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The Reactivity of Tetracarbonylnickel Encapsulated in Zeolite X. A Case History of Intrazeolite Coordination Chemistry

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Abstract

Zeolite X shows a high capacity for tetracarbonylnickel (up to 28 weight percent) such that complete pore filling with 'liquid-like' material takes place. The adsorbed material may be removed simply by evacuation at room temperature. Partial decomposition of the $Ni(CO)_4$ occurs on standing at room temperature under N_2. The resultant orange species is highly reactive and has spectroscopic properties consistent with a coordinatively unsaturated '$Ni(CO)_3$'. Complete and irreversible decomposition by heating to 200 °C *in vacuo* gives a black zeolite, with an undefined metal phase, which is unreactive towards carbon monoxide. Reaction of the zeolite supported $Ni(CO)_4$ with various phosphorus ligands is highly dependent on the original loading level as well as the physical size of the ligands involved. At low loadings two kinds of reactivity are observed: 1) With ligands too large to gain access to the zeolite crystal interior, reaction occurs only in solution and so drags the $Ni(CO)_4$ from the zeolite; 2) With smaller ligands, reaction takes place inside the zeolite cages leading to well-defined, encapsulated, ship-in-bottle complexes which have a stoichiometry dictated by the available space in the cages. At high loading levels, pore blocking phenomena lead to inhomogeneous distributions of encapsulated complexes wherein a complete shell of phosphorus ligand substituted nickel carbonyl species forms at the crystal surface layers and prevents further reaction deeper inside the crystal. The reactivity with large phosphines has been used to study the diffusion of $Ni(CO)_4$ from the zeolite. Monitoring the appearance of the $Ni(CO)_3L$ (where L = phosphine) by 31-P NMR of the supernatant solution shows that $Ni(CO)_4$ leaves the zeolite with a first order rate constant of at least 2×10^{-2} sec^{-1} at 298 K.

Introduction

While homogeneous transition metal catalysts find utility in a large number of organic reactions (hydrocyanation and hydroformylation of olefins, carbonylation of alcohols *etc.*) these materials are often difficult to recover and recycle. Immobilization of such homogeneous catalysts on a solid insoluble support is an approach to surmounting this problem which, in addition, may tend to prevent molecular aggregation or bimolecular self-destruction reactions which lead to deactivation. The challenge is to achieve a supported catalyst which maintains the typically high activity and selectivity of the homogeneous counterpart. One potential system with these properties is offered by zeolite encapsulated catalyst molecules. A catalyst prepared inside the pore system of a zeolite crystal, such that it is entrapped because of its physical size, would be expected to be well dispersed and immobilized yet each individual molecule of such a catalyst should be identical to the solution phase analogue and accessible to substrate molecules via the zeolite pore system. A catalyst which is a true bridge between homo- and heterogeneous systems may be expected.

As an additional bonus, the zeolite support may serve to increase the intrinsic selectivity of the catalyst by virtue of its molecular sieving and orientating effect on the substrate molecules which must diffuse through it to the active sites. Also, and perhaps more excitingly, the restrictive dimensions of the zeolite interior may force an unusual coordination geometry or even coordinative unsaturation upon the entrapped metal catalyst. These latter species may then have unique reactivities and selectivities unparalleled by solution phase catalysts.

We wish to report our observations, aimed at exploring the principles set forth above, on the generation of zeolite encapsulated organometallic species and their modified properties which are a result of the encapsulation. The tetracarbonylnickel/solid support system has been studied prev-

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iously, with particular emphasis on the mechanism of the complex/support interaction [1, 2] and thermal decomposition to the dispersed metal phase [3, 4]. These studies provide background to the present work on nickel carbonyl and nickel phosphine coordination chemistry within the zeolite.

Experimental

Zeolites 13X and 5A were obtained from Alfa-Ventron as pure powders of ~10 micron particles. Tetracarbonylnickel was also obtained from Alfa and was used as received. The zeolite samples were dehydrated prior to use by heating at 400 °C in a horizontal tube furnace under high vacuum for 4 h. The dried zeolites and tetracarbonylnickel were handled only in an inert (N_2) atmosphere glovebox or on a vacuum line in a well ventilated hood. Likewise, all phosphorus ligands were handled under N_2 and all solvents were dried and distilled using standard procedures prior to use.

