Intrazeolite Chemistry of Nickel(0) Complexes and Ni(0,II) Clusters Studied by EXAFS, Solid-State NMR, and FT–IR Spectroscopy

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Abstract: Adsorption, thermal decomposition, and reactivity of Ni(CO)₄ in the cage system of dehydrated zeolite Y has been studied with EXAFS and near-edge spectroscopies, in particular monitoring changes in oxidation states and Ni ligation. Ni(CO)₄ is adsorbed as an intact molecule in cation-free zeolite Y, LiY, and NaY. Symmetry changes of the molecule in LiY and NaY are assigned to the formation of cation–OC–Ni bridges. Thermal treatment of the Ni(CO)₄/NaY adduct leads to loss of CO concomitant with the formation of a bimodal Ni phase. A major part of the Ni forms small clusters (approximately 0.5 to 1.5 nm), in addition to larger crystallites (5–30 nm), sticking at the outer surface of the zeolite crystals. Oxidation of Ni(CO)₄/NaY to NiO/NaY with molecular oxygen occurs almost to completion below 295 K. The small NiO particles are stable to sintering up to 670 K. Nickel–phosphine/NaY adducts have been prepared by direct adsorption from solution [Ni(CO)₄(PMe₃)₂, Ni(CO)₄(PPh₂CHMe₂)], and by synthesis inside the NaY supercage [Ni(CO)₄(PMe₃)₂, Ni(CO)₄(PPh₂CHMe₂)]. The NaY/Ni(CO)₄(PPh₂CHMe₂) adduct is a ship-in-a-bottle complex, i.e., the Ni complex is too large to exit the zeolite supercage. The substitution of carbonyl ligands by phosphines was monitored in the near-edge and EXAFS modulations as well as with 31P MAS NMR. EXAFS is an excellent method to monitor ligand coordination and provides information that is complimentary to IR spectroscopy.

The interplay between organometallic molecules and oxide surfaces has attracted growing attention during the last decade. A major incentive to study these systems is to anchor catalytically active species on heterogeneous supports for the purpose of facile recovery from the reaction mixture. Homogeneous catalysts, if immobilized for instance in the cage system of zeolites, might be expected to be stabilized against aggregation or bimolecular deactivation. Furthermore, the zeolite cage system may favor unique selectivity of a catalytic reaction due to changed complex geometries, transition-state modifications, and/or selective competition for the substrate molecules.

Thermal decomposition of supported Ni(CO)₄ as a precursor for dispersed Ni catalysts and a limited number of attempts to anchor mixed Ni(CO)₄-L complexes directly on partially hydrotreated supports have been reported previously. The reaction of Ni(CO)₄ with NaX zeolite, its thermal stability, and the generation of encapsulated phosphine complexes have recently been studied with IR techniques. The effect of pore blocking at high loading densities and selectivity for ligands of certain size have been demonstrated. The limitations of IR spectroscopy for these systems prevented a definitive identification of the reaction products.

A major challenge for research on supported metal systems is the detailed characterization of the metal environment. In an attempt to understand the behavior of nickel carbonyl compounds in the cage system of faujasites, we have used a combination of EXAFS and X-ray absorption near edge spectroscopy, complemented by 31P MAS–NMR and FT–IR experiments.

Results and Discussion

1. Adsorption of Ni(CO)₄ in Faujasite. Zeolites NaY and dealuminated Y (with Si/Al > 400, hereafter referred to as Y*) readily adsorb Ni(CO)₄ vapor to give saturated samples with compositions NaY(Ni(CO)₄)ₓ and Y*(Ni(CO)₄)ₓ (i.e. 3.9 and 2.9 Ni per supercage). The lower adsorption capacity of Y* may be due to lower crystallinity, or pore blocking by non-framework Al. These saturated zeolites were unstable with respect to loss of Ni(CO)₄; they frequently formed Ni mirrors in the sample vials. Because of this instability, most spectroscopic characterization was one on samples with lower Ni(CO)₄ loadings.

Infrared spectra of Ni(CO)₄ in Y*, NaY, and LiY show striking differences (Figures 1–3). The single carbonyl band observed in Y* (2046 cm⁻¹, Figure 1B) resembles the spectrum of Ni(CO)₄ in the THF solution (Figure 1A). NaY(Ni(CO)₄)₂/NaY has four carbonyl bands at 2132, 2072, 2033, and 2000 cm⁻¹ (Figure 2A). At a loading of 2.2 Ni per supercage, the bands are not as well resolved and the 2072-cm⁻¹ band has shifted to 2066 cm⁻¹ (Figure 2B). In LiY the spectrum changes dramatically as the Ni loading is increased. With 0.25 Ni per supercage, the spectrum resembles NaY(Ni(CO)₄)₂/NaY with four bands at 2129, 2068, 2033, and 1996 cm⁻¹ (Figure 3A). With 2.0 Ni per supercage, the minor band at 2044 cm⁻¹ increases to become the largest band in the spectrum (Figure 3B).

