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Eric Marceau, Laurent Bonneviot, Stanislaw Dzwigaj, Jean-François Lambert, Catherine Louis, et al.. Interfacial Coordination Chemistry for Catalyst Preparation. *Journal of Catalysis*, 2021, 396, pp.104-121. 10.1016/j.jcat.2021.02.002 . hal-03279134

HAL Id: hal-03279134

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Submitted on 6 Jul 2021

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Interfacial Coordination Chemistry for Catalyst Preparation

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Abstract

The concept of interfacial coordination chemistry was one of the innovation for which Michel Che became internationally known during his tenure as full professor at the Université Pierre et Marie Curie. Isolated metal ions on oxide surfaces behave like coordination compounds to which the surface contributes not only via neutral oxo bridges but also via hydroxyl groups. The latter being pH sensitive, the surface can be charged either positively or negatively, allowing selective adsorption of transition metal ions of opposite charge. In the early eighties, examples exploiting these properties for the preparation of oxide/metal supported catalysts were still rare. This review presents Michel Che's early studies, mostly on molybdenum and nickel ions, on which he built, developed and promoted the concept of interfacial coordination chemistry, now widely used in the field of heterogeneous catalysis. This allowed him and his close collaborators to achieve a molecular-scale understanding of several catalyst preparation procedures, such as impregnation, selective adsorption, grafting, deposition-precipitation, and zeolite functionalization. The impact and legacy of the concept of Interfacial Coordination Chemistry on the current design of improved catalytic formulations is also reviewed.

1. Introduction

In the preparation of heterogeneous catalysts, chemistry takes place at the interface between two phases, the most important ones being the liquid-solid and the gas-solid interfaces. It is now difficult to realize how little was known on this chemistry more than forty years ago, when Michel Che started his scientific career as full professor at the Université Pierre et Marie Curie (now Sorbonne Université), at a time when papers on heterogeneous catalysis were mostly rooted in kinetics and physical characterizations, with concepts such as "demanding reactions" developed by Michel Boudart [1]. In contrast, coordination, supramolecular and solid state chemistry were already flourishing fields for which structure-properties correlations at the atomic or molecular level were a prerequisite for publication. The most advanced exploration of heterogeneous catalysis at the molecular level was coming from metal ion-exchanged zeolites. One may cite the emblematic reaction of single electron oxidation by dioxygen of $[\text{Co}(\text{NH}_3)_6]^{2+}$ ion exchanged in Y zeolite, leading to the $[\text{Co}(\text{NH}_3)_n(\text{O}_2^-)]^{2+}$ superoxo complex characterized by Electronic Paramagnetic Resonances (EPR) by Vansant and Lunsford [2]. To our knowledge, the first papers among the very few ones on catalyst design that took advantage of the coordination chemistry concept of "crystal field theory" was published in the sixties by Burwell *et al.*, on cobalt adsorbed on silica [3]. This paper proposed the " $\equiv\text{SiOH}$ and $\equiv\text{SiO}^-$ " writings for the surface silanol and silanolate entities entering the coordination sphere of cobalt as ligands. It has to be noted that at the same time, parallel developments were also occurring in the field of geochemistry, where concepts of molecular inorganic chemistry, such as inner-sphere and outer-sphere complexes were also used for describing surface adsorption [4].

Coming from the famous *Institut de Recherches sur la Catalyse* in Lyon (IRC, now IRCELYON) with a strong background in EPR applied to transition metal ions (TMI), Michel Che naturally developed an interest in the description of the chemistry of supported metal ions at the molecular level, first focusing on $S = 1/2$ ions, Mo^{5+} (d^1) as a defect in bulk oxides or supported on oxides (section 2), as well as Ni^+ (d^9), known to be generated on nickel-exchanged X and Y zeolites in soft reduction conditions (section 3). His first mini-reviews on coordination chemistry of TMI appeared in the mid-eighties, indeed centered on the use of EPR, showing how g and A tensors can help to determine the coordination number and the symmetry of the metal complex, and the denticity of the support, then considered as a flexidentate macroligand leading to the first version of Fig. 1 [5-7] which was refined afterwards [8].

Michel Che, as a skilled spectroscopist, would soon resort to other techniques to characterize precursor ions which are often non-EPR active. Diffuse reflectance UV-visible-NIR spectroscopy was one of them, allowing one for the first time to position surface groups (*i.e.*, silanolates) in the spectrochemical series, as would be done for any classical inorganic ligand [9]. Extended X-ray

Absorption Fine Structure (EXAFS), then a pioneering technique for the characterization of poorly organized materials, gave the first direct proof of metal grafting (i.e., inner-sphere coordination complex formation with surface groups) with the determination of a metal-Si distance in the Ni-O-Si bridges from $[\text{Ni}(\text{en})(\equiv\text{SiO})_2]$ [10]. This first step towards the full molecular description of the coordination of a transition metal complex (TMC), paving the way to the optimization of catalysts preparation by impregnation, selective adsorption, grafting, deposition-precipitation or zeolite functionalization, was followed by a series of thorough investigations on Ni^{2+} ions deposited on different supports and on Pt complexes, evidencing a strong dependence of their chemistry on the presence of chloride ions (sections 4 and 5).

Based on this molecular approach and the integration of concepts of inorganic chemistry to surface adsorption phenomena, Michel Che introduced the notion of Interfacial Coordination Chemistry (ICC) in order to rationalize the various roles of the oxide support upon TMC deposition as well as the nature of ion-support interactions (Figure 1) [8, 11]. In parallel, surface modification using organometallic (π -allyl) complexes was initiated by Yermakov in the early seventies [12]. It was followed by B.C. Gates [13] in the USA and J.M. Basset [14] in France and later by J.M. Thomas [15] mostly considering carbonyl clusters and catalytic applications in a field that will be denoted Surface Organometallic Chemistry (SOMC). Nonetheless, the direct evidence of a metal-support covalent bonding from SOMC came much later with grafted mononuclear pentadienylzirconium [16] and bis(ethylene)rhodium complexes [17]. Both approaches are based on the concept of molecular inorganic chemistry but they mainly differ in the type of catalytic precursors used and the nature of the solvent: mainly organometallic complexes in organic solvent for SOMC and conventional (mostly commercial) TMC soluble in water for ICC. Table 1 is comparing these two fields. Their common scope is to investigate the chemistry of TMCs at oxide support for designing better metal supported heterogeneous catalysts. However, ICC and SOMC differ in their perspective: ICC targets a molecular investigation of the surface interaction of high oxidation state TMC from conventional precursors in order to describe their evolution upon thermal treatments while SOMC is based on the grafting of low oxidation state well-defined organometallic complexes in order to take advantage of their formerly established nuclearity and reactivity.

In 1992 came a major recognition from the catalysis community, as Michel Che was invited to give a plenary lecture at the 10th International Congress on Catalysis held in Budapest: "Interfacial coordination chemistry: concepts and relevance to catalysis phenomena" [8].

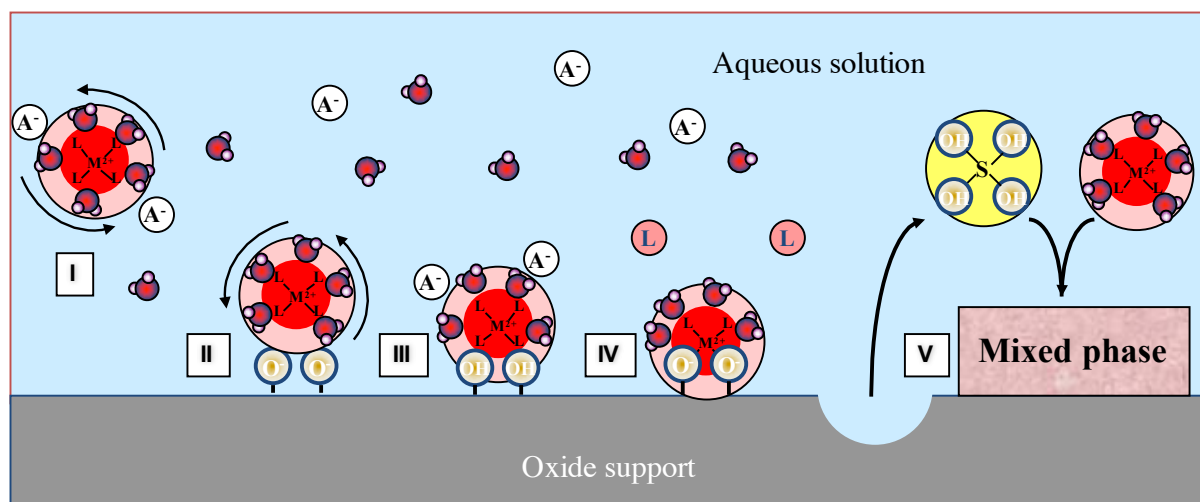


Figure 1 : Schematic representation of the different speciations of transition metal complexes (TMC) at the liquid-solid interface during metal ion deposition involved in heterogeneous catalyst preparation : I) in free rotation without interaction with the surface like in bulk water; II) in mere electrostatic interaction as $\{[M(L)_n]^{m+}, pSO^-\}^{(m-p)+}$ where SO stands for surface hydroxylate groups ($\equiv SiO^-$, silanolate for silica) - note that, for the sake of simplicity, the scheme refers to the case of $n = 4$ (neutral ligands such as NH_3), $m = p = 2$, avoiding remaining counter ion other than the support itself; III) outer-sphere surface complex with H-bonding or van der Waals interaction with surface hydroxyl groups ($\equiv SiOH$, silanol for silica supports); IV) inner-sphere surface complex grafted through one or several support hydroxylates forming for instance the $[M(L)_2(SO)_2]$ neutral surface TMC (see simplification explained in case II); finally, the metal ion can be embedded in mixed phases formed by partial dissolution of the support represented by position V.

Along these decisive steps concerning supported TMC, it rapidly appeared that some experimental conditions (and not necessarily harsh ones) could trigger a partial dissolution of the support followed by a surface re-construction as mixed bulk or molecular phases (Fig. 1). This eventuality, largely ignored at that time, was indeed a critical point as it appeared that some supported TMC were rendered much less accessible and less reducible in these mixed phases than grafted ones (section 6).

Then, coming back to zeolites, the application of Interfacial coordination chemistry concepts led to the design of metal single-sites at framework positions. Indeed, lodging metal ions in the framework position of a zeolite structure was a challenge for most of TMI, vanadium being one of the most difficult case to solve. A successful approach was developed, choosing beta zeolite as a rather open structure, and taking into account the speciation that takes place both in vanadium solution and during aluminum extraction in each of the two post-synthesis treatments needed. This technique developed for vanadium and reported in section 7 was found easily adaptable to many other TMI.

The different parts developed below focus on the chemical concepts that are useful to the preparation of heterogeneous catalysts, showing how much Michel Che's prolific work contributed to a field that

was rather marginal at the beginning of his career. The concept of Interfacial Coordination Chemistry, that Michel Che and the team of researchers that he gathered around him, have developed and perfected along four decades, has been a major step forward to reach a scientific design of heterogeneous catalysts through a molecular control of the nature and the structure of active sites.

<i>Acronym</i>	ICC	SOMC
<i>Name</i>	Interfacial Coordination Chemistry	Surface OrganoMetallic Chemistry
<i>Precursors</i>	Transition metal complexes	Organometallic complexes
<i>Oxidation state</i>	High	Low
<i>Ligand hardness Examples^a</i>	Hard (Pearson) Cl ⁻ , SO ⁻ , SOH, SOH ₂ ⁺ , H ₂ O, NH ₃ , Amines, Polyamines	Soft (Pearson) CO, PR ₃ , Cp, Carbene, Organic ligands
<i>M-L interaction</i>	More ionic	More covalent
<i>Models</i>	Crystal field, molecular orbitals	Molecular orbitals
<i>Stability & reactivity</i>		18 and 18/16 e ⁻ Green rules
<i>Historical tools of characterization^b</i>	EPR, UV-visible	Solid state NMR
<i>Conventional deposition process Solvents</i>	Ion exchange, impregnation, deposition-precipitation.... Water, ethanol, polar solvents	CVD, Impregnation Organic solvents
<i>Air sensitivity</i>	Weak or none (air exposed chemistry and storage)	Strong (storage in leak tight vessels under controlled atmosphere)
<i>Applications</i>	Industrial catalysts design at large scale	Model catalysts Mechanistic studies Determination of effective catalytic metal centers

a) S stands for the ligand provided from the support (Si, Al, Ti, etc...), typically surface hydroxyl groups.

b) First-row transition metals of interest at the beginning of ICC are paramagnetic, rendering the NMR spectroscopy not applicable (see the nice exception of the platinum NMR investigation of part 4). The other techniques are not cited as being not specific to ICC nor to SOMC. Recent techniques are listed in part 8.

