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Solid-state static-echo, MAS-echo, and spikelet-echo ^{95}Mo NMR was utilized to obtain information on reduced/sulfided molybdena-alumina catalysts, as well as the effect of addition of cobalt, cesium, and potassium to "fresh" molybdena-alumina and cobalt to reduced/sulfided molybdena-alumina. We also investigated a used catalyst exposed to thiophene for 24 h. The results obtained for the reduced/sulfided catalysts indicate that the $\text{Mo}^{\text{VI}}\text{-O}$ species present in the "fresh" catalyst undergo only partial reduction and sulfiding, with a portion of the tetrahedral $\text{Mo}^{\text{VI}}\text{-O}$ species remaining unchanged in the reduced and sulfided catalyst. The bulk MoO_3 and octahedral molybdenum species, also present in the "fresh" catalyst, are reduced to Mo(IV) and sulfided to MoS_2 . An unidentified species, possibly MoOS , was also found to be present. Many other minor species are present on the surface which cannot be identified but which represent a high proportion of the molybdenum present on the surface. These could consist of a whole range of Mo(VI) and Mo(IV) mixed oxygen/sulfur compounds. There is no evidence for the presence of MoO_2 , except in one case. Simulation of the static powder line shapes allowed the deconvolution of the various components of the line shapes, thus yielding values of quadrupole parameters as well as relative intensity data. From the spikelet experiments it was ascertained that all species are present as both static adsorbed and dynamically active phases. The used catalyst shows the presence of the tetrahedral molybdenum-oxo species, along with a much reduced MoS_2 resonance (relative to the "fresh" system), perhaps indicating that MoS_2 is the active site in the thiophene HDS experiment and is degraded over time into a range of Mo(IV) and Mo(VI) oxo/sulfur species. In the case of the cobalt promoted "fresh" catalysts, the observed line widths indicated the presence of a paramagnetic coupling. This broadening was also found to be dependent on the method of impregnation of the promoter ion. Spikelet-echo experiments demonstrated the difference in surface chemistry between catalysts prepared by different impregnation techniques, namely, a much stronger Co-Mo interaction in the separately impregnated catalysts. Upon calcination, the usual increase in line width associated with polymerization of the surface molybdena was not observed for the promoted catalyst prepared by separate impregnation. The line width actually decreased for these catalysts, indicating either that the paramagnetic coupling occurred via the dipole coupling provided by the water molecules present on the uncalcined surface or that the cobalt was sequestered by the surface alumina to form CoAl_2O_4 . In the promoted reduced/sulfided catalysts, one observes no MoS_2 resonance in the separately impregnated promoted catalyst, while the MoS_2 is observed in the coimpregnated catalysts. This indicates that the cobalt is closely associated with the MoS_2 phase in the separately impregnated catalysts. In the case of the cesium and potassium promoted "fresh" catalysts, there is a marked increase in the line width of the uncalcined catalysts. The large alkali-metal ions may interact with the molybdenum in such a way as to distort the molybdena species, and thus produce a larger quadrupole interaction, or they donate electron density to the molybdenum thus creating a more shielded environment as well as perturbing the existing electric field gradient. In the calcined catalysts containing cesium or potassium, the line shapes are considerably narrowed, in comparison with the uncalcined catalysts. Comparison with the static and MAS spectra of Cs_2MoO_4 demonstrates the presence of predominantly Cs_2MoO_4 on the surface of high loading catalysts. K_2MoO_4 was also found to predominate at high loadings of potassium. Spikelet-echo experiments of the uncalcined cesium promoted catalysts revealed the presence of a homogeneous broadening mechanism which increases with increasing loading.

Introduction

In previous work,¹ we described in detail the results of a solid-state ^{95}Mo NMR study of the freshly prepared samples of molybdena adsorbed onto γ -alumina, prepared with an impregnation solution of $(\text{NH}_4)_6^{95}\text{Mo}_7\text{O}_{24}$. These "fresh" catalysts are the precursors to the active catalysts involved in hydrodesulfurization (HDS)²⁻⁹ and hydrode-

nitrogenation (HDN).¹⁰ These precursors are active catalysts for these HDS processes but yield only low conversion rates in comparison to the conversion rates obtained after reducing and sulfiding of the precursors. The results we have obtained show the feasibility of using solid-state ^{95}Mo NMR spectroscopy to obtain chemical information on the "fresh" catalysts and various model

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(1) Edwards, J. C.; Adams, R. D.; Ellis, P. D. *J. Am. Chem. Soc.* 1990, 112, 8349.

(2) Schuman, S. C.; Shalit, H. *Catal. Rev.* 1970, 4, 245.

(3) Weisser, O.; Landa, S. In *Sulphide Catalysts. Their Properties and Applications*; Pergamon: Oxford, 1973.

(4) Amberg, C. H. *J. Less-Common Met.* 1974, 36, 339.

(5) Grange, P.; Delmon, B. *J. Less-Common Met.* 1974, 36, 353.

(6) de Beer, V. H. J.; Schuit, G. C. A. In *Preparation of Catalysts*; Delmon, B.; Jacobs, P. A.; Poncelet, G., Eds.; Elsevier: Amsterdam, 1976; p 343.

(7) Ohtsuka, T. *Catal. Rev.-Sci. Eng.* 1977, 16, 291.

(8) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. In *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; p 390.

(9) Grange, P. *Catal. Rev.* 1980, 21, 135.

(10) Ho, T. C. *Catal. Rev.-Sci. Eng.* 1988, 30, 117.

compounds. The one problem which we encountered in the first study was the fact that the inhomogeneously broadened lines are featureless and occur in a very small chemical shift range indicative of polyoxomolybdate species. Magic angle spinning (MAS) and spikelet experiments allowed us to speculate as to the identity of the molybdenum species on the surface. We speculated that on the surface of the uncalcined "fresh" catalysts there were (a) predominately adsorbed surface species which could be tetrahedrally or octahedrally coordinated, (b) intact heptamolybdate clusters at higher loadings, (c) at higher loadings, octahedrally and tetrahedrally coordinated molybdate species which are interacting with the surface and which may be dynamically active, and (d) a small amount of $\text{Al}_2(\text{MoO}_4)_3$. In the calcined "fresh" catalysts there is an overall lowering of the symmetry of the system that takes place owing to the polymerization of the surface species via condensation reactions to form a MoO_3 -like surface polymer. Any dynamically active species are oxidized and polymerized/adsorbed to the surrounding molybdena species. The $\text{Al}_2(\text{MoO}_4)_3$ phase remained intact during the calcination process. We have further evidence for the presence of $\text{Al}_2(\text{MoO}_4)_3$ from a series of solid-state ^{27}Al NMR experiments¹¹ which were carried out in this lab. These findings are in agreement with results obtained for studies of these "fresh catalyst" systems using different analytical techniques, such as Raman spectroscopy,¹²⁻²⁰ Fourier transform (FT) IR,^{21,22} X-ray photoelectron spectroscopy (XPS),^{15,23,24} γ -ray dispersion,²⁵ and liquid-state NMR.^{26,27}

Another point to consider is that the active HDS catalysts consist of reduced and sulfided molybdenum species supported on γ -alumina. This is the form of the catalyst which is of interest to us in this particular study. The fact that $\text{Mo}^{\text{VI}}\text{-S}$ and Mo(IV) species have chemical shift ranges of ~ 2500 and ~ 4500 ppm, respectively,²⁸ will also aid us in our identification of the surface species present on the alumina surface after the "fresh" catalyst has been reduced and sulfided by a 10% mixture of H_2S in H_2 .

There are several review articles on the characterization of "fresh" and "sulfided" HDS catalysts.²⁹⁻³² Gravimetric

(measuring weight loss due to loss of oxygen) and volumetric studies (measuring the amount of H_2 consumed in the reduction process) have been carried out in order to ascertain the stoichiometry of the catalyst.^{33,34} These results confirmed that the $\text{Mo-Al}_2\text{O}_3$ species is reduced at a much slower rate than bulk species, such as MoO_3 , which may be present on the surface.³³ Combined gravimetric and sulfur analyses have indicated that the surface species undergo incomplete sulfiding inferring that a Mo-O-S species is present, or, if MoS_2 is present, only part of the sulfur is in this phase, with the rest being present in a Mo-O-S species. The overall view from characterization techniques such as Raman,¹⁸ EXAFS,³⁵ and ESCA,³⁶ is that there is incomplete sulfidation of molybdenum to form amorphous MoS_2 and a mixed $\text{Mo}^{\text{IV,V}}\text{-O-S}$ species. Also present on the surface is unreduced $\text{Mo}^{\text{VI}}\text{-O}$ species, as well as MoO_2 . An IR study has also claimed that there is a mixed $\text{Mo}^{\text{VI}}\text{-O-S}$ species present on the surface.³⁷ This IR study has been seen as inconclusive, as the catalyst was exposed to air before the spectrum was taken. This is thought to have caused oxidation of the surface species by a large uptake of oxygen. In our study we have utilized solid-state ^{95}Mo NMR spectroscopy to look at model species such as MoO_2 , $(\text{NH}_4)_2\text{MoS}_4$, MoS_2 , and MoO_3 .

The NMR results of the catalytic samples are of 8% Mo-, 12% Mo-, and 16% Mo-loading catalysts. In the case of the 8% Mo samples, both have been calcined before the reduction/sulfidation process, while in the case of the 16% Mo samples, one sample had been calcined while the other was left uncalcined before the reduction/sulfidation process was applied. The reduced and sulfided catalysts are known to age and lose activity with time. For this reason the spectrum of a used catalyst was also obtained in order to determine what changes occur that lower the efficiency of the catalyst, during a thiophene HDS experiment. From our results, we have demonstrated that there are several species present on the surface, among them amorphous MoS_2 , which is the active center of the catalyst, an unaffected tetrahedral $\text{Mo}^{\text{VI}}\text{-O}$ species identical with that found in the fresh catalyst, and an apparent range of $\text{Mo}^{\text{IV}}\text{-O-S}$ and $\text{Mo}^{\text{VI}}\text{-O-S}$ species in different environments. Our results did not demonstrate the presence of MoO_2 on the majority of the catalysts. These results concur with the results obtained for the "fresh" precursor catalysts.¹

We have also focused our attention on the effect of adding promotor ions to the catalysts, namely cobalt in the form of $\text{Co}(\text{NO}_3)_2$, cesium as CsNO_3 , and potassium as K_2CO_3 . It is known that promoted catalysts can yield conversions of 50-60% of the thiophene to C_4 products. Past work performed on Co-Mo- Al_2O_3 systems is covered in several review articles.^{30,38-40} The consensus of opinion

- (11) Edwards, J. C.; Ellis, P. D. To be submitted for publication.
- (12) Wang, L.; Hall, K. W. *J. Catal.* 1980, 66, 251. *J. Catal.* 1982, 77, 232. *J. Catal.* 1983, 83, 242.
- (13) Knözinger, H.; Jeziorowski, H. *J. Phys. Chem.* 1978, 82, 2002.
- (14) Knözinger, H.; Jeziorowski, H. *J. Phys. Chem.* 1979, 83, 1166.
- (15) Zingg, D. S.; Mokovsky, L. E.; Tischer, R. E.; Brown, F. R.; Hercules, D. M. *J. Phys. Chem.* 1980, 84, 2899.
- (16) Cheng, C. P.; Schrader, G. L. *J. Catal.* 1979, 60, 276.
- (17) Brown, F. R.; Makovsky, L. E.; Rhee, K. H. *J. Catal.* 1977, 50, 162.
- (18) Brown, F. R.; Makovsky, L. E.; Rhee, K. H. *J. Catal.* 1977, 50, 385.
- (19) Kasztelan, S.; Payen, E.; Toulhoat, H.; Grimblot, J.; Bonnelle, J. P. *Polyhedron* 1987, 5, 157.
- (20) Quincy, R. B.; Houalla, M.; Hercules, D. M. *J. Catal.* 1987, 106, 85.
- (21) Giordano, N.; Bart, J. C. J.; Vahi, A.; Castellen, A.; Martinotti, G. *J. Catal.* 1975, 36, 81.
- (22) Millman, W. S.; Segawa, K.; Smrz, D.; Hall, K. W. *Polyhedron* 1987, 5, 189.
- (23) Clausen, B. S.; Lengeler, B.; Topsøe, H. *Polyhedron* 1987, 5, 199.
- (24) Hayden, T. F.; Dumesic, J. A. *J. Catal.* 1987, 103, 366.
- (25) Butz, T.; Vogdt, C.; Lerf, A.; Knözinger, H. *J. Catal.* 1989, 116, 31.
- (26) Luthra, N. P.; Cheng, W.-C. *J. Catal.* 1987, 107, 154.
- (27) Sarrazin, P.; Mouchel, B.; Kasztelan, S. *J. Phys. Chem.* 1989, 93, 904.
- (28) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* 1985, 68, 169.
- (29) Hall, K. W., In *Chemistry and Physics of Solid Surfaces VI*; Springer Series in Surface Sciences 5; Vanselow, R., Howe, R., Eds.; Springer Verlag: Berlin, 1986; Chapter 5, p 73.
- (30) Massoth, F. E. *Adv. Catal.* 1978, 27, 265.
- (31) Chianelli, R. R. *Catal. Rev.-Sci. Eng.* 1984, 26, 361.
- (32) Furimsky, E. *Catal. Rev.* 1980, 22, 371.

- (33) Sontag, P.; Kim, D. Q.; Marion, F. C. *R. Acad. Sci., Ser. C* 1964, 259, 4704.
- (34) Massoth, F. E. *J. Catal.* 1975, 36, 164.
- (35) Huntley, D. R.; Parham, T. J.; Merrill, R. P.; Sienko, M. J. *Inorg. Chem.* 1983, 22, 4144.
- (36) Brinen, J. S. *Electron Spectrosc. Relat. Phenom.* 1974, 5, 377.
- (37) Mitchell, P. C. H.; Trifiro, F. *J. Catal.* 1974, 33, 350.
- (38) Ratnasamy, P.; Sivasanker, S. *Catal. Rev.-Sci. Eng.* 1980, 22, 401.
- (39) Topsøe, H.; Clausen, B. S. *Catal. Rev.-Sci. Eng.* 1984, 26, 395.
- (40) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* 1989, 31, 1.
- (41) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* 1948, 73, 679.
- (42) Bloembergen, N.; Dickinson, W. C. *Phys. Rev.* 1950, 79, 179.
- (43) Dickinson, W. C. *Phys. Rev.* 1951, 81, 717.
- (44) McConnell, H. M.; Cheesnut, D. B. *J. Chem. Phys.* 1953, 28, 107, 991.
- (45) Bloembergen, N. *J. Chem. Phys.* 1955, 27, 572.
- (46) O'Young, C.-L. *J. Phys. Chem.* 1989, 93, 2016.

is that in the calcined "fresh" catalysts, a portion of the Co^{2+} is present as both octahedrally ($\text{Co}[\text{O}_h]$) and tetrahedrally ($\text{Co}[\text{T}_d]$) coordinated oxide, with predominantly $\text{Co}[\text{T}_d]$ at low loadings, and the $\text{Co}[\text{T}_d]/\text{Co}[\text{O}_h]$ ratio decreasing with increasing loading. The blue color of the $\text{Co-Mo-Al}_2\text{O}_3$ calcined catalysts suggests that the $\text{Co}[\text{T}_d]$ is CoAl_2O_4 —there has been little evidence for the presence of CoMoO_4 .