Tetracarbonyl loaded zeolites were prepared as follows: 2 grams of dehydrated zeolite were loaded into a tube attached to a high vacuum line and evacuated. Tetracarbonylnickel was placed in a similar tube attached as a side-arm to the zeolite tube and it too was evacuated by 3 cycles of freeze/pump/thawing. The two tubes were attached through a small volume of isolable line such that this volume could be filled with carbonyl vapor (vapor pressure 340 torr), closed off from the bulk carbonyl and then opened to the zeolite. This gave a method of metering the amount of carbonyl absorbed on the zeolite. The carbonyl exposed zeolite was equilibrated at room temperature for at least two days to ensure a homogeneous distribution of carbonyl in the zeolite and then stored at −20 °C in the inert atmosphere dry box until use.

Reaction of the carbonyl loaded zeolite with phosphorus ligands was carried out in a glove box by exposing the zeolite either to neat ligand (when the ligand was a liquid) or to a concentrated toluene solution of the ligand (when the ligand was a solid). These slurries were stirred overnight, filtered and washed extensively with toluene and stored in the glove box prior to characterization.

Infra-red spectra were recorded as nujol mulls (well ground) between KBr plates using a Perkin-Elmer 599 infrared spectrophotometer. UV–Vis spectra were recorded on a Perkin Elmer 559A spectrophotometer as a nujol mull between quartz plates. Both IR and UV–Vis samples were prepared inside the glove box and run immediately after removal from the inert atmosphere.

The sample for NMR work was prepared by taking 500 mg of carbonyl loaded zeolite into 1 ml of dry toluene inside a 10 mm NMR tube inside the glove box. The sample was removed from the glove box, cooled in dry ice/acetone and a solution of 500 mg triphenylphosphine in 1 ml toluene/d-6 acetone (20%) was added. The tube was recapped and then frozen in liquid nitrogen until placed in the NMR spectrometer. After initial shimming at −50 °C, a rapid 31-P NMR spectrum at this temperature showed only unreacted PPh_3. The slurry was warmed to the desired temperature for the kinetic run in the NMR probe. 31-P NMR spectra were recorded with a Nicolet 1180E spectrometer operating at 121.67 MHz. Spectra were recorded as the average of 5 transients every 2 minutes for >2 hours while the temperature was maintained by a standard Bruker temperature controller to ±2 °C. The integrated peak areas were fitted directly to an exponential function to give an estimate of the time constant (rate constant) for the kinetic process.

Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Results and Discussion

The remarkably high affinity of dehydrated X type zeolite for tetracarbonylnickel is demonstrated by allowing the dry zeolite to equilibrate with the carbonyl vapor at room temperature over a period of 1 hour. The zeolite shows a 28% weight increase in this period which corresponds to a 60% filling of the internal void volume with 'liquid' tetracarbonylnickel (density = 1.30 g/cc [5]) which in turn corresponds to an average of 2.75 tetracarbonyl molecules per zeolite supercage. In order to achieve lower loadings it proved necessary to allow the zeolite to contact only a limited amount of the tetracarbonyl vapor as described in the experimental section. In this way, loadings of 28, 13.2, 9.1, 4.8 and 1.6 weight percent were achieved. In marked contrast to this behavior, anhydrous zeolite 5A does not absorb any $Ni(CO)_4$ even when soaked in the neat liquid at room temperature. This zeolite has a pore dimension of only ~5 Å, which is too small to give access to the ~6.5 Å diameter tetracarbonyl. As expected, zeolite X shows no absorption when it is fully hydrated since the internal void volume of the zeolite is fully occupied by water molecules which are not displaced by the $Ni(CO)_4$.

The freshly prepared tetracarbonylnickel (28%) in zeolite X has the infra-red spectrum shown in Fig. 1a with bands at 2045 cm^{-1} corresponding to the T2 symmetry ν_5 band of liquid $Ni(CO)_4$ and a shoulder at 2125 cm^{-1} which appears to correspond to the A_1 symmetry ν_1 band of solid $Ni(CO)_4$ [6]. The appearance of the latter band indicates that the adsorbed $Ni(CO)_4$ feels some orientating effect of the zeolite such that it becomes 'solid-like' – even