Table 1 : Comparison of the most representative characteristics of Interfacial Coordination Chemistry (ICC) and Surface Organometallic Chemistry (SOMC).

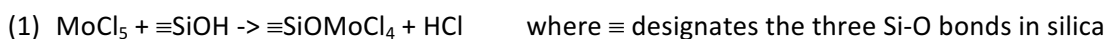
All the ICC concepts detailed below blazed new trails toward improved preparation routes of supported metal catalysts based on the concepts of coordination chemistry. Among the research groups especially active in this research axis at the international level, one can quote the Utrecht group in the Netherlands with John W. Geus, K. de Jong, P. de Jongh [18] and B. Weckhuysen [19], the group of J. R. Regalbuto in the USA [20] and the Patras group in Greece with K. Bourikas, C. Kordulis and A. Lycourghiotis [21]. Some of these works, as well as work carried out by teams with whom Michel Che collaborated directly, are also reviewed in the present contribution.

2. The surface coordination of isolated Mo ions and the role of EPR

Early in his career (starting in Lyon), Michel Che took an interest in the preparation of isolated metal ions on metal oxides, by ion doping or impregnation. Using his technique of choice, EPR, he first focused on paramagnetic $4d^1 \text{Mo}^{5+}$ ions. Molybdenum has only 25% of isotopes with a non-null nuclear spin (i.e. $I=5/2$), ^{97}Mo and ^{95}Mo , but the Mo precursors can be ^{95}Mo -enriched. Through the implementing of EPR at two frequencies (X-and Q-bands) and the simulation of spectra, it has been possible to precisely depict the local environment of Mo by full analysis of Mo^{5+} EPR signals, namely g tensor values of the anisotropic signal, and coupling constants A of the hyperfine tensor (coupling between the spin of the unpaired electron and the ^{95}Mo nuclear spin).

So, in his earliest works on Mo-doped oxides (SnO_2 and TiO_2), prepared either by impregnation followed by calcination at high temperature (800°C), or by burning MoCl_5 with TiCl_4 or SnCl_4 [22-24], EPR confirmed that Mo^{5+} ions were located in substitutional position in the corresponding oxides. This conclusion was reinforced in the case of SnO_2 by the existence of super-hyperfine coupling with the nuclear spin $I=1/2$ of ^{117}Sn and ^{119}Sn (16% of natural abundance) [22]. A more systematic study was conducted for characterizing Mo species at the surface of silica (obtained by impregnation, calcination at 500°C , calcination and H_2 reduction). In this case, the Mo^{5+} EPR signal showed an axial symmetry with $g_{\perp} > g_{\parallel}$. Again, thanks to the use of ^{95}Mo -enriched Mo precursors, the g tensor values and coupling constants were determined [25]. From their comparison with those of a series of reference molybdenyl ($\text{Mo}=\text{O}$) compounds with halide ligands ($g_{\parallel} > g_{\perp}$) and oxygen ligands such as the isopolyanion $\text{Mo}_6\text{O}_{19}^{3-}$ ($g_{\perp} > g_{\parallel}$), it was proposed that isolated Mo^{5+} species on silica were present as molybdenyl species $\text{Mo}^{5+}=\text{O}$ with four O ligands in C_{4v} symmetry [26].

A new preparation method was then developed in the 80's to get highly dispersed Mo species on silica, at variance with the more traditional impregnation of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, which is known to form aggregated Mo oxide entities on this support. This new method involved surface grafting of MoCl_5 in organic solvent or gas phase. EPR was used to investigate *in situ* the chemical process during preparation in gas phase [27]. Grafting had to be performed in air- and water-free conditions because of the high reactivity of MoCl_5 . In contrast with a conventional impregnation in which Mo-support bonds are generated during calcination, bonding was found to occur during grafting, which prevented Mo aggregation during further thermal activation. MoCl_5 gives an isotropic signal at $g = 1.952$ (Figure 2), but during contact with dehydrated silica, a Mo^{5+} EPR signal showing an axial symmetry with $g_{\perp} < g_{\parallel}$ appeared on silica and increased with time (Figure 2). The characteristics of the EPR signal coupled with those of the UV-Visible spectrum also recorded *in situ*, revealed the formation of $[\text{MoOCl}_4]^-$ ion, as a result of the following reaction [27]:



After exposure to air, the initially orange Mo/SiO₂ sample turned blue, because of the co-presence of physically adsorbed diamagnetic dimer Mo₂Cl₁₀, which reacted with air and transformed into a mixed valence Mo⁵⁺-Mo⁶⁺ molybdenum compound (typical intervalence band in the visible range). This compound could be easily washed out with water or ammonia, leaving the sample brown with only grafted Mo in hydrolyzed and partially oxidized states, $\equiv\text{SiOMo}^{\text{V}}(\text{OH})_4$ (EPR signal with $g_{\perp} > g_{\parallel}$) and $\equiv\text{SiOMo}^{\text{VI}}(\text{OH})_5$ [27].

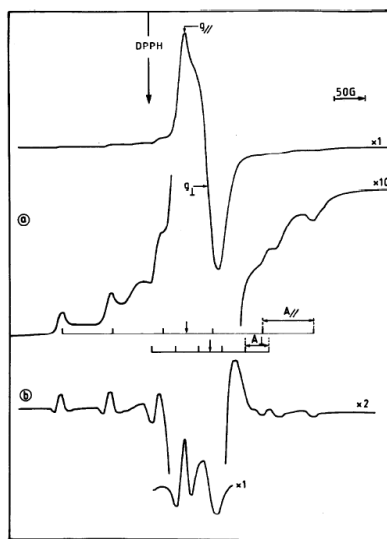


Figure 2: EPR spectra recorded at 77 K of Mo/SiO₂ catalyst during grafting with MoCl₅ vapor at 473 K: (a) first-derivative and (b) third-derivative. Reproduced from ref [28].

After thermal reduction under H₂ and further evacuation at 600 °C, the grafted Mo/SiO₂ samples exhibited a more complex EPR signal, still with $g_{\perp} > g_{\parallel}$ (Figure 3a). The third derivative spectrum as well as EPR measurements at different temperatures and frequencies (X- and Q-bands) revealed the presence of three Mo⁵⁺ species with a molybdenyl structure (Scheme 1) [29].

Several probe molecules were used to characterize their coordination sphere: water, CO and phosphines. For instance, upon stepwise adsorption of water [29], the initial spectrum gradually transformed (Figure 3, Left side): the signal of the more reactive species in Figure 3a transformed into the second signal (Figure 3b), and the latter transformed into the third one (Figure 3c) without changes in the number of spins. Conversely, water desorption at RT, then at 500 °C, allowed one to recover the initial spectrum with three Mo⁵⁺ species.

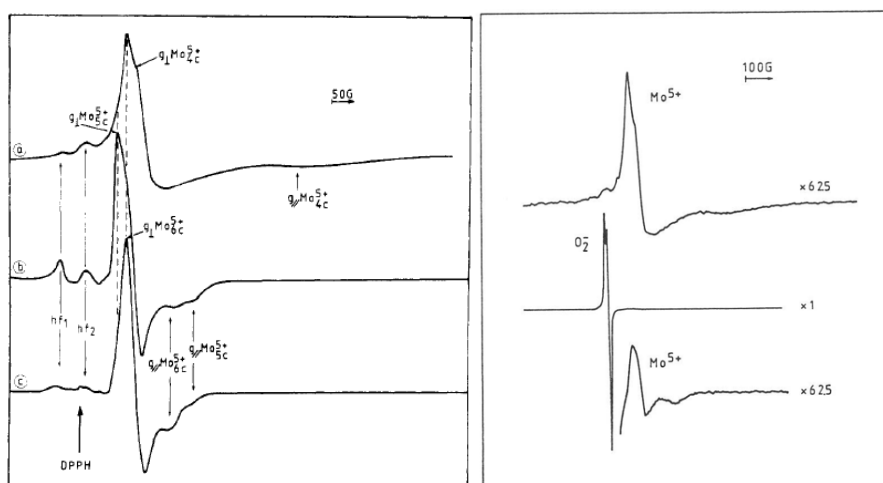
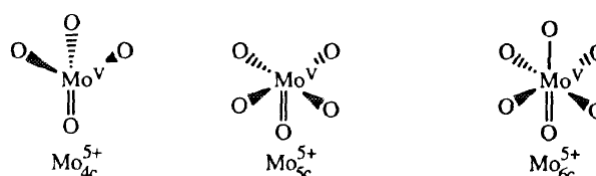


Figure 3: EPR spectra recorded at 77 K of grafted Mo/SiO₂ catalyst:

Left side (a) after reduction at 600 °C; (b) after ~1 Torr water adsorption; (c) after ~18 Torr water adsorption. Reproduced from Ref. [29];

Right side (top) after reduction; (bottom) after O₂ adsorption at low pressure and 77 K. From ref. [30, 31].

The three signals were attributed to Mo⁵⁺ species with three different coordinations: tetra-, penta- and hexa-coordinated (Scheme 1).

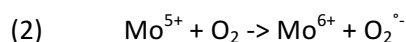


Scheme 1 : Different Mo species proposed from Ref. [32].

The existence of a tetra-coordinated Mo⁵⁺ species, observed for the first time because of the high dispersion of the Mo species onto silica surface thanks to the grafting method (see below), was corroborated using ¹²CO and ¹³CO (90%, I=1/2) as probe molecules, as well as Q-band EPR [29]. The super-hyperfine coupling between the Mo⁵⁺4d¹ electron and the ¹³C nuclear spin led to the appearance of two 1:2:1 triplets which confirmed that 2 CO molecules were completing the coordination sphere of Mo⁵⁺_{4c}. Accordingly, the analysis of the EPR spectrum obtained after adsorption of phosphine P(C₂H₅)₃ (³¹P nuclei, I =1/2, 100%), also indicated that two phosphine molecules were directly bonded to the tetracoordinated Mo⁵⁺_{4c} species [33].

O₂ was also used as a key probe molecule since Michel Che and his coworkers demonstrated that adsorption of dioxygen followed by EPR spectroscopy could be used to evaluate the Mo⁵⁺ dispersion

in reduced Mo/SiO₂ samples [30, 31]. Upon interaction with surface Mo⁵⁺ ions, oxygen is reduced into the paramagnetic radical anion O₂^{•-} showing an anisotropic EPR signal that increases at the expense of the surface Mo⁵⁺ one (Figure 3, right side), according to the following electron transfer reaction:



Discrimination between bulk and surface Mo⁵⁺ ions is then possible, which allows one to quantify the ratio of surface to total TMI while there are very few techniques that are able to give such a direct information.

From the comparison of the Mo⁵⁺ signal intensity before and after oxygen chemisorption, the Mo⁵⁺ dispersion was found to be equal to 80 and 30%, for grafted and impregnated Mo/SiO₂ samples with 1 wt% Mo, respectively. The much higher Mo dispersion in grafted samples was confirmed by other techniques such as photoluminescence [34] and IR spectroscopy [35]. Methanol oxidation, a catalytic reaction known to be structure-sensitive [28, 36-39] also confirmed these results: methyl formate was the main product over grafted Mo/SiO₂ catalysts whereas formaldehyde, which requires multi-Mo sites, was the main one over both Mo/SiO₂ impregnated catalysts and pure MoO₃. Further EPR studies over Mo/SiO₂ catalysts were conducted, focusing on how surface O²⁻ and paramagnetic O⁻, O₂⁻ oxygen species act in a concerted way in the formation of formaldehyde [40].

The high Mo dispersion in the grafted Mo/SiO₂ samples that leads to the presence of low coordinated Mo⁵⁺_{4c} species in the reduced samples (i.e., highly reactive Mo⁵⁺ species) was found appropriate to generate highly intense EPR signals of radical anions O₂^{•-} and O^{•-} and further to study their reactivity [41]. For instance, this was the source of the research work developed by Z. Sojka after his post-doctoral period with M. Che [41].

