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The molecular approach to supported catalysts synthesis: state of the art and future challenges

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Abstract

This contribution addresses some of the molecular-level aspects of classical supported metal catalysts preparation procedures. While the problems selected here have been chosen for their fundamental and practical relevance, important studies due to Knözinger and coworkers will be quoted in each case, and this short review may thus be regarded as a homage to their early activity in the field.

We first briefly discuss the state of current knowledge on the surface species exposed at oxide surfaces, based on the particular case of γ -alumina. While considerable uncertainty remains as to the precise interpretations of spectroscopic data (especially in the presence of an aqueous phase), a concerted research effort might allow a molecular-level mapping of adsorption sites as a function of operating conditions.

We then present the main mechanisms that may be operative in the establishment of metal-support interaction at the oxide–water interface, again with emphasis on the molecular interpretations. The distinction between strong and weak interactions is found not to be very helpful, while distinctions between selective and non-selective, or reversible/irreversible interactions, are more justified at the molecular level. Although our knowledge of these interactions is still lacunary, recent developments raise the hope of important progress in the near future.

Molecular characterization during the later steps of catalyst preparation (thermal activation, calcination, reduction) is much less advanced. However, examples are presented in which the mechanism of initial metal-support interaction (established during the deposition step) has a demonstrated, lasting influence on all further steps of catalyst synthesis, suggesting the practical interest of these studies for fine-tuning of catalysts properties.

Altogether, it appears that the molecular-level characterization of supported metal catalysts preparation is a realistic research program in the middle term. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the field of heterogeneous catalysis, much effort is directed at obtaining molecular-level identification

of adsorbed species on the finished catalyst and reactive intermediates during the catalytic act, and with good reason. In contrast, the preparation of the catalytic materials themselves has long been regarded as purely technical know-how: in fact, it hardly deserved to be called a ‘synthesis’, a term which implies at least the identification of the chemical reactions that are taking place- and there can be

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many of them in the successive steps of preparation, typically involving such unit operations as initial deposition from a transition metal complex (TMC) solution onto the support, followed by drying, calcination, and final reduction or sulfidation.

It is somewhat paradoxical that the newest strategies for catalysts synthesis, such as sol–gel methods or chemical vapor deposition, are often better understood than ‘classical’ preparation procedures starting from metal deposition from an aqueous solution. However, we feel that the time is now ripe for a molecular understanding of unit operations in catalyst synthesis, with the prospect of a chemical control of final catalyst properties. As we will see, the chemistry that takes place when an oxide powder is dipped into a water solution of TMCs is far from simple, and we will encounter many open questions, but sufficient progress has already been made to hope they will eventually be solved.

We will successively treat both partners involved in the first unit operation of metal deposition, the oxide surface (Section 2) and the TMC solution (Section 3), very briefly discussing the extent of our current knowledge on their molecular characterization. We will then consider in some more detail what happens when both are contacted; in other words, we will address the molecular basis for the establishment of the metal–support interaction (Sections 4 and 5). In the final section (Section 7), we will examine the relevance of an identification of the deposition mechanisms for controlling technologically important properties of the finished catalysts.

2. The structure of support oxide surfaces: the example of γ -alumina

In general, in studies on supported catalysts, little attention is paid to the starting structure of the oxides used as catalysts supports, either because the question is thought to be already solved, or because it is felt to be too complicated. Our opinion is that, although specific identifications have been proposed for some surface groups, there is still much uncertainty on the nature of the ‘molecular landscape’ on support surfaces at the nanometric level. To support this contention, we will present a brief overview of

the state of the art concerning the surface of γ -alumina, one of the most common supports.

There is general consensus that the adsorptive and reactive properties of alumina surfaces are governed by surface hydroxyls, i.e. OH species. Vibrational spectroscopy in the mid-IR region has been used for over 40 years in the hope of identifying them and the subject has already been reviewed [1] (another technique of interest would be ^1H NMR, but it has not been widely applied so far) [2]. The OH stretching region indeed shows much structure, evidencing at least five [3] and maybe up to nine [4] separate components.

Several attempts have been made to propose specific assignments of the main OH stretching bands of γ -alumina. Historically, the most influential model is due to Knözinger and Ratnasamy [3], and will later be referred to as the K–R model. We will also discuss the models of Tsyganenko–Mardilovich (T–M) [4], and Busca–Lorenzelli (B–L) [5]. All of these are based on the supposition that the basic surface structure consists in cleavage planes of an underlying spinel lattice, the dangling bonds of which are saturated by OH groups. They differ in the number of configurations that they retain as distinct for OH groups, and the features of these configurations they assume to be relevant for determining the value of the OH stretching frequency (ν_{OH}).

Fig. 1 illustrates the surface configurations that were considered in the K–R and T–M models, together with the corresponding Al_2O_3 ν_{OH} assignments. In both models, surface OHs are distinguished according to their own coordination number, i.e. the number of Al^{3+} ions they are bound to (which seems fairly reasonable), and also according to the coordination number of the latter Al^{3+} ions. Thus, it could be said that the range of vision of the spectroscopic probe (IR of OHs) spans the first neighbors of the hydroxyls (OH–Al), and to a certain degree, their second neighbors (number of anions surrounding the Al^{3+} ions, OH–Al–X, irrespective of whether X is an oxide ion or another OH). Even though the K–R and T–M models are based on the same assumptions, they propose somewhat different assignments for the different ν_{OH} .

