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Contribution from the Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304, and Chemistry Department, Rensselaer Polytechnic Institute, Troy, New York 12180

^{129}Xe NMR Spectroscopy of Molybdenum Carbonyls in Na–Y Zeolite

Cathy L. Tway[†] and Tom M. Apple*[,‡]

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^{129}Xe NMR spectroscopy has been used to characterize the reactions of molybdenum hexacarbonyl in Na–Y zeolite. Upon adsorption of $Mo(CO)_6$ and subsequent dispersion at 323 K, bands of color corresponding to a concentration gradient within the NMR tube are observed. $Mo(CO)_6$ adsorbs and saturates the upper regions of the Na–Y sample, while not saturating lower portions of the sample. From gravimetric measurements, the $Mo(CO)_6$ concentration in the saturated region is approximately 2 molecules/supercage. Evacuation of the sample at 373 K produces a subcarbonyl species which is an adsorption site for xenon. Further heat treatments produce Mo species which are able to migrate out of the supercages. Oxidation of these Mo clusters is observed at 623 K. Reduction of these oxidized species is possible only at elevated temperatures, and although a color change is observed, there is no change in the xenon spectra. This indicates that the chemical reaction is occurring in regions of the zeolite that are inaccessible to xenon. On the basis of the NMR spectra and adsorption data, we propose that Mo is able to migrate into the sodalite cages and/or the hexagonal prisms of the Na–Y structure.

Introduction

^{129}Xe NMR spectroscopy was introduced by Fraissard in the early 1980s as a means to characterize microporous materials.[1-5] The ^{129}Xe nucleus is spin $^1/_2$ and is present in 26% natural abundance. Any perturbation of the spherical electron cloud is seen by the nucleus and gives rise to a very large chemical shift. Xenon is inert and thus provides a noninvasive probe of zeolite chemistry. Due to its size, xenon may access the supercages in the faujasite structure but not the sodalite cages and hexagonal prisms. Therefore, ^{129}Xe NMR spectroscopy can be used to study the location of adsorbate species,[6] crystallinity,[7] and metal migration.[8]

Recently, there has been renewed interest in the reactions of metal carbonyls with inorganic supports.[9-13] Zeolites offer an advantage over many of the other supports in that the regular arrangement of pores helps to establish the binding sites for the molybdenum carbonyl species. These systems offer the possibility of encapsulating the metal carbonyls and introducing homogeneous catalytic properties to a heterogenous catalyst. In addition, adding metals to catalyst supports in this manner may produce higher metal dispersion or very small particles exhibiting "quantum size effects".

The reactions of $Mo(CO)_6$ with a variety of supports has been reviewed recently.[12] In Na–X and Na–Y zeolites, $Mo(CO)_6$ forms a stable subcarbonyl complex after heating at 373 K. This complex has been studied by a number of techniques.[14-18] The stoichiometry of this species has been determined to be $Mo(CO)_3$ by temperature-programmed decomposition techniques.[15-17] The subcarbonyl is believed to be stabilized by interactions between molybdenum and the oxygen atoms in the zeolite lattice.[17] Through size-selective chemical reactions with the similar $Cr(CO)_3$ subcarbonyl species, Ozkar et al.[19] was able to determine that the subcarbonyl is located within the supercages of the zeolite.

Further heating at elevated temperatures causes complete decarbonylation of the carbonyl.[17,18] In Na–Y zeolite, zerovalent Mo is produced upon decarbonylation whereas, in H–Y, zeolite oxidation of the Mo occurs, presumably through reactions with the hydroxyls in the zeolite.[18] For $Mo(CO)_6$ in Na–Y, decarbonylation at 473 K produces molybdenum that is easily oxidized by exposure to O_2 at room temperature. However, following decarbonylation at 673 K, oxidation of the molybdenum species is not facile at room temperature.[18] X-ray diffraction and transmission electron microscopy (TEM) studies show no evidence of molybdenum migration to the exteriors of the zeolite crystals.[16,20] X-ray photoelectron spectroscopy (XPS) indicates there is no enrichment of molybdenum on the zeolite crystal exteriors, suggesting that the molybdenum is stabilized within the zeolite after decarbonylation.[20,21] The behavior of molybdenum is very different from that of many other metal species within zeolites which sinter and migrate to the zeolite exterior.[8,22]

Recently, Coddington et al.[23] have used ^{129}Xe NMR spectroscopy to study the formation of Mo clusters in zeolites via $Mo(CO)_6$ decomposition. The purpose of this work is to further characterize the reactions of $Mo(CO)_6$ in Na–Y zeolite via ^{129}Xe NMR spectroscopy. The NMR data allow the determination of the location of the subcarbonyl species. In addition, the siting of species produced by adsorption of oxygen and hydrogen by decarbonylated molybdenum has been investigated.