In the reduced and sulfided form there is disagreement as to the nature of the cobalt species. One of the hypothesized models is the intercalation model, suggested by De Beer and Schuit,⁶ in which the sulfiding process breaks up the molybdena monolayer forming small, discrete MoS_2 crystallites. The cobalt reacts with the MoS_2 to form a CoMoS_2 intercalation species. However, the most favored model is one in which the promoter cobalt is present as cobalt ions adsorbed to the edges of the MoS_2 crystallites. Cobalt that is not adsorbed to the MoS_2 is thought to be present as Co_3S_8 and as cobalt ion coordinated to the tetrahedral alumina sites (CoMoO_4).

These promoted catalysts have been found to be more effective when a separate impregnation method is used in their preparation; i.e., the γ -alumina is impregnated with the heptamolybdate solution, dried, and then impregnated again with a separate $\text{Co}(\text{NO}_3)_2$ solution and then dried again. In order to ascertain if there are any difference which can be observed between this preparation method, and one involving coimpregnation with a heptamolybdate/ $\text{Co}(\text{NO}_3)_2$ solution, we have performed experiments on catalysts prepared by both of these methods at different cobalt loadings.

One problem, however, is the paramagnetic nature of Co^{2+} , which can cause a broadening of the ^{95}Mo resonances of molybdenum-cobalt interaction species, along with a paramagnetic shift which can remove the resonance from your effective spectral window. The interaction between unpaired electron magnetic moments and nuclear magnetic moments occurs via dipole-dipole¹⁷⁻¹⁹ coupling and Fermi contact coupling.^{20,21} These electron-nucleus magnetic interactions can affect both nuclear relaxation times (causing inhomogeneous broadening due to the reduction of the molybdenum spin-spin relaxation time, T_2) and observed shifts. In this investigation, we have utilized the solid-state ^{95}Mo NMR spectroscopy of these promoted systems in order to compare them with the unpromoted catalyst results obtained previously. Our philosophy, owing to the presence of paramagnetic cobalt, was that if we could not deduce anything concerning the surface structure from the spectra themselves, we might be able to deduce some information from any resonances, observed in the unpromoted catalysts, that may be "missing" in the promoted catalyst spectra, owing to a paramagnetic interaction. In our experiments, we have only observed a slight (2–3 kHz) overall broadening of the observed "fresh" catalyst resonances upon introduction of Co^{2+} promoter ions. Also, attempts to observe the model compound CoMoO_4 were unsuccessful, and the investigation of the promoted, reduced/sulfided catalysts yielded spectra in which the resonances in the –600 to –2200 ppm range, assigned previously to MoOS/MoS_2 , were reduced in intensity or not present at all.

With respect to the effects of alkali-metal promoters (potassium and cesium), we have tried to determine if there is a phase transformation of the molybdenum, upon

calcination, to form Cs_2MoO_4 or K_2MoO_4 , as suggested by O'Young.²² Alkali-metal promoters are used to improve the selectivity and activity of many catalysts. The effects of these promoters have been studied by many groups,²³⁻²⁵ and in general, it is believed that the alkali-metal ions can donate electrons to the transition metals in order to enhance their back- π -bonding capabilities. In this work, we will study the solid-state ^{95}Mo NMR of 12% $\text{Mo-Al}_2\text{O}_3$ catalysts promoted with different loadings of cesium, and a single loading of potassium.

In both cases, with the cobalt and cesium promoted catalysts, we have obtained the spikelet-echo spectra of the uncalcined and calcined catalysts in order to try and deduce if the increases in line width observed in the promoted, uncalcined catalysts (compared to the unpromoted catalysts) is due to homogeneous or inhomogeneous broadening. It was also hoped that we might be able to differentiate between different species on a chemical shift basis by observing superimposed "spikelet combs" due to different molybdenum species.

Experimental Section

The reduced and sulfided active catalysts were prepared from the "fresh" precursor catalysts previously prepared by the impregnation of γ -alumina with an appropriate concentration of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solution.¹ The molybdenum employed in our experiments was 94.9% ^{95}Mo -enriched molybdenum metal, obtained from Isotec, Inc. The sample of ^{95}Mo -enriched $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was prepared by dissolving the molybdenum metal powder in hot concentrated HNO_3 , and the resulting yellow precipitant was dissolved in a few milliliters of 6 M HCl . The liquid was then allowed to evaporate and the resulting powder was placed in a furnace at 800 K for 3 h yielding $^{95}\text{MoO}_3$. The $^{95}\text{MoO}_3$ was then dissolved in an $(\text{NH}_4)\text{OH}$ solution which was pH adjusted to pH 5.2. The $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was collected after crystallization from this solution and characterized by laser Raman⁶⁰ and FT-IR.⁶¹ The $\gamma\text{-Al}_2\text{O}_3$ was obtained from Aesar and was found to have a surface area of 115 m^2 when analyzed with a surface area analyzer made by Quanta-Chrome. It should be noted that the alumina that was used is technically a transition alumina rather than γ -alumina. The 10% H_2S in H_2 gas used in the reduction/sulfidation was produced by Matheson.

Preparation of $\text{MoO}_3\text{-Al}_2\text{O}_3$ Catalysts. It was calculated that a 16% weight for weight loading of ammonium heptamolybdate on γ -alumina is the equivalent of a monolayer coverage.¹ A typical preparation involved dissolving the appropriate weight of ^{95}Mo -enriched heptamolybdate dissolved in ~15 mL of water. Approximately 1 g of γ -alumina was placed in a plastic weigh boat, and a few milliliters of solution was added to the alumina in order to make a slurry. The sample was then heated in an oven at 50 °C until dry, then 3 mL of solution was added again and the sample dried. This process is continued until all the solution is used. This methodology leads to a more uniform coverage of the alumina surface. The sample was then dried at 120 °C for 4 h. A part of the sample was saved and is henceforth called the *uncalcined sample*. The other portion of the catalyst is then calcined at 550 °C, in air, for 18 h—this sample is referred to as the *calcined sample*.

The $\text{Co-Mo-Al}_2\text{O}_3$ catalysts were prepared by two different methods.

Separate Impregnation. In the catalysts we studied, a 12% Mo loading was used. The γ -alumina was impregnated and dried at 120 °C, consecutively with pore volume aliquots of an appropriate molar solution concentration of heptamolybdate as described previously.¹ The final dried molybdena/ γ -alumina catalyst was impregnated again with a $\text{Co}(\text{NO}_3)_2$ solution containing either 4% Co or 8% Co by weight. These catalysts were then dried at 120 °C and investigated as the uncalcined

(47) Kantschewa, M.; Delannay, F.; Jeziorowski, H.; Delgado, E.; Eder, S.; Ertl, G.; Knözinger, H. *J. Catal.* 1984, 87, 482.

(48) King, D.; Peri, J. B. *J. Catal.* 1983, 79, 164.

(49) Rankin, J. L.; Bartholomew, C. H. *J. Catal.* 1986, 100, 533.

(50) Tytko, K.-H.; Schönfeld, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1975, 30b, 471.

(51) Miller, F. A.; Carlson, G. A.; Bentley, F. F.; Jones, W. H. *Spectrochim. Acta* 1960, 16, 156.

(52) Wildervanck, J. C.; Jellinek, F. *Z. Anorg. Chem.* 1964, 328, 309.

catalyst. A portion of each catalyst was then calcined at 500 °C for 16 h to yield the calcined catalysts.

Coinpregnation. The γ -alumina was impregnated with pore volume aliquots of an appropriate solution of $\text{Co}(\text{NO}_3)_2$ /heptamolybdate (12% Mo and 4% Co or 8% Co, by weight). The dried catalyst was investigated as the uncalcined catalyst, and a portion of these catalysts were calcined at 500 °C for 16 h to yield the calcined catalyst samples.

Cesium and Potassium Promoted Catalysts. The Cs-Mo- Al_2O_3 catalysts were prepared by first making a calcined 12% Mo- Al_2O_3 catalyst, followed by impregnation with the appropriate solution of CsNO_3 (8%, 16%, 32% (w/w)). These catalysts were then dried at 120 °C for 3 h and calcined at 500 °C, in air, for 16 h. The 32% K-12% Mo- Al_2O_3 catalyst was prepared in an identical manner to the cesium promoted catalysts.

Preparation of the Reduced and Sulfided Catalyst. The samples chosen to undergo the reduction/sulfiding process were the 8% Mo/ γ - Al_2O_3 (calcined, impregnation solution at pH 5.2), 8% Mo/ γ - Al_2O_3 (calcined, impregnation solution at pH 8.2), and 16% Mo/ γ - Al_2O_3 (calcined and uncalcined samples, impregnation solutions at pH 5.2). These samples were loaded into a quartz tube and placed in a furnace, a stream of 10% H_2S in H_2 was passed over the sample for 4 h while the furnace was at 400 °C. There were no special precautions made to keep the catalyst in an oxygen-free environment.

Kinetic Measurement and Preparation of the Used Catalyst. A sample containing 0.100 g of a 12% Mo- Al_2O_3 (calcined, impregnation solution at pH 5.2, 40–100 mesh) was reduced and sulfided by the same method described previously, in a flow microreactor. A stream of 2.7% thiophene in H_2 (30 mL/min) was flowed over the catalyst, and the products were analyzed by a dedicated HP-5890A gas chromatograph. The catalytic activity was measured over a 24-h period. The conversion rate calculated at the 24-h mark was taken as the conversion rate of the catalyst. This value corresponded to a 9% conversion of thiophene to C_4 products. When the low surface area of the support is taken into account, this value corresponds to a moderate to low activity when compared to other unpromoted active catalysts. The catalyst was investigated by NMR after this kinetic measurement was carried out, and the activity of the catalyst was seen to be dropping.

Preparation of Model Compounds. A sample of ammonium thiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$) was obtained from John H. Enemark at the University of Arizona. The sample of MoS_2 was prepared by a method described by Wildervanck et al.,⁵² which involves heating ammonium thiomolybdate in a quartz boat, at 1000 °C, under a flow of He gas, for 6 h. The sample of MoO_2 was obtained by heating MoO_3 at 400 °C, for 10 h.

A sample of CoMoO_4 was made by crystallization from a mixture of two stoichiometric solutions of $\text{Co}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{MoO}_4$, respectively. A sample of $\text{Cs}_2(\text{MoO}_4)$ was made by crystallization from a solution of MoO_3 dissolved in a stoichiometric CsOH solution. CsNO_3 was obtained from Aldrich, and the $\text{Co}(\text{NO}_3)_2$ was obtained from Fisher.

NMR Spectroscopy. The solid-state ^{95}Mo FT-NMR spectra were obtained at 26.06 MHz, on a Varian XL-400 spectrometer operating in the so-called "wideline" mode. The spectra were obtained in a broad band, tunable Doty 7-mm MAS probe, obtained from Doty Scientific (Columbia, SC). A 30-MHz low pass filter was utilized in order to remove any spurious signals from the transmitter rf. All chemical shifts are reported with respect to a 2 M Na_2MoO_4 reference solution at pH 11. The nonselective $\pi/2$ pulse width was determined from this solution, a typical value being around 9 μs . The forward transmitter pulse power was 625 W with a typical reflected power of ~ 60 W. In order to observe the central $\pm 1/2$ transition exclusively we have employed the selective solid-echo sequence^{53–56}

$$(\pi/2)_s - \tau_1 - (\pi)_s - \tau_2 - \text{acquire}$$

Here the subscript s refers to a selective pulse. The selective pulse width is obtained by dividing the nonselective pulse width

by a factor of $(I + 1/2)$ —in this case, for ^{95}Mo , $(I + 1/2) = 3$. The accuracy of this selective pulse width was ascertained by performing a pulse width array on a solid sample of enriched heptamolybdate, and a maximum was observed at the selective $\pi/2$ pulse width value. Typical values for the echo delays were 60 μs for τ_1 , and 5 μs for τ_2 , in order to observe the top of the echo, without the effects of acoustic ringing being observed. Typical values for $(\pi/2)_s$ were around 3 μs . Recycle delays were between 80 and 50 ms. A 16-step phase cycle was used to remove artifacts caused by imperfect pulses. The sweepwidth used was 250–400 kHz. The same solid-echo 16-step phase cycle pulse sequence was used for the MAS experiments. The only difference being that the echo delay, τ_1 , was made equal to the reciprocal of the spin speed.

In a recent note, Man and co-workers⁵⁷ alluded to a potential problem when utilizing selective pulses in quadrupolar systems. Namely, when one has a mixture of species with differing quadrupole coupling constants, one may have problems associated with the quantitative details of the experiment. This problem occurs when ω_Q (proportional to the quadrupole coupling constant) for some of the species is large compared to ω_H , while for others ω_Q is small relative to ω_H . In this situation the rf pulse cannot be considered as selective. If one has mixed states, then the quantitation can be obtained by using a small flip angle excitation instead of selective $\pi/2$ pulses.⁵⁷ This situation is easy to diagnose with a nutation experiment.^{58–60} We have performed such experiments on all of our surface precursors and have found that all of the observable ^{95}Mo is in the limit where $\omega_Q \gg \omega_H$. Hence, relative quantitation via the selective solid-echo approach is a valid method.

The spikelet-echo experiment has been used to good effect in the past^{1,57,68} and involves the digitization of a whole train of spin echoes. Upon Fourier transformation this leads to a "spikelet spectrum", which shows the presence of different species by inconsistencies in the "spikelet spacings" (caused by chemical shift differences), and the "spikelet line widths" (caused by the different spin-spin relaxation rates observed by the different species). Sweepwidths used were 200 or 500 kHz, 1920 or 3932 data points were collected, recycle delay of 50 ms, τ_1 and τ_2 were equal to 60 μs , while the echo train delay was 150 μs . The echo train consisted of 16 or 32 π pulses and the receiver was blanked for 5 μs and a delay of 95 μs inserted before and after each echo train pulse in order to remove breakthrough due to receiver blanking. The special experimental and processing aspects of this experiment are discussed elsewhere.^{1,57}

^{95}Mo is a quadrupolar nucleus with nuclear spin $I = 5/2$ and a relatively high natural abundance (15.8%). Its relatively small quadrupole moment, Q , of $0.12 \times 10^{-24} \text{ cm}^2$ (or $0.011 \times 10^{-24} \text{ cm}^2$ depending on the source), means that the obtained central $\pm 1/2$ transition, second-order perturbed quadrupolar line shapes, are not too broad. In our experiments, the catalyst samples were made with ^{95}Mo -enriched material in order to improve the sensitivity of the experiment, which because of the enrichment was increased by a factor of 40.

Line Shape Simulation. The model compound and catalyst line shapes were simulated by using an interactive graphical curve fitting program, written in C, developed in this laboratory. This program has been used previously to simulate solid-state static

(57) Man, P. P.; Klinowski, J.; Trokiner, A.; Zanni, H.; Papon, P. *Chem. Phys. Lett.* 1988, 151, 143.

(58) Samoson, A.; Lippmaa, E. *J. Magn. Reson.* 1988, 78, 255.

(59) Yannoni, C. S.; Kendrick, R. D. *J. Chem. Phys.* 1981, 74, 747.

(60) Man, P. P.; Theveneau, H.; Papon, P. *J. Magn. Reson.* 1985, 64, 271.

(61) Janssen, R.; Tijink, G. A. H.; Veeman, W. S. *J. Chem. Phys.* 1988, 88, 518.

(62) Geurts, F. M. M.; Kentgens, A. P. M.; Veeman, W. S. *Chem. Phys. Lett.* 1985, 120, 206.

(63) Samoson, A.; Lippmaa, E. *Chem. Phys. Lett.* 1983, 100, 205.

(64) Samoson, A.; Lippmaa, E. *Phys. Rev. B: Condens.* 1983, 28, 6567.

