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Supported metal catalysts preparation

Francesco Pinna*

Department of Chemistry, University of Venice, Calle Larga S. Marta 2137, 30123 Venezia, Italy

Abstract

The paper describes the most widely used methods for the preparation of supported metal catalysts. The influence of the operating variables on the catalyst properties is analyzed and discussed. Finally two characterization methods, often applied to assist the preparation of supported metal catalysts, are briefly outlined. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Supported; Metal catalyst; Preparation

1. Introduction

The aim of the preparation of catalytic materials that can be employed on an industrial scale is to obtain a product with high activity, selectivity and stability. To this purpose, the active phase – in our case the metal – must be in a sufficiently high dispersed form which results in a large specific surface area and consequently in a maximum specific activity. In order to reach this objective the active metal component is usually deposited on the surface of a support, a highly porous and thermostable material (with a high surface area and suitable mechanical strength) which is able not only to disperse the metal, but also to increase its thermal stability and hence the catalyst life.

The common preparation methods of dispersed metal catalysts require a combination of different unit operations, some of them not entirely understood, which can be described as: (i) introduction of the metal precursor on the support by impregnation or ion-exchange, coprecipitation and deposition precipitation, (ii) drying and calcination, and (iii) reduction.

2. Impregnation methods

In its essential features, this procedure requires that the support is contacted with a certain amount of solution of the metal precursor, usually a salt, then it is aged, usually for a short time, dried and calcined. According to the amount of solution used, two types of impregnation can be distinguished: one called "incipient wetness" or "dry" impregnation because the volume of the solution containing the precursor does not exceed the pore volume of the support. In the simplest way, the impregnating solution is sprayed on the support which is maintained under stirring and has been previously evacuated. By removing the air trapped in the inner pores, a deeper penetration of the solution is allowed and a consequent more uniform distribution of the metal precursor should be attained. In principle this method appears to be simple, economic (especially when using solutions of costly active components) and able to give a reproducible

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*Corresponding author. Tel.: +44 1792 295862; fax: +44 1792 295862.

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metal loading which is however limited by the solubility of the metal precursor. However, when higher concentration of the metal are required, this limitation can be overcome by carrying out consecutive impregnation steps.

The second type of impregnation, called ''wet'' or ''soaking'', involves the use of an excess of solution with respect to the pore volume of the support. The system is left to age for a certain time under stirring, filtered and dried. This procedure is applied especially when a precursor–support interaction can be envisaged. Therefore, the concentration of the metal precursors on the support will depend not only on the concentration of the solution and on the pore volume of the support, but also on the type and/or concentration of adsorbing sites existing at the surface.

2.1. *Ion-exchange*

Inorganic oxides such as Al_2O_3, SiO_2, TiO_2, MgO, which are commonly used as support materials, tend to polarize and to be surface charged once suspended in an aqueous solution. This charge will be controlled by the pH of the solution according to these schematic equations:

$$\mathrm{M{-}OH} + \mathrm{H^+A^-} \Leftrightarrow \mathrm{M{-}OH_2^+A^-} \tag{1}$$

$$\mathrm{M{-}OH} + \mathrm{OH^-} \Leftrightarrow \mathrm{M{-}O^-} + \mathrm{H_2O} \tag{2}$$

In acidic media Eq. (1) the adsorption surface site (M–OH) is positively charged and will be covered by anions, while in basic media Eq. (2) the acidic surface site (M–OH) will be negatively charged and covered by cations. For each oxide a peculiar pH at which the surface will not be charged will then exist. This pH is called [1] PZC (zero point of charge) or IEPS (isoelectric point) and in Table 1 a summary of isoelectric points available in the literature is reported [2].

The knowledge of the isoelectric point is very useful in the design of catalysts since it allows to foresee the adsorption features of the different oxides as a function of the pH of the impregnating solution. For instance, if we immerse γ-Al_2O_3 (PZC=8) in a solution with a pH above its PZC, its surface will be negative polarized and will adsorb cations, while the opposite will happen if the pH of the solution is below the PZC, it will be positively charged and anionic species will adsorb on the surface. Depending on their surface charge in the solution, some oxides will mainly adsorb cations (silica, silica–alumina, zeolites), anions (magnesia, lantania) and both (alumina, chromia, titania, zirconia). Fig. 1 shows the variation of zeta potential for silica and alumina gels with the pH [1].

