Interfacial coordination chemistry. Current status and applications

Christine Lepetit *, Michel Che

Laboratoire de Réactivité de Surface, URA 1106 CNRS, Université P. et M. Curie, 4, Place Jussieu, 75252 Paris Cedex 05, France

Abstract

After definitions of interfacial coordination chemistry (ICC) and surface organometallic chemistry (SOMC), their main characteristics and applications are compared. The common concepts of ICC and classical coordination chemistry, as well as the specific features of ICC are illustrated through some examples. Finally, possible applications of ICC to catalyst preparation, adsorption and relations to catalysis are given.

Keywords: Adsorption; Coordination chemistry; Interfaces; Materials; Preparation; Transition metal ions

1. Introduction

In the present paper, we will consider the applications of coordination chemistry concepts to oxide surfaces mainly in the context of catalysis and related fields such as catalyst preparation and adsorption.

Recently, Van Santen [1] distinguished three possible approaches in catalysis: (i) catalytic engineering at the macroscopic level dealing with processes, reactors, mechanical resistance and shape of the catalyst; (ii) studies at the mesoscopic level of catalyst preparation and activation with emphasis on kinetics and measurements of catalytic activity in microflow reactors; (iii) and finally studies at the microscopic or 'molecular' level on reaction pathways. In the latter case, the aim is to identify the catalytic active site and to determine the elementary steps of the reaction and the bonds between the active center, surface atoms and substrate which are formed or broken. The

active site–substrate recognition concept is useful. This approach is based on 'atomic scale' characterization of the catalysts and on studies of model systems including theoretical investigation which allow to determine the stability of proposed intermediates and support spectroscopic information. Such a basic approach was determinant in the improvement of coordination chemistry and homogeneous catalysis and is expected to provide the same benefits to heterogeneous catalysis.

Two emerging fields are trying to meet these requirements while developing coordination chemistry concepts at the interface: surface organometallic chemistry (SOMC) and interfacial coordination chemistry (ICC), both part of transition metal chemistry. In what follows, we will define interfacial coordination chemistry as the branch of inorganic chemistry concerned with the combined behaviour of cations and their ligands, when some or all of those belong to a solid, at a solid–fluid or solid–solid interface, while surface organometallic chemistry specifically refers to

---

* Corresponding author. e-mail: cml@ccr.jussieu.fr

compounds at interfaces where a metal–carbon bond is present.

The distinction between these two fields is similar to that of their solution analogues and Table 1 gives their main characteristics, although recent results suggest that there are several examples at variance with this classification and that this distinction should not be taken too literally.

In the present paper, we will illustrate the current status of ICC through some examples by comparison with classical solution coordination chemistry taken as the reference and show how it is relevant to fields such as catalyst preparation, selective ion adsorption and catalysis.

2. Solution coordination chemistry [2]

We will focus here on transition metal (TM) complexes, because the partly filled metal d orbitals lead to properties (optical and magnetic) which strongly depend on the environment of the metal center. Those properties can thus be used to provide information on the changes of environment occurring during any perturbation (ligand exchange, redox process). Moreover, we will consider complexes in high symmetry (O_h, T_d or D_{4h}) simply because available tools, particularly crystal field theory, work best for such high symme-

tries but with additional effort can be applied to lower ones [2].

2.1. Experimental results

The experimental results described here are restricted to those which have found their analogues in ICC which will be the object of the second part (Section 3) of this paper.

Optical properties of transition metal complexes

The colors of TM complexes were noticed very early and are in striking contrast to those of other compounds. Absorption spectra can be explained in simple terms by the splitting of the atomic d orbitals of the metallic center in the presence of ligands. For octahedral complexes, the strength of metal–ligand interactions may be described by the crystal-field strength (Δ_0), while the covalent character can be estimated from the Racah parameter B, related to the interelectron repulsion [2] (vide infra).

Ligand spectrochemical series

In classical coordination chemistry, for a given metal ion in a given symmetry, ligands can be arranged in order of increasing induced crystal-field strength. This order is generally independent of the metal ion. It is therefore possible to list the

Table 1
Comparison of the main characteristics and applications of the two domains of interfacial coordination chemistry (ICC) and surface organometallic chemistry (SOMC)

|	Interfacial coordination chemistry (ICC)	Surface organometallic chemistry (SOMC)
Metal oxidation state	high	low
Ligands	hard (Pearson) σ donor–π donor Cl^-, SO^- [a], SOH [a], SOH_2^+ [a], H_2O, NH_3	soft (Pearson) σ donor–π acceptor CO, PR_3, organic ligands
M–L interactions	more ionic	more covalent
Models	crystal field, molecular orbitals	molecular orbitals 18e$^-$ stability rule 16–18e$^-$ reactivity rule
Applications	ligands slightly perturbed **catalyst preparation** selective ion adsorption	ligands perturbed organic synthesis **catalysis**

[a] S stands for support metal ions.
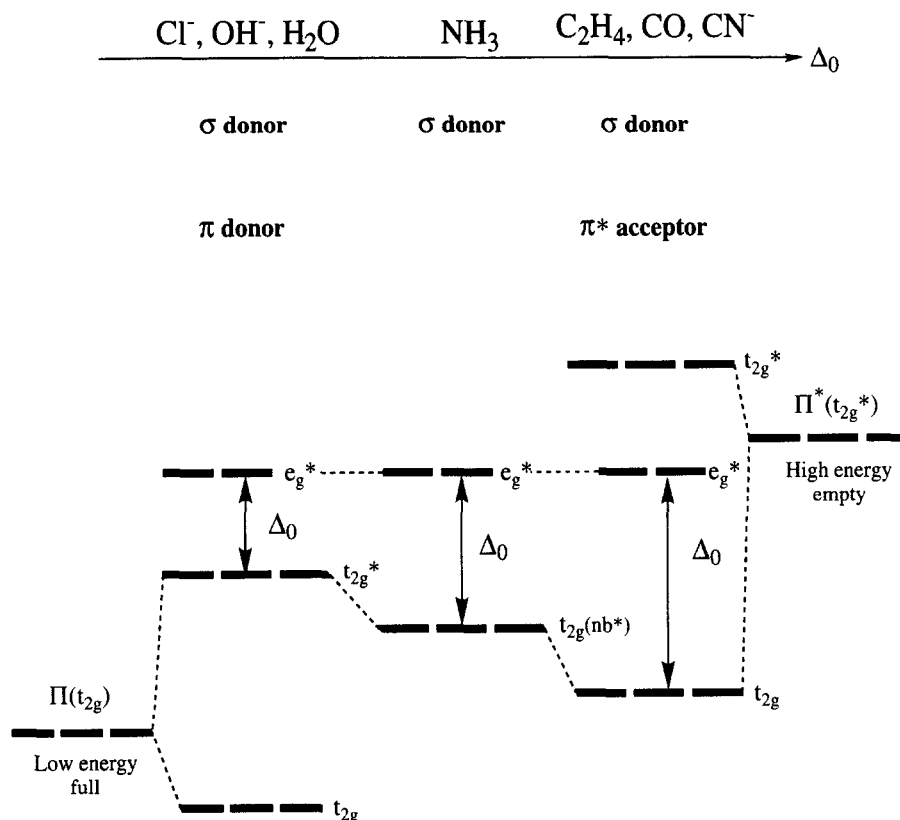
Fig. 1. Ligands spectrochemical series established for TM complexes in O_h symmetry. Relation to electronic properties of the ligands. Adapted from Refs. [2] and [4]. * nb stands for non bonding.

ligands by increasing field strength in a ligand spectrochemical series [3]. Since it is not possible to obtain a complete field strength scale of all ligands with the same metal ion, the so-called ligand spectrochemical series has been constructed from overlapping sequences, each of them illustrating a portion of it.

