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VARIABLE TEMPERATURE ^{13}C MAS NMR OF $KFe_2Mn(CO)_{12}$ IN THE SOLID STATE AND AS A *CATALYST PRECURSOR* ON A CARBON SUPPORT

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Nuclear magnetic resonance for catalyst characterization, $KF_2Mn(CO)_{12}$ as catalyst precursor

Variable temperature ^{13}C MAS NMR spectra are reported for ^{13}CO-enriched $KFe_2Mn(CO)_{12}$ as a solid and also as dispersed clusters on a carbon support. The spectrum of $KFe_2Mn(CO)_{12}$ at 300 K agrees with the proposed structure for this cluster and shows that the cluster is static. Two bridging carbonyl resonances are clearly resolved and, by comparison with ^{13}C MAS NMR spectra of $Mn_2(CO)_{10}$ and $Fe_2(CO)_9$, all terminal resonances for the cluster can be assigned. When the cluster is supported on carbon, two broad resonances are observed at room temperature which are assignable to $KFe_2Mn(CO)_{12}$ and a decomposition product, $Mn_2(CO)_{10}$. The carbonyl ligands in both supported clusters are completely averaged, and $KFe_2Mn(CO)_{12}$ on the carbon surface demonstrates fluxional behavior similar to that observed for the cluster in solution. For this fluxional process, activation energies of 0.6 kcal/mol and 0.5 kcal/mol are estimated for carbon-supported $KFe_2Mn(CO)_{12}$ and $Mn_2(CO)_{10}$, respectively.

1. Introduction

Mixed-metal carbonyl clusters offer a promising route to produce bimetallic or promoted heterogeneous catalysts. Stoichiometric Fe-Mn carbonyl clusters are of special interest because of their high selectivity to light olefins in the CO hydrogenation reaction [1]. This capability has prompted a thorough study of carbon-supported Fe-Mn clusters using DRIFTS, Mössbauer spectroscopy, TEM/EDS, and calorimetry [2–4]. Information about the state of these metal carbonyl cluster precursors during the preparative process would be helpful in both improving catalyst preparation and understanding the chemical state of the metal in these catalysts. The initial synthesis step for such a catalyst involves the adsorption of the cluster onto the support. We have characterized the nature of

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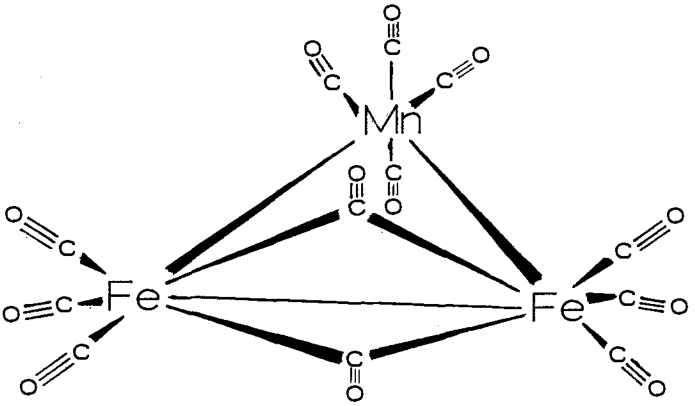

Fig. 1. Proposed structure of $KFe_2Mn(CO)_{12}$.

carbon-supported $KFe_2Mn(CO)_{12}$ using variable temperature ^{13}C MAS-NMR and have compared it to the neat, solid cluster. The high surface area carbon was chosen because it can be cleaned in H_2 to give oxygen- and sulfur-free surfaces.

The crystal structure of the $[Fe_2Mn(CO)_{12}]^-$ anion has not been reported. The cluster has been suggested to be isostructural with $Fe_3(CO)_{12}$ on the basis of solution IR spectroscopy [5] and Mössbauer spectroscopy [6]. This structure is shown in fig. 1. Anders and Graham [5] pointed out that the IR spectrum of $[Et_4N]^+[Fe_2Mn(CO)_{12}]^-$ in THF is very similar to that of $[Et_3NH]^+[HFe_3(CO)_{11}]^-$. The crystal structure of $[HFe_3(CO)_{11}]^-$ is similar to that of $Fe_3(CO)_{12}$ [7,8], except that one of the two bridging CO ligands is replaced by a bridging hydride [9].