Ni(CO)₄ can be displaced from NaY(Ni(CO)₄), by washing with THF. After a Ni–zeolite sample is stirred for 18 h in THF, all of the Ni(CO)₄ is found in the THF solution. The polar THF must be more strongly adsorbed than nonpolar Ni(CO)₄.

Recent IR studies of metal carbonyls in zeolites suggested stabilization of carbonyl ligands to give small metal clusters and metal subcarbonyls. For example, the generation of yellow/
orange species "Ni(CO)₃" has been reported from the reversible interaction of Ni(CO)₄ with NaX zeolite or Al₂O₃. However, IR studies alone cannot provide a definitive characterization of the metal coordination sphere.

We present here the first EXAFS spectra of Ni(CO)₄ adsorbed in different Y zeolites. Figure 4 compares both near edge spectra
and the Fourier transformed EXAFS modulations (Fts) of Ni(CO)$_4$ in dealuminated Y and NaY. The complete match of both edge spectra and EXAFS Fts between the two samples indicates that adsorption of the carbonyl into the different forms of zeolite Y leads to essentially identical metal carbonyl species. No oxidation of the Ni is observed upon adsorption into the zeolite. Comparison of these edges with that of neat Ni(CO)$_4$ shows similar magnitude differences in the particle size distribution occur. Gravimetric studies also show that all carbonyl ligands are desorbed at 373 K. The amount of loaded metal corresponds to the starting content and remains constant upon heating between 373 and 673 K.

The Fourier transform of sample VAC323 is compared to that of neat Ni(CO)$_4$ per supercage and heated up to 323 K in vacuo for 2 h (VAC323) loses weight corresponding to a coordinatively unsaturated system with CO/Ni = 1, accompanied by a color change from white to dark grey. No evidence has been found for loss of nickel metal since no metal mirror appeared. If NaY is saturated with 3.9 Na$^+$ ions, this fit provides the deviation from the reference spectrum can be explained by the cation occupations. In dehydrated NaY there are an average of 3.8 Na$^+$ ions per supercage in site II. Even at high Na loadings, every Ni(CO)$_4$ is bound to a sodium ion. However, in NaY that has been exchanged with Li$^+$ there are an average of 1.6 Na$^+$ and 0.9 Li$^+$ per supercage in site II. Because there are fewer cations in the supercage of LiY, not every Ni(CO)$_4$ can bind to a cation at high Ni loadings.

### 2. Thermal Decomposition of Ni(CO)$_4$ in Y Zeolite.

Ni loaded with 2.0 molecules of Ni(CO)$_4$ per supercage and heated up to 323 K in vacuo for 2 h (VAC323) loses weight corresponding to a coordinatively unsaturated system with CO/Ni = 1, accompanied by a color change from white to dark grey. No evidence has been found for loss of nickel metal since no metal mirror appeared. If NaY is saturated with 3.9 Na$^+$ ions, a similar decomposition experiment results in a metal mirror at the reactor wall. The corresponding XANES of VAC323 is compared with the edge of NaY(Ni(CO)$_4$)$_2$ in Figure 6A. A dramatic reduction in the first absorption maximum indicates increased occupation of bonding orbitals upon removal of $n$-acceptor ligands as expected. The increase in pre-edge absorption can be understood in similar terms. These edge changes are indicative of the formation of metallic Ni, though some residual bound CO is still observed. If the sample is evacuated at 373 K for 2 h (VAC373), further changes occur in the edge region (Figure 6B). Complete loss of CO is now observed as evidenced by comparison of the edges to that of Ni foil (Figure 6C). Continued heating to 673 K produces no further changes in the edge region. Gravimetric studies also show that all carbonyl ligands are desorbed at 373 K. The amount of loaded metal corresponds to the starting content and remains constant upon heating between 373 and 673 K.

The Fourier transform of sample VAC323 is compared to that of VAC373 in Figure 6D and allows for a similar interpretation as obtained from the K-edge results discussed above. After heating at 373 K no evidence for bound CO is observed and only minor differences in the particle size distribution are seen.