Table 1

Oxide	IEPS	Adsorption
Sb_2O_5	<0.4	Cations
WO_3	<0.5	
SiO_2	1.0–2.0	
U_3O_8	≈4	Cations or anions
MnO_2	3.9–4.5	
SnO_2	≈5.5	
TiO_2	≈6	
UO_2	5.7–6.7	
γ-Fe_2O_3	6.5–6.9	
ZrO_2 hydrous	≈6.7	
CeO_2 hydrous	≈6.75	
Cr_2O_3 hydrous	6.5–7.9	
α-, γ-Al_2O_3	7.0–9.0	
Y_2O_3 hydrous	≈8.9	Anions
Fe_2O_3	8.4–9.0	
ZnO	8.7–9.7	
La_2O_3	≈10.4	
MgO	12.1–12.7	

For simple cation adsorption, the equilibrium

$$\mathrm{M{-}OH^+} + \mathrm{C^+} \Leftrightarrow \mathrm{M{-}OC^+} + \mathrm{H^+}$$

is controlled by the pK_a of the surface acidic group and shifts to the right at high pH of the solution. The affinity of the functional group for the metal ions will control the strength of the adsorption and will depend on the charge and radius of the cations ($C^{4+}>C^{3+}>C^{2+}>C^{+}\approx H^{+}$).

For simple anionic adsorption, the equilibrium

$$\mathrm{M{-}(OH)^-} + \mathrm{A^-} \Leftrightarrow \mathrm{M{-}A^-} + \mathrm{(OH)^-}$$

will depend as before on pH, but this time it will shift to the left for a high pH. The strength of the adsorption will increase with the anionic polarizability and ionic charge (e.g. $SO_4^{2-} > I^- > Br^- > Cl^- > F^-$). In conclusion, according to Brunelle adsorption model [1], based only on electrostatic interactions, the most important variables to be controlled are: (i) type

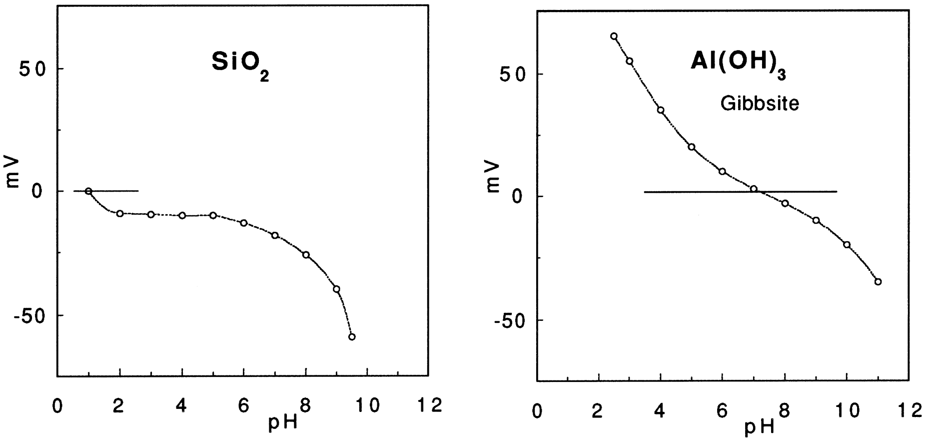
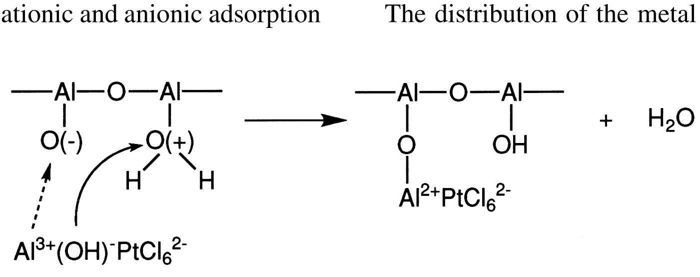


Fig. 1. Zeta potential curves vs. pH for SiO_2 and $Al(OH)_3$ (Gibbsite) gels.

and concentration of the metal precursor, (ii) pH of the aqueous solution, (iii) type of support, its isoelectric point and/or the pH-dependent evolution of the surface polarization of the support. The latter can be obtained by electrophoretic velocity measurements – i.e. the velocity of a charged particle in an electric field, which is related to the PZC – and by measurements of adsorption at constant pH.

