Formation of Iridium Carbonyl Complex in NaY Zeolite

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The structure of iridium carbonyl complexes trapped within the zeolite cavities and the reactivity of these species towards the methanol carbonylation have been investigated. $Ir(NH_3)_5Cl^{2+}$-exchanged NaY zeolite upon thermal decomposition is converted into an $Ir(OH)_x$ species. The carbonylation of iridium was followed by quantitative measurement of the ^{12}CO uptake, infrared spectra of the reaction with ^{12}CO, ^{13}CO, and a mixture of $^{12}CO-^{13}CO$. $Ir(I)(CO)_3$ was found to be very active and selective for the vapor phase carbonylation of methanol at atmospheric pressure in the presence of methyl iodide.

INTRODUCTION

During the past few years increasing attention has been devoted to the design of catalysts having the advantages of both homogeneous and heterogeneous catalysts (*1–4*). The usual approach in this field has consisted of anchoring or immobilizing transition metal complexes on a functionalized organic or inorganic support (*1–4*). An alternative means is to use ion exchange to incorporate the transition metal complex into the structure of a layer-lattice silicate. Rhodium complexes electrostatically bonded to mineral hectorite has thus been used for olefin hydrogenation (*5*). The use of synthetic zeolites for anchoring metal complexes also appears very promising since cationic species may be uniformly dispersed within the zeolite lattice by ion exchange and furthermore strongly held to the solid by ionic forces (*6*). Faujasite-type zeolites have been used for this purpose. However, for large or bulky metal complexes the steric effect can be a serious limitation since the metal complex must diffuse through the 8-Å diameter 12-membered rings to enter the supercage. This difficulty can be overcome by synthesizing within the zeolite cavities the desirable metal complex. Mantovani *et al.* (*7*) have prepared a rhodium carbonyl cluster trapped in NaY zeolite by reacting the Rh(III)-exchanged form with a mixture of H_2 and CO. The resulting catalyst was found to be very active for the hydroformylation of olefins. Similarly the formation of dicarbonyl rhodium (I) species within the zeolite cavities has been reported (*8*). Evidence for the formation of a rhodium acyl complex from reaction between Rh(III)–NaX zeolite, carbon monoxide and methyl iodide has also been presented (*9*).

The present study was undertaken to show further that synthesis of metal carbonyl complexes within the zeolite cavities is a useful route for heterogenizing homogeneous catalysts. In the present paper we report results of a study on the carbonylation of iridium ions in NaY zeolite. The probable structure of the iridium carbonyl compounds entrapped within the cavities is discussed.

EXPERIMENTAL

NaY zeolite was supplied by Union Carbide–Linde Co. The iridium form was prepared by ion exchange at 353 K with a solution of chloropentammine iridium (III) dichloride purchased from Johnson Matthey Co. The exchange level was controlled by using the appropriate amount of the $Ir(NH_3)_5Cl^{2+}$ complex. The samples

were then filtered out, thoroughly washed and dried at 313 K. The actual iridium content was determined by atomic absorption spectroscopy. Two samples with respectively 2.6 and 7.7 iridium cations per unit cell were thus prepared.

Quantitative studies of the reaction between carbon monoxide and iridium cations encaged in the zeolite were performed with a conventional glass volumetric system. During the reaction the pressure was monitored using a Texas Instruments precision pressure gauge. The CO uptake was determined using 1 g of Ir–NaY sample which was introduced in the reactor, heated in a stream of oxygen to 523 K at a rate of 0.5°/min and finally evacuated at 523 K. In some cases the pretreatment temperature was raised to 773 K. The CO uptake and CO_2 formed during the carbonylation of Ir(III) were measured only after equilibrium had been reached. The carbonylation reaction was performed at 298 and 443 K.

For infrared measurements the samples were pressed into 18-mm-diameter disks of about 6 mg/cm². The wafer was placed in a sample holder and introduced in the greaseless infrared cell described previously (8). Two samples were heated in a stream of oxygen and then *in vacuo* at 523 and 773 K respectively, using the same procedure as for the volumetric measurements. Spectra were recorded both before and after carbon monoxide adsorption. Infrared spectra were recorded on a Perkin–Elmer 580 spectrometer with a resolution of 2.8 cm⁻¹.