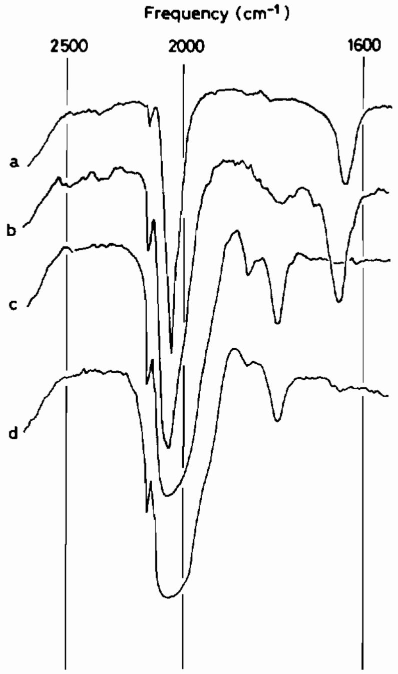

Fig. 1. Infra-red spectra of 28 weight percent tetracarbonylnickel in zeolite X as a function of time. (a) 1 hour; (b) 4 hours; (c) 60 hours; (d) 168 hours after original exposure to Ni(CO)$_4$.

at room temperature (m.p. Ni(CO)$_4$ = −17.2 °C). As this cream-colored zeolite is allowed to sit in room light and at room temperature, under N_2 in a sealed vial, it turns orange-red in ~24 hours. As this color change occurs the IR band at 2045 cm^{-1} broadens to the low wavenumber side (Fig. 1b), and then changes overall appearance (Fig. 1c–d). After 7 days the IR spectrum appears to have stabilized. Most striking is the complete loss of all OH absorptions from the original zeolite (residual water, not removed by the dehydration procedure gives a band at 1650 cm^{-1}) and the appearance of two new absorptions at 1840 cm^{-1} and 1775 cm^{-1} in a region appropriate for metal bridging carbonyls. The orange zeolite has a UV–Vis spectrum (nujol mull/transmittance) with a peak at 380 nm tailing into the visible region. Exposure of the orange zeolite to CO leads to a regeneration of the original cream color and restoration of the sharp Ni(CO)$_4$ IR spectrum, with loss of other major features that had developed. Finally, exposure of the orange zeolite to air leads to rapid lightening to a very pale green with concurrent heat evolution. This material has an IR spectrum showing no carbonyl bands but a clean absorption from CO_2 at 2350 cm^{-1}.

Interpretation of these observations rests largely on the electronic spectrum, which is very reminiscent of the coordinatively unsaturated NiL_3 species which are formed with very bulky phosphorus ligands [7]. These tricoordinate complexes typically have a strong UV absorption around 400 nm which tails into the visible region and results in the orange color. Accordingly, we assign the present orange species to 'Ni(CO)$_3$' adsorbed in zeolite X. Such an interpretation is similar to that offered for the Ni(CO)$_4$ on alumina system [1]. Such a coordinatively unsaturated species ought to be extremely reactive and might be expected to attack neighboring Ni(CO)$_4$ molecules to form metal carbonyl cluster species with bridging CO ligands. This would give rise to the new IR absorptions observed. The loss of water which is apparently concurrent with generation of 'Ni(CO)$_3$' suggests that these reactive species may also attack residual water molecules to generate nickel(II) and formate/formaldehyde species leaving a 'dehydrated' zeolite. Reversal of color and spectral changes by CO is consistent with these interpretations and the apparently facile air oxidation of the Ni(0) to Ni(II) and concurrently of the CO to CO_2 is also consistent with the presence of very reactive 'Ni(CO)$_3$' species. From these preliminary observations, it is clear that the zeolite is inducing production of novel species which have no solution phase analogues and in particular in the generation of moderately long-lived, coordinatively unsaturated metal species.

When the Ni(CO)$_4$ loaded zeolite is heated *in vacuo* at 300 °C for 2 hours, the material turns black as nickel metal is deposited inside the zeolite. This approach to the generation of highly dispersed nickel metal catalysts has been explored previously [1–4] where evidence for the intermediacy of subcarbonyl species has been presented. Attempts to reverse the decomposition reaction by exposure of the freshly produced Ni/zeolite to 1 atmosphere of CO at temperatures from 25 to 100 °C failed. No IR bands attributable to coordinated carbonyl ligands were detected after 8 h of reaction. It appears, therefore, that the black zeolites which nominally bear nickel atoms actually have these metal sites strongly aggregated and/or strongly interacting with the zeolite lattice such that treatment with CO is incapable of overcoming this interaction under the conditions tried. It may be possible to use higher pressure and/or temperatures to overcome this resistance to reaction.

