatier [14], who said that the intermediate compound formed by one reactant at the surface must be stable enough to be formed but not too stable since it must decompose to yield the products. This can be correlated with the heat of adsorption of reactants and products, governed by the electronic factors, which should be neither too strong nor too weak to give the optimum coverage for species competing at the surface, or for the products to desorb. The ammonia synthesis, competition between N_2 , H_2 and NH_3 , and the selective hydrogenation of unsaturated hydrocarbons, competition between H_2 and hydrocarbons, are good examples for that. This is illustrated for the hydrogenation of ethylene on metal wires (Fig. 1); the rate is maximum for Rh, for which the heat of adsorption of ethylene provides the optimum coverage in C_2H_4 and H_2 .

It was early believed that an electron was transferred in the chemisorption process from the reactant to the metal surface, or the reverse. This proposition allows to understand the popularity of the RBT of alloys in which the d-band holes of one metal are filled by the valence electrons of a second metal. The valence shell electronic configuration of Pd in atomic form is of $4d^{10}5s^0$ type; in metallic Pd, approx. 0.36 electrons of the d-shell are in the s-band. This leaves an equivalent number of holes in the d-band. The filling of the 4d shell on alloying can therefore arise either by a flow of charge from s-band of Pd or a charge transfer from a second component. Actually, it was recognized later that: (i) the chemisorption bond on metal is covalent for the main; and (ii) the extent of electron transfer from one component to the other upon alloying is very small, if so. Nevertheless, the degree of electronic interaction between valence electrons of the two

components in alloys depends on the enthalpy of formation ΔH_f , it will be low if ΔH_f is positive, but strong if ΔH_f is negative (see [1] for more details).

In an extensive study about the electronic properties of Pd alloyed with 20 elements as Mg, transition metals, lanthanides and actinides, Fuggle et al. [16] concluded that (i) in alloys with electropositive elements the Pd d-band is filled and moved away from the Fermi level with narrowing of the d-band width; (ii) as the electronegativity difference between the elements is decreased there is a greater overlap in the band energies of Pd and second metal; (iii) the filling of bands is largely due to changes in the hybridization of the Pd d-band, and the actual charge transfer of Pd d electrons is probably small. XPS studies of Pd₈₀Ge₂₀ glassy alloys also showed strong modifications of the Pd d-band, which is filled in the alloys [17]. This was not due to charge transfer from Ge to Pd, but to intra-atomic charge transfer from 5s to 4d orbitals of Pd. The reverse was reported when Zn was vapor-deposited on a Pd surface [18]. The XPS experiments provided evidences that redistribution of charge occurred in Pd with shift from 4d to 5s orbitals, which strengthened the Pd–Zn bimetallic bond. Ab initio SCF calculations on Pd₃Zn₁₀ clusters reached the same conclusions: small charge transfer between Pd and Zn but redistribution of charge from 4d to 5s Pd levels. From quantum chemical calculations on Pd₁Cu₁₂ and Pd₄Cu₆ clusters, Fernandez-Garcia et al. [19] proposed a similar scheme for an intra-atomic charge redistribution from 4d to 5sp states at Pd sites. Surface Pd atoms became slightly negatively charged. This electronic modification of Pd would be in agreement with XANES experiments on PdCu/KL-zeolite catalysts [20]. These results disagree with the interpretation of IR-CO experiments on PdCu/Al₂O₃ [21], and XPS experiments on PdCu/Pumice [22], from which no electronic modification of Pd by Cu was claimed, but only a dilution of Pd surface. These few examples emphasize the great variety of situations for electronic modifications upon alloying Pd with a second component. The electronic interpretation of alloying effect was then forsaken at the benefit of geometric considerations, i.e. dilution of the active sites. Anyway, even if there are clear evidences that the extent of electron transfer is generally low upon alloying, the consequence of dilution of the active metal into smaller ensembles by a second component is the ap-

pearance of discrete levels in the valence band and in many cases the rehybridization of the orbitals.

In any case, if one wishes to put in evidence electronic effects in catalysis by alloys, it is necessary to consider reactions in which the geometric effects are of small importance, i.e. those known as occurring on a site of small size (vide infra). This is the case for the hydrogenation of alkenes, alkynes and alkadienes.

Electronic modifications upon alloying Pd was invoked to interpret the better selectivity observed in the selective hydrogenation of alkadienes and alkynes to alkenes [23]. For instance, in the hydrogenation of 1,3-butadiene and 1-butene on Pd-based catalysts, Sarkany et al. reported that the rate of *n*-butane formation was suppressed to a greater extent than was the consumption of 1,3-butadiene when Pd was alloyed with Zn [24] or Co [25]. This was ascribed to a decrease in the strength of butene and butadiene complexation. This behavior can be illustrated by Fig. 2. As discussed above about the electronic factors in catalysis by metals, the maximum of catalytic activity is expected for an optimum strength of adsorption, neither too strong nor too weak. This was exemplified in the case of ethene hydrogenation on Group VIII metals (Fig. 1). The same concept applies by choosing a catalyst and changing the reactant within an homologue family (Fig. 2). In that case, alkyne are too strongly bonded to react fast enough. The challenge is to fine-tune the properties of the metal phase to decrease the strength of adsorption of the alkyne, so that it reacts faster. In this frame, the alkene will be less reactive and a higher selectivity to this target compound will be achieved more easily according to the consecutive formal reaction scheme: alkyne (or alkadiene) → alkene → alkane.