Fig. 2 shows the relevant surface configurations in the B–L model. Here, third neighbors are included in the picture to some extent, because, for some

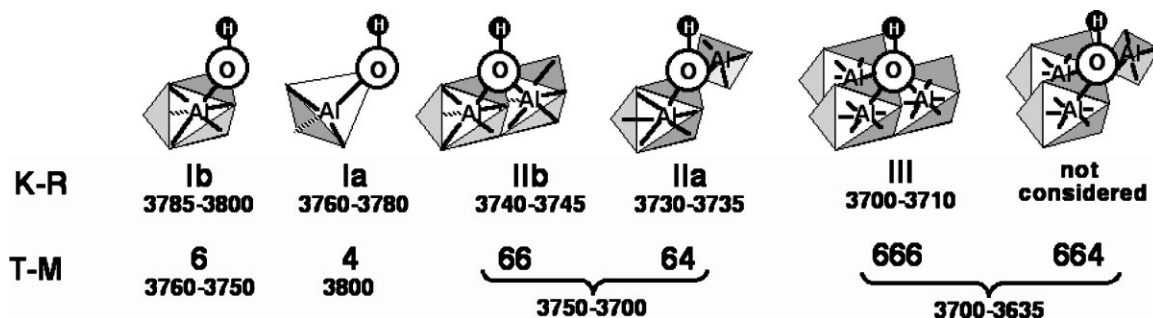


Fig. 1. Relevant configurations for surface hydroxyls on the surface of γ -alumina in the model of: (a) Knözinger and Ratnasamy (K-R, [3]); (b) Tsyganenko and Mardilovich (T-M, [4]). Proposed assignments for ν_{OH} stretching frequencies are also given.

configurations, it is considered important to determine if the Al^{3+} ions are adjacent or not to a lacunary cationic site — such sites must be present at least in the bulk, according to the stoichiometry of Al_2O_3 ; in other words, OH-Al-X-Al is distinguished from $\text{OH-Al-X-}\square$. This distinction is not made for OHs in coordination number 1, 2 and 3 (types II and III in the K-R model), maybe because there would be too many possibilities; incidentally, the high structural diversity of these species could explain why the corresponding bands are much broader.

The implicit hypotheses made in all three models are not limited to the number of neighbors that must

be included in the description of a given surface configuration around OH. Another basic assumption is the neglect of dipole–dipole coupling, which, in opposition, was considered to be the dominant factor in the now superseded model of Peri ([6], and Fig. 3a in the present paper). In fact, the paper of Tsyganenko–Mardilovich [4] underlines that geminal OH pairs (HO-Al-OH) must be found on some faces (see Fig. 3b), but states that dipole–dipole coupling may be safely ignored even then, although without strong justification.

More important, and already mentioned, is the fact that the unperturbed spinel lattice is supposed to extend up to the very surface. This hypothesis is

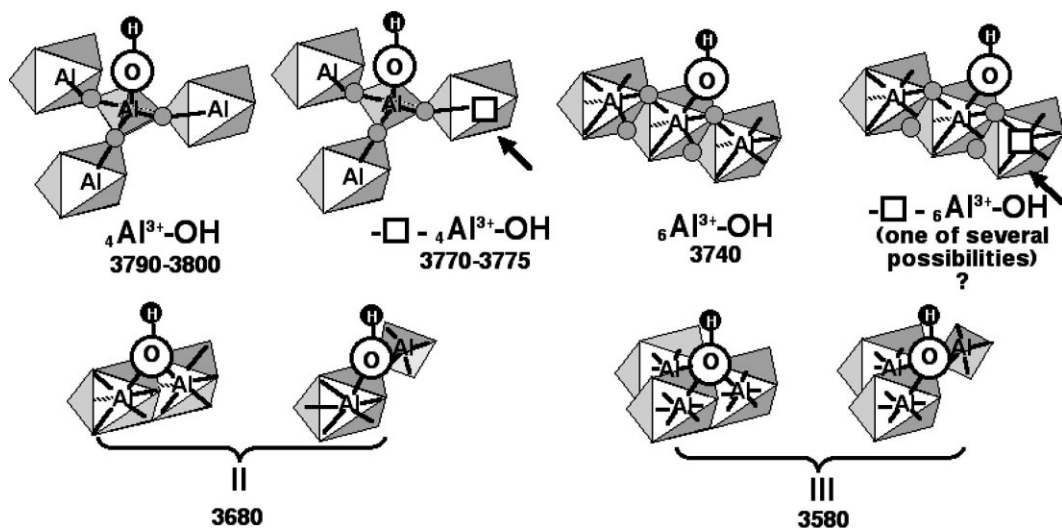


Fig. 2. Relevant configurations for surface hydroxyls on the surface of γ -alumina in the model of Busca–Lorenzelli (B-L, [5]), with proposed ν_{OH} assignments.

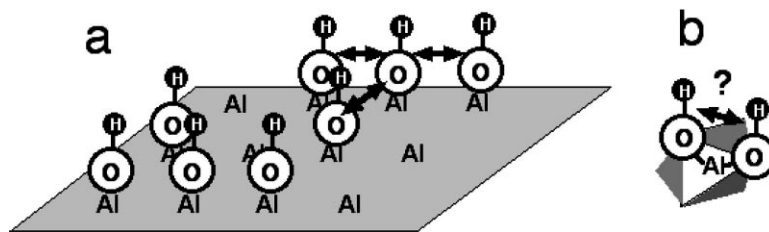


Fig. 3. (a) Dipole–dipole coupling between surface hydroxyls of γ -alumina in Peri's model [6]; (b) a configuration presenting geminal OHs in the T–M model ((110) face, D-layer), where dipole–dipole coupling was considered to be negligible.

explicitly stated in ref. [4]. Indeed, Reller and Cocke [7] have observed on one specific γ -alumina fringe patterns compatible with spinel microcrystals preferentially exposing (110) planes, but the crystallites are too small for selected area electron diffraction. Thus, so far, there is no incontrovertible direct evidence for alumina surfaces having perfect structures of spinel faces. At the contrary, there are some indications that the core structure may be significantly altered at the surface; this is the conclusion reached from molecular dynamics simulations of the equilibrium structure of small alumina particles [8]. Even on the sole basis of IR spectroscopy, Morterra et al. [9] concluded that one of the prominent OH species, actually the most reactive one, was ascribable to a 'crystallographically defective configuration', whose structure was, however, left unspecified.