(65) Kentgens, A. P. M.; Lemmens, J. J. M.; Geurts, F. M. M.; Veeman, W. S. *J. Magn. Reson.* 1987, 71, 62.

(66) Trokiner, A.; Man, P. P.; Thèveneau, H.; Papon, P. *Solid State Commun.* 1985, 55, 929.

(67) Cheng, J. T.; Ellis, P. D. *J. Phys. Chem.* 1989, 93, 2549.

(68) Garroway, A. N. *J. Magn. Reson.* 1977, 28, 365.

(53) Solomon, I. *Phys. Rev.* 1958, 110, 61.

(54) Weisman, I. D.; Bennett, L. H. *Phys. Rev.* 1969, 181, 1341.

(55) Bonera, G.; Avogadro, A.; Borsa, F. *Phys. Rev.* 1968, 165, 171.

(56) Warren, W. W., Jr.; Norberg, R. E. *Phys. Rev.* 1967, 154, 277.

Table I. Singularity Positions and Line Width Data for the Model Species, "Fresh", and Sulfided/Reduced Catalysts

sample	singularity positions, ppm	line width $W_{1/2}$, kHz
PbMOO ₄ ^a	51, 20	4.42
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O ^a	535, 133, 34, -41, -135	13.15
MoO ₃ ^a	120, 19, -104, -371	9.20
12% Mo-Al ₂ O ₃ , calcined, pH 5.2	-131	19.26
8% Mo-Al ₂ O ₃ , calcined, pH 8.2	-127	19.28
8% Mo-Al ₂ O ₃ uncalcined, pH 5.2	-96	16.37
8% Mo-Al ₂ O ₃ calcined, pH 5.2	-100	19.57
MoS ₂	-609, -2302	~53.00
MoO ₂	9, 848, 1533, 2400	~88.00
(NH ₄) ₂ MoS ₄	2181	1.45
16% Mo-Al ₂ O ₃ , calcined, pH 5.2, reduced & sulfided	-142, -599, -2141	
16% Mo-Al ₂ O ₃ , uncalcined, pH 5.2, reduced & sulfided	-136, -577, -2142	
4.5-kHz MAS	1130, 776, 204, -151	
	-322, -750, -1780	
8% Mo-Al ₂ O ₃ , calcined, pH 5.2, reduced & sulfided	-70, -625, -2140	
8% Mo-Al ₂ O ₃ , calcined, pH 8.2, reduced & sulfided	1842, -216, -622, -2220	
12% Mo-Al ₂ O ₃ , calcined, pH 5.2 reduced & sulfided, used in HDS of thiophene	-104, -700	

^a See ref 1.

Table II. Quadrupole Parameters and Relative Normalized Areas of Model and Catalyst Samples Obtained from IGCFF Simulation of the Static Powder Line Shapes

sample ^a	Q_{cc} , MHz	η_Q	singularity positions, ppm	normalized concn, %
MoS ₂ (1a,b)	6.72	0.16	-609, -2302	
MoO ₂ (1c)	7.80	0.00	2400, 9	
16% uncalcined, R/S (2)				
1	3.19	0.82	-136	8
2	8.61	0.07	-577, -2142	18
3	3.13	1.00	-577	14
Gaussian				60
16% calcined, R/S (3)				
1	3.19	0.82	-142	13
2	8.30	0.08	-599, -2141	26
3	3.13	1.00	-599	18
Gaussian				43
8% calcined, R/S pH 5.2 (4)				
1	3.19	0.82	-70	23
2	8.30	0.08	-625, -2140	14
3	3.13	1.00	-625	15
Gaussian				48
8%, calcined, R/S pH 8.2 (5)				
1	3.19	0.82	-216	19
2	2.39	0.80	-622, -2220	9
3	6.50	0.08	-622	7
Gaussian 1				59
Gaussian 2			1842	6

^a Numbers in parentheses are the figure number for the spectrum.

⁸⁷Rb and ⁹⁵Mo NMR spectra.^{1,69,70} In the context of this work, the simulation program was used to simulate the MoO₂ and MoS₂ line shapes, assuming the line shape is the sum of the second-order quadrupole and chemical shift anisotropy interactions in which the two tensor PAS frames are assumed to be either coincident or noncoincident. The catalyst samples were simulated by taking into account only the quadrupole interaction (Q_{cc} , η_Q). The deconvoluted catalyst line shapes indicate the presence of three species along with an inhomogeneous distribution of species, represented by a Gaussian-like line shape.

The quadrupole parameters were obtained for one of the catalyst samples, and these values were used as initial guesses in the simulations of the remaining catalysts. The program uses a double simplex algorithm which can vary any combination of the offset, width, and scale of the calculated line shape to obtain the best fit and then uses the associated error values of the fit to simplex the desired NMR parameters. In the case of calculated quadrupole line shapes, only the offset and scale are varied, whereas all three parameters are varied for the Gaussian line shapes. Thus the program allows one to extract the relative intensity of each component present in the various catalyst line shapes.

Results

The singularity position data of the static, and a few MAS experiments, expressing the positions of the observed singularities of the line shapes are displayed in Table I, along with the line width data (full width at half height (fwhh)). The quadrupole parameters obtained from the line shape simulations are displayed in Table II, along with the relative intensity approximations for the catalyst line shape components. Line width data from the promoted catalyst experiments is given in Table III.

Discussion

Background on the "Fresh" Catalyst Surface Structure. We must first discuss what the surface structure of the "fresh" catalyst is like in order to be able to identify any surface species that remained unchanged during the reduction and sulfiding process. In previous publications, we have investigated a range of model compounds^{1,70} and by line shape simulation extracted the quadrupole and chemical shielding information from the line shapes.

One of the major trends that was found during previous studies^{1,70} of ⁹⁵Mo is that the presence of highly symmetrical environments, such as purely octahedral or tetra-

(69) Cheng, J. T.; Edwards, J. C.; Ellis, P. D. *J. Phys. Chem.* **1990**, *94*, 553.

(70) Edwards, J. C.; Zubieta, J.; Shaikh, S. N.; Chen, Q.; Bank, S.; Ellis, P. D. *Inorg. Chem.* **1990**, *29*, 3381.

Table III. Static Powder Line Shape Line Width Data for the Calcined and Uncalcined Promoted Catalyst Samples

catalyst	catalyst state	impregnation method	line width (fwhh ^a), kHz
12% Mo	uncalcined		13.39
12% Mo, 8% Co	uncalcined	coimpregnation	15.16
12% Mo, 4% Co	uncalcined	coimpregnation	16.16
12% Mo, 8% Co	uncalcined	separate	22.88
12% Mo, 4% Co	uncalcined	separate	20.94
12% Mo	calcined		21.47
12% Mo, 8% Co	calcined	coimpregnation	17.32
12% Mo, 4% Co	calcined	coimpregnation	16.44
12% Mo, 8% Co	calcined	separate	21.03
12% Mo, 4% Co	calcined	separate	17.03
12% Mo, 16% Cs	uncalcined	separate	15.59
12% Mo, 32% Cs	uncalcined	separate	16.29
12% Mo, 8% Cs	calcined	separate	17.43
12% Mo, 16% Cs	calcined	separate	7.13
12% Mo, 32% Cs	calcined	separate	4.59
12% Mo, 32% Cs	calcined	separate	0.88
(4 kHz MAS)			
12% Mo, 32% K	calcined	separate	2.97
Cs ₂ MoO ₄			2.37
Cs ₂ MoO ₄			0.94
(4 KHz MAS)			

^a fwhh, full width at half height of line shape.

hedral species (having low Q_{cc} values) adsorbed to the surface, is readily demonstrated by the MAS experiment in which the resonances due to these sites narrow considerably and, thus, allow the discernment of these sites. This demonstrated trend will be important in later discussions of the possible surface species present in the "fresh", promoted, and reduced/sulfided catalysts.

From the previous study of the "fresh" catalyst,¹ the structure of the molybdenum surface species seems to consist of a range of species. In the uncalcined catalysts, there are species present corresponding to tetrahedrally and octahedrally coordinated molybdate adsorbed to the alumina. Which of these two species predominates is dependent on the method of preparation. At higher loadings (>12% Mo), there is evidence for the intact adsorption of heptamolybdate clusters, as well as the presence of dynamic surface species. Another species that may be present is $Al_2(MoO_4)_3$, especially at higher loadings.

A general loss of symmetry occurs upon calcination, probably due to a polymerization of the surface species via a condensation reaction, to form a MoO_3 -like species. The dynamic surface species, present at higher (above monolayer) loadings, are either adsorbed to the surface, polymerized to the surface polymer being formed on calcination, or oxidized to a MoO_3 -like species too large to be dynamic. Thus, we feel that there are a wide range of octahedral and tetrahedral species on the surface.

Model Species. There are several model species that could be used to describe the state of the molybdenum on the surface of the reduced and sulfided catalyst. The first of these species is molecular MoS_2 , shown in Figure 1a, which is a Mo(IV) species. MoS_2 has a layer structure in which the NMR-equivalent Mo^{4+} ions are found in a 6-fold trigonally prismatic surrounding.⁷¹ The layers are held together by van der Waals forces giving MoS_2 good lubricating properties. The d-orbital splitting in a trigonal prismatic crystal field has a singly degenerate lowest energy level with two doubly degenerate higher energy levels. As Mo^{4+} has 2d electrons, the lowest energy level is filled making MoS_2 diamagnetic and thus amenable to NMR observation. The spectrum obtained for MoS_2

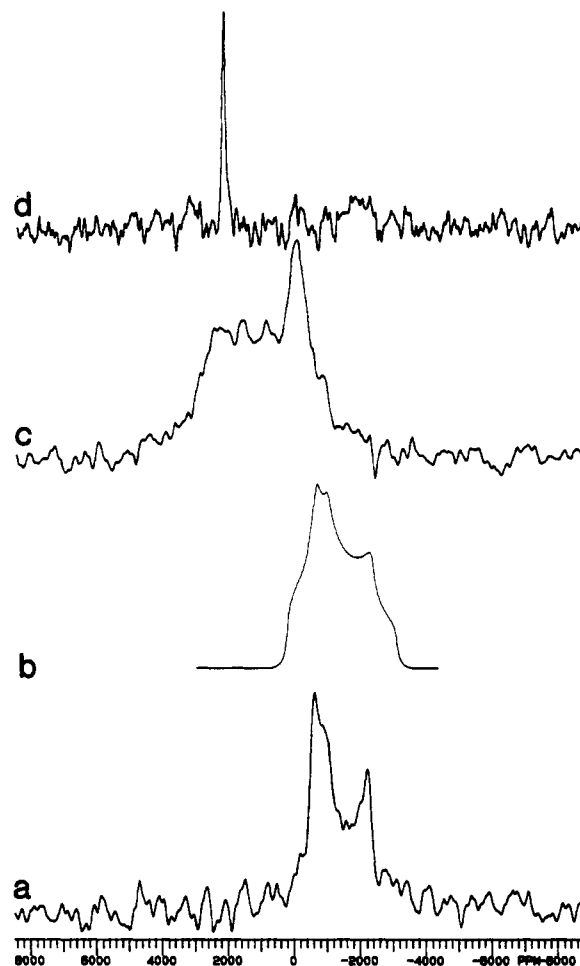


Figure 1. Static powder and simulated spectra of the central $\pm 1/2$ transition of the model compounds for the reduced and sulfided catalyst surfaces: (a) the spectrum of MoS_2 , 38 536 transients, recycle delay = 5 s, LB = 4000 Hz; (b) the simulation of the MoS_2 line shape produced by an IGC program; (c) the spectrum of MoO_2 , 9279 transients, recycle delay = 5 s, LB = 4000 Hz; (d) the spectrum of $(NH_4)_2MoS_4$, 6840 transients, recycle delay = 12 s, LB = 800 Hz. Note: the simulation is not on the same scale as the experimental line shape.

indicates that it has a high Q_{cc} , a low asymmetry parameter, and a considerable chemical shielding anisotropy. The singularity positions of the two observable discontinuities at -609 and -2300 ppm should make it easy to identify the presence of molecular MoS_2 in the catalyst samples. Figure 1b shows a simulation of the MoS_2 line shape corresponding to a Q_{cc} of 6.72 MHz, $\eta_Q = 0.16$, a chemical shielding interaction whose three principal components are $\sigma_{11} = -866$ ppm, $\sigma_{22} = 470$ ppm, $\sigma_{33} = 973$ ppm, and Euler angles $\alpha = -33^\circ$, $\beta = 67^\circ$, $\gamma = -40^\circ$. It should be noted that this is a perfect example of a line shape which cannot be simulated without the inclusion of the noncoincidence of the quadrupole and chemical shielding tensors. Also, the simulation contains shoulders at both extremes of the line shape which are not clearly represented in the experimental line shape. These shoulders are reduced in intensity in the experimental line shape owing to consequences of finite pulse length and the large width of the MoS_2 line shape.

During the reduction/sulfidation procedure, it is thought that one of the precursors to MoS_2 is MoO_2 . MoO_2 has been shown to consist of edge sharing distorted octahedra in which the structure of the MoO_2 strings brings about site inequivalence—two inequivalent molybdenum sites

(71) Takeuchi, Y.; Nawacki, W. *Schweiz. Mineral. Petrogr. Mitt.* 1964, 44, 105.

are found to be present.⁷² Thus, we have obtained the static spectrum of MoO₂ (Figure 1c) which displays a broad two-component resonance (fwhh = 88 kHz), corresponding to Q_{cc} values of about 6–7 MHz, and an axially symmetric asymmetry parameter ($\eta_Q = 0.0$) (simulated spectrum not shown). The chemical shift is to lower shielding with peak maxima appearing in the range +2400 to +9 ppm. As will be shown later, there is no corresponding resonance in any of the catalyst sample line shapes, thus ruling out the possibility of the presence of MoO₂ on the catalyst surface.