Experimental Section

Rinsed Linde LZY-52 molecular sieves were used as the starting material. All samples were evacuated in a glass vacuum manifold to a residual pressure of less than 5×10^{-5} Torr. All reductions were carried out on the same vacuum system under static H_2 (Linde 99.999%) which was dried by passing through Drierite and molecular sieves prior to exposure to the sample. Oxidations were performed using static O_2 (Linde 99.999%). H_2 and O_2 uptakes were monitored with a capacitance manometer (MKS Instruments Inc.). Research grade xenon was obtained from Cryogenic Rare Gas and used without further purification. All samples were evacuated prior to adsorption of xenon.

All Na–Y samples were put into 8 mm o.d. NMR tubes described below and evacuated at 623 K under vacuum (5×10^{-5} Torr). For all

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[†] University of Nebraska—Lincoln.

[‡] Rensselaer Polytechnic Institute.

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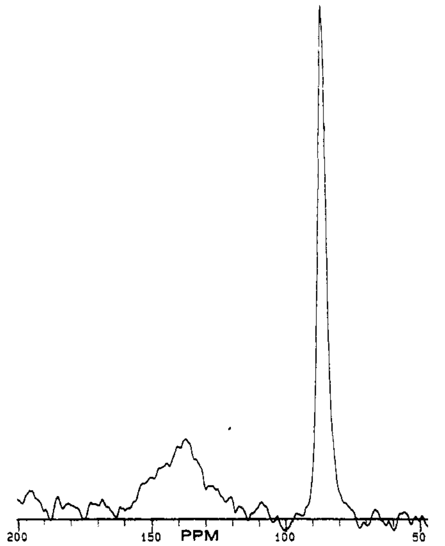

Figure 1. ^{129}Xe NMR spectrum of $Mo(CO)_6$ in Na–Y zeolite (310 Torr of Xe).

experiments, 0.5 g of zeolite was used. Vapor from $Mo(CO)_6$ (Aldrich Chemical Co., Inc.) which was previously degassed was introduced to the Na–Y in the glass vacuum system while the Na–Y was immersed in liquid N_2. Typically, 0.1 g of $Mo(CO)_6$ was used in the experiments; however, not all of the adsorbate was retained by the zeolite due to losses during evacuation. After loading was complete, the NMR tube was sealed with an ultratorr fitting and heated at 323 K overnight to disperse the $Mo(CO)_6$. Excess $Mo(CO)_6$ was removed by evacuation at room temperature. The subcarbonyl was formed by heating the sample at 373 K under vacuum until the pressure returned to base pressure. Mo content was determined gravimetrically after complete decarbonylation. Because the adsorption of $Mo(CO)_6$ is heterogeneous, it was necessary to determine the volume of the sample impregnated with Mo by measuring the length of the adsorbate band. The length of this band was generally between half and two-thirds of the entire sample length. The percentage of the sample impregnated with Mo was also determined by physically removing the adsorbate-loaded band and then weighing the remaining Na–Y in the sample tube. Only the amount of Na–Y containing Mo species was used in the xenon isotherm calculations. ^{129}Xe NMR spectra were acquired using a Varian VXR-200 NMR spectrometer operating at 55.337 MHz for ^{129}Xe. The number of transients collected ranged from 1000 to 3000, depending upon the xenon overpressure. Repetition rates were varied while signal intensity was monitored, and a relaxation delay of 1.0 s was determined to be appropriate for use on all samples. This value is similar to those reported in the literature.[3,5–8] Chemical shifts were referenced to a secondary standard consisting of xenon in Na–Y, the resonance of which had previously been referenced to that of xenon gas at zero pressure using Jameson's equation.[24] The magnet was locked in all experiments by using 8 mm o.d. NMR sample tubes equipped with J. Young valves inserted within 10 mm i.d. NMR tubes filled with D_2O.[25]

Results

Immediately after the Na–Y zeolite is exposed to $Mo(CO)_6$ vapor, a yellow band appears in the uppermost region of the sample, with the bottom of the sample remaining the white color of Na–Y. After the sealed tube is heated at 323 K to disperse the $Mo(CO)_6$, the color becomes more intense and more of the Na–Y zeolite becomes yellow. These colored bands do not appear to diffuse down the length of the sample, even after 6 months.