XPS measurements were performed using a Vacuum Generators ESCA III spectrometer equipped with a reaction chamber. A multichannel pulse height analyzer equipment enabled the signal to noise ratio to be increased. The zeolite was pressed on a grid attached to a sample holder and introduced in the reaction chamber. The binding energies for the iridium were corrected using $Si(E_b(2s) = 154.0$ eV) or $O(E_b(1s) = 532.4$ eV) as internal standards. All binding energies were accurate to within 0.2 eV.

RESULTS

Infrared Studies

The infrared spectrum of the iridium-exchanged NaY zeolite showed bands at 1360 cm⁻¹ characteristic of NH_3 molecules bound to iridium, and at 1640 cm⁻¹ attributed to physically adsorbed water molecules and to the ν_5 degenerate bending vibration of NH_3 bound to iridium. As the calcination temperature was raised from ambient to 773 K, a marked decrease in the intensities of the 1640- and 1360-cm⁻¹ bands was observed resulting from the desorption of water and the decomposition of the $Ir(NH_3)_5Cl^{2+}$ complex. At 523 K adsorbed water and NH_3 ligands were almost completely removed while hydroxyl groups vibrating at 3640 cm⁻¹ appeared.

At moderate temperatures (393–453 K), apart from the remaining ν_2 symmetric bending vibration at 1360 cm⁻¹ due to NH_3 ligands, a new band at 1900 cm⁻¹ appeared in the ir spectrum, which was subsequently eliminated upon evacuation at 453 K and restored upon NO adsorption on the activated sample.

On addition of carbon monoxide (5 Torr) at ambient temperature to Ir–NaY pretreated at 523 K, very little change occurred in the infrared spectrum. Only a weak broad band appeared around 2100 cm⁻¹ (Fig. 1a). In contrast, upon exposure to 5 Torr of CO at 443 K, twin strong bands at 2102–2086 and 2030–2001 cm⁻¹ developed (Fig. 1b). Simultaneously bands at 1640 and 2360 cm⁻¹ appeared. These absorptions are characteristic of water and carbon dioxide physically adsorbed. It is worth pointing out that the ir bands at 1640 and 2360 cm⁻¹ developed as the temperature of carbonylation was raised from ambient to 443 K, but they were never detected when the sample was contacted with CO at room tempera-
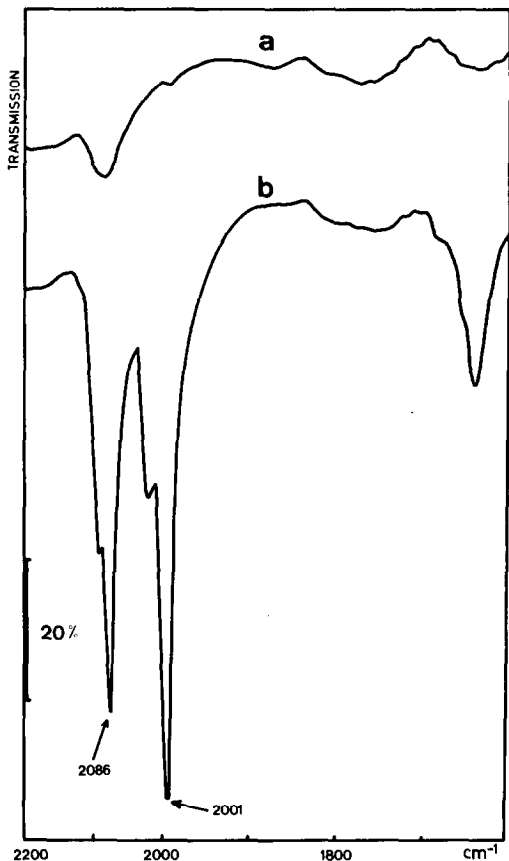
FIG. 1. Infrared spectra in the carbonyl stretching region for CO reaction with IrY zeolite: (a) at 298 K; (b) at 443 K.

trum of the iridium carbonyl when an equimolecular mixture of $^{13}CO/^{12}CO$ was used. Bands at 2086, 2075, 2060, 2036, 2001, 1978, and 1956 cm^{-1} were observed. When IrY was reacted with 90% ^{13}CO-enriched carbon monoxide at 5 Torr pressure and 443 K, two strong bands at 2036 and 1956 cm^{-1} were observed.

