# IR and Theoretical Studies of Monocarbonyl Ni Complexes Formed by Adsorption of CO at Low Pressure on Silica-Supported Ni$^{II}$ Ions

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***Abstract:*** This work reports on the reactivity of coordination vacancies of Ni$^{II}$ ions grafted onto the tridentate silica support (Ni$^{II}_{3c}$ ions) with respect to CO used as a probe molecule. The adsorption of CO at 77 K in the 0.3 to 3.5 Pa CO pressure range is studied by FTIR on two samples differing in the dispersion of nickel. Quantum chemical calculations by the DFT method are performed to investigate, using a cluster approach, the binding of Ni to silica and, after CO adsorption, the geometry of the resulting carbonyl Ni complexes. Silica is modeled by using clusters composed of three types of monodentate ligands, SiO$^-$, SiOSi and/or SiOH, found on the surface of silica. This work is devoted to the monocarbonyl complexes. Whatever the sample, only one type of monocarbonyl is formed from Ni$^{II}_{3c}$ ions. It is shown that the charge of the silica cluster is the major parameter influencing the CO IR frequency whereas the nature and the size of the silica cluster do not affect the CO bond length, confirming that local electrostatic interactions predominate. Only the 1− charged silica cluster Si$_5$O$_3^-$, composed of SiO$^-$, 2SiOSi fragments, respectively, reproduces the Ni−O distances derived from EXAFS for the Ni$^{II}_{3c}$ grafted site and gives CO frequencies in good agreement with the experimental values. It is shown that CO is stabilized by a magnetic transition from the $^3$Ni$^{2+}$ triplet to the $^1$Ni$^{2+}$ singlet state occurring upon adsorption.

## Introduction

The metal/oxide interface[1] has become a very important subject in surface science studies because of its relevance to a variety of technological applications, from microelectronics to coating and protection of metals and from nonlinear optics to gas sensor applications.[2] However, oxides are difficult to study by surface science techniques because their nonconductive and brittle nature causes experimental difficulties related to sample charging and heating. An approach that has been used to facilitate the study of oxides and metal−support (oxide) interactions is to prepare thin films on a metal surface.[3,4]

As pointed out by Pacchioni and co-workers,[2] another approach is the controlled dispersion from aqueous solutions of transition metal (TM) complexes onto the support.[5] This is particularly interesting since these complexes can be used as molecular probes to investigate the nature of their interaction with oxide supports.[6] By a careful control of the experimental conditions, it has been possible to show that an oxide can act as a counterion,[5a,b] a receptor,[6b,7] a ligand,[8a,b] or a reactant[9] and that the nature of the "TM complex−oxide" interaction can be described with the concepts of electrochemistry, supramolecular chemistry, coordination chemistry, or geochemistry[6b] respectively.

During the past decade, interest in chemical reactions occurring at the metal oxide−aqueous solution interfaces has increased significantly because of their importance in a variety of fields including atmospheric chemistry, heterogeneous ca-

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talysis and photocatalysis, chemical sensing, corrosion science, environmental chemistry and geochemistry, metallurgy and ore beneficiation, metal oxide crystal growth, soil science, semiconductor manufactoring and cleaning, and biology.[10]

From this variety of fields, heterogeneous catalysis is of special interest because it is at the crossroads of chemistry.[6] As a matter of fact, catalyst preparation is largely concerned with inorganic chemistry when transition metal complexes, precursors of the catalytically active sites, are deposited from their aqueous solutions onto oxide supports. After removal of the solvent and careful thermal activation, selective and active solid materials are obtained[6b,c,11] which can be used for the benefit of chemistry for instance to catalyze molecular reactions,[12] be they from the fields of petrochemistry, fine chemicals, or environmental chemistry, thus bridging the gap between solid-state chemistry and molecular chemistry.

Among all catalyzed reactions, those involving carbon monoxide, a most suitable synthon, have been the subject of many studies.[12,13] At the industrial level, they concern both homogeneous catalysis (e.g. hydroformylation of olefins, amination of CO and carbonyl compounds)[13] and heterogeneous catalysis (e.g. oxidation of CO from exhaust gas, steam reforming, watergas shift reaction, methanol synthesis, CO hydrogenation).[12] Carbon monoxide is also of fundamental interest because it can be used to probe the interfacial coordination chemistry of transition metal ions grafted onto oxide surfaces.[6,14] By gradually filling the coordination vacancies, the number of the latter can be determined by spectroscopic techniques such as NMR, IR, and EPR.[6,13] Such coordination vacancies are most important because they largely determine the way catalytic sites operate.[6,13]

The present paper deals with the characterization of surface carbonyl species by means of IR spectroscopy aided by theoretical calculations. These species are formed at a gas–solid interface by adsorption of carbon monoxide on isolated $Ni^{II}$ ions tricoordinated to silica. These ions, referred to as $Ni^{II}_{3c}$, are obtained by deposition onto silica of ammine or ethanediamine Ni complexes in aqueous solution followed by a suitable activating treatment at 973 K. Silica was chosen as a support as it offers a large number of different types of grafting sites.[15] The characterization of the $Ni^{II}_{3c}$ ions by EXAFS and Diffuse Reflectance UV–visible spectroscopy (DRS) was previously reported for the activated samples.[5a,16] No EXAFS measurements were performed after CO adsorption. The interest of producing these silica-supported isolated $Ni^{II}_{3c}$ ions is that they can be selectively photoreduced by hydrogen into isolated $Ni^{I}_{3c}$ ions,[17,18]

which can catalyze olefin oligomerization.[19a] By contrast, less unsaturated ions such as tetracoordinated $Ni^{II}_{4c}$, which are the main species produced after an activating treatment at 773 K, were shown to be hardly photoreducible.[19b]

This paper is devoted to the identification of the monocarbonyl $Ni^{II}$ complexes produced by adsorption of CO at low pressure (0.3 to 3.5 Pa). The occurrence of di- and/or tricarbonyls at higher CO presure will be discussed in a future paper. To obtain further insight into the geometry of the monocarbonyl $Ni^{II}$ complexes identified by IR, and into the interaction of the $Ni^{II}$ ions with the support, a modeling of selected molecular clusters simulating the amorphous silica surface and the monocarbonyl $Ni^{II}$ complex is performed by using quantum DFT calculations. Following the interesting approach of Ramprasad et al.,[20] cluster models of Ni bound ions are investigated versus the net charge of the monocarbonyl complexes and the coordination number of $Ni^{II}$ ions. The combined IR data and theoretical calculations show that the convenient silica-based cluster which best reproduces the geometry of the grafted $Ni^{II}_{3c}$ ion (symmetry and Ni–O distances derived from DRS and EXAFS, respectively) and the experimental CO frequencies has a 1– charge.

