

Role of oxide surface in coordination chemistry of transition metal ions in catalytic systems

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Abstract - On going from the solution into the bulk of an oxide through the fluid-solid interface, it is possible to encounter four types of coordination chemistry (CC) for a transition metal ion (TMI) : solution coordination chemistry, extraframework ion CC, surface framework ion CC and solid state CC. In each case, the reactivity of the TMI is discussed on the basis of its structure, accessibility and mobility, and the oxide surface is seen to act either as a solvent, ion or ligand. TMI's located in zeolites or clays exhibit behaviours related to either one of the four previous types of CC depending on the experimental conditions.

INTRODUCTION

A large number of heterogeneous catalysts consist of an active phase containing transition metal ions and supported on an oxide carrier (ref.1). They are usually very active but the selectivity is always a major concern. On the contrary, homogeneous catalysts are known to be much more selective and their behaviour is better understood because of the possibility of applying the models and concepts of coordination chemistry (ref.2). Although several attempts have been made to use those concepts for heterogeneous systems (ref.3,4), it has been rather difficult so far to draw general conclusions mainly because of our lack of understanding of the role played by the solid oxide toward the TMI's.

The usual approach to bridge the gap between infinite and tridimensional solid state and discrete coordination compounds has been to thoroughly investigate the chemistry of metal or oxide (ref.5) clusters and more recently that of supraclusters (ref.6). One expects to observe a continuous variation of the TMI properties which can be described at least qualitatively by quantum mechanics (ref.7).

In this work, we have adopted a different approach to bridge the gap mentioned above by investigating how the CC concepts are changed on moving from the solution to the solid through the water-oxide interface. TMI's are successively located in solution, on, at the surface and finally in the bulk. It will be seen that the oxide phase can act not only as a ligand but also as an ion or a ligand. Along this succession, the modification of structure, accessibility and mobility of the TMI's lead to identify four types of CC : solution CC, extraframework ion CC, surface framework ion CC, and solid state CC (ref.8).

We further want to stress that in the present approach, the catalysts preparation only requires simple chemicals such as mononuclear complexes, aqueous solution and conventional oxide supports. This differs from the supported homogeneous catalysis approach where more involved inorganic or organometallic compounds or clusters are grafted onto oxide carriers, very often by means of organic solvents (ref.3).

RESULTS

Solution coordination chemistry (SCC)

In aqueous solution, TMI's are complexed (Fig.1, type-I) by water and/or other molecules present which all are ligands (L). This defines the inner sphere of solvation usually called coordination sphere. One defines also an outer sphere of solvation formed by a layer of water molecules, with which the complex can move (i.e rotate and translate) within the liquid medium. The reactivity of a TMI depends on its ability to be coordinatively unsaturated in order to i) admit in its coordination sphere (CS) one or several reactive ligand(s), ii) catalyze their transformation into (a) given product(s), iii) and finally release the product(s) recovering its original unsaturated state. The generality of the ligand dissociation-association process has led to formulate the 16- and 18-electron rule (ref.9a) for reactivity of transition metal complexes. This rule has been very useful in discernment of preferred reaction pathways in homogeneous catalysis (ref.2).

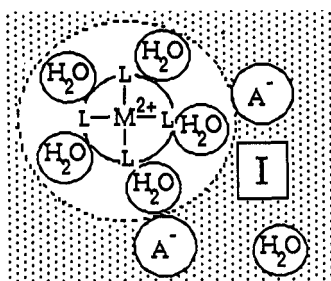


Fig. 1. Type-I model for a TMI in solution.

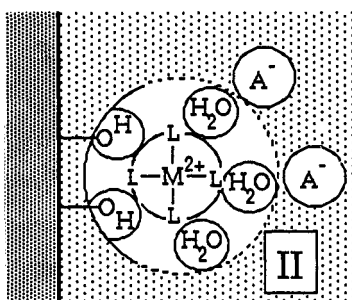


Fig. 2. Type-II model for a TMI solvated by the oxide surface.

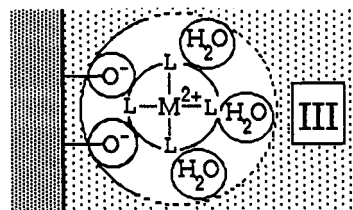


Fig. 3. Type-III model for a TMI ion exchanged on an oxide surface.

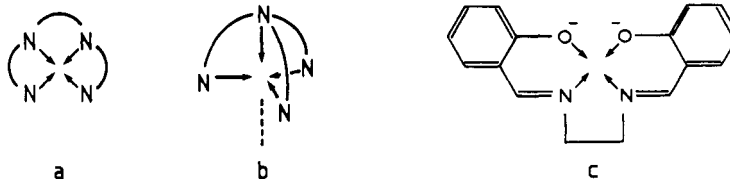
In a catalytic cycle, we can define four types of ligands : reactants, products, spectator ligands and stabilizing ligands. The stabilizing ligand, usually the solvent, allows to maintain the complex in the catalytic cycle by inhibiting any side reaction. In particular, in their unsaturated state, complexes can readily form dimers (usually stable and blocking the access of reactants to the active site) following the reaction :



where the square stands for a ligand vacancy in the CS (represented by the curve line) of the transition metal M. Reaction (1) may be inhibited by the use of bulky ligands.