The synthetic strategy for the generation of encapsulated or ship-in-bottle metal coordination complexes requires the *in situ* production of such complexes via the reaction between an adsorbed metal species and the component ligands. To investigate the production of such materials a freshly prepared batch of Ni(CO)$_4$ loaded into zeolite X (28%) was exposed to a variety of phosphorus ligands as described above. The resultant materials were characterized by their infrared spectra of which three typical examples are shown in Fig. 2.

Fig. 2. Infra-red spectra of 28 wt % $Ni(CO)_4$ in zeolite X after exposure to phosphorus ligands. (a) triphenylphosphine; (b) triethylphosphine; (c) triethylphosphite.

With very large phosphines such as triphenyl or tricyclohexyl the isolated zeolite reaction product shows no infrared bands in the carbonyl region (Fig. 2a). These ligands are apparently too large to enter the zeolite and so remain in the external solution during the treatment. However, since the adsorption of materials such as $Ni(CO)_4$ into zeolites is a reversible equilibrium, there will be a finite concentration of $Ni(CO)_4$ desorbed as the zeolite is slurried into solution. Indeed this small amount of desorbed material may be detected by IR spectroscopy of the supernatant liquid after the zeolite is slurried in a pure solvent. When a large phosphine is present in the solvent, a substitution reaction between it and the liberated $Ni(CO)_4$ leads rapidly to large phosphorus substituted complexes, incapable of reentering the zeolite. The substitution reaction has the effect of reducing the solution concentration of $Ni(CO)_4$ below its equilibrium value and therefore shifts the $Ni(CO)_4$ concentration in the zeolite towards complete desorption. The overall effect is that the large phosphine drags all of the adsorbed $Ni(CO)_4$ out of the zeolite.

With a small phosphine such as triethyl (Fig. 2b) or phosphite such as trimethyl the behavior is quite different. Now the ligand can easily enter the zeolite interior where it can encounter and react with the adsorbed $Ni(CO)_4$ forming substituted carbonyl complexes (as evidenced by their infrared spectra). In these cases, the resultant complexes are not removed from the zeolite even by extended extraction with toluene or methylene chloride. In the case of the trimethylphosphite, the complex is not removed even after evacuation at room temperature for 60 hours. These complexes represent examples of novel 'ship-in-bottle' species where the metal species is kept inside the zeolite purely because of its physical size. In the case of triethylphosphine, the IR spectrum appears to be a composite resulting from absorptions from $Ni(CO)_2L_2$ and $Ni(CO)L_3$ [8], but with no residual $Ni(CO)_4$, behavior which is very similar to that in solution [9]. With trimethylphosphite the IR spectrum indicates that a mixture of mono, di and tri substituted complexes (predominantly di) is present [10] but also that a considerable proportion of the $Ni(CO)_4$ is left unreacted. This stands in contrast to the solution phase behavior where a substitution level of 3 phosphite ligands is rapidly attained [9]. Clearly, the zeolite is restricting the reactivity of the tetracarbonyl as a result of pore blocking (*vide infra*).

The behavior of the zeolite system with the ligand triethylphosphite was unexpected in light of the above results. After soaking the $Ni(CO)_4$ loaded zeolite in neat ligand for 24 h, the IR spectrum (Fig. 2c) showed essentially no change; the IR absorption was only slightly broadened from that of the original $Ni(CO)_4$ zeolite and almost equally strong. If this ligand were too large to access the interior of the zeolite, then it ought to behave like the tricyclohexyl- or triphenyl-phosphines and drag all of the $Ni(CO)_4$ out of the zeolite leaving an IR spectrum like Fig. 2a. On the other hand, if the ligand can enter the pores then substituted carbonyl complexes ought to form as in the cases of triethylphosphine and trimethylphosphite. This puzzling result becomes clear when the loading level of the original zeolite is taken into consideration. Five different loading levels of $Ni(CO)_4$ in zeolite X – 1.6, 4.8, 9.1, 13.2, 28 weight percent – were soaked in $P(OEt)_3$ overnight. The IR spectra of these samples are shown in Fig. 3a–e.