It might be argued that the degree of crystallinity of the surface layer(s) is not of fundamental importance since the assignments proposed for OH stretching vibrations only depend on local structures in the vicinity of the hydroxyls, which might very well be the same on crystalline and amorphized surfaces. Unfortunately, this is not a foregone conclusion: perturbed surface layers could also contain some new OH configurations, not considered in spinel-based surface models, such as OHs borne by five-coordinated Al^{3+} ions (Fig. 4). Indeed, five-coordinated Al must be present in some cases since it has been detected in γ -alumina by ^{27}Al NMR [8,10]. More systematic studies, combining IR with CP-MAS and REDOR ^{27}Al NMR, possibly also with ^1H NMR, are needed to solve this problem.

The question of surface amorphization, or at least of a strong modification with respect to regular crystal faces, has sometimes been treated, but rather as a possible consequence of Al–OH condensation

after thermal treatments at elevated temperatures [4]. The field of application relevant for the present paper involves, instead, alumina in contact with bulk aqueous solutions. Here too, very strong reorganization may occur: alumina is in equilibrium with its dissolution products, and dissolution of surface species most likely involves as a first step the hydrolysis of some $\text{Al}_{\text{surface}}\text{–O–Al}_{\text{bulk}}$ bonds, with the formation of new OH species. Here, in situ observation of surface OH species is extremely difficult because classical vibrational spectroscopy fails at these so-called 'buried' interfaces, although the new SFG technique raises some hope for the future [11].

If the identification of individual surface hydroxyls is so imprecise, it should be no surprise that our knowledge of their mutual disposition is even fuzzier. Yet, it seems that the adsorption of many molecules or ions on alumina requires groups of two or more OHs ([12,13] — see also Section 4); therefore, in order to identify adsorption sites and predict adsorption capacities, it would be useful to understand exactly what kind of OHs may form such groupings and how many of them are expected on a given surface. The obtention of such an understanding may be considered as a long-term research program, although some speculations on the matter can already be found sometimes in the literature.

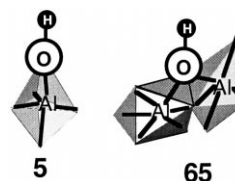


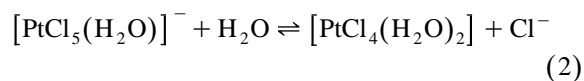
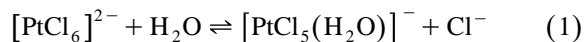
Fig. 4. New hydroxyl configurations that could occur if five-coordinated Al's are present on the alumina surface (see text).

We are, thus, left with the inescapable conclusion that the question of surface groups identification in alumina is far from being solved, and will probably keep on giving rise to much controversy in the forthcoming years. In fact, recent results have even complicated the problem, for instance by raising the question of interstitial OHs created by dissociative water adsorption [14]. We are, thus, in great need of a concerted research effort combining molecular modeling, spectroscopic investigations (^1H and ^{27}Al NMR) under well-controlled conditions and the use of reference compounds containing well-defined hydroxyl groups: an interesting possibility in this respect would be the $[\text{Al}_{13}\text{O}_4(\text{OH})_{24+x}(\text{H}_2\text{O})_{12-x}]^{7+}$ polycations immobilized in the interlayer space of pillared clays, which apparently present homogeneous ‘type IIB’ hydroxyls [15].

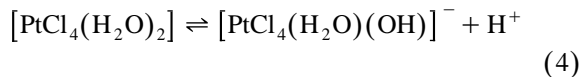
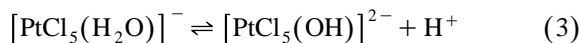
While we have used the case of alumina as an illustrative example, similar remarks could be made for other oxide supports, most noticeably for amorphous silicas [16].

3. Transition metal speciation in precursor solution

Metal deposition involves the interaction of two partners: the oxide surface and the TMC solution. Very often, the TMC chosen as precursor is a simple one; for instance, if a nickel nitrate solution is used, nickel will overwhelmingly be present as the hexa-aqua complex, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. Even in less trivial cases, metal speciation, i.e. its distribution between the different possible chemical species, is generally well understood in homogeneous solutions, and quite accurate equilibrium constants for most speciation reactions are available. There are some exceptions: for instance, in a recent study of Pt deposition on alumina from hexachloroplatinic acid solutions [17], it was found necessary to determine first the equilibrium constants for the following reactions:



... (these insertions of water ligands are called ‘aquation’ reactions), and



... (acid–base reactions), before understanding the deposition process itself. This is because aquation of hexachloroplatinic acid had been little studied, and only before the advent of ^{195}Pt NMR, the only technique that allows easy measurements of equilibria — in contrast with interhalogen substitution reactions, which are known in much more detail [18].

In fact, there is no insurmountable problem preventing the detailed understanding of such simple systems. When this has not yet been achieved, it may be because they are (or look), in fact, too simple to attract the attention of specialists in coordination chemistry.

4. A quick review of TMC/oxide support adsorption mechanisms

We may come now to the chemistry that is taking place during the deposition of TMCs. First, we have to establish a clear terminological distinction between preparation procedures (such as incipient wetness impregnation, equilibrium deposition followed by filtration...) which refer to the sequence of steps (unit operations) applied and controlled at the macroscopic level, and adsorption mechanisms, which are identified at the molecular level and will be discussed below.

The different mechanisms for adsorption of charged species (including TMCs) from an aqueous solution onto an oxide support have long been known [19], and their systematization in the field of supported catalysts preparation was attempted by Che et al. using the concept of *interfacial coordination chemistry* [20–23]. We refer to some recent review papers [24,25] for a detailed presentation of this idea; only the most relevant features of the three main adsorption mechanisms will be recalled here.