It is important to realize that, in favorable cases, both reactant(s) and product(s) are temporarily attached to the metal center. In contrast, spectator ligands which are permanently bonded to the metal, have to be chosen for their electronic (or steric) properties to achieve the reaction, control its selectivity and avoid poisoning. From a general point of view, the ligands may be mono- or polydentate, flexible or rigid (sterically demanding), electrodonor or acceptor. The open chain ligand triethylenetetramine, trien (scheme 1, a), is a flexible and sterically non demanding tetradentate ligand, whereas triethylaminetriamine, tren (scheme 1, b), one of the so-called "tripod" ligands, although flexible tends to favour trigonal bipyramidal structures. By contrast, the highly conjugated phthalocyanine, Schiff base as the bis(salicylaldehyde) ethylene diimine, salen (scheme 1, c), are rigid and sterically demanding ligands by imposing a square planar structure (ref.9b).

Scheme 1



Scheme 1 *a* = trien, *b* = tren with full line = $-(\text{CH}_2)_2$ and *c* = salen ; carbon and hydrogen atoms are not represented for the sake of simplification

These various properties of ligands make it possible to design more selective homogeneous transition metal catalysts. In the following, we will see how this coordination chemistry of a TMI is modified on approaching an oxide surface.

Extraframework ion coordination chemistry (EFICC)

In most cases, supported metal oxide catalysts are prepared by impregnation of the oxide carrier with an aqueous solution of the metal salt.

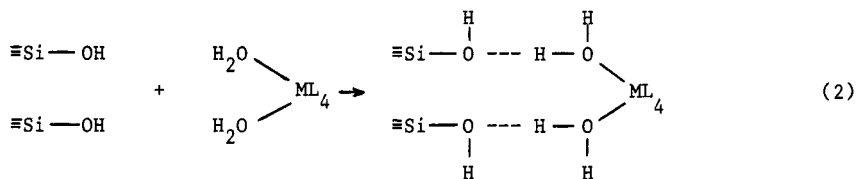
During this process, four types of position can be envisaged for the TMI with respect to the liquid-solid interface (Fig. 1, 2, 3 and 4). By reference to the situation in free water (type-I), modifications of the TMI environment may occur i) in the outer sphere of solvation, the oxide acting as a solvent (type-II) or counterion (type-III) ii) in the coordination sphere, the oxide becoming a ligand (type-IV).

(a) The oxide surface as a solvent

In the liquid medium, the TMI complex is able to move (rotate and/or translate) freely. This mobility is strongly modified in the pores of an oxide due to the perturbation produced by the liquid-solid interface. This is attributed to the immobilization of the two first layers of water at the interface (ref.10) explained by the formation of hydrogen bonds between water and surface silanol groups ($=\text{SiOH}$) (ref.11). This perturbation which changes the structure of water (lower freezing temperature and higher viscosity than bulk water) decreases as one moves away from the surface. This "anomalous" water does not crystallize and cations can be trapped within this glassy matrix which has a thickness of 8 or 10 water layers. These effects have been evidenced on a set of copper impregnated silicas with a mean pore diameter ranging

from 4 to 100 nm (ref.12). Cu^{2+} ions ($3d^9$, $S = \frac{1}{2}$) were located by EPR. For silica with pores smaller than 6 nm and below $\sim 313\text{K}$, the few layers of water available have the thickness of the glassy matrix where Cu^{2+} is characterized by an axially symmetric EPR signal. In pores larger than 6 nm, a second signal, typical of Cu^{2+} in bulk water, is superimposed on the first one. Both signals are assigned to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ but in the first layers of water, the rotation or reorientation rate was found to be 1.5 times slower than in bulk water. In the example above, there is no specific Cu^{2+} adsorption at the surface. The only interaction between Cu^{2+} and the surface is indirect and occurs via the "anomalous" water (type-I, Fig.1).

In addition, a direct interaction is likely to occur between the TMI complex and the surface through hydrogen bonding between surface hydroxyl groups which can enter the TMI outer sphere of solvation and the H_2O ligands (Fig.2, type-II). The resulting $\mu - (\text{H}_2\text{O})_2$ bridging ligands will be equivalent to that evidenced in the stable $\text{cis-}\alpha - [(\text{pico})_2\text{Cr}(\text{H}_3\text{O}_2)_2\text{Cr}(\text{pico})_2]^{4+}$ complex, a dimer of the $\text{cis-}\alpha - \text{bis}(2 \text{ picolylamine})\text{aqua}(\text{hydroxo})$ chromium (III) complex (ref.13). By analogy, the surface reaction can be written as :

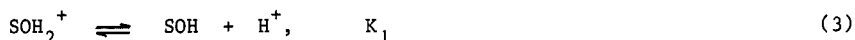


where $L = \text{H}_2\text{O}$ are the ligands, M the TMI and the dotted lines represent hydrogen bonds.

Hydrogen bonds also exist between H_2O molecules of the solvent and the ligands L not involved in the interaction with the surface. Since the OH surface groups and the H_2O solvent molecules lead to hydrogen bonding typical of solvation, the solid surface through its silanol groups can be looked at also as a solvent. The difference of solvation of a TMI in solution within a pore or on the surface is likely to be weak. Immobilization of the complex on the surface oxide which necessitates a stronger bonding than that created through reaction (2), occurs spontaneously on Al_2O_3 and MgO during impregnation (ref.12). Such a shift toward a specific adsorption can be also created on silica in water-ammonia solution and this is described next.