However, it must be noted that EPR spectroscopy is not a widespread characterization technique in the field of heterogeneous catalysis and there are very few groups using EPR spectroscopy for catalyst characterization. The number of published papers related to EPR of Mo⁵⁺ has been decreasing in recent years (from 50-69 papers per 5 years from 1970 to 2004 to 35-40 papers after 2005). The reasons for this declining interest are diverse : (i) EPR is a very sensitive technique, so traces of Mo⁵⁺ can be detected and not necessarily be significant in Mo-containing samples, (ii) this technique must be associated to other ones to provide an overview of all possible other Mo oxidation states present in the samples [35]; (iii) EPR is most suited for low concentrated samples since for highly concentrated samples or when the Mo⁵⁺ ions are not isolated from each other, the EPR signal broadens due to spin-spin interaction and shorter relaxation times; (iv) quantitative evaluation of spin number is difficult for solid state samples.

Nevertheless, the work of Michel Che and co-workers on EPR of Mo^{5+} has been the source of many following works for questioning the surface chemistry of Mo in the context of heterogeneous catalysis. The Mo^{5+}_{4c} , Mo^{5+}_{5c} , Mo^{5+}_{6c} terminology has been widely adopted, and the assignments of the EPR Mo^{5+} signals have never been questioned. Among more recent works, one can quote:

- the molecular assignment of Mo^{5+} EPR signal to Mo species with short Mo=O bond [42];
- the identification of the type of Mo^{5+} species formed during an electron transfer from an absorbed molecule or a catalytic reaction for example for the ethanolsis of Kraft lignin [43]
- the investigation of the Mo^{6+} redox properties in Mo-based catalysts for selective oxidation reactions [44]
- The study of the unusual high amount of Mo(V) present in mixed Nb(V)-Mo(VI) oxides obtained by calcination at high temperature (700-900°C) [45]
- The characterization of model redox systems in surface science with the identification of Mo^{5+} point defects on MgO(100) films grown on Mo(100) single-crystal surfaces after thermal treatment in UHV [46].

Beyond the EPR studies on the coordination chemistry of paramagnetic metal ions supported or inserted into oxides, Michel Che studied other systems. In collaboration with several colleagues, Tench first, then Dyrek, Giamello, Anpo, Sojka, Adamski and Murphy, he focused on electron transfers and especially on the formation of anionic reactive oxygen species (ROS) on metal oxides (O^- , O_2^- , O_2^{2-} , O_3^-). This is detailed in a second review of this special issue [41].

3. Coordination chemistry and reactivity of isolated nickel ions

In parallel with this early work on molybdenum systems, Michel Che and his coworkers implemented a whole set of electron magnetic resonance techniques to investigate the formation of Ni^+ ions inside (Ni^{2+} , Ca^{2+})-containing zeolites X, and their migration when exposed to CO [47-49]. $\text{Ni}(\text{H}_2)^+$ ions, characterized by EPR and ENDOR, were produced by reduction of Ni^{2+} ions with hydrogen at 200°C [47]. Examination of the hyperfine structure of the EPR signals upon adsorption of ^{13}C O revealed the existence of $\text{Ni}(\text{CO})_2^+$ and $\text{Ni}(\text{CO})_3^+$ species in the zeolite supercages, depending on the CO pressure. The reduction of these isolated nickel ions by hydrogen atoms at 273 K led to the quantitative formation of 1 nm Ni(0) nanoparticles, characterized by ferromagnetic resonance [48]. This strategy (isolating homodispersed ions via a chemical method, to ultimately yield homodispersed particles) would become one of the unifying threads running through Michel Che's work on the synthesis of supported metal catalysts.

The formation of Ni^+ complexes was subsequently extended to other supports, such as silica, proving that the structural characteristics of zeolites were not a prerequisite for the stabilization of these reputedly unstable species. The key point was to isolate Ni^{2+} ions at the onset of the catalyst synthesis, a result which could not be achieved by conventional impregnation methods [50]. To reach this end, a specific synthesis procedure, based on ion exchange and inspired by the preparation of Pt catalysts, was detailed in a patent filed in 1982 [51]. Silica was first treated with an aqueous solution of monovalent alkali or ammonium cations, at a pH greater than about 10. The resulting solid was then exposed to a basic aqueous solution containing a divalent nickel salt and a complexing agent (ammonia, amines). The isolation of the Ni^{2+} ions was guaranteed by their electrostatic interactions with the deprotonated surface groups of silica, and by the inability of Ni^{2+} ions, protected by the amine ligands, to undergo condensation at high pH. This seminal procedure, grounded on physical and coordination chemistry concepts, is the starting point toward later developments by Michel Che's group in interfacial coordination chemistry in general, and in the preparation of dispersed nickel nanoparticles in particular.

EPR is known for its sensitivity to paramagnetic species such as Ni^+ ions, but these ions amounted to only 4% of the total nickel ions in NiCaX zeolites [49]. In order to cover the chemistry of Ni^{2+} ions as well, EPR and infrared spectroscopy were used in combination to identify the different Ni^{2+} -CO and Ni^+ -CO complexes formed in zeolites and on silica as a function of temperature and CO pressure, and to monitor their interconversion [52, 53]. A new mode for nickel reduction, initially developed for molybdenum catalysts, was introduced in these works: UV irradiation in H_2 at 77 K, using a high-pressure mercury lamp. The immobilization of the Ni^+ complexes on supports led to their beneficial application in the dimerization of ethylene and propylene [54]. Because of the conditions of reduction, the transformation of nickel ions into Ni metallic particles was inhibited [55], solving one of the problems encountered in the Dimersol homogeneous process of alkene dimerization. The careful analysis of g-tensors allowed Michel Che's team to associate a high activity in ethylene dimerization to the presence of $\text{Ni}(\text{O}_{\text{sup}})_2(\text{CO})_2(\text{C}_2\text{H}_4)$ and $\text{Ni}(\text{O}_{\text{sup}})_2(\text{CO})(\text{C}_2\text{H}_4)_2$ complexes of trigonal bipyramid structure, in which O_{sup} is an oxygen from the support. These complexes were the results of ligand addition and substitution, as would occur in homogeneous catalysis. But unlike catalysts produced by the surface organometallic chemistry route, in which the complex is first synthesized in solution before being deposited onto the support, the catalyst was built here from a supported precursor species, and, as such, related to interfacial coordination chemistry. The O_{sup} surface atoms were supposed to impose a particular coordination and geometry to the Ni^+ precursor species prior to the reactant adsorption. In this conceptual approach, the support could thus be considered as a sterically demanding, polydentate macro-ligand [7]. Both the strategies of reduction in mild conditions, and quantification

and identification of the active sites, were still referred to as pioneering in recently published reviews focusing on alkene oligomerization using isolated supported Ni ions [56, 57] a domain that has now expanded to cover spectroscopic measurements in operando conditions (EPR, FTIR) [58, 59].

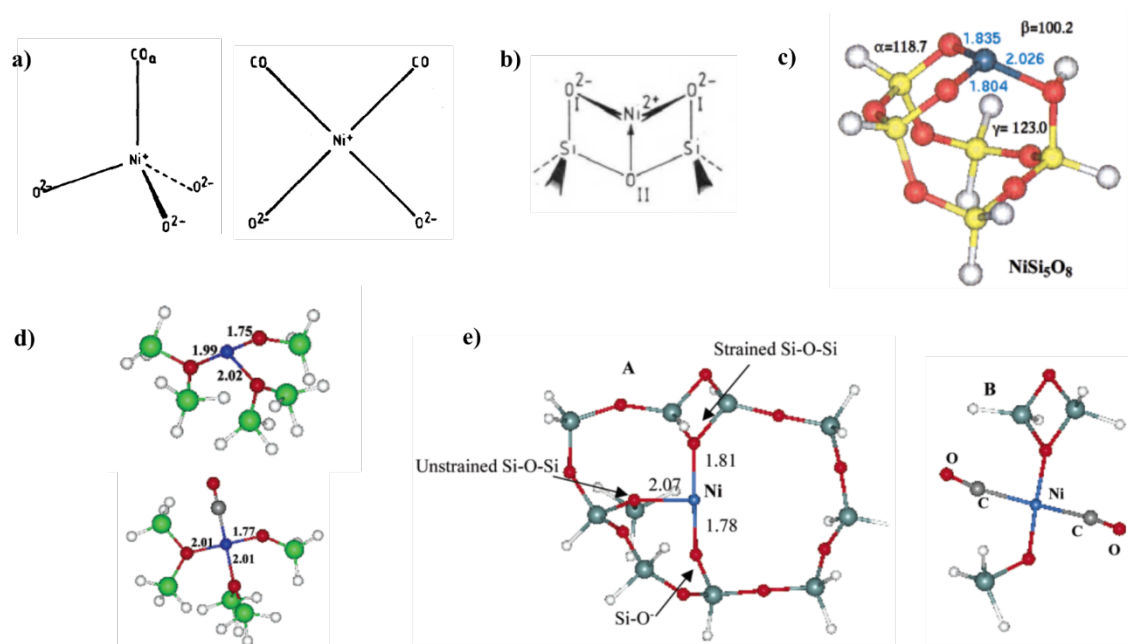


Figure 4. Visualizing a concept in progress: evolution of the description of silica-supported isolated nickel ions. a) geometry of mono- and dicarbonyl Ni⁺ complexes deduced from EPR measurements [54]; b) alleged coordination mode of bare supported Ni²⁺ ions on silica [55]; c) DFT model of a supported Ni²⁺ ion based on a closed cluster [60]; d) DFT model of a supported Ni²⁺ ion and a monocarbonyl complex based on an open cluster [61]; e) DFT model of a supported Ni²⁺ ion and a dicarbonyl adduct based on silica rings [62].

Silica-supported Ni⁺ ions were also shown to catalyze the trimerization of acetylene to benzene [63]. The limits of interpretation of EPR and IR spectra led to resorting to extended Hückel and ab initio calculations to confirm the nature of the benzene complexes. Calculations were based on molecular hydroxo complexes, for the sake of simplicity. Both methods were consistent in predicting an unusual η²-coordination of benzene tilted over the Ni⁺ ion [64].

This introduction of theoretical chemistry represented a step forward in the exploration of the reactivity of supported nickel complexes, but models built on hydroxo complexes would not allow answering an underlying question: the geometry of the local environment around nickel ions in the silica-supported precursor species, which determined the system properties. The first stage in the modelling of a silica environment by DFT required the construction of tri-coordinating Si₅O₃⁻ closed or open clusters containing siloxane bridges and silanolates, to coordinate Ni²⁺-CO adducts in a manner

that reproduced the interatomic distances and the CO stretching frequencies experimentally measured by EXAFS and infrared spectroscopy, respectively [60, 61]; this approach based on realistic fragments, that confronted molecular modelling and spectroscopic data for a more accurate description of silica-supported complexes, was being developed at the beginning of years 2000s before periodic slabs became more commonly used to model the support thanks to growing computer power [65]. This preliminary model was then refined and extended to dicarbonyl species, by embedding the fragment in an environment comprising a large silica ring and a small, strained, neighboring 2T ring, as can exist on the surface of silica [62]. The reactivity of NO on these tripodal Ni²⁺ complexes was ultimately studied [66], concluding a large and coherent body of work that spanned over a period of almost 30 years and that would further expand, for example through the works of the Krakow and Torino groups [67]. At each stage, this work had included new sophisticated methodologies of analysis, and from the investigation of the puzzling migration of Ni²⁺ ions in zeolites, led to the description at the atomic level of isolated supported complexes and of their first- and second-sphere environment (Fig. 4).

A secondary consequence of this work on isolated SiO₂-supported Ni²⁺ complexes was the emergence of the concept of “chemical glue”, that described in an imaged manner the fact that transition metal ions (in this case, Ni⁺ or Ni²⁺ ions) acted as anchoring sites for reduced Ni particles at the interface with the support [68, 69]. A two-step procedure was developed to prepare 2-6 nm Ni nanoparticles, starting with isolated grafted Ni²⁺ of ions in strong interaction with the support onto which nickel species introduced by impregnation would later condense. While isolated ions would be formed when ion-exchange using stable and inert [Ni(en)₃]²⁺ chelates (en = ethylenediamine) was implemented in the first step, phyllosilicate nuclei would grow when nickel was introduced by impregnation with nickel nitrate or ion-exchange with Ni-NH₃ complexes [70, 71]. This finding opened the way to the works on impregnation and deposition-precipitation that will be described below.