The electron micrograph of VAC323 (Figure 7) shows octahedral Ni crystals of 5–30-nm diameter, sticking at the outer surface of the zeolite matrix. Contributions of the 3rd and 4th Ni-Ni shell in the EXAFS Fts (Figure 6D) of this sample must

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**Table 1. Bond Distances and Coordination Numbers of Ni Species in Zeolites As Derived from Fitting Fourier-Filtered EXAFS Data**

<table>
<thead>
<tr>
<th>sample</th>
<th>distance/Å</th>
<th>coordination no. back-scatterer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foil</td>
<td>2.492</td>
<td>12 Ni(0)</td>
</tr>
<tr>
<td>VAC323</td>
<td>2.47</td>
<td>5.3 Ni(0)</td>
</tr>
<tr>
<td>VAC373</td>
<td>2.46</td>
<td>6.2 Ni(0)</td>
</tr>
<tr>
<td>VAC673</td>
<td>2.48</td>
<td>7.6 Ni(0)</td>
</tr>
<tr>
<td>NaY (Ni(PMe$_3$)$<em>2$)$</em>{2.95}$</td>
<td>+0.02$^b$</td>
<td>3.96 $^P$</td>
</tr>
</tbody>
</table>

$^a$ In addition to the above fitting parameters, the fits included allowances for changes in the Debye–Waller factor and in threshold energy. In all cases the changes of these parameters were small and chemically reasonable. $^b$Since the Ni-P distance of this compound in solution is unknown, this fit provides the deviation from the reference data, estimated to be 2.30 Å.
Figure 6. Ni K edge spectra (A, B, C) and Fourier transformed, $k^3$ weighted EXAFS modulations (Fts) of Ni(CO)$_4$ heat treated in NaY, $R' = R + R' \Delta k$, with $R'(k)$ being the phase shift. (A) Edges of NaY(Ni(CO)$_4$)$_2$ (dashed) and VAC323 (solid line). (B) Edges of samples VAC323 (--), VAC373 (---), and VAC673 (+). (C) Edges of sample VAC673 (--) and Ni foil (---). (D) Fts of samples VAC323 (--) and VAC373 (---). (E) Fts of samples VAC373 (--) and VAC673 (---).

be due to the larger particles that are detected in the TEM. Fitting of the backtransformed EXAFS modulations to Ni foil demonstrates that the first Ni–Ni scattering amplitude amounts to less than 50% of the bulk value (Table I). This value for the backscattering amplitude relates to an average particle size of 1.0 nm. However, the bulk-like outer-shell Ni–Ni backscattering amplitude in the EXAFS data and the electron-optical observations indicate the presence of a fraction of larger Ni crystallites in this sample. On the basis of the first Ni–Ni amplitude, a maximum of 50% of the Ni atoms could be present as bulk-like particles ($\geq 5$ nm). For the remainder of the Ni phase, this extreme distribution would imply the complete absence of Ni–Ni neighbors, i.e., atomic dispersion with oxygen coordination by the zeolite framework. Since no appreciable oxygen coordination is detected in the Fts (in the expected Ni–O distance of approximately 0.20 nm), the authors favor a more realistic, bimodal size distribution with a major size fraction between ca. 0.5 and 1.5 nm (not detected in the electron microscope) and a fraction of large (5–30 nm) particles sticking at the outer surface of the zeolite crystals. It seems very likely that the small Ni particles have a size in the vicinity of the zeolite supercage dimensions (1.3 nm), since the rigid zeolite framework presents a barrier against agglomeration of the Ni phase.

Comparison of the later stages of thermal treatment (samples VAC373 and VAC673) in Figure 6E reveals a significant increase of Ni–Ni neighbor populations (Table I). This is indicative of an agglomeration process as expected for elevated temperatures.

EXAFS studies concerning the characterization of supported nickel metal particles have been reported. Hydrogen reduction of Ni/Si(OH)$_4$ gels yielded Ni particles with diameters between 2 and 10 nm, whereas larger particles were produced with a gas evaporation technique. The magnitude of the EXAFS radial distribution function was found to decrease substantially with decreasing particle size. It becomes clear that careful decom-
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3. Oxidation of Nickel Carbonyl in Faujasite. If the adduct NaY(Ni(CO)₄)₂ (i.e., with 2 molecules per zeolite supercage) is exposed to an excess of molecular oxygen (relative to Ni) at 77 K and slowly warmed up to 295 K, the color of the sample changes from white to grey (OXR295). Evacuation at 373 K reduces the weight down to the expected value for a complete oxidation to NiO (OXR373). This weight remains unchanged upon further heating at 673 K for 12 h (OXR673).

