

LETTERS

Evidence for Interfacial Molecular Recognition in Transition Metal Complexes Adsorption on Amorphous Silica Surfaces

Souhir Boujday, Jean-François Lambert,* and Michel Che†

Laboratoire de Réactivité de Surface, UMR 7609 - CNRS, Université Pierre et Marie Curie (Paris VI), 4, place Jussieu, 75252 Paris CEDEX 05, France

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A series of Ni(II) complexes containing polyamines and 1, 2, or 3 labile aqua ligands ($[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$, $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$) were selectively adsorbed on the same silica support. In all cases, saturation coverages derived from adsorption isotherms were far below one physical monolayer and UV-visible and EXAFS spectroscopy suggested adsorption by grafting on specific surface sites. The density of adsorption sites was different for all three complexes, suggesting that molecular recognition phenomena, probably implying interactional complementarity between surface and adsorbate, are operative in the adsorption mechanism.

Introduction

Molecular recognition has been a crucial concept in biology and biochemistry since its introduction by Emil Fischer in 1894 with the key-lock mechanism.¹ More recently, this phenomenon was extrapolated to chemistry,^{2–5} giving rise to the notions of supramolecular chemistry, self-assembly, and host–guest chemistry. Ever since, growing attention has been paid to molecular recognition and related phenomena, including cases where only inorganic molecules are implicated.^{6,7} One particular aspect of supramolecular chemistry that has not been transferred so far to the field of inorganic chemistry is the “docking” of small molecules on the surface of large particles presenting different potential adsorption sites.⁸ A well-documented example is the interaction of oligosaccharides with the surface of lectins,⁹ where the key to molecular recognition is constituted by an “epitope” of the oligosaccharide containing three polar groupings that specifically bind to complementary sites on the protein surface: not only is a specific adsorption site recognized on the protein surface, but the orientation of the docking molecule is

imposed as well. Here, we show that an inorganic analogue to this situation might be provided by the specific adsorption of transition metal complexes (TMCs, with molecular weights of a few hundred daltons, comparable to oligosaccharides) on the surface of nanometric-size oxide particles.

Ideas derived from the field of molecular recognition have been applied previously to rationalize de novo synthesis of porous materials,^{10–12} but not, to our knowledge, adsorption of metal complexes on preformed oxides.

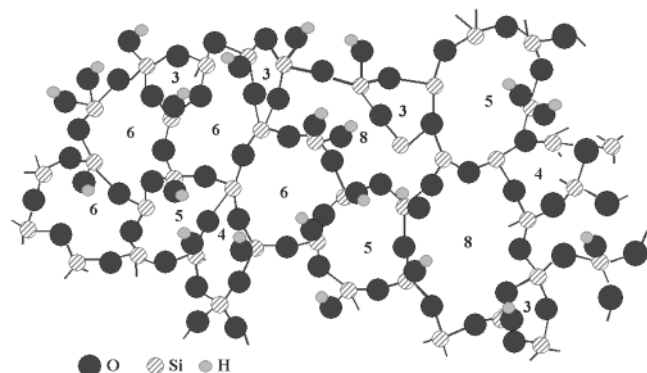
Although oxide particles are 2 or 3 orders of magnitude heavier than typical proteins, they also present a high degree of structural complexity, as discussed later. Specific adsorption phenomena have been the object of longstanding interest in the fields of geochemistry and soil science.¹³ However, the precise characterization of TMC/surface interaction has proved an elusive goal and nothing remotely approaching the oligosaccharide/lectin example quoted above has been achieved so far.

Recently, we have been led to consider that molecular recognition phenomena could also be involved in the synthesis of heterogeneous catalysts, for which a first step is usually the deposition of a TMC on the surface of a preformed support oxide.

† Institut Universitaire de France.