The novelty of the paper lies in the fact that the system investigated both experimentally and theoretically is not a model but a real system composed of an amorphous oxide support with dispersed TM ions and an adsorbed phase. This system is modeled in order to find the best fit able to reproduce results coming from DRS (symmetry),[16] EXAFS (Ni–O distances),[5a] and IR (CO frequencies). Despite the complexity of the system, it will be shown that the important chemical entities which mainly determine the system properties are the surface groups of the oxide support which are bonded to the TM ion in the same way as the donor atoms of the ligands bonded to the TM ion mainly determine the properties of a molecular complex.

## Experimental Section

**Sample Preparation.** Two types of silica-supported Ni samples were prepared by cation-exchange with hexaamminenickel(II), $[Ni(NH_3)_6)]^{2+}$, and with tris-ethanediaminenickel(II), $[Ni(en)_3]^{2+}$ with en = $H_2N–CH_2–CH_2–NH_2$, according to procedures previously described[5a] using a nonporous silica Aerosil 380 Degussa (specific surface area = 380 $m^2\cdot g^{-1}$) as a support. These samples are hereafter respectively referred to as ENi(NH$_3$) and ENi(en). The Ni loading of both samples was 2.0 wt %.

**Sample Pretreatment.** Samples were activated following a procedure previously described:[5a] heating (a) in $O_2$ (150 Torr) (1 Torr = 133.3 Pa) from room temperature (RT) to 773 K (100 K. h$^{-1}$) and (b) in $O_2$ (150 Torr) at 773 K for 2 h, (c) outgassing in a vacuum up to 973 K (100 K. h$^{-1}$), and finally (d) outgassing in a vacuum at 973 K for 15 h. After this activation procedure, neither $Ni^0$ nor $Ni^I$ species were detected by ferromagnetic resonance and EPR, respectively. The above-mentioned samples are referred to as activated samples.

**IR Measurements.** For the IR measurements, the samples were pressed in self-supporting pellets (15 mg·cm$^{-2}$) and placed into an IR cell adapted for low-temperature measurements, connected to a vacuum-sorption line, and allowing thermal treatments and adsorption–desorption experiments to be carried out in situ.

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The IR spectra were recorded on a Bruker IFS 66V FTIR spectrometer with 4 cm$^{-1}$ resolution and 256 co-added scans. The IR spectra of CO adsorbed at 77 K are reported in absorbance with the spectrum of the activated pellet taken as the background.

**Gases.** High-purity $O_2$, $^{12}CO$ (Matheson) gases were employed, with no further purification except liquid nitrogen trapping; 99% $^{13}C$-enriched CO gas (Icon), with a small fraction of $^{13}C^{18}O$ (7%) was employed to prepare $^{12}CO-^{13}CO$ isotopic mixtures.

**Methodology for Modeling Calculations.** Theoretical calculations may help to determine the geometric and spectroscopic parameters of the supported complex and provide information on the chemical bonding with the oxide support. Thus, for metal particles prepared by decarbonylation of metal carbonyl clusters,[21-24] the density functional theory (DFT) was successfully used to validate the structural model of rhenium subcarbonyls adsorbed on MgO.[24] DFT calculations have proven their efficiency in predicting geometries and IR CO frequencies for transition metal carbonyl complexes.[25-33] Cluster models were already used to model by ab initio calculations the adsorption of CO on Lewis sites on MgO and NiO[34] and to investigate the interaction of Cu and Pd atoms with regular and defect sites of $SiO_2$ surface.[2,35] The cluster approach was successfully employed also for Cu-exchanged zeolites,[20] where theoretical calculations of vibrational frequencies of CO were performed on mono- and dicarbonyl Cu complexes of various charges.

Calculations were performed with the Gaussian 94 program.[36] The geometrical parameters of the monocarbonyl Ni complexes were optimized independently at the DFT level by using the Becke's Three Parameter Hybrid Method with the Lee−Yang−Paar Correlation Functional (B3LYP)[37] and checked by vibrational analysis. The basis set used was a Double-Zeta plus Polarization basis (DZVP2).[38] The results were not corrected for basis set superposition error (BSSE) or zero point energy vibrational effects, leading thus to an overestimate of bond strengths.