The Ni K edges of these samples are identical as shown in Figure 8A, indicating that the oxidation of Ni(CO)₄ in zeolite to Ni(II) species is extremely facile. The strong intensity of the first absorption maximum represents the "white line" of Ni(II). If the Fits of the respective EXAFS modulations are compared, only small differences are observed between the low temperature product OXR295 and the samples treated at elevated temperatures (Figure 8B). Upon fitting to the backtransformed EXAFS modulations of the reference compounds, the first and the third marked peaks of the Ft from OXR295 are assigned to Ni-O and Ni-Ni backscatters at distances typical for bulk NiO. A third peak, located between the former ones, is due to Ni-Ni distances in direct bonding, indicating that a small fraction of the Ni is still in the zerovalent state. The amplitude of the NiO contribution amounts to about 50% of the bulk value, which translates into a particle size distribution around 1 nm, provided the distribution is monomodal and the degree of disorder is comparable to bulk NiO (Table I). An inspection of the corresponding electron micrograph (Figure 9) shows that only very few NiO crystallites are located outside the zeolite interior, thus the major fraction of the Ni must be stabilized within the zeolite cage system. This is in marked contrast to the significant migration of metal which is observed upon thermal decomposition of the carbonyl/zeolite adduct. It is evident that the NiO/NaY system is remarkably stable against sintering since neither the degree of oxidation nor the average particle size change upon heating up to 673 K (Table 1).

4. Adsorption of Ni-Carbonyl-Phosphine Complexes in Y Zeolite. Both Ni(CO)₃(PMe₃) and Ni(CO)₃PMe₃ are readily adsorbed from hexane by NaY. A space-filling model of Ni(CO)₃PMe₃ in the NaY supercage shows that the Ni complex should be able to pass through the 12-ring opening into the supercage (Figure 10). The saturation loading levels are 1.48 Ni
The low-frequency mode (E) is more strongly affected than the high-frequency mode (A) when complexes are introduced into the zeolite. This makes the 31P NMR shift remain largely unaffected when a complex is removed from the zeolite. In favorable cases with narrow line widths, chemical shift differences as small as 2-3 ppm can be resolved by solid-state MAS-NMR. In contrast to the NMR results, the infrared spectra show the complete conversion of the phosphine in the zeolite. Therefore, the IR spectrum is useful for the assignment of the structure. For example, a carbonyl band at >2000 cm⁻¹ is a clear indication of a Ni(CO)₄ species. Once this effect is appreciated, the IR spectrum is useful for the assignment of the structure. For example, a carbonyl band at >2000 cm⁻¹ is a clear indication of a Ni(CO)₄ species.

IR spectra and 31P NMR spectra are summarized in Table II. The 31P NMR shift remains largely unaffected when a complex is removed from the zeolite. In favorable cases with narrow line widths, chemical shift differences as small as 2-3 ppm can be resolved by solid-state MAS-NMR. In contrast to the NMR results, the infrared spectra show the complete conversion of the phosphine in the zeolite. Therefore, the IR spectrum is useful for the assignment of the structure. For example, a carbonyl band at >2000 cm⁻¹ is a clear indication of a Ni(CO)₄ species.

**Table II. Spectroscopic Data for Ni-Phosphine Complexes in NaY**

<table>
<thead>
<tr>
<th>Sample</th>
<th>ν(CO)/cm⁻¹</th>
<th>31P NMR/ppm</th>
<th>Ligand shift, A-B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>complex (A)</td>
<td>free ligand (B)</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Ni(CO)₃(P(t-Bu)₃)₀.₅</td>
<td>2046, 1942</td>
<td>+91.1</td>
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<tr>
<td></td>
<td>Ni(CO)₃(P(t-Bu)₃)₀.₅</td>
<td>2067, 1972</td>
<td>+90.9</td>
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<tr>
<td>II</td>
<td>NaY(Ni(CO)₃PMe₃)₀.₄₈</td>
<td>2059, 1975</td>
<td>-19.3</td>
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<td>NaY(Ni(CO)₃PMe₃)₀.₂₅</td>
<td>2065, 1952, 1958</td>
<td>-18.5</td>
</tr>
<tr>
<td></td>
<td>Ni(CO)₃PMe₃</td>
<td>2070, 1996</td>
<td>-19.8</td>
</tr>
<tr>
<td></td>
<td>Ni(CO)₃PMe₃</td>
<td>2069, 1994</td>
<td>-19.9</td>
</tr>
<tr>
<td>III</td>
<td>NaY(Ni(CO)₂(PMe₃)₂)₀.₉₇</td>
<td>1965 (sh), 1954</td>
<td>-17.4</td>
</tr>
<tr>
<td></td>
<td>Ni(CO)₂(PMe₃)₂</td>
<td>1989, 1880</td>
<td>-17.5</td>
</tr>
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<td></td>
<td>Ni(CO)₂(PMe₃)₂</td>
<td>2002, 1941</td>
<td>-18.2</td>
</tr>
<tr>
<td>IV</td>
<td>NaY(Ni(CO)₂PPh₂(CHMe₂)₀.₉₃</td>
<td>2075, 1995, 1948</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td>Ni(CO)₂PPh₂(CHMe₂)</td>
<td>2067, 1990 (CH₃CN)</td>
<td>-19.3</td>
</tr>
<tr>
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<td>Ni(PMe₃)₄</td>
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<td></td>
<td>Ni(PMe₃)₄</td>
<td>-</td>
<td>-22.2</td>
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</table>