A part of the spectrochemical series that will be useful hereafter is given below:

$$Cl^- < H_2O < NH_3 < en$$
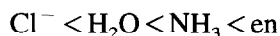
where en stands for ethylenediamine.

This scale may be rationalized on the basis of the σ- and π-donor or acceptor properties of the ligands. Weak σ- and strong π-donor properties are expected to yield small crystal field, while strong σ-donor and weak π-donor or strong π-acceptor character of a ligand are expected to be associated with a large crystal field (Fig. 1).

Nephelauxetic effect

As stated above, the covalent character of the metal–ligand bond may be estimated from the Racah parameter [4]. The value, (B), of the latter is found to be smaller in the complex than that in the free ion (B_0). This is the indirect evidence for the sharing of electrons between ligands and the central TM ion. The smaller the nephelauxetic parameter $\beta = B/B_0$, the more covalent the ligand–TM ion bonding in the complex. A nephelauxetic series [2,5] may be set up for both various metal ions and various ligands indicating the order of increased nephelauxetic effect. Hence this effect may be taken as a measure of the tendency towards covalent bonding.

The lower interelectron repulsion in the complex may be attributed to an increased distance between electrons, since the molecular orbitals are of larger size (in greek, nephelauxetic means 'cloud expansion') as compared to the atomic
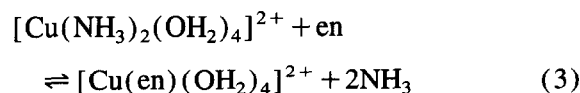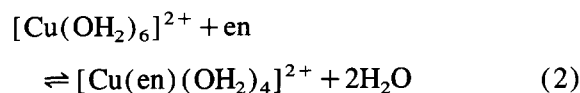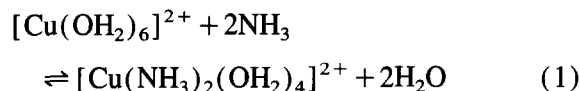
orbitals of the free TM ion. Ligands which can easily delocalize electrons over a large space are most effective in this manner.

Magnetic properties

For a given TM ion, the ground electronic state in the complex depends on the crystal-field strength. Weak crystal field are expected to yield high-spin complexes, whereas strong crystal field preferentially generate low-spin complexes [2].

Chelate effect

Complexes with polydentate (chelating) ligands are generally more stable thermodynamically than those of identical coordination number but with monodentate ligands, assuming the donor atoms are the same in both cases. The entropy change is the driving force for the displacement of monodentate ligands by chelating ones, as illustrated hereafter:

$$[Cu(OH_2)_6]^{2+} + 2NH_3$$
$$\rightleftharpoons [Cu(NH_3)_2(OH_2)_4]^{2+} + 2H_2O \quad (1)$$
$$[Cu(OH_2)_6]^{2+} + en$$
$$\rightleftharpoons [Cu(en)(OH_2)_4]^{2+} + 2H_2O \quad (2)$$
$$[Cu(NH_3)_2(OH_2)_4]^{2+} + en$$
$$\rightleftharpoons [Cu(en)(OH_2)_4]^{2+} + 2NH_3 \quad (3)$$

The standard thermodynamic energy values corresponding to reactions 1, 2 and 3 are given in Table 2.

Upon substitution of monodentate ligands such as H_2O by NH_3, the reaction energy variation ($\Delta G^0 = \Delta H^0 - T\Delta S^0$) is mostly related to the enthalpy term (reaction 1, Table 2). The substitution of monodentate water ligands by the bidentate en ligand is accompanied by a variation of both enthalpy and entropy terms (reaction 2, Table 2). However, the substitution of monodentate ligands NH_3 by a bidentate analogue (en) is an entropy-driven reaction only (reaction 3, Table 2).

Table 2

Reaction	ΔH^0 (kJ/mol)	ΔS^0 (J/K·mol)
1	-46.4	-8.4
2	-54.4	$+22.6$
3	-8.0	$+31$

Hapticity

For organic ligands, such as benzene or cyclopentadiene, that can act as polyelectron donors, Cotton [6] suggested the *hapto* nomenclature (from greek : to fasten) to describe the number of atoms by which the ligand is attached to the TM ion (i.e., the hapticity η). For example, benzene is involved in numerous organometallic complexes where its hapticity may vary from one to six [7].

2.2. Theories

In classical coordination chemistry, crystal-field and molecular orbitals theories are the most popular. In the former, the interactions between the metal ion and the ligands are considered as purely electrostatic (ionic). Although this simple theory accounts for a large amount of data, it is only a model. It is not realistic since the bonding in TM complexes also has a covalent character. The latter theory describes the molecular orbitals of the complex as a combination of the orbitals of the free ion with atomic or/and molecular orbitals of the ligands. Metal–ligand interactions are described in terms of σ- or $\sigma + \pi$-bonding.

3. Interfacial coordination chemistry – current status

Transition elements are the best candidates to study ICC. As a matter of fact, they can act both as catalytic sites and as probes of their own interactions with an oxide support, not only in the course of catalyst preparation but also upon further thermal treatment and catalytic reaction. Any change in their coordination sphere may affect

their optical or magnetic properties and may therefore be followed by spectroscopic techniques.

Our studies have been limited to oxide supports so far, but similar results may be expected for instance with sulfides, since sulfur exhibits similar σ and π-donor properties as oxygen.

3.1. Concepts of coordination chemistry applied to TM complexes interacting with oxide surfaces

From electrostatic adsorption to grafting

An ion can be associated with an oxide surface as an outer-sphere or an inner-sphere complex [8] as shown on Fig. 2 for octahedral complexes at the liquid–oxide support interface. In the former case, there is only an electrostatic interaction between the TM complex and the surface while in the latter case, a iono-covalent bond between the metal and the surface is formed, the surface acting as a supermolecular ligand.