Volumetric Studies

The CO uptake by the iridium-exchanged Y zeolite was determined as follows: 1 g of IrNaY (2.9 wt% Ir) sample dehydrated *in vacuo* at 523 K was contacted with CO at room temperature for several hours. The amount of CO irreversibly adsorbed, derived from the isotherm of adsorption, was 5 μmole CO/g. Since 1 g of the sample contained 150 μmole of iridium, clearly only a small
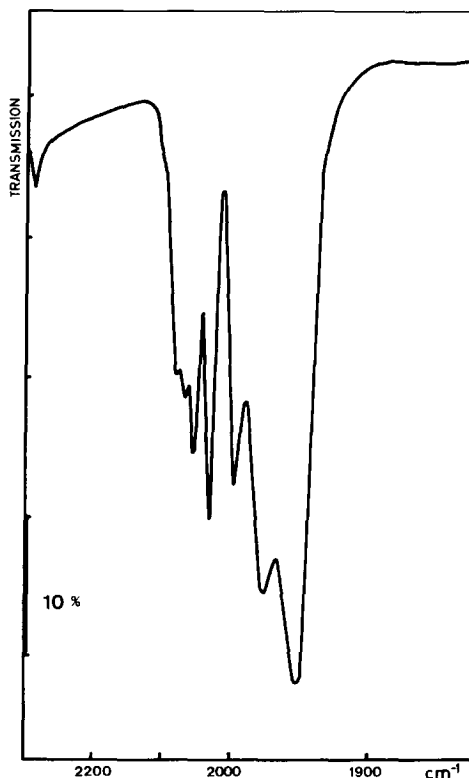
ture for several days. These results indicate that the adsorbed H_2O and CO_2 detected on the carbonylated IrY sample were generated during the carbonylation reaction at 443 K.

To obtain more direct and unambiguous information about the nature of the iridium carbonyl species responsible for the ir spectrum shown in Fig. 1b, we studied the adsorption of an equimolecular mixture of $^{13}CO/^{12}CO$. It is known that the symmetry of a metal carbonyl species containing more than one equivalent CO will be reduced upon substitution of some ^{12}CO for ^{13}CO. The lowering of the symmetry of the species will give rise to new ir absorptions in the carbonyl stretching region. Figure 2 illustrates the ir spec-

FIG. 2. Infrared spectrum in the carbonyl stretching region for $^{12}CO-^{13}CO$ reaction with IrY at 443 K.

fraction of the iridium was involved in the adsorption process at room temperature. Furthermore, this is in good agreement with the infrared data showing that under the same experimental conditions only a small ν_{CO} band was observed. The IrNaY sample was then reacted with CO at 443 K for several hours until there was no change in the total pressure. The sample was then cooled to room temperature, the condensable gas was trapped in a liquid nitrogen trap and the amount of CO consumed was measured. It appeared that 605 μmole of CO had reacted with 1 g of IrNaY (2.9 wt% Ir). The amount of the condensed gas, identified as CO_2 by mass spectrometry, was 180 μmole. From these volumetric data the stoichiometric ratio for the carbonylation reaction at 443 K is CO:Ir $\simeq$ 4.0 and CO_2:Ir $\simeq$ 1.2.

Figure 3a depicts the XPS spectrum of the Ir $4f \frac{5}{2}$ and Ir $4f \frac{7}{2}$ levels of an $[Ir(NH_3)_5Cl]^{2+}$–HY sample thermally treated in oxygen and then in vacuo at 523 K. In this study the H form of Y zeolite was used to avoid the overlapping of the Na $2s$ ($\sim$66 eV) and the Ir $4f \frac{5}{2}$

FIG. 3. XPS spectra of Ir $4f \frac{5}{2}$ and Ir $4f \frac{7}{2}$ levels (a) IrNaY thermally treated at 523 K; (b) (a) + CO at 443 K.

peaks. The iridium peaks were found at 66.1 eV and 62.9 eV. Along with these peaks, a peak at about 200 eV corresponding to the binding energy of Cl $2p$ (not represented in Fig. 3) was observed while the peak corresponding to nitrogen was absent, which suggests that the coordinated ammonia ligands were removed while some chlorine ions were still present following the thermal treatment at 523 K. Furthermore, it was observed that the peak area of Ir $4f$ remained almost constant following thermal treatment from 293 up to 523 K, which indicates that there is no change in the iridium distribution, within the zeolite, following thermal treatment. Figure 3b illustrates the results when Ir–HY was exposed to CO at 443 K. The carbonylation reaction caused the shift in binding energies of Ir $4f \frac{5}{2}$ and Ir $4f \frac{7}{2}$ to 65.2 and 61.8 eV. These negative shifts in the binding energies indicate that a reduction of iridium cations has occurred.

