Co(CO)$_3$NO Encapsulated in Zeolite NaY; a Novel Shape-selective Fischer–Tropsch Catalyst

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The sorption of the title compound into the pores of NaY zeolite is studied by i.r. and ^{13}C magic angle spinning n.m.r. spectroscopy; after appropriate activation, the supported cobalt system is a shape-selective catalyst for the hydrogenation of carbon monoxide to alkenes with a cut-off at C$_8$.

The direct conversion of hydrogen–carbon monoxide mixtures (synthesis gas) into organic products *via* the Fischer–Tropsch (F–T) family of reactions has for many years been recognized as an important goal in catalytic research.[1] There has also been in recent years a developing focus on increasing the selectivity of F–T chemistry, both with respect to the nature of the chemical products and to the molecular weight distributions. As many organic chemical processes carried out within the confines of a zeolite can be directed towards products of certain sizes and/or geometries (shape selectivity),[2] much research is therefore being directed towards the use of zeolite-supported and similar shape-selective F–T catalysts.[3]

Unfortunately, the reasons for unusual product distributions from F–T reactions are at present not well understood.† In an effort, therefore, to complement earlier work[3] on the use of zeolite-encapsulated, volatile cobalt carbonyls as shape-selective F–T catalysts, we have initiated an investigation of Co(CO)$_3$NO (1)[4] as a catalyst precursor. Compound (1) is a dark orange-red, volatile (b.p. 50 °C), hydrophobic liquid. It is isoelectronic with Ni(CO)$_4$ and pseudotetrahedral (C_{3v}) in structure, with a molecular diameter of about 6.3 Å. It is thus sufficiently small that it is readily and rapidly absorbed by NaY zeolite (pore diameter 7.4 Å, supercage diameter 13 Å), but not by Linde 5A molecular sieves (nominal pore diameter 5 Å).‡ To impregnate the NaY supports with (1), 0.3 ml of (1) was injected through a septum into a flask containing 5 g of the zeolite under nitrogen. The mixture was then shaken at room temperature for 10 h. All NaY products of this treatment, which contained about 2% cobalt by weight, were

orange, the colour of dilute solutions of (1). That they do indeed contain (1) physisorbed within the confines of the zeolite was suggested by the fact that much of the cobalt compound can be removed by pumping on the material (10^{-2} mmHg) at room temperature for 24 h.

The nature of the sorptive process was surmised on the bases of the Nujol mull i.r. (Figure 1) and the ^{13}C magic angle spinning (m.a.s.) n.m.r. (Figure 2) spectra of the zeolite-encapsulated compound. As can be seen from Figure 1, the i.r. spectrum in the triple bond region exhibits broad ν(CO) at 2113 and ~2050 cm^{-1}, and a broad ν(NO) at ~1800 cm^{-1}. Superimposed on these broad absorptions are well resolved ν(CO) at 2100 and 2034 cm^{-1} and a ν(NO) at 1806 cm^{-1}, which are the absorptions of (1) leached from the support and dissolved in the Nujol. The broad bands to be attributed to sorbed (1) suggest that the encaged complex experiences a range of attractive interactions with the zeolite matrix, presumably between the ligand oxygen lone pairs and Lewis acid sites of the zeolite.[5] The changes in frequencies on sorption are small and thus the sorptive interactions are undoubtedly weak, in agreement with the apparent ease of removal of (1) from the zeolite. As the ν(CO) and ν(NO) of (1) shift to higher and lower frequencies, respectively, on sorption, it seems likely that the major attractive interaction is *via* the nitrosyl oxygen.[6]

$$Co(CO)_3NO$$
$$(1)$$
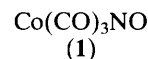
This conclusion is substantiated by the room temperature, 50.3 MHz ^{13}C m.a.s. n.m.r. spectrum of (1) in NaY, which exhibits a resonance of Lorentzian lineshape at δ 203.5 with Δν ~150 Hz (Figure 2b), considerably *narrower* than the
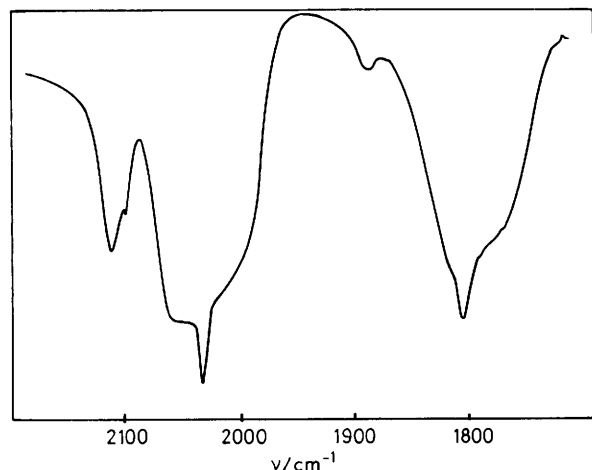

Figure 1. I.r. spectrum (Nujol mull) of (1) encapsulated in NaY zeolite.

