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EXAFS STUDY OF NICKEL TETRACARBONYL AND Ni-CLUSTERS IN ZEOLITE Y[1]

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ABSTRACT
Adsorption and thermal decomposition of $Ni(CO)_4$ in the cage system of zeolite Y have been studied with EXAFS, electron microscopy and IR spectroscopy. $Ni(CO)_4$ is adsorbed as an intact molecule in both cation-free zeolite Y and NaY. Symmetry changes of the molecule in NaY are assigned to the formation of Na^+--OC-Ni bridges. Thermal treatment of the $Ni(CO)_4$/NaY adduct leads to loss of CO concomitant with the formation of a binodal Ni phase. A major part of the Ni forms clusters with diameter between 0.5 and about 1.5 nm, in addition to larger crystallites (5-30 nm), sticking at the outer surface of the zeolite matrix.
The Ni-Ni scattering amplitude indicates increasing average particle size with increasing temperature.

INTRODUCTION

Thermal decomposition of supported $Ni(CO)_4$ as a precursor for dispersed Ni catalysts has been reported previously (1-3), in addition to a limited number of attempts to anchor mixed $Ni(CO)_nL_m$ complexes directly on partially hydroxylated oxide surfaces (4). Little is known regarding the interaction of the complex with the matrix and formation of the metal phase. In an attempt to understand the reactivity of nickel carbonyl compounds in the cage system of faujasites, we have used a combination of EXAFS, X-ray absorption near edge spectroscopy (XANES) and transmission electron microscopy. The results are compared with those obtained with IR spectroscopy.

EXPERIMENTAL

Materials: Zeolite Y from Strem Chemicals (Linde LZ-Y52), with the unit cell composition $Na_{55}(AlO_2)_{55}(SiO_2)_{137}\ xH_2O$, was dehydrated at 670 K under 10^{-5} torr for 12 hours (heating rate 2 K/min) and handled under nitrogen in a drybox. Dealuminated zeolite Y' was prepared according to (5) and dehydrated in a similar procedure. $Ni(CO)_4$ from Alfa was used as received.
Vapor phase loading: 0.5 g of dehydrated zeolite were weighed 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 with 3 freeze-pump-thaw cycles under low intensity light. A calculated amount of carbonyl vapor was admitted to the zeolite and allowed to equilibrate for 30 min. at 295 K, followed by evacuation for 30 min. Gravimetric and manometric control of this process revealed that the dosing technique allows a predictable loading of the zeolite with volatile compounds.

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Thermal decomposition: Samples of the carbonyl/zeolite adduct (300 mg) were heated under vacuum, with a rate of 1 K/min, up to 323, 373 and 673 K (samples VAC323, VAC373 and VAC673) and held at these temperatures for 2 hours and 12 hours (673 K).
Methods: IR spectra were taken with a Nicolet 5DX8 FT-IR spectrometer in a Barnes controlled atmosphere diffuse reflectance IR cell with CaF_2 windows.
EXAFS experiments were carried out at the X11-A beamline at the National Synchroton Light Source with a stored electron energy of 2.5 GeV at currents between 40 and 100 mA. Spectra of samples, embedded in paraffine or sealed in polyethylene cells, were taken in a dewar with Kapton™ windows at ca. 100 K. The data were analyzed according to published procedures (6). Background removal was accomplished using a cubic spline function and the resultant EXAFS modulations were weighed by k^3 and Fourier transformed over a range of 2 to 16 K.
Transmission electron micrographs of the zeolites were taken on a Hitachi H600 instrument from microtomed sections of 70 to 90 nm thickness. The samples were embedded in Epon 812 under exclusion of air.

RESULTS AND DISCUSSION

1. Adsorption of Nickel Tetracarbonyl in Faujasite.

We present here the first EXAFS spectra of $Ni(CO)_4$ adsorbed in different faujasites. Fig. 1 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 the Fts between the two samples indicates that adsorption of $Ni(CO)_4$ 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 $Ni(CO)_4$ as well as comparison of the magnitude of the strong outer shell scattering due to linear CO indicates little distortion of the CO ligands.
The IR CO-stretching pattern of $Ni(CO)_4$ in Y' resembles that of the neat carbonyl, whereas in NaY four different bands appear at 2120, 2065, 2030 and 2010 cm^{-1}. If combined with the EXAFS results, this observation can be understood in terms of symmetry changes due to Na^+--OC-Ni interactions in NaY zeolite which are absent in Y'. Comparable interactions are discussed for the adsorption of metal carbonyls on alumina and for carbonyl-ion pairing (7, 8).

2. Thermal Decomposition of Nickel Tetracarbonyl in Faujasite.

NaY loaded with 2.0 molecules of the carbonyl per supercage and heated up to 323 K in vacuo for 2 hours (VAC323) loses weight corresponding to a coordinatively unsaturated system with CO/Ni = 1, accompanied by a color change from white to dark grey. The corresponding XANES of VAC323 is compared with the edge of $NaY/Ni(CO)_4/_2$ in Fig. 2a. A dramatic reduction in the first absorption maximum indicates increased occupation of bonding orbitals as expected upon release of pi-acceptor ligands. 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 hours (VAC373), complete loss of CO is now observed as evidenced by comparison of the edges to that of Ni foil. 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 Fourier transform of sample VAC323 is compared to that of VAC373 in Fig. 2b. Slight differences in outer shell amplitudes are visible in addition to a small peak in VAC323 corresponding to the Ni-C distance found in $Ni(CO)_4$ (Fig. 1). This peak is tentatively assigned to residual CO ligands which are only removed upon evacuation at 373 K.
The electron micrograph of VAC323 (Fig 3) shows octahedral Ni crystallites 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 (Fig. 2b) must be due to the large particles that are detected in the TEM. The first Ni-Ni scattering amplitude amounts to only 50% of the bulk value, and the upper limit of bulk-like particles in this system is therefore 50%. This assumtion would imply atomic dispersion - most likely with oxygen coordination - of the remaining Ni fraction. Since no oxygen coordination is detected in the Fts, a consistent model involves a binodal Ni phase with a major size fraction at about zeolite supercage dimensions and a fraction of large (5 - 30 nm) crystallites sticking at the outer surface of the zeolite matrix.