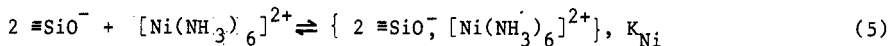
(b) The oxide surface as an ion

Oxides in aqueous suspension are generally electrically charged as shown directly by electrophoresis experiments. This is attributed to the amphoteric dissociation of the surface hydroxyl groups following the reactions :



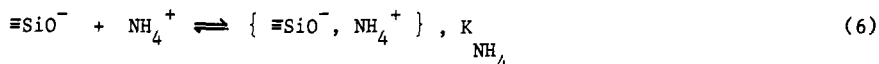
where K_1 and K_2 are the equilibrium constants of process (3) and (4). At a characteristic $\text{pH} = (\text{p}K_1 + \text{p}K_2)/2$ called the isoelectric point (IEP), the oxide surface has a zero net charge (ref.14). The surface becomes positively charged at a pH below its IEP allowing adsorption of anions (ref.15). By contrast, the negatively charged surface adsorbs cations at a pH above its IEP.

In the latter case, the oxide surface which acts as a macroanion is able to separate the cations from their counterions (Fig.3, type-III model). This cation exchange process has been studied in more detail in our laboratory for the nickel-silica system in water-ammonia solution and investigated by UV-vis spectroscopy (ref.16). The concentration of the NO_3^- counterion was monitored by the band at 33000 cm^{-1} assigned to the $(n \rightarrow \pi^*)$ transition. The concentration of Ni^{2+} ions was followed by one of the spin allowed d-d transitions, ${}^3A_2(F) \rightarrow {}^3T_1(g)(P)$ at 25000 cm^{-1} characteristic of octahedral coordination and referred to as ν_3 . After exchange and centrifugation, the $[\text{NO}_3^-]/[\text{Ni}^{2+}]$ concentration ratio was two times smaller in the gel than in the initial exchange solution. Therefore, only part of the Ni^{2+} ions are adsorbed and separated from their counterions while the remaining Ni^{2+} ions are in the exchange solution trapped inside the pores of the gel. A subsequent washing with a water-ammonia solution was necessary to remove the trace amounts of NO_3^- and the unexchanged Ni^{2+} ions. With washing solutions, having an ammonia concentration high enough to maintain the predominance of the hexaammine and pentaammine complexes, no appreciable shift of the ν_3 band was observed for the adsorbed species. No ligand substitution occurs in the CS of the exchange cation. This represents a pure electrostatic adsorption process consisting in the formation of a "surface ion pair" between the surface macroanion and the adsorbed complex ion such as :



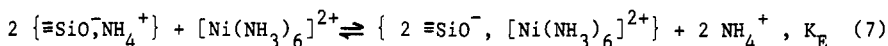
where K_{Ni} is the equilibrium constant of process (5).

The same type of equilibrium can be written for the NH_4^+ ions which are also present in water-ammonia solution :



where K_{NH_4} is the equilibrium constant of process (6).

The competition level between NH_4^+ and Ni^{2+} ions allows to control the amount of nickel adsorbed on silica following reaction (7), a combination of (5) and (6) :



where K_E is the equilibrium constant of process (7).

The experimental determination of K_E requires the titration of the solution before and after the exchange so as to obtain the amount of adsorbed Ni^{2+} . There is however no simple method available to determine the amount of adsorbed NH_4^+ . Since the percentage N_E of surface silanol groups effectively exchanged depends on the normality $N = 2[\text{Ni}^{2+}] + [\text{NH}_4^+]$ of the solution, several experiments were carried out at N and N_E constant, with an excess of NH_4^+ giving a high competition level ($N/2[\text{Ni}^{2+}] = 25-50$) in solution. In such conditions, K_E and N_E were determined using a graphic method (ref.17). For nickel, at a normality of 1 mol. l^{-1} , N_E is equal to 90% and K_E to 1.9. One can try to fit these data with the electrical double layer model developed by Davis et al. (ref.18) for electrostatic adsorption on oxides. This semi-empirical model represents the space between the surface groups (negative charges) and cations (positive charges) as a condenser with a capacitance C . A calculation provides the surface charge density, the amount of adsorbed cations and the capacitance C . The best fit leading to $N_E = 90\%$ and $K_E = 1.3$, is obtained with $\text{p}K_{\text{Ni}} = 12.3$, $\text{p}K_{\text{NH}_4} = 6.2$ and $C = 3 \text{ Fm}^{-2}$. The values for C and $\text{p}K_{\text{NH}_4}$ are consistent with the available literature (ref.18). This good agreement confirms the role of macroanion played by the oxide surface. The latter can also function as a macroligand by entering into the coordination sphere of TMI's and this is discussed next.

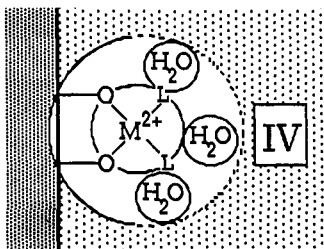
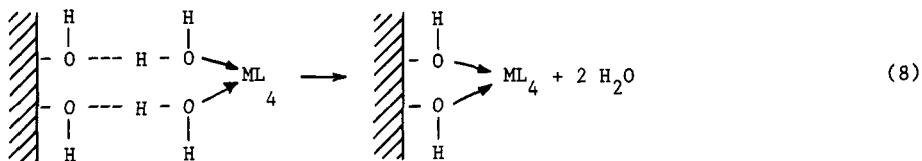


Fig.4. Type-IV model for a TMI grafted to surface oxygens

(c) The oxide surface as a ligand

As a solvent or a macroanion, the oxide surface interacts only within the TMI outer sphere of solvation. When it becomes a ligand, the oxide surface enters the CS (Fig.4, type-IV) and involves a chemical bonding between the TMI and the surface which is stronger than either one of the preceding hydrogen (Fig.2, type-II) or electrostatic (Fig.3, type-III) bonding.