Another possibility is that the molybdenum is not reduced but simply sulfided. This could lead to $[\text{Mo}^{\text{VI}}\text{S}_4]^{2-}$; with this in mind we looked at a sample of (NH₄)₂MoS₄ (Figure 1d) which yielded an extremely narrow line ($W_{1/2} = 1.45$ kHz) at a chemical shift of -2181 ppm. The narrow line bears testimony to the high tetrahedral symmetry of $[\text{MoS}_4]^{2-}$.⁷³ Other mixed Mo^{VI}-O-S species were investigated but seemed to display relaxation time problems; i.e., they displayed long T_1 (spin-lattice relaxation times) values. Owing to this problem, spectra of these species could not be obtained. The isotropic chemical shifts of these mixed Mo-O-S species are known from liquid-state NMR²⁸ to be 497, 1067, 1654, and 2259 ppm for $[\text{MoO}_3\text{S}]^{2-}$, $[\text{MoO}_2\text{S}_2]^{2-}$, $[\text{MoO}_3\text{S}]^{2-}$, and $[\text{MoS}_4]^{2-}$, respectively. We may be able to obtain spectra of these species in the near future, when we have refined our initially successful attempts to cross polarize to ⁹⁵Mo.^{74–76}

Investigation of Sulfided/Reduced Catalyst Samples. Upon investigation of the catalyst samples, it has become apparent that the idea of MoS₂ being the predominant species present on the surface is not borne out by our results. We first of all investigated two 16% Mo-Al₂O₃ catalysts. The first of these had been uncalcined prior to the reduction/sulfiding process (Figure 2a). The simulated spectrum is shown in Figure 2c, corresponding to four components shown in the deconvoluted spectrum (Figure 2d). The quadrupole parameters corresponding to the components are displayed in Table II. A Gaussian function was used to represent the inhomogeneously broadened line which underlies the three major components. The component appearing at -150 ppm was due to a Q_{cc} of 3.19 MHz ($\eta_Q = 0.82$), the component of -600 ppm was due to a Q_{cc} of 3.13 MHz ($\eta_Q = 1.00$), and the third component, which yields singularities at -580 and -2140 ppm, corresponds to a Q_{cc} of 8.61 MHz ($\eta_Q = 0.07$). This third component has similar line shape characteristics to MoS₂, and hence we associate this species with surface adsorbed MoS₂. It should be noted that the quadrupole interaction is larger than was observed for the bulk MoS₂, indicating that the molybdenum is in a different environment. The deconvolution of the components can yield approximations as to the relative amounts of the different species present on the surface. We can assume that we are observing all the molybdenum on the surface because we have ascertained that we used a relaxation delay that was greater than $5T_1$ for all the components present on the surface. This was done by comparing the signal intensities of spectra obtained with relaxation delays of 50 and 500 ms, which turned out to be almost identical in signal intensity. In the case of this catalyst, only ~18% of the molybdenum is present in the MoS₂ phase and ~60% is present in the inhomogeneously

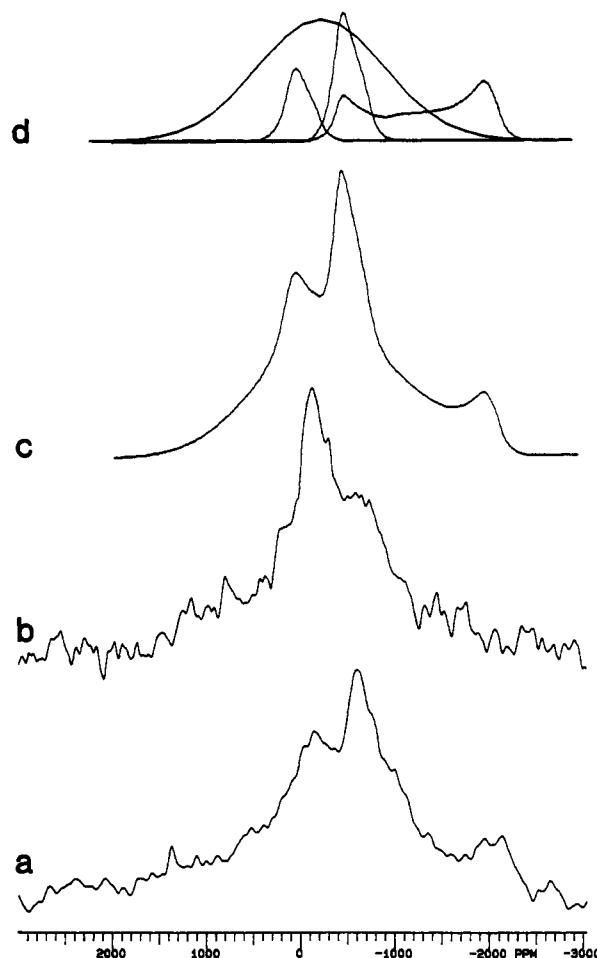


Figure 2. Static powder, MAS, and simulated spectra of the central $\pm 1/2$ transition of the reduced and sulfided, uncalcined 16% Mo-Al₂O₃ catalysts: (a) the static powder spectrum of the uncalcined, reduced and sulfided catalyst, 534 000 transients, recycle delay = 50 ms, LB = 2000 Hz; (b) the 4.5-kHz MAS spectrum, 642 546 transients, recycle delay = 50 ms, LB = 1500 Hz; (c) the simulated line shape; (d) the deconvolution of the four components of the line shape. Note: the simulation is not on the same scale as the experimental line shape.

broadened line shape caused by the presence of a range of species, ~14% is present as the unidentified component at -600 ppm, and ~8% is present as the phase at -150 ppm. These percentages have errors on the order of 10%. The inhomogeneously broadened line is assigned to a wide range of Mo(0, II, IV, and VI) species with oxygen, sulfur, and mixed ligand environments, the sum of whose line shapes is represented by the broad resonance. The component at -600 ppm is outside the Mo^{VI}-O and Mo^{VI}-O-S range; thus, we will associate this phase with a Mo^{IV}-O-S species which has been observed on the alumina surface in other studies. Figure 4b shows the 4.5-kHz MAS spectrum of the catalyst and demonstrates the narrowing of the component at ~-150 ppm.

The static powder spectrum of the corresponding 16% Mo-Al₂O₃ sample which was calcined prior to reduction and sulfidation is shown in Figure 3a. It looks similar to the spectrum observed previously for the uncalcined catalyst. This might be expected as the reducing/sulfiding process takes place at 400 °C and will, therefore, calcine the sample as the process proceeds, thus producing a similar species coverage of the surface being treated. The simulated spectrum is shown in Figure 3c and the corresponding deconvoluted spectrum is shown in Figure 3d. The quadrupole parameters of two of the deconvoluted components of this line shape are identical with those

(72) Magnéti, A. *Ark. Kemi, Mineral. Geol.* 1967, 24A, 1.

(73) Lapasset, J.; Chezeau, N.; Belouigne, P. *Struct. Rep.* 42A, 305.

(74) Edwards, J. C.; Ellis, P. D. *Magn. Reson. Chem.* 1990, 28, S59–67.

(75) Edwards, J. C.; Ellis, P. D. Submitted to *J. Phys. Chem.*

(76) Edwards, J. C.; Ellis, P. D. Unpublished results to be submitted for publication.

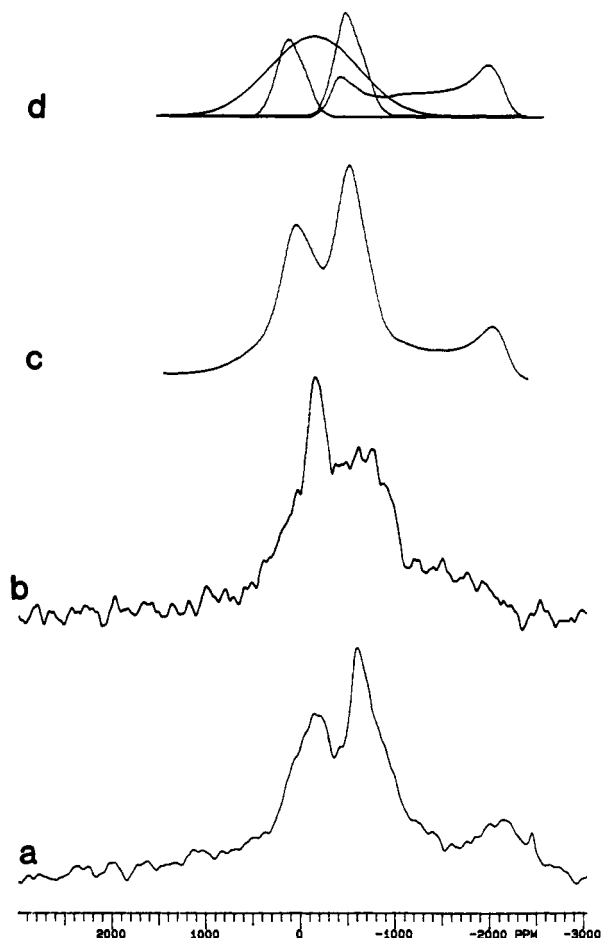


Figure 3. Static powder, MAS, and simulated spectra of the calcined 16% Mo-Al₂O₃, reduced and sulfided catalyst: (a) the static powder spectrum, 1.07×10^6 transients, recycle delay = 50 ms, LB = 2000 Hz; (b) the 4.5-kHz MAS spectrum, 735 398 transients, recycle delay = 50 ms, LB = 1500 Hz; (c) the simulated spectrum; (d) the deconvolution of the four components of the line shape. Note: the experimental and simulated spectra are not on the same scale.

obtained for the uncalcined catalyst (Figure 2), the only difference is the smaller value of Q_{cc} (8.30 MHz) obtained for the component with two singularities at around -600 and -2141 ppm (assigned MoS₂). The 4.5-kHz MAS spectrum (Figure 3b) again demonstrates the narrowing of the component at ~ -150 ppm.

Interestingly, the line shape analysis of the experimental line shapes leads to the extraction of a Q_{cc} for the MoS₂ phase which is much larger than observed in the bulk MoS₂ sample. This may indicate, not surprisingly, that the surface MoS₂ environment is very different to that found in the bulk salt.

The only noticeable difference between the static powder spectra of the two catalysts is yielded by the deconvoluted simulation spectrum. The relative intensities of the peak which appears at ~ -150 ppm and the broad underlying line shape are noticeably different in the two spectra, with 26% of the molybdenum present as the component to higher shielding (-600 to -2141 ppm) in the precalcined catalyst. The calcined catalyst contains a smaller broad resonance indicating the presence of relatively less unresolved Mo^{VI} or IV-O-S species (representing 43% of the molybdenum) than in the uncalcined catalyst. There also appears to be a considerable difference in the amounts of the molybdenum species responsible for the resonance at -150 ppm (13% present as this component in the calcined catalyst).

The resonance at -150 ppm is in the chemical shift range of the original "fresh" catalyst resonance, while the lines at -600 and -2141 ppm are about the same as those found in the MoS₂ spectrum. It should also be noted that no resonance appears in the 2180 ppm region thus ruling out the presence of [MoS₄]²⁻. The broad inhomogeneously broadened line underlying the spectrum indicates that there could also be a range of Mo^{VI}-O-S or Mo^{IV}-O-S species present. Thus we can assign the peaks at around -150 ppm to an unreduced/unsulfided Mo^{VI}-O species which was present in the "fresh" catalyst. The peaks at around -600 and -2141 ppm are the two discontinuities of a MoS₂ phase, while the broad underlying resonance is the sum of the contributions of many different Mo^{IV} and VI-O-S species and perhaps even Mo(II) and Mo(0) species. The identity of the third component, found at ~ -600 ppm, is thought to be MoOS based on the chemical shift range which is indicative of a Mo(IV) species intermediate between MoO₂ and MoS₂.

Ratnasamy et al.⁷⁷ in a gravimetric/IR study, claimed that they saw three different molybdenum species present on the surface of a reduced catalyst. They claimed there was a nonreducible phase of tetrahedral molybdenum, an easily reduced phase of bulk MoO₃, and an intermediately reducible state—probably adsorbed octahedral molybdenum. In our original study,¹ we also found the possible presence of these three forms of molybdenum on the surface of the "fresh" catalyst. Thus, we have an explanation of the reduced/sulfided catalyst spectrum. The peak due to an unchanged species that was present in the "fresh" catalyst, at -150 ppm, may correspond to the adsorbed tetrahedral molybdenum surface species that remained in the nonreduced form during the reduction/sulfidation process. This seems to be supported by the observed narrowing of this resonance during the MAS experiment, indicating the presence of a low Q_{cc} value species, such as an adsorbed tetrahedral molybdate. The component due to MoS₂ was caused by MoS₂ formed from octahedral molybdenum present in the uncalcined catalysts (primarily adsorbed octahedral molybdenum but also including heptamolybdate clusters or cluster fragments) and also the MoO₃-like species, found in the calcined "fresh" catalysts, which have been reduced and sulfided. The broad underlying, inhomogeneously broadened line shape is the sum of all the molybdenum environments on the surface which have been either partially reduced, partially sulfided, or reduced beyond the +4 oxidation state, to form Mo(II) and Mo(0) species.

In an attempt to see if lower loadings and variation of the pH of the impregnation solution used to prepare the "fresh" catalyst would effect the spectra, the spectra were obtained for two different 8% Mo-Al₂O₃ catalysts, which were both calcined prior to reduction/sulfidation but were prepared at different pH.

The first of these is an 8% Mo catalyst prepared at a pH of 5.2 and calcined prior to the reduction/sulfiding procedure (Figure 4a). The simulated spectrum and deconvoluted spectrum are shown in parts b and c of Figure 4, respectively. It can be seen that 23% of the molybdenum is present in the tetrahedral Mo^{VI}-O phase, 48% as the range of Mo^{0,II,IV,VI}-O-S species, 15% as MoOS, and 14% as the MoS₂ phase. At pH 5.2 the predominant species in the impregnation solution is the octahedral [Mo₇O₂₄]⁶⁻ species. The spectrum shows a sharp contrast to that obtained for the 16% Mo catalysts. The intensity ratio of the MoS₂ and unreduced tetrahedral molybdenum peaks

(77) Ratnasamy, P.; Ramaswamy, A. V.; Banerjee, K.; Sharma, D. K.; Ray, N. J. *Catal.* 1975, 38, 19.

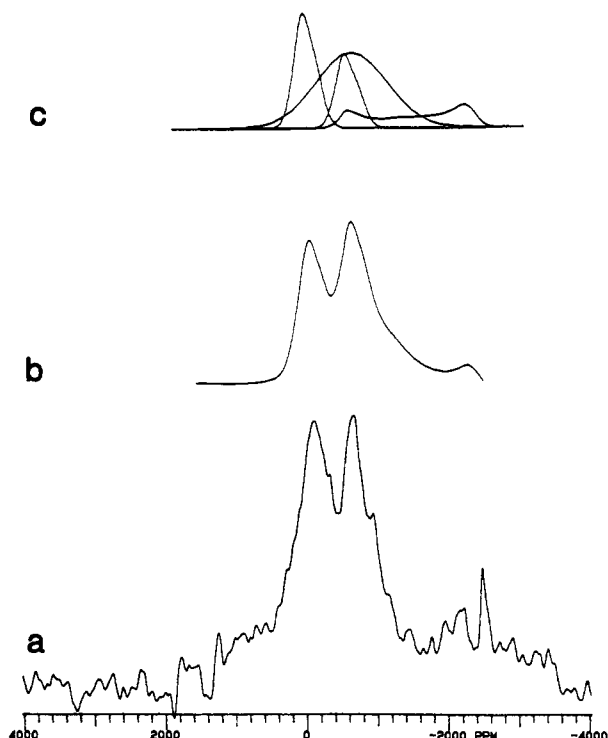
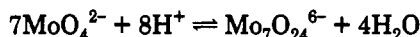


Figure 4. Static powder and simulated spectra of the central $\pm 1/2$ transition of the calcined 8% Mo- Al_2O_3 catalyst, prepared at pH 5.2: (a) static spectrum, 779 550 transients, recycle delay = 80 ms, LB = 2000 Hz; (b) simulated spectrum; (c) deconvolution of the four components of the line shape. Note: the simulated and experimental spectra are not on the same scale. is almost reversed. In the 16% Mo catalysts there appears to be more MoS_2 present than tetrahedral $\text{Mo}^{\text{IV}}\text{-O}$ by about a factor of 2–2.5:1. This difference can be explained by the fact that at higher loadings $\geq 16\%$ Mo there is a much larger concentration of octahedral molybdenum sites on the surface due to the precipitation of intact heptamolybdate clusters on the alumina surface,⁷⁸ which are readily reduced/sulfided to MoS_2 . Knözinger and Jeziorowski¹⁴ put forward the idea that, at pH 5.2, the isoelectric point of the alumina would cause dissociation of the predominant $[\text{Mo}_7\text{O}_{24}]^{6-}$ clusters to $[\text{MoO}_4]^{2-}$ (which is the predominant species present in solution above pH 8.0), as follows



Thus, the adsorbent is equilibrated to tetrahedral $[\text{MoO}_4]^{2-}$ by the basic nature of the alumina surface environment. Thus, in the lower loading catalysts you will observe adsorption of both octahedral and tetrahedral molybdenum. However, as the loading increases, the equilibrium reaction occurring at the surface would shift or stop as the basicity of the environment is reduced by the H^+ produced in the equilibrium reaction. Thus, at higher loadings one would expect, initially, to observe the adsorption of tetrahedral molybdenum over octahedral. Then, as the equilibrium reaction shifts, one would expect to see predominantly adsorption of octahedral molybdenum. At higher loadings, therefore, one would expect to see a relatively larger amount of octahedral molybdenum on the surface than in the lower loading catalysts. In turn, this should lead to the observation of higher relative amounts of MoS_2 in the high loading reduced/sulfided catalysts.