4. Fundamental studies of Interfacial Coordination Chemistry

As stated in the introduction, the notion of interfacial coordination chemistry was central to Michel Che’s reflection on supported metal catalysts preparation: the already well-established field of transition metals ions coordination chemistry in homogeneous phases (solid crystals or solution) could help understand the reactions and behavior at the surface of solid supports. This led to testable predictions that could be explored using well-chosen model systems. It also led to a unified view of transition metals adsorption phenomena, where previously only fragmented insights were available: while electrostatic adsorption phenomena had already reached the mainstream of catalytic science

with the work of Brunelle [72], no general frame of reflection was accepted to make the link with such phenomena as “grafting”.

For instance, a central feature of TMC is the existence of a ligand-induced splitting of d orbitals that is described in the frame of the crystal field theory. The crystal field splitting Δ , an energetic parameter, can be deduced from the UV-visible absorption spectrum where d-d electronic transitions are often very conspicuous. The underlying theory is not trivial but it is well-understood following systematic studies of TMC spectra in the 1950s and 1960s. In order to determine if the changes in coordination of catalytic metal ions brought about by their adsorption on supports had similar effects on their spectroscopic properties, first ammine Ni^{2+} complexes [9], then $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ [73], were selected as model systems. The bidentate ethylenediamine ligand, denoted (*en*), is stably bound to the nickel ion due to the chelate effect, while the two H_2O (aqua) ligands are labile. The nitrate salt of this complex was deposited from aqueous solutions on different supports such as amorphous silica, alumina, a zeolite (Y faujasite) and a pillared clay, followed by drying at room temperature. Systematic shifts in the energies of the d-d transitions were observed, indicating that the two aqua ligands had been substituted by surface groups of the support. Thus, the adsorption of the nickel precursor consisted in a simple ligand substitution reaction, leading to Inner Sphere Complex (ISC) formation with the surface:



where $(\text{SO})_{\text{surf}}$ designates a surface oxygen-containing group of the support. Along with the determination by EXAFS of a Ni-Si distance and the effective number of Ni-O-Si formed [10], terms often used in the literature such as “grafting” were given a more precise meaning.

Furthermore, all supports did not have the same crystal field strength. Indeed, surface groups could be fitted in the *spectrochemical series* of ligands as follows:

$\Delta_o(\text{Cl}) < \Delta_o(\text{AlO}) < \Delta_o(\text{ZO}) < \Delta_o(\text{SiO}) \cong \Delta_o(\text{H}_2\text{O})$, showing that alumina surface groups were weaker field ligands than those of silica, with the zeolite groups in an intermediate position. It was possible to rationalize this order on the basis of another parameter that could be calculated from the energies of d-d transitions, namely the nephelauxetic ratio β . It was found that $\beta(\text{AlO}) < \beta(\text{ZO}) < \beta(\text{SiO}) \cong \beta(\text{H}_2\text{O})$, indicating that the weaker-field groups were also better π -donors (in addition to the σ -donating ability present in all ligands). This spectrochemical series of supports has been confirmed in part by later works. Espinosa-Alonso et al. [74] have observed a bathochromic shift for OH^- substitution by aluminolate groups in square planar Pd (II) complexes, confirming the low field position of surface (AlO^-) in the spectrochemical series. Vivier et al. [75] studied the grafting of $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+/2+}$ on alumina both by UV-Vis spectroscopy and cyclic voltammetry. This approach allowed to go further into the

understanding of interfacial coordination chemistry, confirming that aluminol groups are weak-field ligands because they have π -donating in addition to σ -donating electronic properties, as is the case e.g. of halogeno ligands in solution-phase coordination chemistry.

Interestingly, the clay support gave rise to a quite different behavior. Here the predominating adsorption mechanism was cation exchange into the interlayers rather than ISC formation, and when aqua ligands were eliminated, the peculiar surroundings of the nickel cations between the layers favored the formation of square-planar $[\text{Ni}(\text{en})_2]^{2+}$ complexes with no obvious coordination to clay oxide groups. The interfacial chemistry of these systems is summarized in Figure 5.

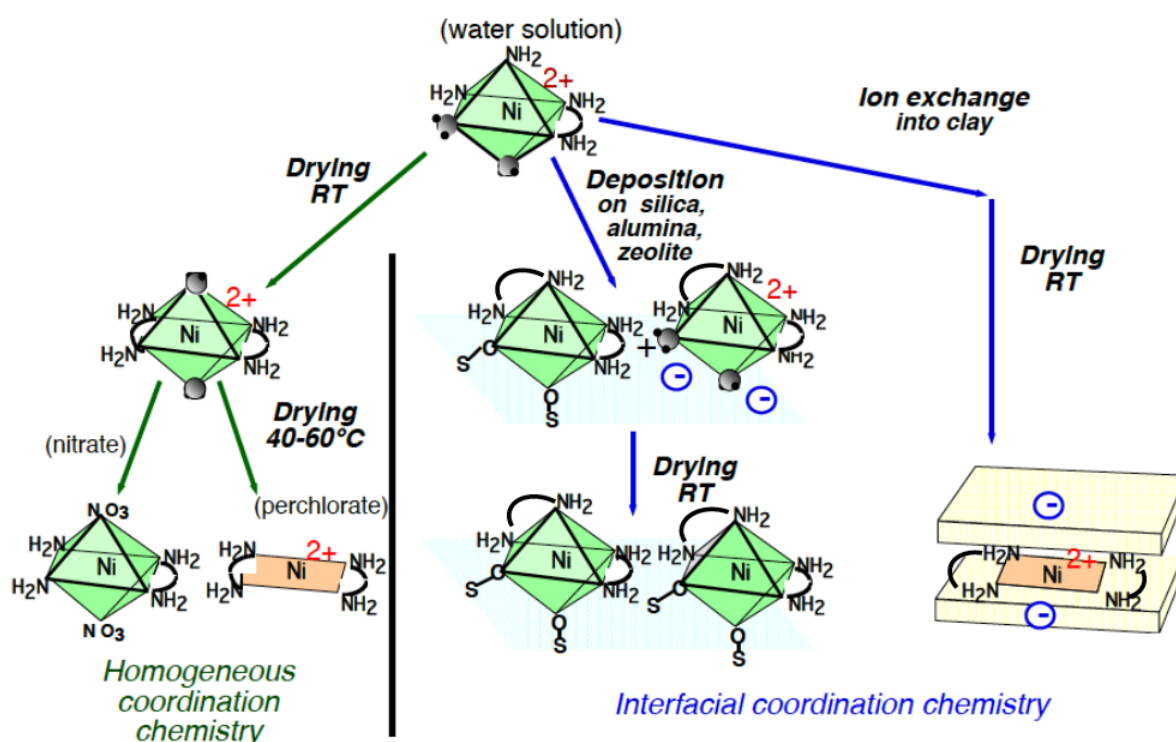


Figure 5. A graphical summary of the various reactions relevant to the chemistry of $[\text{Ni}(\text{en})_2\text{L}_2]$ complexes, in reference salts (left), on silica/alumina surfaces (center), and in clay interlayers (right).

The composition of the coordination sphere of a transition metal ion does not only have consequences on its spectroscopic properties, but also on its reactivity, especially in redox reactions. Here again the underlying theory is well-understood in classical, homogeneous phase coordination chemistry. ISC formation with π -donating ligands such as those of alumina should make the TMC stronger reductants (and/or weaker oxidants). In order to check if this was indeed happening, nickel was replaced by a transition metal having two stable oxidation states, i.e., cobalt ($\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ couple) [75]. The redox potentials were measured by cyclic voltammetry, both for the precursor complexes in solution and the complexes deposited on alumina. Aqueous cis- and trans- $[\text{Co}^{\text{III}}(\text{en})_2\text{Cl}_2]^+$ had redox potentials of -0.17V and -0.35V (vs. calomel electrode) respectively; upon deposition, both converged to

$\text{cis}[(\text{AlO})_2\text{Co}(\text{en})_2]_{\text{surf}}^{x+}$, indicating the cis-directing effect of the surface, and the redox potential of this inner-sphere complex indeed went down significantly, to -0.65V.

In industry, operationally simple procedures such as impregnation from an aqueous phase are selected whenever possible. Michel Che's intuition was that this apparent simplicity could hide an underlying complex chemistry at the molecular level. In particular, the nature of the TMC adsorption sites is most often unknown: writing them e.g. as 2 (SO) groups (see equation (3) above) is a reflection of our limited knowledge. In an effort to use TMC as probes of the adsorption sites [76, 77], three nickel complexes were selected: $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, already encountered, $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$, and $[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$, where (dien) is the tridentate diethylenetriamine ligand. Since these complexes respectively have 2, 3 and 1 labile aqua ligands, they were theoretically susceptible of forming ISC with the same number of surface ligands. ISC formation was indeed confirmed by EXAFS at the Ni K edge, showing that the silica surface can act as a mono-, bi- or tridentate ligand. The quantification of this phenomenon through the measurement of adsorption isotherms was compatible with site adsorption, as they followed a Langmuir dependence with well-defined saturation coverages. A complementary approach of the coverage-dependent chemistry of ISC, based on adsorption isotherms and UV-visible spectroscopy, was proposed at the same period by the Patras group for the optimization of the preparation of nickel and cobalt catalysts on alumina and titania [78-80].

The saturation coverages were different for all three complexes, and did not correspond to trivial ratios. This suggests that each complex "recognizes" its own adsorption site, and that adsorption may involve something more complex than simple ligand substitution. Indeed, the best interpretation of all macroscopic and spectroscopic data leads to the interaction schemes shown in Figure 6:

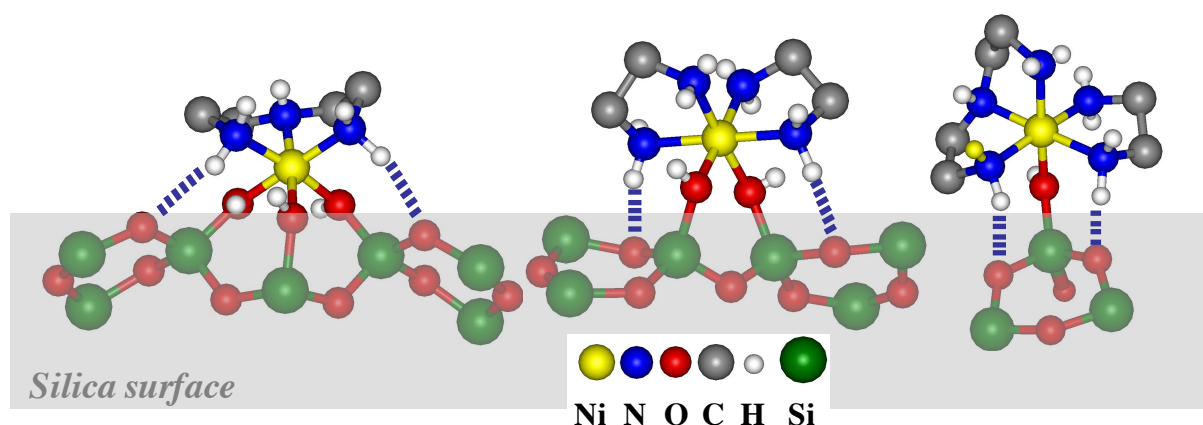


Figure 6: Possible models for molecular recognition with interactional complementarity between complexes $[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$, $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, and $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$ and surface sites of silica.

Here, adsorption involves a group of 1, 2 or 3 silanols acting as ligands, together with H-bond accepting groups (possibly siloxanes) in a well-defined geometrical relation to them. Thus, the adsorption of TMC on silica could involve a kind of molecular recognition based on interactional complementarity [81] – something as apparently trivial as nickel deposition on an inorganic support would then put into play a chemistry as complex as the one that is responsible for e.g. substrate recognition by an enzyme.

While obviously a detailed molecular identification of TMC adsorption sites is difficult and requires sharply focused work, there are other hints in the literature that specific grafting sites may be present at rather low concentrations on support surfaces, e.g. for square planar Pd^{II} complexes/ γ -Al₂O₃ systems [82]. For Co^{II} complexes ([Co(neo)]²⁺, where (neo) is the 2,9-dimethyl 1,10-phenanthroline ligand) supported on porous silicas, an interesting lead was proposed by Watton et al.: grafting sites could be dependent on pore diameter, with larger pores silicas containing more sites as shown by saturation values of adsorption isotherms [83]. Practical consequences of this view for the control of the impregnation step are presented in section 5.