One way of creating interactions between the TM complex and the surface is ionic exchange [10]. This method is based on the amphoteric properties of surface hydroxyl groups which depend on the pH as follows:

$$SOH_2^+ \;\rightleftharpoons\; SOH \;\rightleftharpoons\; SO^- + H^+$$
$$pH < pH_i \qquad pH \approx pH_i \qquad pH > pH_i$$
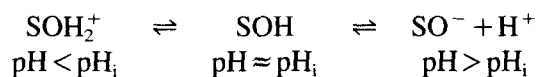
where pH_i is the isoelectric point. The resulting surface charges may attract ions (charged complexes) of opposite charge. Such adsorbed complexes in electrostatic interaction with the surface may then substitute some of their original ligands by surface ligands. The resulting inner-sphere complexes are then grafted, i.e., chemically bonded to the oxide surface.

The potential-energy curves related to electrostatic adsorption (Ad) or grafting (G) are given in Fig. 2. The horizontal line represents the zero of potential energy corresponding to an octahedral complex $[ML_6]^{2+}$ far from the oxide support surface. Above this line, energy has to be supplied, and below it, energy is liberated. The enthalpy of physical adsorption (Van der Waals, hydrogen bonding or electrostatic interaction between the $[ML_6]^{2+}$ complex and the oxide surface) is weak
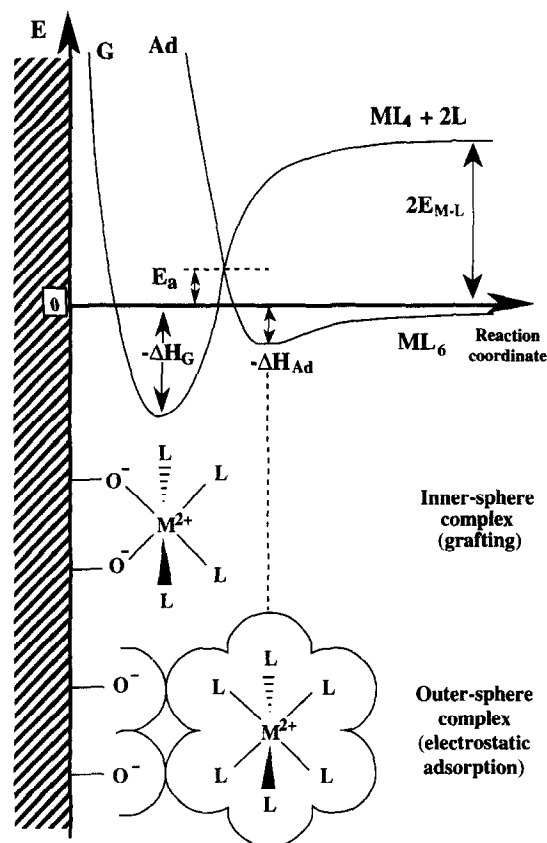

Fig. 2. Representation of an octahedral inner-sphere and of an octahedral outer-sphere complex of a transition metal M located at the interface of a negatively charged oxide surface and of an aqueous solution (high pH) and corresponding potential energy diagrams. Adapted from Ref. [9].

and represented (curve Ad) by $-\Delta H_{Ad}$ ranging from a few to a few tens of $kJ \cdot mol^{-1}$. There is no activation energy and the minimum is rather far from the surface. In Fig. 2, the circles around O^- and the $[ML_6]^{2+}$ outersphere complex represent Van der Waals radii.

The curve G corresponds to grafting leading to an inner-sphere complex. It is related to the process:

$$2\,SO^- + [ML_4]^{2+} \rightarrow [ML_4(SO)_2]$$
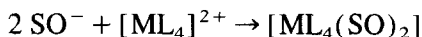
and for this reason, it begins at a height $2E_{M-L}$ above the origin of potential energy corresponding to the following reaction:

$$[ML_6]^{2+} \rightarrow [ML_4]^{2+} + 2L$$
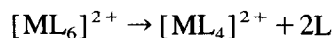
As the $[ML_4]^{2+}$ complex approaches the oxide surface, it becomes stabilized by the formation of

two chemical bonds and the potential energy therefore falls down. The depth of the minimum $-\Delta H_G$ corresponds to the enthalpy of grafting, which lies in the range of chemical bond enthalpies, i.e., a few hundreds of $kJ \cdot mol^{-1}$ and the corresponding distance from the oxide surface is substantially shorter than for the minimum of curve Ad.

The activation energy E_a for grafting arises because both curves intercept above the potential energy zero. Grafting occurs without providing the $[ML_6]^{2+}$ complex the energy $2E_{M-L}$ necessary to break two M–L bonds to produce $[ML_4]^{2+}$ which would require a high temperature. The importance of physical adsorption (curve Ad) is that it allows the $[ML_6]^{2+}$ complex to come close enough to the oxide surface without the need to acquire the energy $2E_{M-L}$; then at the intersection of the curves, the transition from physical adsorption to grafting takes place, which can be represented in this case by the process:

$$2\,SO^- + [ML_6]^{2+} \rightarrow [ML_4(SO)_2] + 2L$$
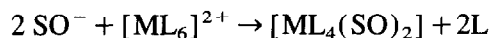
Optical properties – splitting of d orbitals

For oxide-supported TM complexes, the color may be correlated to the structure of the complex. Moreover color changes may be used to probe the outer-sphere/inner-sphere transition as in the case

of silica-supported Ni^{2+} complexes [10] where the samples turn from magenta to light-green upon grafting $[Ni(NH_3)_6]^{2+}$ onto silica and formation of phyllosilicates [11]. The substitution of ammonia ligands by two or several silica surface ligands (SiO^-) decreases the ligand field with a shift of the color to the red.

Classical coordination-chemistry theories may be applied to complexes involving the support as a supermolecular ligand. The electronic spectra of supported TM complexes may be assigned considering the splitting of d orbitals. The grafted *cis*-$[Ni(en)_2(AlO)_2]$ complex was prepared by impregnation of *cis*-$[Ni(en)_2(H_2O)_2]^{2+}$ on γ-alumina [12]. The corresponding Diffuse Reflectance spectrum (DRS) obtained in the UV–visible range is typical of an octahedral Ni^{2+} complex. As expected from the simplified correlation diagram for a d^8 ion subjected to a crystal field of octahedral symmetry (Fig. 3), the DRS exhibits three spin-allowed transitions ν_1, ν_2 and ν_3 respectively located at 965, 600 and 370 nm of which the first one gives the crystal-field strength $\Delta_0 = 10D_q$.