Of course, this is a very simple model which does not take into account some additional parameters [3], like the heterogeneity of the surface hydroxyl groups, which can give specific adsorption of the catalyst precursors and might play an important role during the preparation of multimetallic catalysts. In addition metal adsorption is often performed with precursors which are complex ions by themselves or can give complex ions in solution. For instance, chlorometallic ions can be subjected in solution to the formation of aquo-complexes or to reaction of hydrolysis or reduction. These complex ions may give rise to big deviations from the simple ion-exchange equilibria. Useful data on the strength of cationic and anionic adsorption in different environments are available in [4]. Another thing that has to be remembered is that at very high and/or low pH (where usually the maximum exchange is obtained), the solubility of the oxides might occur. For instance, it has been demonstrated [5] that the adsorption of H_2PtCl_6 on γ-Al_2O_3 occurs with an acid attack on the support, formation of Al^{3+} ions, which can easily hydrolyze to $Al(OH)_2$ and in turn can be readsorbed with $PtCl_6^{2-}$ after formation of a complex $Al^{3+}(OH^-)PtCl_6^{2-}$. The adsorption may involve the presence of a surface acid–base couple according to Scheme 1.

From the previous consideration, the amount of metal that can be deposited with this method of wet impregnation is limited because multilayer adsorption is not possible, unless intermediate calcination is performed. In general wet impregnation is used for the preparation of low-loading catalysts and in particular expensive precious metal catalysts, where, generally speaking, the active metal phase should be highly dispersed in order to obtain high activity. The distribution of the metal precursor will be based



Scheme 1.

on the density of the exchanging sites in the support. With low metal loading and high density of adsorbing sites on supports in granules, pellets, extrudates (where diffusion effects are encountered), the distribution of the precursor will be inhomogeneous [6]. Deposition will take place mainly at the external layers of the support particles. By the addition of ions capable of competing with the metal precursor for the same adsorbing sites, a better distribution, more uniform, can be obtained. In some cases, depending on the type of reaction, it will be useful to have the active metal in the inner part of the particle support: in this case the addition of ions different from the metal precursor, adsorbing faster and more strongly on the support, will prevent the deposition of the precursor at the outer shell of the particle, due to a blocking of the external surface sites. In case of strong interaction of the metal precursor and the support, any redistribution will be prevented during the following drying step, therefore the localization of the active phase will be mainly controlled during the impregnation step. For instance, in the preparation of Pt/Al_2O_3, because of the strong interaction between alumina and chloroplatinic acid, which is a commonly used platinum precursor, platinum will be deposited, as shown in Fig. 2(i), on the outer shell of the particle (the so-called egg-shell deposition). This non-uniform distribution is in fact desirable when the catalysts will be used for reactions that are diffusion limited. When a more homogeneous distribution is needed, HCl (or HNO_3, CH_3COOH), that adsorbs on the same sites as the $PtCl_6^{2-}$ species, is added to the impregnating solution. For bifunctional Pt–Cl/Al_2O_3 naphtha reforming catalysts, HCl is coimpregnated with H_2PtCl_6: in this case the penetration of $PtCl_6^{2-}$ species increases and chlorine is added to the support as active component which enhances the acidic properties of the catalysts [7]. In case of applications for reactions which have negative order rate dependence on reactant concentration (Fig. 2(iii) and Fig. 3(iv)) or processes where poisoning present on the reactant stream are adsorbed and strongly retained on the outside surface (Fig. 2(ii)), a more buried distribution of the metal component is preferred. As an example, Pt/Al_2O_3 with a controlled subsurface Pt distribution (the so-called egg-white type distribution) is very active [8] in the oxidation of pollutants in automobile exhaust gas. Such a type of distribution [9] can be achieved by the addition to the precursor solution of organic acids, like oxalic, tartaric, citric, that will adsorb more strongly than chloroplatinic acid. By increasing the acid strength, the metal distribution changes from (ii) to (iv).

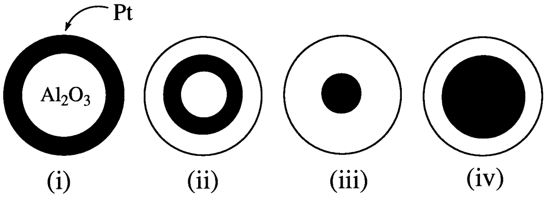


Fig. 2. Profiles of metal concentration in the pellet.