The second of these calcined 8% Mo- Al_2O_3 catalysts was prepared with an impregnation solution at pH 8.2.

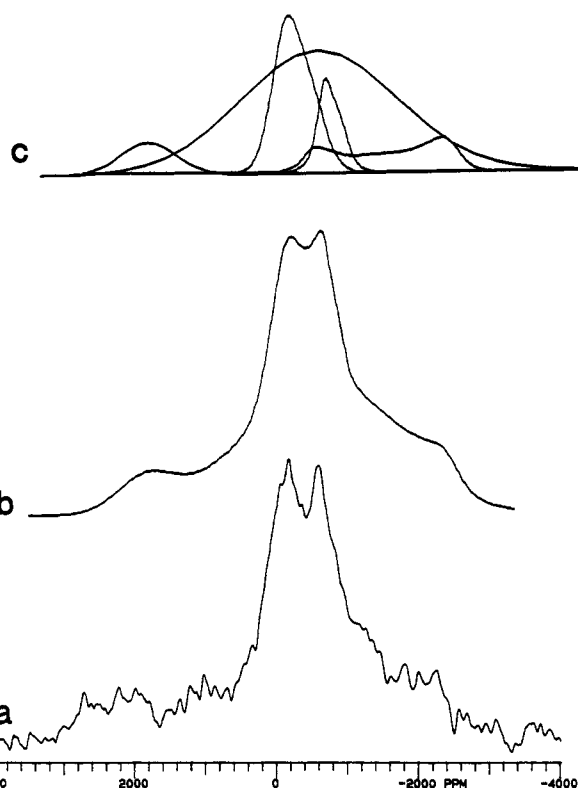


Figure 5. Static powder and simulated spectra of the $\pm 1/2$ central transition of the 8% Mo- Al_2O_3 catalyst prepared at pH 8.2: (a) static spectrum, 796 770 transients, recycle delay = 50 ms, LB = 2000 Hz; (b) simulated spectrum; (c) the deconvolution of the four components of the line shape. Note: the experimental and simulated spectra are not on the same scale.

The predominant species present in the impregnation solution is the tetrahedral $[\text{MoO}_4]^{2-}$. The spectrum (Figure 5a) shows a close similarity to the sample prepared at pH 5.2, mentioned previously. However, the surface hydroxyls do not present a mechanism for the equilibrium production of $[\text{Mo}_7\text{O}_{24}]^{6-}$ during the impregnation, at this pH. Thus, one would expect to observe the almost exclusive adsorption of tetrahedral molybdate in the “fresh” catalyst. This should then lead to a marked difference in the relative intensities of the two components at -115 and $-621/-2141$ ppm, in favor of the tetrahedral molybdenum in the reduced/sulfided catalyst. In practice, it is not as simple as this, and from the spectra of this reduced/sulfided catalyst the presence of MoS_2 bears testimony to the presence of octahedral molybdenum. However, it is clear from the relative intensities that some MoS_2 is present, the relative intensity of the component at -150 ppm is much greater than it was for the catalyst prepared at pH 5.2, in line with the presence of a higher proportion of tetrahedral molybdenum. This observation was also made in our study of “fresh” catalysts prepared at this pH.¹ It may be that a complex chemistry is occurring at the surface—perhaps the small fluctuations in the pH at the surface caused by the deprotonation of the hydroxyls by the solution OH^- , followed by charge balancing by the solution counterions (NH_4^+), causes the $[\text{MoO}_4]^{2-}/[\text{Mo}_7\text{O}_{24}]^{6-}$ equilibrium to favor $[\text{Mo}_7\text{O}_{24}]^{6-}$ and thus adsorption of octahedral molybdenum.

One difference in the two spectra of the “pH 5.2” and “pH 8.2” catalysts is that the catalyst prepared at pH 8.2 displays several resonances in the range 974, 1842, and 2171 ppm, which could indicate the presence of mixed $\text{Mo}^{\text{VI}}\text{-O-S}$ species, especially $[\text{MoS}_4]^{2-}$, or even the presence of MoO_2 . Figure 5b shows the simulated spectrum obtained from the IGC program, while Figure 5c shows

(78) Medema, J.; Van Stam, C.; de Beer, V. H. J.; Konings, A. J. A.; Koningsberger, D. C. *J. Catal.* 1978, 53, 386.

the deconvolution of the five-component line shapes which were used to describe the catalyst line shape. From the deconvoluted spectrum, we can see that the resonances at around 1842 ppm can be described as a Gaussian line shape representing 5% of the molybdenum present on the surface. The MoS_2 phase is present as 9% of the total molybdenum, and the sharply defined singularity at -2220 ppm led to a smaller calculated value of Q_{cc} (6.5 MHz) for this species. The tetrahedral $\text{Mo}^{\text{VI}}\text{-O}$ species was present as 19% of the total and the species at -215 ppm was present as 7% of the total. By far the greatest amount of molybdenum (59%) was found to be present as the range of species giving rise to the inhomogeneously broadened line shape, represented by a second Gaussian line shape.

It should be noted that in the lower loading catalysts, the relative intensity of the tetrahedral molybdenum peak at -150 ppm is much greater than the corresponding resonance in the higher loading catalysts. This perhaps indicates that two different adsorption regimes can occur. At lower loadings the favorable adsorption mechanism may be via the tetrahedral molybdenum, whereas the adsorption of octahedral molybdenum increases with increasing loading.

Spikelet-Echo Experiments. One other method of investigating the surface structure of the catalysts was used, namely spikelet-echo experiments. Such experiments can yield not only chemical shift differences (potentially scaled) of the various surface species but also dynamical information, yielding insights as to the surface binding and surface kinetics, of adsorbed species. This method was used previously¹ to obtain dynamic data on the surface species present in the "fresh" catalyst. From these experiments one hopes to obtain T_2 (or $T_{1\rho}$) information on the species present which will manifest itself in the line widths of the spikelets. It should be stressed, however, that the chemical shift data that is obtained is limited due to the scaling of the chemical shift that occurs due to the short cycle time of the echo train. The chemical shift of the species will be preserved if the π -pulse repetition rate frequency is small in comparison with the chemical shift separation in hertz. In this case, however, the pulse repetition rate is on the order of 3.30 kHz while the maximum chemical shift separation of the MoOS species, the range of unidentified molybdenum species, and the tetrahedral $\text{Mo}^{\text{VI}}\text{-O}$ species are on about the same order of magnitude. Thus, one would not expect to be able to distinguish these species on a chemical shift basis, and this is borne out experimentally. However the chemical shift range of MoO_2 and MoS_2 , compared to the other three species, might allow one to distinguish their presence on a chemical shift basis. Thus, one should be able to distinguish between different species both on a line width basis, and a chemical shift basis, by observing the extent of the spikelet spectra, the presence of superimposed "combs" of spikelets and the T_2 differences.

We have performed the spikelet-echo experiment on the two 16% $\text{Mo-Al}_2\text{O}_3$, as well as the used catalyst (see later). Parts a and b of Figure 6 show the spikelet spectra of the uncalcined and calcined 16% Mo catalysts, respectively. Both spectra show the presence of several, distinct adsorbed species, indicated by the interconnecting comb of modulo 3.3 kHz narrow resonances. The spectra do not readily demonstrate the presence of any dynamically active species. The spikelet spectra can be compared to the spikelet spectra obtained for the "fresh" catalysts,¹ and this allows one to determine if there are any similarities between the two. This comparison demonstrates the fact that the comb of intense spikelets extends across a much larger

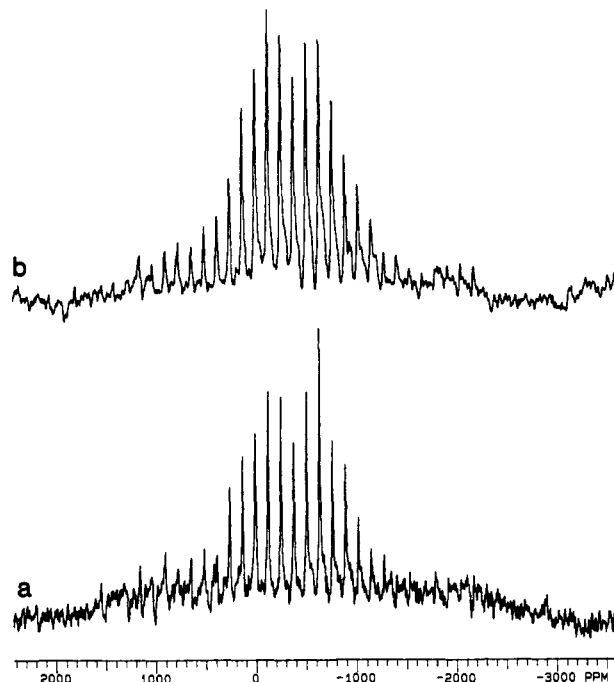


Figure 6. Spikelet-echo spectra obtained for the 16% $\text{Mo-Al}_2\text{O}_3$ catalysts: (a) uncalcined catalyst, 700 000 transients, recycle delay = 50 ms, LB = 150 Hz; (b) the calcined catalyst, 761 300 transients, recycle delay = 50 ms, LB = 150 Hz.

frequency range than is found in the "fresh" catalyst. This is indicative of the fact that the chemical shift range of three of the components (the $\text{Mo}^{\text{VI}}\text{-O}$, MoOS , and inhomogeneously broadened resonances) is not large enough to prevent the scaling of their chemical shifts. However, close inspection of the -600 to -2300 ppm range reveals the presence of a smaller comb of spikelets chemically shifted to higher shielding from the more intense spikelet comb. These small, chemically shifted spikelets represent MoS_2 . What is of interest is the increase in signal intensity between the catalyst which was calcined prior to reduction/sulfiding (Figure 6b) and that which was not (Figure 6a). The MoS_2 phase is much more prominent in the precalcined catalyst. These differences in intensity may be due to the presence of more statically adsorbed species in the precalcined catalysts and may indicate that the rolling base line of the uncalcined catalyst (Figure 6a) is due to dynamically active species.

Investigation of a Used Catalyst. Having performed some thiophene HDS kinetic measurements on a reduced and sulfided 12% $\text{Mo-Al}_2\text{O}_3$ catalyst, which had been calcined prior to being reduced and sulfided, we decided to investigate the state of a used catalyst. The spectrum we obtained (Figure 7a) clearly indicates the reduction in the intensity of the MoOS/MoS_2 resonances at -600 ppm. This is due to the slow deterioration of the catalyst over the period of the HDS experiment. This would seem to support MoS_2 (or perhaps MoOS) being the active site of the catalyst. Another difference in the spectrum is the relative intensity of the underlying inhomogeneously broadened line. Its decrease in intensity would tend to support the idea that the MoOS/MoS_2 has decomposed to an unspecified species thus causing a reduction in the efficiency of the catalyst. Thus, one cannot speculate from this result as to which of the MoS_2 or MoOS species is the active phase in the catalyst.

The idea of the partial decomposition of both the MoOS and MoS_2 phases is supported by the spikelet spectra obtained for this sample (Figure 7b). The spikelets in the -509 to -1022 ppm range are much reduced in comparison

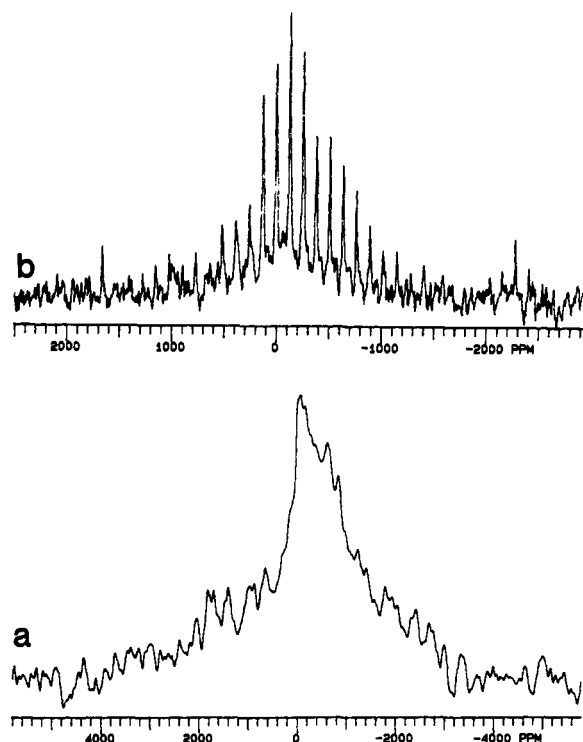


Figure 7. Static powder and spikelet-echo spectra of the used 12% Mo-Al₂O₃ catalyst: (a) static powder spectrum, 2×10^6 transients, recycle delay = 50 ms, LB = 2000 Hz; (b) the spikelet-echo spectrum, 700 000 transients, recycle delay = 40 ms, LB = 200 Hz.

with the spectra obtained for the reduced and sulfided 16% Mo-Al₂O₃ catalysts, as are the chemically shifted spikelets in the -1022 to -2290 ppm range, perhaps indicating the loss of parts of MoOS and MoS₂ phases. Another interesting feature is the relative increase in the amount of dynamic species (represented by the broad underlying component) present, compared to the spikelet spectra obtained for the reduced and sulfided 16% Mo-Al₂O₃ catalysts.

One hypothesis for the loss of intensity in the MoOS/MoS₂ phases is that use of the catalyst in HDS reactions slowly breaks up the surface bound MoS₂ and MoOS phases into smaller, dynamically active phases which are not as effective in the HDS processes.

