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Communications

Nature of γ-Alumina-Supported Molybdenum Subcarbonyls As Determined by Cross Polarization–Magic Angle Spinning ^{13}C NMR Spectroscopy

Sir:

Alumina-supported molybdenum subcarbonyls have been detected by cross polarization–magic angle spinning (CP MAS) ^{13}C NMR spectroscopy. The results obtained give additional insight into the structure and dynamics of an important class of catalyst precursors and demonstrate the viability of CP MAS ^{13}C NMR for probing the surface chemistry of metal carbonyls.

Reports from other laboratories on the utilization of ^{13}C NMR for the characterization of supported metal carbonyls have been reported only in symposia proceedings.[1-3] Broad-line NMR work on group 6 carbonyls in Na–Y zeolite indicates that molecular reorientation within the zeolite is more rapid than for the bulk solid.[1] Recently it has been shown that CP MAS ^{13}C can be used to detect intrazeolitic rhodium carbonyls.[3]

The nature of λ-alumina-supported metal carbonyls has been well studied by using a variety of techniques[4-13] including stoichiometry of decomposition,[4-7] infrared spectroscopy,[9,12,13] and catalysis.[4,8,10] This body of knowledge makes molybdenum subcarbonyls an attractive model system for an NMR study of supported metal carbonyls.

Basically, two problems must be overcome when MAS NMR is applied to these systems—signal sensitivity and extreme air sensitivity. Even with relatively large surface areas[14] and monolayer coverage, the number of ^{13}C spins in the sample is very small. Also, T_1's for solid group 6 metal carbonyls are extremely long.[15] We measure T_1 for $Mo(CO)_6$ to be 480 s in the solid by the progressive saturation technique.[16] Fortunately, metal carbonyls are easily enriched in ^{13}C by exchange with ^{13}CO. Furthermore, homonuclear dipolar interactions (^{13}C–^{13}C) are small compared to the chemical shift anisotropy in metal carbonyls since adjacent carbons are ca. 3 Å apart. We find that enrichments in ^{13}C up to 45% gives no additional broadening in the MAS ^{13}C NMR spectrum of binary metal carbonyls. The sensitivity problem introduced by the long T_1 for metal carbonyls is overcome by the cross polarization technique.[17] This is possible for metal subcarbonyls supported on hydroxylated or partially dehydroxylated aluminas where there is a high concentration of protons on the surface. Quite fortuitously, unsubstituted group 6 carbonyls physically supported on alumina can also be seen by MAS ^{13}C NMR. Cross polarization is not a viable means for overcoming long T_1's because in the absence of a direct bond to the surface the ^{1}H–^{13}C dipolar interaction is very weak. However, T_1 is shortened dramatically for physisorbed metal carbonyls, obviating the need for cross polarization. We measure T_1 for $Mo(CO)_6$(phys) to be 120 ms by the inversion recovery technique.[16]

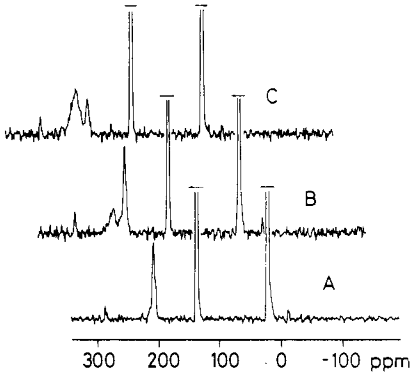

Figure 1. CP MAS ^{13}C NMR spectra of $Mo(CO)_6$ on γ-alumina. Spectrum A was obtained after activation at 30 °C for 1 h. Spectrum B was obtained on a separate sample heated to 100 °C for 1 h. Spectrum C was obtained on a separate sample heated to 100 °C for 3 h. In each spectrum, two very large peaks appear; these are due to hexamethylbenzene, which was added to the samples for magic angle and chemical shift calibration.