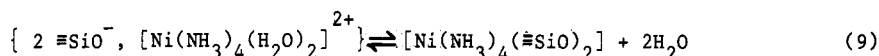
The resultant specific adsorption depends on the Lewis base character of surface oxygens. This can explain why it occurs on Al_2O_3 and MgO (ref.12) during impregnation but not on silica. The product of reaction (2) which is not very stable on those surfaces can easily react further according to process (8) :



Reaction (8) consists in the elimination of water from the $\mu\text{-(H}_2\text{O)}_2$ ligand to form a $\mu\text{-(OH)}$ bridging ligand between the surface and the metal center. Such reaction is known as "olation" when one considers the first step of precipitation of aqua ions in solution or "aging" of hydroxides in the solid state (ref.19,20).

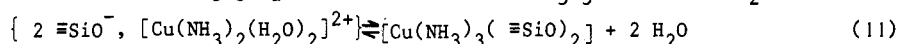
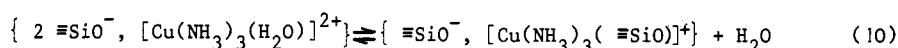
The adsorption described above may occur at a pH below the IEP and involves surface hydroxyl groups. Above the IEP, in the "surface ion pair" (Fig.3, type-III), the $\equiv\text{SiO}^-$ groups may substitute one or two ligands of the electrostatically adsorbed complex. This has been studied by UV-vis spectroscopy for Ni^{2+} ions adsorbed on silica during the washing and drying steps of preparation (ref.4,16). In the $[\text{Ni}(\text{NH}_3)_{6-(n+m)}(\text{H}_2\text{O})_n(\equiv\text{SiO})_m]^{2-m}$ complex which stays octahedral, the substitution degree can be monitored by means of the ν_3 band. A shift toward

low energies of -480 and -300 cm^{-1} is observed for the substitution of NH_3 by H_2O and H_2O by $\equiv\text{SiO}^-$, respectively. When the concentration of NH_3 in the washing solution or during the drying step is lowered sufficiently so as to enter the range of stability of the tetraammine complex, the TMI can undergo grafting following reaction (9) :

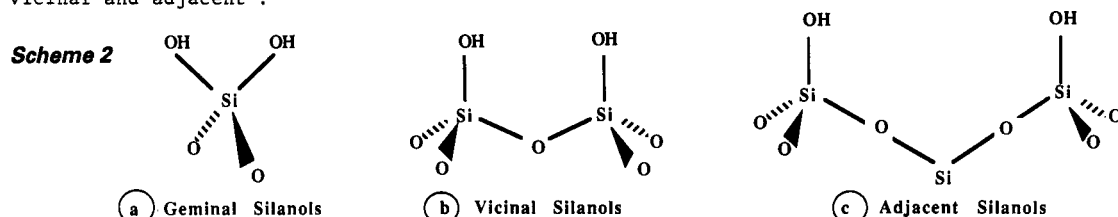


Reaction (9) creating a more intimate binding with the surface is expected to shift reaction (7) to the right hand side and increase the amount of adsorbed metal. This has been verified for Cu^{2+} ions exchanged on silica in presence of various complexes of the type $[\text{Cu}(\text{H}_2\text{O})_n(\text{NH}_3)_m]^{2+}$ ($n+m = 4$) (ref.17). While the $[\text{NH}_4^+]$ and $[\text{Cu}^{2+}]$ concentrations and the competition level were kept constant, the pH was varied from 5.5 to 10 by increasing the NH_3 concentration so as to work successively in the range of stability of the diammine and triammine complexes.

Above pH = 9, the tetraammine complex is electrostatically adsorbed as described previously and the amount fixed, 0.38 wt % in our conditions, does not vary. Below pH = 9, i.e., when the $[\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O})]^{2+}$ complex appears, the amount fixed increases while the electrical double layer model predicts a decrease. For instance, at pH = 8.2, there is about 4 times more copper adsorbed (0.55 wt %) than theoretically predicted (~ 0.15 wt %). At pH = 6.7, the $[\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ complex is the most stable and the discrepancy further increases since it is found that 1.7 wt % is adsorbed while the theory predicts virtually no adsorption. Below pH = 6.5, the metal loading finally decreases due to the competition with protons titrating $\equiv\text{SiO}^-$ groups following equation (4). In these experiments, only a fraction of copper is fixed and the results are consistent with equilibria (10) and (11) as follows :

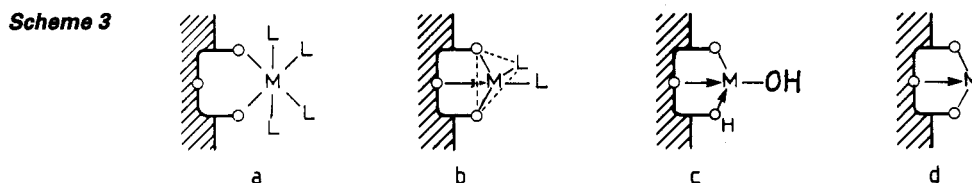


The existence of reactions (9) to (11) raises the question on the nature of surface groups able to behave as bidentate ligands. On silica, there are three types of silanol pairs, geminal, vicinal and adjacent :