DISCUSSION

In a recent paper Primet et al. (8) have shown that the chemical composition of $Rh(NH_3)_5Cl^{2+}$ cations introduced in NaY zeolite by ion exchange remained almost unchanged as long as the sample was not calcined. Similarly the present infrared study, in addition to XPS measurements, shows that the fresh iridium-exchanged zeolite contains the $[Ir(NH_3)_5Cl]^{2+}$ obviously localized within the supercage. Subsequently the disappearance of the ir band at 1360 cm^{-1} indicates that the NH_3 ligands are readily removed by the thermal treatment at 523 K. Similarly, XPS has shown that the nitrogen peak disappeared following the calcination at 523 K. In contrast, the XPS peak at 200 eV, attributed to the chlorine $2p$ binding energy, remained almost unchanged as the sample was outgassed from 293 K up to 523 K. Thus the infrared and XPS results suggest that subsequently to the thermal decomposition at 523 K of the $[Ir(NH_3)_5Cl]^{2+}$

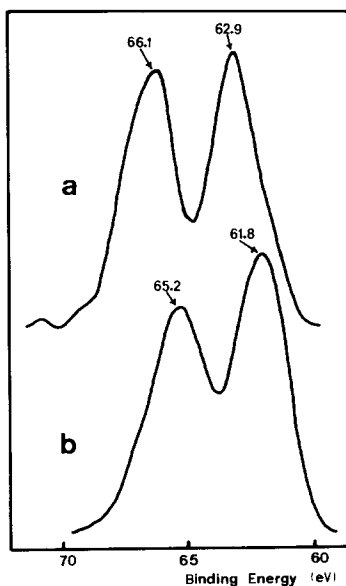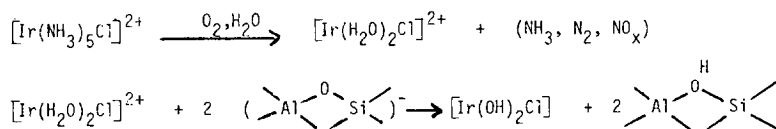complex only the chlorine ligand remained bonded to iridium. The band at 3640 cm^{-1} appearing after the calcination at 523 K has been assigned to acidic hydroxyl groups (10). Thus the calcination not only removed NH$_3$ ligands, but simultaneously produced acidic OH groups. It is now well accepted that multivalent-cation exchanged Y zeolites present Brønsted acidity due to the hydrolysis of water molecules bound to the cation. Acidic hydroxyl groups on iridium Y zeolite should arise from the progressive removal of the ammine ligands either as free molecules or oxidized forms (N$_2$, NO$_x$) and their concomitant substitution by H$_2$O molecules. These undergo further heterolysis into hydroxide ions which bind to the cations and into protons which bind to the lattice oxide ions. The overall mechanism may be pictured as:

$$[Ir(NH_3)_5Cl]^{2+} \xrightarrow{O_2,H_2O} [Ir(H_2O)_2Cl]^{2+} + (NH_3, N_2, NO_x)$$

$$[Ir(H_2O)_2Cl]^{2+} + 2 \left({>}Al \overset{O}{<} Si{<} \right)^{-} \longrightarrow [Ir(OH)_2Cl] + 2 {>}Al \overset{\overset{H}{O}}{<} Si{<}$$

Alternatively, the monohydroxychloro complex of iridium (III) might form due to the cleavage of a single water molecule per iridium.

The fact that the ν_{OH} due to these hydroxychloro complexes of iridium (III) has not been detected is not surprising. Indeed a band in the range 3580–3550 cm^{-1} is expected (10) but is only detectable for extensively exchanged zeolite, and depending on its frequency may or may not be easily removed from the other two bands at 3550 and 3640 cm^{-1}. It is worth noting that those iridium metal ions, which were fully hydrolyzed with the loss of ammonia, were thus converted into neutral hydroxychloro iridium complexes trapped within the zeolite cavities without any change in the oxidation state of iridium.