Using the change in mass after the complete decarbonylation of the sample and the length of band, it is possible to calculate the amount of molybdenum present in the yellow band. The molybdenum content is approximately 2.1 Mo atoms/supercage of zeolite. This value is very similar to the saturation loading reported by others.[16,19] A typical ^{129}Xe NMR spectrum of a sample is shown in Figure 1. Two separate xenon resonances are observed. From prior work with Na–Y zeolite, the sharp resonance at 85 ppm corresponds to xenon residing within Na–Y containing no molybdenum subcarbonyl species. The broad resonance centered at 138 ppm is assigned to the species in the yellow band. This assignment was also confirmed by moving the sample in the NMR coil and monitoring the changes in intensities of the resonances.

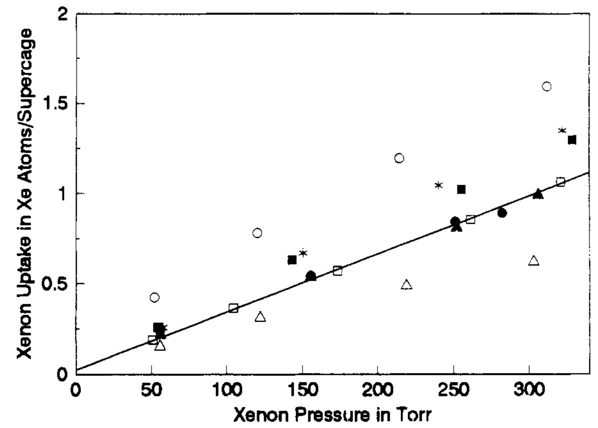

Figure 2. Plot of xenon uptake vs xenon pressure: □, Na–Y; △, $Mo(CO)_6$ in Na–Y; ○, $Mo(CO)_3$ in Na–Y; ✱, Mo in Na–Y; ■, Mo in Na–Y after heating at 623 K for 17 h; ▲, Mo in Na–Y after oxidation at 623 K; ●, Mo in Na–Y after reduction at 623 K.

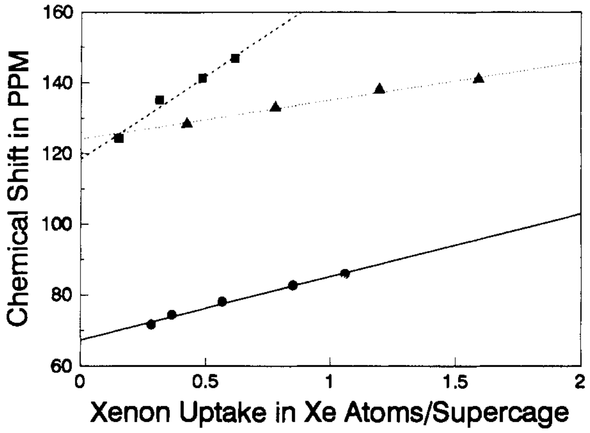

Figure 3. Plot of xenon chemical shift vs xenon uptake: ●, Na–Y; ■, $Mo(CO)_6$ in Na–Y; ▲, $Mo(CO)_3$ in Na–Y.

Xenon uptake is diminished following the $Mo(CO)_6$ adsorption and dispersion steps (Figure 2). Figure 3 shows the relationship between the ^{129}Xe chemical shift and the xenon concentration inside the zeolite.

Heating and evacuating the sample at 373 K produce a stable subcarbonyl that has been previously determined to be $Mo(CO)_3$.[15,17,19] The yellow band turns orange following this treatment, while the white band remains unchanged. A typical ^{129}Xe NMR spectrum is shown in Figure 4. Two resonances are observed at all xenon overpressures, with the upfield one corresponding to xenon residing in Na–Y without molybdenum species and the downfield resonance corresponding to xenon interacting with $Mo(CO)_3$ species inside the zeolite.