The two lowest loadings show IR spectra with a pair of carbonyl absorptions at 2015, 1970 cm^{-1} of equal intensity and NO residual signal at 2045 cm^{-1} from the $Ni(CO)_4$ precursor. This spectrum is closest to that reported [11] for $Ni(CO)_2[P(OEt)_3]_2$ 2034, 1975 cm^{-1} (but does not correspond exactly to any known $Ni(CO)_x[P(OEt)_3]_{4-x}$ species) [6]. The three higher loading zeolites show no split carbonyl absorption but instead a single, broad band is present at 1995, 2012, 2035 cm^{-1} for the 9.1, 13.2 and 28 weight percent samples, respectively. These results indicate that at loadings of less than 9 wt.% the $P(OEt)_3$ ligand can gain free access to ALL $Ni(CO)_4$ molecules in the zeolite and react via carbonyl displacement as expected. However, unlike the equivalent solution phase reaction, which proceeds to the trisubstituted product [9], substi-

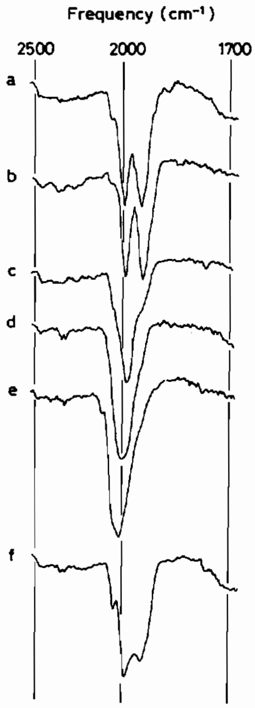

Fig. 3. Infra-red spectra of Ni(CO)$_4$ in zeolite X at different loading levels after exposure to triethylphosphite. (a) 1.6; (b) 4.8; (c) 9.1; (d) 13.2; (e) 28 wt %. Spectrum (f) shows the 28 wt % loaded zeolite after evacuation at 50 °C for 24 hours.

tution in the zeolite stops when only two phosphite ligands are attached to the nickel. This selectivity to the disubstitued product is apparently clean and is most likely a function of the supercage diameter being too restrictive to allow further substitution.

At loadings of >9 wt % the problem of pore clogging becomes important. The supercages are now ~75% occupied by Ni(CO)$_4$ molecules so that, while reaction with P(OEt)$_3$ at the surface layers can occur as before, this generates an outer skin on the zeolite crystal which is heavily plugged by Ni(CO)$_2$[P(OEt)$_3$]$_2$ complexes. These complexes, at this density, effectively seal off the interior of the crystal from the phosphite, thereby generating an unreactive core of Ni(CO)$_4$ at the crystal center. The IR spectra of such materials, therefore, represent a superposition of spectra for Ni(CO)$_4$ and Ni(CO)$_2$L$_2$. As the loading increases, the penetration of phosphite into the crystal will be shallower and more of the Ni(CO)$_4$ will remain unreacted. The resultant spectra show that the carbonyl absorption maximum moves successively closer to the frequency of the totally unreacted Ni(CO)$_4$ material.

Evacuation of the 28% loaded and phosphite treated sample at 50 °C for 24 hours gave a dark material with the IR spectrum shown in Fig. 3f. This spectrum, although weak, resembles that of the equivalent 1.6% loaded material (Fig. 3a) and implies that the Ni(CO)$_4$ core of the zeolite could be decomposed, liberating CO and leaving Ni atoms. This leaves the phosphite complex for detection by IR, unmasked by the Ni(CO)$_4$ absorption.

Both this latter sample and the 1.6% loaded sample (likewise evacuated at 50 °C for 24 hours) were subjected to XPS and chemical analyses. The results are summarized in Table I.

These data indicate that the surface layer probed by XPS (~50 Å) contains >4 times more phosphorus than the bulk analysis predicts for the 28% sample whereas the surface layer is actually depleted in phosphorus in the 1.6% sample. The nickel seems to be fairly homogeneously distributed in both samples. The 1.6% sample has a good correspondence of P/Ni with that ratio predicted on the basis of the IR spectrum. The 28% sample, on the other hand, shows a reasonable ratio in the surface layers but a strong deficiency of phosphorus in the bulk of the zeolite particle. These results confirm the explanation given above of pore-plugging at high loading densities. This system serves as a caution in this whole field of intrazeolite synthesis and catalysis: loading densities can be a critical parameter in determining reactivity.