2.2. Geometric effect

The first element of this model lies in the pioneering works from Kobozev [27], Poltorak and Boronin [28]. They showed that some reactions need more than one surface atom to proceed. Moreover, a specific arrangement between these atoms will be even required to generate the active site [29]. This geometric model was more recently revisited by several authors [30–32], naming it as “ensemble-size” model. The basic idea is that the rate is function of the probability to find an ensemble of *n* free and neighbor atoms on

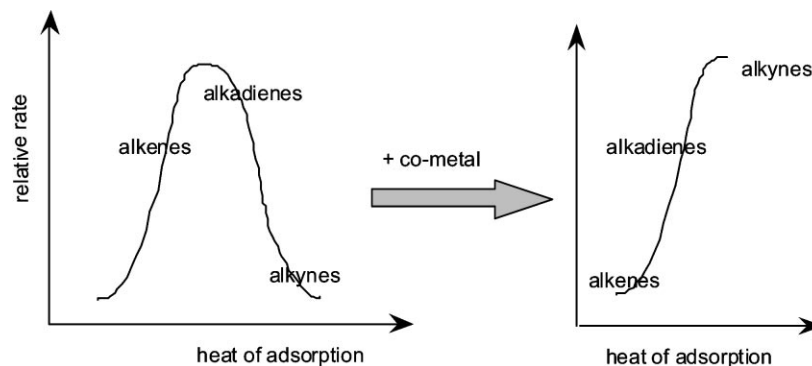


Fig. 2. Relative rate of alkene, alkadiene and alkyne hydrogenations as a function of the heat of adsorption on Pd catalysts [26].

which the adsorption of the reactant(s), and the further transformations, can occur. In the illustration of Fig. 3, the hydrogenolysis of ethane needs several neighbor metal atoms to accommodate the multi-bonded HCC^* reactive intermediate and the five H^* abstracted, 12 on Ni catalysts according to Dalmon and Martin [32]; in contrast the reactive adsorption of ethylene could proceed on a single atom.

Since the simple and attractive hypothesis of RBT in alloys has failed to stand the test of time, the “ensemble-size” model became very helpful to interpret the behavior of alloys. When applied to alloys between an active component A and an inactive one B, the ensemble-size model in its simplest form reflects the dilution in ensembles of smaller size of the active surface A by B; these smaller ensembles of A being less prone to activate the reactant(s). The immediate consequence of this phenomenon is a sharp decrease of the turn over frequency (TOF). The TOF

is the number of molecules transformed per unit time and per surface metal atom A; the number of surface metal atom being titrated by hydrogen chemisorption for instance. Concurrently to the TOF decrease, no modification of the kinetic parameters, activation energy, enthalpies of adsorption and entropy changes, should occur. Obviously, the fall of TOF should be all the more so that preferential segregation to the surface of the inactive component B occurs. In the classical treatment of diluting an infinite surface A by B, the probability to find an ensemble of neighboring n A atoms is given by [1,33,34]:

$$P = (1 - \theta_B)^n \quad \theta_B : \text{surface coverage by B} \quad (1)$$

This ideal relationship is true when A and B are randomly distributed on an infinite surface. The situation becomes more complicated when the distribution of A and B is not random. Upon alloying A and B if ΔH_f is positive the components tend to form clusters, at variance when ΔH_f is negative ordering prevails. Random distribution of A and B is favored when ΔH_f is slightly negative.

Another limitation to the ideality represented by Eq. (1) is the finite size of metal particles in real catalysts [34]. Moreover, the surface of small metal particles are composed of sites with different topologies: low index planes, kinks, edges, corners, etc. The distribution of the different components of the bimetallic particles could be ordered, and one component would occupy sites of a given topology preferentially [10,35]. This was demonstrated by Monte-Carlo calculations for Pt alloyed with Cu, Ag or Au [36], and by the

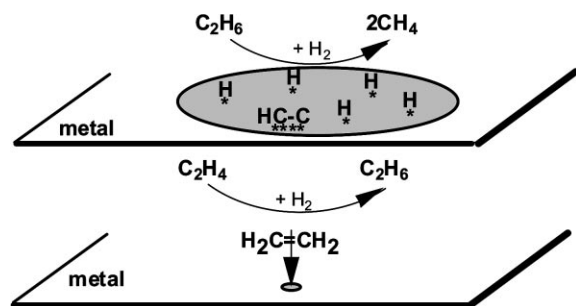


Fig. 3. Schematic representation of the ensemble size required for the hydrogenolysis of C_2H_6 and the hydrogenation of C_2H_4 .

Density Functional Theory calculations for Rh alloyed with Ge, Sn or Pb [10]. Such a behavior was suggested to occur also in PdRh/Al₂O₃ where Pd would occupy preferentially the low coordination sites in PdRh bimetallic particles [37].

A very efficient approach to probe the dilution of A by B is the IR-monitored chemisorption of CO [1]. This is a particular powerful tool in the case of Pd-based catalysts. The IR spectrum of CO adsorbed on reduced Pd surface exhibits two intense bands in the range 2100–2050 and 2000–1800 cm⁻¹. The former is ascribed to various forms of linearly adsorbed CO on Pd atoms, and the latter to CO bridging two or more adjacent Pd atoms. The dilution of Pd by an inactive component can be put in evidence by (i) a shift of ν_{CO} to lower values; and (ii) a decrease of the relative intensity of bands corresponding to bridged species [1]. This was first clearly demonstrated by Soma-Noto and Sachtler [38] on supported PdAg alloys. Moreover, a very elegant method, adsorption of ¹²CO/¹³CO mixture, allows to discriminate in the ν_{CO} shift what is due to dilution effect and what comes from ligand effect (electronic effect) [39].

PdCu system is a typical example where IR-CO experiments were applied with success. The first and main conclusion was a dilution of Pd by Cu in a random fashion [20,21,40–43]. However, on PdCu/SiO₂ catalysts prepared from mixed acetylacetonate precursors it was further postulated that the Cu atoms are preferentially located on the edges of the small crystals and (or) on the (1 0 0) open faces, rather on the (1 1 1) facets [42]. This idea of preferential migration of Cu on low coordination sites will be supported by ion scattering spectroscopy on various PdCu alloys [44], theoretical studies on PdCu single crystals [45] and cubo-octaedral aggregates [46]. Moreover, the absence of any ν_{CO} shift at low ¹²CO coverage in ¹²CO/¹³CO IR experiments on Pd and PdCu alloys was interpreted as a very low ligand effect in this system [39]. However, from XANES and IR-CO experiments [20] and quantum chemical calculations [19], it was claimed that an intra-atomic charge redistribution between 4d and 5s states of Pd occurs upon alloying with Cu.