Figure 10. Model of Ni(CO)₃PMe₃ in the NaY supercage: (A) framework model; (B) model including zeolite van der Waals radii.

Figure 11. (A) 31P MAS-NMR spectrum shows the complete conversion of the phosphine in the zeolite. The sidebands in Figure 11A are due to the incomplete averaging of the chemical shift anisotropy by the magic angle spinning. When this sample was washed with THF, only the Ni(CO)₄ was displaced from the zeolite. The Ni(CO)₄ is expected since they are both small enough to pass through the 12-ring opening of the supercage (Figure 12). This material is comparable to a ship phase loading of excess Ni(CO)₄.
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Figure 11. $^{31}$P MAS-NMR spectra of (A) NaY(Ni(CO)$_3$(Ph$_2$PCHMe$_2$)) and (B) NaY(Ph$_2$PCHMe$_2$).

Figure 12. Model of Ni(CO)$_3$(Ph$_2$PCHMe$_2$) in the NaY supercage: (A) framework model; (B) model including zeolite van der Waals radii.

in the bottle; the reactants are small enough to enter the zeolite supercage but the product is too large to exit.

A modification of the above procedure was used to prepare zeolite entrapped Ni(CO)$_3$P(t-Bu)$_3$. P(t-Bu)$_3$ and Ni(CO)$_4$ were added to the zeolite sequentially from hexane solution. The $^{31}$P MAS-NMR spectrum of the zeolite product has a resonance at 91.1 ppm equal to the chemical shift of Ni(CO)$_3$P(t-Bu)$_3$ in solution and a resonance at 62.5 ppm that is assigned to unreacted phosphine in the zeolite (Table II, Figure 13). It should be noted that unreacted phosphine cannot be detected by either IR or Ni EXAFS. The IR spectrum of NaY(Ni(CO)$_3$P(t-Bu)$_3$)$_{0.5}$ has at least five bands in the carbonyl region (Figure 14). The complexity of the spectrum may be due to a mixture of cation-bound species (Na$^+$--OC--Ni) and cation-free species as was observed with Ni(CO)$_4$ in LiY. There may also be a splitting of the E mode in the cation-bound species. Splitting of the E mode is sometimes seen even in solution spectra of Ni(CO)$_3$L complexes.$^{14}$

The Ni K edge and the Fts of NaY(Ni(CO)$_3$P(t-Bu)$_3$)$_{0.5}$ are compared to those of authentic Ni(CO)$_3$P(t-Bu)$_3$ in Figure 15. The edges match perfectly, indicating that a similar electron density is present at the Ni central atoms of both species. If the radial distribution functions are compared, a close match is observed for the magnitudes of the first (Ni--C) and third (Ni--O) peak (Figure 15B). The differences present in the second peak (Ni--P) are assigned to small artifacts caused by the convolution of three strong backscattering patterns; it is known that side lobes of strong shell contributions add in the Fts if the shells are close in R space. Individual peaks could not be filtered out to yield neighbor distances and coordination numbers due to lack of sufficient resolution. However, the backtransformed region of the three backscatterers compared well with that of the reference.

The sequential addition of Ni(allyl)$_2$ and excess PME$_3$ to NaY from pentane solution yields zeolite-entrapped Ni(PME$_3$)$_2$. The $^{31}$P MAS--NMR spectrum of this sample shows a peak for unreacted PME$_3$ and a peak close to the position expected for Ni-(PME$_3$)$_2$ (Table II). A space-filling model shows that there is enough space to accommodate the Ni complex inside the NaY supercage without any van der Waals contacts (Figure 16).