The trinuclear carbonyl cluster, $Fe_3(CO)_{12}$, is partially fluxional in the solid state at ambient temperatures, and a ^{13}C MAS NMR spectrum consistent with a static structure has been reported only at a temperature near −93°C at 22.6 MHz [10]. At ambient temperatures, a six-line pattern is observed which has been deduced as being the result of a rotation of the triangle of iron atoms within the distorted icosahedron or carbonyl ligands to average pairs of carbonyl groups [10,11].

In solution, $[Fe_2Mn(CO)_{12}]^-$ behaves in a manner similar to $Fe_3(CO)_{12}$ [12,13] in that only a single resonance is observed in ^{13}C NMR spectra at temperatures down to −85°C [12]. Thus carbonyl ligands in both clusters are completely averaged in solution. We now report variable temperature ^{13}C MAS NMR results which demonstrate that $KFe_2Mn(CO)_{12}$ is static in the solid state at ambient temperatures yet the cluster is completely fluxional when supported on carbon.

2. Experimental

$KFe_2Mn(CO)_{12}$ was prepared by refluxing $Fe(CO)_5$ (Aldrich) and $KMn(CO)_5$ in THF [5]. The $KMn(CO)_5$ was produced by stirring a THF solution of

$Mn_2(CO)_{10}$ (Pressure Chemical) with NaK alloy. All reactions and manipulations were performed under nitrogen. The resulting dark-blue solution was filtered through a glass frit and the THF was removed by vacuum distillation to yield microcrystalline $KFe_2Mn(CO)_{12}$ powder. The blue-back compound was characterized by IR (THF) and solution ^{13}C NMR (acetone-d6), and the spectra were in agreement with those in the literature [5,12]. The $KFe_2Mn(CO)_{12}$ was enriched with ^{13}CO (Monsanto Research Corp., 99%) by stirring a THF solution of the cluster with 10 mg of 5% Pd/C (Engelhard). From the amount of ^{13}CO added to the flask, the enrichment level could not have exceeded 10%. The ^{13}CO enrichment was great enough to distort the IR spectrum of the complex; however, the solution ^{13}C spectrum remained unchanged, indicating that no decomposition had occurred to yield other carbonyls. The ^{13}CO-enriched $KFe_2Mn(CO)_{12}$ was dissolved in dry, degassed THF and added dropwise with stirring to the carbon support (CSX-203) under an argon atmosphere. The solvent was removed by evacuation overnight at room temperature.

A sample of $Mn_2(CO)_{10}$ (Pressure Chemical) was packed into a 9.5 mm Delrin rotor (Chemagnetics), and the ^{13}C MAS NMR spectrum was obtained at 25.0 MHz on a Chemagnetics M-100S using 90° pulses and a 5-s pulse delay. A Chemagnetics CMC-300A was used to obtain the 74.0 MHz ^{13}C MAS NMR spectrum of $Fe_2(CO)_9$ (Aldrich). 30° pulses were used with a 4-s pulse delay. This sample was contained in a 7.5 mm zirconia rotor (Chemagnetics) which had an end cap and fluted spinner end made from Kel-F. A 25.0 MHz ^{13}C MAS NMR spectrum was obtained for the ^{13}CO-enriched $KFe_2Mn(CO)_{12}$ at ambient temperature using a 9.5 mm Kel-F rotor (Chemagnetics). The 74.9 MHz NMR spectrometer was equipped by Chemagnetics for variable temperature operation, and ^{13}C MAS NMR spectra were obtained for $KFe_2Mn(CO)_{12}$ (packed in the 7.5 mm zirconia rotor) in the range from $-10\,^{\circ}C$ to $22\,^{\circ}C$ using a CO_2/ethanol slush bath to cool the dry house air used for the drive and bearing gases. Temperatures up to 41°C (the maximum allowable temperature) were attained using the temperature controller heater. At both 74.0 and 25.0 MHz, 90° pulses and a 10-s pulse delay were used. Changing the pulse delay time did not alter the relative intensities of the signals indicating that all the resonances possessed similar T_1 values. As determined by both solution ^{13}C and MAS NMR, substantial amounts of THF were present in the $KFe_2Mn(CO)_{12}$ powder. At first, this was thought to be due solely to residual THF which was not removed under vacuum; however, the THF molecules must have been in close contact with individual carbonyl clusters because CP-MAS spectra could be obtained. This suggests that the $KFe_2Mn(CO)_{12}$ clusters crystallized along with at least one THF molecule as a nearest neighbor.