Figure 2. Room temperature 50.3 MHz ^{13}C n.m.r. spectra of (1) (a) in chloroform solution and (b) encapsulated in NaY zeolite (with magic angle spinning).

† For discussions of relevant factors, see refs. 3(d) and 3(e).

‡ Zeolites were dried at 10^{-2} mmHg for 24 h at 500 °C (NaY) or 100 °C (5A). Spectroscopic studies were carried out with powdered supports (600 mesh), catalytic studies with 1/16″ pellets.
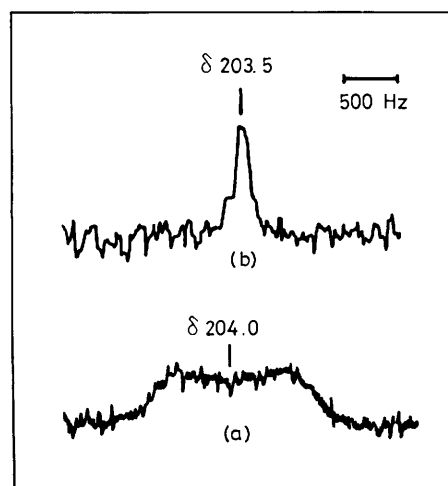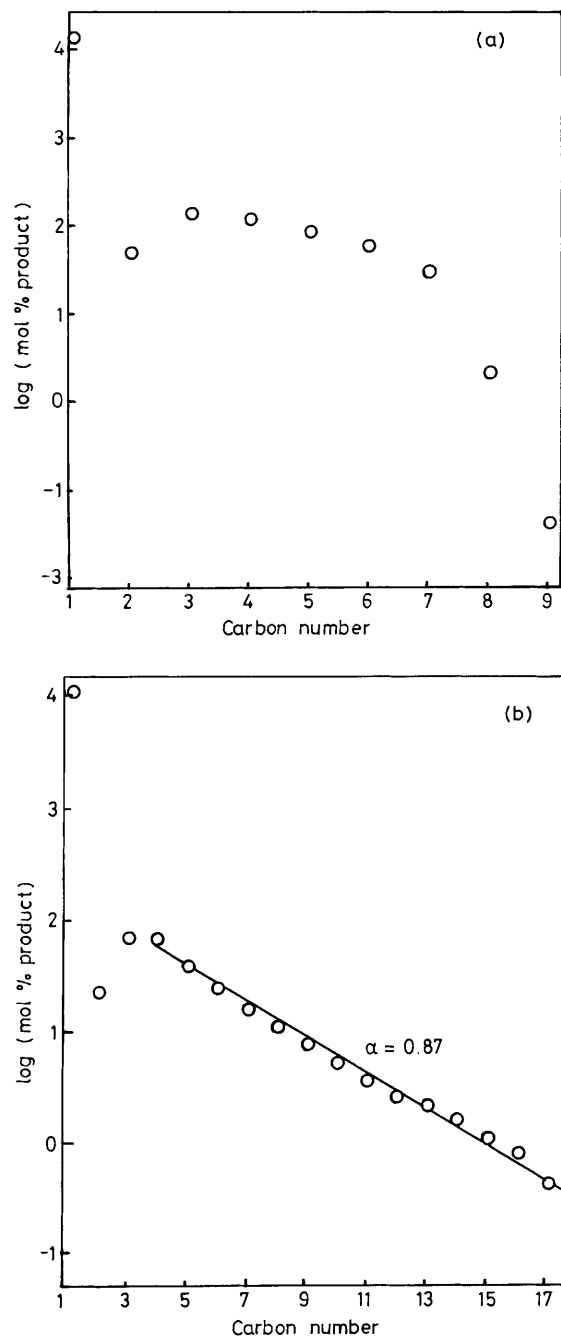
Figure 3. (a) Anderson–Schulz–Flory plot of products from catalyst generated under mild reductive conditions, showing truncated product distribution. (b) Plot showing 'normal' product distribution.

result is consistent with the cobalt complex experiencing somewhat more hindered movement in the zeolite matrix than in solution. In accord with this interpretation, the resonance of (1) in solution at −48 °C also exhibits a resonance of Lorentzian shape, with a line width reduced to about 580 Hz.