TABLE 1: Parameters Related to the Adsorption of Ni(II) Amine Complexes on Silica (Aerosil380 Degussa)

nickel complex	$[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$	$[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$	$[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$
no. of grafted complexes/nm ²	0.20	0.35	0.15
complex area (nm ²)	0.30	0.17	0.27
saturation coverage as % of physical monolayer	7	5	4
% of silanols involved in grafting	4	14	10

**Figure 1.** Amorphous silica surface, adapted from Garofalini.¹⁷

To test this idea, we have selected a series of related TMC/oxide systems, where the oxide was an amorphous fumed silica, and the TMCs were octahedral complexes of Ni(II) with amine and aqua ligands, with coordination spheres ($\text{NiN}_{6-x}\text{O}_x$). The aqua ligands in such complexes are very labile.¹⁴ Previous research has shown that their adsorption mechanism does indeed involve substitution of aqua ligands by surface groups of the oxide support, i.e., formation of an inner sphere complex with the surface.¹⁵ Selected complexes differed in the number (x) of labile ligands: $x = 1$ for $[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$, $x = 2$ for $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, $x = 3$ for $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$ ($\text{en} = \text{NH}_2(\text{CH}_2)_2\text{NH}_2$, $\text{dien} = \text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$).

Materials and Methods

The support was an Aerosil380 silica (Degussa) with specific surface area = 380 m² g⁻¹. The Ni(II) complexes were synthesized in the aqueous phase by successive dissolution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and stoichiometric amounts of the required polyamines.¹⁵

Room-temperature adsorption isotherms were measured for the three Ni(II) complexes under conditions of constant ion strength (fixed by addition of KNO_3) and carbon dioxide exclusion. After equilibration of the solution/silica mixtures under stirring, the solid phase was separated by centrifugation and washed several times with distilled water to eliminate reversibly adsorbed complexes. This procedure is sometimes called “selective adsorption” in catalysis literature.¹⁶ Elemental analyses were carried out by atomic absorption (Centre d’Analyse du CNRS, Vernaison) on room-temperature dried solids, and their diffuse reflectance UV–vis–NIR spectra were recorded on a Cary 5 spectrometer (Beckman). ²⁹Si NMR spectra were recorded on a Bruker MSL400 spectrometer, with a 100 s delay and 0.5 μs pulse length.

Results and Discussion

Structural models of the amorphous silica support are available from molecular simulations, as illustrated in Figure 1.¹⁷ They show a surface composed of two basic types of building blocks, siloxanes (Si–O–Si) and silanols (Si–OH), and are in general agreement with the limited experimental results provided by neutron scattering¹⁸ and ²⁹Si MAS NMR.¹⁹ The diversity of possible arrangements of these building blocks is apparent in Figure 1, especially as regards the groupings and

mutual disposition of the more reactive silanols. ²⁹Si MAS NMR allows discrimination between geminal silanols (−90 ppm) and terminal silanols (−102 ppm). It also provides the total amount of silanols, and thus, the silanol density on the silica surface. The silica used in this work has 5 silanols per nm², in agreement with previous data,²⁰ and its geminal SiOH/total SiOH ratio is approximately equal to 10%.

Significant amounts of Ni complexes were irreversibly retained and Langmuir-type adsorption isotherms, characterized by the existence of a saturation coverage, were observed in all three cases. Table 1 lists the saturation coverages corresponding to the three Ni(II) amine complexes under study and compares them to the complex areas and the number of available silanols on the silica surface. A first point to be made is that observed saturation coverages have nothing to do with physical monolayers: the number of complex molecules that would correspond to a uniform close packing on the surface was estimated from molecular modeling (using the Cerius2 package, Accelrys), and the saturation coverages represent only a small fraction of the latter. Furthermore, there seems to be no correlation between complex area and saturation coverage (Table 1).

Two main adsorption mechanisms could give rise to irreversible adsorption on the silica surface: electrostatic adsorption in the double layer created by the negative charges of the deprotonated silanols, and inner-sphere complex formation or “grafting”, which is a form of site adsorption.

Two main arguments lead us to exclude electrostatic adsorption:

(i) the saturation coverages are significantly different for the three complexes; an electrostatic adsorption mechanism should induce similar coverages for all complexes because they bear identical electric charges, and the pHs of the three solutions are similar at 7.20 to 7.30, which must induce similar surface concentrations of negative charge on silica;

(ii) elemental analysis shows that the cation of the indifferent electrolyte (K^+) is not retained on washing, as it would be if the adsorption mechanism was a simple charge compensation;

We may note that, conversely, a significant amount of the counterion (ClO_4^-) is adsorbed together with the Ni(II) complex; the question of whether it adsorbs independently, or as a ternary adduct, remains open, and this coadsorption neither proves nor disproves pure electrostatic adsorption.