Our procedure for handling these materials completely avoids exposure to air. The metal carbonyl is decomposed on

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(18) The alumina pretreatment before addition of pentane solutions of $Mo(CO)_6$ was as follows: for partially dehydroxylated alumina (PDA) the alumina was heated to 450 °C for 1 h in flowing helium.[9] For dehydroxylated alumina (DA) the alumina was heated to 950 °C for 1 h in flowing helium.[9]

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γ-alumina[18] in an ultrapure helium-flow reactor.[9] An advantage of this technique is that CO evolution can be measured directly. The reactor is sealed under helium and taken into a Vacuum Atmospheres drybox where the supported carbonyl is transferred under nitrogen to a Kel-F bullet type sleeve rotor that is sealed with Plasticine.[19] Samples prepared in this manner show no deterioration by NMR over a period of several days.[20] A typical set of CP MAS ^{13}C NMR spectra for molybdenum hexacarbonyl supported on partially dehydroxylated alumina under various conditions are shown in Figure 1.[21,22]

Spectrum A shows the result of activation for 1 h at 30 °C. Samples activated at this temperature are bright yellow. The CP MAS ^{13}C NMR spectrum shows one resonance in the carbonyl region at 203 ppm.[23,24] This is 2 ppm downfield from $\mathrm{Mo(CO)_6}$(phys), which is also present in the sample (vide infra). This we assign to $\mathrm{Mo(CO)_5}$(ads), which is proposed by Brenner and Burwell as an intermediate in the formation of $\mathrm{Mo(CO)_3}$(ads).[5] This species should have an octahedral coordination geometry with a surface hydroxyl group occupying the sixth coordination site at molybdenum. If this is the case, then we expect to see the axial and equatorial carbonyl ligands in a ratio of 1:4. Our failure to see a unique axial resonance is due either to an accidental degeneracy of signals or to a dynamic process involving axial–equatorial CO exchange. Preliminary low-temperature NMR results show slight broadening of this resonance at −40 °C, which may be consistent with a dynamic process.

Activation of $\mathrm{Mo(CO)_6}$ on alumina at 100 °C for 1 and 3 h leads to spectra B and C, respectively. Both of these samples are yellow-brown. A new broad resonance can be seen to grow at 223 ppm. This we assign to $\mathrm{Mo(CO)_3}$(ads), again after Brenner and Burwell.[5] The chemical shift of this species corresponds well to literature values for (arene)$\mathrm{Mo(CO)_3}$.[24] One resonance is expected if the group has C_{3v} symmetry, two are expected if the group has only mirror-plane symmetry, and three resonances are expected for a tricarbonyl group with no symmetry. On partially dehydroxylated alumina, it is difficult to imagine $\mathrm{Mo(CO)_3}$(ads) at sites with threefold rotational symmetry. Thus more than one resonance should result for this species. Our results suggest a fluxional tricarbonyl group. This is well precedented for metal tricarbonyl fragments.[25]

The tricarbonyl group, $\mathrm{Mo(CO)_3}$(ads), has in some cases been postulated to be dimeric; i.e., $\mathrm{Mo_2(CO)_6}$(ads).[12,13] Comparison of model compounds $\mathrm{Cp_2Mo_2(CO)_6}$[23] and (arene)$\mathrm{Mo(CO)_3}$ shows chemical shifts of 228.6 and ~222 ppm, respectively. Furthermore, the latter compound shows coalescence of carbonyl resonances at temperatures below 0 °C while the former shows coalescence close to 100 °C. Although this is not proof, certainly the results for $\mathrm{Mo(CO)_3}$(ads) more closely resemble the mononuclear model complexes.