2.3. Mixed-sites

It is somehow difficult to give an unequivocal definition of the mixed-sites. One can tentatively propose

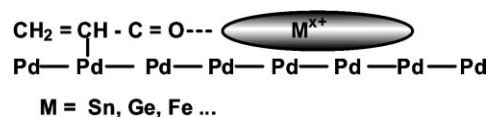


Fig. 4. Schematic representation of the activation of the C=O bond in α,β -unsaturated carbonyls on Pd-M^{x+}.

that a mixed-site is an active site where both components of the alloys participate in the catalytic transformation. In some cases, such a site can show a higher catalytic activity than any of the pure metals, without real alteration of the individual electronic properties. This situation can be illustrated in alloys between two transition metals: a better catalytic activity was proposed for C₂H₆ hydrogenolysis in mixed Pd–Ni sites composed of six Ni atoms diluted in the Pd matrix [47].

Very interesting also is the case of Pd-promoter in which the promoter is not fully reduced in the running conditions of the reaction. In this situation, mixed-site can be described as Pd–M^{x+}. Synergistic effects in such sites have been claimed to occur during the liquid phase hydrogenation of α,β -unsaturated aldehydes, although Pd was not the commonly used active metal for this reaction [1,48]; this is illustrated in Fig. 4. The promotion effect is due to a positively charged cationic species M^{x+} activating the C=O bond, which becomes easily hydrogenated. The building of this mixed-site is very similar to what is occurring in the well-known strong metal support interaction (SMSI) [49]. SMSI occurs when Pt, Pd, Rh, ... deposited on some reducible supports, TiO₂, Nb₂O₅, ... are reduced at high temperature. There is a partial reduction of the support, e.g. TiO₂, with the migration of TiO_x adspecies onto the surface of metallic particles. This phenomenon leads to a dilution of the metal surface (Pt, Pd, ...) into smaller ensembles, and the creation of mixed-sites Pd-(TiO_x)^{δ+}. Some electronic modifications of the noble metal have also been claimed [49].

2.4. The problem of the β -PdH phase

A peculiar behavior of Pd concerns its ability to form hydride phases, which could explain to some extent the catalytic properties in hydrogenation of unsaturated hydrocarbons [50]. The solubility isotherms and X-ray results clearly show the existence of two

solid solutions, named α and β , under normal conditions [51]. The latter tends to disappear as the size of Pd particles decreases to the nanometer scale [52–54]. The presence of β -PdH phase in the catalyst considerably increases the acetylene hydrogenation rate to ethane, and is concurrently accompanied by a low selectivity to ethylene [53]. The decomposition of the β -PdH phase results in a sharp increase toward the ethylene selectivity, and electronic effects were mainly accounted for the interpretation of these behaviors. Upon incorporation of a second metal such as Cu [55], Sn or Pb [56], and its diffusion into the bulk due to appropriate thermal treatments, the suppression of the β -PdH phase was postulated for supported bimetallic catalyst. In both cases, in parallel to the disappearance of β -PdH there was a decrease of the TOF for the hydrogenation of 1,3-butadiene on PdCu [55], and of isoprene on PdSn and PdPb catalysts [56]. There was also a concurrent increase for the selectivity to alkenes.

2.5. Some comments

It comes out that the influence of co-metal on the Pd performances can be interpreted in terms of geometric or electronic effects, the occurrence of mixed-sites and the disappearance of β -PdH. On the other hand, it is well known that some classes of reactions are more or less sensitive to some of these factors. For instance, the electronic factors play a definite role in the selective hydrogenation of unsaturated hydrocarbons, whilst geometric considerations are prevailing in the hydrogenolysis of alkanes; besides, the occurrence of mixed-sites is a dominating factor in the selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols. As a consequence, for a given catalytic formulation, i.e. Pd–Sn, interpretation of the Sn influence on Pd properties depends directly on the reaction considered.

As above-mentioned it is worth noting that the influence of co-metal on Pd performances will be crucially affected by (i) the degree of intimate interaction between the two components in the same aggregates; and (ii) the chemical state of the co-metal. In the following section, we will give an outlook on the ways by which the different methods used to synthesize the catalysts could affect these factors. Finally, a last section will provide a short overview about the influence

of co-metal on Pd performances in various classes of reactions, which are treated in more details in other part of this review book.

3. Preparation of Pd-based alloys catalysts

There are two main steps in bimetallic catalysts preparation. The first consists of depositing the active component precursors as a divided form on the support, whereas the second consists of transforming these precursors into the required active phase. It is worth noting that industrially a large majority of deposition methods involve aqueous solutions and liquid–solid interface. The activation of the deposited precursors will obviously have a clear impact on the chemical nature and the mutual interaction between the two components, e.g. Pd and co-metal M. One can anticipate that treatments in a mild reducing medium at low temperature will maintain the ionic states to some extent, whilst reduction at high temperature in pure hydrogen will promote pure alloy formation, and intermetallic compounds when possible. In the following, we will not treat this aspect and the attention will be focused on the influence of the deposition method. The deposition method of both Pd and M precursors can be tentatively categorized within three general methods:

1. The non-selective deposition (NSD) in which there is no interaction between Pd and M precursors during the deposition process.
2. The selective deposition (SD) in which one precursor, of the co-metal M in the very general case, is selectively deposited onto the metallic particles of the other component.
3. The deposition of heterobinuclear organometallic complexes, or inorganic salts, of Pd and M.

As for the activation process, the choice of both deposition method and support will affect the vicinity of Pd and M in the same aggregates, as well as their chemical state. When NSD is used, a close vicinity between the two components is not always achieved in the final reduced catalyst, and a wide family of mono- and bimetallic particles of different compositions exists at the support surface. This is the main reason for the development of SD methods and deposition of heterobinuclear complexes to achieve a closer interaction

between the two components. In-fine the knowledge of the architecture of the active site for a given reaction will help to decide what kind of deposition will achieve the rational design of the selective catalyst.