Fundamental investigations into interfacial coordination chemistry in Michel Che's group were not limited to nickel complexes. Indeed, valuable insights were obtained from quite different systems such as hexachloroplatinate on alumina, even though the original motivation for these studies were very practical since they were aimed at reforming catalysts improvement [84, 85]. Platinum has the advantage of a spin ½ isotope, ¹⁹⁵Pt (33% natural abundance). This allows one to follow its speciation by NMR, a technique that can be extremely sensitive to molecular environment, especially for heavy atoms. And indeed, H₂PtCl₆/Al₂O₃ was the first system for which *outer*-sphere complexes (OSCs) were unequivocally observed, such as Al–OH₂⁺ ⋯ [PtCl₆]²⁻ and Al–OH₂⁺ ⋯ [PtCl₅(OH)]²⁻, where the minimal influence of surface groups in the outer sphere (solvation, not coordination sphere) could still induce significant changes of chemical shift. Outer-sphere bonding is quite dynamic, with bonds being constantly broken and reformed, so that the platinum complex is still mobile enough to be observed in NMR. Upon thermal activation, though, the surface groups replace two chloride ligands to form grafted inner-sphere complexes that are not observable any more due to their low symmetry and lack of mobility.

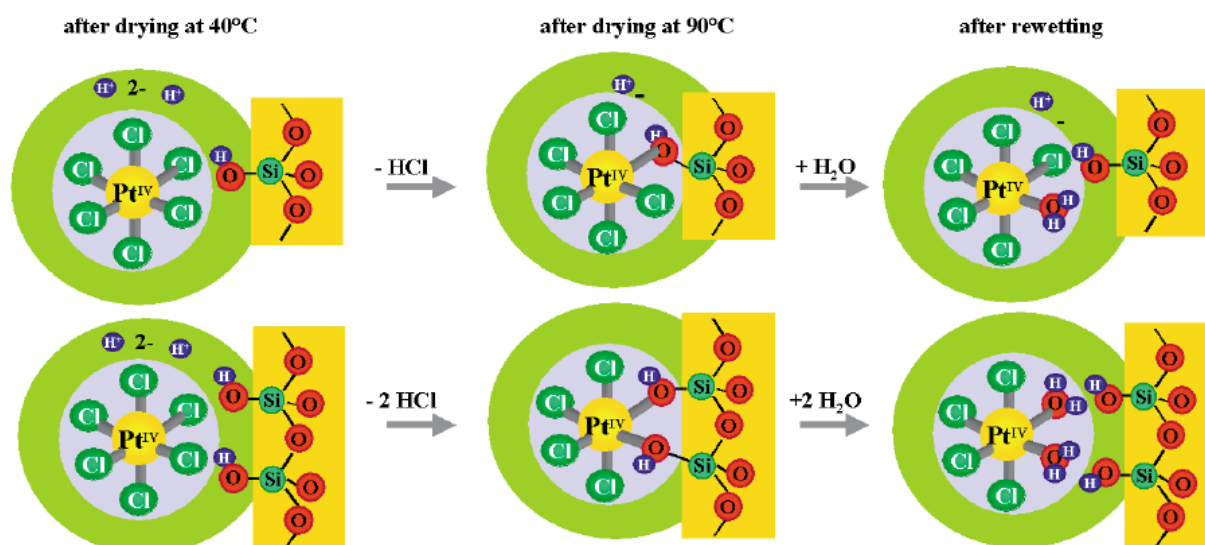
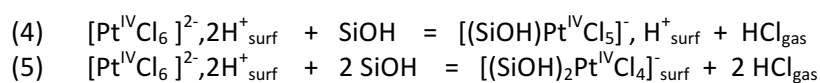


Figure 7: Evolution of platinum adsorption mode in $\text{H}_2\text{PtCl}_6/\text{SiO}_2$ systems: upon drying at 40°C , formation of OSC; upon drying at 90°C , formation of ISC by grafting; upon rehydration, OSCs are formed again.

Hexachloroplatinate speciation was also followed by NMR on silica [86]. Here, upon drying, the protons of hexachloroplatinic acid reacted with the chloride ligands to form labile HCl, inducing ISC formation, along:



However, contrary to alumina, grafting was reversible upon exposure to water, as aqua ligands could displace the surface (SiOH) ligands. These transformations are summarized in Figure 7.

It was found that the elimination of HCl could be quantitatively controlled by partial NaOH titration, and thus, indirectly, the relative amounts of hexa-, penta- and tetrachloride complexes. Remarkably, upon further reduction by gas-phase H_2 in TPR conditions, each precursor species had a specific reduction temperature: $[\text{Pt}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]$ (formed by rehydration) was reduced at 10°C , $[(\text{SiOH})\text{Pt}^{\text{IV}}\text{Cl}_5]^{-}$ at 170°C , and $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ only at 220°C . Thus, here again the molecular-level understanding of surface coordination chemistry of precursor ions was not a mere pastime for theoreticians, but had very significant consequences in terms of reactivity. The idea that different Pt surface species have different reducibilities, and that this allows controlling of the final Pt dispersion and consequent catalytic performance, was developed by Mironenko et al. who used mild hydrothermal treatments to create new chloroplatinate grafting sites on γ -alumina (bridging OH groups having a characteristic IR frequency) [87].

The ligand exchange chemistry of the chloroplatinate/alumina system was further studied by Regalbuto et al. [88, 89]. They proposed slightly different interpretations taking into account the effect

of the surface on local pH and chloride concentrations. Furthermore, they used the fundamental knowledge garnered on Pt complexes speciation and their influence on adsorption mechanisms to devise practically useful supported catalysts preparation procedures resulting in high dispersions of Pt metal in the final reduced catalysts. Thus, strong electrostatic adsorption (SEA) could be induced by pH control starting from $[\text{Pt}^{\text{II}}(\text{NH}_3)_4]^{2+}$, $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$, as well as $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ precursors on alumina [90, 91], but also on carbon supports [92], and the concept was extended to several other systems [93-96]. A modification of this method for incipient wetness impregnation was called charge-enhanced dry impregnation (CEDI) [97], and other simple tools of speciation control such as counterion concentration could be used fruitfully [98]. In most of these cases, adsorption data could be rationalized by electrostatic adsorption models, without substitution of the platinum ligands by support surface groups (i.e., without Inner Sphere Complex formation). There is no reason however to establish a sharp separation between these cases, and those where grafting does occur. Both are examples of precise molecular-level characterization of the adsorption phenomena; and transitions from electrostatic interactions to grafting are often observed upon further catalyst treatments, when high temperature treatments are involved.

Other researchers showed that $\text{Cl}^-/\text{H}_2\text{O}$ ligand exchange plays a major role in directing chloroplatinate precursors adsorption on growing Pt^0 nanoparticles [99]: UV-Visible and ^{195}Pt NMR allowed to follow the formation of $[\text{Pt}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ from $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$ and then $[\text{Pt}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]^0$, and the latter, neutral complex was preferentially adsorbed and reduced on Pt (111) planes, causing the growth of (100) limiting faces, and thus cubic morphologies of the nanoparticles.

Furthermore, it was demonstrated that the presence of chloride ions in the preparation of Pt catalysts had important consequences for an industrial application, catalytic methane combustion. While Pt catalysts prepared by thermal decomposition of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ usually displayed well-dispersed 1-3 nm particles, the coexistence of chloride ions and ammine Pt(II) complexes in the impregnation solution (when alumina was chlorided, or when $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ was chosen as precursor salt) led to the crystallization of poorly soluble salts such as $[\text{Pt}(\text{NH}_3)_4]_3[\text{P}(\text{NH}_3)_3\text{Cl}]_2\text{Cl}_8$ (resulting from a mere substitution of Cl^- to NH_3 in only 2 $[\text{Pt}(\text{NH}_3)_4]^{2+}$ complexes over 5), ultimately decomposing into large 7-15 nm Pt particles presenting a low activity. A similar detrimental association between Cl^- ions and ammine Pt complexes, resulting in a poor Pt dispersion stemming from ligand exchange, was fully explored by the Regalbuto's group in recent studies [20, 100]. Whatever the Pt dispersion, catalysts prepared from chloride-containing complexes were initially poorly active in methane combustion, owing to poisoning of the metal particles by residual Cl atoms. The activity increased with time-on-stream because of the progressive removal of Cl by the water produced during the reaction [101-103].

5. Chemistry of Impregnation

The developments around interfacial coordination usually involved individual transition metal complexes introduced by ion-exchange or equilibrium adsorption. However, as mentioned above, supported metal catalysts in industry are rather prepared by impregnation, which consists of filling the pore volume of the support with a solution of precursor metal complexes, with two main differences compared with the above-mentioned procedures: i) because pH conditions may not be fixed by an external intervention, as can be done to thermodynamically favor the formation of one specific complex, several complexes may coexist at equilibrium in the impregnation solution, and equilibria can shift upon grafting of the complexes onto the support or upon crystallization of the precursor salt [104, 105]; ii) because of the absence of a washing step, all the species introduced with the metal ion in the impregnation solution (ligands, counterions, additives) remain present in the support porosity [106, 107]. The chemical system is thus more complex, but the situation was turned beneficial with respect to catalyst preparation by treating these species as chemical partners that interact and react with each other in the wet porosity or during thermal treatments (Fig. 8a). One has to note that most of the examples given below are referring to the deposition of cations (Ni^{2+} and Co^{2+}) but a similar approach was pursued by the Patras group with anionic precursors (tungstates, molybdates and chromates) [108-110].

At low nickel loadings, using ethylenediamine (*en*, cf. section 4) as a chelating ligand in impregnation solutions prepared from nickel nitrate proved to inhibit the formation of nickel aluminate on $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts, a phase that is not reduced below 950°C , yielding otherwise poorly dispersed Ni particles (Fig. 8b, left) [106, 107]. The key point was to perform the thermal treatment following impregnation in an inert atmosphere, in order to conserve *en* ligands bonded to Ni^{2+} ions up to 230°C . *In situ* UV-Visible-NIR and DRIFT spectroscopies evidenced an interfacial complex of suggested formula $[\text{Ni}(\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_3^+)_2(\text{OAl})_2]$, in which the ligands acted as stabilizing, bridging species between the Ni^{2+} ion and alumina (Fig. 8c) [106, 107, 111]. *en* ligands were subsequently decomposed by reaction with the oxidizing nitrate counterions, but the early diffusion of Ni^{2+} ions into alumina had been inhibited. The reduction temperature of the surface Ni^{2+} ions to metallic nickel was lowered by 450°C compared to a nickel aluminate phase, yielding much smaller particles (Fig. 8b, right).

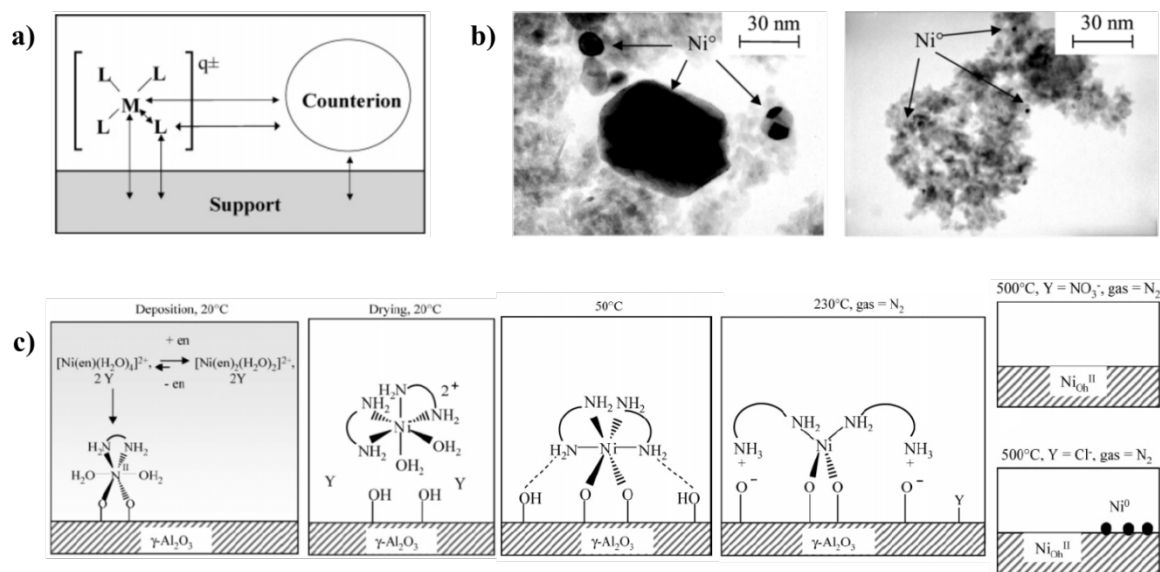


Figure 8. a) Scheme of the possible interactions between chemical partners during the preparation of a catalyst by incipient wetness impregnation [106]; b) TEM micrographs of Ni/Al_2O_3 catalysts prepared by impregnation of nickel nitrate, reduced at 950°C (left), and by impregnation of $[Ni(en)_2(H_2O)_2](NO_3)_2$, reduced at 500°C (right) [107]; c) Evolution of nickel speciation during the preparation of a catalyst by impregnation of $[Ni(en)_2(H_2O)_2](NO_3)_2$ followed by thermal treatment in N_2 ($Y : NO_3^-$ or Cl^-) [106].