The carbon-supported, ^{13}CO-enriched $KFe_2Mn(CO)_{12}$ was packed in a 9.5 mm Kel-F rotor (Chemagnetics) in an argon atmosphere drybox. Variable temperature ^{13}C MAS NMR spectra were obtained for this sample on a GN-300WB spectrometer (General Electric) equipped with a Chemagnetics CP-MAS probe, solids accessories and a temperature controller. Dry house nitrogen was used for the drive and bearing gases which were cooled with liquid nitrogen to achieve subambient temperatures. The lower temperature limit for the MAS probe was 123 K. A spectrum of the carbon-supported cluster could not be obtained by ^{13}C CP-MAS NMR, and THF was not detected in the sample using either ^{13}C MAS NMR or ^{13}C CP-MAS NMR.

3. Results and discussion

The 74.9 MHz ^{13}C MAS NMR spectrum of solid $KFe_2Mn(CO)_{12}$ at 22°C is shown in fig. 2(a). Besides the carbonyl resonances and spinning sidebands, there are impurity signals due to stopcock grease at 1.5 ppm and THF at 68.7 and 26.4

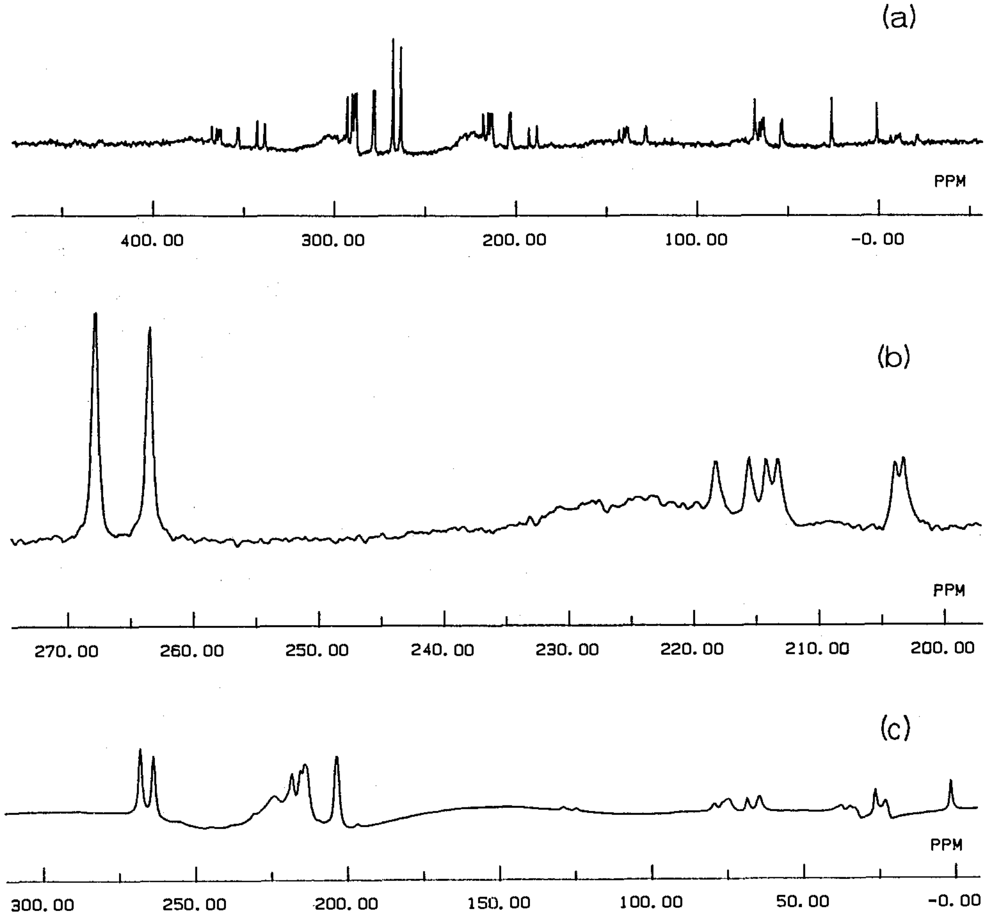

Fig. 2. (a) 74.9 MHz ^{13}C MAS NMR spectrum of $KFe_2Mn(CO)_{12}$ at 22°C. (b) an expanded portion of spectrum 2 (a) showing only the central carbonyl resonances. (c) 25.0 MHz ^{13}C MAS NMR spectrum of $KFe_2Mn(CO)_{12}$ at 22°C.

ppm. The static nature of the carbonyl ligands is immediately apparent as a result of the very intense array of spinning sidebands for the carbonyl ligands. The spinning rate was about 5500 Hz and varying the temperature of the sample between −10 °C and 41 °C did not alter the spectrum. The spectrum in fig. 2(b) is an enlarged portion of fig. 2(a) showing only the carbonyl region containing the central resonances of the spinning sideband pattern.