The calculated harmonic frequencies are corrected by a scaling factor taking into account the anharmonicity. For the CO stretching mode,
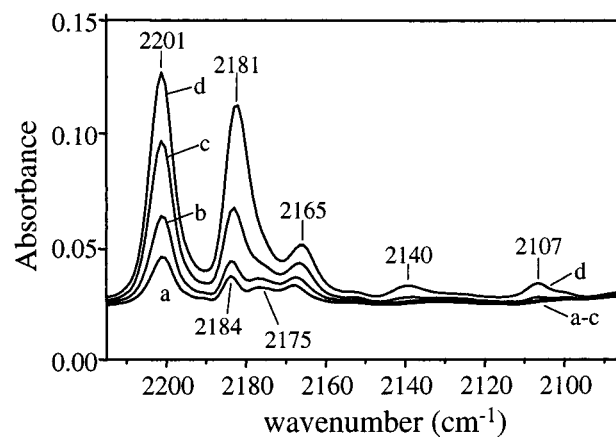
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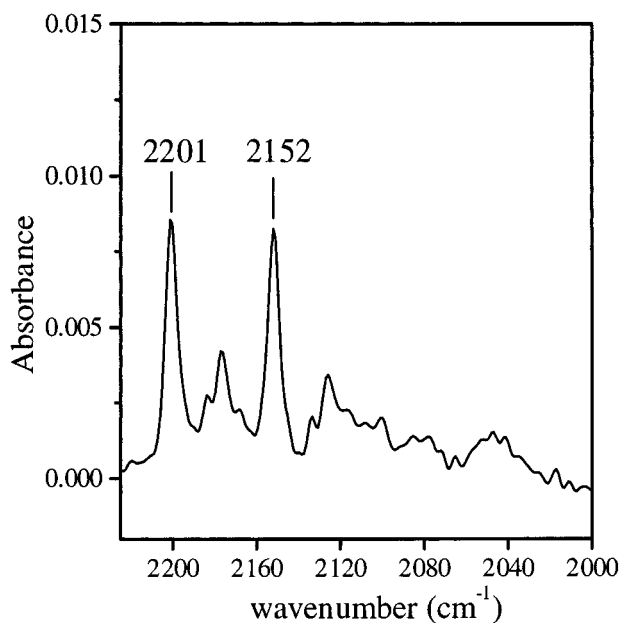
**Figure 1.** Infrared spectra of $^{12}CO$ adsorbed at 77 K on ENi(NH$_3$) under low CO pressure: (a) $3 \times 10^{-1}$, (b) $6 \times 10^{-1}$, (c) 1, and (d) 3.5 Pa.

this factor is derived from the free CO molecule since it fits well the experimental data.[39] The ratio of the experimental (2143 cm$^{-1}$) to the harmonic frequency (2170 cm$^{-1}$) is equal to 0.988. For convenience, in this work, the calculated CO frequencies were scaled with this factor (×0.988) in order to be compared with the experimental values, assuming the anharmonicities of the carbonyl complexes to be equal to that of the free CO molecule.

As a first test, geometries and vibrational spectra of known coordination complexes such as Ni(CO)$_4$, Fe(CO)$_5$, and Cr(CO)$_6$ were optimized and their IR frequencies calculated. The optimized geometries agree with those derived from IR and the calculated CO stretching frequencies fit the experimental ones with an accuracy equal to or better than 1%. Hence, the chosen method appears to be adequate for our study.

The results concerning the grafted Ni$^{II}$$_{3c}$ ion and the carbonyl Ni$^{II}$ complexes are reported for the most stable spin configuration, i.e., a triplet and a singlet, respectively.

## Results

**(A) Infrared Study. (1) Adsorption of CO. (1.1) IR Spectra of $^{12}CO$ Adsorbed on Activated ENi(NH$_3$) and ENi(en).** The admission of small doses of $^{12}CO$ at 77 K ($p(CO) < 4$ Pa) on the activated ENi(NH$_3$) sample produces two main bands at 2201 and 2184−2181 cm$^{-1}$, growing in intensity with increasing CO pressure (Figure 1). In this pressure range, the band at 2184 cm$^{-1}$ remains weaker in intensity than that at 2201 cm$^{-1}$.

A very weak and broad absorption is observed around 2175 cm$^{-1}$ together with a weak band at 2167 cm$^{-1}$ (Figure 1a,b). The absorption around 2175 cm$^{-1}$ is progressively masked by the low-frequency side of the dominant 2181 cm$^{-1}$ peak. The band at 2167 cm$^{-1}$ shifts to 2165 cm$^{-1}$ with increasing CO pressure, whereas two weak components at 2140 and 2107 cm$^{-1}$ appear for higher CO pressures (Figure 1c,d). All bands disappear by outgassing CO at 77 K and are reversibly restored by a subsequent CO adsorption. The same spectra are obtained for the activated ENi(en) sample (spectra not reported for the sake of brevity).

**(1.2) IR Spectra of $^{12}CO-^{13}CO$ (50:50) Adsorbed on Activated ENi(NH$_3$).** At very low $^{12}CO-^{13}CO$ pressure ($3 \times 10^{-1}$ Pa), the spectrum exhibits two main absorptions at 2201 and 2152 cm$^{-1}$, corresponding to the bands observed when only $^{12}CO$ or $^{13}CO$ are respectively adsorbed (Figure 2). Minor components, very poorly resolved, are also present in the 2185−2160 and 2140−2115 cm$^{-1}$ ranges.

**Figure 2.** Infrared spectrum of $^{12}CO-^{13}CO$ (50:50) adsorbed at 77 K on ENi(NH$_3$) under $3 \times 10^{-1}$ Pa.

**(2) Attribution of the IR Bands. (2.1) Preliminary Remarks on the Nature and Relative Amounts of the Different Types of Ni$^{II}$ Ions.** Depending on the Ni deposition method, previous studies by EXAFS[5a] and DRS[16] have shown that Ni$^{II}$/SiO$_2$ materials exhibit various types of Ni$^{II}$ ions *after an activating pretreatment at 973 K*, differing in their coordination number (three, four, five, or six oxygen ligands in the first shell) and in their state of dispersion on the support (isolated ions or small NiO particles). Among the different species, Ni$^{II}_{3c}$ ions are the most abundant and because of their state of low coordination are likely to be the sites leading to the Ni carbonyl complexes and therefore to the associated IR bands. This is corroborated by the fact that the spectra of Ni carbonyl complexes differ for samples pretreated at 773 K, which contain mainly Ni$^{II}_{4c}$ ions.[16]

In our samples, the 2201 cm$^{-1}$ band, which is the most intense at low CO coverage, should be attributed to carbonyl Ni complexes formed from such abundant Ni$^{II}_{3c}$ sites. Minor bands at 2165 and 2140 cm$^{-1}$, which undergo a limited increase in intensity with increased CO pressure, must rather be assigned to Ni$^{II}$ carbonyl complexes formed from other low-coordinated ions Ni$^{II}_{nc}$ present in small amounts.

It may be noticed that bands at 2180 and 2107 cm$^{-1}$ already observed at low CO coverages (Figure 1c,d) are assigned to dicarbonyl species as discussed in a forthcoming paper.