The ion exchange procedure of preparation of zeolites [10] or hydrous oxide ion exchangers [11], can be regarded as special case of ionic adsorption, with the difference that in this case cations (usually NH^{4+}, Na^+) are involved in the exchange instead of protons.

3. Precipitation methods

3.1. Coprecipitation

In this procedure the solutions containing the metal salt and a salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxides and/or carbonate. After washing, these can he transformed to oxides by heating. Typical examples of industrial catalysts prepared by this procedure are Ni/Al_2O_3 and Cu–Zn oxide/alumina, both used in large scale productions: the first in the steam reforming process and the second in the methanol synthesis and in low-temperature shift. The choice of the salts and/or alkali depends mainly on availability at a moderate cost, the solubility in the solvent (water), and, most important, on avoiding the introduction of compounds that can cause negative effects in the final catalyst. For instance, except in particular cases, chlorine ions are known as common poisons and their presence has to be avoided as well as sulfate, which can be reduced to sulfide during the last step of activation. Therefore, nitrate salts or organic compounds, such as formate, oxalate are preferred although some problems can arise with them too. In fact, the latter are expensive and during calcination may not completely decompose. Nitrate are inexpensive and particularly soluble in water, but calcination has to be controlled because of the exothermic evolution of nitrogen oxides. As to the alkali, Na^+, K^+, NH_4^+ hydroxides, carbonates and bicarbonates can be used as precipitating agents, although ammonium hydroxide is often preferred because of the absence of cation residue.

By coprecipitation a uniform distribution on a molecular scale of the different active species in the final catalyst could be attained, at least in principle. Many variables have to be controlled: very important is an efficient mixing, the procedure and order of addition of the different solutions, the temperature, the ageing time of the precipitate (which may help filtration by transferring a gelatinous precipitate in a more crystalline one), the filtering and washing procedure (during washing the precipitate may peptize, i.e. redisperse into a colloidal gel difficult to filter). Since we are dealing with a multicomponent system, the pH (value and variations) has to be carefully controlled in order to avoid precipitation of the component at a different sequence, thus affecting the final structure of the solid.

Scaling up at industrial level the coprecipitation procedure increases the problems previously discussed: for instance an efficient mixing of large volumes of solution, or a uniform control along the catalyst bed of the variables (temperature, water vapor pressure) during the thermal treatment to obtain the oxide, may become difficult. In order to be used in industrial reactors, commercial catalysts have to be formed or shaped as pellets, extrudates, spheres, tablets, etc. Some of these cannot be obtained without the addition of suitable additives. The final materials must have satisfactory strength, porosity and uniform size.

In spite of the problems outlined above, several industrially important catalysts are still prepared by coprecipitation. Precipitation is the preferred procedure for preparing supported catalysts with a metal loading higher than 10–15%.

4. Deposition–precipitation

This procedure is in principle similar to the coprecipitation method previously described: it consists in the precipitation of a metal hydroxide or carbonate on the particles of a powder support through the reaction of a base with the precursor of the metal. The main problem is to allow the precipitation of the metal hydroxide particles inside the pores of the support: therefore the nucleation and growth on the support surface will result in a uniform distribution of small particles on the support. On the contrary, rapid nucleation and growth in the solution bulk will lead to large crystallites and inhomogeneous distribution, since the large particles will be unable to enter into the pores, but will deposit only on the external surface. In order to obtain the best results, an efficient mixing should be used together with a slow addition of the alkali solution in order to avoid the build-up of local concentration. It has been found [12] that the best base is urea, which is usually added at room temperature: by rising the temperature at 90°C, urea slowly hydrolyzes generating ammonium hydroxide homogeneously through the solution. The pH of the solution remains practically constant as the rate of precipitation is higher than that of hydrolysis. Best results in terms of homogeneous distribution are also obtained when an interaction between the support and the active precursor takes place: for instance the formation of Cu or Fe hydrosilicate, instead of hydroxides, has been pointed out [12] on the surface of silica.

After the deposition–precipitation step, the material is filtered, washed, dried and formed as in the coprecipitation procedure. Tentatives of applying the deposition–precipitation method to a pre-formed support have been performed with interesting results, for example in the case of Ni/Al_2O_3 catalysts [13]. The only problem is the impossibility up to now, to obtain catalysts with high concentration of metal.