Analysis and Assignment of the Carbonyl Infrared Bands

We first consider the absorption band near 2100 cm^{-1} observed for the CO–IrY adduct formed at 25°C. Vaska (11) has reported that [IrCl$_3$(Ph$_3$P)$_2$]complex reacts with CO at 25°C to yield an iridium (III) monocarbonyl complex [IrCl$_3$(CO)(Ph$_3$P)$_2$] showing a ν_{CO} band at 2079 cm^{-1}. The corresponding iridium (I) monocarbonyl species IrCl(CO)(Ph$_3$P)$_2$ shows an ir band at 1970 cm^{-1} (12). Thus the ir band at 2100 cm^{-1} could be assigned to CO attached to an Ir(III). The small intensity of this ir band indicates that only a small fraction of the total iridium complexes within the zeolite cavities were concerned in the carbonylation at 25°C. The carbonylation of iridium-exchanged zeolite is favoured by the temperature as indicated by the appearance of two strong additional bands at 2086 and 2001 cm^{-1} when the sample was treated with CO at 443 K. These two bands can be attributed to a single iridium carbonyl compound (species I) on the basis that their relative intensities remained constant with the reaction temperature and the iridium loading.

In metal carbonyls, the number of infrared active stretching vibrations may be derived on the basis of the local symmetry of the carbonyl groups (13). Hence, for L$_x$M(CO)$_2$ compounds with C_{2v} symmetry, two ir bands are expected corresponding to the A_1 symmetric and B_1 antisymmetric stretching modes. Their relative intensities are given by $I_{A_1}/I_{B_1} = \cot^2(\Theta/2)$, where Θ is the bond angle. Similarly, two stretching vibrations of A_1 and E modes occur for the L$_x$M(CO)$_3$ compounds of C_{3v} local symmetry, with

relative intensities $I_{A_1}/I_E = \frac{1}{4}(3 \cot^2 (\Theta/2) - 1)$. To discriminate C_{2v} dicarbonyl and C_{3v} tricarbonyl compounds a general procedure consists of a partial substitution of ^{12}CO groups by ^{13}CO so as to lower the local symmetry. With $L_xM(^{12}CO)_2$, $L_xM(^{13}CO)_2$ (C_{2v} symmetry) and $L_x M(^{12}CO)(^{13}CO)$ (C_s) are obtained. For each structure, there are two stretching vibrations, the frequencies of which may be calculated from the experimental values of $L_xM(^{12}CO)_2$ assuming that the bond angle remains invariant upon substitution (13). Table 1 gives the ν_{CO} frequencies calculated if one has assumed $M(CO)_2$ species.

From this table, it appears that the number and the frequencies of the ir bands observed upon ^{12}CO–^{13}CO exchange is inconsistent with the $L_x M(CO)_2$ model.

On the other hand, ^{12}CO–^{13}CO exchange of $L_xM(^{12}CO)_3$ gives mono-, di-, and trisubstituted derivatives: $L_x M(^{12}CO)_2(^{13}CO)$, $L_xM(^{12}CO)(^{13}CO)_2$, and $L_xM(^{13}CO)_3$. In the mono- and disubstituted compounds, the local symmetry of the carbonyl is lowered from C_{3v} to C_s lifting the degeneracy of the E mode into

A' and A'' modes. If, upon substitution, the bond angle remains invariant, the A'' mode of the monosubstituted derivatives has the same energy as the E mode of the unsubstituted ones, and similarly the A'' mode of the disubstituted compounds has the same energy as the E mode of the trisubstituted ones.

The frequencies calculated from the experimental values of $L_xM(^{12}CO)_3$ are reported in Table 2.

These results prove unambiguously that a tricarbonyl iridium species is formed upon carbonylation of Ir (III) ions located in the zeolite. Moreover, volumetric studies have shown the consumption of 4 molecules of CO per Ir atom and the formation of about 1 CO_2 molecule.