The behavior of the Ni(CO)$_4$/zeolite/large phosphine system, which leads to complete desorption of the Ni(CO)$_4$, suggested a novel method for the estimation of the diffusional behavior of this organometallic species in the zeolite. By monitoring the appearance of the phosphine substituted nickel species in solution, the kinetics of the tetracarbonyl leaving the zeolite should be estimable. Following the procedure described in the experimental section,

TABLE I. XPS and Analytical Data for NiX/P(OEt)$_3$ Zeolites.

Original Ni(CO)$_4$ Loading	Technique	Ni/Si ratio	P/Ni ratio	P/Si ratio
1.6 wt %	XPS	<0.01	0.0	<0.04
1.6 wt %	Bulk Analysis	0.03	2.0	0.06
28.0 wt %	XPS	0.10	3.0	0.30
28.0 wt %	Bulk Analysis	0.13	0.5	0.07

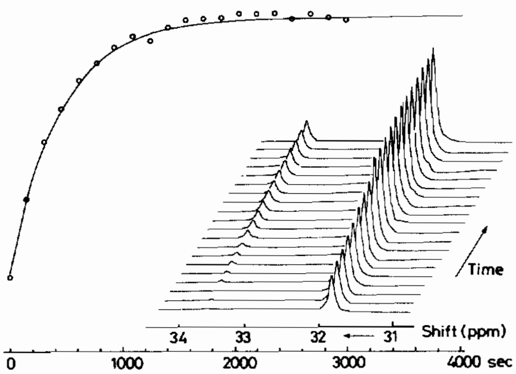

Fig. 4. Plot of integrated peak intensity of $Ni(CO)_3L$, where $L = PPh_3$, from the 31-P NMR spectra as a function of time at 0 °C. The solid line through the points is a computer fit to a simple exponential function (time constant = 450(5) sec) and the insert shows the actual spectra (major peak = $Ni(CO)_3L$; minor peak = $Ni(CO)_2L_2$).

31-P NMR spectra were accumulated and showed an exponential increase with time in a peak corresponding to the monosubstituted nickel carbonyl $Ni(CO)_3PPh_3$ [12] (Fig. 4). At longer reaction times, a second peak begins to appear at the position corresponding to $Ni(CO)_2(PPh_3)_2$. The production of phosphine substituted species is quantitative based on the amount of $Ni(CO)_4$ introduced and the final zeolite, if isolated by filtration and washed with excess toluene, shows no carbonyl absorption bands. The first order rate constant corresponding to the appearance of $Ni(CO)_3PPh_3$ is estimated at $2.0(1) \times 10^{-2}$ sec^{-1} at 298 K. This value is essentially identical to the rate constant for the simple substitution reaction of PPh_3 for CO in $Ni(CO)_4$ [13] which implies, therefore, that it is CO dissociation from $Ni(CO)_4$ and not the diffusion of the nickel species which is being monitored by this experiment. This, in turn, means that it is the substitution kinetics which are rate limiting and that the diffusion kinetics are considerably faster. This same conclusion holds under all conditions and temperatures studied and serves only to set a lower limit on the diffusion rate constant of $>5 \times 10^{-2}$ sec^{-1}. This is surprisingly fast (half life <30 sec) at room temperature and continues to be a subject of investigation. Presumably, if $Ni(CO)_4$ could be incorporated into a smaller pore zeolite then the diffusion kinetics should become rate limiting and hence measurable by this NMR technique.

Conclusions

The behavior of organometallic species, such as $Ni(CO)_4$, entrapped within a zeolite framework has been shown to be a consequence of the entrapment. Both the behavior of the species itself and its substitution chemistries are altered from those observed in solution. Evidence for the generation of the novel species '$Ni(CO)_3$' in the zeolite with its concurrent reactivity fosters the belief that new, catalytically active organometallic species can be generated inside zeolites. Work in these laboratories on the synthesis and properties of this new generation of hybrid catalysts has also realized examples of increased selectivity in both hydrogenation of olefins [14] and oxidation reactions of hydrocarbons [15]. That work and the work presented above serve to foster the expectation that the principles outlined in the introduction section will indeed be borne out through the generation of an exciting new family of zeolite encapsulated metal complex catalysts.

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