Including oxide surfaces into the ligand spectrochemical series

As the surface may act as a supermolecular ligand, the question arises as to whether it may be
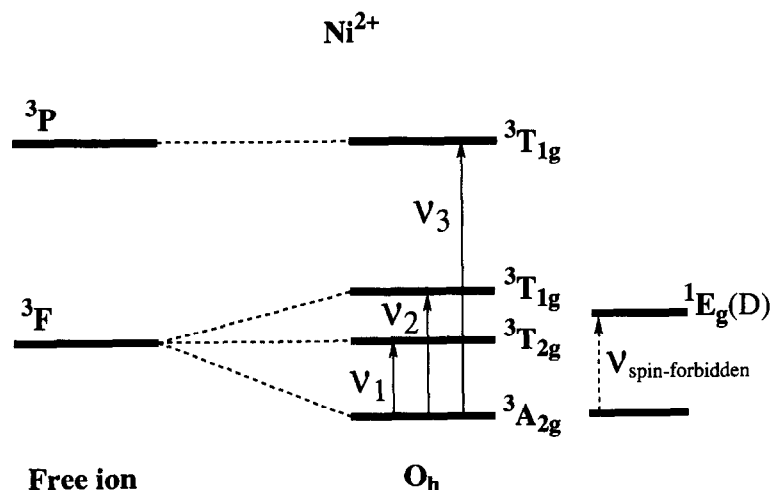

Ni^{2+}

Fig. 3. Simplified correlation diagram between the energy levels of the Ni^{2+} free ion (d^8) and those of the same ion subjected to a crystal field of octahedral symmetry. Solid-line arrows indicate spin-allowed electronic transitions and dotted-line arrows correspond to spin-forbidden ones. From Ref. [4] p. 82.

inserted in the ligand spectrochemical series. This is not an easy task since we are dealing with mixed complexes with different types of ligand (from the liquid and solid phases), and each of them contributes differently to the overall crystal field experienced by the TM ion. Earlier attempts had failed to give conclusions in agreement with theoretical expectations [13].

The problem can however be solved, providing that firstly the surface complexes along the different preparation steps are prepared and identified, and secondly the rule of average environment [14] is applied [10]. This rule applies when the ligands of an octahedral complex are replaced by ligands nearby in the spectrochemical series. In this case, the energies of the levels which originate from the splitting of the octahedral levels are not different enough to cause real splitting of the 'octahedral' bands. According to this rule, the decrease of the crystal-field strength upon substitution of NH_3 by a weaker ligand such as H_2O in the $[Ni(NH_3)_6]^{2+}$ complex is assumed to be a linear function of the number of NH_3 ligands.

Studies of ligand substitution in octahedral Ni^{2+} complexes yield a part of the answer. Bathochromic shifts (i.e., towards lower energies or higher wavelengths) of the DRS absorption bands of the octahedral $[cis\text{-}Ni(en)_2(H_2O)_2]^{2+}$ complex were observed upon impregnation of this complex onto silica and γ-alumina [12], suggesting that both water ligands are replaced by two SiO^- and two AlO^- ligands respectively. Larger shifts observed on γ-alumina relative to silica, favoured the following order of ligand strength:

$$AlO^- < SiO^- < H_2O$$

Another sequence of the series may be obtained from square-planar Pd^{2+} complexes [15]. The bathochromic shifts observed upon adsorption of $[Pd(NH_3)_4]^{2+}$ on silica (SiO^-) [16,17], γ-alumina (AlO^-) [18] or NaY zeolite (ZO^-) [19] (i.e. substitution of two NH_3 ligands by two surface ligands) suggest the following order of ligand field:

$$AlO^- < ZO^- < SiO^- < H_2O < NH_3$$

It may be noticed that as expected, aluminosilicate NaY is a ligand of intermediate strength between alumina and silica.

Finally, Rakai et al. [20] observed a slight hypsochromic shift (i.e., towards higher energies or lower wavelengths) upon grafting $[PdCl_4]^{2-}$ onto alumina, yielding the following spectrochemical series:

$$Cl^- < AlO^- < ZO^- < SiO^- < H_2O$$
$$< NH_3 < en$$

Oxide surfaces may therefore be regarded as weak field ligands in between halides and aqua ligands. The position of oxide surfaces in this spectrochemical series has been explained in terms of their σ-donor and π-donor properties being weaker than those of halides which results in a larger splitting of d orbitals. The d orbitals splitting due to oxide surfaces is nevertheless smaller than that produced by weaker π-donor ligands such as H_2O.

The next step would be to establish a support spectrochemical series including various oxides and sulfides. A better definition of the ligand nature of oxide supports is expected to lead to a better understanding of the redox properties of oxide-supported TM ions, important in reducibility studies and redox catalysis.

EXAFS and thermo-programmed reduction studies have largely confirmed the change of TM ion–support interactions from electrostatic upon adsorption to iono-covalent upon grafting. In the latter case, the supermolecular nature of the oxide support is another aspect of supramolecular chemistry [21].

Nephelauxetic effect

The Racah parameter (B) has been evaluated for several octahedral Ni^{2+} complexes involving molecular or supermolecular ligands. The values are compared in Table 3. B was determined from the DRS absorption bands and the table [22] which gives the ratio D_q/B versus ν_3/ν_1. B is

Table 3

Complex	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	B (cm^{-1})	Ref.
Free Ni^{2+}				1080	[4]
[Ni(en)$_3$]$^{2+}$	855	547	345	812	[4]
cis-[Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$	925	568	355	871	[23]
cis-[Ni(en)$_2$(AlO)$_2$]	965	600	370	836	[12]
[Ni(en)(H$_2$O)$_4$]$^{2+}$	970	616	370	842	[23]
[Ni(CHXN^a)$_2$(H$_2$O)$_2$]$^{2+}$	936	570	360	855	[24]
[Ni(CHXN^a)(H$_2$O)$_4$]$^{2+}$	970	621	370	842	[25]
Ni(CHXN^a)(H$_2$O)$_2$(SiO)$_2$	986	–	389	757	[24]

^{a} CHXN = 1,2-diaminocyclohexane (C$_6$H$_{10}$(NH$_2$)$_2$).

readily obtained since $\nu_1 = \Delta_0 = 10D_q$. This calculation procedure avoids the use of ν_2, the position of which may be perturbed by the proximity of a spin-forbidden transition.

When ethylenediamine is substituted by two water ligands, B increases indicating an increase of the ionicity according to the scale of the ionic nature of the bond:

Ni–en < Ni–H$_2$O
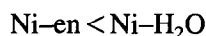
[Ni(CHXN)$_n$(H$_2$O)$_{6-n}$]$^{2+}$ and [Ni(en)$_n$(H$_2$O)$_{6-n}$]$^{2+}$ ($n = 2$ or 4) have very close B values indicating that the ionicity of Ni–CHXN and Ni–en bond are very similar. The size of the alkyl chain does not seem to have an influence on the interelectron repulsion.

By contrast, B decreases upon substitution of one CHXN ligand by two water ligands. Moreover, B decreases although it was expected to increase upon substitution of H$_2$O by AlO$^-$ or upon substitution of CHXN by SiO$^-$ as the following ionic bond order was expected:

Ni–CHXN ≈ Ni–en < Ni–H$_2$O

< Ni–OSi < Ni–OAl
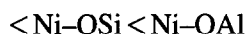
These unexpected results may indicate substantially distorted octahedral geometries in the corresponding complexes. The electronic levels (absorption bands) are therefore shifted and the determination of B, valid for a given high symmetry, is no longer rigorous.

