Catalysis Letters 19 (1993) 121–130

Observation of $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ in hydrotreating catalyst precursors by solid-state ^{27}Al NMR

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Received 19 January 1993; accepted 1 April 1993

A previously unobserved octahedral ^{27}Al MAS NMR resonance has been detected in re-hydrated calcined Mo/Al_2O_3 hydrotreating catalyst precursors. This resonance is attributed to the presence of hydrated forms of aluminum molybdate such as $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ ($n = 1$ or 2). The cross-polarization relaxation parameters, obtained from variable contact time experiments, yielded information on the relative sizes of the $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ domains in the catalysts with different molybdenum loadings. Analysis of the ^{27}Al MAS NMR spectra of $P–Mo(8)/Al_2O_3$ and $P–Mo(12)/Al_2O_3$ (wt% P = 0.0–12.0) shows that a function of the phosphate in the 12 wt% Mo catalyst is to prevent the re-hydration of the molybdate phases on the calcined catalysts.

Keywords: Solid-state ^{27}Al NMR; cross-polarization; hydrotreating catalyst precursors; hydrated aluminum molybdates

1. Introduction

The importance of molybdenum based catalysts for the petrochemical industry has prompted much research aimed at understanding the nature of the various molybdenum oxide species present on the alumina surface[#1] [1–3]. Concurrent with these fundamental studies, there has been much work carried out to elucidate structure–activity relationships [4–6]. All this research has shown the surface structure of Mo/Al_2O_3 based catalysts to be very complex. And there is still the need for a more detailed understanding of the various molybdenum oxide species that form on the alumina surface, and how these species are effected by the presence of promoters.

A technique which is being used increasingly to study Al_2O_3 supported catalyst precursors is solid-state ^{27}Al NMR [7–9]. It has been shown that $Al_2(MoO_4)_3$ can

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[#1] For review articles see ref. [1].

be readily detected using ^{27}Al single pulse/magic angle spinning (SP/MAS) NMR experiments. In agreement with XRD [10] and XPS [11] studies of Mo/Al_2O_3 materials, the amount of $Al_2(MoO_4)_3$ detected by solid-state ^{27}Al NMR was found to be dependent on the molybdenum loading, and the presence of promoter species such as phosphate. Additionally, Narayana et al. have reported ^{27}Al DOR (double rotation) NMR data showing that there are four inequivalent Al^{3+} sites in the crystal lattice of $Al_2(MoO_4)_3$ [12]. Thus, solid-state NMR is emerging as a very powerful tool for characterizing amorphous and small crystallite phases which cannot be detected by techniques such as XRD or laser Raman.

Recently, Haller et al. have demonstrated the use of solid-state ^{27}Al, ^{31}P and ^{95}Mo NMR to study the hydration effects of $Al_2(MoO_4)_3$ and $AlPO_4$ phases in hydrotreating catalysts [8]. The importance of hydration effects was reported by Wachs et al. [13] who showed that surface molybdenum oxide species become hydrated upon exposure to air, while others have shown that the nature of the MoS_2 phases on sulfided Mo/Al_2O_3 based catalysts is dependent on the state of the calcined precursor [14].

During the course of our work on phosphate promoted $Mo–Ni/Al_2O_3$ catalyst precursors we observed a previously unreported resonance in the ^{27}Al cross-polarization (CP) MAS NMR spectra of rehydrated Mo/Al_2O_3 and $P–Mo/Al_2O_3$ catalyst precursors. In order to elucidate the nature of the species giving rise to this resonance, we have studied a series of $P–Mo/Al_2O_3$ catalysts in which the molybdenum loading is varied from 8.0 to 12.0 wt% and the P loading is between 0.0 and 12.0 wt%. We have synthesized a hydrated aluminum molybdate compound which appears from XRD and elemental analysis to be $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ ($n = 1$ or 2), and compared its ^{27}Al CP/MAS spectrum with those produced by the $P–Mo/Al_2O_3$ materials. Variable contact time experiments have been used to determine the relative sizes of dispersed phases on the catalyst surface. The results of this study provide evidence for the presence of a hydrated form of the aluminum molybdate on the surface of calcined $P/Mo/Al_2O_3$ materials which have been allowed to rehydrate. They also show that the presence of phosphate on the 12 wt% Mo containing catalysts prevent the re-hydration of the molybdate phases after calcination.

2. Experimental

The catalysts were prepared by the aqueous incipient wetness impregnation technique. Norton 6375C γ-alumina (20/40 mesh) was used as the support: surface area of 221.8 m^2/g, and a pore volume of 1.4 cm^3/g. Phosphoric acid and ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) were used as the starting materials. The $P/Mo/Al_2O_3$ samples were prepared by impregnation of γ-Al_2O_3 with a solution of H_3PO_3, followed by drying at 110°C for 16 h. The dried catalysts were then impregnated with appropriate solutions of ammonium heptamolybdate, dried

at 110°C for 16 h, and finally calcined in flowing air (60 cm^3/min) at 500°C for 3 h. All the catalysts were allowed to rehydrate in the laboratory environment prior to the NMR analysis. The metal loadings were confirmed by elemental analysis.

The sample of $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ ($n = 1, 2$) was prepared by the method employed by Jones [15]: 5 g of $Na_2MoO_4 \cdot 2H_2O$ obtained from Alfa Products was dissolved in 25 ml of water and $AlCl_3$ was slowly added with constant stirring until a white precipitate formed. The precipitate was filtered, washed with water and left to dry in air. A portion of the sample was calcined at 500°C in flowing air (60 cm^3/min). The aluminum/molybdenum content was obtained by elemental analysis.