In an often quoted paper, written some 20 years ago [26], Brunelle popularized the notion of a pH

dependent surface charge for oxides in contact with a water solution. He underlined that as a consequence of the existence of amphoteric surface groups, the same oxide can electrostatically retain anions at low pH values, and cations at high pHs. The resulting electrostatic adsorption is formalized in the frame of the *double layer* theory (see Fig. 5) — the first layer is just the surface of the oxide, which bears positive or negative charge according to whether it is protonated or deprotonated, and the second, or *diffuse layer*, is the region of the solution where ion concentrations are significantly affected by the electric potential ($\phi(x)$) generated by the surface charge (σ).

It is misleading to write a ‘chemical equilibrium’ corresponding to electrostatic adsorption, because no bonds are made or broken (see Section 4.1 for a further discussion, however).

The idea of a pH-dependent electrostatic adsorption was an important progress to understand metal precursors adsorption and has been widely accepted ever since, but other well-established results of colloid chemistry have not made their way into the mainstream of heterogeneous catalysis so easily.

In particular, colloid chemists have recognized for decades that pure electrostatic adsorption cannot ac-

count for most systems of practical interest. In consequence, they developed the so-called ‘triple-layer’ models, wherein a part of the adsorbed ions are held at a fixed distance to the surface by some kind of *specific* adsorption; the latter is also called *site adsorption* because it is localized in a plane situated some distance away from the surface, the ‘Stern layer’, in opposition to the non-localized electrostatic interaction to which it is superimposed. Surprisingly, little attention has been given to the precise nature of this specific adsorption (although hydrogen bonding immediately comes to mind) but its occurrence is proved by an ample body of data. Beyond the plane of specific adsorption extends a diffuse layer; two quite different cases may be considered, as illustrated in Fig. 6, taking a negatively charged surface plane to fix ideas. In Fig. 6a, the amount of specifically adsorbed cations is insufficient for compensation of the negative surface charge, and the diffuse layer again contains an excess of cations. In Fig. 6b, in opposition, the cation density in the Stern layer is high enough to produce charge overcompensation, with the seemingly counterintuitive result that anions, i.e., ions of the same charge as the surface plane, are held in the diffuse layer. One way of

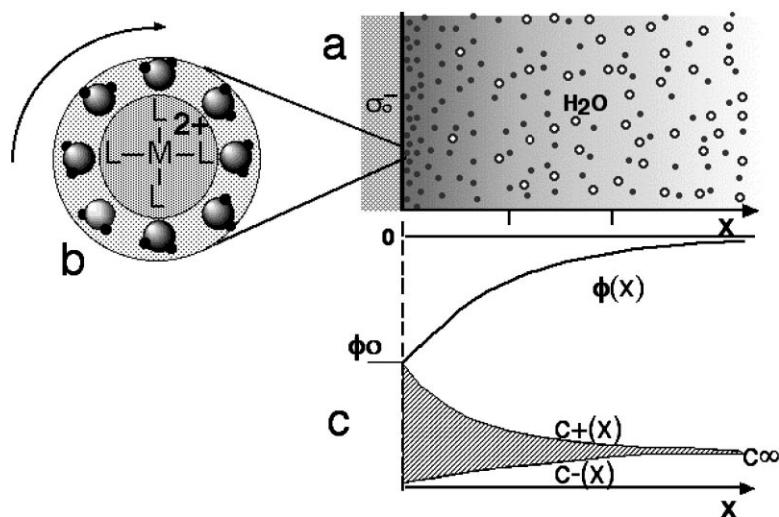


Fig. 5. Electrostatic adsorption, as represented by the double-layer model: (a) graphical illustration of the surface layer and the diffuse layer (full circles, cations in solution; empty circles, anions in solution); (b) a close-up view of a cation in the diffuse layer, as seen at the molecular level [25]; (c) evolution of electrostatic potential and ionic concentrations in the diffuse layer, as a function of the distance x to the surface. The cationic charge excess of the diffuse layer is shaded.

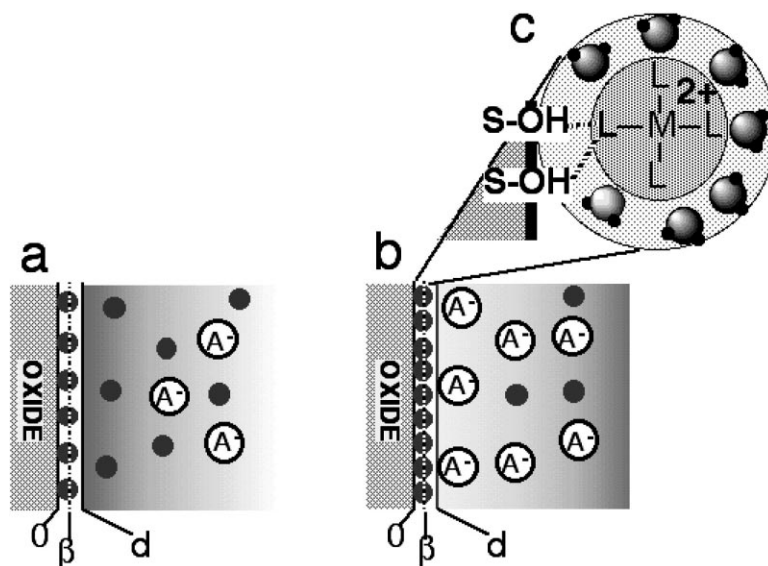
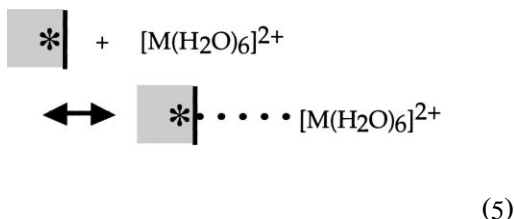


Fig. 6. The triple-layer model of adsorption, integrating electrostatic and specific adsorption. Full circles, cations; empty circles, anions in solution. The surface plane (0), the Stern layer (β) and the front of the diffuse layer (d) are indicated: (a) specific adsorption without overcompensation (excess of cations in diffuse layer); (b) specific adsorption with overcompensation (excess of anions in diffuse layer); (c) molecular interpretation of specifically adsorbed metal ions in the Stern layer [25].

writing an equilibrium of specific adsorption would be

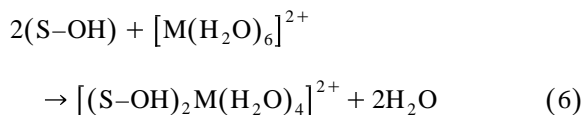


Here, the star represents a localized surface site whose nature is generally unknown, and the dotted line represents some also unknown, but supposedly noncovalent, interaction.