Magnetic properties

In zeolite CoY, upon introduction of acetonitrile (strong field ligand), the low-spin octahedral complex [Co^{II}(CNCH$_3$)$_6$]$^{2+}$ ($S = 1/2$) is formed and unambiguously characterized by electron paramagnetic resonance (EPR) [26] through the hyperfine structure (due to the interaction of the unpaired electron with the nuclear spin $I = 7/2$ of ^{59}Co) and the absence of fine structure ($S = 1/2$). This is an example of outer-sphere complex in which the zeolitic framework is acting as counter-anion.

A high-spin Fe^{II} complex with nitric oxide was observed in Y zeolite [26]. The EPR spectrum is typical of an ion in $S = 3/2$ and $M_s = \pm 1/2$ spin state with a zero field splitting D $\gg h\nu$. The axial g tensor ($g_\perp = 4.07$ and $g_\parallel = 2.003$) could be assigned either to [Fe^{III}(NO$^-$)]$^{2+}$ or [Fe^I(NO)$^+$)]$^{2+}$ with three unpaired electrons. The reduction of the iron ion by nitric oxide being evidenced by IR spectroscopy, the EPR signal was therefore associated to the high-spin [Fe^I(NO)$^+$)]$^{2+}$ complex.

Chelate effect

The surface may act as a monodentate or polydentate ligand.

Upon grafting of trans-[Co(en)$_2$Cl$_2$]$^+$ on silica, the formation of the surface trans-[Co(en)$_2$Cl(SiO)]$^+$ complex was observed [27] with the silica surface acting as a monodentate supermolecular ligand.

When acting as a chelating bidentate ligand, silica has a ligand behaviour very close to that of the oxalate (C$_2$O$_4$)$^{2-}$ ligand [28]. The grafting reaction of cis-[Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$ onto silica (reaction 4) is an entropy-driven reaction like reaction 3 (Section 2, subheading: *Chelate effect*). The enthalpy variation upon substitution of two water ligands by two SiO$^-$ ligands is very small, since the donor atom (oxygen) is the same in both cases. The driving force of the substitution is the entropy increase upon replacement of two monodentate water ligands by the bidentate supermolecular silica ligand:

$$2\,SiO^- + cis\text{-}[Ni(en)_2(H_2O)_2]^{2+} \rightleftharpoons$$

$$cis\text{-}[Ni(en)(\equiv SiO)_2] + 2\,H_2O \quad (4)$$
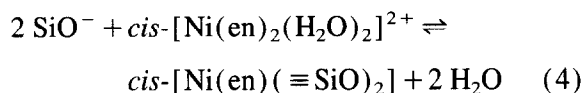
The unsaturated $(O)_3Ni^{II}$ complex, involving a tridentate supermolecular silica ligand through three of its surface oxygen atoms, which can be produced upon thermal treatment of a surface octahedral complex such as $[Ni(NH_3)_2(H_2O)_2(SiO)_2]$ or $cis\text{-}[Ni(en)_2(SiO)_2]$, has been characterized by diffuse reflectance spectroscopy [29] and EXAFS [30].

Hapticity

As in classical coordination chemistry, benzene exhibits several modes of coordination to oxide-supported TM ions. For instance, η^6-complexes were characterized with alkali metal ions in zeolites [31].

Silica-supported Ni^I–dihapto(η^2)benzene complexes have been recently observed in our laboratory [32]. In these complexes, Ni^I interacts with only two carbon atoms of the benzene ring as shown by infrared spectroscopy. The bathochromic shift ($-20\;cm^{-1}$) of the C–C stretching vibration relative to the free C_6H_6 molecule is consistent with a ring–edge bound complex [33]. Unlike η^6-arene complexes, this lower coordination mode of benzene is not very common, although it was already observed in solution for Cu^{II}, Ag^I or Os^{II} complexes [33,34].

Extended Hückel and ab initio calculations based on the density functional theory were carried out onto the model complexes [(benzene)$Ni^I(OH)_3]^{2-}$ and [(benzene)$Ni^I(OH)(OH_2)_2$] in order to investigate the bonding mode of benzene to silica-supported Ni^I ions. In these model complexes, the contribution of the silica support is restricted to hydroxyl groups or water molecules. Both calculation methods agree in predicting an η^2-coordination of benzene. Moreover, the calculations allow a better geometrical description of the stable dihaptobenzene complexes. The discussion of the calculations in terms of molecular orbitals interaction, allows to understand the factors responsible for the low coordination mode of benzene.

3.2. Specific features of ICC

We described above how the experimental results of classical coordination chemistry could find their analogues in ICC. The latter has however its specificities with no equivalence in solution coordination chemistry as illustrated hereafter.

Solid–liquid interface

This type of interface is used most generally in catalyst preparation. As already mentioned above, the initial interaction of the TM complex with the surface is often created by electrostatic adsorption. Upon grafting, mixed ligand complexes involving both mobile ligands from the solution (generally ligands are hard in the Pearson's classification in conventional catalyst preparation methods using aqueous solutions) and rigid supermolecular oxide surface ligand are formed. The latter may be mono- or polydentate. When acting as a bidentate ligand, the surface is chelating and cis complexes are generally favoured. Tridentate supermolecular ligands, leading to fac isomers, may be envisaged as well.

Solid–gas interface after thermal treatment and/or evacuation

Using suitable thermal treatments, it is possible to generate on the surface low symmetry complexes and coordination vacancies. This is a unique property since the reactivity of such vacancies toward ligand addition/substitution is the driving force for the adsorption of probes or reactants and catalysis on surface TM complexes. By contrast, coordination vacancies are difficult to create at the solid–liquid interface as the solvent generally fills in the insaturations.

For example, using a suitable thermal treatment, it was possible to prepare isolated three-coordinated $Ni^{2+}(O)_3$ ions supported on silica [29], alumina [35] and A zeolite [36]. They were characterized by diffuse reflectance spectroscopy in the UV–visible range and EXAFS [30]. They have no analogue in solution. Similarly, by grafting of chromic acid on silicalite followed by thermal reduction by CO, Spoto et al.

[37] were able to prepare and characterize isolated three-coordinated $Cr^{2+}(O)_3$ ions.

Upon evacuation at an appropriate temperature, the framework of faujasite-type zeolite may act as a bi- or tri- or even hexadentate supermolecular ligand depending on the zeolitic site [38] where the metallic cation is located. The TM cation lying in S_I site (hexagonal prism) is surrounded by an octahedron of oxygen atoms from the supermolecular hexadentate zeolite ligand.

The supermolecular ligand may play a major role in inhibiting the aggregation of complexes that would be otherwise observed in solution. Species in unusual oxidation state such as Ni^I [29] or Cu^I [39] may be stabilized on a support such as silica, the supermolecular ligand avoiding dismutation reactions which would occur easily in solution.