Promoted Catalysts. Cobalt Promoted "Fresh" Catalysts. First, we will concentrate on the "fresh" Co-Mo-Al₂O₃ catalysts. The colors of the catalyst samples can suggest the type of bulk species formation that has occurred during the impregnation and drying processes, when compared to the colors of the various model compounds that have been suggested to be present on the surface. CoMoO₄ is purple (or olive green), CoAl₂O₄ is blue, CoO is brown, Co₂O₃ is brown. All the uncalcined fresh Co-Mo catalysts that were made had a purple coloration which intensified with loading, while the calcined catalysts were a blue color. The colors of the catalyst suggest that the predominant cobalt species is CoAl₂O₄. (The promoted reduced and sulfided catalysts were black, which does not allow easy interpretation, as all our reduced/sulfided catalysts are black). As we have mentioned previously, the paramagnetic cobalt ion could effect the observed ⁹⁵Mo resonance by either broadening, or shifting, the resonance. In Figure 8 we show the effect of an 8% Co loading, prepared by co- or separate impregnation, with 12% Mo-Al₂O₃. The unpromoted catalyst (Figure 8a), has a line width (fwhh) of 13.39 kHz, while the coimpregnated 8% Co-12% Mo-Al₂O₃ catalyst (Figure

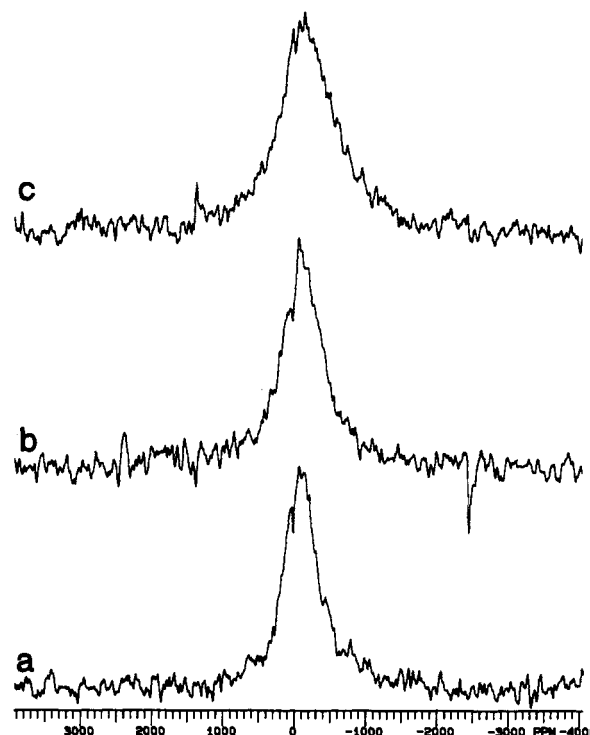


Figure 8. Central $\pm 1/2$ transition static powder line shapes of uncalcined 12% Mo-Al₂O₃ catalysts, with and without Co promoter ions: (a) without Co, 300 000 transients, recycle delay = 50 ms; (b) 8% Co present, prepared by coimpregnation, 190 000 transients, recycle delay = 40 ms; (c) 8% Co present, prepared by separate impregnation, 400 086 transients, recycle delay = 40 ms. Line broadening was 750 Hz in each case.

8b) has a line width of 15.16 kHz, and the 8% Co-12% Mo-Al₂O₃ prepared by separate impregnation (Figure 8c) has a line width of 22.88 kHz. These, and other line width values, are given in Table III. From our previous work on these "fresh" catalyst systems,¹ the typical values for the uncalcined catalyst line widths were on the order of 13-15 kHz. What is clear, from our results here, is that there is a definite broadening of the resonances upon addition of cobalt and that the broadening is dependent on the method of impregnation. It would appear that there is a much greater Co-Mo interaction in the catalysts prepared by separate impregnation which is demonstrated by the broader resonance owing to a larger paramagnetic coupling to the ⁹⁵Mo. This difference is not, however, observable by simple observation of the color of the catalysts, which look identical for both methods of impregnation.

From an integrated signal intensity stand point, there is not much difference in the signal intensities of the two promoted catalysts. However they do differ from the intensity observed in the unpromoted catalyst. In the coimpregnated catalyst one is observing 72% of the molybdenum, whereas in the separately impregnated catalysts one is observing only 64% of the molybdenum. Note, the error involved in these integrated signal intensities is around 10%; thus, the two catalysts are equal in intensity to within experimental error. These intensity figures were obtained by comparing the promoted catalyst integrated signal intensities with the signal intensity from an unpromoted 12% Mo-Al₂O₃ and adjusting for the weight of the sample.

Investigation of the calcined catalysts (Figure 9) yields some results which, again, are in contrast to the results that were obtained in our previous investigation of "fresh" catalysts.¹ The unpromoted catalyst (Figure 9a), shows a line width of 21.47 kHz. This line width increase, upon

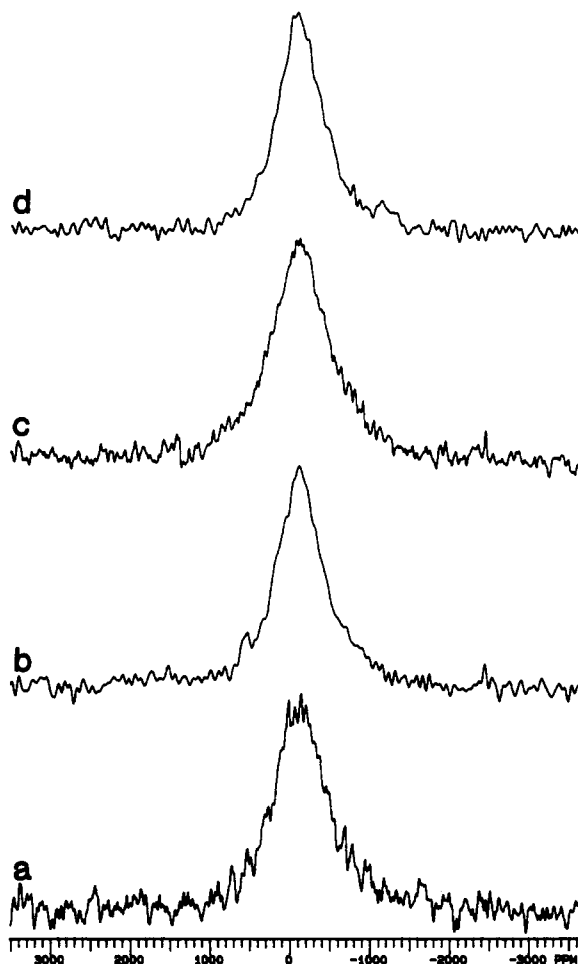


Figure 9. Central $\pm 1/2$ transition static powder line shapes of calcined 12% Mo- Al_2O_3 catalysts, with and without Co promoter ions: (a) without Co, 267 000 transients; (b) 8% Co present, prepared by coimpregnation, 460 815 transients; (c) 8% Co present, prepared by separate impregnation, 490 000 transients; (d) 4% Co present, prepared by separate impregnation, 459 554 transients. In each case the recycle delay was 50 ms, and the line broadening was 750 Hz.

calcination (13.39–21.47 kHz), is consistent with the results obtained previously for all the unpromoted catalysts, which all showed such an increase upon calcination. The coimpregnated 8% Co-12% Mo- Al_2O_3 catalyst (Figure 9b) also increased in line width by 2.16 kHz. However, the separately impregnated 8% Co-12% Mo- Al_2O_3 (Figure 9c) and 4% Co-12% Mo- Al_2O_3 catalysts decreased considerably in line width (~ 5 kHz) upon calcination, to line widths comparable to those observed for the non-promoted catalysts. This decrease could arise from several possibilities for the chemistry occurring at the surface: The cobalt-molybdenum paramagnetic interaction could be occurring across large distances (>20 Å), via the water molecules present on the uncalcined alumina surface which could act as a dipolar bridge, allowing magnetization to flow from the relatively far removed cobalt to the molybdenum. Upon calcination this water is removed, thus removing the paramagnetic interaction and causing the line widths to narrow. Another possibility is that the cobalt is sequestered by the surface alumina during the calcination process to form a CoAl_2O_4 , which would account for the blue coloration of these catalysts. Alternatively, the cobalt becomes more intimately associated with the molybdenum upon calcination and removes a component from the spectrum, leaving a narrowed resonance due to the molybdena not associated with the cobalt. Why the

paramagnetic interaction only apparently dominates the separately impregnated catalysts is not difficult to rationalize. The integrated signal intensities of the uncalcined catalyst line shapes informs us that we are losing approximately 30% of the molybdenum signal in both cases, and for the calcined catalysts one is observing 72% of the molybdenum in the separately impregnated catalyst and 82% of the molybdenum in the coimpregnated catalyst (again, the error associated with the intensity values is $\sim 10\%$). These are very similar values and do not reveal any striking differences between the two types of catalyst. What is interesting is that more signal is observed after calcination, indicating that hydroxyl dipole-bridge coupling mechanism, and the alumina sequestration of cobalt, may in fact be occurring. However, it seems unlikely that one is losing a component due to a stronger paramagnetic interaction. It would appear that the losses in signal that occur in the calcined catalysts, compared to the unpromoted catalyst, reflect the relative amounts of the molybdenum-cobalt interaction species that can be found in the two types of catalyst. Thus, it must be the surface chemistry involved in the two methods of impregnation that is causing the differences in the line shape behavior and the relative integrated signal intensities that are observed. As will be explained below, the differences can be rationalized if one considers certain adsorption scenarios that could occur in the two impregnation methods.

In the separate impregnation method, the molybdena is adsorbed to the γ -alumina surface by condensation reactions with the alumina hydroxyls. The 12% Mo- Al_2O_3 catalyst represents a $3/4$ monolayer coverage, although in reality, the coverage will be considerably less owing to the effects of multilayer formation and cluster deposition. Thus, when the $\text{Co}(\text{NO}_3)_2$ solution is used to impregnate the molybdena-alumina catalyst, the Co^{2+} is likely to adsorb to, or interact with, either the alumina surface or the molybdena surface. Thus, a close arrangement of cobalt on molybdena species may account for the paramagnetic broadening of the ^{95}Mo resonance. Upon calcination, the cobalt could be partially sequestered by the alumina surface to form CoAl_2O_4 , or there could be formation of Co-Mo interaction species which we are not observing. Attempts to observe the ^{95}Mo spectrum of a Co-Mo interaction species, namely CoMoO_4 , were unsuccessful, probably owing to the paramagnetic interaction that must be involved in this species. Therefore, it is unlikely that one would observe its formation on the alumina surface. Thus, what we may be observing in the calcined catalysts prepared by separate impregnation is the subsurface molybdena and the surface molybdena that has not been involved in a reaction to form a Co-Mo interaction species, such as CoMoO_4 . One would expect these molybdena, removed from any cobalt interaction, to yield a line shape similar to that of the unpromoted catalyst. In other research,⁷⁹ we have found that the electric field gradient (EFG) of the surface molybdena species, which are coordinated to one to two hydroxyls, is greater than that observed in the subsurface molybdena species. This was found by performing *ab initio* molecular orbital calculations on hypothetical $[\text{MoO}_6]^{6-}$, $[\text{MoO}_4]^{2-}$, and $[\text{MoO}_3\text{OH}]^-$ and comparing the magnitudes and asymmetry parameters of the calculated EFG tensors. In other work performed on aluminas,^{79,80} this trend was demonstrated by the simulation of ^{27}Al resonances obtained exclusively from surface alumina sites by cross polarization from the surface hydroxyls. Thus, if these

(79) Huggins, B. A.; Ellis, P. D. Unpublished results.

(80) Morris, H. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 6045.

calculations are applicable to the surface situation, removal of a large portion of the surface molybdena resonances, in the separately impregnated catalyst, by the paramagnetic interaction, might yield a narrower resonance due to the lower Q_{cc} values associated with the subsurface molybdena species.

In the case of the coimpregnated catalysts, the molybdenum and cobalt ions will compete with each other to coordinate to the surface. There will be preferential adsorption of cobalt at Lewis base sites⁸¹ and adsorption of molybdena via condensation reactions. In contrast to the separately impregnated catalyst, the molybdena will be deposited on the surface on top of a relatively large number of the cobalt promoter ions. Therefore, one can expect a much greater interaction between the cobalt and the subsurface molybdena species, along with a reduction of the cobalt interaction with the surface molybdena species, in the coimpregnated catalysts. This situation probably leads to as much higher formation of CoAl_2O_4 in these catalysts, upon calcination. If the CoAl_2O_4 is stable to reduction/sulfidation treatment, these possible adsorption mechanisms could be important in our continuing discussion of the promoted reduced/sulfided catalysts. Also, on the basis of the molecular orbital calculation results, one would expect the line shape behavior of these catalysts to be very similar to the unpromoted catalysts, as one is losing paramagnetically coupled molybdena resonances from both the surface and subsurface layers.

Another interesting observation was the presence of some structure not observed previously in the calcined catalyst line shapes, for the 8% Co-12% Mo- Al_2O_3 (Figure 9b at ~ 550 ppm), and 4% Co-12% Mo- Al_2O_3 (Figure 9d at ~ -1150 ppm) promoted catalysts. Whether these singularities represent line shape contributions from Co-Mo species is a question that cannot be answered based on the results at our disposal.

Spikelet-Echo Experiments Performed on Cobalt Promoted "Fresh" Catalysts. We ran the spikelet-echo experiment on the cobalt promoted, uncalcined, "fresh" catalysts, and Figure 10 shows the comparison of the spectra obtained for the unpromoted 12% Mo- Al_2O_3 (Figure 10a), the 8% Co-12% Mo- Al_2O_3 (coimpregnation, Figure 10b), and the 8% Co-12% Mo- Al_2O_3 (separate impregnation, Figure 10c). As can be seen from the spectrum of the unpromoted catalyst, there are "spikelet combs" indicating the presence of at least two species and possibly a third, which are chemically shifted enough that the chemical shift is not scaled by the experiment. In all the spectra the most intense spikes appear at 267, 130, 1, -134, -257, -400, and -530 ppm. The less intense comb of spikelets appear to higher shielding at -53, -184, -310, -448, and -562 ppm. Both the species are statically adsorbed species; however, the species responsible for the most intense spikes appear to have longer T_2 values associated with them as they are narrower than the less intense spikes. The less intense spikes may be caused by Al_2MoO_4 , while the more intense spikes are caused by adsorbed molybdena species with similar chemical shifts.

The promoted catalysts display a much more varied chemistry, especially the catalyst prepared by coimpregnation of the catalyst. With the coimpregnated catalyst, the spikes at higher shielding (-53, -184 ppm, etc.) are much more intense than in the unpromoted catalyst, and there are at least two more features to the line shape, namely a broad underlying component, and a new range of spikelets to lower shielding from the most intense spikelets, at 178, 50, and -84 ppm. The broad underlying

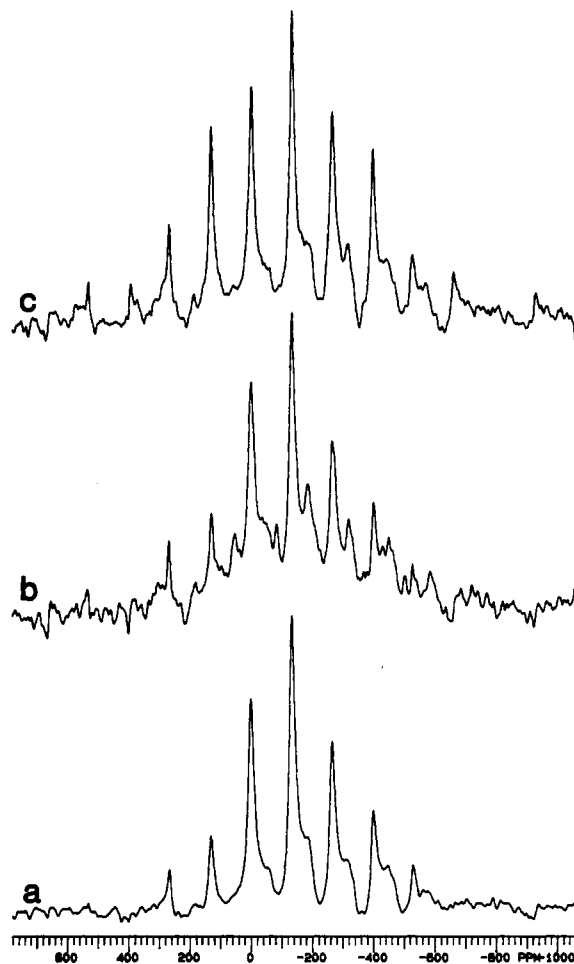


Figure 10. Spikelet-echo spectra obtained for the uncalcined 8% Co-12% Mo- Al_2O_3 catalysts: (a) unpromoted 12% Mo- Al_2O_3 catalyst, 100 000 transients; (b) 8% Co-12% Mo- Al_2O_3 catalyst prepared by coimpregnation, 250 000 transients; (c) the 8% Co-12% Mo- Al_2O_3 catalyst prepared by separate impregnation, 200 000 transients. In each case the recycle delay was 50 ms, and the line broadening was 200 Hz.

component is due to a molybdenum phase whose T_2 relaxation time has been reduced by contact with the cobalt. The new range of spikelets is a new species that we have not seen before. The most intense spikelets are twice as broad (805 Hz) as those observed in the unpromoted catalyst (425 Hz), again indicating a general decrease in the T_2 relaxation times of most of the molybdenum on the surface.