Before focusing on various methods for precursor deposition, we will shortly present a case study, supported PdFe catalyst reduced in similar conditions, demonstrating the incidence of deposition protocol on the physico-chemical properties of the material. In PdFe/Al₂O₃ prepared from NSD of inorganic salts, fully reduced PdFe alloys and Fe³⁺ coexist [57,58]. However, it has been claimed that the dipping sequence affects the Fe³⁺ proportion which increases when H₂PdCl₄ is deposited first, then FeCl₃ [58]. When SiO₂ is used as support, PdFe is also present as a dispersed metallic phase, but part of Fe will be then present as Fe²⁺ [59]. When a high purity graphite support was used for the NSD of inorganic salts, the supported metal particles consist of thermodynamically stable segregated state of metallic Fe and PdFe alloys [60], in accordance with the bulk immiscibility of the two phases [51]. This emphasizes the influence of the support on the chemical state of the two components: a weak metal-support interaction, with the graphite support, allows the creation of bimetallic structures predicted from bulk behavior, yet not found when refractory oxide supports are employed. The use of PdFe heterobinuclear carbonyl complexes for the preparation of PdFe/SiO₂ catalysts leads to bimetallic particles composed of PdFe alloy and Pd-Fe³⁺ pairs with great intimacy [61]. Finally, PdFe/Al₂O₃ prepared from underpotential deposition (UPD) of Fe³⁺ onto a pre-reduced parent Pd/Al₂O₃ allows the selective deposition of Fe⁰ near Pd sites of low coordination [62].

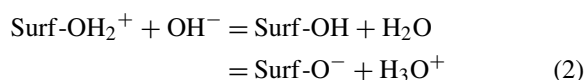
3.1. Non selective deposition of the precursors

This method mainly applies when M is a transition metal. The basic principle of NSD of Pd and M precursors, together or successively, is such that the interaction of both precursors with the solid surface was stronger than between the two precursors. On that account the two deposited precursors are separated on the support and surface diffusion will be necessary to yield the “bimetallic” aggregates during the activation process. NSD will use the same deposition methods as for monometallic catalysts, which are described

in details in several reviews ([1,63–66], and references therein). According to the final degree of metallic dispersion targeted, the deposition will be done by ion-exchange, chemical grafting or wet impregnation. The two formers allow deposition of atomically distributed precursors which leads to highly dispersed metallic phase upon subsequent reduction. In contrast, aggregates of the precursors are formed by impregnation, yielding larger metallic particles. As mentioned above, the methods using aqueous medium and inorganic complexes are much more popular in industry.

3.1.1. NSD by ion exchange

Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another species. The support containing ion A is immersed into an excess volume of a solution containing ion B that is to be introduced. Ion B gradually penetrates into the pores of the support and replaces ion A, which passes into solution, until an equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution. Oxide surfaces, and charcoal in some cases, contacted with water are generally covered with hydroxyl groups, Surf-OH, where Surf stands for Al, Si, Ti, ... The following equilibria exist in aqueous solution:



The resulting surface charge, which arises from an excess of one type of charged site over the other, is a function of the solution pH. A given value of pH exists for which the particle is not charged overall. This value is characteristic of the oxide and is called the zero point charge (ZPC) of the oxide. The metal precursors generally used are transition metal complexes (TMC), e.g. Pd(NH₃)₄Cl₂ or PdCl₄K₂. In aqueous solution, TMC is surrounded by H₂O in the outer solvation sphere, whereas the ligand L (Cl, NH₃, ...) is in the inner coordination sphere (Fig. 5). The method of preparation will be based on the different kinds of ion-support interaction (ISI) between TMC and the support surface [67], through the concept of the interfacial coordination chemistry (ICC) [68]. In the ion exchange, an electrostatic interaction occurs between transition metal ion (TMI) and the support after exchange of TMC with H₃O⁺ in the case of a positively

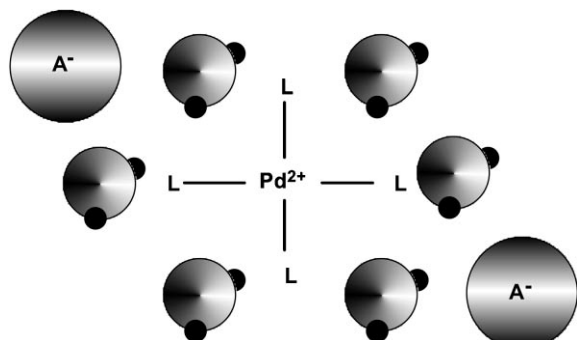
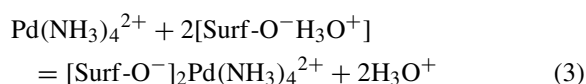


Fig. 5. Schematic representation of a cationic transition metal complex (TMC).

charged surface:



the same interaction obviously applies for the TMC of the co-metal M.

The support surface acts as a supramolecular counter-anion. The resulting ISI is generally strong and leads to nano-sized (1–2 nm) particles after activation. The homogeneous distribution of both TMIs of Pd and M through the grain of the support will be a key factor for their further interaction in the same aggregates. A similar strength of interaction between both TMIs and support will promote this homogeneous distribution.

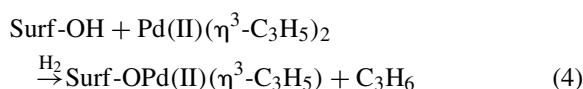
Another drawback associated with the strength of ISI could be the necessity of a high reduction temperature (i) to favor surface diffusion of the various species to aggregate; and (ii) to reach the metallic state for both components. Some sintering can then occur. On that account, the choice of a ligand L with high reducing power can partially solve this problem. It has thus been claimed that homogeneous nanometric bimetallic PdAu particles located in the supercages of Y zeolite can be obtained from co-exchange of HY with $\text{Pd}(\text{en})^{2+}$ and $\text{Au}(\text{en})_2^{3+}$ (en = ethylenediamine) [69]. The ethylenediamine ligand allows the in situ reduction of Pd and Au in inert atmosphere without significant sintering.

Providing the ion exchange capacity of the surface has not been exceeded, the sequence of deposition of both TMCs is of no importance; however, co-exchange is generally preferred.

3.1.2. NSD by grafting

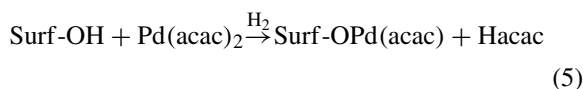
The grafting of organometallic complexes on a support can be achieved generally through the chemical reaction with surface hydroxyl groups, with the removal of one or more organic ligands from the inner coordination sphere of the metal complex ([66,70], and references therein). The method of deposition results in many cases in a strong interaction which leaves the metal phase either atomically dispersed or as nanometric sized particles, after activation treatments usually in mild conditions. The acetylacetonate and π -allyl are the most frequently organic Pd complexes used. The co-grafting, or successive grafting, of Pd and M organic complexes has been scarcely reported, and a few selected examples will be shortly described hereafter.