Solid–gas interface after adsorption

After thermal treatments, low symmetry complexes with coordination vacancies are obtained. Upon gas adsorption, again mixed ligand complexes involving both mobile ligands from the gas phase and the rigid supermolecular ligand from the solid support oxide are obtained. The affinity of the metallic center to gas phase ligands is due to the thermodynamically favoured process of bond formation. In some cases, bonds are lost between the metal center and the oxide surface. Nevertheless at least one bond with the surface is maintained. This can be illustrated in the series $Ni^I(CO)_n(O)_p$ where O stands for a silica surface oxygen atom ($1 \leq n \leq 4$ and $1 \leq p \leq 3$) characterized using EPR [40]. CO addition and/or CO/O substitution are observed upon increasing the CO pressure. Similarly, using EPR, it was shown that four-coordinate silica-supported Mo^{5+} ions may add one or two water molecules to yield the corresponding five- and six-coordinate mixed ligand inner-sphere complexes [41].

Finally, whatever the nature of the interface, it is important to note that the oxide surface is also a polyligand, since many TM complexes may be grafted simultaneously, in contrast to what can be observed in classical coordination chemistry.

In this study, the supermolecular ligand is limited to SO^- (negatively charged surface), SOH or SOH_2^+ (positively charged surface) surface species. These species are weak σ-donor/π-donor (SO^-, SOH) or σ-donor only (SOH_2^+) ligands and lead to high-spin complexes. The reactivity of the corresponding complexes and their applications described in the next section, will therefore depend on the properties of the supermolecular ligand as described in Table 1.

4. Applications

As shown in Table 1, ICC deals mainly with transition metal ions in high oxidation state coordinated to hard σ donor–π donor ligands or σ donor only ligands. The metal–ligand interaction is mostly ionic and the ligands are only slightly perturbed. Consequently, ICC may be applied to catalyst preparation and selective ion adsorption as it is illustrated hereafter.

4.1. Catalyst preparation

The first step in the preparation of heterogeneous catalysts generally consists in creating an interaction between the active site precursor (a TM complex for example) and the support. The strength of the so-created ion support interaction (ISI) is expected to greatly influence the following steps of the preparation and the final state of the catalyst.

Weak ISI's include physically adsorbed complexes on a surface, hydrogen-bonded complexes or adsorbed complexes on a charged surface (outer-sphere complexes). The mobility and aggregation of such weakly interacting species is possible and often observed during the following steps of the preparation.

By contrast, in inner-sphere complexes, there is a strong (iono-covalent) bond between the metal ion and the support (supermolecular ligand). These strong ISI are expected to lead to a better stabilization of the active species.

Isolated supported ions, either electrostatically adsorbed, H-bonded or involved in inner-sphere complexes may be described in the context of ICC. For supported polynuclear species, supported oxides or intermediate compounds such as phyllosilicates, the ISI becomes more complex and may be described in the context of supported solid state chemistry.

One may take advantage of the variety of ISI's to prepare catalysts. For example, depending on the nature (chelate or not) of the ligand present in the coordination sphere of Ni^{2+} during competitive cationic exchange at high pH, one may deposit respectively isolated complexes on the silica support (the latter acts then as a supermolecular ligand) or obtain phyllosilicates (the support acting here as a reactant) [11,30,42].

ISI's are also involved in metal–support interaction and can be used as a chemical glue to stabilize and promote supported metal particles as illustrated in the next section.

4.2. Nucleation and particle growth

A two-step method for the preparation of metal particles of controlled size, with the obtention of decreasing particle size for increasing metal content was recently reported in the case of the Ni/SiO$_2$ [43]. Nickel in strong interaction with the support (phyllosilicate or grafted Ni) is produced first, then nickel in weak interaction is introduced by impregnation. Nickel ions in strong interaction with the support act as nucleation sites for the particle growth arising from Ni ions in weak interaction. The lower the concentration of nucleation sites, the larger the Ni particle size (Fig. 4).

4.3. Selective ion adsorption

Interaction of Cu^{II} in the aqueous phase with pillared clays obtained from natural or synthetic saponite was studied using adsorption measurements and electron paramagnetic resonance [44]. It was shown that the formation of inner-sphere complexes between copper ions and the surface ligand is preferred over ion-exchange or copper
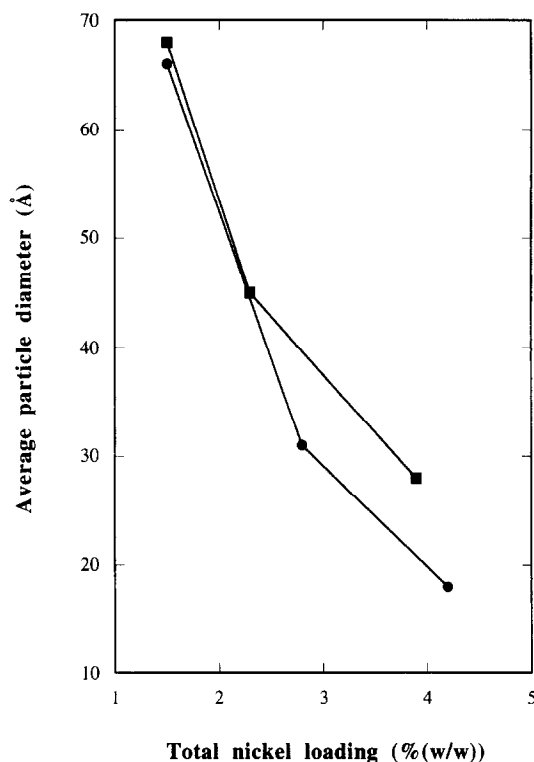

Fig. 4. Average diameter of metal particles versus the total nickel loading for a given amount of nickel and an increasing loading in nickel nuclei: (a) impregnated nickel nitrate (1.5% (w/w)) over isolated ex-Ni^{II}(en)$_2$(O)$_2$ supported on silica, (b) impregnated nickel nitrate (1.5% (w/w)) over phyllosilicates. From Ref. [43].

hydroxide precipitation. Since the formation of inner-sphere complexes is more efficient than ion exchange, the applications of such materials for the fixation of heavy metals during soil depollution is very promising. The same results have been obtained for the interaction of Cd^{II} with pillared clays [45].

4.4. Catalysis

As discussed in the introduction of this paper, transition-metal chemistry can be subdivided into two main fields: ICC and SOMC. In Pearson's classification, hard ligands (hard bases) form more stable complexes with TM ions in high oxidation state (hard acids). The behaviour of such complexes can be described by means of ICC concepts (Table 1). Soft ligands (soft bases) give more stable complexes with TM ions in low oxidation state. The behaviour of such complexes can

be discussed in the context of SOMC (Table 1).