Compound (1) was immobilized on the zeolite support (*i.e.* activated for catalysis) in two ways. Treatment of (1) sorbed in NaY with hydrogen (1 atm, static system) for 24 h at 90 °C resulted in the zeolite turning black; the i.r. spectrum exhibited new, reasonably well resolved ν(CO) at 2059 and 1992 cm^{-1} and ν(NO) at 1774 cm^{-1}, in addition to the above-mentioned absorptions of loosely sorbed (1). Alternatively the NaY-encapsulated (1) was heated *in vacuo* for 24 h at 85 °C to give a black material, the i.r. spectrum of which exhibited ν(NO) at 1892(m) and 1808(s) cm^{-1} but no ν(CO). The product of the reductive activation would appear on the basis of its i.r. spectrum to result from mono-substitution of CO,[4] as occurs with Ni(CO)$_4$.[5] The nature of the product of vacuum decomposition is not known, but the frequencies and relative intensities of the observed ν(CO) are very similar to those of several supported cobalt dinitrosyl systems.[8] The spectra also exhibited broad absorption bands at frequencies >2200 cm^{-1} which may be attributed to byproduct species such as isocyanate ion or N$_2$O,[9] while the spectrum of the hydrogenated product also exhibited sharp bands at 2356 and 2342 cm^{-1}, which can probably be attributed to CO$_2$.[10]

The supported cobalt systems described above have been found to exhibit very interesting properties as F–T catalysts.§ Activation of (1) in NaY by 1 atm of H$_2$ for 24 h at 90 °C, followed by further treatment within the reactor with flowing H$_2$ for 2 h at 180 °C, 3 atm, yielded a catalyst whose overall hydrocarbon product distribution was as shown in the Anderson–Schulz–Flory plot of Figure 3a.[11] As can be seen, a precipitous drop in selectivity for C$_9$ and higher hydrocarbons was observed. In addition, it was found that the alk-1-ene : alkane ratios for the C$_3$ and higher hydrocarbons was consistently >1, *i.e.* 10 and 2.4 for C$_3$ and C$_4$, respectively. In contrast, activation under more forcing conditions (initial H$_2$ treatment at 120 °C) yielded a catalyst which was characterized by lower alk-1-ene : alkane ratios (0.9—2) and which exhibited a standard Anderson–Schulz–Flory plot (Figure 3b).

As mentioned above, the origins of shape-selectivities such as those observed here are at present controversial. Both metal dispersion and geometrical constraints are considered to be strong candidates,† and recent work on alumina-supported cobalt by Reuel and Bartholomew[12] has indeed clearly demonstrated an inverse correlation between the molecular weight distribution of the hydrocarbon products and the metal dispersion. Our method of catalyst preparation, with low cobalt loadings, is expected to lead to a high degree of dispersion¶ and the narrowest product distribution is in fact obtained with that catalyst for which immobilization of the cobalt was accomplished under relatively mild conditions (85 rather than 120 °C). However pore constraints to hydrocarbon chain growth must also be important; while Reuel and Bartholomew observed essentially Anderson–Schulz–Flory distributions of products even for their lowest dispersions,[12]

resonance observed in chloroform solution at room temperature (Figure 2a). The broadened doublet resonance (Δν ∼1700 Hz) observed in solution is as expected for a spin 1/2 nucleus coupled to a spin 7/2 ^{59}Co which is relaxing slowly because of the almost cubic, pseudotetrahedral environment.[7] Within the zeolite, however, the cobalt apparently experiences significant 'self-decoupling' from the carbon, leading to narrowing of the carbon resonance, an observation best interpreted in terms of more rapid quadrupolar scalar relaxation of the cobalt in the zeolite and hence a longer rotational correlation time for the cobalt. Thus the n.m.r.

our product distribution is noticeably truncated at C_9.** We note in concluding that the high alkene:alkane ratios observed for our systems are also consistent with alkene (the primary products on cobalt[1]) formation in a hydrogen-poor environment, *i.e.* within the zeolite pores.

References

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** Catalysts formed at higher temperatures may be expected to contain less well dispersed metal, thus possibly rationalizing the results of Figure 3b. Consistent with this, we find that hydrogen decomposition of (**1**) at 85 °C on 5 Å molecular sieves, which cannot absorb and thus disperse the organocobalt compound, results in an F–T catalyst which produces a normal distribution of alkanes.