**(2.2) Band at 2201 cm$^{-1}$: Monocarbonyl Ni$^{II}_{3c}$−CO.** The band at 2201 cm$^{-1}$ shown in Figure 1 does not appear to be correlated with any other absorption. In the presence of a $^{12}CO-$

$^{13}CO$ (50:50) mixture, its intensity is reduced by one-half. The $^{13}CO$ component observed at 2152 cm$^{-1}$ is at the expected frequency[40] and has the same intensity as that of the $^{12}CO$ component (Figure 2). These features clearly indicate that the 2201 cm$^{-1}$ band is to be associated with a monocarbonyl complex.

**(2.3) Band at 2165 cm$^{-1}$: Monocarbonyl Ni$^{II}_{nc}$−CO ($n$ = 4, 5).** This weak band (Figure 1), not correlated with any other absorption, may be assigned to monocarbonyl adducts formed from a minor fraction of Ni$^{II}_{4c}$ or Ni$^{II}_{5c}$ ions detected by DRS.[16] The position of this band is less shifted than that of the 2201 cm$^{-1}$ component with respect to that of free CO (2143 cm$^{-1}$), indicating a decrease of the strength of the cationic electrostatic field,[41] in agreement with the higher number of oxygen atoms in the coordination spheres of Ni$^{II}_{4c}$ or Ni$^{II}_{5c}$ ions.

**(2.4) Band at 2140 cm$^{-1}$: Monocarbonyl Ni$^{II}$−CO on the Surface of Small NiO Particles.** The weak component at 2140 cm$^{-1}$ observed in Figure 1 appears as a single band and thus should also be assigned to a monocarbonyl complex, formed from another type of surface site present in a small amount. Unlike the 2201 and 2165 cm$^{-1}$ monocarbonyl bands, this weak component appears located at a frequency slightly lower than that of free CO.

An ill-defined band centered in the 2160−2130 cm$^{-1}$ region has been assigned to CO molecules adsorbed on Ni$^{2+}_{5c}$ ions exposed on the (100) plane of ill-crystallized NiO particles whereas a coverage dependence of the CO frequency is observed for sintered NiO samples (2152−2136 cm$^{-1}$ when $\theta$ varies from 0 to 0.5).[42a]

The 2140 cm$^{-1}$ band that is not coverage dependent can be related to the presence of very small NiO particles, <10 Å, detected on our samples by EXAFS[5a] and EPR.[43] However, the small NiO particle size strongly suggests that the adsorption sites are Ni$^{2+}$ ions in low coordination rather than Ni$^{2+}_{5c}$ ions located on exposed (100) planes of NiO. This attribution will be corrobated in a further paper.

**(B) Modeling Calculations. (1) Choice of a Model Representing the Silica Surface.** In a previous work of our group,[44] the ability of several cycles representing the silica surface to reproduce the geometry (symmetry and Ni−O distances) of the Ni$^{II}_{3c}$ site was tested. Among these model cycles, the Si$_5$O$_8$ cluster, which is a ten-membered ring with two adjacent SiO$^-$ (silanolate groups) and one SiOH, corresponds to a neutral NiSi$_5$O$_8$ complex and reproduces well the geometry of the grafted Ni$^{II}_{3c}$ ion. However, adding one CO to this neutral complex gives rise to a monocarbonyl complex with a CO bond length much more elongated than that of free CO (see Table 3). The corresponding CO frequency is lower than that of free CO, and does not agree with the experimental result. Thus, to

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**Table 1.** Optimized Parameters for Monocarbonyl Ni$^{II}_{3c}$ Complexes at the B3LYP Level

| cluster model | C−O[a] bond length l(Å) | Ni−C bond length l(Å) | Ni−C−O angle (deg) | CO[b] binding energy (kcal·mol$^{-1}$) |
|---|---|---|---|---|
| (OH)(H$_2$O)$_2^-$ | 1.136 | 1.887 | 179 | −33 |
| Si$_4$O$_3$H$^-$ | 1.137 | 1.820 | 177 | −9 |
| Si$_5$O$_3^-$ | 1.138 | 1.846 | 177 | −10 |

[a] Calculated value for free CO: 1.146 Å. [b] CO binding energy = $E_{\text{carbonyl complex}} - E_{\text{Ni(II)complex}} - E_{\text{free CO}}$.

**Table 2.** Calculated CO Stretching Frequencies for Monocarbonyl Ni$^{II}_{3c}$ Complexes

| monocarbonyl Ni$^{II}_{3c}$ complex | calcd CO$^a$ freq (cm$^{-1}$) |
|---|---|
| [Ni$^{II}$(OH)(H$_2$O)$_2$ (CO)]$^+$ | 2224 |
| [Ni$^{II}$(Si$_4$O$_3$H) (CO)]$^+$ | 2215 |
| [Ni$^{II}$(Si$_5$O$_3$) (CO)]$^+$ | 2204 |

$^a$ To be compared with experimental CO frequency = 2201 cm$^{-1}$

**Table 3.** Calculated CO Bond Length for Various Monocarbonyl Ni$^{II}_{3c}$ Complexes

| monocarbonyl Ni$^{II}_{3c}$ complexes | fragments or cycles bound to Ni$^{II}_{3c}$ | CO$^a$ bond length (Å) |
|---|---|---|
| [Ni$^{II}$(Si$_5$O$_3$ H$_{15}$)(CO)]$^+$ | SiO-, 2SiOSi | 1.138 |
| [Ni$^{II}$(Si$_4$O$_3$ H$_{13}$)(CO)]$^+$ | SiO-, SiOH, SiOSi | 1.137 |
| [Ni$^{II}$(Si$_4$O$_3$ H(OH)$_{12}$)(CO)]$^+$ | SiO$^-$, SiOH, SiOSi | 1.138 |
| [Ni$^{II}$(Si$_5$O$_3$ H$_{12}$)(CO)]$^0$ | 2SiO$^-$, SiOSi | 1.145 |
| [Ni$^{II}$(Si$_5$O$_8$ H$_9$)(CO)]$^+$ | SiO$^-$, 2SiOH (cycle) | 1.136 |
| [Ni$^{II}$(Si$_5$O$_8$ H$_2$ (OH)$_7$)(CO)]$^+$ | SiO$^-$, 2SiOH (cycle) | 1.137 |
| [Ni$^{II}$(Si$_5$O$_8$ H$_8$)(CO)]$^0$ | 2SiO$^-$, SiOH (cycle) | 1.145 |
| [Ni$^{II}$(Si$_3$O$_3$ H$_7$)(CO)]$^0$ | 2SiO$^-$, SiOH | 1.145 |