Soft ligands because of their high polarisability may be strongly perturbed upon bonding to soft TM ions. SOMC is thus directly concerned with catalysis. This is illustrated by the example of olefin dimerization catalyzed by supported nickel complexes, given below. Because of their low polarisability, hard ligands are only slightly perturbed upon bonding to hard TM ions. ICC is thus not directly concerned with catalysis. TM ions in high oxidation state do nevertheless participate in certain catalytic reactions such as the selective oxidation of hydrocarbons. When this is the case, TM ions are assisted by oxygen ions (for instance O^- and O^{2-} species). The example of methanol oxidation catalyzed by supported molybdenum catalysts will illustrate this type of redox catalysis.

Olefin dimerization

Well-defined trialkylphosphine (TAP) Ni^I complexes supported on silica have been prepared [46] and fully characterized using a combination of spectroscopic techniques. $(O)_2Ni^I(PR_3)$ (where O stands for a silica surface oxygen atom and R = Me, Et, c-C_6H_{11}(cy) or phenyl) have been shown to be active in ethylene and propylene dimerization and a concerted-coupling mechanism has been proposed [47,48] (Fig. 5).

The catalytic properties depend on (or may be controlled by) the ligands present in the Ni^I coor-

dination sphere. The stability and selectivity for α-olefins of the catalyst increase with the electron-donating properties of the TAP ligand. Among the TAP ligands we used, tricyclohexylphosphine (Pcy$_3$) lead to the most stable catalyst with the best selectivity for α-hexenes [48]. The distribution of the reaction products depends on the bulkiness (cone angle) of the TAP. The presence of Pcy$_3$ in the coordination sphere of Ni^I favours the formation of branched dimers over linear ones [48].

The concerted-coupling mechanism involving the interconversion of 15 and $17e^-$ species (Fig. 5), was recently confirmed by computer simulation of the conversion–time profile [49]. Kinetic parameters such as rate constant (k), equilibrium constant of formation of the metallacycle (K) and rate constant of deactivation (k_p) have been evaluated.

Methanol oxidation

Catalytic oxidation of methanol is a versatile probe network reaction. It allows the simultaneous identification of surface redox and acid properties. It is structure sensitive, i.e., the distinction between crystal planes exposed can be made. It is dispersion sensitive since the selectivity of isolated and clustered active centers is different [50].

Objectives to be met are to determine the elementary steps of the reaction at the molecular level
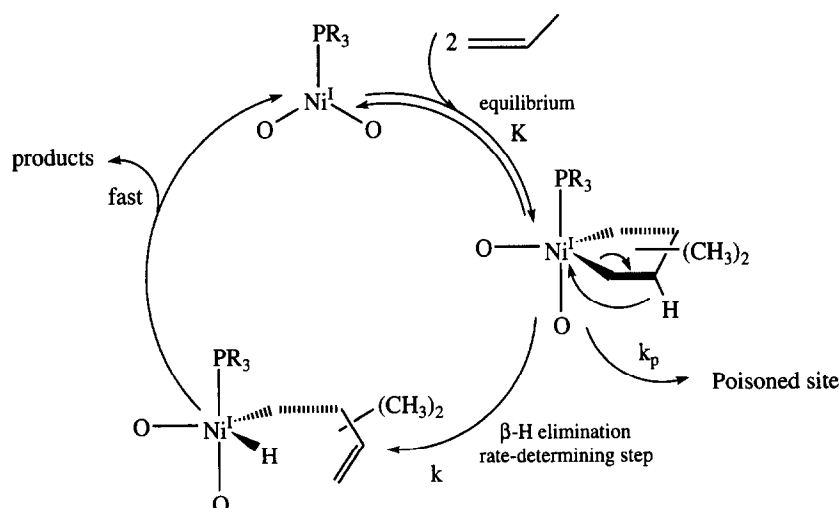

Fig. 5. Catalytic cycle proposed for propylene dimerization over $(O)_2Ni^I(Pcy_3)$ catalysts. From Refs. [48] and [49].

and to obtain evidence for the migration of surface intermediates.

A new approach has been proposed recently [51] and cycles of model reactions between methanol and in situ generated O^- species, both adsorbed on the surface of grafted Mo/SiO_2 catalysts have been studied by EPR. The O^- species was used to bypass the rate-determining step, i.e., the abstraction of methyl hydrogen, in order to investigate the subsequent steps of the process. This study has shown that the reaction takes place within the inner-sphere of isolated coordinatively unsaturated Mo^{5+}/Mo^{6+} redox couples as the reaction active centers. The following elementary steps have been evidenced:

1. ligand to ligand hydrogen transfer and proton transfer
2. ligand to metal electron transfer
3. migration of $\cdot CH_2OH$ intermediates. The latter provide a reasonable explanation for the dispersion sensitivity of methanol oxidation.

Other examples

Other examples of heterogeneous catalysis involving inner-sphere complexes are presented hereafter.

Recently, Kazansky et al. [52] prepared a silica-supported Mo–carbene ($Mo=CH_2$) by interaction of cyclopropane with low coordinated Mo^{4+} ions in photoreduced Mo/SiO_2 catalysts. They were the first to isolate and characterize a supported carbene. Carbene species have been proposed as the active site of olefin metathesis especially from homogeneous catalysis studies. The preparation of the supported carbene results in a sharp increase of the specific activity of the silica–molybdena catalyst. IR data show fast reversible transformation of $Mo=CH_2$ to $Mo=CH-CH_3$ thus providing the first direct spectroscopic confirmation of a chain carbene mechanism of propene metathesis.

Anpo et al. [53] prepared well-defined Cu^+ complexes anchored to silica or ZSM5. The EPR, IR and photoluminescence results suggest that these complexes play a significant role as active

species in the photocatalytic decomposition of NO into N_2 and O_2.

Cr^{2+} ions grafted to amorphous silica or the internal surface of silicalite have been shown to polymerize ethylene giving rise to living $(CH_2)_n$ polymer [54]. On $Cr^{2+}/silicalite$, the limited pore size depresses the growth of the polymeric chain, thus allowing a more accurate study of the initiation step using IR spectroscopy. It is confirmed that no methyl groups are formed during the initiation step.

5. Conclusion

In the present review, interfacial coordination chemistry (ICC) and surface organometallic chemistry (SOMC) have been first defined and their main characteristics given. After a brief recall of the experimental results and theories of classical coordination chemistry, the current status of ICC was presented, starting with the application of the concepts of classical coordination chemistry to TM complexes interacting with solid–liquid and solid–gas interfaces. This was made possible, using TM ions as probes of their own interactions with oxide surfaces onto which they are deposited when supported catalysts are prepared. Oxide surfaces were shown to act as supermolecular mono- or polydentate ligands. It was possible to include them in the ligand spectrochemical series as weak σ-donor and π-donor ligands and to propose the beginning of a support spectrochemical series. Several aspects were then considered such as nephelauxetic effect, magnetic properties, chelate effect and hapticity. The specific features of ICC were summarized before a few typical applications of ICC to catalysts preparation, adsorption and relations to catalysis were discussed.