The broad peak at about 223 ppm is due to "wet" $KFe_2Mn(CO)_{12}$ which formed via centrifugation of the sample in the spinning rotor. Indeed, when the rotor was opened for inspection, two phases were present; a dry layer compacted along the walls of the rotor and a very viscous, wet layer towards the rotor interior. The chemical shift of the broad peak agrees with the solution value of 223.3 ppm [12], except that the peak is broadened by the viscosity of the "wet" layer.

The two resonances at 267.7 and 263.4 ppm are readily assignable to bridging carbonyl ligands for two reasons. First of all, the resonances occur well downfield in the bridging region. Secondly, an inspection of the intense array of spinning sidebands [14,15] indicates that the chemical shift anisotropy (CSA) of these two signals is less than 250 ppm, while the other carbonyl resonances possess a CSA of about 400 ppm. The CSA values of 250 and 400 ppm are expected for bridging and terminal carbonyl ligands, respectively [16]. It is this difference in CSA between the bridging and terminal carbonyls which causes the distortion of the relative intensities of these signals, and this effect has been discussed previously by Harris [17]. The intensity distortions are reduced to some extent in a spectrum obtained at 25.0 MHz, shown in fig. 2(c), as the sample spinning rate of about 3300 Hz is faster relative to the CSA. The possibility that the terminal carbonyl carbons possess longer T_1 values was ruled out because spectra obtained with longer pulse delays yielded identical relative intensities.