In the field of supported catalysts, the first clear instance of specific adsorption with charge overcompensation was provided by Spanos et al. [27] for the heptamolybdate/alumina system; it was later shown that similar phenomena occur in polytungstate/alumina systems as well [28–30]. At the same time, Knözinger et al. [31,32] have also applied triple layer adsorption models to the adsorption of hexachloroplatinate and palladium(II) tetraammine on alumina, even attempting to evaluate equilibrium constants for the specific adsorption reactions, and thus, predict

interfacial speciation. In spite of these successes, it seems that the triple layer has not gained widespread recognition as yet.

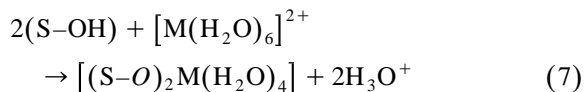
More intimate than specific adsorption is another mechanism called inner-sphere adsorption by colloidal chemists, in which some of the original ligands of the transition metal in solution are replaced by surface groups. This is easily written as a chemical equilibrium (in fact, it is a simple ligand exchange reaction as considered in classical coordination chemistry), e.g.



where (S–OH) is a surface hydroxyl group.

Because this reaction is the simplest one can write in the frame of valence bond theory, it is often proposed speculatively when no better evidence is available. It is generally called ‘grafting’ in heterogeneous catalysis, rather than ligand exchange, by analogy with the modification of oxide surfaces with organic moieties which was known earlier and also implies the formation of covalent bonds.

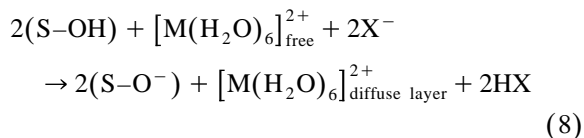
In many cases (at least when the matter has been studied in detail), there is reason to believe that inner-sphere adsorption is coupled with deprotonation of the implied surface groups:



where (S–O) stands for a surface S–O[−] group formed by deprotonation of (S–OH)

4.1. Metal adsorption: strong versus weak, or specific versus non-specific?

Research papers whose main focus is not on the preparation of the catalytic systems are often satisfied with classifying initial metal adsorption as ‘strong’ or ‘weak’. It may seem straightforward to quantify this distinction on the basis of the adsorption energy, i.e. the ΔG° of the adsorption reaction. When considered more closely, this program raises many problems, however. For instance, is electrostatic interaction weak or strong? A counterion in the double layer at a distance x from the surface plane has an electrostatic energy of $ZF\phi(x)$, where Z is the ion charge and F is the Faraday (96,500 coulomb/mole). Taking a (rather high) value of $\phi^\circ = 200$ mV, the adsorption energy of counterions in the double layer, as defined above, would be anywhere between 0 and -40 kJ/mole, which seems imprecise but could be averaged to a rather weak value. However, it is obvious that removing all of the counterions from the diffuse layer is physically impossible, as this would lead to a huge uncompensated electric charge on the surface. The solution to that paradox is that, as already mentioned, a chemical equilibrium cannot be written if electrostatic adsorption is considered alone, but only in conjunction with the surface charge buildup reaction, e.g.



where X[−] is OH[−] or maybe the anion introduced together with the metal complex, if it is basic.

Values of ΔG° for the above reaction may be quite negative because they include the contribution

from an acid–base reaction (deprotonation here, or protonation when one considers positive charge buildup). Electrostatic adsorption would then have to be considered as strong, and it is certainly true that electrostatically adsorbed ions will not desorb to any appreciable extent if washed with pure water (i.e., the reverse of reaction (8) will not or hardly occur). On the other hand, if the system is contacted with a solution containing other ions of the same charge, say B²⁺, extensive displacement of $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ will take place, because in this simple model $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ and B²⁺ have exactly the same electrostatic energy, namely $2F\phi(x)$. ‘Specific adsorption’, as defined above, involves rather weak forces — in principle. For instance, a typical H-bond (in water) has an energy of 15 kJ/mole [33], but in many instances several H-bonds act cooperatively, providing both the specificity of the adsorption and a more negative ΔG_{ads} . Thus, TMC-surface bonding in Eq. (5) above could consist in the formation of several H-bonds between metal ligands and surface species, resulting in ΔH_{ads} in the order of -30 to -45 kJ/mole. As regards the entropy variation (ΔS_{ads}) on adsorption by H-bond formation, this is an extremely complicated question, as is amply proved by biochemical studies [34], and we will, therefore, not venture to propose a precise estimate for ΔG_{ads} .

Consider now the third adsorption mechanism, i.e. inner-sphere adsorption. Some experimental measurements of ΔG_{ads} have been reported, although there are rather few of them. Their obtention needs tedious work to determine the precise stoichiometry of the reaction (cf. Eqs. (6) and (7) above), and to unravel intrinsic thermodynamic values (concerning the substitution reaction proper) from superimposed electrostatic effects. Published values are not very negative, in the -20 to -30 kJ/mole range [12,35]. In fact, as underlined by Che [23], the surface groups of oxide ligands may be classified in the spectrochemical series as weak-field ligands, even weaker than water; thus, the crystal field stabilization energies (see [36], Chapter IX, for example) decrease on adsorption, with the result that the enthalpy difference in reaction (6) may well be unfavorable. In one case, where the matter was studied precisely (not concerning a transition metal complex, but $[\text{Pb}(\text{H}_2\text{O})_x]^{2+}$ on TiO₂ and Fe₂O₃), it turned out that