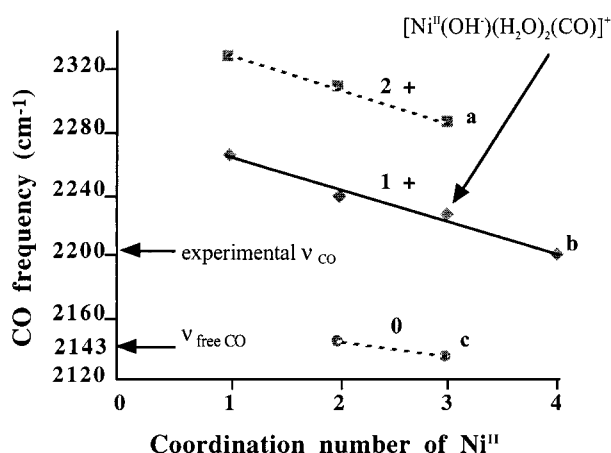$^a$ Calculated value for free CO: 1.146 Å.



**Figure 3.** CO frequency of the monocarbonyl Ni$^{II}$ complex versus the coordination number of Ni$^{II}$ and the charge of the complex: (a) 2+ charged complexes [Ni$^{II}$(H$_2$O)$_n$]$^{2+}$ with 1 < n <3; (b) 1+ charged complexes [Ni$^{II}$(OH)(H$_2$O)$_n$]$^+$ with 0 < n <3; and (c) 0 charged complexes [Ni$^{II}$(OH)$_2$(H$_2$O)$_n$]$^0$ with 0 < n <1.

understand the reasons for this disagreement, we have investigated simple clusters representing the amorphous surface, to evaluate the influence of separate parameters such as the charge (0, 1+, 2+) of the complex and the coordination number of Ni$^{II}$ ions on the CO frequency of the monocarbonyl complex.

To investigate the effect of the charge, very simple monodentate ligands such as OH$^-$ and H$_2$O were first used to model the silica surface: the OH$^-$ ligand represents the negatively charged SiO$^-$ (silanolate), whereas H$_2$O represents the neutral SiOH (silanol) and Si−O−Si (siloxane bridge). In addition, to evaluate the influence of the coordination number of the Ni$^{II}$ ion on the CO frequency, Ni$^{II}_{nc}$ sites (n = 1−4) were investigated. Even nonrealistic sites such as Ni$^{II}_{1c}$ were investigated from a theoretical point of view. The carbonyl complexes were optimized without imposing any geometrical constraint.[45]

Figure 3 shows the dependence of the calculated CO frequencies on the coordination number of the Ni$^{II}$ ion in the

monocarbonyl complex after optimization of the geometry for different charges of the complex. It appears that, for a fixed coordination number, the charge of the complex has a strong effect on the CO frequency (about 100 cm$^{-1}$) whereas, for a fixed formal charge of the complex, the addition of a neutral ligand such as H$_2$O has a smaller effect (about 10 cm$^{-1}$). The CO frequency is shown to decrease almost linearly with increased coordination number. Whatever the coordination number of the Ni$^{II}$ ion, a neutral complex does not give a positive shift of the frequency with respect to that of free CO (2143 cm$^{-1}$), in contrast with the experimental data. The 2+ charged complexes should also be excluded because the positive shift is too high. The 1+ charged complexes give the most satisfactory results for Ni$^{II}_{3c}$ and Ni$^{II}_{4c}$ ions; the CO frequency found for the prevailing Ni$^{II}_{3c}$ site (2224 cm $^{-1}$) fits the experimental value (2201 cm$^{-1}$) with an accuracy of 1%.

To summarize, only the positively charged complexes give an upward shift of the CO frequency with respect to that of free CO. Recent DFT calculations on silica-supported Mo, where silica is modeled with the same ligands, corroborate this result.[46]

We can now compare the calculated and the experimental frequencies of the monocarbonyl complexes. Noticeably, the positive shift of the CO frequency of the 1+ charged monocarbonyl Ni$^{II}_{3c}$ complex (+58 cm$^{-1}$) lies in the range of experimental and calculated values reported for M$^+$CO complexes where M = Li$^+$, Cu$^+$, Ag$^+$, Au$^+$ ($\delta\nu$ = +35−65 cm$^{-1}$).[47]

The above-mentioned results obtained by modeling the silica surface groups stabilizing the Ni$^{II}$ ion with very simple ligands suggest that (i) the Ni$^{II}$ ion in the monocarbonyl complex remains tricoordinated to the silica support and (ii) the overall charge of the complex is 1+, which implies that the Ni$^{II}_{3c}$ site contains one negative ligand (SiO$^-$) and two neutral ones (SiOSi and/or SiOH). In previous studies,[5a,16] the grafted Ni$^{II}_{3c}$ ion was assumed to be in a distorted site with one long ($d_{Ni-O} \approx 2.00 \pm 0.01$ Å) and two short ($d_{Ni-O} \approx 1.75 \pm 0.03$ Å) Ni−O distances. The Ni−O distance corresponding to the silanolate ligand is the shortest one, in agreement with the strong electrostatic interaction. However, the choice of two equivalent adjacent SiOH ligands is inappropriate since the samples being activated at 973 K are highly but not completely dehydroxylated. For this reason, we have chosen in a first approximation to build a cluster model representative of the silica surface, containing one SiO$^-$, one SiOH, and one SiOSi. This cluster referred to as (SiO$^-$, SiOH, SiOSi) involves three different Ni−O distances. After geometry optimization, the Ni−O distances are found to be 1.75, 1.83, and 2.02 Å, respectively (Figure 4 A$_1$). This cluster model is referred to as Si$_4$O$_3$H where the coordination of each Si atom is completed with H atoms (Si$_4$O$_3$H$_{13}$).