Replacing nitrates by chloride counterions, increasing the proportion of *en* ligands to 3, increasing the nickel loading, or using hydrogen-rich ligands such as cyclohexanediamine had another effect [106, 111, 112]. As the oxidizing species present in the porosity were now absent or acted as limiting reactants, the hydrogen liberated by decomposition of the $-CH_2-NH_2$ terminations, or of the cyclohexane rings, was sufficient to directly reduce Ni^{2+} ions into 2-6 nm Ni nanoparticles. A final treatment in H_2 was however necessary to clean the metal surface from carbonaceous deposits. The resulting Ni/Al_2O_3 catalysts were shown to be more active in CO methanation than catalysts prepared by impregnation of nickel nitrate [113].

For two other systems, this strategy was less successful in terms of metal dispersion, but with interesting outcomes from the chemistry standpoint. Extension to the preparation of Co/Al_2O_3 catalysts revealed a sequence of reactions taking place during impregnation and drying, involving not only the metal cations, the *en* ligands and the counterions, but also oxygen dissolved in the impregnation solution. Starting from a $[Co(en)_2(H_2O)_2](NO_3)_2$ composition, it is not dispersed species but, through the shift of successive equilibria, large crystals of the $[Co(en)_3](NO_3)_3$ salt that crystallized in the porosity [104]. When $[Ni(gly)_2(H_2O)_2]$ ($gly = NH_2-CH_2-COO^-$), a neutral complex that would interact with the alumina surface only by hydrogen bonds [114], was used for impregnation, the decomposition in argon led to an unexpected phase: hexagonal close packed metallic nickel stabilized by outer graphitic layers [115].

Polyfunctional molecules containing –OH groups (sorbitol, glucose) were finally tested at a high concentration as additives for the preparation of Ni/Al₂O₃ catalysts by impregnation [116]. Circular dichroism measurements showed that unlike polyamines, these molecules were not acting as ligands, but as co-solvents via second-sphere interactions. The dispersion of nickel nitrate over the surface of the support was associated to an increase of the viscosity of the impregnation solution that would prevent a recrystallization of the salt, a consequence more of a physical effect than of a chemical one.

As was the case for deposition-precipitation, this molecular interpretation of impregnation can be read in a context of mutual inspiration and cross-fertilization of ideas with the work carried out in the Inorganic Chemistry and Catalysis group from Utrecht University (John W. Geus, Krijn P. de Jong, P. de Jongh, Bert M. Weckhuysen, and their collaborators). In the same period, alternative methods of thermal treatments involving gases different from air (N₂, NO) were developed and rationalized by the Utrecht group to optimize both nickel or cobalt dispersion, and the distribution of the metal particles over the support [117-119], while the work initiated by Espinosa-Alonso et al. in microspectroscopy would build on the surface chemistry and decomposition of Ni-*en* complexes to explore the dynamics of impregnation within catalyst bodies [120-122].

6. Role of support dissolution : case studies on silica and alumina

The concept of Interfacial coordination chemistry has also led to reconsider the role of oxidic supports used in heterogeneous catalysis, no longer seen only as a mere physical or chemical dispersing agent for the active phase, but as a genuine reactant during catalyst preparation through the release of its constituents. This dissolution can be a consequence of the physico-chemical conditions during active phase deposition (pH, temperature, time....), but can also be promoted by the active phase itself as demonstrated later.

Support reactivity was first studied by the group of Michel Che [123, 124] through the Deposition-Precipitation with Urea (DPU) procedure initially developed by Geus et al. [125] for producing Ni/SiO₂ catalysts with high and homogenous dispersion. DPU in the presence of nickel nitrate and of a silica suspension involves a thermohydrolysis of urea which leads to a gradual and homogenous pH increase up to a moderate value of 5.4. This results in Ni deposition through silica dissolution and subsequent formation of layered Ni (hydroxy)silicate (phyllosilicates). These phenomena were also observed during a simple impregnation at room-temperature with Ni ammine complexes, at a basic pH lower than 9.5, value above which the formation of the stable [Ni(NH₃)₆]²⁺ complex would inhibit the Ni-silicate formation [123, 124]. The same inhibition was also observed with protecting ligands such as ethylenediamine as described in the previous sections [126]. It was also pointed out that Ni-phyllosilicate

formation could occur during the washing and drying steps, highlighting the fact that each preparation step was crucial for controlling the state of the final catalyst. As a matter of fact, different parameters were shown to be key to the formation of a mixed surface phase upon catalyst preparation: pH, oxide/water contact time, support specific surface area, since they control both the thermodynamic (solubility) and kinetics (rate) of silica dissolution. High pH and high specific surface area of silica favored the formation of surface phyllosilicates at the expense of Ni hydroxide [127].

However, for deposition-precipitation with specific conditions ($T=90^{\circ}\text{C}$, ambient pressure), kinetics imposed the type of surface phyllosilicates formed, preferentially the least thermodynamically stable 1-1 phyllosilicate (serpentine), made of a brucite-type sheet containing Ni(II) in octahedral coordination and a sheet containing linked tetrahedral SiO_4 units.[128] Later on, Burattin et al.[129] gave a full molecular picture of the processes occurring during the preparation of Ni/SiO₂ catalysts with DPU (Figure 9). The first step occurs at the silica/solution interface and can be described as an electrostatic adsorption of the aquo Ni complex (step 1) followed by an heterocondensation between the surface OH of silica and monomeric hydroxo aqua Ni(II) complexes (steps 2-3 in Fig. 9), giving rise to adsorbed Ni species that can condense with each other (step 4) to yield a surface layer that can be described either as a brucitic layer of Ni(OH)₂ or as a first slab of a 1-1 Ni phyllosilicate. Then two routes compete, depending on the amount of dissolved silicic species. For high surface area silica, dissolution is kinetically favored, leading to a large concentration of Si monomers (steps 5 and 6) than will condense with dissolved Ni species, polymerize (heterocondensation, steps 7 and 8) and yield 1:1 Ni phyllosilicates that can grow on the surface layer initially formed. For low surface area silica, the dissolution rate of silica is low, and oligation reactions between hydroxo aqua Ni(II) complexes (homocondensation) is favored, yielding supported Ni hydroxide Ni(OH)₂ (steps 2, 9 and 10). In both cases, the initial monolayer acts as a nucleation site for the subsequent phase, which also explains the influence of the silica specific surface area and porosity on the morphology of the supported phase.

Such a fundamental approach has practical consequences for the control of the final catalyst, since it was shown that samples containing nickel hydroxide lead to Ni particles with broader size distributions and larger average sizes (i.e. $\phi \approx 5$ nm) than the samples containing mainly 1:1 nickel phyllosilicate (i.e. $\phi < 5$ nm). These differences can be related to the higher decomposition temperature of phyllosilicates to NiO, which will lead to a fast reduction and low sintering of the latter [130]. A high resistance to sintering is a key feature of these catalysts, and it can be further explained by strong metal-support interactions present both at the oxide state (NiO) through the formation of the brucitic layer at the interface, and at the metallic state (Ni⁰) where it is supposed that some unreduced Ni ions play the role of anchoring sites for metal particles.

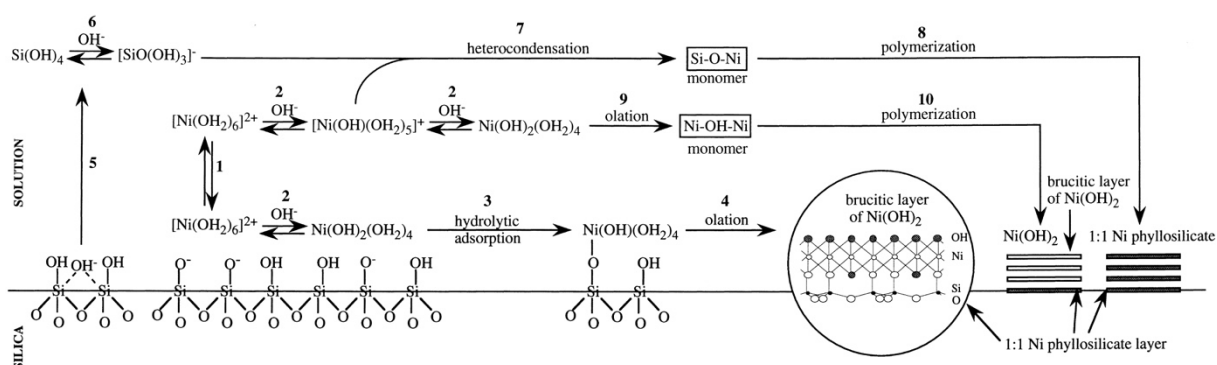


Figure 9 : Molecular-level mechanism for the deposition-precipitation of Ni(II) on silica. Reproduced from ref.[129]

Dissolution phenomena, and their consequences on interfacial coordination chemistry, are not restricted to silica. Clause and coworkers later showed that the same type of surface precipitation could occur with alumina, which is yet believed to be a poorly soluble oxide [131]. In that case, deposition of Ni(II) and Co(II) amine complexes leads to the formation of hydrotalcite surface precipitates (layered double hydroxides), which are the Al counterpart of phyllosilicates. Interestingly, it was clearly demonstrated that the formation of these types of surface precipitates occurs through a dissolution-precipitation mechanism, even in mild conditions (ambient temperature, pH close to the isoelectric point of the support, reasonable contact times, i.e. a few hours), which reveals that support dissolution can be a major player even with poorly soluble oxides in non-aggressive conditions. It was postulated that the dissolution can be kinetically promoted by the initial adsorption of the metal ions (Co(II), Ni(II)) and consequent weakening of Al(III)-O bonds. Hence, the kinetic and thermodynamic solubility of the bare oxide does not appear as a sufficient descriptor for explaining the reactivity of catalytic supports. Estimation of the overall thermodynamic driving force for the formation of mixed surface phases needs to take into account both the metal and support atoms. The potential occurrence of these types of dissolution-precipitation phenomena for a variety of other catalytic systems can be assessed by looking at the existence of natural mixed phases, which can be used as a first guide in order to consider the possible formation of surface precipitates.

Deposition-precipitation (DP) is now a routine technique of catalyst preparation and has been used with many different types of supports. Ni-based catalysts have been prepared with DP on HBEA zeolites giving homogeneous ($2.5 \pm 0.7\text{nm}$) and thermally-resistant Ni particles due to high metal/support interactions leading to highly stable catalysts in hydrodeoxygenation reactions [132]. Non-silica based supports have been also used such as carbon nanofibers where it was shown that surface functionalization (oxidation leading to the formation of surface carboxylic groups) was essential for the deposition process in order to obtain well-dispersed metallic Ni particles [133]. The original work of Geus et al. [125] and Che and

co-workers on DP was also the basis for the development of an improved preparation route for Au-based catalysts. Haruta et al. [134] first prepared highly active Au/TiO₂ catalysts for low temperature CO oxidation by a procedure denoted imperfectly DP since it was carried out at a fixed pH (adjusted with NaOH) instead of an increasing pH brought about by the thermohydrolysis of urea. In this case, the Au content was limited to 1 wt%. Later on, Zanella et al. [135, 136] followed the conventional DP route starting from HAuCl₄ and urea and succeeded in maintaining a small and homogeneous size for Au nanoparticles (2-3 nm) while being able to substantially increase the weight loading of Au up to 8 wt%.

The nature of the mixed surface phase formed upon support dissolution also depends on the type of catalytic metal precursor (cationic or anionic) present in solution. It was demonstrated above, that in the case of transition metal cations (Ni²⁺, Cu²⁺...) a bulk surface precipitate is obtained (phyllosilicate or hydrotalcite for example), whereas in the case of oxoanions (i.e. molybdates or tungstates) it will be shown below that support dissolution generally leads to the formation of molecular mixed entities (such as heteropolyanions).