In contrast, definite evidence for nickel grafting is provided by spectroscopic methods. Figure 2a–c presents the UV–visible spectra of nickel complexes in aqueous solution and adsorbed on silica, respectively. In the case of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ (Figure 2.b), the three d–d transitions expected for octahedral Ni(II)¹⁵ are observed. After deposition on silica and drying, they are significantly shifted to lower energies, which indicates a change in the coordination sphere, more precisely, a replacement of the aqua ligands in the coordination sphere of nickel by lower crystal field ligands.

These ligands are most probably constituted by SiOH (silanols) and/or SiO^- (silanolate) groups, rather than by relatively unreactive siloxanes; their degree of protonation is not known with certainty, and therefore the generic term “silanols” must be understood hereafter to refer to either SiOH or SiO^- .

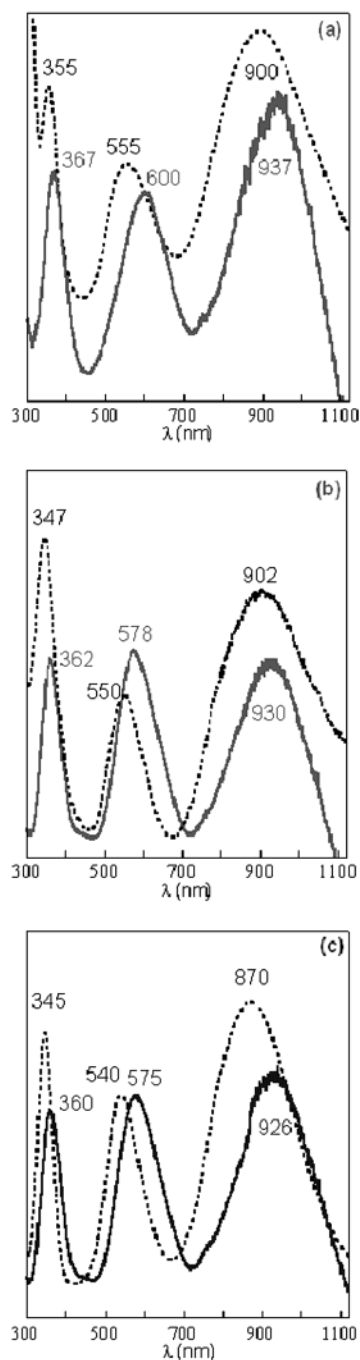


Figure 2. UV-visible-NIR spectra of Ni(II) complexes, in solution (transmission; dotted line), and adsorbed on silica (diffuse reflectance; continuous line): (a) $[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$; (b) $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$; (c) $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$.

Similar observations are made for the other two Ni(II) complexes (Figure 2.a,c) whereas a parallel study on the interaction of $[\text{Ni}(\text{en})_3]^{2+}$, which has no labile ligands, with the silica surface indicates that no substitution occurs (the adsorption mechanism is electrostatic in the latter case). An EXAFS study at the Ni K edge confirmed the grafting, which was manifested by the appearance of second nearest neighbor Si atoms at a distance of 3.2 Å from the Ni(II) center; their optimized number after adsorption (1.0, 1.8, and 3.0, for $[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$, $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$, respectively) corresponded well to the number of labile H_2O ligands before adsorption (1, 2, and 3), suggesting a simple ligand substitution mechanism. Thus, not only the silica surface can act as a ligand

for supported Ni(II) complexes, but it will behave as a monodentate, bidentate, or tridentate ligand according to the nature of the adsorbed complex. In addition, the data confirm that surface ligands are silanols rather than siloxanes, because the latter would result in more than one Si second neighbor per entering ligand.

A remarkable feature of the spectra of the adsorbed Ni(II) complexes is the small width of the d-d bands, comparable or even inferior to those observed for the aqueous precursor complexes. This strongly suggests that after completion of the selective adsorption procedure, the molecular environments of all Ni(II) ions on the surface are very homogeneous. In view of the large variety of local structures that exist on the silica surface (see Figure 1), it can be concluded that only some of those are selected by the Ni(II) complexes and only these specific local configurations constitute the adsorption sites. Indeed, as shown in Table 1, only a small fraction of the total silanols is implied in the adsorption process.