The grafting of $\text{Pd}(\text{II})(\eta^3\text{-C}_3\text{H}_5)_2$ can be described by the following reaction:



A similar reaction applies for the π -allyl complex of the co-metal M. A double bonded metal complex is usually obtained with Cr, Mo and W, and a single bonded metal complex is obtained with Ni, Pd and Pt. A heavily loaded PdNi/SiO₂ catalyst was thus prepared by successive ligand exchange of first $\text{Pd}(\text{II})(\eta^3\text{-C}_3\text{H}_5)_2$ then $\text{Ni}(\text{II})(\eta^3\text{-C}_3\text{H}_5)_2$ complexes in *n*-pentane solution. Both complexes interact separately with the OH groups of silica surface [71]. PdNi bimetallic particles were obtained in the 1–2 nm range, even after reduction at 823 K. The surface is enriched in Pd and a synergistic effect was observed in the ethane hydrogenolysis (mixed sites). The use of $\text{Pd}(\text{II})(\eta^3\text{-C}_3\text{H}_5)_2$ and (E)-2-ethyl-1-hexenyl-Cu(I) was claimed to favor the formation of alloy particles in PdCu/pumice catalysts [22].

The co-deposition of $\text{Pd}(\text{II})$ -2,4-pentanedionate ($\text{Pd}(\text{acac})_2$) and $\text{Mn}(\text{II})(\text{acac})_2$ was recently described and leads to the formation of PdMn alloys particles surrounded by manganese oxide after reduction of a PdMn/SiO₂ catalyst [72]. As in the case of π -allyl complexes, the interaction of $\text{Pd}(\text{acac})_2$ obeys the reaction [73]:



In order to compare the benefit gained by using heterobinuclear complexes, a PdMo/MgO catalyst was prepared from co-grafting MgO with PdCl₂(PhCN)₂ and Mo(CO)₆ [74]. The co-grafting leads to weaker Pd–Mo interaction and larger PdMo particles after reduction, as compared to the deposition of heterobinuclear complexes.

3.1.3. NSD from impregnation

The most frequently case is the use of inorganic salts in aqueous solution. The support is contacted with a solution of TMC (Fig. 5), and some H₂O molecules are then removed out from the solvation sphere of TMI. The weakness of the ISI in this deposition procedure usually leads after activation to metal particles of sizes larger than 4–5 nm. Two cases can be distinguished, depending on whether the pore space of the support contains only ambient air at the beginning (capillary impregnation), or whether it is already filled by the solvent from the impregnation solution (diffusional impregnation) [65]. In the particular case of alloy catalysts preparation, an important parameter is the deposition sequence of Pd and co-metal precursors. It may govern (i) the spatial distribution of both precursors within the pore space and the final vicinity of the two components; and (ii) their chemical state after the reduction process. In the case study of PdCu/Al₂O₃ prepared from Pd(acac)₂ and Cu(NO₃)₂, according to the timing for Cu introduction, different phases were obtained [21]. When Cu(NO₃)₂ was deposited on Pd/Al₂O₃, a cherry model particle with a Pd core and Cu outershell was found. On the other hand when Pd(acac)₂ was deposited onto CuO/Al₂O₃, a large fraction of alloyed PdCu particles with a PdCu interdispersed surface layer was obtained.

3.1.4. Miscellaneous

We will briefly describe some alternative methods which were reported for the preparation of Pd-alloyed supported catalysts: (i) the so-called polyol process; (ii) the photocatalytic deposition; and (iii) the sol–gel method. The aim, when developing these alternative methods, was to promote well-dispersed heavily loaded metallic phases and/or to form true bimetallic aggregates.

The so-called polyol process was applied to prepare PdAg/Al₂O₃ catalysts [75]. It consists of using ethane-diol or propane-diol as solvent of inorganic

precursors, and as mild reducing agent. Well dispersed PdAg bimetallic particles were thus obtained after heating an ethyleneglycol solution at 353 K.

The photocatalytic deposition consists of irradiating a photosensitive semiconductor surface in the presence of a noble metal salt. The metal can be thus deposited as small metal particles at room temperature. It was applied for the preparation of PdPt/TiO₂ catalysts from their chloride precursors [76]. After UV irradiation for 24 h, 1–3 nm PdPt metal particles of heterogeneous compositions were obtained. However, the obtention of true bimetallic particles requires the favorable situation of comparable reduction rates for both precursors.

Several attempts have been made to prepare Pd-based supported catalysts by the sol–gel method starting from the inorganic salt in an alkoxide solution of the support precursor. PdCo/SiO₂ was obtained from the gelation of Co and Pd nitrates in an ethyleneglycol solution of Si(OC₂H₅)₄ [77]. PdCo fully reducible bimetallic particles were formed. Improvement in the process was claimed when organically substituted alkoxides capable of forming chelates with Pd and Ag ions were formed [78]. PdAg particles of 2–3 nm dispersed inside the silica particles have been prepared.

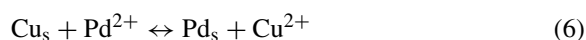
3.2. Selective deposition of the co-metal precursor (SD)

This covers methods of wide applicability ranging from the deposition of clear non-metal, e.g. Si or Se, to early transition metals, e.g. Cr, on supported Pd particles. In contrast to NSD of Pd and M, in the SD the aim is to create an interaction between Pd and the M precursor much stronger than that of M precursor with the support. This is achieved through a highly selective interaction between the M precursor, inorganic salt or organometallic complex, with a prerduced supported Pd catalyst. The SD methods can be categorized within two types of approaches. The first methods involve inorganic salts in aqueous solution, and are based on the principle on “redox” reactions. They are mainly applied for transition metals. Methods of the second type, occurring in gas phase or in apolar organic solvent, involve organometallic complexes, and are based on surface chemical reactions.