inner-sphere metal adsorption was indeed entropy-driven, having both ΔH_{ads} and ΔS_{ads} positive [35]. Once again, the reasons for this entropy increase are far from understood, and their discussion will not be attempted here. The point we want to stress is that all three adsorption mechanisms (electrostatic, specific adsorption, and inner-sphere/grafting) may imply adsorption energies of the same order of magnitude, so that there is no mechanistic basis for a distinction between strong and weak adsorption. There are, however, definite and important distinctions concerning: (1) specificity, which is nonexistent for electrostatic adsorption, but high for inner-sphere adsorption, and also for outer-sphere complex formation — this is of course why the latter is called ‘specific adsorption’ by colloid chemists; (2) reversibility: desorbing electrostatically adsorbed metal complexes requires providing ions of the same charge to compensate the charge of the surface, and desorbing grafted metal complexes may require providing protons; thus, metals adsorbed along these two mechanisms will not be removed by the usual procedure of washing with distilled water. On the other hand, outer-sphere adsorbed metal complexes have no such requirements for desorption nor do they seem to have a high activation energy (ΔG^\ddagger) and they will probably not be retained by the surface when the system is submitted to a washing treatment. In other words, a molecular understanding of adsorption mechanisms is required in order to predict the likely effect of a simple elementary step in the catalyst preparation procedure.

4.2. Identification of surface sites in site adsorption mechanisms

Both outer sphere and inner sphere adsorption have been termed site adsorption mechanisms, because their specificity can only be explained by a localized interaction of the adsorbed ion or molecule with a precise type of surface species, or a group of surface species, that constitute the adsorption site. The identification of adsorption sites is not a trifling question, as it will determine the maximum density of adsorbed metal ions, and most probably, their further reactivity. Thus, as already mentioned, outer sphere TMC-surface bonding in Eq. (5) above could

consist in the formation of several H-bonds implying the coordinated water molecules in the TMC as H-bond donors, and some surface groups of the oxide as H-bond acceptors. Analogs have been known from the field of supramolecular chemistry [37]. Fig. 7 shows how $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is specifically bound to a crown-ether through four hydrogen bonds from the protons of the aqua ligands to the ether oxygens in the cycle.

It is easy to imagine the corresponding species on an oxide surface, since similar arrays of H-bond acceptor groups may probably be found among the many hydroxyls and oxide ions that are exposed at the surface. It is much harder to obtain conclusive spectroscopic evidence for the existence of such outer-sphere complexes. One of the few instances where a precise structure was proposed for a metal complex specifically adsorbed on an oxide surface is to be found in the work of Bargar et al. [38] for $[\text{Pb}(\text{H}_2\text{O})_x]^{2+}$ on $\alpha\text{-Al}_2\text{O}_3$ (0001). To obtain a candidate structure for adsorbed lead (Fig. 8), a single crystal of alumina exposing a well-defined face had to be used, and the surface sensitive GI-XAFS spectroscopy had to be applied, which is definitely not routine work.

It is easier to characterize spectroscopically inner-sphere adsorption than outer-sphere adsorption, since the immediate environment of the adsorbed metal is more deeply perturbed in the former case. Several spectroscopic probes have been used to that purpose according to the system under consideration, for instance UV–VIS spectroscopy of d–d transitions in Ni(II)/oxides [39], ^{195}Pt NMR for $[\text{PtCl}_6]/\text{Al}_2\text{O}_3$ [40], or EPR for Cu(II)/oxides [41], to quote

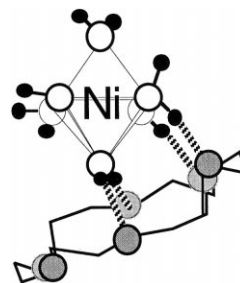


Fig. 7. The pattern of hydrogen bonding between $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and crown ether 18-C-6 (from [37]): an analogue of specifically adsorbed ions on oxide surfaces?

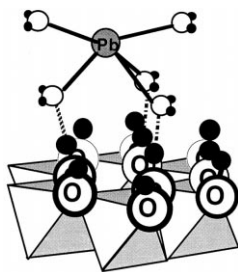


Fig. 8. The structure of $[\text{Pb}(\text{H}_2\text{O})_x]^{2+}$ adsorbed on α -alumina by formation of an outer-sphere complex, after Bargar et al. [38].

only a few recent studies from our research group. Most of the time, the composition of the coordination sphere of the adsorbed complex can be determined with reasonable certainty, establishing the reality of inner-sphere adsorption and maybe its stoichiometry. Local spectroscopic probes of the metal center hardly extend beyond the coordination sphere, and therefore, it is difficult to determine the precise nature of the surface groups that act as ligands: if they are OH groups, then what kind of OHs, and how are they disposed with respect to each other? As in the case of outer-sphere adsorption, the very few instances where inner-sphere adsorption sites have been tentatively identified concern model systems, e.g. in the $[\text{Co}(\text{H}_2\text{O})_x]^{2+}/\alpha\text{-Al}_2\text{O}_3$ (1102) system, where the cobalt ion was proposed to be coordinated to no less than four surface groups: one μ^3 -oxide ion, one bridging (μ^2) OH, and one terminal OH [42].

