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Adsorption and Thermal Decomposition of $Ni(CO)_4$ on Various Oxides: A Novel Preparation of Dispersed Metallic Nickel Catalysts

The possibility of anchoring coordination compounds on organic or inorganic supports has received a great deal of attention in recent years (*1*). When the coordination complex is a metal-carbonyl compound, its thermal decomposition leads to the formation of dispersed metal crystallites as evidenced for Mo, Re, and Ru-carbonyl compounds adsorbed in Y-zeolite (*2*). Hence, such systems are worth further investigation, mainly with respect to the characterization of the complex–support interaction, the nature and mastering of the decomposition mechanisms, and the study of the metallic phase and of its catalytic activity.

The present note reports briefly a study of the adsorption of $Ni(CO)_4$ on various oxidic materials, eventually followed by thermal decomposition. ^{13}C-nuclear magnetic resonance (CNMR) is used to monitor the strength of the complex–support interaction. It is shown that stable and porous metallic Ni crystallites can be obtained even on an inert and nonporous support as alumina fibers.

$Ni(CO)_4$ was supplied by Alfa-Ventron. Supports were alumina fibers (Saffil, I.C.I.), γ-alumina (Merck), NaY-zeolite (Linde, SK-40), and NH_4Y-zeolite obtained by exchange of the NaY form (up to 85.7%) in NH_4^+-normal solutions. De-ammoniation of the NH_4Y material at 673 K leads to the HY-zeolite. Prior to adsorption, all supports were dehydrated and activated to a maximum temperature of 673 K and a vacuum of $2–5 \times 10^{-6}$ Torr. After activation, the various oxides were equilibrated with the vapor pressure of $Ni(CO)_4$ at 298 K. A reference sample was prepared by dissolving $Ni(CO)_4$ vapor in $CDCl_3$ containing 1% of TMS (tetramethylsilane).

^{13}C-NMR spectra were recorded using a WP-60 Bruker Fourier transform spectrometer equipped with a specially designed external lock deuterium-probe. Particular attention was paid to the optimization and calibration of the CNMR spectra as described in detail elsewhere (*3*). Accumulation times were kept below 2–3 hr because of the slow decomposition of $Ni(CO)_4$ on the supports used. $Ni(CO)_4$ on alumina fibers was decomposed at 473 K (20 K above the reported decomposition temperature) and scanning electron micrographs (SEM) were obtained using a Jeol JSM-35 instrument.

Figure 1 shows the CNMR spectra of $Ni(CO)_4$ obtained in solution or following its adsorption on the various supports. Chemical shifts and approximate linewidths for the ^{13}C-resonance of the C=O groups are presented in Table 1. With reference to the chemical shift observed in solution, a remarkable variation is apparent. On NaY-zeolite, a positive shift (towards lower field) is found (+1.4 ppm) while a negative shift (to higher field) characterizes the other systems. For those, the chemical shift differences follow the general trend of surface acidities, i.e., $\Delta\delta = -1.0$ ppm on Saffil alumina, -1.6 ppm on γ-alumina, and -8.9 ppm on HY-zeolite.

These results can be rationalized on the basis of the ^{13}C paramagnetic contribution

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to the chemical shift [for a recent review see Ref. (*4*)]. Neglecting as a first approximation the variation in the average radius of the $C(2p)$ orbital and in the bond order of the carbon atom of the CO molecule, one only has to consider the average excitation energy between the diamagnetic ground state and the lowest paramagnetic excited state. Studies conducted in solution show that substituents favoring the back-bonding between the Ni and C atoms (n or π-donor substituents) cause a positive shift of the resonance because of the stabilization of the lowest excited state π^* of CO. By contrast, electron withdrawing groups give rise to negative shifts by destabilizing the same π^* state. Hence, the active site on NaY-zeolite must be considered as an electron donor and could correspond to lattice oxygen anions. On the contrary, electron acceptor (acidic, eventually protonic) sites must be involved on the other supports: alumina fibers, γ-alumina, and HY-zeolite in their respective order of increasing acidity.