When the NMR spectra of samples A–C are recorded by using a single carbon 90° pulse with or without proton decoupling (i.e., no cross polarization), residual physisorbed $\mathrm{Mo(CO)_6}$ is observed at 201 ppm in each sample. The presence of residual $\mathrm{Mo(CO)_6}$ is probably a function of our reaction conditions. The NMR samples contain nearly monlayer coverage by molybdenum subcarbonyl.[21] For these high coverages the reaction times used were not sufficient to completely convert to the tricarbonyl. Also, a relatively low helium sweep rate (30 mL/min) was used in these reactions. This is consistent with the equilibrium postulated by Brenner and Burwell (eq 1).[5] If the reaction is stopped prematurely,

$$\mathrm{Mo(CO)_6(phys)} \underset{+\mathrm{CO}}{\overset{-\mathrm{CO}}{\rightleftarrows}} \mathrm{Mo(CO)_5(ads)} \underset{+\mathrm{CO}}{\overset{-\mathrm{CO}}{\rightleftarrows}} \mathrm{Mo(CO)_3(ads)} \quad (1)$$

then $\mathrm{Mo(CO)_6}$(phys) can be generated in the sealed rotor. Furthermore, we can confirm that on small samples and low weight percent loadings (250 mg of alumina, <2 wt % $\mathrm{Mo(CO)_6}$) nearly 3 equiv of CO/equiv of Mo is evolved at 100 °C after 2 h.[26]

The NMR results for $\mathrm{Mo(CO)_6}$ decomposed on hydroxylated alumina are substantially the same as reported for partially dehydroxylated alumina. However, for $\mathrm{Mo(CO)_6}$ on dehydroxylated alumina, we find that $\mathrm{Mo(CO)_3}$(ads) and $\mathrm{Mo(CO)_5}$(ads) cannot be detected by MAS NMR. This is due to the obvious lack of nearby protons for cross polarization experiments and an apparent increase in T_1 caused by anchoring the subcarbonyl to the surface. On dehydroxylated alumina we can easily obtain a spectrum for $\mathrm{Mo(CO)_6}$(phys) using the single-pulse sequence described above. The chemical shift is the same as for $\mathrm{Mo(CO)_6}$(phys) on partially dehydroxylated alumina, i.e. 201 ppm.

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Registry No. $\mathrm{Mo(CO)_6}$, 13939-06-5; alumina, 1344-28-1.

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(19) Plasticine is modeling material manufactured by Colorforms, Ramsey, NJ 07446.

(20) The samples did not bleach over a period of 4 days when prepared in this fashion, and the spectrum obtained on an aged sample gave the same relative intensity for the observed signals. Samples exposed directly to air bleached within a few minutes.

(21) All NMR samples were prepared to contain a monolayer of molybdenum carbonyl, ca. 6 wt. % $\mathrm{Mo(CO)_6}$,[4] by impregnation from pentane solution. Excess $\mathrm{Mo(CO)_6}$ was removed by sublimation in flowing helium at 25 °C.

(22) NMR spectra were recorded on a JEOL FX60Q-S spectrometer. The solids accessory was manufactured by Chemagnetics.

(23) This correlates well with monosubstituted molybdenum carbonyl derivatives $\mathrm{LMo(CO)_5}$.[24]

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(26) The average value for five runs in which the loading was between 0.8 and 1.8 wt % $\mathrm{Mo(CO)_6}$ was 2.95 ± 0.06 equiv of CO/equiv of Mo.

Iridium–Nitrogen Bond Cleavage in the Photolysis of Carbonylnitrosylbis(triphenylphosphine)iridium

Sir:

The identification of metal isocyanate (M–NCO) species on metal surfaces has led to the proposal of their involvement as intermediates in the metal-catalyzed pollution removal reaction of nitric oxide and carbon monoxide as ammonia and carbon dioxide.[1] A homogeneous model for isocyanate formation from the interaction of CO and NO at a metal site is reaction 1.[2] This reaction has been proposed to proceed

$$[\mathrm{Pt(PEt_3)_2(NO)(NO_2)}] + 2\mathrm{CO} \rightarrow \underset{\mathbf{2}}{[\mathrm{Pt(PEt_3)_2(NCO)(NO_2)}]} + \mathrm{CO_2} \quad (1)$$

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