If supported $Mo(CO)_3$ is heated under vacuum or inert gas flow at 473 K, complete decarbonylation occurs.[15,18] In this study, the samples were activated at 623 K under vacuum. After this treatment, the samples turn black with the white Na–Y band present at the bottom of the tube. Xenon uptakes for these samples are greater than those of Na–Y itself, though not as great as that of the $Mo(CO)_3$. A representative ^{129}Xe NMR spectrum is shown in Figure 5. A number of xenon resonances are observed. Further heat treatment at 623 K affects the sample very little, although the resonances attributed to molybdenum species appear to have moved upfield somewhat (Figure 5).

Introduction of O_2 to these samples at room temperature does not change the sample appearance. ^{129}Xe NMR spectroscopy

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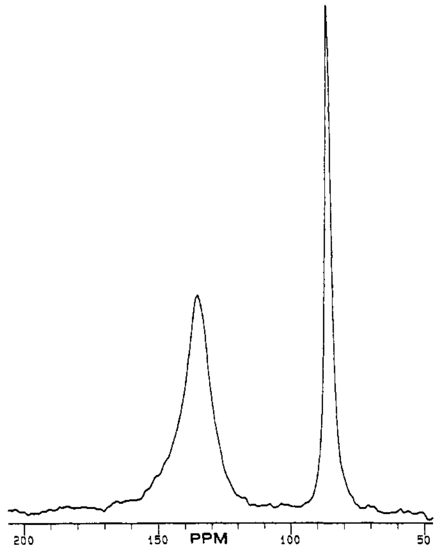

Figure 4. ^{129}Xe NMR spectrum of $Mo(CO)_3$ in Na–Y zeolite (305 Torr of Xe).

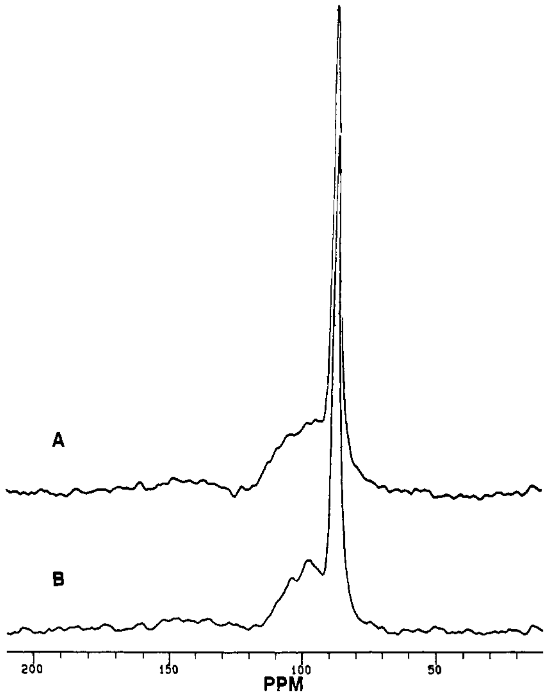

Figure 5. ^{129}Xe NMR spectra of fully decarbonylated molybdenum in Na–Y zeolite: (A) after heating 17 h at 623 K and 329 Torr of Xe; (B) after heating 1 h at 623 K and 322 Torr of Xe.

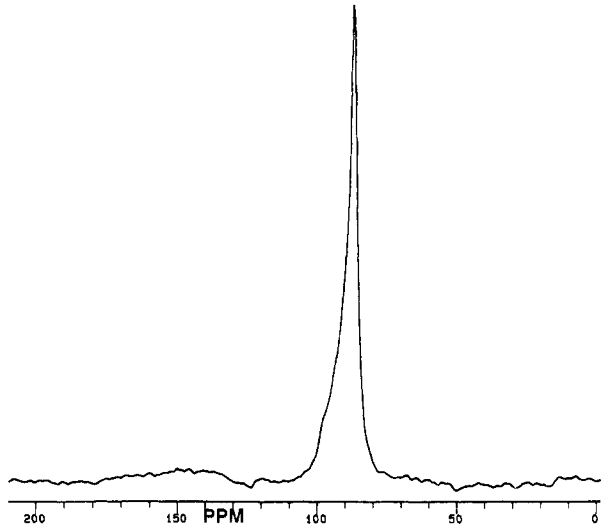

Figure 6. ^{129}Xe NMR spectrum of fully decarbonylated molybdenum in Na–Y zeolite after exposure to O_2 at 298 K and 320 Torr of Xe.