Intensity distortions of ^{13}C MAS NMR signals due to differences in CSA are dramatically demonstrated by the 74.9 MHz ^{13}C MAS NMR spectrum of $Fe_2(CO)_9$ shown in fig. 3. The central resonances are at 236.4 and 204.2 ppm, and the spinning sidebands are marked with an asterisk. The left sideband is due to the signal at 204.2 ppm and the right sideband is due to the resonance at 236.4 ppm. The spinning rate was 4500 Hz. The bridging signal at 236.4 ppm is much

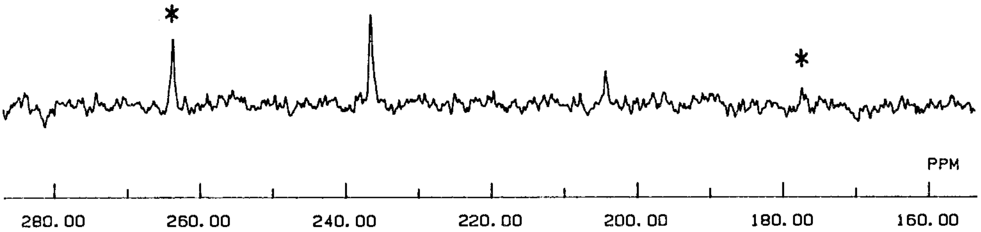

Fig. 3. 74.9 MHz ^{13}C MAS NMR spectrum of $Fe_2(CO)_9$ at 22 ° C. Spinning sidebands are marked with an asterisk.

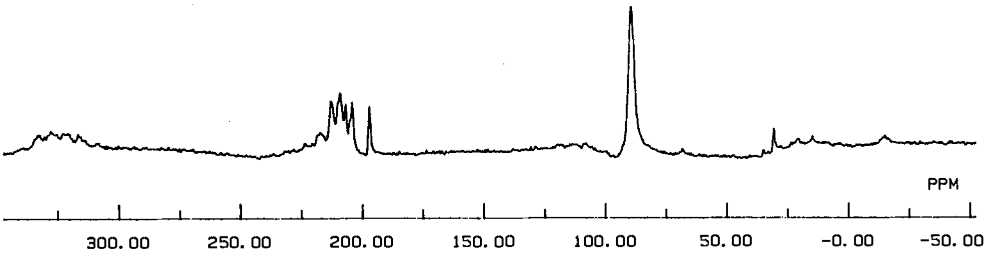

Fig. 4. 25.0 MHz ^{13}C MAS NMR spectrum of $Mn_2(CO)_{10}$ at 22° C.

more intense than the terminal signal at 204.2 ppm; however, a previously reported spectrum obtained at 15.0 MHz [18] yielded the correct integrated intensities of 3 : 6 for the bridging and terminal carbonyl resonances, respectively.

The assignments of the six resolved terminal carbonyl resonances at 218.0, 215.4, 214.0, 213.1, 203.8 and 203.2 ppm in fig. 2(b) are not so straightforward. The group of four peaks at 218.0, 215.4, 214.0, and 213.1 ppm resembles a similar group of four peaks (213.0, 209.1, 206.8, and 204.4 ppm) detected in the ^{13}C MAS NMR spectrum of $Mn_2(CO)_{10}$ shown in fig. 4. The fifth resonance of the cluster is at 196.8 ppm and the very intense peak at 89.3 ppm is due to the Delrin rotor. $Mn_2(CO)_{10}$ has a staggered, all-terminal structure [19] with five crystallographically distinct carbonyl groups which account for the five resonances. Thus $Mn_2(CO)_{10}$ can be considered to be a model compound for the $Mn(CO)_4$ fragment in the $KFe_2Mn(CO)_{12}$ cluster, while the two overlapping signals at 203.8 and 203.2 ppm are attributable to the terminal CO ligands in the two $Fe(CO)_3$ fragments (fig. 1). These values agree well with the chemical shift of the terminal CO ligands in $Fe_2(CO)_9$ (204.2 ppm). With these assignments the calculated average chemical shift is 218 ppm and is close to the reported solution value of 223.3 ppm [12].