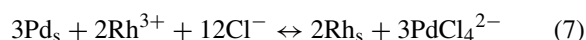
3.2.1. SD by redox methods

These preparations of bimetallic catalysts have been recently reviewed by Barbier ([79] and references therein). Three different approaches exist: (i) the direct redox reactions (DRR) between metallic and ionic species of both components; (ii) the redox reaction with adsorbed species (RRA); and (iii) the underpotential deposition (UPD). Moreover, under well-defined conditions, the second metal can be deposited selectively on specific sites of the parent metal particles. By using pre-adsorbed hydrogen and RRA, Pt was deposited on low coordination sites of prereduced Pd particles, whereas by using the DRR, the adsorption of Pt occurred on the Pd facets preferentially [80].

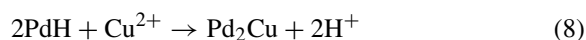
Practically the preparation of bimetallic catalysts using DRR can be extensively used for depositing a noble metal with a high standard electrochemical potential onto a non-noble metal with a lower standard electrochemical potential, e.g. Pd²⁺ on metallic Raney Cu [81]:



The extent of Pd²⁺ deposition on Cu metal (or on a metal of lower potential) depends on the equilibrium constant of Eq. (6). Finally, the redox properties can be modified by using different ligands which alter the standard redox potential and consequently the equilibrium by chelating metallic ions. As an example, Pd²⁺ can be deposited on Rh particles according to Eq. (6). However, the reverse is true in the presence of chloride ions which induce a complexation of Pd²⁺:



Bimetallic catalysts can also be prepared by using a reductant that preadsorbs selectively on the parent metal, in static or dynamic conditions (RRA). The ions of the second metal are reduced by this reagent, and the two metals interact. Hydrogen, preadsorbed on noble metals, is commonly used to prepare bimetallic catalyst by RRA. For instance this technique has been used to prepare PtPd/Al₂O₃ [80], and PdCu/C [82]:



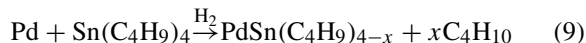
In the techniques described above, the deposition of the modifier occurs at electrochemical potentials which are lower than the equilibrium potential of the

modifier. Under such conditions, the deposition of the modifier takes place as a three-dimensional deposit. By contrast, the UPD characteristically forms submonolayer adatoms structures. In fact, the UPD technique has been used empirically in organic chemistry in order to increase the selectivity in liquid-phase hydrogenation catalysis by the addition of modifier cations. Under the hydrogenating conditions and in a protic solvent, UPD of these modifiers to adatoms explains the changes of selectivity. This aspect has been fairly discussed upon modification of supported Pd catalysts by addition of Ge⁴⁺, Pb²⁺, Cu²⁺, Fe³⁺ and Sn²⁺ [13,82,83], as well as the state of the modifier in the reaction conditions: reduced adatoms or adsorbed ions [13].

3.2.2. SD from organometallic complexes

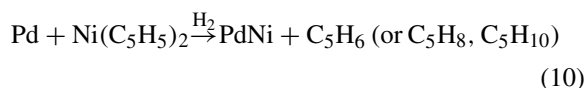
This method of deposition has been reviewed in details by several authors [83–86]. A generic name was proposed to describe this route for preparing bimetallic catalysts: the surface organometallic chemistry (SOMC). SOMC consists of a chemical reaction occurring at a metal surface between an organometallic complex and a zero-valent metal, which results in a covalent bonding between the metal and a fragment of the organometallic moieties. SOMC can be carried out in both gas or liquid phases, generally in an apolar solvent for the latter. SOMC differs from organochemical vapor deposition (OMCVD) in that the reaction of SOMC yields less than a monolayer coverage of the metal surface, whereas OMCVD is used to prepare multilayered materials. The organometallic complexes most frequently used belong to the alkyl-, metallyl- and carbonyl complexes, even though other compounds have been employed. The first attempt in this approach could probably be found in the reaction of dicyclopentadienyl–Ni on a Ni⁰ surface with the help of hydrogen [87], but the method was really successfully applied in the case of bimetallic systems in 1984 [88–91]. The reaction involves the organometallic compound MR_n (M being Ge, Sn, Pb, Se, Zn, Si, ... where R is CH₃, C₂H₅, C₄H₉, C₅H₅, phenyl ...) and the surface of reduced supported metal in the presence of preadsorbed or flowing hydrogen. This is exemplified in the case of α-alumina-supported Pd catalysts which were modified by tetra-*n*-butyl M complexes (M = Ge, Pb, Sb, Sn) [92]. The reaction was carried out by contacting

prereduced Pd/Al₂O₃ with a *n*-heptane solution of the M alkyls complexes at 360 K:



The anchored $-\text{Sn}(\text{C}_4\text{H}_9)_{4-x}$ moieties release the remaining butyl fragment(s) upon heating to give Sn adatoms first, and further on bulk PdSn alloys whenever possible. The modification of Pd with Si, Sn, Sb, Pb and Ge has thus been described [86,92–95]. An interesting aspect, not fully explored, in this surface modification with organometallic complexes is when the SOMC is stopped at the level of Eq. (9). Alkyl fragments then remain bonded to the M modifier, itself anchored to the metal surface. It has been shown that in well-defined conditions this fragment is thermally stable up to fairly high temperatures [85]. Unexpected selectivities were thus found in some reactions, e.g. the hydrogenation of citral to geraniol on RhSn(C₄H₉)₂/SiO₂ [96]. Albeit attractive, no example was yet reported about catalysis on such modified Pd surface.

There are some examples of modification by Ni [97] and Ru [98] of Pd-based catalysts through SOMC between Pd metal and metallocenes. This reaction is very similar to that of alkyl metals:



Finally, the use of metal carbonyls allows the selective deposition by sublimation of early transition metals. PdCr/SiO₂ were prepared by this way, using the sublimation of Cr(CO)₆ on prereduced Pd/SiO₂ [99].

3.3. The deposition of heterobinuclear complexes

Elements of these approaches for preparing bimetallic catalysts can be found in some reviews [100,101]. Two goals have initiated researches towards the use of heterobinuclear complexes as precursors for bimetallic catalysts. The first is the fine tuned control of an homogeneous composition in the nuclearity of bimetallic particles. As compared to catalysts prepared by NSD methods, mixed-metal cluster-derived catalysts should retain more bimetallic ensembles. The second goal is to maintain a high degree of dispersion of the transition metal in the presence of an oxophilic co-metal, giving

strong interaction with the oxide support. However, the use of heterobinuclear complexes is limited by the availability of high nuclearity clusters and by the narrow choice of metallic couples. The different types of interaction of these complexes with the support are the same as previously described for the NSD methods.