5. Drying

After impregnation, the material undergoes a drying treatment which is generally performed at temperatures between 80°C and 200°C in order to eliminate the solvent used in the previous impregnation step. Different variables such as the rate of heating, final temperature and time of treatment, type of atmosphere, can influence the process and have to be selected according to the different systems. It has been pointed out that this step can affect, even severely, the results obtained during the impregnation procedure (in case of weak or no interaction between the metal precursor and the carrier surface) in terms of distribution of the active precursor. The significant factors which influence the process and make the redistribution of the metal compounds possible are different and complex: for instance, the rate of nucleation, rate of heating, degree of liquid saturation, viscosity, volume and forms of pores, distribution of pore size, etc. A simplified model which takes into account a uniform type of pores, has been previously described [14] showing how the active phase will concentrate at the inner part of the particle or at the external surface as a function of the rate of drying. If the drying rate is very slow the evaporation of the solvent (usually water), which starts at the external surfaces, allows the diffusion of the salt into the liquid deeper in the pore. This results in an increase of concentration of the solution in the inner pore: after precipitation the metal precursor is mainly located at the bottom of the pore. On the contrary, too high drying rates will generate temperature gradients and will force the solution towards the outer layer of the particles, where the precipitation will occur. In order to obtain a uniform distribution, the rate of drying has to be higher than the rate of homogenization of the solution. In practice the situation is more complicated [15] because we are dealing with a complex porous system.

6. Calcination

This treatment consists of heating the catalysts in oxidizing atmosphere at a temperature usually as high or a little higher than that encountered during reaction. Calcination has the purpose of decomposing the metal precursor with formation of an oxide and removal of gaseous products (usually water, CO_2) and the cations or the anions which have been previously introduced. In the case of industrial production, calcination is useful for the removal of extraneous materials, like binders or lubricants, which have been used during the previous forming operations (extrusion, tabletting, etc.). Besides decomposition, during the calcination (i) a sintering of the precursor or of the formed oxide, and (ii) a reaction of the latter with the support can occur. In fact, in case of alumina as the support, a calcination performed at temperatures around 500–600°C, can give rise to reaction with divalent metal (Ni, Co, Cu) oxide with consequent formation on the surface of metal aluminates which are more stable than the oxides and so might require a higher temperature of reduction than that needed for the oxides. However, this is not a problem if the reduction temperature is not going to cause excessive sintering: in fact after reduction, the final catalysts will be well dispersed due to this textural effect. For instance, in the case of Pt/Al_2O_3 systems a volcano type correlation has been found between the metal dispersion and the catalytic properties vs. the calcination or reduction temperature [16]. The optimal dispersion is obtained at about 400–500°C, when an interaction between the $PtCl_6^{2-}$ ions and the surface, in oxidizing atmosphere, is supposed to occur with the removal of some chlorine ligands and the exchange with oxygen atoms of the support. A calcination at temperatures higher than 600°C leads to a catalyst with lower dispersion because the oxychloride Pt complex decomposes to Pt oxide species that are mobile on the surface and tend to sinter.

When dealing with bimetallic catalysts, a severe control of calcination temperature is required in order to avoid the formation of two separate oxides or segregation of one of the component.

7. Reduction

With this operation the metal oxide, or sometimes the metal precursor, is transformed into a metal by thermal treatment in hydrogen (or diluted hydrogen) flow. In some catalysts the reduction is performed in solution by chemical reagent such as formaldehyde or hydrazine. As in the previous thermal treatments, variables like the rate of heating, final temperature and time of reduction, hydrogen concentration and flow have to be carefully chosen depending on the type of metal, catalytic system and reaction to be performed. The quality of the reduction gas or mixture is very important: water vapor has to be as low as possible because it can be detrimental for a high dispersion of the metal. For the same reason hydrogen flow has to be high enough to remove from the support the water formed during the reduction. Direct reduction of the metal precursor, for instance metal chlorides, is avoided although the latter are more easily reduced than the corresponding oxides: the hydrochloric acid would be very corrosive in the presence of small amounts of water vapor.

Usually the catalysts are reduced to metals by the producer and then stabilized or passivated before shipping, by oxidation of a thin film of metal which can be easily removed in the reactor. This passivation is usually performed with a diluted oxidant mixture (1–2% O_2 in inert gas like N_2).