Acknowledgements

References

[1] R.A. Van Santen, Theoretical Heterogeneous Catalysis, World Scientific, Singapore, 1991, p. 1.

[2] For a review see, for instance: K.F. Purcell and J.C. Kotz, Inorganic Chemistry, 2nd Ed., Saunders, Philadelphia, 1991; F.A. Cotton, G. Wilkinson and P.L. Gauss, Basic Inorganic Chemistry, 3rd Ed., John Wiley, New York, 1995; F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 5th Ed., John Wiley, New York, (1988); J.E. Huheey, Inorganic Chemistry, Principles of Structure and Reactivity, 4th Ed., Harper Collins, New York, 1993; N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1987.

[3] K. Fajans, Naturwissenschaften, 11 (1923) 165.

[4] A.B.P. Lever, Inorganic Electronic Spectroscopy, Studies Phys. Theor. Chem., Vol. 33, 2nd Ed., Elsevier, Amsterdam, 1984.

[5] C.K. Jørgensen, Oxidation Numbers and Oxidation States, Springer, New York, 1969, p. 106.

[6] F.A. Cotton, J. Am. Chem. Soc., 90 (1968) 6230.

[7] E. Maslowsky, Jr., J. Chem. Ed., 70 (1993) 980.

[8] W. Stumm, Chemistry of the Solid–Water Interface, Wiley, New York, 1992, p. 21.

[9] M. Che and Y.G. Shul, Science and Technology in Catalysis, Kodansha, Tokyo, 1995, p. 21.

[10] L. Bonneviot, O. Legendre, M. Kermarec, D. Olivier and M. Che, J. Colloids Interf. Sci., 134 (1990) 534.

[11] M. Kermarec, J.Y. Carriat, P. Burattin, M. Che and A. Decarreau, J. Phys. Chem., 98 (1994) 12008.

[12] M. Hoogland, J.F. Lambert and M. Che, to be published.

[13] M.B. McBride, Adv. Soil Sci., 10 (1989) 1.

[14] C.K. Jørgensen, Acta Chem. Scand., 10 (1956) 887; Struct. Bonding, 1 (1966) 234.

[15] J.F. Lambert and M. Che, to be published.

[16] M. Bouchemoua, Thèse de 3ème Cycle, Université P. et M. Curie, Paris VI, (1986).

[17] W. Zou and R.D. Gonzalez, Catal. Lett., 12 (1992) 73.

[18] F. Devisse, Thèse de Doctorat, Université P. et M. Curie, Paris VI, (1994).

[19] Z.C. Zhang, W.M.H. Sachtler and H.Y. Chen, Zeolites, 10 (1990) 784.

[20] A. Rakai, Thèse de Doctorat, Université P. et M. Curie, Paris VI, (1989).

[21] J.M. Lehn, Supramolecular Chemistry, Concepts and Perspectives, VCH, Weinheim, 1995.

[22] Ref. [4], p. 507 and 738.

[23] D.L. Leussing, J. Phys. Chem., 66 (1962) 1544.

[24] T. Setoyama and M. Che, to be published.

[25] D.L. Leussing, Inorg. Chem., 2 (1963) 77.

[26] J.H. Lunsford, Magn. Reson. Colloids Interf. Sci., 61 (1980) 67.

[27] R.L. Burwell, Jr, R.G. Pearson, G.L. Haller, P.J. Tjok and S.P. Chock, Inorg. Chem., (1965) 1123.

[28] M. Che, Proc. 10th Int. Congr. Catal., Budapest, Hungary, 1992, A, 1993, p. 31.

[29] D. Olivier, L. Bonneviot, F.X. Cai, M. Che, M., P. Gihr, M. Kermarec, C. Lepetit-Pourcelot and B. Morin, Bull. Soc. Chim. Fr., 3 (1985) 370.

[30] J.Y. Carriat, Thèse de Doctorat, Université P. et M. Curie, Paris VI, (1994) p. 37.

[31] A. de Mallmann and D. Barthomeuf, Zeolites, 8 (1988) 292.

[32] C. Lepetit, M. Kermarec, M. Che and J.M. Thomas, Colloids Surf., A 72 (1993) 265.

[33] (a) T.J. Pinnavaia and M.M. Mortland, J. Phys. Chem., 75 (1971) 3957. (b) W.D. Harman and H. Taube, J. Am. Chem. Soc., 109 (1987) 1883.

[34] R.W. Turner and E.L. Amma, J. Am. Chem. Soc., 88 (1966) 1877.

[35] D. Cornet, J.F. Hemidy and C. Mariette, N.J. Chim., 8 (1984) 159.

[36] K. Klier and M. Ralek, J. Phys. Chem. Solids, 29 (1968) 951.

[37] G. Spoto, S. Bordiga, E. Garrone, G. Ghiotti and A. Zecchina, J. Mol. Catal., 74 (1992) 175.

[38] D.W. Breck, J. Chem. Educ., 41 (1964) 678.

[39] M. Amara, M. Bettahar, L. Gengembre and D. Olivier, Appl. Catal., 35 (1987) 153.

[40] L. Bonneviot, D. Olivier and M. Che, J. Mol. Catal., 21 (1983) 415.

[41] C. Louis and M. Che, J. Phys. Chem., 91 (1987) 2876.

[42] L. Bonneviot, O. Clause, M. Che, A. Manceau and H. Dexpert, Catal. Today, 6 (1989) 39.

[43] M. Che, Z.X. Cheng and C. Louis, J. Am. Chem. Soc., 117 (1995) 2008.

[44] L. Bergaoui, J.F. Lambert, H. Suquet and M. Che, J. Phys. Chem., 99 (1995) 2155.

[45] L. Bergaoui, J.F. Lambert, H. Suquet and M. Che, J. Chim. Phys., 92 (1995) 1486.

[46] C. Lepetit, M. Kermarec and D. Olivier, J. Mol. Catal., 51 (1989) 73.

[47] F.X. Cai, C. Lepetit, M. Kermarec and D. Olivier, J. Mol. Catal., 43 (1987) 93.

[48] C. Lepetit, M. Kermarec and D. Olivier, J. Mol. Catal., 51 (1989) 95.

[49] C. Lepetit, J.Y. Carriat and C. Bennett, Appl. Catal. A, 123 (1995) 289.

[50] J.M. Tatibouet, Catal. Rev., to be published.

[51] Z. Sojka and Che, J. Phys. Chem., 99 (1995) 5418.

[52] V.B. Kazansky and B.N. Shelimov, Res. Chem. Interm., 15 (1991) 1.

[53] M. Anpo, M. Matsuoka, Y. Shioya, H. Yamashita, E. Giamello, C. Morterra, M. Che, H.H. Patterson, S. Webber, S. Ouellette and M.A. Fox, J. Phys. Chem., 98 (1994) 5744.

[54] A. Zecchina, G. Spoto, G. Ghiotti and E. Garrone, J. Mol. Catal., 86 (1994) 423.