Variable temperature ^{13}C MAS NMR spectra for carbon-supported $KFe_2Mn(CO)_{12}$ are shown in fig. 5, and the spectral parameters are given in the figure caption. The only features present in the 289 K spectrum are two broad peaks at about 214 and 205 ppm. There are no spinning sidebands. These features indicate that the signals are due to motionally averaged species since the anisotropy of the carbonyl resonances is dramatically reduced. The carbonyl cluster(s) responsible for the broad resonances are not merely species solvated by the residual THF in pores of the carbon support since no THF was detected in the sample by either MAS NMR or CP-MAS NMR. Complementary DRIFTS studies also did not detect any residual THF [2]. We did not detect any static carbonyl clusters which were rigidly immobilized on the surface; however, we cannot rule out the possibility of a small number of such species which would be difficult to detect due to their increased T_1 values.

As the temperature is lowered, both signals begin to broaden as the rate of the averaging slows; thus the rate of the averaging is in the fast-exchange regime [20].

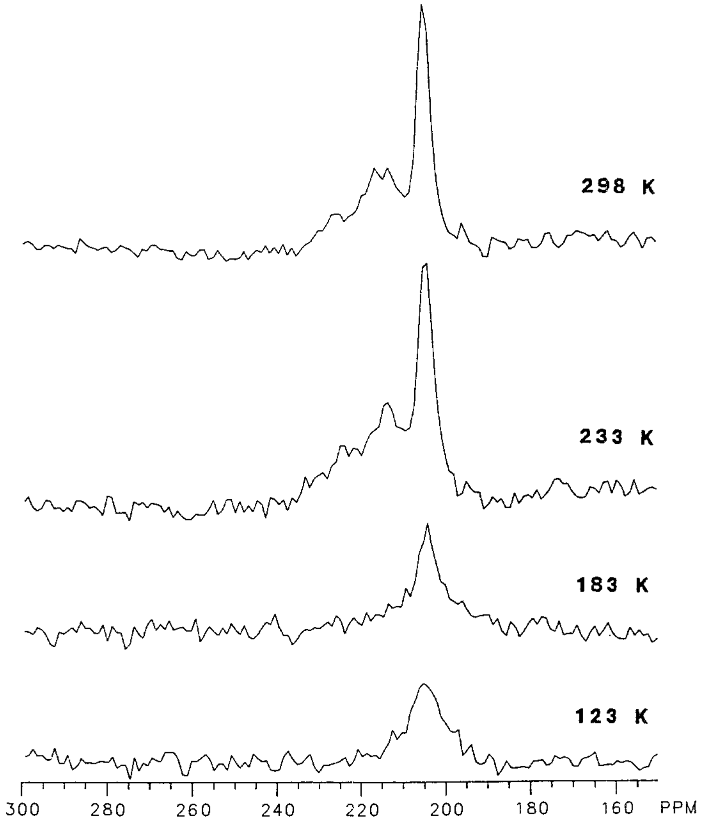

Fig. 5. Variable temperature ^{13}C MAS NMR spectra of carbon-supported ^{13}CO enriched $KFe_2Mn(CO)_{12}$.
Spectral parameters: 298 K 45° pulse width, 10 s pulse delay
233 K 90° pulse width, 10 s pulse delay
183 K 45° pulse width, 2 s pulse delay
123 K 45° pulse width, 2 s pulse delay.

At 183 K and 123 K, the peak near 214 ppm has essentially vanished, whereas the peak at about 205 ppm continues to broaden. It would be expected that as the rate of motional averaging decreased, the T_1 of a species would increase; however, the use of shorter pulse widths and/or longer pulse delays did not change the appearance of the 183 K or 123 K spectra although these spectra had poorer signal to noise ratios. This suggests that signal broadening is responsible for the disappearance of the signal at about 214 ppm. Thus, the slow exchange regime [20] is not reached at the temperatures accessible in our spectrometer (lower limit 123 K), and lower temperatures are necessary in order to detect static spectra of the two surface carbonyl species. The linewidths for the signals at various temperatures are given in table 2.