5. Slow reactions that alter metal speciation at the interface

The processes that have been considered so far in Section 4 are definitely adsorption reactions, in that the TMC maintains a recognizable identity throughout. However, it often occurs that new mixed phases (containing the metal as well as elements derived from the support) are detected after the deposition step, the best-known case being constituted by nickel phyllosilicates in the synthesis of Ni/SiO₂ [43,44]. More generally, mixed molecular species may be formed without giving rise to a separate solid phase; they are of course more difficult to evidence in this case, and this is the reason why, for instance, the

formation of the heteropolyanion $[\text{Mo}_6\text{Al}(\text{OH})_6\text{O}_{18}]^{3-}$ by simple contact of heptamolybdate solutions with alumina was not evidenced until 1997 [45], in spite of much previous work on such systems (a review of the work carried out until 1988 may be found in [46]). The mechanism of mixed species formation is not yet fully characterized. It involves reaction in the aqueous phase of $[\text{Mo}_7\text{O}_{24}]^{6-}$ with $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ions formed by dissolution of the aluminic material. Carrier et al. [47] have shown that advantage can be taken of the slow kinetics of heteropolyanion formation to control molybdenum speciation: leaving the molybdate solution/alumina mixture to equilibrate for several hours will result in total conversion of Mo into $[\text{Mo}_6\text{Al}(\text{OH})_6\text{O}_{18}]^{3-}$, while stopping the reaction immediately after contact by freeze-drying will leave it as the original $[\text{Mo}_7\text{O}_{24}]^{6-}$. Not unexpectedly, the two systems obtained in this way will behave quite differently later on: after calcination at 400°C, $[\text{Mo}_6\text{Al}(\text{OH})_6\text{O}_{18}]^{3-}/\text{Al}_2\text{O}_3$ shows large crystals of MoO₃, while Mo species in the calcined sample from $[\text{Mo}_7\text{O}_{24}]^{6-}/\text{Al}_2\text{O}_3$ remain well dispersed. Two lessons can be drawn from this example: (i) it is worthwhile to study the kinetics of interfacial reactions at the oxide–water interface [25], because their understanding during the deposition step may provide new tools to control the properties of the finished catalyst; (ii) catalysis scientists have something to learn from geochemists, who have been studying such problems for a long time [48].

Another example of the importance of interfacial kinetics is the $[\text{PtCl}_6]^{2-}/\text{Al}_2\text{O}_3$ system, where the initial adsorption of chloroplatinic species can be rationalized in a triple layer model; if, however, the system is aged for 10–20 h at room temperature (or less at higher temperatures), inner sphere adsorption slowly becomes predominant [17,40,49].

6. Is it worth the trouble? Memory effects in further steps of catalysts synthesis

An objection that is often raised towards in-depth studies of the metal deposition step is that they may have some fundamental interest, but little practical relevance since further treatments of the catalyst

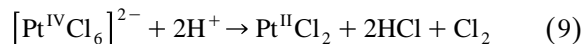
prior to its use involves thermal activation at rather high temperature, which is likely to force all catalytic systems with the same composition into the same equilibrium state, irrespective of their previous history. This objection cannot be brushed aside and is likely to be justified in some cases... but certainly not all.

A complete answer would have to take into account all phenomena that occur during drying, calcination, reduction... at the same molecular level as was done for the initial metal deposition. Unfortunately, we are not able to systematically fulfill this program at the present time, because the molecular identification of species formed during thermal treatments of catalysts is still in its infancy. Our claim for the existence of memory effects in the synthesis of supported catalysts then has to rely on specific examples where controlled changes in the metal deposition mechanism translates into variations of the finished catalyst. The reader who is familiar with industrial catalyst preparation will probably not be surprised that such instances can indeed be found, because careful examination of the preparation procedures (when possible!) often reveals that a number of empirical recipes have to be applied in order to obtain a high-performance final catalyst.

This suggests that the system may remember for a long time the initial preparation conditions.

We will now briefly describe some specific examples providing strong evidence for this contention.

Recent work from our laboratory indicates that thermal transformations of adsorbed chloroplatinic species are strongly dependent on the nature of their initial interaction with the support. When the adsorption mechanism is electrostatic and/or outer sphere, such as happens on silica, *self-reduction* can occur even under an oxidizing atmosphere along



Because the high mobility of the intermediate PtCl_2 allows the coalescence of molecularly dispersed species into large particles, the catalyst after the calcination step will contain metallic Pt of very low dispersion, which will not be improved by further reduction under H_2 [50].

On the other hand, when the chloroplatinates are adsorbed by an inner sphere mechanism as on γ -alumina (cf. Section 5 above), the grafted $[(\text{AlOH})_2\text{Pt}^{\text{IV}}\text{Cl}_4]$ species are, for some as yet unknown reason, immune to self-reduction. Reduction to the metallic state, thus, does not occur before contact with H_2 , and it then gives Pt particles of much higher dispersion. However, treatment of the alumina surface with aqueous HCl prior to chloroplatinate deposition can inhibit platinum grafting, so that the thermal behavior of the $[\text{PtCl}_6]^{2-}$ /chlorinated Al_2O_3 system is more reminiscent of $[\text{PtCl}_6]^{2-}/\text{SiO}_2$ than of $[\text{PtCl}_6]^{2-}$ /untreated Al_2O_3 .

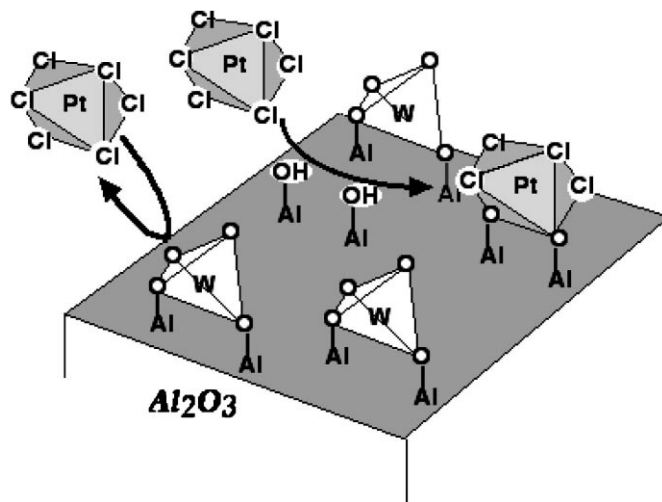


Fig. 9. Successive adsorption of monotungstate and $[\text{PtCl}_6]^{2-}$ on γ -alumina [50].