In comparison, the spikelet spectrum of the separately impregnated catalyst does not appear to be as rich in chemistry differences from the unpromoted catalyst as the coimpregnated catalyst. It looks basically the same as the unpromoted catalyst except that the most intense spikes extend to higher shielding with spikes appearing at -664 and -700 ppm. Also, some weak spikelets appear to unusually low shielding for Mo(VI) species, at 182, 392, and 532 ppm. This may be a paramagnetically shifted $\text{Mo}^{\text{VI}}\text{-O}$ species.

From these results, it appears that the broadening of the solid-echo static powder line shapes, observed in the coimpregnated catalysts, is due to a reduction of the T_2 relaxation time. The chemistry involved in the formation of this catalyst is more complicated than that observed for the separately impregnated catalyst. In the case of the separately impregnated catalyst, the same basic molybdenum environments appear to be present as in the unpromoted catalyst although the homogeneous broad-

(81) Knözinger, H.; Ratnasamy, P. *Catal. Rev.—Sci. Eng.* 1978, 17, 31.

ening appears to be greater; i.e. there is an increase in the quadrupole interaction which is giving rise to broader lines. One must, however, be aware that similar chemistry may be occurring in both catalysts. The differences that one observes may be caused by the average cobalt-molybdenum distance. In the coimpregnated catalysts, one may have a greater average value for the cobalt-molybdenum distance (as a result of adsorbate islanding) whose effect upon the line shapes can be discerned in the T_2 values of the system, as they do not interact so strongly as to remove the molybdena signal.

On the other hand, the cobalt ions may be more closely associated with the surface molybdenums in the separately impregnated catalysts, leading to the broadening, or complete removal, of the signal from the spikelet experiment line shape. Another difference in the chemistry is the presence of subsurface Al-Co-Mo interaction species, which may be contributing to the spikelet spectrum of the co-impregnated catalyst.

Investigation of Cobalt Promoted Reduced/Sulfided Catalysts. As stated previously, in our investigation of these catalyst samples we must take the philosophy that we are interested in what is not observed when the catalysts are promoted with cobalt. We must compare the results that we obtain for the promoted catalysts with the results of the unpromoted reduced/sulfided catalysts. Figure 11a shows the static powder spectrum of a 16% Mo- Al_2O_3 catalyst which was reduced and sulfided. The reduced/sulfided 8% Co-12% Mo- Al_2O_3 catalyst, prepared by coimpregnation (Figure 11b), shows quite clearly the presence of MoS_2 . In contrast, the 8% Co-12% Mo- Al_2O_3 (Figure 11c) and 4% Co-12% Mo- Al_2O_3 (Figure 11d) prepared by separate impregnation show a much reduced MoS_2 resonance, if at all. This is in line with the hypothetical adsorption mechanisms described previously. The MoS_2 in the separate impregnation catalysts must be closely associated with the cobalt present, while in the coimpregnation catalyst the cobalt is present predominantly as CoAl_2O_4 and has a lesser interaction with the MoS_2 phase. This might explain why it has been found that the separate impregnation method produces catalysts which have much greater reaction rates than those produced by coimpregnation. The promotion by the cobalt occurs by the interaction of cobalt with the edges of the active MoS_2 crystallites.

Finally, the singularity present at -140 ppm (Figure 11a,b) has been assigned to adsorbed, tetrahedral $\text{Mo}^{\text{VI}}\text{O}$ which remains unchanged by the reducing/sulfiding procedure. In the case of the 8% Co-12% Mo- Al_2O_3 catalyst, prepared by separate impregnation, the remaining resonance at -140 ppm should correspond to this same species. In other work performed on the "fresh" catalysts,¹ we compared the slow spinning (4-5 kHz) MAS spectra of "fresh" catalysts prepared with impregnation solutions at pH 5.2 and 9. These catalysts should have predominantly octahedral and tetrahedral species present on the alumina surface, respectively. It was found that the slow spinning MAS spectra obtained for the two catalysts could not correspond to the same species and that one was observing peak maxima corresponding to octahedral molybdena at \sim -200 ppm and tetrahedral molybdena at \sim -100 ppm.¹ We have compared the 4.6-kHz MAS spectrum of the 8% Co-12% Mo- Al_2O_3 catalyst, prepared by separate impregnation (Figure 12c), with the slow spinning speed MAS spectra of the fresh uncalcined catalysts prepared at pH 5.2 (Figure 12a) and pH 9 (Figure 12b). As one can see, the reduced and sulfided 8% Co-12% Mo- Al_2O_3 catalyst is very similar in shape, and in

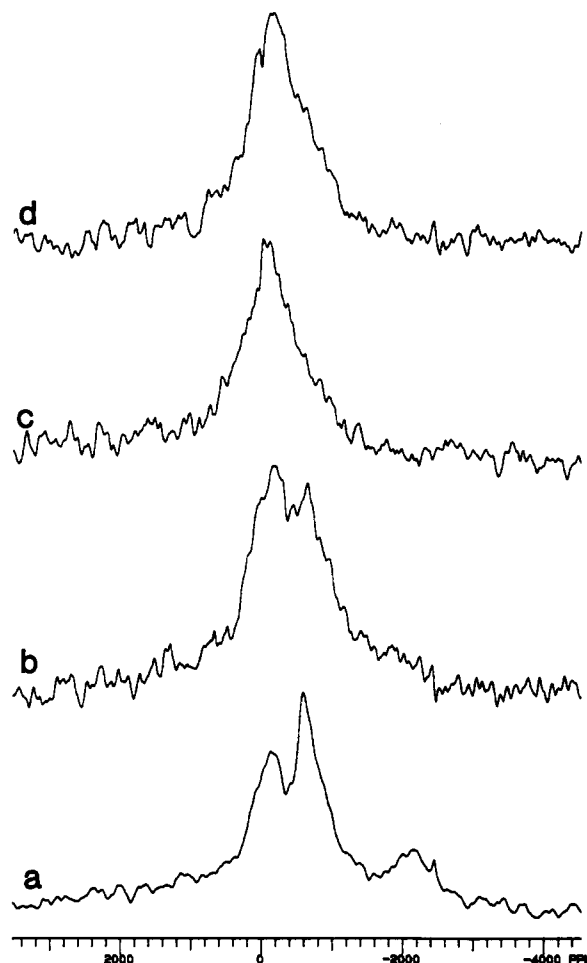


Figure 11. Central $\pm 1/2$ transition static powder spectra of reduced and sulfided Mo- Al_2O_3 catalysts, with and without cobalt promoter ions: (a) 16% Mo, without Co, 1070 000 transients, recycle delay = 60 ms, LB = 2000 Hz; (b) 12% Mo-4% Co, prepared by coimpregnation, 825 370 transients, recycle delay = 40 ms, LB = 1500 Hz; (c) 12% Mo-4% Co, prepared by separate impregnation, 513 333 transients, recycle delay = 40 ms, LB = 1500 Hz; (d) 12% Mo-8% Co, prepared by separate impregnation, 579 711 transients, recycle delay = 40 ms, LB = 1500 Hz.

the chemical shift of the peak maxima, to the catalyst prepared at pH 9 (Figure 12b). This supports the previous assignment of these resonances in the "fresh" catalyst and the reduced and sulfided catalysts to the tetrahedral Mo(VI) oxide.¹

Cesium and Potassium Promoted Catalysts. We have obtained the solid-state ^{95}Mo NMR spectra of Cs_2MoO_4 (Figure 13), as this has been postulated to be present on the surface of the calcined cesium promoted catalyst, from thermogravimetric analysis, NO chemisorption, and FT-IR results.⁴⁶ However, there was no direct evidence to support this hypothesis. The ^{95}Mo NMR resonance of Cs_2MoO_4 is typical of a tetrahedrally coordinated molybdate, with its narrow (fwhh = 2.4 kHz) line shape indicative of the low Q_{cc} involved. The peak maximum appears at a shift of -19.6 ppm. In the uncalcined promoted catalysts (Figure 14b,c), one does not observe a narrow Cs_2MoO_4 resonance. However, when the 16% Cs (Figure 14b) and 32% Cs (Figure 14c) loading promoted catalysts are compared with the unpromoted catalyst (Figure 14a), although the fwhh are similar (see Table III), there is a definite overall broadening of the promoted catalyst line shapes, especially at the base of the line shape. Unlike the cobalt, the cesium promoter is diamagnetic, and thus one is observing all the molybdenum on the

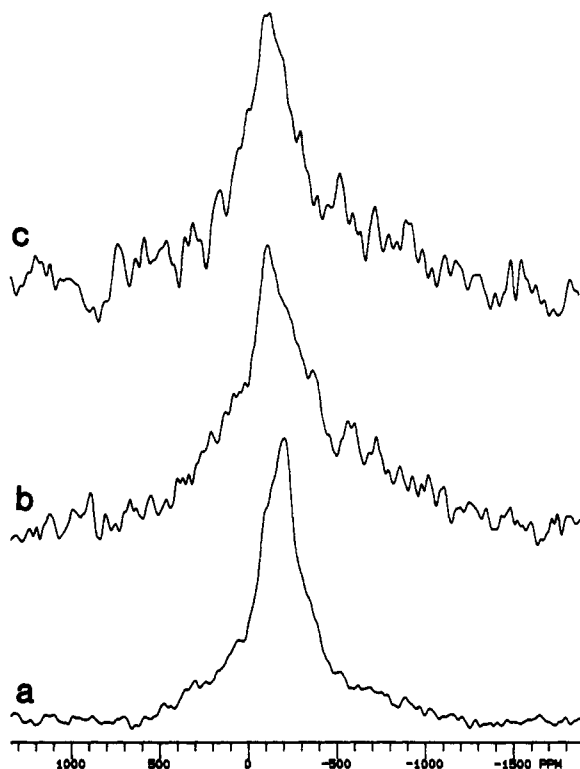


Figure 12. Comparison of the central $\pm 1/2$ transition magic angle spinning spectra of 12% $\text{Mo-Al}_2\text{O}_3$ catalysts, prepared at different impregnation solution pH, and a promoted catalyst prepared by separate impregnation: (a) 4.4-kHz MAS of 12% Mo catalyst prepared at pH 5.2, 386 000 transients; (b) 4.2-kHz MAS of 12% Mo catalyst prepared at pH 9.0, 387 000 transients; (c) 4.57-kHz MAS of 8% Co-12% Mo prepared at pH 5.2 and then reduced and sulfided, 715 946 transients. The recycle delay was 40 ms and the line broadening used was 750 Hz.

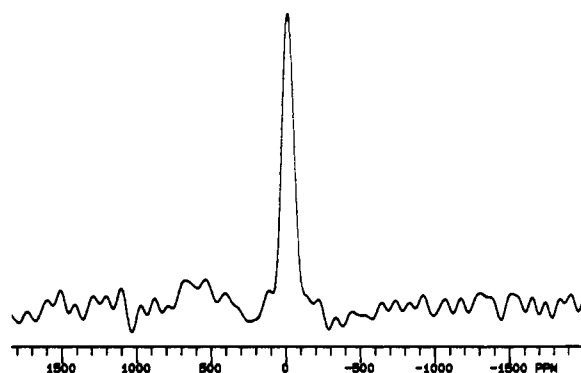


Figure 13. Static powder spectrum of Cs_2MoO_4 , 12 500 transients, recycle delay = 5 s, 100-Hz line broadening.

surface (supported by the integrated intensity data obtained from our experiments). Thus, the broadening could be due to one (or both) of two factors. The cesium ions could be interacting with the molybdena species in such a way that they are causing distortion of the molybdenum environment, and thus producing a larger Q_{cc} .⁷⁰ Alternatively, they could be donating electron density to the molybdenum center and thus perturbing the electric field gradient about the molybdenum producing a larger Q_{cc} .

The calcined catalysts (Figure 15), however, clearly show that upon calcination the Cs-Mo interaction species is changed to Cs_2MoO_4 . In the unpromoted catalysts (Figure 15a), one always observes an increase in the line width upon calcination, as the surface molybdena are polymerized via condensation reactions. The promoted catalysts, however, when $\text{Cs}/\text{Mo} > 1$, narrow considerably to line

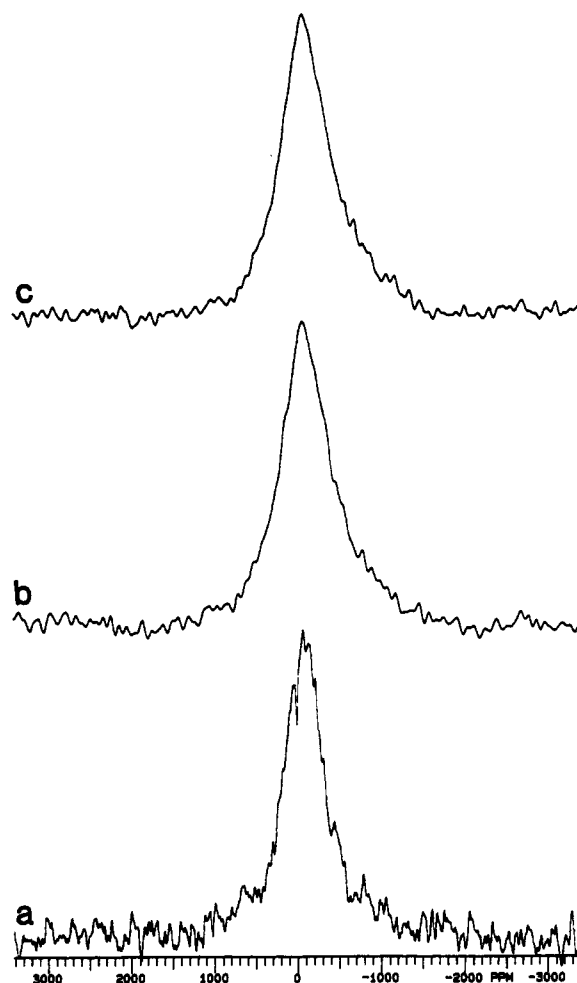


Figure 14. Static powder spectra of uncalcined 12% $\text{Mo-Al}_2\text{O}_3$ catalysts: (a) with no promoter ion, 300 000 transients, recycle delay = 50 ms; (b) with 16% Cs (w/w), 564 871 transients, recycle delay = 40 ms; (c) with 32% Cs (w/w), 724 892 transients, recycle delay = 40 ms. A line broadening of 750 Hz was used for all spectra.

widths comparable to that observed for the Cs_2MoO_4 resonance (see Table III). The peak maxima position of these catalysts also moves to lower shielding, toward the shift observed for the Cs_2MoO_4 model compound. The amount of molybdena which undergoes this phase transformation to tetrahedral molybdate is dependent on the atomic ratio of the promoter ion and the molybdena. At low loadings, $\text{Cs}/\text{Mo} < 1$ (8% Cs, Figure 15b), most of the molybdena is unchanged and a line shape similar to that of the unpromoted catalyst is obtained, although a small amount of tetrahedral molybdate is visible in the line shape at ~ -65 ppm. At moderately high cesium loadings ($\text{Cs}/\text{Mo} > 1$, 16% Cs, Figure 15c), a large proportion of the molybdena is present as tetrahedral molybdate (resonance peak maximum at -42 ppm), indicated by the narrow resonance which is superimposed on the broader resonance caused by unchanged surface polymerized molybdena. At $\text{Cs}/\text{Mo} > 2$ (32% Cs, Figure 15d), almost all the molybdenum is present as tetrahedral molybdate, with the tetrahedral resonance peak maximum at -13 ppm, and only a very small underlying broad resonance is observable. These levels of interaction are in agreement with the results obtained by O'Young.⁴⁶ However, where O'Young could only deduce the presence of Cs_2MoO_4 by indirect means, we can directly observe the narrow tetrahedral molybdenum resonance, and by simulation one could decon-