As a matter of fact, it was demonstrated by liquid-state ²⁷Al NMR that the simple contact between alumina and an heptamolybdate ([Mo₇O₂₄]⁶⁻) solution led to the formation in solution of an aluminomolybdic heteropolyanion [Al(OH)₆Mo₆O₁₈]³⁻ (Anderson structure, also noted [AlMo₆] thereafter), here again in pH conditions which are supposed to be non-aggressive for alumina (pH between 4 and 6.5) [137]. The kinetics of this dissolution-complexation phenomenon was relatively fast, since this heteropolyanion was identified in solution after only one hour of contact time at pH 4 at room temperature. It was also shown that the initial Mo precursor, heptamolybdate, reacts quantitatively with dissolved aluminum, since the only identifiable molybdic species in solution at pH 4 at equilibrium is the [AlMo₆] Anderson compound (Figure 10), which means that the initial catalytic precursor is fully converted in solution during deposition. This counter intuitive result can be rationalized by considering that the complexation reaction between heptamolybdate and dissolved aluminum increases the thermodynamic solubility of the oxide support by shifting the alumina dissolution reaction to the right, which can be summarized by the term ligand-promoted support dissolution. These results demonstrate again that the solubility of the bare oxide is a poor descriptor of the support reactivity during metal impregnation. The subsequent deposition of the mixed aluminomolybdic species on the surface of the alumina was also verified with ¹H-²⁷Al CP-MAS NMR spectroscopy. The same type of conclusions was obtained with WO_x/Al₂O₃ catalysts, for which the formation of Keggin-type heteropolytungstates was demonstrated [138].

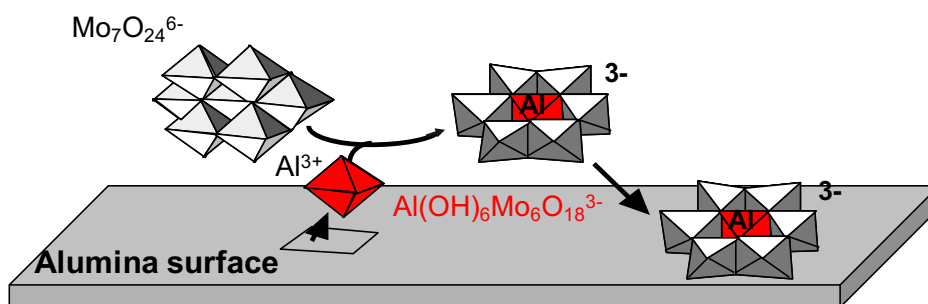


Figure 10 : Dissolution-complexation during molybdate deposition on alumina. Adapted from ref. [137].

At a more applied level, this fundamental study of the impregnation chemistry during $\text{MoO}_x/\text{Al}_2\text{O}_3$ catalyst preparation has important implications for the control of Mo dispersion after activation [139]. Indeed, incipient wetness impregnation of heptamolybdate leads not only to the formation of the Anderson $[\text{AlMo}_6]$ heteropolyanion, but also to its surface precipitation as an ammonium salt, $(\text{NH}_4)_3[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$, due to the generally high concentration of Mo in the impregnation solutions ($[\text{Mo}] > 1 \text{ M}$) and the low solubility of the Anderson salt. Ensuing calcination leads to the decomposition of the surface salt and the formation of ill-dispersed MoO_3 oxide particles.

Bergwerff et al. [19] later showed that these differences are not limited to oxidic phases, since precipitation of the $[\text{AlMo}_6]$ Anderson salt also leads to poorly dispersed MoS_2 slabs in hydrodesulfurization (HDS) catalysts, and consequently lower hydrodesulfurization activity. The same type of conclusions (poor dispersion and low hydrodesulfurization activity) were obtained for the co-impregnation of Ni and Mo on Al-SBA-15 mesoporous supports due to the concomitant precipitation of $[\text{AlMo}_6]$ and $[\text{NiMo}_6]$ species [140]. Current approaches to optimize the dispersion and activity of hydrodesulfurization catalysts implies notably to control $[\text{AlMo}_6]$ formation through various strategies including the optimization of the impregnation solution (use of chelating ligands, additives...) [19, 141]. Another approach is also to inhibit support dissolution by minimizing the oxide/water contact time by freeze-drying the catalyst after impregnation [139].

The potential formation of surface heteropolyanion was also later invoked by Scheithauer et al. in tungstated zirconia catalysts (WO_x/ZrO_2) based on the work mentioned above. These authors conjectured that Zr^{4+} ions from the support could be incorporated in the WO_x overlayer requiring charge compensation from protons which would explain the protonic acidity of these materials [142].

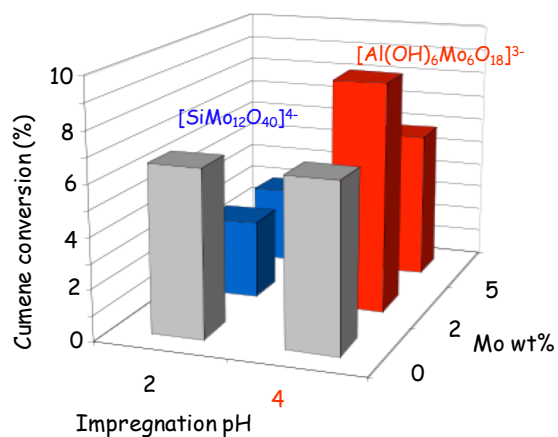


Figure 11 : Cumene conversion (atmospheric pressure, 300°C) for Mo/SiO₂-Al₂O₃ catalysts prepared by wet impregnation of ammonium heptamolybdate at pH 2 and pH 4 on a Grace-Davison ASA with 87% SiO₂-13% Al₂O₃ [143].

Dissolution phenomena for mixed oxide supports such as amorphous silica-alumina (ASA) adds a level of complexity since selective dissolution of either Al³⁺ or Si⁴⁺ can be promoted by Mo oxoanions through the respective formation of [AlMo₆] or a silico-molybdc heteropolyanion (i.e. Keggin-type [SiMo₁₂O₄₀]⁴⁻), and in turn impacts the acidity of the silica-alumina as revealed by cumene cracking (Figure 11) [143]. In the case of a wet impregnation (excess solution) at pH 4, it was proposed that for low molybdenum contents, the formation of [AlMo₆] leads to a mild dealumination of the ASA support with an increase in the strength of the acidic sites. At higher molybdenum contents, the larger dealumination leads to a decrease in the number of sites that is not compensated by the increase of their strength. On the contrary, for a wet impregnation at a highly acidic pH (i.e. pH = 2), for which the formation of [SiMo₁₂O₄₀]⁴⁻ is favored, the severe dealumination of the support at such acidic pH leads to a decrease in the acidity whatever the molybdenum content.

The impact of support dissolution with Mo-based silica-alumina catalysts was also demonstrated in metathesis applications. It was shown that the formation of [AlMo₆] in these systems was detrimental for Mo dispersion since it leads to the genesis of MoO₃ and Al₂(MoO₄) inactive species [144]. The molecular understanding of Mo speciation at the impregnation stage led to the derivation of a new preparation strategies by using either an additive (oxalic acid) or an alternative Mo precursor (Mo hydrates) in order to minimize the formation of [AlMo₆] and the subsequent formation of inactive species upon calcination resulting in enhanced metathesis activity [145].

Finally, it is also worth mentioning that the bare oxide support is not necessarily inert in aqueous suspensions, which can have crucial consequences in aqueous-phase reactions occurring in severe conditions (hydrothermal biomass conversion or Fischer-Tropsch synthesis for example) [146].

Considering γ -Al₂O₃ which is the predominant oxide support used at the industrial scale, it has been demonstrated by Michel Che's group that γ -Al₂O₃ can undergo chemical degradation (or *weathering* in the terms of Earth Science) when contacted with an aqueous solution which leads to the formation of hydroxides (Al(OH)₃) and/or oxy-hydroxides (AlOOH) along with a profound structural change of the initial support [147]. Weathering was demonstrated to occur through a dissolution/heterogeneous precipitation of the hydroxide on the initial γ -Al₂O₃ particles [147, 148]. Mesoporous aluminas are especially sensitive to this phenomenon of dissolution and conversion to aluminum hydroxide [149, 150]. It was also demonstrated by other groups that the profound structural changes of γ -Al₂O₃ after an hydrothermal treatment can have a drastic impact on the state of supported metal catalysts by lowering metal-support interactions and in turn, decreasing metallic dispersion as demonstrated for Al₂O₃-supported Pt [87] and Ni [151] catalysts.

As a result of the previous fundamental studies, new strategies are currently being developed in order to drastically decrease and even inhibit alumina weathering in order to design stable alumina supports for industrial applications in hydrothermal conditions. Several successful approaches have been implemented involving for example surface functionalization with inorganic dopants (Mg²⁺, Zr⁴⁺, Ni²⁺, Si⁴⁺) [152] or selective carbon deposition which is proposed to block the most reactive alumina surface sites [153].

7. Design of single-site metal zeolite catalysts

Finally, going back to the first research interests of Michel Che for the design of isolated metal cations on oxide supports, and the use of molecular-scale spectroscopic methods including EPR, another research direction emerged for the controlled elaboration of single site metal-zeolite catalysts with metal atoms in framework position [154]. Isolated metal single-site materials, in which metal atoms are atomically dispersed on supports, promise to achieve the highest metal efficiency from every atom of such materials. In the case of supported systems, generally prepared by impregnation, obtaining single-site catalysts is challenging since the difficulty resides in the so-called speciation, which is "the distribution of an element amongst defined chemical species in a given system" [155]. The speciation concerns both the aqueous solution and the oxide support. The challenge is to design metal single-site catalysts with isolated and well dispersed metal active centers, whereas the speciation of metal precursors and support sorption sites are usually diverse. For the latter, the complexity of oxide supports can be avoided by selecting zeolite systems. The high silica BEA zeolite, with Si/Al ratio of 11 and aluminum atoms sufficiently diluted in the zeolite matrix, was chosen. In addition, this zeolite: i)

has a three-dimensional structure, ii) possesses pores larger than those of ZSM-5 and iii) exhibits high thermal and acid stability [156].

In order to reach the single-site goal, a two-step post-synthesis procedure was chosen and firstly applied to obtain vanadium-containing Si-BEA zeolites, as illustrated in Figure 12 (Left). It involves two successive steps: i) removal of the aluminum atoms from the framework upon treatment of BEA zeolite at 353 K for 4 h by a 13 N nitric acid solution (removal confirmed by chemical analysis, which showed that the Si/Al ratio increased to over 1000), and creation of vacant T-atom sites (T for tetrahedral) and associated silanol groups [154, 157] and ii) incorporation of vanadium at room temperature from low molality aqueous NH_4VO_3 solution at pH = 2.5, into the vacant T-atom sites created in the first step. The choice of the experimental conditions was determined by the fact that the metal atoms to be incorporated into the framework should be, like the removed aluminum atoms, positively charged and mononuclear. The predominance diagram of vanadium(V) [158] shows that the only appropriate species is VO_2^+ , limiting the domain to low molality and pH.