Therefore, it is suggested that the CO_2 was formed upon reduction of Ir(III) into Ir(I) with a simultaneous formation of an iridium (I) tricarbonyl according to the following scheme:

$$Ir(III)(OH)_2 + 4\ CO \rightarrow$$
$$Ir(I)(CO)_3 + CO_2 + H_2O.$$
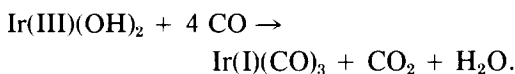
Thus the carbonyl complex is most probably an iridium tricarbonyl. Whether an

TABLE 1

Comparison of the Experimental CO Frequencies with Those Calculated for $L_xM(CO)_2$ Species

Compounds	$L_xM(^{12}CO)_2$	$L_xM(^{12}CO)(^{13}CO)$		$L_xM(^{13}CO)_2$	
Symmetry group	C_{2v}	C_s		C_{2v}	
CO stretching modes	A_1	A'		A_1	
	B_1	A'		B_1	
Calculated frequencies (cm^{-1})		2072^a	2068^b	2046^a	2036^b
		1971^a	1972^b	1952^a	1956^b
Experimental frequencies (cm^{-1})	2086	2075		2036	
	2001	1978		1956	
		2060			
		1966			

^{a} Force constant = 17.38 m dyne · Å^{-1} (0.174 N · m^{-1}) for ^{12}CO and ^{13}CO as calculated from frequencies of unsubstituted $L_xM(^{12}CO)_2$.

^{b} Force constant = 17.38 m dyne · Å^{-1} (0.174 N · m^{-1}) for ^{12}CO and 17.31 m dyne · Å^{-1} (0.173 N · m^{-1}) for ^{13}CO as calculated from totally ^{13}CO-exchanged compound.

Note. $\Theta = 105°5$ as calculated from I_{A_1}/I_{B_1}.

TABLE 2

Comparison of the Experimental CO Frequencies with Those Calculated for $L_x M(CO)_3$ Species

Compounds	$L_x M(^{12}CO)_3$	$L_x M(^{12}CO)_2(^{13}CO)$		$L_x M(^{12}CO)(^{13}CO)_2$		$L_x M(^{13}CO)_3$	
Symmetry group	C_{3v}	C_s		C_s		C_{3v}	
CO stretching modes	A_1	A'		A'		A_1'	
	E	A''		A''		E	
		A'		A'			
Calculated frequencies (cm^{-1})		2079^a	2075^b	2065^a	2060^b	2038^a	2036^b
		2001^a	2001^b	1957^a	1956^b	1957^a	1957^b
		1964^a	1966^b	1977^a	1979^b		
Experimental frequencies (cm^{-1})	2086	2075		2060		2036	
	2001	2001		1956		1956	
		(1966)		1978			

[a] Force constant: 16.64 m dyne · Å^{-1} (0.166 N · m^{-1}) for ^{12}CO and ^{13}CO as calculated from frequencies of $L_x M(^{12}CO)_3$.

[b] Force constant − 16.64 m dyne · Å^{-1} (0.166 N · m^{-1}) for ^{12}CO and 16.61 m dyne · Å^{-1} (0.166 N · m^{-1}) for ^{13}CO as calculated from frequencies of totally ^{13}CO exchanged compound.

Note. $\Theta = 87°2$ as calculated from I_{A_1}/I_E.

oxygen ion or the halide balances the positive charge on the iridium is still not clear. However, as both chemical analysis and XPS measurement provide evidence for the presence of the halide in a ratio 1 : 1 with respect to iridium, it is highly probable that the carbonyl complex is indeed the iridium tricarbonyl halide, generated by the concomitant reduction and carbonylation of the hydroxo iridium halide Ir(III)X(OH)$_2$.

In this study we have conclusively shown using volumetric measurements and ir spectroscopy combined with spin-labeling techniques that well-defined iridium tricarbonyl species entrapped within the zeolite supercages are formed. The ability of this carbonyl to catalyse methanol carbonylation was tested. Zeolite-entrapped Ir(I)(CO)$_3$ exhibited a high activity, selectivity and stability towards the vapor phase carbonylation of methanol to form methyl acetate at 443 K and atmospheric pressure and in the presence of the methyl iodide promoter. The spectroscopic data (*14*) suggested that the promoter added oxidatively to the iridium tricarbonyl as a rapid step. The carbonyl-

ation kinetics showed a zero order with respect to CO and methyl iodide and a first order with respect to methanol.