The Ni K edge of an authentic solution sample of Ni(PME$_3$)$_2$ is compared to the zeolite adduct in Figure 17a. As with the samples discussed previously, there is a good match between the edges of reference and zeolite adduct sample. The phosphine ligands decrease the electron density on the Ni atom as dramatically visualized in the overlay of the Ni(CO)$_4$ edge and the Ni(PME$_3$)$_2$ edge (Figure 17B). The first absorption maximum in the carbonyl edge vanishes and a weak maximum at lower
energy is observed. The EXAFS radial distribution function of the adduct. Since the Ni-C distance in Ni(allyl), is close to the Ni-P bond distance (0.21-0.22 nm), it cannot be ruled out that the reaction was incomplete. Owing to the high reactivity of Ni(allyl)* phosphine nickel complexes have been prepared in solution. On the basis of the UV spectrum of Ni(PET3)3 (λmax = 500 nm), we would expect Ni(PMe3)3 to be purple, whereas our zeolite sample is pale yellow. Further analysis of the backtransformed backscatterer region (Table I) demonstrates that the decrease in amplitude is not due to a decrease in coordination number but is a result of static disorder. A tentative explanation for this disorder would be elongation of one of the Ni-P bonds as a result of bulky phosphines, this gives nickel-phosphine complexes that are too large to exit the zeolite.

Experimental Section

All operations involving dehydrated zeolites, Ni(CO)4, and phosphines were done either in a Vacuum Atmospheres glovebox under nitrogen or on a high-vacuum line.

Materials. Zeolite NaY from Strem Chemicals (Linde L.Z.Y52), with the unit cell composition \( \text{Na}_{12}\text{Al}_2\text{O}_{12}\text{SiO}_4\cdot 17\text{H}_2\text{O} \), was dehydrated at 670 K under \( 10^{-5} \) Torr for 12 h (heating rate 2 deg K/min) and handled under nitrogen in a drybox (< 0.5 ppm). LiY was prepared by exchanging 10 g of NaY zeolite three times with 300 mL of 10% LiNO3 solution for 60 min at 360 K. The zeolite was dehydrated by heating to 870 K (1 deg K/min) at \( 10^{-5} \) Torr and maintaining at 870 K for 8 h. Dealuminated zeolite Y* was prepared essentially according to Grobet et al.24 using a vertically mounted tube furnace for the SiCl4 and steam treatments. Analysis gave a unit cell composition of \( \text{Na}_{12}\text{Al}_2\text{Si}_{12}\text{O}_{40}\cdot 8\text{H}_2\text{O} \).

Ni(CO)4 from Alfa and PMe3 and P(t-Bu)3 from Strem were used as received. THF was distilled from sodium benzophenone ketyl under argon. All other solvents were sparged with argon, passed through activated 4A molecular sieve until use. Ni(allyl)3 was prepared as a pentane solution by a literature procedure.25 The Ni concentration was determined by treating an aliquot with dry oxygen to give a dark precipitate which was analyzed for Ni.

Sample Preparation. Vapor-Phase Loading with Ni(CO)4. Half a gram of dehydrated zeolite were weighted into a quartz sample holder in the drybox, introduced into a vertical quartz reactor, and evacuated at \( 10^{-5} \) Torr for 30 min. Ni(CO)4 was degassed at the same vacuum line by carrying out 3 freeze-pump-thaw cycles under low-intensity light. A calculated amount of Ni(CO)4 vapor was admitted to the zeolite and allowed to equilibrate for 30 min at 295 K, followed by evacuation for 30 min. The evacuation step was omitted for some samples. This was especially important for samples of dealuminated Y since evacuation resulted in partial loss of the Ni(CO)4.

phosphine complexes can be synthesized inside the zeolite supercage by sequential addition of the phosphine and the Ni reagent. In the case of bulky phosphines, this gives nickel-phosphine complexes that are too large to exit the zeolite.

Summary

The combined use of EXAFS, X-ray near edge spectroscopy, MAS-NMR, and IR yields consistent information about the oxidation state, agglomeration processes, and intrazeolite chemistry of organonickel compounds adsorbed in the cage system of Y zeolites.