We have thus established that the Ni(II) polyamine complexes specifically recognize well-defined local configurations on the silica surface, probably involving one or more silanol groups, as their specific adsorption sites, and that their interaction with these adsorption sites implies the substitution of one or several labile (aqua) ligands. As regards the precise nature of those local configurations, only speculative hypotheses may be offered at this point. Among the three complexes selected for this study, we expected $[\text{Ni}(\text{en})(\text{dien})(\text{H}_2\text{O})]^{2+}$ to be the least demanding because it can accommodate only one SiOH group in its coordination sphere upon substitution of the single water ligand. However, it does not yield the highest saturation coverage of the three tested complexes (0.20 nm^{-2} , instead of 0.35 nm^{-2} for $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$). On the other hand, the most sterically demanding complex, $[\text{Ni}(\text{dien})(\text{H}_2\text{O})_3]^{2+}$, which needs three silanol groups to enter its coordination sphere, does indeed yield the lowest saturation coverage: in summary, there is no simple correlation between the number of surface ligands necessary for grafting and the maximum amount of complex that can be grafted.

We therefore conclude that the picture of Ni(II) complex adsorption by a simple inner-sphere complex mechanism (substitution of one or several SiOH surface ligands for the initially present aqua ligands) is in fact oversimplified. For a quantitative rationalization of adsorption data, the cooperative action of some distinct molecular phenomenon must be invoked. One obvious possibility is the formation of some hydrogen bridges between, e.g., the amine protons as H-bond donor groups (D), and some surface siloxanes and/or silanols as H-bond acceptors (A). This type of H-bridge was indeed observed by DRIFT during the interaction of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ with alumina.²¹ Although these N-H...O bridges are usually quite weak,²² they should be strengthened by the complexation of the lone electron pair of the amine. The resulting situation is schematically illustrated in Figure 3, which outlines the possibility of *interactional complementarity* between the Ni(II) complex and the silica surface. In this view, the adsorption site would involve not only two silanols able to act as ligands but also a number of H-bridge accepting groups (assumed equal to 2 in Figure 3). Although hypothetical, this model has clear analogues in the field of combinatorial chemistry of homogeneous systems.²³ It is also compatible with observations from the field of geochemistry: careful investigations have shown that, in the adsorption of $[\text{ML}_x]^{2+}$ systems on dispersed oxides, so-called "spectator" ligands may indeed play an active role in the process of transition metal complex adsorption.²⁴

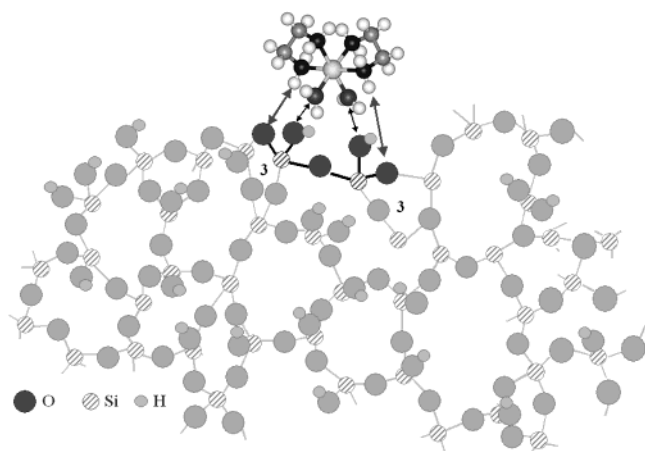


Figure 3. Possible interaction mechanism between $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ and a silica surface site, outlining the principle of interactional complementarity. The arrows indicate ligand substitution of two surface silanols for two aqua ligands with formation of covalent bonds, and H-bond donor/acceptor interactions.

In conclusion, the view of metal catalyst precursor deposition that we advocate here involves the occurrence of well-defined organizational principles, similar to those operating in simple biological systems, in what usually appears as a low-technology industrial preparation procedure. If this view is correct, it opens interesting prospects for molecular tailoring of catalytic sites in oxide-supported systems, especially because many of the available data on the subsequent thermal evolution of such catalysts indicate that the initial metal speciation plays a long-lasting role in determining the properties of the catalytic system.²⁵ In addition, there are clear similarities between our conclusions and those reached previously on other TMC/oxide systems, particularly on $\text{Pd}(\text{II})/\text{Al}_2\text{O}_3$ by Contescu et al.,²⁶ where the importance of geometrical constraints during adsorption–impregnation was underlined.

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