The activity, stability and selectivity of this active precursor illustrate the use of zeolite to stabilise well-defined transition metal complexes which can be used in a variety of catalytic processes. The zeolite appears not only as a unique solid matrix to host transition metal complexes but also as a particularly interesting reaction medium for them.

APPENDIX: METHOD OF CALCULATION

$M(CO)_2$

1. The two CO groups are equivalent: point group C_{2v}

$$\Gamma_{\nu_{CO}} = A_1 + B_1 \qquad \text{two ir bands.}$$

ν_{CO} fundamental frequencies:

$$\lambda(A_1) = (\mu O + \mu C)(1 + \cos \Theta)(f + f'),$$

$$\lambda(B_1) = (\mu O + \mu C)(1 - \cos \Theta)(f - f'),$$

where

$$\lambda = 4\pi^2 c^2 \nu^2, \qquad c = \text{speed of light},$$

$$\nu = \text{wavenumber}$$

$\mu O = 1/16, \quad \mu C = 1/12 \ (^{12}CO),$
$$\text{or } 1/13 \ (^{13}CO).$$

Θ: bond angle, f: force constant, f': interaction constant for cis-CO groups

Relative intensities:

$$\frac{I_{A_1}}{I_{B_1}} = \cot^2 \frac{\Theta}{2} \cdot$$

The Θ value was determined from the experimental intensities. From the experimental frequencies of the ^{12}CO species, it is possible to calculate f and f'.

2. The two CO are different: point group Cs.

$$\Gamma_{\nu CO} = 2A'$$

(this occurs for $M(^{12}CO)(^{13}CO)$.

ν_{CO} fundamental frequencies

$\lambda(A') = (\mu O + a)f + af' \cos \Theta + \Delta^{1/2}/2,$

$\lambda(A') = (\mu O + a)f + af' \cos \Theta - \Delta^{1/2}/2,$

where

$$a = \frac{1}{2}\left(\frac{1}{12} + \frac{1}{13}\right),$$

$$\Delta = \left(\frac{1}{12} - \frac{1}{13}\right)^2 f^2$$
$$+ 4\left(\frac{1}{16} + \frac{1}{12}\right)\left(\frac{1}{16} + \frac{1}{13}\right)f'^2$$
$$+ 4aff'\left(\frac{1}{16} + a\right)\cos \Theta + a^2f^2 \cos^2\Theta.$$

$M(CO)_3$

1. The three CO groups are equivalent: point group C_{3v}

$$\Gamma_{\nu CO} = A_1 + E \qquad \text{two ir bands.}$$

ν_{CO} fundamental frequencies

$\lambda(A_1) = |\mu O + \mu C(1 + 2 \cos \Theta)| \ (f + 2f'),$

$\gamma(E) = |\mu O + \mu C(1 - \cos \Theta)| \ (f - f').$

Relative intensities

$$\frac{I_{A_1}}{I_E} = \frac{1}{4}[3 \cot^2 (\Theta/2) - 1];$$

f, f', and Θ are calculated from the experimental data (intensities and frequencies of the ^{12}CO species).

2. One CO is different from the two others: point group Cs

$$\Gamma_{\nu CO} = 2A' + A''$$

ν_{CO} fundamental frequencies. A' modes:

$$\gamma(A') = (B + \Delta^{1/2})/2,$$
$$\gamma(A') = (B - \Delta^{1/2})/2,$$

with

$B = [2 \mu O + \mu C_2 + \mu C_1(1 + \cos \Theta)]f$
$\quad + [\mu O + \mu C_1(1 + \cos \Theta) + 4a \cos \Theta]f'$

$\Delta = [\mu C_2 f - \mu C_1(1 + \cos \Theta)f$
$\quad - (\mu O + \mu C_1(1 + \cos \Theta))f']^2$
$\quad + 8 [af \cos \Theta + (\mu O + \mu C_2$
$\quad\quad + a \cos \Theta)f'][af \cos \Theta$
$\quad\quad + (\mu O + \mu C_1(1 + \cos \Theta))f'].$

A'' mode:

$$\lambda(A'') = [\mu O + \mu C_1(1 - \cos \Theta)](f - f'),$$

where

μC_1: relative to the two equivalent CO,

μC_2: relative to the CO different,

a, Θ, f, f': as defined previously.

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