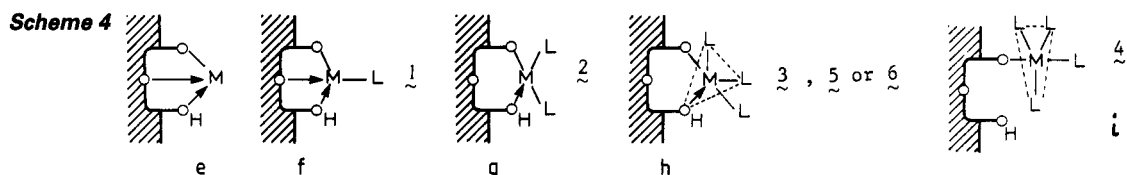
Various types of silanol pairs on a silica surface

The distance between two oxygens in the adjacent pair is too large to bind a TMI ($> 0.5 \text{ nm}$) while it is too small (0.26 nm) for the geminal pair. Therefore, on a structural basis, the vicinal pair is to be preferred with a value of about 0.3 nm which imposes a minimum of distortion in the octahedral (case of nickel) or square planar (case of copper) grafted complex as depicted in scheme 3a.



Various types of coordination of extraframework M^{2+} (Ni^{2+} for instance) ions with surface oxygens. L stands for ligand (H_2O for instance). The oxygen within the surface represents a bridging oxygen between two silicium ions while the other two oxygens are those belonging to a vicinal silanol pair.

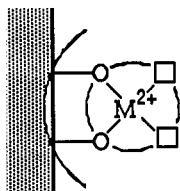
An UV-vis study shows that Ni^{2+} ions exchanged on silica do not form nickel oxide under calcination in dry oxygen up to 973 K . The ions remain isolated and their coordination number decreases from 6 to 3 when the calcination temperature increases from 293 to 973 K (ref.21a,21b). Their symmetry changes progressively from octahedral to trigonal bipyramid, tetrahedral, and finally trigonal pyramid (scheme 3 a-d, respectively). Along this series, an increasing distortion appears since the rigid oxide by taking more importance as a ligand (scheme 3, a-d) imposes its coordination to the Ni^{2+} ions. The oxide surface acts as a tridentate ligand by addition of a dative bond with the bridging oxygen of the vicinal silanol pair (scheme 3b) to the initial two ionic bonds created during the grafting process (reaction (9) and scheme 3a).



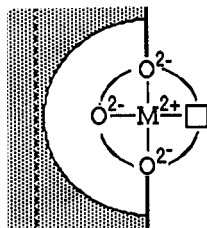
Various types of coordination of $M^+(Ni^+)$ ions obtained by reduction of tricoordinated M^{2+} ions (scheme 3d) ($L = CO$) attached to a vicinal silanol pair

It is important to note that the preceding change of coordination upon calcination is reversible if water is admitted into the CS of Ni^{2+} ions and that one can scan from scheme 3d, to 2b and finally 2a (ref.21b).

After reduction in H_2 at 443 K or under UV irradiation either in H_2 at 77K or in CO at 293 K (ref.22) of the tricoordinated Ni^{2+} ions (scheme 3d), the coordination of the resulting Ni^+ ($3d^9$) ions (scheme 4e) was studied by EPR using $^{13}C(I = \frac{1}{2})$ labelled CO (ref.23). On increasing the CO pressure, a series of Ni^+ complexes are reversibly formed: tetrahedral $[Ni(O_s)_3(CO)]^+$, 1 (scheme 4f), square planar $[Ni(O_s)_2(CO)_2]^+$, 2 (scheme 4g) and trigonal bipyramidal $[Ni(O_s)_2(CO)_3]^+$, 3 (scheme 4h) and $[Ni(O_s)(CO)_4]^+$, 4 (scheme 4i). In the preceding formulas O_s stands for a surface O^{2-} ion, or a bridging O^{2-} ion or an OH group (scheme 4). It is seen that the oxide surface changes from a tri- to bi- and monodentate ligand via two inequivalent surface oxygens (O_s) which belong to a vicinal silanol pair and the bridging oxygen between the two silicium ions (scheme 2b) (ref.23). It is thus a very versatile ligand.



V Fig.5.



VI Fig.6.

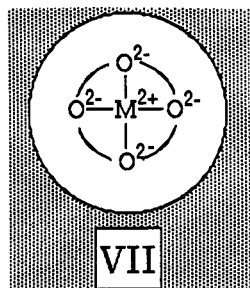


Fig.7

Fig.5. Type-V model for a TMI grafted on an oxide surface after heat treatment to create ligand vacancies (represented by the squares)

Fig.6. Type-VI model for a TMI in framework position at the surface of an oxide solid solution

Fig.7 Type-VII model for a TMI in framework position within the bulk of an oxide solution

In figure 5, the bidentate case is given by type-V where the ligand vacancies can be filled up with CO to obtain complex 2. The Ni^+ ions also bind and dimerize ethylene. Thus, when C_2H_4 is adsorbed at increasing pressure on species 2, complexes $[Ni(O_s)_2(CO)_2(C_2H_4)]^+$, 5, and $[Ni(O_s)_2(CO)(C_2H_4)_2]^+$, 6, are successively observed by EPR. Only the latter leads to dimerization showing that two C_2H_4 per Ni^+ are required before the reaction proceeds.