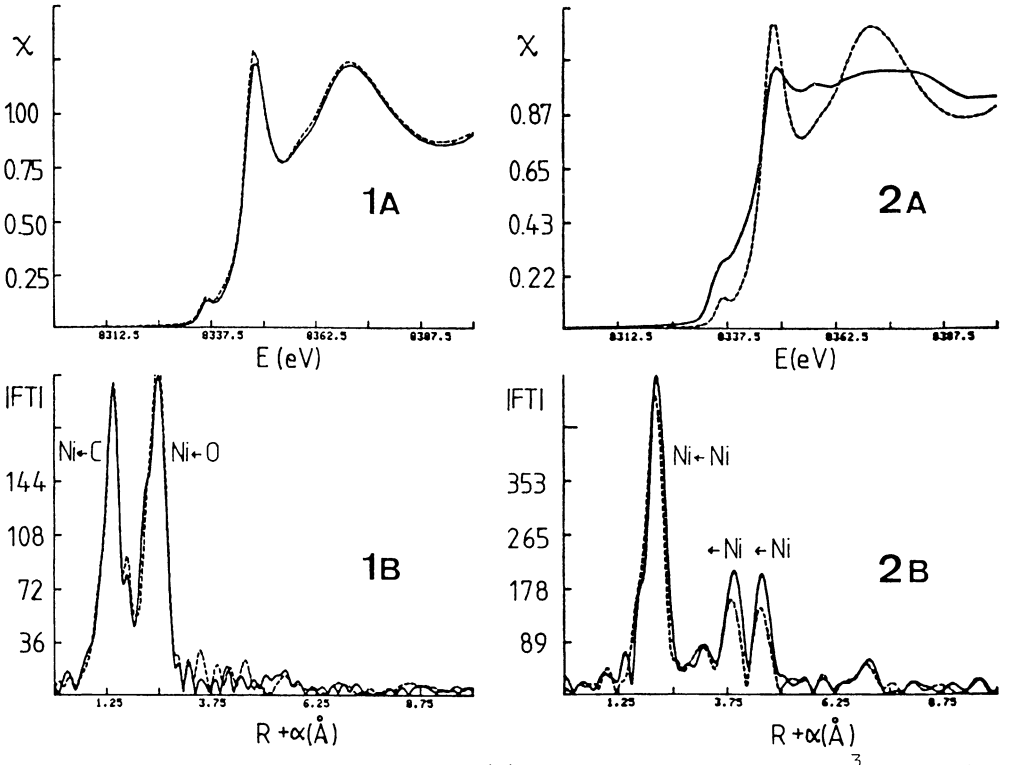

Figure 1 and 2. Ni K edge spectra (A) and Fourier transformed, k^3 weighted EXAFS modulations (B).
1. $Ni(CO)_4$ in NaY (-) and dealuminated Y' (--).
2A. Edges of $NaY/Ni(CO)_4$ (2 per supercage) (--) and sample VAC323 (-).
2B. Fts of samples VAC323 (-) and VAC373 (--).

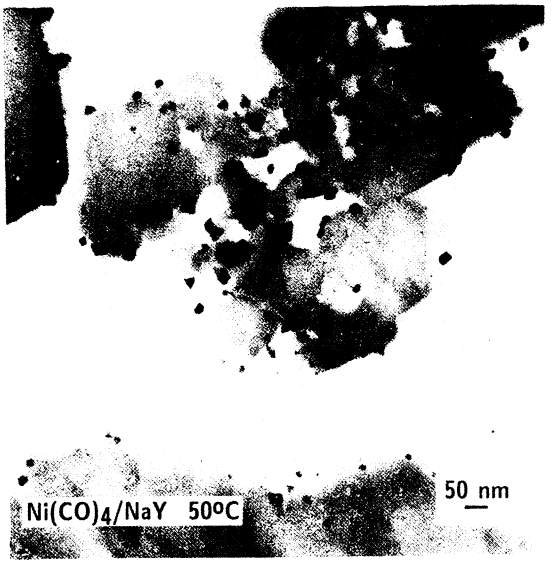

Figure 3.

Transmission electron micrograph of sample VAC323.

Comparison of the later stages of thermal treatment (samples VAC373 and VAC673) reveals a significant increase of Ni-Ni neighbor populations. 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 (9, 10). Hydrogen reduction of $Ni(II)/Si(OH)_4$ gels yielded Ni particles with diameters between 2 and 10 nm (9), whereas larger particles were produced using a gas evaporation technique (10). The magnitude of the EXAFS radial distribution function was found to decrease substantially with decreasing average particle size (10).
It becomes clear that careful decomposition of $Ni(CO)_4$ adsorbed in zeolites provides a valuable technique for the preparation of small nickel particles.

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