A commonly used technique [17,18] to study the reduction process is the temperature programmed reduction (TPR).

8. Temperature programmed reduction (TPR)

This useful technique is mainly used for investigation and characterization of metal catalysts. The standard apparatus commonly used is reported in Fig. 3.

In principle, during the TPR experiment, a reducing mixture (5% H_2/Ar) flows through a fixed amount of catalyst [B] (where the active metal is in its oxidic or other reducible form) contained in a reactor which is linearly heated. The amount of hydrogen consumed during the reaction is given by the difference of its concentration in the mixture before and after reduction and is measured by a TCD detector [A]. In order to obtain quantitative data, the gas mixture leaving the reactor passes through a cold trap [C] before going to the TCD detector, to remove H_2O or other reduction products and a proper calibration has to be performed, for instance by injecting known amounts of H_2 through a sampling valve [D]. The change in hydrogen concentration and temperature with time are recorded: a typical TPR profile shows one or more peaks for each different reduction process. In order to avoid artifacts in the TPR profile, care has to be taken to control such experimental parameters as gas flow rate, mass of sample, particle size, heating rate.

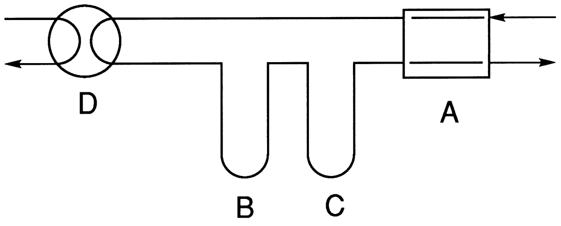


Fig. 3. Scheme of a temperature programmed reduction apparatus.

TPR experiments provide very useful information to decide the proper reduction conditions of the metal oxide precursor and to recognize the presence of different precursor phases, their oxidation state and their interaction with the support. So TPR patterns can be used to study and optimize catalyst pretreatment. In the industrial laboratories TPR is used as a quality control device to determine the efficacy of the preparation procedures.

In case of bimetallic catalysts, TPR is very useful to characterize the state of the metallic components, giving informations on their mutual effect and on the factors which influence the formation of an alloy.

9. Metal surface area characterization by selective chemisorption

Catalyst characterization plays an important role in the process of catalyst design. Many analytical techniques are now available for a complete characterization of the structure and the dimensions of finely dispersed particles on a porous support. Here we will describe only one classic and most frequently used technique, i.e. the study of the metal dispersion and the extent of the free-metal surface area through selective chemisorption. This method plays an important role both in the laboratory research for the development of new catalysts and in the industrial production. In fact, since in most cases, the final goal in the preparation of supported metal catalysts is to reach a high dispersion, the determination of the exposed metal area after preparation and during different steps of reaction, has resulted as a good guide for optimizing the preparation technique. On the other hand, in the industrial practice such measurements are applied as control routine for quality and reproducibility, besides playing a role in trouble shooting.

Chemisorption is based on the formation of a strong chemical bond between the adsorbate molecules with the exposed metal surface. The selected gas molecule is chemisorbed under conditions which allow the formation of a monolayer coverage of gas on the metal surface without significant uptake by the nonmetallic part (support) through physical adsorption.

This requires both a careful selection of a suitable gas molecule and of the experimental conditions and procedures, and the knowledge of the stoichiometry of adsorption. Different useful reviews on the estimation of metal dispersion and covering various aspects of gas chemisorption are available in the literature [19–21].

The most used gas for chemisorption measurements is hydrogen, which has been used by the US ASTM for measuring the dispersion of Pt/alumina samples and by the research Group on Catalysis, European Council for the EUROPT-1 (Pt/silica) catalysts. Carbon monoxide and oxygen are also used especially when hydrogen chemisorption gives rise to problems.

Once the gas has been chosen, the amount of adsorbed gas at the monolayer is measured either by volumetric/static or chromatographic/dynamic techniques. In the first one a classical high vacuum BET apparatus is used and usually two isotherms are measured: the first measures both chemisorbed and the physisorbed gas, the second (run after pumping in proper condition) measures only the physically adsorbed gas. From the difference of the two isotherms the volume of the chemisorbed gas can be derived. The chromatographic or "pulse-flow" technique is a dynamic method derived from gas chromatography. The apparatus is the same as that previously described for TPR (except for the H_2O adsorbing trap, which is missing here): the gas to be adsorbed is sent as a pulse in a stream of carrier gas and measured by a TC detector. By knowledge of the volume injected, the amount of gas adsorbed at the monolayer is obtained by the number of injected volumes. This flow method is generally faster, more convenient and less expensive of the static systems, although it allows only the measure of the gas which chemisorbs fast and irreversibly.