Four types of ligands may control the coordination and reactivity in olefin dimerization (ref.4,23): reactants (C_2H_4), products (1-butene), spectator ligands (CO, phosphines) able to assist the reaction via electronic and steric effects and finally the oxide macro-ligand, which is a very versatile ligand (ref.8,21a).

In scheme 3 for Ni^{2+} ions or 4 for Ni^+ ions, a dative bond between a surface oxygen O_s and the metal center can be created in place of a bond between a gas phase molecule (H_2O , CO or PR_3) and the metal center. The surface oxygen atoms enter, from the outersphere on the solid side, into the CS of the TMI and play the role of a solvent-ligand able to (temporarily) occupy a vacancy.

When the mobile entities, belonging to the outer and inner spheres, are removed by heat and/or vacuum treatment TMI's in state of low coordination are generated. Their stabilization often occurs by their migration into the surface to produce ions in framework positions. The behaviour of those surface framework ions is treated in the next paragraph.

Surface framework ion coordination chemistry (SFICC)

At the surface of microcrystalline oxide solid solutions, TMI's are in framework position (Fig.6, type-VI) i.e., within rather than on the surface as described in the preceding part.

The best model to illustrate SFICC is represented by high surface area (50–200 m²/g) NiO-MgO or CoO-MgO solid solutions which can be prepared as microcrystalline cubelets where 98–96 % of the surface ions are located on {100} faces and 2–4 % at edges or corners (ref.24,25).

When one increases the cubelet size by sintering in dry air (typically at 1373 K for 12h), the surface area as well as the fraction of TMI's at edges and corners drastically decrease. By contrast, hydrothermal treatments lead to an increase of the relative concentration of TMI's at edges and corners allowing to study their properties (ref.26a).

(a) TMI's located in faces

At {100} faces, Ni²⁺ or Co²⁺ ions are in a C_{4v} square pyramidal symmetry as evidenced by UV-vis-NIR spectroscopy (ref.24,25). They interact weakly with CO which adsorbs only at 77K (ref.24,25). At high coverage, the C-O stretching frequency shifts toward low energies from 2118 to 2090 cm⁻¹ for the Co-CO system. This shift is in the direction opposite to that expected for dipole-dipole interaction between vibrators characterized by very close stretching frequencies. In dilute CoO-MgO solid solutions, this downward shift is best explained in terms of an electronic effect which reinforces the back donation of the Co-CO bond due to the σ electron donation from CO molecules adsorbed on Mg²⁺ neighbours (ref.24). The inductive effect which propagates in the plane of the oxide surface increases the donor properties of surface Co²⁺ ions through the outer sphere.

Co²⁺ ions located at {100} faces have been found recently to function as heterogeneous oxygen carriers. IR and EPR studies show (ref.26b,27) that oxygen adsorption at 77K onto Co²⁺ ions leads by electron transfer to the formation of a superoxide ion O₂⁻ stabilized on a Co³⁺ ion in a bent end-on position. This is similar to the oxygen adduct of cobalt complexes in solution (ref.28) where Co²⁺ ions are bonded in the equatorial plane to porphyrins via 4 nitrogen atoms or Schiff bases via 2 nitrogen and 2 oxygen atoms (see scheme 1c). The fifth position of the C_{4v} square pyramidal symmetry is occupied by a Lewis base which for the CoO-MgO solid solution is an O₂⁻ anion.

(b) TMI's at edges and corners

TMI's located at edges and corners of the cubelets are in state of low coordination, 4 and 3, respectively. They are less stabilized by the lattice than those located at faces or in the bulk (ref.29a). Ni²⁺ at edges or corners are reduced in hydrogen at 673 K while when they are located in faces their reduction occurs in the 673–973 K range and above 973 K for Ni²⁺ located in the bulk (ref.29b).

Adsorption of CO on these TMI's occurs at room temperature. Their reactivity is so high that they are reduced to the zerovalent state leading to extraframework mono- and polynuclear species. This suggests that the frontier between SFICC and EFICC can in some cases be very difficult to draw.

In solid solutions, TMI's also occupy bulk positions and this is discussed in the next section.

Solid state coordination chemistry (SSCC)

TMI's can migrate from the surface into the bulk of the oxide carrier during calcination in a location where they no longer are accessible to gas phase reactants (Fig.7, type VII). As impurities in semi-conductors, bulk TMI's are able to modify the catalytic properties of the surface (ref.30). Such electronic modifications are propagated from the bulk to the surface TMI's through their outer sphere. On a molecular basis, inductive effects or electron transfers require the knowledge of the local symmetry of the TMI.

For instance, an EPR study of Mo doped TiO₂ (ref.31) or SnO₂ (ref.32) shows that part of Mo ions are stabilized in the 5+ oxidation state. The EPR characteristics of Mo⁵⁺ are consistent with an hexacoordinated state at a substitutional site with D_{2d} symmetry. In Mo/SnO₂ system, the unpaired electron of Mo⁵⁺ ions is delocalized onto orbitals of Sn⁴⁺ ions belonging to the Mo⁵⁺ outer sphere. This is evidenced by the presence of a superhyperfine structure due to the ¹¹⁷Sn and ¹¹⁹Sn isotopes (I = ½) whose natural abundance is around 15 %.

DISCUSSION

The structure of the environment, the accessibility and the mobility of a TMI are determined by its inner (coordination) and outer spheres. Such properties are modified when the TMI moves across the interface from the solution into the oxide. Those modifications are related to the solvent, counterion and ligand properties of the oxide.