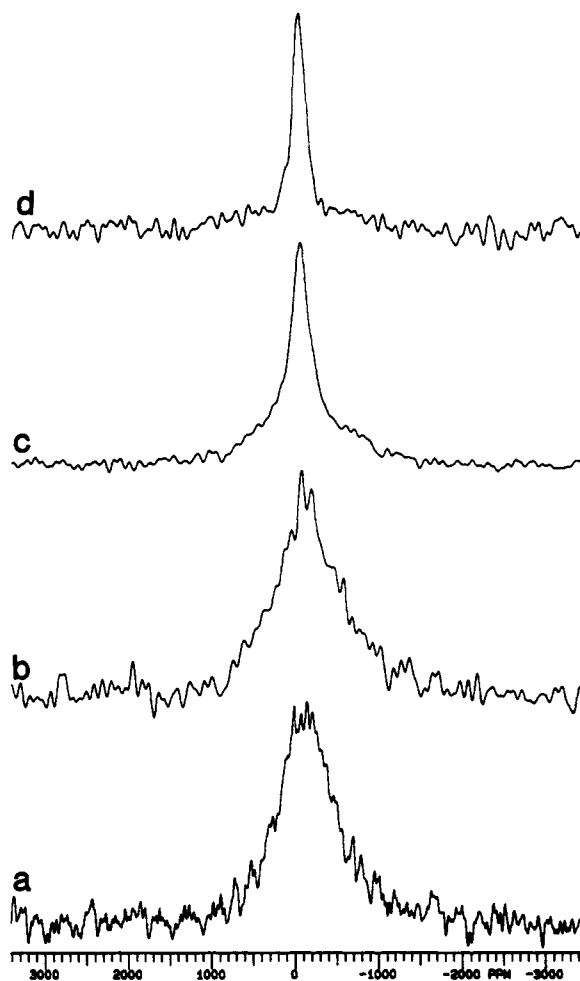


Figure 15. Static powder spectra of calcined 12% Mo-Al₂O₃ catalysts: (a) without promoter ions, 267 000 transients, recycle delay = 50 ms; (b) 8% Cs, 488 930 transients; (c) 16% Cs, 590 443 transients; (d) 32% Cs, 473 160 transients. For all spectra a line broadening of 750 Hz was used, and for the promoted catalysts the recycle delay was 40 ms.

volute the components of the line shape and obtain the relative amounts of Cs₂MoO₄ and unchanged surface molybdena.

In order to ascertain if the same phase transformation occurred from surface bound molybdena to alkali-metal molybdate upon calcination of potassium promoted catalysts, we obtained the static powder spectrum of a 32% K-12% Mo-Al₂O₃ catalyst (Figure 16a). As can be seen from the narrow resonance (fwhh = 2.97 kHz) that is observed, there was indeed formation of K₂MoO₄. However, there appear to be two singularities in the spectrum at 14 and -33 ppm. This may indicate the formation of two types of K₂MoO₄ on the surface with different chemical shifts.

Also in Figure 16, we have the comparison of the static (Figure 16b) and 4-kHz MAS (Figure 16c) NMR spectra of the 32% Cs-12% Mo-Al₂O₃ catalyst with the 4-kHz MAS spectrum obtained for the Cs₂MoO₄ model compound (Figure 16d). The MAS spectra clearly indicate that there is Cs₂MoO₄ present on the surface of the promoted catalyst, with the peak maxima appearing at -10 and -65 ppm for the catalyst sample and at -5 and -50 ppm for the Cs₂MoO₄ sample. Both samples demonstrate the effective narrowing (see Table III) of tetrahedral line shapes which occurs during MAS experiments.^{1,70}

Spikelet-Echo Experiments Performed on Cesium Promoted Catalysts. In order to ascertain if the broadening observed in the *uncalcined* cesium promoted cat-

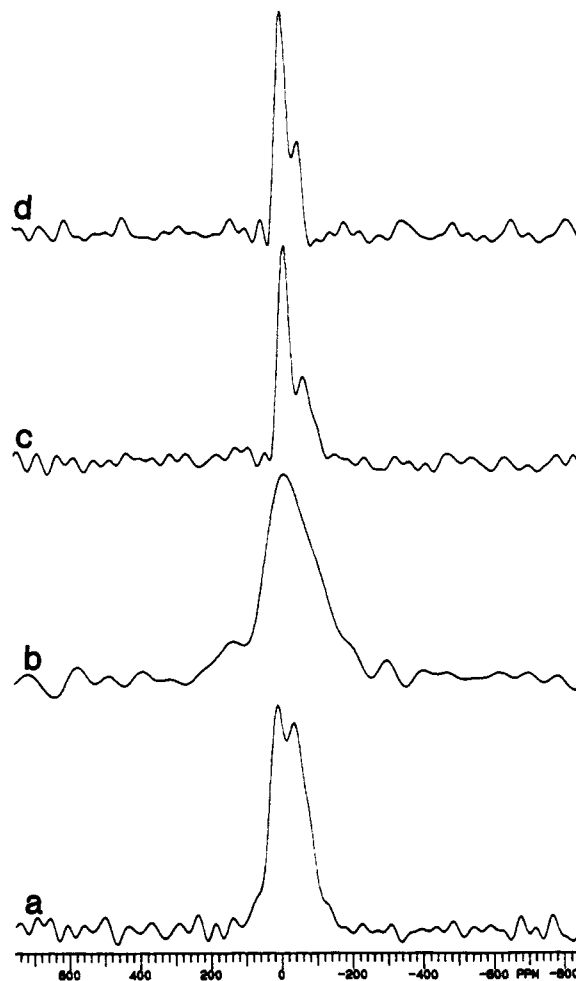


Figure 16. Static powder spectra of cesium and potassium promoted 12% Mo-Al₂O₃ catalysts: (a) 32% K (w/w), 150 000 transients; (b) 32% Cs (w/w), 473 160 transients. Also, the comparison of the ~4-kHz MAS spectra of (c) 32% Cs-12% Mo-Al₂O₃, 477 563 transients, and (d) Cs₂MoO₄, 3072 transients, recycle delay = 5 s. A line broadening of 100 Hz was used, and the recycle delay was 40 ms for the catalyst samples.

alysts is inhomogeneous or homogeneous in origin, we have performed spikelet-echo experiments on the 16% Cs (Figure 17b) and 32% Cs (Figure 17c) catalysts. The spectra are compared to the unpromoted catalyst whose line shape appears in Figure 17a. In the unpromoted catalyst spectra, one can readily observe the most intense range of spikelets (at 267, 130, 1, -134, -265, -400, and -530 ppm); however, in the promoted catalysts these spikelets extend further to higher and lower shielding. This extension of the shift range informs one of the homogeneous nature of the broadening that one is observing for the uncalcined promoted catalysts. The broadening is, therefore, due to an increase in the quadrupole interaction brought about by the donation of electrons to the molybdenum center by the cesium promoter. It should be noted that the signals of the spikelets at the extreme edges of the combs are much stronger in the 32% Cs catalyst, indicating a higher concentration of the species causing these spikelets. The superimposed comb of less intense spikelets, that was observed to higher shielding in the unpromoted catalysts, is also present in the promoted catalysts, as is another comb of spikelets at 421, 312, 178, and 51 ppm. It appears that the overall chemistry of the molybdenum species in the uncalcined promoted catalysts is very similar to that observed in the unpromoted catalyst, except that the quadrupole interaction is increased because of the electric field gradient increase, caused by donation

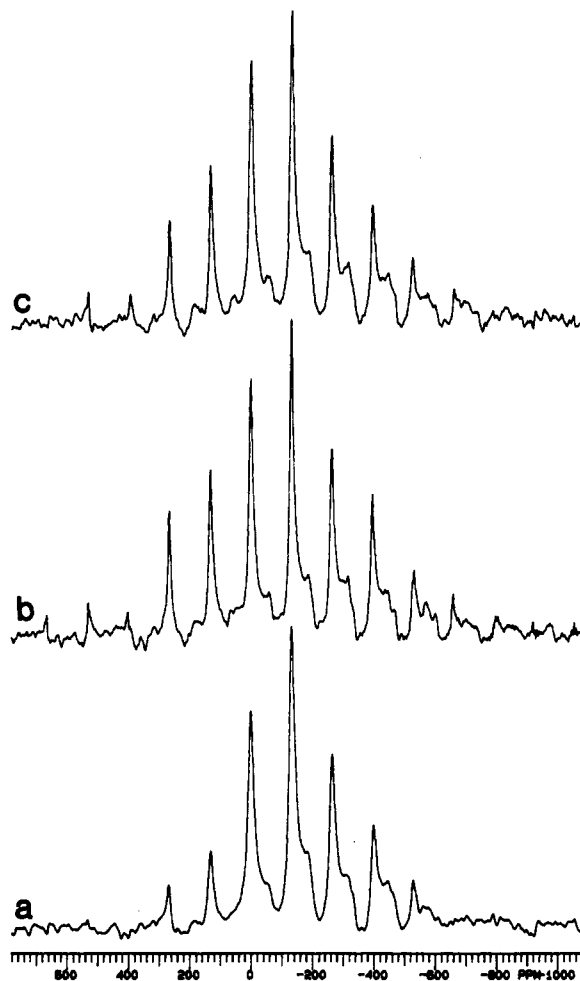


Figure 17. Spikelet-echo spectra obtained for the uncalcined $X\%$ Cs-12% Mo- Al_2O_3 catalysts ($X = 16$ and 32): (a) unpromoted 12% Mo- Al_2O_3 catalyst, 100 000 transients; (b) 16% Cs promoter, 176 000 transients; (c) 32% Cs promoter, 176 000 transients. All the spectra were obtained with a recycle delay of 50 ms and line broadening of 200 Hz.

of electron density from the cesium to the molybdenum. However, if one looks closely at the spikelet spectra of the unpromoted catalyst, one can observe two, or possibly three, species, while for the promoted catalysts one can observe three, or possibly four, species. This difference in the number of possible species is perhaps indicative of the formation of a Cs-Mo species.

Summary and Conclusions

We have shown that upon reduction and sulfiding of the fresh catalyst there are four (and sometimes five) main molybdenum species found on the surface of the alumina. Firstly, there is a tetrahedral molybdenum-oxo species, which remains unchanged from its form in the "fresh" catalyst. Secondly, MoS_2 is found on the surface having been formed by the reduction and sulfidation of adsorbed octahedral molybdenum sites as well as any bulk MoO_3 or adsorbed clusters, found on the "fresh" catalyst. However, the quadrupole interaction is larger indicating that the MoS_2 environment is different from that found in the bulk species. Thirdly, a phase is present at around -600 ppm for which we have no model compound or catalyst results which allow us to make an unequivocal assignment. The chemical shift position makes a Mo(IV) species the most likely candidate, in particular MoOS. Finally, a range of mixed oxidation states and mixed ligation Mo-O-S, Mo-O, and Mo-S species are present. The presence of Mo(0)

and Mo(II) species cannot be ruled out and seems likely considering the intensity of the broad underlying resonance in the static powder spectra. Interestingly, only one of our spectra demonstrated the presence of a component that could possibly be assigned to MoO_2 on the surface of the alumina.

These results support the conclusions we made as to the structure of the molybdenum surface species present in the "fresh" catalyst.¹ We also seem to be in agreement with the idea that either the MoOS or the MoS_2 species (or both) act as the active sites in the various HDS processes that these catalysts are engaged in. It seems that the MoOS and MoS_2 phases either decompose over time to the mixed oxidation state/structure/ligand species which combine to form a broad line underlying the spectrum or the adsorbed MoOS/ MoS_2 species are broken up during the HDS reactions into smaller dynamically active species which are not as effective as catalysts for the HDS processes. We can also account for the differing concentrations of MoS_2 versus tetrahedral molybdenum by taking into account the adsorption chemistry occurring during the impregnation and calcination process. Interestingly, we have demonstrated once again that the idea that only deposition of $[\text{MoO}_4]^{2-}$ salt occurs at high impregnation pH is erroneous, as the adsorption of octahedral and tetrahedral molybdenum is clearly occurring. One final speculation is that the lack of differences between the amounts of MoS_2 versus tetrahedral molybdenum in the uncalcined and calcined sample may indicate that the polymerization that occurs upon calcination does not change the overall symmetry of the individual molybdenum species but merely distorts the molecular environments.

The solid-echo and spikelet-echo results obtained on the cobalt promoted catalysts indicate that a considerable difference exists between the Mo-Co interactions in catalysts prepared by coimpregnation of the molybdenum and cobalt and by separate impregnation. The paramagnetic interaction of the Co^{2+} ion with the molybdena is more marked in the catalysts prepared by separate impregnation. However, the chemistry involved in the coimpregnated catalyst is seemingly much more complex, although one might be observing long range paramagnetic interactions (which lead to broadening of the observed line shapes) in one case and short range interactions in the other (which lead to complete removal of the signal from the line shape). However, upon calcination the differences in the line shapes (and thus the chemistry) are more apparent, as the separate impregnation catalysts actually narrow on calcination. This could indicate the removal of the resonances due to the surface molybdena, which are thought to have larger quadrupole interactions associated with them than the subsurface molybdena. However, the overall signal intensity for the two catalysts increases upon calcination, although the two signal intensities are very similar. This indicates that the paramagnetic interaction is partially coupled via the water present on the uncalcined catalysts which acts as a dipole bridge. Also, the spikelet-echo experiments revealed the presence of a species present only in the coimpregnated catalyst; this species was probably a subsurface Al-Co-Mo interaction species.

After reduction and sulfiding, the separate impregnation catalysts demonstrate no MoS_2 resonance in the NMR line shape, indicating that the cobalt is closely associated with the MoS_2 , while the MoS_2 resonance is observed in the coimpregnation catalysts. It was also possible to support the assignment of the resonance at -140 ppm to tetrahedral $\text{Mo}^{\text{VI}}\text{-O}$, by comparison of the MAS spectrum

of a cobalt promoted, reduced, and sulfided catalyst with that of a 12% Mo-Al₂O₃ catalyst prepared at pH 9 (solely [MoO₄]²⁻ in the impregnation solution).

It was readily demonstrated that molybdena-alumina catalysts promoted by alkali-metal ions (cesium and potassium) yield phases of Cs₂MoO₄ and K₂MoO₄ upon calcination. The degree of conversion to these tetrahedral molybdate phases is directly related to the ratio of the alkali metal and molybdenum. We have been able to observe cross polarized spectra of the promoted catalysts,⁷⁵ which will help further disentangle the chemistry involved in these promoted catalyst systems. Further information may be forthcoming from solid-state ¹³³Cs NMR of these systems.

We have demonstrated here that solid-state ⁹⁵Mo NMR spectroscopy can be used effectively to extract useful

structural information from molybdenum systems which have been difficult to investigate in the past.

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Registry No. MoO₃, 1313-27-5; Co, 7440-48-4; Cs, 7440-46-2; K, 7440-09-7; ⁹⁵Mo, 14392-17-7.