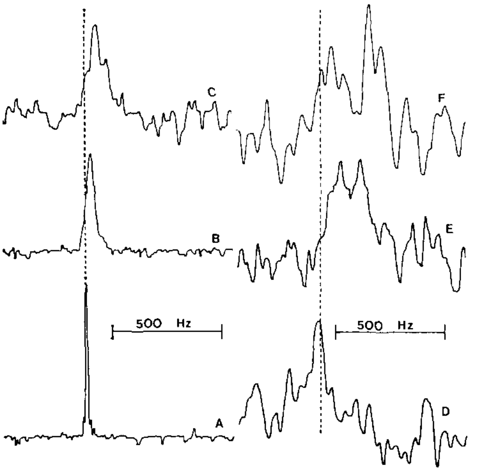

FIG. 1. ^{13}C-NMR spectra of $Ni(CO)_4$ in various environments: (A) solution in $CDCl_3$; (B) alumina fibers (Saffil); (C) γ-alumina; (D) NaY-zeolite; (E) HY-zeolite (with broad band ^{1}H decoupling); (F) HY-zeolite (without ^{1}H decoupling). The vertical dotted lines indicate the position of the unshifted ^{13}C-resonance of $Ni(CO)_4$ as observed in solution.

TABLE 1

^{13}C Chemical Shifts and Linewidths for $Ni(CO)_4$ in Various Environments (T = 294 K)

System	δ^a (ppm)	ΔH^b (Hz)
$CDCl_3$ solution	192.0	25
γ-Al_2O_3	190.4	65
Alumina fibers (Saffil)	191.0	50
NaY-zeolite	193.4	50
Hy-zeolite	183.1^c	70

[a] Maximum error due to use of external lock system is about 0.1 ppm (*3*). Chemical shifts are expressed in ppm from TMS.

[b] Linewidths are not corrected for instrumental line broadening (about 18 Hz).

[c] Dipolar coupling to one ^{1}H has been detected in this case. ($H = H_0 \pm 1.058$ Oe).

It is important to note that this explanation only holds if the CO groups are not involved directly in the bonding of $Ni(CO)_4$ to the supports, i.e., that change in the bonding is occurring through the Ni atom interaction with the oxidic surface. This conclusion is supported by two other features of the CNMR spectra. First, adsorption of $Ni(CO)_4$ on HY-zeolite leads to a line split into two components of which the separation depends on the amplitude of the broad band decoupling radiation applied at the ^{1}H resonance frequency. Therefore, the observed doublet must be attributed to dipolar coupling of ^{13}C with one ^{1}H on the surface. The ^{13}C to ^{1}H distance that corresponds to such a dipolar coupling value is 0.235 nm. Assuming that the $Ni(CO)_4$ molecule is adsorbed flat on a surface hydroxyl group (so as to obtain a square compressed pyramid with the proton at its top) and that the "hopping" motion of the molecule from hydroxyl to hydroxyl is rather restricted (which is reasonable in view of the relative dimensions of $Ni(CO)_4$ and of the sodalite and super-cages in the zeolite), one calculates readily a ^{1}H–Ni distance of 0.151 nm which compares extremely well with an expected Ni–H bond length of 0.16 nm. Finally,