Solvent properties of the oxide

The solvent properties concern the outer sphere of a TMI. There are two types of EFICC related to the liquid- or gas-oxide interface. In the former case, TMI's located in the first layers of water or on the surface are solvated by means of hydrogen bonds between H₂O molecules or hydroxyl surface groups and ligands of the CS (Fig.1 and 2, type-I and -II). There is a slight reduction of the TMI mobility as compared to the situation in bulk water. At the gas-oxide interface, the removal of the mobile ligand during drying and calcination leads to

the suppression of the outer sphere on the gas phase side (Fig.5, type-V). On silica, for instance, the outer sphere contains Si^{4+} and O^{2-} ions which are part of $\equiv\text{SiOH}$ and $\equiv\text{Si-O-Si}\equiv$ groups. As exemplified in schemes 3 and 4, these two surface groups may enter the CS of Ni^{2+} or Ni^+ ions to compensate vacancies created by elimination of mobile ligands L. In EFICC, this behavior mimics the role of ligand-solvent known for SCC.

At the surface or in the bulk of solid solutions, for SFICC or SSCC, the second shell or outer sphere contains cations to compensate the negative CS of, for instance, NiO_6^{10-} octahedr: bulk complex in NiO-MgO system, the oxide acting as a ionic solvent.

Ion properties of the oxide

It is remarkable that the nature of the surface charge is determined by a single parameter, the pH, which can thus be considered as a "surface charge selection switch": the positive charge being obtained at $\text{pH} < \text{IEP}$ and the negative one at $\text{pH} > \text{IEP}$. Once charged, the oxide surface is able to attract counterions and glue them by electrostatic bonding. This role of a pure macro-ion, excluding the role of ligand, can be played only with respect to TMI's when those are in extraframework positions.

Beside the primary effect of surface charge selection, the pH has another effect, i.e., that of determining the stability of a particular complex. This is a very important aspect since the results on copper complexes indicate that the extent to which grafting occurs strongly depends on the nature of the complex. It appears that the presence of water creates a weak point in the CS facilitating the grafting process. (reactions 10 and 11).

Ligand properties of the oxide

In SCC, with monodentate and sterically non demanding ligands, the metal imposes the symmetry to its environment leading to nearly perfect conventional symmetries (octahedral, tetrahedral or square planar). Sterically demanding ligands are necessary to stabilize particular structures (square planar, trigonal bipyramid...). When the oxide enters the CS of a TMI and acts as a rigid macroligand, mono or polydentate, it distorts the TMI environment and generates particular structures. This distortion increases and low coordinated states are generated when solution or gas phase mobile ligands are removed. The oxide is either an anionic ligand via $\equiv\text{SiO}^-$ groups (Fig.4, type-IV) for a neutral ligand via dative bonds with $\equiv\text{SiOH}$ or $\equiv\text{Si-O-Si}\equiv$ groups (schemes 3 and 4). Very accessible TMI's are produced but owing to the bonding with the surface, TMI-TMI bond formation (reaction 1) is inhibited. These TMI's are also very reactive. For instance, tricoordinated extraframework Ni^+ ions on silica, can bind molecular hydrogen (ref.22) as recently observed also for coordination compounds of iridium (ref.33a) or selectively dimerize olefins via a 17-19 electron process (ref.23).

In solid solutions, the TMI environment is clearly imposed by the host oxide which is a sterically demanding ligand. In the bulk, for SSCC, the TMI coordination number is 4, 6 or 8 and depends on the $r_M/r_{\text{O}^{2-}}$ ratio of the ionic radii of the metal cation and the anion O^{2-} (ref.33b). At the surface, the surface framework ions are accessible and have, for instance, 1, 2 or 3 vacancies on {100} faces, edges and corners, respectively, in MO-MgO systems.

Up to this point, our discussion has been mainly concerned with conventional oxides but it is striking to note that the four different types of CC can all be encountered in a single system like two- or three- dimensional crystallized oxides such as clays and zeolites as discussed below.

Clay coordination chemistry (CCC)

In clay chemistry, lamellar silicates provide examples of bidimensional oxides. For instance, in dioctahedral smectites, a layer consists in the association of two tetrahedral (T) sheets, formed by SiO_4 units, separated by an octahedral (O) sheet composed of $\text{AlO}_4(\text{OH})_2$ units. Between TOT layers, solvents and electrolytes may penetrate and occupy extraframework positions. In the montmorillonite-type of smectite, some of the Al^{3+} are substituted by Mg^{2+} ions, creating for each substitution a negative charge and a cation octahedral vacancy on the layer. This allows cation exchange within the interlayer space in extraframework positions.

Upon heat treatment ($\sim 200^\circ\text{C}$) of Li exchanged smectite, the small Li^+ ions migrate into the octahedral sheets and neutralize the layer charges leading to the suppression of the exchange properties of the clay. This is known as the Hofman-Klemen effect (ref.34) widely used to titrate the vacancies of the octahedral sheet. Very recently, this effect has been observed for Ni^{2+} ions above 400°C and evidenced by wide angle X-ray diffraction (ref.35). In the latter experience, Ni^{2+} ions exhibit EFI- and SS-type of CC.

Zeolite coordination chemistry (ZCC)

Zeolites are microporous crystallized aluminosilicates where cations can be exchanged in defined extra-lattice positions inside cavities connected by windows or channels (Fig.8). Migration of molecules or cations may occur within the structure provided that their size is smaller than the apertures (ref.36). Those special properties allow zeolites to exhibit the three previous types of CC as exemplified by the faujasite type.