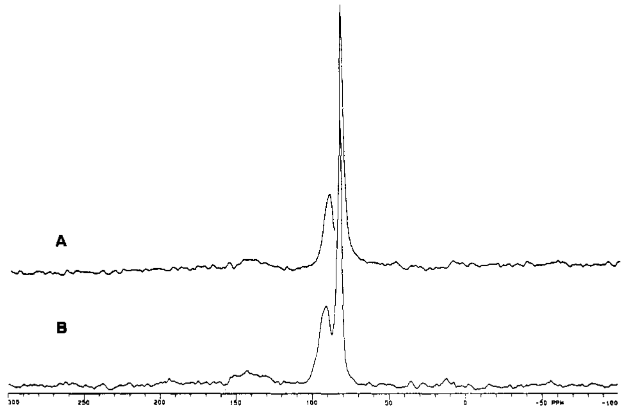

Figure 7. ^{129}Xe NMR spectra of fully decarbonylated molybdenum in Na–Y zeolite: (A) after oxidation at 623 K and 251 Torr of Xe; (B) after subsequent reduction and evacuation at 623 K and 256 Torr of Xe.

reveals that some change has occurred in these samples during this treatment (Figure 6). The peaks due to molybdenum species have now moved very far upfield and are nearly identical to that of the Na–Y. During oxidation at room temperature, a ratio of 0.2 mol of O/mol of Mo is observed.

When O_2 is introduced to the sample at 623 K, significant oxidation occurs and the black part of the sample becomes pale gray while the white part remains unchanged. The xenon uptake diminishes greatly after this procedure and is now identical with that of Na–Y containing no molybdenum, as is shown in Figure 2. ^{129}Xe NMR spectra feature two very sharp resonances and a very broad resonance far downfield (Figure 7). The most upfield resonance is that of xenon residing in Na–Y without any molybdenum species, and the other sharp resonance is due to some oxidized molybdenum species.

There is no significant uptake of H_2 at room temperature following the oxidation treatment, and there is no difference in the sample appearance. Reduction proceeds at 623 K, causing the sample to turn bronze in color. However, xenon uptake and ^{129}Xe NMR spectra are nearly identical to those of the sample prior to reduction (Figures 2 and 7).

Discussion

The production and long-term stability of the colored bands present in these samples suggest that there is some type of Mo bonding to the zeolite. Because molybdenum is coordinately saturated as a hexacarbonyl, there must be an initial loss of at least one CO ligand during the adsorption or dispersion steps. Yong et al.[16] have reported the loss of CO during the adsorption of $Mo(CO)_6$ in Na–Y zeolite although Ozkar et al.[19] found no loss of CO until samples were heated at temperatures greater than 323 K. Temperature-programmed decomposition studies of $Mo(CO)_6$ with a variety of X- and Y-type zeolites indicate that the initial decomposition temperature is affected by the Si/Al ratio of the zeolite and the corresponding difference in oxygen basicity.[15] Thus, the discrepancies in these studies may be due to slight differences in the starting zeolites.

Although there has been no other report of concentration bands in $Mo(CO)_6$ adsorption in zeolites, the appearance of such a distinct concentration gradient down the length of the NMR tube is not at all surprising on the basis of prior ^{129}Xe NMR studies of adsorbed species in Na–Y zeolite. Gedeon et al. observed that the adsorption of H_2O in Na–Y proceeds in a similar manner, where the uppermost regions of the sample are saturated and the lower regions of the sample have virtually no adsorbed H_2O.[2] Recently, Chmelka et al. reported the same adsorption phenomenon in the adsorption of organic molecules in Na–Y.[6] Yong et al.[16] found that after the initial saturation loading of $Mo(CO)_6$ in Na–Y, the N_2 uptake diminished to less than 1% of the original value. Similarly, diminished xenon uptake was observed in this study following the adsorption of $Mo(CO)_6$, as is shown in Figure 2.

The relationship between the ^{129}Xe chemical shift and the xenon concentration inside the zeolite following the $Mo(CO)_6$ adsorption is similar to that observed by Gedeon et al.[2] when Na–Y zeolite was saturated with H_2O (Figure 3). Therefore, the assignment of the yellow band to zeolite with a saturated concentration of molybdenum subcarbonyl species is further supported by ^{129}Xe NMR data.