Upon adsorption, Ni(CO)4 undergoes symmetry changes due to CO cation bonding. Small nickel-phosphine complexes can be adsorbed from hydrocarbon solution. Alternatively, nickel-
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Intrazeolite Chemistry and Synthesis of NaY(Ni(CO)3PMe3)1.48 (i.e., with an average loading of 1.48 molecules per supercage). A solution of Ni(CO)4PMe3 was prepared by combining Ni(CO)4 (0.683 g, 4.0 mmol) and PMe3 (0.304 g, 4.0 mmol) in 50 mL of hexane. After 2 h, dehydrated NaY zeolite (1.595 g, 1.00 mmol supercages) was added while stirring. The solution concentration of Ni(CO)4PMe3 was monitored by IR spectroscopy of filtered aliquots. After 20 h, the solution concentration was no longer changing. The saturation loading of the zeolite was calculated as 1.48 Ni per supercage. The zeolite was filtered and dried briefly on the frit.

Synthesis of NaY(Ni(CO)4)PMe3/2.925. Ni(CO)4 (18.8 mL, 0.10 M) and PMe3 (20.1 mL, 0.20 M, 100% excess) were combined in a 200-mL flask. The solution was frozen and the flask was evacuated and closed off with a high-vacuum Teflon stopcock. The solution was heated to 348 K for 2 h. An IR spectrum showed complete conversion to Ni(CO)3(PMe3)2. Dry NaY zeolite (1.179 g, 0.627 mmol) was added with stirring, and after 48 h a saturation loading of 0.97 Ni per supercage was obtained. The zeolite was filtered and dried briefly on the frit.

Synthesis of NaY(Ni(CO)4)PPh2(CHMe)2/0.25 and NaY(Ni(CO)4)PMe3/0.25. Dry NaY (0.833 g, 0.522 mmol of supercages) was stirred in 25 mL of hexane for 15 min. A solution of PPh2(CHMe2) (0.030 g, 0.131 mmol) in 5 mL of hexane was added dropwise over a period of 5 min. The UV spectrum of a filtered aliquot showed that all of the phospine had been adsorbed after 20 min. The zeolite was filtered and dried at <10^-5 Torr for 2 h. The evacuated zeolite was exposed for 60 min to the full vapor pressure from a container of liquid Ni(CO)4 held at 273 K. ^3P MAS-NMR spectroscopy showed complete reaction of the PPh2(CHMe2), and IR spectroscopy showed an excess of Ni(CO)4 in the zeolite. A small sample (ca. 0.050 g) was stirred in 2.0 mL of THF for 2 h. The filtered zeolite showed IR bands only for entrapped Ni(CO)4PPh2(CHMe2) (Table II). A similar procedure was used to prepare NaY(Ni(CO)4)PMe3/0.25 except that the THF washing caused a partial loss of Ni(CO)4PMe3 so that the Ni loading in the sample characterized by IR (Table II) was <0.25 Ni per supercage.

Synthesis of NaY(Ni(CO)4)P(r-Bu)/0.25. Dry zeolite (1.00 g, 0.626 mmol supercages) was suspended in 25 mL of hexane and stirred for 10 min. A solution of P(r-Bu)3 (63 mg, 0.311 mmol) in 25 mL of hexane was added dropwise to the zeolite suspension while stirring. The mixture was stirred for 12 h at 295 K. Under stirring, a solution of Ni(CO)4 (0.10 M in hexane, 6.3 mL, 100% excess) was added dropwise and the suspension was stirred for 12 h. The pale yellow zeolite was filtered and dried briefly on the frit.

Synthesis of NaY(Ni(PMe3))1.25. Dry zeolite (1.00 g) was suspended in 25 mL of pentane and stirred for 30 min. The Ni(allyl)2 solution (2.96 mL, 0.106 M) was added dropwise to the zeolite suspension while stirring. The mixture was stirred for 45 min during which time the yellow solution decolorized and the zeolite became orange. A solution of PMe3 (12.6 mL, 0.20 M, 100% excess) was added dropwise over a period of ca. 2 min and the suspension was stirred for 12 h. The yellow zeolite was filtered and dried briefly on the frit.

Reference solutions of all Ni compounds were prepared for the EXAFS studies.

Analytical Methods. IR Spectroscopy. IR spectra were taken with a Nicolet SDXB FT-IR spectrometer, in sample holders equipped with CaF2 windows. It was found that Ni(CO)4 was displaced from the zeolite by THF, hexane, or Nujol hydrocarbons. Therefore, IR spectra of Ni(CO)4-zeolite samples were recorded as thin dry powders between CaF2 plates. The edges of the plates were sealed with high-vacuum grease to exclude air. Zeolite–Ni-phosphine samples could be examined in Nujol mull. Solution spectra were recorded in pentane or hexane. Typically 200 scans were accumulated with a resolution of 2 cm^-1.