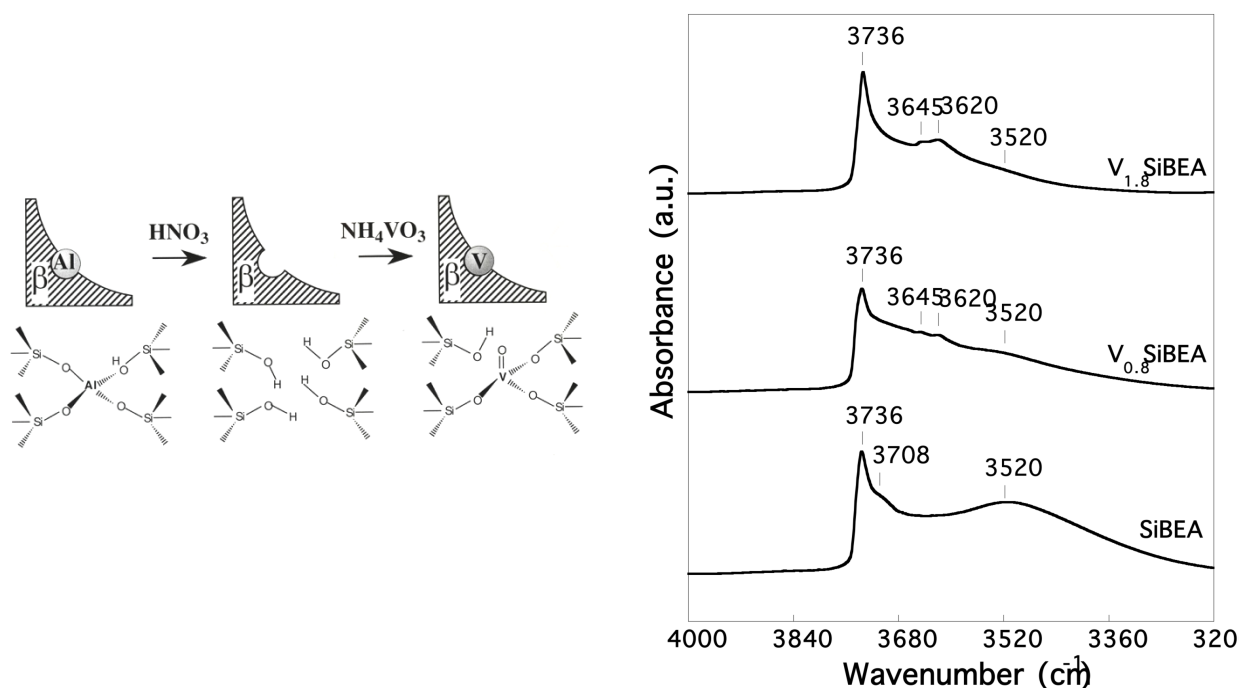


Figure 12. Left: Description of the two-step postsynthesis procedure [154] and of the associated sites. Right: FTIR spectra recorded at room temperature of SiBEA, $\text{V}_{0.8}\text{SiBEA}$ and $\text{V}_{1.8}\text{SiBEA}$ in the O-H stretching region after calcination of the samples at 773 K for 8 h in flowing oxygen followed by outgassing (10^{-3} Pa) at 573 K for 6 h [159]. The intensities of the IR spectra have been normalized with respect to the intensity of framework overtones located within the $2000\text{--}1800\text{ cm}^{-1}$ range (not shown) used as internal standards.

After contact of SiBEA with an aqueous NH_4VO_3 solution at room temperature for 3 days (pH = 2.5, $c = 1 \times 10^{-3}\text{ mol L}^{-1}$), chemical analysis showed that all the V atoms present in the initial solution had been

loaded into the SiBEA framework, up to a limit of 1.75 V atoms per unit cell [154, 157]. The incorporation of vanadium did not affect the zeolite crystallinity, but modified the d_{302} spacing which increases with V loading [154]. Because of the relative values of the Al-O, Si-O and V-O bond lengths (1.790, 1.660 and 1.755 Å respectively) [154], this expansion of the lattice strongly suggested that vanadium had been incorporated into the zeolite framework. Furthermore, vanadium was not removed by washing at room temperature with an aqueous solution of ammonium acetate (NH_4OAc) [157]. This incorporation led to a decrease of intensity of the IR bands of the SiO-H groups, in particular hydrogen bonded groups at 3520 cm^{-1} , suggesting that these silanol groups had reacted with the V precursor (Figure 12 (Right)) [154, 157]. Vanadium in the SiBEA zeolite was mostly present as isolated pseudo-tetrahedral vanadium(V) species, with a non-hydroxylated pyramidal structure $(\text{SiO})_3\text{V}=\text{O}$ (Figure 12 (Left)) [154, 157]. The appearance of two small IR bands at 3620 and 3645 cm^{-1} [157] suggested that V_xSiBEA also contained V(V) sites with V(V)O-H groups with a hydroxylated pyramidal structure $(\text{SiO})_2(\text{HO})\text{V}=\text{O}$. Pyridine adsorption measurements showed that these V(V)O-H groups possessed a Brønsted acidic character [159]. The tetrahedral environment of vanadium was confirmed by the single peak at *ca.* 1.6 Å (without phase-shift correction) observed in the Fourier transform of normalized k^3 -weighted EXAFS spectra and the coordination number of 4 oxygen atoms [160]. Finally, the DR UV-vis spectrum of V_xSiBEA exhibited two main bands at 270 and 340 nm [154, 157, 161-163]. Because of the absence of d-d transition in the range 600-800 nm and of any V(IV) ($3d^1$) EPR signal, the two bands were assigned to $\pi(t_2) \rightarrow d(e)$ and to $\pi(t_1) \rightarrow d(e)$ oxygen-tetrahedral V(V) charge transfer transitions, involving bridging (V-O-Si) and terminal (V=O) oxygen, respectively [164].

All these results evidenced that the two-step post-synthesis procedure allows one to obtain V_xSiBEA zeolites with isolated and framework pseudo-tetrahedral vanadium (V) species.

The two-step post-synthesis procedure in its aqueous version was also applied with success to incorporate other elements into BEA such as Co(II) ($3d^7$) [165, 166], Fe(III) ($3d^5$) [167, 168], Cu(II) ($3d^9$) [169, 170], and Cr(III) ($3d^3$) [171, 172] and the catalytic properties of the resulting systems investigated, particularly in the selective reduction of NO by alcohols or propane [165, 168-170, 173] or the oxidative dehydrogenation of propane [172]. These results allowed one to reconsider the common belief that incorporation of transition metals into the framework of zeolites led to catalysts with low activity and stability.

To incorporate Nb(V) and Ta(V) (both d^0) as single species, an organic liquid route was applied in the second step of the post-synthesis procedure, using niobium pentaethoxide $\text{Nb}(\text{OC}_2\text{H}_5)_5$ [174] or tantalum pentaethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$ [175]. To incorporate Ti(IV) ($3d^0$), a gaseous precursor such as TiCl_4 was used [176, 177]. Three important advantages were associated with the application of this latter precursor: i) the speciation of titanium was restricted to a single species, ii) there was no longer any

need of a solvent, iii) the precursor had the same tetrahedral symmetry as that of the site it should occupy after incorporation into the SiBEA structure. In line with the results described for other d^0 systems, the molecular processes associated with each of the two steps of the post-synthesis procedure globally followed the sequence and description given for vanadium. Recently Ziolk and her group built on the above strategy with the alternative postsynthesis methods to incorporate group five metals (vanadium, niobium and tantalum) into different zeolite structures in order to design zeolites with novel and attractive catalytic and photocatalytic properties [178].

There are now countless reports where zeolites are used as supports for designing isolated metal single-sites in many catalytic processes because of their highly uniform structures [179-181]. The emergence of isolated single atom catalysts demonstrates that the field is moving toward manipulating metal atoms in a controllable way for the synthesis of materials with the desired structure and properties [182].

8. Perspectives

The different works reported above are based on the concept of Interfacial Coordination Chemistry largely developed and promoted by Michel Che. This new approach has been decisive in setting fundamental grounds to the know-how attached to the different unit operations in catalyst preparation. Current developments in the field can be seen as a direct continuation of his approach, and a greater level of complexity can be tackled thanks to the new tools that have been made available to the community in the last decade, for the exploration of different length scales, time scales, and experimental conditions.

First, the precise description of the grafted metallic ions and of the support surface sites has benefited from great progress of computational chemistry, with consequences in the comprehension of the phenomena that determine the nucleation and growth of supported phases. This topic is developed by another paper of the present issue by Corral Valero and Raybaud [183]. Theoretical calculations were initially largely devoted to the understanding of the working catalytic site, but many recent examples can be found that are dedicated to the genesis of the active phase, be it at the solid/liquid (impregnation) or solid/gas (drying, calcination, activation) interfaces. Computational chemistry can now bring more insight into the ICC concept by proposing : i) an atomic description of the local structure of the various surface sites of the support seen as a ligand, be it a covalent oxide like silica or silica-alumina, or an ionic oxide like alumina, ii) the optimized geometry of adsorbed metal precursors as well as the effect of promoters/additives (such as organic ligands) on this adsorption mode, iii) a

molecular comprehension of the support effect on the particle size, morphology, orientation... during the catalyst activation (reduction, sulfidation...).

Development of ICC was made possible thanks to the use of complementary spectroscopic techniques available in the lab (UV-vis, EPR, NMR...) in order to yield a molecular description of the active phase upon thermal treatments. However, the intrinsic limitations of these techniques made the analysis difficult when the speciation of the metal was complex, and when the evolution of the supported ions needed to be followed at increasing temperature. The development of In-Situ/Operando synchrotron-based techniques such as EXAFS and XANES has now allowed one to take a step forward in the full understanding of activation parameters required to transform the grafted complex into the catalytic site. More recently, time-resolved techniques (Quick-EXAFS) have brought even more insight into the kinetics of phase transformation and multiplicity of species involved [184]. Time-resolved spectroscopy results in a very large amount of data with tens of spectra recorded per minute, and integration of chemometric tools in XAS data analysis has proved to be essential to unravel the formation of active species. By using procedures such as the Multivariate Curve Resolution with Alternating Least Squares analysis (MCR-ALS), it is now possible to quantify and extract pure spectra of species present as an initial mixture, or of intermediate species, each of them evolving simultaneously or consecutively toward the building of the supported phases. In the case of CoMo/Al₂O₃ catalysts, MCR-ALS led to the identification of 5 intermediate species and interconversion mechanisms that would otherwise be impossible to isolate [184]. The combination of XAS and MCR-ALS chemometric analysis now yields a detailed molecular view of the activation, reactivity and possible deactivation of catalysts.

Finally, one has to note that ICC was developed as a local, molecular-scale approach, best fitted to systems that could be described as "single sites" throughout the catalyst. The heterogeneity of shaped industrial catalyst and the diffusion processes associated to the preparation of extrudates could not really be taken into account. Nevertheless, Bergwerff et al. [19] showed with the help of Raman microspectroscopy that support-dissolution (as developed in section 6) was key to explain the heterogeneous distribution of the active phase in industrial extrudates. The combination of ICC concepts and imaging techniques at different length scales [185] is certainly a promising way for a rational understanding and control of the spatial distribution of the active phase on technical shaped catalysts.

9. Concluding remarks

Our tribute to Michel Che for his development of Interfacial Coordination Chemistry is centered on the chemistry concepts developed by him and his group over several decades, in order to reach a molecular-scale design of heterogeneous catalytic materials and control of their preparation. It also

highlights the appropriate choice of a diversity of characterization techniques depending on the proof that is sought. EPR has always been a central technique with UV-Visible spectroscopy but application of EXAFS as early as the eighties was also a decisive move for setting the ground of Interfacial coordination chemistry.

It also has to be stressed that a distinct feature of Michel Che's scientific approach was to continuously dialog with other scientists coming from different fields of chemistry (coordination chemistry, electrochemistry, geochemistry, supramolecular chemistry...) in order to integrate common concepts that led to the development of interfacial coordination chemistry as a distinct field and as a unifying concept, that could make it possible to go beyond the collection of particular cases, to consider support and metal complexes as chemical partners evolving together along the catalyst preparation, and to establish some fundamental grounds behind know-how practices which were applied in the large-scale preparation of industrial catalysts.

Another related aspect, and not the last, was his search for illustrative words in order to clarify definitions, nomenclatures and classifications. One can quote, among others, the discussion about grafting vs. anchoring [186] or the term Ligand-Promoted Support Dissolution [137].

This review also highlights the legacy of the concept of Interfacial Coordination Chemistry with numerous examples of current strategies for a rational control of catalyst preparation.

Obviously, Michel Che' group was indeed an outstanding and inspiring place to learn and develop science. We, his PhD students, postdoctoral fellows, visiting professors and close collaborators can be grateful to him for his scientific legacy that is currently influencing our research.

Acknowledgements

This review is a tribute to the pioneering contribution of Michel Che to the field of Interfacial Coordination Chemistry applied to heterogeneous catalyst preparation which would not have been possible without the dedication of many colleagues in Paris, in addition to the co-authors of the present article: D. Delafosse who was decisive in Michel Che's moving from Lyon to Paris, P. Rabette, D. Olivier and M. Kermarec who welcomed him in Paris and became very close friends to him, F. Averseng, D. Costa, A. Davidson, R. Franck, J. Fournier, C. Lepetit, P. Massiani, B. Morin, Y. Millot, M.J. Peltre, J.M. Tatibouët. Long-lasting collaborations in this field also took place at the international level and most importantly in Krakow (K. Dyrek, Z. Sojka and co-workers), Munich (H. Knözinger and co-workers), Osaka (M. Anpo and co-workers), Moscow (B. Shelimov) and Turin (S. Coluccia, E. Giamello and co-workers). All the PhD students and Post-Docs mentioned in the following references are also warmly acknowledged.

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