As CO is removed from the sample by gentle heating under vacuum, the amount of xenon that is adsorbed increases dramatically. In fact, samples containing the $Mo(CO)_3$ species actually adsorb more xenon than Na–Y zeolite itself, which is shown in Figure 2. The enhanced xenon adsorption is probably not due to strong interaction with the molybdenum carbonyl but, instead, can be best explained by the surface curvature model, which predicts that smaller pores will have stronger van der Waals interactions with xenon.[26] The presence of two $Mo(CO)_3$ moieties per supercage causes the effective supercage size to be diminished, and therefore, Na–Y containing $Mo(CO)_3$ will adsorb more xenon at a given xenon pressure than Na–Y itself. These results are very similar to those observed by Ito et al.,[27] which showed that lightly coked H–Y adsorbs more xenon than H–Y containing no coke. The enhanced xenon adsorption clearly indicates that the subcarbonyl must be located either in the supercages or in the channels which connect them, in agreement with the work of Ozkar et al.[19]

In this study, the $Mo(CO)_3$ samples were activated at 623 K under vacuum to produce completely decarbonylated molybdenum metal species. The xenon uptakes for these samples are greater than that of Na–Y containing no metal, indicating that the molybdenum species are present in locations accessible to xenon (Figure 2). The ^{129}Xe NMR spectra feature a number of xenon resonances. The different resonances may be due to heterogeneity in the distribution of molybdenum throughout the sample. Further heat treatments at 623 K cause some of the xenon resonances to move upfield, suggesting that the molybdenum species may be migrating out of areas accessible to xenon (Figure 5).

Following the 623 K heat treatment, the samples were exposed to O_2 at room temperature. The upfield movement of the xenon resonances attributed to molybdenum species after the introduction of O_2 to the sample at room temperature is somewhat surprising. Very little oxygen is chemisorbed at room temperature (0.2 mol of O/mol of Mo), and no change in the sample appearance is observed, suggesting that the alteration of the ^{129}Xe NMR spectrum is not due to changes in the molybenum oxidation state but to movement of molybdenum. Abdo et al.[18] saw no evidence of oxidation at room temperature of molybdenum species which were activated at 673 K.

Oxidation at 623 K is very rapid. Xenon adsorption isotherms and ^{129}Xe NMR data suggest that the oxidized molybdenum species are not in regions of the zeolite directly accessible to xenon. The xenon uptake in these oxidized samples is identical to that of Na–Y containing no molybdenum (Figure 2). A representative ^{129}Xe NMR spectrum is shown in Figure 7. Figure 7 also shows a representative ^{129}Xe NMR spectrum of the same sample after it has been reduced at 623 K. The two spectra are nearly identical. In addition, the xenon uptake for the reduced sample is the same as that of the oxidized sample (Figure 2). Yet the samples are very different in appearance. These observations further suggest that the molybdenum species are either in the sodalite units or in the D6R rings rather than in the supercages. However, ^{129}Xe NMR spectroscopy may not be sensitive to the chemical changes occurring in the reduction and oxidation of Mo.

The molybdenum does not appear to be moving outside the zeolite crystallites, as there is no change in the xenon adsorption isotherms following repetitive oxidation and reduction cycles. In addition, the oxidation and reduction steps at 623 K are completely reversible with no changes in the ^{129}Xe NMR spectra, suggesting that the molybdenum species are stabilized within the zeolite lattice. This finding is in agreement with prior XPS and TEM studies.[20,21]

Conclusion

^{129}Xe NMR spectroscopy has proven to be a useful technique in the characterization of the reactions of $Mo(CO)_6$ in Na–Y zeolite. This technique enables the direct determination of the location of the $Mo(CO)_3$ subcarbonyl species within the supercages of the zeolite material. Adsorption of $Mo(CO)_6$ yields a saturation coverage of 2 Mo species/supercage.

Migration of the fully decarbonylated molybdenum species has been monitored. The results of this work suggest that the molybdenum species are mobile in the presence of O_2 and move to positions inside the sodalite cages.

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Registry No. $Mo(CO)_6$, 13939-06-5; $Mo(CO)_3$, 55979-29-8; ^{129}Xe, 13965-99-6; Xe, 7440-63-3.

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