EXAFS Studies. The EXAFS experiments were carried out at the X-11A beamline at the National Synchrotron Light Source with a stored electron energy of 2.5 eV at currents between 35 and 100 mA. Spectra were taken of (i) covalent compounds embedded at 310 K in dodecane/acetone (1:1), (ii) Ni(CO)4/zeolite adducts in 1-mm sealed polyethylene cells, and (iii) solution references in 1-mm sealed polyethylene cells, in a Dewar with Kapton windows at ca. 100 K. In most cases, IR spectra were recorded after the EXAFS experiment to confirm the stability of the samples. The data were analyzed according to published procedures. Background removal was accomplished by using a cubic spline function and the resultant EXAFS modulations were weighted by k^2 and Fourier transformed over a range of 2 to 16 k. Typically, the EXAFS data of the zeolite-encapsulated Ni complexes were directly compared with the respective reference compounds. Additionally, individual coordination shells were examined by comparison of the backtransformed EXAFS modulations of the samples to well-defined reference compounds (Ni foil, NiO, Ni(CO)4, etc.). Coordination numbers and bond distances were obtained from an iterative fitting routine using experimentally determined phase and amplitude functions from both reference and unknown. Variable fitting parameters included:

Matrix Photochemistry of
($\eta^5$-Cyclopentadienyl)bis(ethene)rhodium and
($\eta^5$-Cyclopentadienyl)(ethene)carbonylrhodium: A Test-Bed
for Intermediates in C–H Activation

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Abstract: The photochemical reactivities of CpRh(C2H4), (1) and CpRh(C2H4)CO (2) (Cp = $\eta^5$-C5H5) have been examined in low-temperature matrices with IR and UV/vis detection. Photodissociation of ethene from 1 in inert matrices (Ar or CH4) yields the coordinately unsaturated CpRh(C2H4), the reaction is reversed by long-wavelength irradiation. The identity of CpRh(C2H4) is demonstrated by 2H labeling of ethene and cyclopentadienyl groups. The IR results support a “bent”, ground-state geometry for CpRh(C2H4). UV photolysis of 1 in CO matrices releases ethene and generates 2 and CpRh(CO), sequentially. The corresponding reaction in nitrogen matrices leads to CpRh(C2H4)(N2). On photolysis of 1 in CO-doped methane matrices, CpRh(CO)(CH3)H is formed in addition to substitution products. Complex 2 undergoes loss of either CO, yielding CpRh(C2H4), or of C2H4, yielding CpRh(CO)2, on UV photolysis in argon matrices. These reactions are reversed by long-wavelength photolysis, but in more concentrated matrices CpRh(C2H4)(CO) is formed as an additional product. In nitrogen matrices both CpRh(C2H4)(N2) and CpRh(CO)(N2) are generated. In methane matrices CpRh(C2H4) is still detected on UV photolysis, but CpRh(CO) is replaced by the product of oxidative addition of methane, CpRh(CO)(CH3)H. Long-wavelength photolysis removes CpRh(C2H4) but increases conversion to the (methyl)hydride complex. These experiments demonstrate that oxidative addition of methane must proceed via CpRh(CO). The role of CpRhL (L = C5H5, CO) intermediates in solution reactions is discussed.

Some of the most successful of recent C–H activation reactions are thought to involve the dissociation of a small molecule from organometallic rhodium and iridium complexes in the primary step. Photochemical reactions of ($\eta^5$-C5R5)MLH and ($\eta^5$-C5R5)ML2 and thermal reactions of ($\eta^5$-C5R5)ML(H)R' species (R = H, Me; R' = alkyl; L = CO, phosphine, etc.; M = Rh, Ir) with alkanes have recently been postulated to proceed through ($\eta^5$-C5R5)ML, 16-alkene intermediates. Such fragments have excited considerable theoretical interest because of their carbeneoid character and because both triplet and singlet states are available to them. Attempts have been made to calculate the (ring-centroid) ML angle of the fragment and its dependence on spin state and to define those factors that stabilize the singlet state relative to the triplet. However, experimental observation of these fragments has been extremely limited.

Photochemical matrix-isolation experiments on Cp*Ir(CO)2 (Cp* = $\eta^5$-C5Me5) failed to induce CO loss in inert matrices, probably because of in-cage recombination. This conclusion has been confirmed in detailed studies of ($\eta^5$-C5R5)ML(CO)2 byRest

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