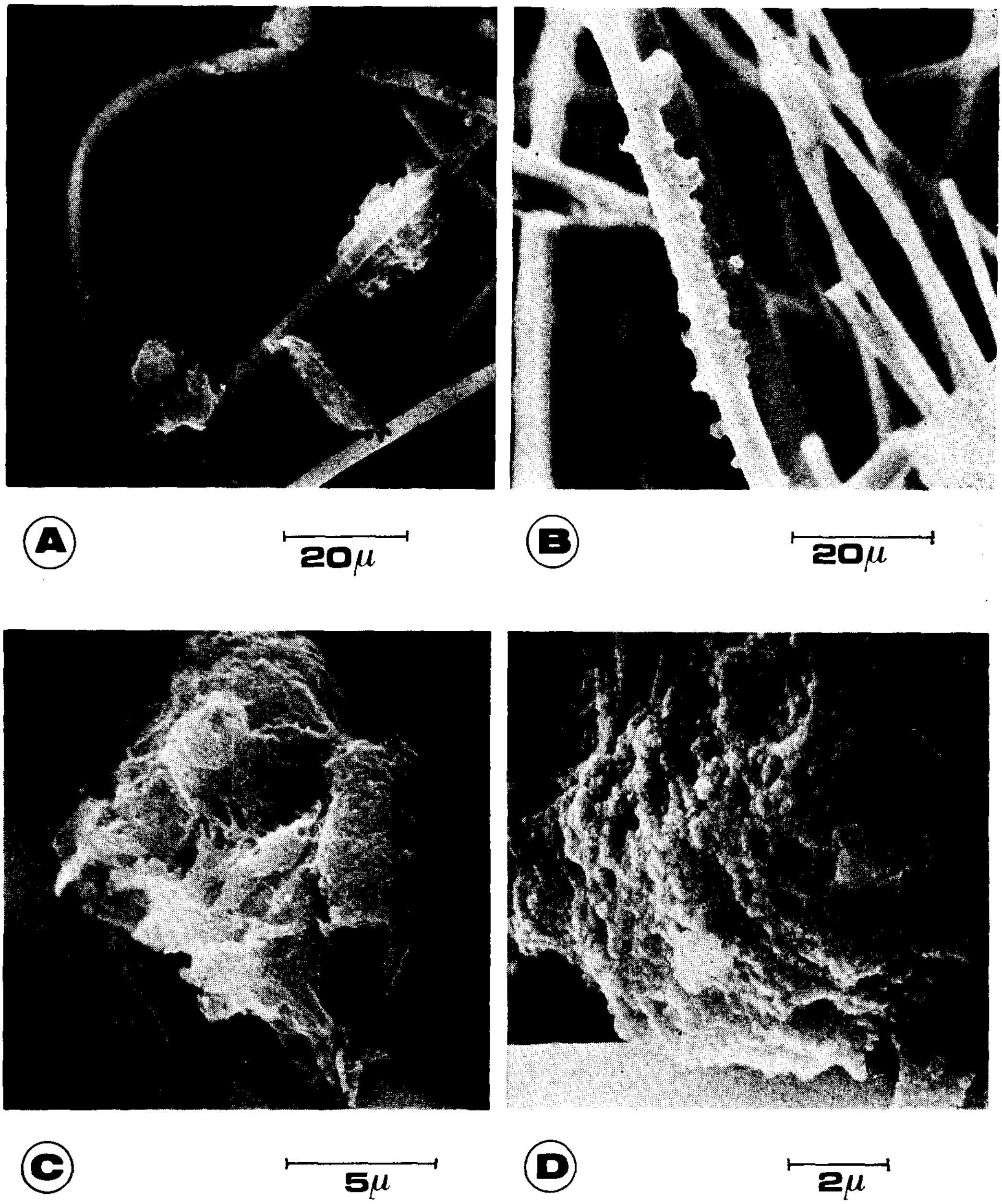

FIG. 2. Scanning electron micrographs of Ni on Saffil catalysts (see text for description).

the chemical shift observed for $Ni(CO)_4$ on HY-zeolite (183.1 ppm) (*6*) is rather close to that of free CO (181.3 ppm) indicating that back-bonding into the π^* state is rather weak in this case. That would result in an activation of the CO ligands which is confirmed by the higher decomposition rate observed on this support.

Ni metal particles obtained by thermal decomposition of the $Ni(CO)_4$–Saffil system were examined by scanning electron microscopy (SEM) leading to most interesting conclusions as evidenced from Fig. 2A to D. Ni crystallites (diameter 5–15 μm) are directly supported by the alumina fibers (Fig. 2A), probably as a consequence of an initial nucleation stage at some asperities (Fig. 2B). Use of higher magnification shows that the Ni crystallites must be considered as highly microporous (Fig. 2C) or as ensembles of tiny spheres (Fig. 2D) which are surprisingly uniform in size (50–200 nm). The so-obtained Ni crystallites are in many respects (including size, morphology, and texture) identical to those obtained by clustering of Ni atoms in organic media [vapor codeposition (*5*)], which have proved to be active hydrogenation and disproportionation catalysts.

The novel procedure reported here for the preparation of Ni catalysts certainly deserves more attention along the lines pointed out in the first paragraph of this note. The method is also capable of improvements and extensions, notably with respect to the preparation of multimetallic catalysts by direct clustering of the metals in the zero-valent state. The note specifically illustrates the power of CNMR as a tool for the characterization of the complex–support interaction in the precursor as well as the possibility of using rather inert supports, such as alumina fibers, for the clustering of the metal atoms. Further work is in progress which deals with the preparation of a more dispersed system (Ni on Saffil), the characterization of all the Ni systems described in this note, and the possible use of other metal-carbonyl compounds, as such or as mixtures.

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