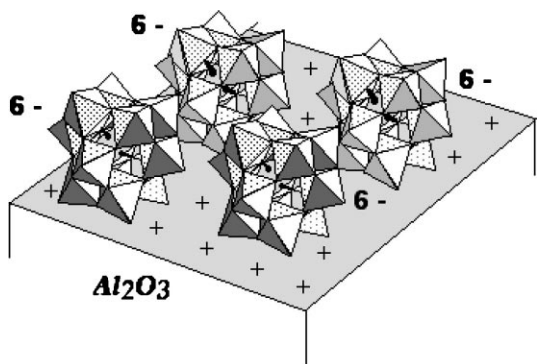


Fig. 10. Adsorption of metatungstate on γ -alumina [51].

A more intricate case is that of the bimetallic $[\text{PtCl}_6]^{2-}/\text{WO}_x/\text{Al}_2\text{O}_3$ system. We have studied a synthesis procedure in which the alumina surface is first modified by tungstate deposition, followed by washing, drying, chloroplatinate deposition, a second drying step and thermal treatments [51,52]. The sequence of events occurring during these successive steps was found to strongly depend on the nature of the initial tungstate salt used for deposition, and on their deposition mechanism:

- Monotungstate (WO_4^{2-}) was adsorbed in small amounts by an inner-sphere mechanism. The ad-

sorption sites were apparently the same as those active for chloroplatinate grafting, so that there was some amount of competition between both species (Fig. 9). However, only a small fraction of potential $[\text{PtCl}_6]^{2-}$ adsorption sites were blocked, and the amount of Pt that did adsorb behaved much in the same way as on the untreated Al_2O_3 surface.

- Metatungstate ($\text{H}_2\text{W}_{12}\text{O}_{40}$) $^{6-}$ was mostly electrostatically adsorbed and remained mobile on the surface. It could, however, effectively screen the Pt adsorption sites because of its high negative charge, preventing Pt grafting during deposition and even later (Fig. 10). As a result, $[\text{PtCl}_6]^{2-}$ self-reduction was not prevented and metallic Pt was already present after the calcination step. Therefore, it could activate hydrogen at low temperatures in the final H_2 reduction, catalyzing tungsten reduction, and giving rise to a SMSI effect (Pt decoration with WO_x suboxides).
- Paratungstate ($\text{H}_2\text{W}_{12}\text{O}_{42}$) $^{10-}$ adsorbed specifically, probably as outer-sphere complexes, and with charge overcompensation (cf. Section 4). The diffuse layer then contained the initial counterions of the tungstates, which were NH_4^+ and could not be removed by the washing procedure; thus, a

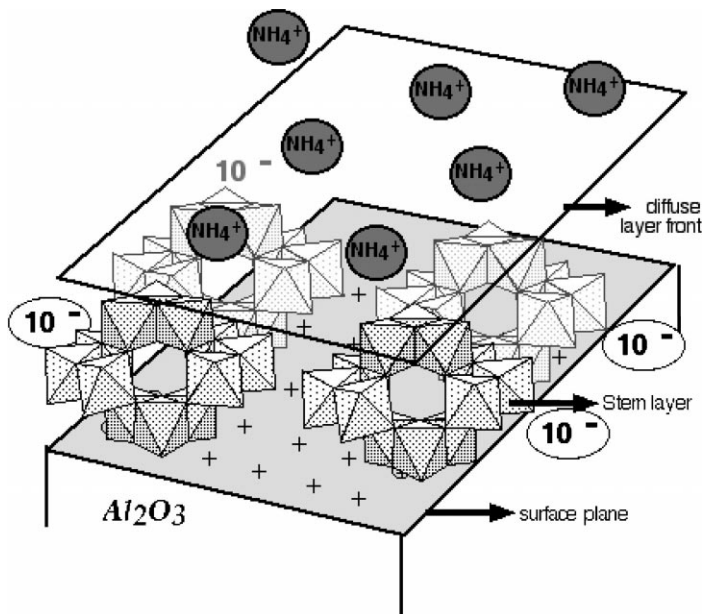


Fig. 11. Adsorption of paratungstate on γ -alumina [51]; application of the triple-layer model.

good part of the platinum species reacted to form large crystals of $(\text{NH}_4)_2\text{PtCl}_6$ (Fig. 11). This phase underwent self-reduction even more easily than in the previous case, with similar consequences but a much higher average size for Pt^0 particles.

These contrasted evolutions will be discussed in more depth in forthcoming papers, together with their consequences on the adsorption of small molecules and the catalytic activity. The brief summary presented here is sufficient to provide an idea of the cascade of events that take place as a consequence of initially different adsorption mechanisms. Let it be mentioned that experiments were performed to isolate the effect of tungsten loading from that of tungsten speciation, and that the latter was found to be predominant.

The reader may find it worthwhile to compare the latter results with those recently published by Knözinger et al. on the WO_x/ZrO_2 system [53].

7. Conclusion

The overview presented above was meant to give a feeling of the current state of the art as regards the first steps of supported catalysts preparation by classical procedures. While we generally have sufficient knowledge of the molecular speciation of metal precursors in the starting solution (with a few exceptions), the same cannot be said for the state of the support oxide surfaces, for which many important questions are still unanswered. As regards the molecular description of the interaction between metal precursors and oxide surfaces, the extent of our ignorance is still greater. However, a good understanding of the types of reaction that can occur at this water–oxide interface has already been developed in the field of coordination chemistry, and a requirement for further progress is that this understanding find its way into the mainstream of catalysis research.

The instances of precise molecular identification of adsorbed metal complexes are still scarce, but the recent appearance of such models is cause for hope. We now have the conceptual framework and charac-

terization techniques necessary to achieve this goal, if we start working on it.

As regards the further transformations of the adsorbed species during later stages of catalyst preparation (thermal treatments), the molecular-level understanding of metal speciation is a more distant prospect, but it is not impossible. We have to realize that the chemistry involved is more complicated than might be thought at first sight, and an incentive to study that chemistry is the identification of instances where the initial nature of the metal–oxide interaction is remembered throughout the preparation procedure, and plays a key role in determining technologically important properties of the finished catalyst.

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