Diffuse Reflectance FTIR spectroscopy (DRIFTS) studies on carbon-supported $KFe_2Mn(CO)_{12}$ have shown that the cluster partially decomposes during

Table 1
Ambient temperature ^{13}C MAS NMR data for carbonyl clusters

Carbonyl cluster	^{13}C MAS NMR resonances (ppm)	Assignment
$KFe_2Mn(CO)_{12}$	267.7, 263.4	bridging CO
	218.0, 215.4, 214.0, 213.1	$Mn(CO)_4$ group
	203.8, 203.2	$Fe(CO)_3$ groups
$Fe_2(CO)_9$	236.4	bridging CO
	204.2	terminal CO
$Mn_2(CO)_{10}$	213.0, 209.1, 206.8, 204.4, 196.8	terminal CO

impregnation to give $Mn_2(CO)_{10}$ [2], and Mössbauer studies of this catalyst showed only the initial cluster and superparamagnetic, zero-valent iron particle [3]. This then allows the assignment of the peaks at 214 and 205 ppm to carbon-supported $KFe_2Mn(CO)_{12}$ and $Mn_2(CO)_{10}$, respectively, and these values are close to the average values of 218 ppm and 206 ppm calculated from the solid-state spectra.

In solid $Fe_3(CO)_{12}$ at ambient temperatures, rotation of the iron triangle within the distorted icosahedron of carbonyl ligands averages pairs of carbonyl ligands to yield a six-line spectrum. Clearly, this process does not occur in ambient temperature spectra of $KFe_2Mn(CO)_{12}$. Rotation of the metal triangle might be unique to the trinuclear cluster, $Fe_3(CO)_{12}$, since this cluster possesses a disorder involving the metal triangle, whereas $KFe_2Mn(CO)_{12}$ may not [21]. On a clear carbon surface, the $KFe_2Mn(CO)_{12}$ cluster behaves as it does in solution, i.e., all twelve of the CO ligands are averaged to yield a single resonance.

It is possible to calculate activation energies for these motional processes from the variable temperature MAS NMR spectra [20,22]. Since the MAS NMR linewidth, Δ, is a function of temperature, a plot of ln Δ vs $1/T$ yields an activation energy. Using the data in table 2, activation energies of 0.6 kcal/mol for the motional process involving carbon-supported $KFe_2Mn(CO)_{12}$ and 0.5 kcal/mol for carbon-supported $Mn_2(CO)_{10}$ were calculated, but it should be emphasized that these values are only rough estimates. The E_a value estimated for carbon-supported $KFe_2Mn(CO)_{12}$ is below the upper limit value of 5 kcal/mol

Table 2
Variable temperature ^{13}C MAS NMR linewidths for carbon-supported $KFe_2Mn(CO)_{12}$ and $Mn_2(CO)_{10}$

Temperature	$KFe_2Mn(CO)_{12}$ resonance linewidth (Hz)	$Mn_2(CO)_{10}$ resonance linewidth (Hz)
298 K	1400	263
233 K	1800	286
183 K	–	432
123 K	–	902

estimated for $Fe_3(CO)_{12}$ in solution [8,13], and it is also considerably lower than the value of 10 kcal/mol estimated for solid $Fe_3(CO)_{12}$ [10]. However, it is close to the value of about 1 kcal/mol estimated for solid $Fe(CO)_5$ [23]. The existence of such a low activation barrier for the rearrangement of carbonyl ligands in carbon-supported $KFe_2Mn(CO)_{12}$ may be due to the absence of both solvent interactions (as expected for a complex in solution) and crystal packing forces which would exist in the solid. Various mechanisms have been proposed for fluxionality in the $[Fe_2Mn(CO)_{12}]^-$ cluster in solution [12] and similar processes may be occurring in the carbon-supported cluster. Lower temperature studies are necessary to better define this motional process.

In conclusion, $KFe_2Mn(CO)_{12}$ is static at ambient temperatures in the solid state, but when supported on carbon, the intact cluster on the surface is completely fluxional in a manner similar to that in solution. These results further support the analogy we have drawn between the chemistry of metal carbonyl clusters on clean, oxygen-free carbon surfaces and that in solution [24].

Acknowledgments

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