Those solids possess cavities of different sizes which can act as microreactors at the molecular scale and present a strong analogy with cryptate chemistry (ref.37).

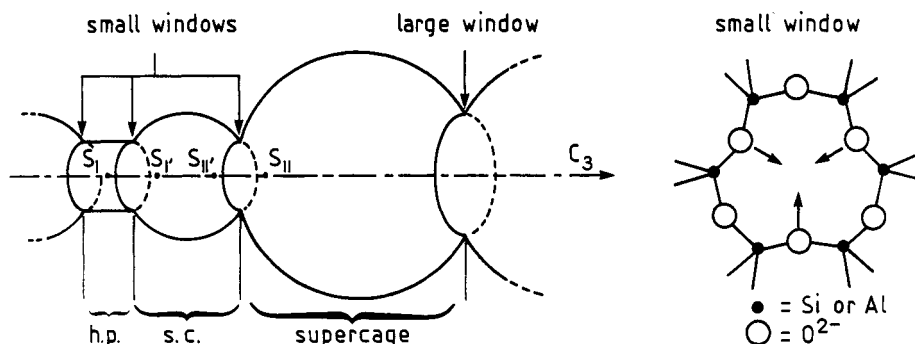


Fig.8 Alignment of the faujasite cavities along the C_3 axis (h.p = hexagonal prism, s.c = sodalite cage) and representation of the tridentate small window.

During the exchange procedure, Cu^{2+} ions enter with their coordination sphere into the supercages (Fig.8) through the large window (0.8-0.9 nm). With a capacity of 28 water molecules and 1.14 nm internal diameter (ref.38), those cages can accommodate the $[Cu(H_2O)_6]^{2+}$ complex with its outer sphere of solvation. An EPR study (ref.39) shows that the rotation rate of the complex is 10 times slower than in bulk water (to be compared with a factor of 1.5 times found in pores of silica see ref.42) due to the close vicinity of the cavity walls. Through this strong restriction of TMI's motion, zeolites act as anionic solvent where SCC can be realized. Under heat treatment, TMI's located in the supercages loose their mobile water ligands and move toward sites S_{II} , S_{II}' and S_I' where they bind to three lattice oxygens of a small window (Fig.8).

In the sodalite cage (S_I' and S_{II}' sites), TMI's are accessible to small polar molecules (H_2O , NH_3 or NO) but they usually have to migrate toward S_{II} sites in the supercages to completely fulfill the conditions of EFICC. In hidden sites S_I inside the hexagonal prism, the TMI is hexacoordinated by lattice oxygens and immobilized in the structure. This is typical of SSCC where a TMI is not accessible to reactants. One can also find SFICC for MeAPO-type zeolites where TMI's (Me = Mn, Fe, Co) have been incorporated in framework position during the synthesis procedure (ref.40).

CONCLUSION

The role of the oxide in the chemistry of a TMI moving from the solution into the oxide across the interface has been described by means of the basic concepts of CC. The progressive loss of mobility, accessibility and reactivity of TMI's has been related to the modifications occurring in their inner (coordination) and outer spheres where the oxide can act as a solvent, ion or ligand.

The role of the oxide as solvent can now be emphasized. Apart from the obvious role of entrapping TMI containing solution within its pores, the oxide can first, through hydrogen bonding (Fig.2, type-II) solvate TMI's in the same way as water does. Second, it can act as a solvent by temporarily entering the CS of a TMI during a catalytic reaction cycle. Third, it can act as a solid solvent by dissolving TMI's (ref.41) as soon as ionic mobility appears, around the Tammann temperature usually taken as half the fusion temperature (ref.42).

Using the pH as a "charge selection switch", the oxide surface can be either negatively or positively charged, reactions (4) and (3), and adsorb cations and anions, respectively. In the adsorption process, "surface ion pairs" are formed where the oxide surface acts as a counterion.

While full coordination is achieved in either solution CC or solid state CC, there is a possibility at the interface to generate highly unsaturated ions in extra- or surface framework positions where the oxide is a versatile or sterically demanding ligand, respectively. The catalytic active sites can be modelled by the proper choice and balance of four types of ligands: the rigid surface ligand which stabilizes and immobilizes the TMI via its hydroxyl groups, or terminal or bridging oxygens, permanently attached spectator ligands (phosphines for instance) which can influence the reaction through their electronic and steric effects, and finally the reactants and products which have to be mobile ligands if the reaction is to proceed further. Though less flexible for the choice of ligands, the so-called "interface catalysis" on oxides has three advantages over homogeneous catalysis: first, metal-metal bonds formation via reaction (1) is inhibited by fixation of the TMI on or at the surface, second, the separation "catalyst-products" is easier for heterogeneous systems and third, the temperature window for reactivity to be observed is larger for heterogeneous catalysts.

Moreover, this work has also shed some light on the thickness of the fluid-oxide interface. It includes the double layer and can be extended to 8-10 water layers away on the fluid side, while on the solid side, it contains not only the nearest neighbours (inner sphere) but also the next nearest neighbours (outer sphere) (Fig.6, type-VI).

It has been possible to identify four types of CC, each documented by results concerned with one typical oxide system. There are by contrast oxides which are capable to exhibit all four types of CC and such is the case of clays and zeolites. These systems are quite unique owing to their internal space and cavities which can be used at a molecular level as microreactors to promote typical reactions. The time is not far where, upon suitable and careful modifications at the steric and electronic levels these systems will function as enzyme systems (ref.43-45).

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