Once the monolayer has been established, the chemisorption stoichiometry (X_m), has to be known. X_m has been defined [19], as the average number of surface metal atoms associated with the adsorption of each adsorbate molecule. In addition the number of metal atoms per unit area of surface (n_s) has to be known. At the monolayer coverage, if n^s_m is the total adsorbed uptake expressed in molecules, the total surface area A is given by

$$A = n^s_m X_m n_s^{-1}.$$

The number of surface atoms per unit area (n_s) for a polycrystalline surface [19] depends on the surface structure and the usual approximation is the assumption that the metal surface is formed from equal proportion of the main low-index planes [(1 1 1), (1 1 0) and (1 0 0)]. The chemisorption stoichiometry (X_m) for hydrogen is almost always 2 since the hydrogen molecule adsorbs dissociatively on metals and each hydrogen atom is adsorbed on one metal atom. Carbon monoxide stoichiometry can change from 2 to 1 since an associative chemisorption in a bridge or a linear form can occur, i.e. covering two or one metal atom, respectively. With oxygen values from 2 to 1 or even lower (0.75) can be found according to the type of metal.

The evaluation of the total adsorbate uptake (n^s_m) at the monolayer coverage is subjected to some uncertainties, if using a volumetric system. In fact a slow chemisorption with increasing pressure is sometimes observed that has been ascribed to (i) impurities in the support or on the surfaces of the metal particles, (ii) contribution from physical adsorption on the support, (iii) spillover of the gas adsorbed to the support. Therefore, a correction has to be made for the intrinsic adsorption on the support and an extrapolation to zero pressure gives a good estimate of n^s_m.

The optimum temperature and pressure for carrying out the adsorption isotherms will depend on the catalytic system and are usually established experimentally. Usual condition for hydrogen chemisorption on Pt supported system are 0–25°C and 10–300 Pa.

The hydrogen–oxygen titration method [22] is commonly used for measuring the metal surface area. It has been proposed that the hydrogen titration of an oxygen-covered Pt surface occurs with the following stoichiometry:

$$\mathrm{Pt{-}O} + 3/2\mathrm{H_2} \rightarrow \mathrm{Pt{-}H} + \mathrm{H_2O}$$

Therefore, the sensitivity of this method is three times higher than normal chemisorption

$$\mathrm{Pt} + 1/2\mathrm{H_2} \rightarrow \mathrm{Pt{-}H}$$

A certain number of transition metals, when contacted with hydrogen, form bulk hydrides: one of these is palladium which is able to absorb hydrogen atoms in the bulk giving rise to β-hydride palladium systems. In this case hydrogen cannot be used unless chemisorption is carried out at 100°C and at sufficiently lowpartial pressure of H_2 to avoid bulk hydride formation [23]. The H_2–O_2 titration (carried out at 100°C) has also been reported to be a useful and convenient method, but carbon monoxide chemisorption is usually considered more adequate, although the uncertainties due to the stoichiometry cannot be disregarded.

From the knowledge of the free-metal area (A), the mean particle diameter (d_v) can be obtained. For spherical particles:

$$d_v = 6V/A,$$

where V is usually calculated by the knowledge of the mass of metal in sample and its density.

In case of bimetallic catalysts the measure of the free surface area by chemisorption may become complicated. In fact in certain systems (Pt–Pd, Pt–Rh) it is only possible to obtain the total free surface area because the two components have similar behavior in chemisorption capacity.

In other bimetallic combinations, for instance involving IB metals, the volume of gas chemisorbed (H_2, CO) cannot be quantitatively related with the free surface area because only one component of the bimetallic system is "active" in the chemisorption. Otherwise, when the two metals (Pt–Fe, Pd–Fe) have different chemisorption behavior towards the gas molecules, some informations on the surface composition, although semi-quantitative, can be obtained by using proper adsorbate and experimental conditions. When dealing with bimetallic systems the use of other methods (XRD, TEM) for obtaining the free-metal area is strongly advisable.

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