In a second approximation, the choice of two siloxanes (SiOSi) leads after geometry optimization to a silica cluster shown in Figure 4A$_2$ and referred to as Si$_5$O$_3$ (Si$_5$O$_3$ H$_{15}$), with one short (1.75 Å) and two long Ni−O distances (2.02 and 1.99 Å). For both models, the average calculated Ni−Si distance (3.2 Å) is consistent with the experimental one (3.14 ± 0.1 Å) derived from EXAFS for the grafted Ni$^{II}_{3c}$ ion.

Calculations of the monocarbonyl complexes were made with these two clusters and the choice of the adequate cluster will

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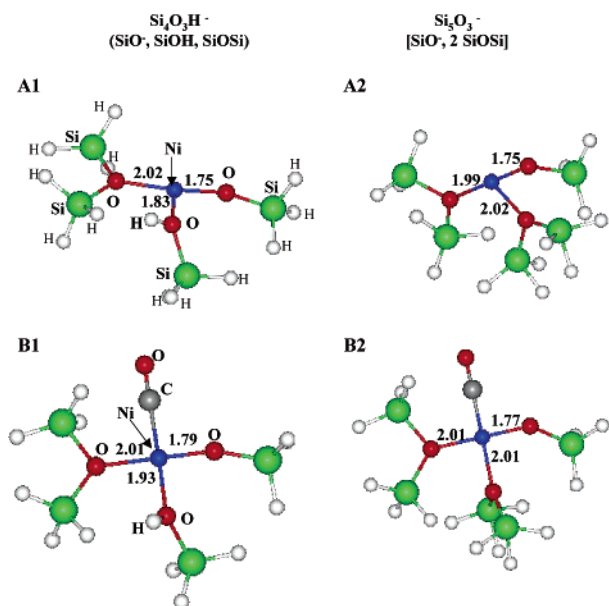
**Figure 4.** Optimized structure (B3LYP) of the tridentate $Si_4O_3H^-$ cluster-($A_1$). Optimized structure (B3LYP) of the corresponding monocarbonyl $Ni^{II}$ complex ($B_1$). Optimized structure (B3LYP) of the tridentate $Si_5O_3^-$ cluster ($A_2$). Optimized structure (B3LYP) of the corresponding monocarbonyl $Ni^{II}$ complex ($B_2$). Distances on $A_1$ and $A_2$ are given in Å.

be discussed later. The carbonyl complexes were then modeled, setting Si- - -Si distances at the values found for the grafted $Ni^{II}_{3c}$ ion with the $Si_4O_3H$ and $Si_5O_3$ clusters, (6.0 and 6.2 Å) and (4.6, 6.2, 5.3 Å), respectively, to take into account the constraints of the annealed silica.

**(2) Monocarbonyl $Ni^{II}_{3c}$ Complex. (a) Triplet → Singlet Transition.** The ground state of the $Ni^{II}_{3c}$ ion is a triplet, and corresponds to a weak ligand field as known for silica as a ligand.[6b,c] The following scheme based on calculations shows that the triplet is more stable than the singlet state by 11 kcal·mol$^{-1}$. The addition of CO induces a stronger ligand field by destabilization of the $d_{z^2}$ orbital and therefore gives rise to a low-spin configuration (singlet). The formation of the mono-carbonyl complex in the triplet state $^3[Ni^{II}(Si_4O_3 H_{13})(CO)]^+$ is slightly endothermic (+3 kcal·mol$^{-1}$). The adsorption of CO causes the evolution of the system until the difference in energy between the triplet and singlet surfaces becomes low enough to favor the triplet → singlet transition that stabilizes the monocarbonyl complex. A similar transition was experimentally observed, by ESR upon CO adsorption on $Co^{II}(s=^3/_2)$/ZSM5 zeolite, inducing a high-spin to low-spin transition to $Co^{II}(s=^1/_2)$/state.[48] This transition is not observed for the carbonyl complex of $Mo^{II}/SiO_2$.[46]
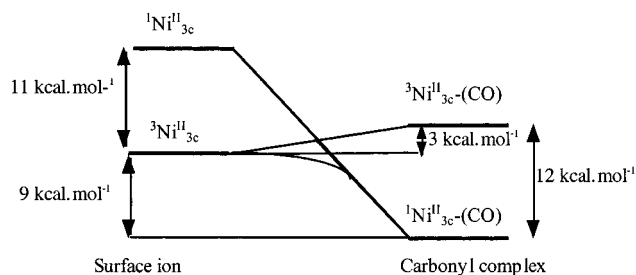


**(b) Geometrical Parameters.** In this section, we compare the calculated geometrical parameters (symmetry, distances,

angles) and the CO binding energies using cluster models built with simple entities (OH$^-$, H$_2$O) and with two silica clusters built with monodentate fragments (SiO$^-$, SiOSi, SiOH) and (SiO$^-$, 2SiOSi) referred to as $Si_4O_3H$ and $Si_5O_3$ respectively (Table 1). Figure 4 shows the geometry of the monocarbonyl complex with the silica-like clusters only. The geometry is square-planar like for the $[Ni^{II}(OH)(H_2O)_2(CO)]^+$ complex optimized without constraints and slightly tetrahedral for the $[Ni^{II}(Si_4O_3H)(CO)]^+$ and $[Ni^{II}(Si_5O_3)(CO)]^+$complexes (Figure 4, $B_1$ and $B_2$). In both cases, the Ni$^{II}$ ions remain tricoordinated to the support. The C–O bond length is shorter than that of free CO, in agreement with the experimental results (a frequency higher than that of free CO indicates a shorter C–O distance) and the Ni–C–O angle is slightly lower than 180°.

The substitution of OH$^-$, H$_2$O ligands by SiO$^-$, SiOSi ligands has a very small effect on the C–O bond length but more strongly influences the Ni–C distance, which is shown to decrease (Table 1). As expected, the Ni–O bond lengths are slightly modified in the monocarbonyls (Figure 4). Similar results were reported for silica-supported Mo ions.[46] Although EXAFS measurements were not performed for monocarbonyls, the calculated Ni–O distances can be trusted because the calculated CO frequency reproduces well the experimental CO frequency (see paragraph below).