Carbonyl complexes are probably the most widely used heterobinuclear organometallic complexes. PdFe/SiO₂ were prepared by impregnation of silica with [Fe₄Pd(CO)₁₆][TMBA]₂ and [HFe₆Pd₆(CO)₂₄][TMBA]₃ in organic solvent [61]. Interdispersed Pd–Fe alloys and superficial Pd–Fe³⁺ pairs are present in the reduced particles. Similarly, PdCo/C catalysts were obtained after impregnation of active carbon with a CH₂Cl₂ solution of [DPPE][PdCo₂(CO)₇] [102]. Very high dispersion of Pd in PdMo/MgO materials was retained even after treatment of the samples under drastic conditions by using [Pd₂Mo₂(Cp)₂(CO)₆(PPh₃)₂] [74]. The oxophilic Mo exists preferentially at the interface between MgO and metal particles and stabilizes the bimetallic clusters against sintering.

Attempts have been undertaken to synthesize mixed acetylacetonate complexes in defined proportions of the two metals. This was successfully achieved for PdCu/SiO₂ from Pd_xCu_{1-x}(acac)₂ [43]. However, the same group did not succeed in the case of PdMn/SiO₂ catalysts [72]. A similar approach was described for the preparation of PdCu/Al₂O₃ from mixed Pd cuprate PdCu(OAc)₂ in ethanol solution [42].

4. Influence of co-metal on some selected reactions

Hereafter, we will exemplify the influence of co-metal M on the performance of Pd in supported catalysts. The classes of reactions chosen are those for which Pd constitutes a reference active metal [103]: (i) the selective hydrogenation of highly unsaturated aliphatic hydrocarbons; (ii) the hydrogenation of aromatics; (iii) the hydrogenation of N-containing compounds; and (iv) the hydrodehalogenation in both aliphatic and aromatic series.

4.1. Selective hydrogenation of highly unsaturated aliphatic hydrocarbons

This class of reactions mainly addresses to the selective hydrogenation of alkynes, alkadienes and

related compounds to the corresponding alkenes. Pd metal exhibits the best catalytic properties for these reactions and can even be improved by the addition of a co-metal [104]. The first clear example of promoting Pd by addition of a second metal deals with the well-known Lindlar catalyst PdPb/CaCO₃ for the selective hydrogenation of alkynes [105]. More recently, better performances in these reactions were reported upon alloying Pd with Pb [95,106–109], Sn [107,110,111], Ag [75,112,113], Cu [114–116], Co [25,117], Cr [99], Sb [107], Fe [118], Au [112], Zn [24] and Tl [109]. The promoting effect of co-metal on selectivity was almost always interpreted as follows:

1. An electronic or ligand effect and/or the disappearance of the β -PdH phase, both being intimately related. The presence of the modifier at the surface and in the bulk produced a change of the relative adsorption strength of the alkynes or alkadienes and the alkene, which resulted in an increased reactivity for alkynes and a decreased reactivity for alkenes (Fig. 2).
2. A geometric effect which results from the dilution of the Pd surface layer decreasing the probability of strongly multi-bonded alkylidene intermediate formation. This species has been proposed as responsible for the direct hydrogenation of alkynes to alkanes.

In the hydrogenation of styrene to ethylbenzene, an increase in activity and sulfur resistance was observed after both Co or W addition to Pd/Al₂O₃ [119]. It was ascribed to the formation of very active Pd–Co and Pd–W mixed sites. On the other hand, the addition of Pt to Pd/pumice exhibited a negative effect in the selective hydrogenation of 1,3-cyclooctadiene to cyclooctene [120,121].

4.2. Hydrogenation of aromatics or hydro-dearomatisation (HDA)

It is generally agreed that PtPd on acidic supports exhibit a higher activity and a better sulfur tolerance in HDA than the monometallic Pd and Pt homologues, as mentioned in a recent review [122]. It is generally accepted that the sulfur resistance is related to the electron-deficient character of Pt atoms in the bimetallics. This electron deficiency comes from (i) the dilution of Pt in the Pd matrix; and (ii) the acidic

properties of the carrier. The dilution of Pt atoms in a Pd surface was put in evidence by IR spectroscopy of adsorbed CO [123–125], and EXAFS [126–128]. However, from EXAFS experiments also, Fujikawa et al. [129] concluded that the higher activity of PtPd/SiO₂–Al₂O₃ comes from Pd species dispersed on Pt particles. As a conclusion, it comes out that an intimate interaction between Pt and Pd is required to achieve good performances, and details of the preparation strongly influences the degree of alloying between them. Perfectly homogeneous composition of PtPd particles supported on SiO₂ were thus obtained by using mixed PtPd acetylacetonates as precursors [121]. A maximum of sulfur resistance was observed for a Pd₂₀Pt₈₀ bulk composition, corresponding to a nearly 50/50 composition of the outmost surface layer. A topological segregation of Pd at corner and edge sites was also proposed in PdRh/Al₂O₃ catalysts to account for a better sulfur resistance than Pd or Rh alone in the hydrogenation of benzene [130].

In PdRu/SiO₂ catalysts, a ligand effect was proposed between Pd and Ru which changed markedly the stereoselectivity in the hydrogenation of *o*-xylene [131].

4.3. Hydrogenation of nitrogen-containing compounds

In the hydrogenation of aliphatic nitriles, Pd catalysts yield preferentially tertiary amines [132]. In the gas phase hydrogenation of butyronitrile, the promotion of Pd by Ni in PdNi/NaY catalysts increased the specific rate and the yield to the primary amine with respect to Pd and Ni alone [133]. This was attributed to a higher reduction degree of Ni and the presence of mixed ensembles at the surface of bimetal clusters. By contrast, the addition of Ag did not affect the selectivity [133]. The addition of Co to Pd/C increased also the rate in the liquid phase hydrogenation of propionitrile [134].

The industrial catalyst for the hydrogenation of nitrobenzene is a trimetallic catalyst PtPdFe supported on C [135]. The positive effect of Fe could be attributed to the activation of the N–O bonds by Feⁿ⁺ in mixed site Pd–Feⁿ⁺ as proposed in the hydrogenation of 2,4-dinitrotoluene on PdFe/SiO₂ [136].