Whatever the model used, the formation of the monocarbonyl $Ni^{II}$ complexes is exothermic. The CO binding energy in the $[Ni^{II}(Si_4O_3H)(CO)]^+$ and $[Ni^{II}(Si_5O_3)(CO)]^+$complexes is close to −9 kcal·mol$^{-1}$. Taking into account the BSSE and zero point energy corrections that are expected to be less than 5 kcal·mol$^{-1}$, the value of the corrected CO binding energy will decrease to about −5 to −6 kcal·mol$^{-1}$, which is consistent with a reversible CO adsorption.[49]

**(3) Frequency Calculations.** Table 2 shows that the CO frequency of the monocarbonyl $Ni^{II}$ complex calculated with the $Si_5O_3$ cluster (2204 cm$^{-1}$) fits best the experimental value (2201 cm$^{-1}$).

**(4) Effect of the Cluster Size.** The calculated CO frequency of both $[Ni^{II}(Si_4O_3H_{13})(CO)]^+$ and $[Ni^{II}(Si_5O_3 H_{15})(CO)]^+$ complexes (where the silica clusters are summarized as $Si_4O_3H$ and $Si_5O_3$ in Table 2) was shown to fit well the experimental CO frequency (Table 2). The effect of the cluster size on the CO bond length was also investigated (Table 3). The size of the cluster is increased either by replacing the H atoms by OH groups in the $[Ni^{II}(Si_4O_3 H_{13})(CO)]^+$ complex or by using the $Si_5O_8$ cycle previously reported.[44] For comparison, the CO bond length was also calculated for the corresponding neutral monocarbonyl $Ni^{II}$ complexes.

The value of the CO bond length is very close to that of free CO in the neutral complexes, whereas it decreases in the 1+ charged complexes, whether the cluster is made up of monodentate ligands or a cycle. This trend (decrease of the CO bond length when the charge of the complex increases) has already been observed in carbonyl Cu complexes.[20]

**Discussion**

We will first justify the choice of the $Si_4O_3H^-$, $Si_5O_3^-$ clusters taken as the tridentate silica ligand of the $Ni^{II}_{3c}$ site, in comparison with larger cycle clusters reported in a previous

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study.[44] Then we will comment on the decrease of the CO frequency with the coordination number of the Ni[II] ion.

**Pertinence of the 1− Charged Clusters as Models of Silica.** In this work, we have first chosen to use silica clusters composed of small monodentate ligands although larger tridentate cluster $Si_xO_y$ cycles, where the difference $y − x$ corresponds to the number of terminal oxygens, may appear to be more realistic to represent the silica surface. Amorphous silica is often represented by silica-based clusters of the form $Si_xO_y(OH)_2$[15a] or by $(SiO)_n$ rings (or $Si_xO_y$ cycles).[15b,44] In a recent work of our group,[44] several cycles were tested and it was shown that the cycle reproducing best the geometry of the grafted $Ni^{II}_{3c}$ ion involved at least 5 or 6 Si. In particular the $Si_5O_8$ cycle composed of 2 $SiO^−$ and 1 SiOH ligands is shown to best reproduce the environment of Ni. Thus in our work, the validity of this model is tested by using CO as an experimental probe to determine the number of coordination vacancies of Ni[II] ion with the aim of investigating several parameters which are transferable to other oxide-supported TM complexes. Since calculations of the CO frequencies of the corresponding carbonyl complexes are time-consuming when using such large clusters: Silica is first modeled by a cluster composed of three types of monodentate fragments $SiO^−$, SiOSi, and/or SiOH which exist on the surface of annealed silica. However, as shown in the preceding section (Table 3), the CO bond length of the monocarbonyl complex (and therefore the CO frequency) does not markedly depend on the size of the cluster but is strongly influenced by the charge of the complex. Indeed, replacing the H atoms saturating the Si atoms by OH groups appears to be more satisfying from a chemical point of view but does not significantly increase the CO bond length (1/1000 Å). Whatever the nature of the cluster, monodentate ligand, or cycle, it appears that the neutral monocarbonyl complex that has two $SiO^−$ groups (corresponding to a 2− charged silica cluster) gives a CO bond length close to that of free CO.

By contrast, only the 1+ charged monocarbonyl complex gives a CO bond length close to that observed for $[Ni^{II}(Si_4O_3H)(CO)]^+$ and $[Ni^{II}(Si_5O_3)(CO)]^+$ complexes. For this latter complex, the calculated CO frequency fits the experimental CO frequency with an accuracy better than 0.1%, which validates the DFT approach and the choice of a 1− charged silica cluster. The conclusions of the recent work of Pacchioni et al.[46] where only positively charged silica supported Mo(IV) complexes of the form $[(OH)_4OSi_2O_2−Mo]^{2+})$ give a positive shift of the CO frequency with respect to that of free CO are in line with our own results.

The presence of one or two siloxane SiOSi bridges in these clusters seems reasonable since the samples outgassed at 973 K are highly dehydroxylated. The positive charge of the above-mentioned complexes is likely to be compensated by a silanolate group in the vicinity of the complexes. The presence of some $SiO^−$ groups at the surface of silica is not surprising since the deposition of nickel occurs in basic medium favoring the deprotonation of silanol groups.[50] Moreover, the high outgassing temperature treatment undergone by the samples maintains a high (but incomplete) dehydroxylation degree of silica and prevents protonation of the $SiO^−$ groups.

**Choice of the $Si_5O_3^−$ Silica Cluster.** Both $Si_4O_3H^−$ and $Si_5O_3^−$ clusters corresponding to ($SiO^−$, SiOH, SiOSi) and

(SiO^−, 2SiOSi) fragments, respectively, do not fully account for the EXAFS Ni−O distances, the first one leading to three Ni−O distances while the second one gives rise to one short and two long distances. What is the more realistic cluster? Considering the $Si_4O_3$ $H^−$ cluster, it appears that the OH is bridging Ni and Si (Figure 4, **A₁**). We must verify if the presence of an OH group bound to Ni is consistent with experimental and calculated results. One can estimate the concentration of OH bound to Ni in our sample. Although the surface density of OH groups of our activated samples was not evaluated from their IR spectra, one can estimate its value from the work of Zhuravlev.[51] This author has calculated the average concentration of OH groups in various amorphous silicas dehydroxylated by vacuum outgassing at several temperatures and shows that it is independent of the type of silica.[51] For a silica outgassed at 700 °C the concentration was found to be 1.1 $OH/nm^2$. Our 2% Ni containing sample activated at 700 °C has 0.7 $Ni/nm^2$. This estimation means that 64% of the available OH would be bound to Ni in the $Si_4O_3H^−$ cluster. Besides, the experimental spectrum of our sample activated at 700 °C exhibits only a sharp band at 3745 $cm^{-1}$ assigned to isolated terminal SiOH groups (spectrum not shown).[52] However, the calculated spectrum of the $[Ni^{II}(SiO^−)(SiOH)(SiOSi)]^+$ complex indicates the presence of an OH band shifted by −90 $cm^{-1}$ with respect to the frequency of the SiOH band at 3745 $cm^{-1}$ with an intensity ratio $I_{3655}/I_{3745} = 1.7$, which implies that the ratio of the extinction coefficients $\mu_{NiOH}/\mu_{SiOH} = 2.66$. This calculated frequency (3655 $cm^{-1}$) is consistent with that reported in the literature for NiOH groups (3645 $cm^{-1}$).[9c] These data indicate that a NiOH band would clearly appear in the spectrum of the Ni-activated sample. Therefore, the non-observation of this NiOH band excludes the presence of a OH group in the vicinity of $Ni^{II}_{3c}$ ions.

Although both clusters give satisfactory calculated CO frequencies for the monocarbonyl complex, the first cluster can be excluded on this basis.

Finally, it is interesting to discuss the type of surface complexes we are dealing with. Earlier studies have shown that the $O^{2-}$ surface species of silica behaves as a σ donor−π donor 2 e− ligand.[6b,18] Thus, according to rules given by Tollman,[53] the $Si_5O_3^−$ cluster offering three $O^{2-}$ for bonding to Ni[II] ($3d^8$) can be considered as a 6 e− tridentate ligand, leading to a very unsaturated $Ni^{II}_{3c}$ surface complex with a total of 14 e−. After adsorption of CO at low pressure and counting CO as a 2e− ligand, the Ni monocarbonyl is a 16 e− complex.

**Effect of the Coordination Number and of the Charge of the Ni[II] Complex on the CO Frequency of the Monocarbonyl Complex.** The calculated CO frequencies are shown to be higher than that of free CO and correspond to a shortening of the CO bond length (Figure 3). The classical bonding scheme suggests that the CO−$Ni^{II}_{3c}$ bond associated with 5σ-donor (CO)−d acceptor ($Ni^{II}_{3c}$) orbital interaction is dominantly σ in character and involves polarization forces due to the high charge carried by the cationic center.[41] The nature of the bonding in M(CO)+ and M(CO)2+ carbonyl complexes where the M → CO π back-donation is considered to be negligible, was largely debated.[2,42c] According to recent theoretical ab initio calculations, the positive shift of the stretching CO frequency with respect to free CO could mainly be explained by the electrostatic interaction of

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the ionic charge leading to a change in the polarization of the molecular orbitals of CO rather than by the CO → M $\sigma$ donation.[34b,47,54]

## Conclusion

In this work, the controlled dispersion of $Ni^{II}$ ions on amorphous silica was performed via the solid−liquid interface approach. The two samples $ENi(NH_3)$ and $ENi(en)$ differing in the degree of dispersion of these $Ni^{II}$ ions were studied. An appropriate activation treatment was selected so as to obtain isolated tricoordinated $Ni^{II}_{3c}$ ions with a single Ni(II) oxidation degree. The reactivity of the coordinatively unsaturated $Ni^{II}_{3c}$ ions was then tested toward CO used as a probe molecule at 77 K to maintain the Ni(II) oxidation state.

It was shown by FTIR that, whatever the precursor used, the CO probe sees one type of site because the same monocarbonyl complex is formed from $Ni^{II}_{3c}$ ions.

A cluster approach was used to model silica with clusters composed of three types of monodentate ligands, $SiO^-$, SiOSi, and/or SiOH, found on the surface of silica. This work complements the preceding one where $Si_xO_y$ clusters were investigated to model silica as a tridentate ligand of $Ni^{II}$ ions.[44]

The originality of our approach is that it takes into account the amorphous character of the support. This is the reason the samples were already characterized by EXAFS and DRS spectroscopies in order to get information on the neighbors of $Ni^{II}_{3c}$ ions, whereas in previous works, silica was modeled by idealized extended planes of cristalline cristobalite.[55]

The reliability of the small-cluster models was tested by their ability to reproduce the Ni−O distances derived from EXAFS and for the monocarbonyl complexes by the consistency of the calculated energies with experimental observations (reversibility at 77 K of the formation of the monocarbonyl $Ni^{II}$ complexes) and their ability to reproduce the experimental CO frequencies. It is shown that the charge of the silica cluster strongly influences the CO frequency whereas the size of the cluster (ligands or cycle) does not affect the CO bond length. In other words, only the ligands directly bound to the $Ni^{II}$ ion have a major effect on the CO frequency. This suggests that, with respect to the transition metal ion, the surface groups of solid ligands play the same role as the donor atoms of molecular ligands.

The best candidate is the $Si_5O_3^-$ cluster, which reproduces the short (≈1.75 Å) and long (≈ 2.02 Å) NiO distances found by EXAFS for the activated samples and gives a calculated CO frequency for the corresponding monocarbonyl $[Ni^{II}(Si_5O_3)(CO)]^+$ complex, in good agreement with experimental results.

This cluster represents a very simplified view of the structural complexity of the silica surface. In a forthcoming paper dealing with dicarbonyls, we will first try to reproduce the experimental statistical results by using this cluster, then the complexity of the surface structure of amorphous silica will be taken into account by embedding this cluster in various cycles representing silica.

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