The hydrogenation of nitrates in aqueous solutions on PtPd/C leads to the formation of N₂O, N₂ and

hydroxylamine, which can be obtained in high yields [137]. Ge promotes the activity of Pd/C and of PtPd/C which are the best catalysts for the obtention of hydroxylamine. It has been proposed that the catalyst in the steady-state is an alloy.

The hydrogenation of nitrates and nitrites to N_2 in contaminated drinking water is promoted by addition of Cu to Pd catalysts [138–140]. The formation of ammonium ions is minimized and the beneficial effect was explained in terms of mixed sites Pd–Cu. Tin and indium would promote more efficiently Pd for nitrate reduction than Cu [141].

4.4. Reactions involving CO

Supported Pd catalysts are attractive due to their activity and selectivity to methanol in the CO hydrogenation. Methane can be formed as by-product and the high selectivity of Pd catalysts has been related to the inability of Pd to chemisorb CO dissociatively [142]. However, recent studies from Gotti and Prins [143] demonstrated that Pd on ultra pure silica hardly produced methanol from CO and H_2 . They proposed that some conflicting previous reports about the selectivity to methanol could be explained from impurities present in the support. When Ni [71,144] and Co [78,145] are added to Pd and reduced at temperatures to favor the formation of alloys, the formation of higher hydrocarbons prevails with a product distribution showing a signature reminiscent to Fisher–Tropsch catalysts. This behavior was ascribed to the suppression of “Pd carbide” due to alloy formation, and a better dissociative adsorption of CO [145]. By contrast, when Pd is alloyed with small amount of Fe ($Fe/Pd \leq 1$), a higher selectivity to methanol was found [61,146]. Fe^0 acts as an inert breaker of the Pd ensembles responsible for bridging CO chemisorption and CO dissociation. Concurrently the presence of Pd– Fe^{3+} pairs favors the activation of CO bond for insertion with Pd–H and Pd–alkyl intermediates. Fe-rich catalysts derived from Fe_4Pd binuclear clusters were not selective catalysts [61]. The promotion of Pd/SiO₂ by alkali, and low temperature reduction, for methanol formation from syn-gas was also interpreted in term of Pd ensembles dilution [147]. Sulfidation of PdMoK/Al₂O₃ catalysts yielded materials exhibiting good selectivity for higher alcohol synthesis (C_{2+}) from CO + H_2 [148].

The reductive carbonylation of CH_3OH with CO and H_2 is enhanced upon alloying Pd and Co [102]. This is explained by a higher reduction degree of Co mediated by Pd, and the formation of close neighborhood of hydrogen activation sites and carbonylation centers in more active bimetallic Pd–Co sites.

The reaction between NO and CO to give selectively N_2 and CO_2 is very important for three ways catalysts in order to substitute expensive and scarce Rh, which is the most active metal for that reaction. Pd alone is poorly efficient, but the addition of Mo [149,150], Mn [151], Cu [152] or Cr [153] increases the activity and the selectivity to N_2 , at the expense of N_2O . Various interpretations of the promoter effect have been proposed. Cu maintains Pd in a zero-valent state in the reaction conditions and the dissociation of NO will be favored [152]. Upon Mo addition, mixed sites Pd– Mo^{n+} will be formed on which Pd activates CO, and NO dissociates through the redox cycle Mo^{4+}/Mo^{6+} [150]. It was proposed that on Pd alone the surface is mainly covered by NO and that the Cr addition will increase the CO coverage, and consequently the rate [153].

4.5. Hydrodehalogenation

Pd and Ni are the preferred metals for the hydrodechlorination (HDCl) in both aromatic and aliphatic series [103,154]. In recent works, a special attention was paid to the selective HDCl of chlorofluorocarbons (CFCs) to hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) [154]. It was shown that the addition of Bi and Tl to Pd/SiO₂ increased the selective HDCl of CCl_2FCF_2Cl to CH_2FCCF_2Cl and CH_2FCHF_2 [155]. The promotion was interpreted in terms of geometric effects, dilution by Bi and Tl of Pd surface into small ensembles less prone to hydrodefluorination. A similar interpretation might be suggested for the improved HDCl of CCl_2F_2 to CH_2F_2 upon addition of Au to Pd/MgF₂ [156]. When Al and Zr were added to Pd/graphite, a higher selectivity to CH_2F_2 was also reported in HDCl of CCl_2F_2 [157]. It was proposed that AlF_x and ZrF_x species, formed during the reaction, migrated onto the Pd particles. The resulting close interaction between Pd and AlF_x species induced an electronic modification of Pd which made the reactive desorption of F_2C^* with H^* easier [157]. In the same reaction the

addition of Re to Pd/Al₂O₃ had little influence and a partial fluorination of the carrier (AlF_x species) during the reaction was found to increase the selectivity [158]. Iron addition to Pd/graphite favored the formation of CF₂CF₂ from CCl₂F₂ [159].

Geometric effects, i.e. the dilution of Pd surface into smaller ensembles, were claimed for causing the change of activity and selectivity in HDCl of CH₂Cl₂ on PdRe [160] and of CHCl₂CH₃ on PdAg [77].

Electronic effects were mainly invoked to account for the modifications in selectivity and activity in the gas phase HDCl of chlorobenzene on PdRh/Al₂O₃ [161], and of 1,2,4-trichlorobenzene on Pd/Al₂O₃ modified by Sn, Pb, Sb and Ge [162]. The HDCl in the liquid phase of polychloroanilines and polychlorophenols yielded selectively the *meta*-chloro derivatives upon addition of Ag, Bi, Zn, . . . on Pd/charcoal [163].

5. Concluding remarks

There is no single interpretation to explain the effect of co-metal on the performance of Pd catalysts. Depending on the nature of both the co-metal and the reaction, the beneficial presence of a co-metal can be interpreted in terms of geometric effects, electronic effects and/or mixed sites. Moreover, in many cases, the promotion of catalytic properties will be directly related to the method of catalyst preparation, which affects the chemical states of both Pd and co-metal as well as their spatial distribution. A very important aspect will be the clear identification of the active site architecture, in order to choose the most appropriate synthesis route which will selectively yield this active site in the catalytic material.

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