The NMR spectra were acquired on a Varian Unity-300 spectrometer at a resonance frequency of 78.42 MHz for ^{27}Al, and 300 MHz for ^{1}H. The spectra were obtained using CP [16,17] and MAS [17,18], as well as single pulse techniques. In all cases high power proton decoupling ($B_1 = 50$ kHz) was employed. A Doty Scientific 7 mm High Speed CP/MAS probe, and a Chemagnetics 7 mm CP/MAS probe were used at spinning rates of 6–7 kHz. The spectra were referenced to the isotropic resonance (0 ppm) of a solid sample of $KAl(SO_4)_2$ observed single pulse MAS (SP/MAS). The single pulse experiments were obtained using a $\pi/24$ ^{27}Al pulse. The CP technique allows selective observation of the surface aluminum species in a heterogeneous catalyst, as the only aluminum in dipolar contact (roughly, within 7 Å) with a proton spin reservoir at the surface [19]. Therefore, one observes a spectrum free from interference by the bulk alumina. Contact times were optimized and found to be 0.5 ms for pure γ-Al_2O_3, and 0.2 ms for treated alumina. Relaxation delays of 1 s were used, a ^{1}H $\pi/2$ pulse of 5 μs, and an acquisition time of 20 ms. The spectral width was 100 kHz. The variation of signal intensity with contact time was investigated, where the observed signal intensity for a given contact time, τ_{cp}, is described by the equation

$$M(\tau_{cp}) = [M_\infty - (M_\infty - M_0)\exp(-\tau_{cp}/T_{Al-H})]\exp(-\tau_{cp}/T_{1\rho}^H) + M_0\,,$$

where T_{Al-H} is the cross-relaxation time, and $T_{1\rho}^H$ is the spin-locked spin-relaxation time constant. T_{Al-H} is related to the strength of the ^{27}Al–^{1}H dipolar interaction which is proportional to $1/r^3$, where r is the Al–H internuclear distance, as well as the number of neighboring protons [17,18]. By running the variable contact time experiment one can extract the values of T_{Al-H} and $T_{1\rho}^H$ for each species present. In order to deduce the relative amount of observed aluminum present as the species giving rise to the resonance at 13 ppm, lineshape deconvolutions were carried out using the Varian VNMR software – the component lineshapes were not constrained in any manner during the analysis.

The XRD patterns were collected using a Scintag, PAD IV, theta/2-theta diffractometer. The diffractometer is equipped with a 2° divergence slit, a 0.3 mm receiving slit, and an intrinsic germanium solid-state detector. The samples were ground to a 100 mesh particle size and top loaded into the cell. The following run

conditions were used: power: 45 kV, 40 mA; source: Cu Kα; range: 5°–70° 2-theta at 0.03 chopper size at a continuous rate of 0.5° per min. Assignment of the diffraction patterns was achieved using the library of patterns supplied with the instrument.

3. Results and discussion

Fig. 1 shows the CP/MAS spectra of a series of P–Mo(8)/Al_2O_3 catalysts, where the phosphorus loadings are 0, 1, 2, and 3 wt%. P(0)Mo(8)/Al_2O_3 yields signals at 13 and 4 ppm. The 4 ppm resonance can be assigned to the surface octahedral aluminums associated with the alumina lattice. The 13 ppm resonance, to our knowledge, has not been reported previously. The intensity of the 13 ppm resonance is seen to decrease slightly with higher phosphorus loading (fig. 1). Also, as the phosphorus loading is raised, the octahedral surface aluminum resonance is seen to shift to higher shielding while the overall linewidth of the resonance increases. This indicates that a range of octahedral aluminum species are present such as those bonded to phosphate and molybdate, as well as unreacted octahedral alumina sites. This is in agreement with our previous work, which showed that monomeric and polymeric phosphates, as well as aluminum phosphates and alumi-

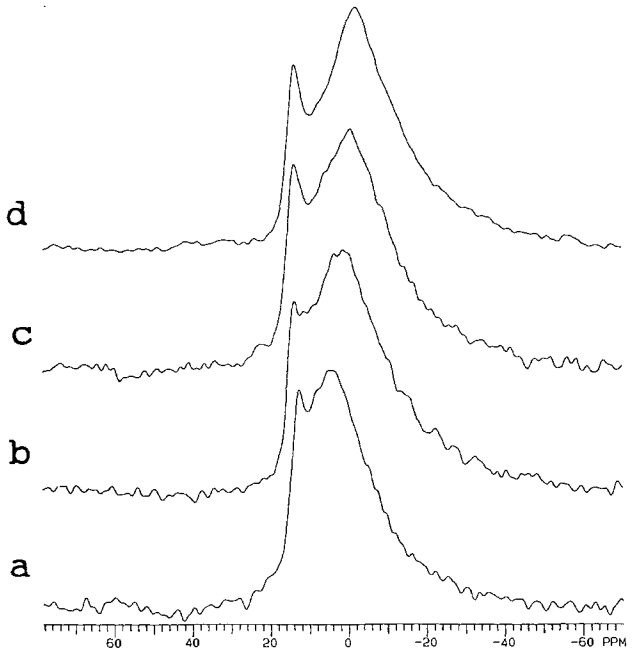

Fig. 1. ^{27}Al CP/MAS spectra of P(x)Mo(8)/Al_2O_3, where (a) $x = 0$ wt%, 2654 transients, (b) $x = 1$ wt%, 4192 transients, (c) $x = 2$ wt%, 5415 transients, and (d) $x = 3$ wt%, 16384 transients. Recycle delay was 1 s, contact times were 250 μs.

num molybdates are formed on the alumina surface, all of which would perturb the shielding of the octahedral sites differently [9].

Fig. 2 shows the ^{27}Al CP/MAS spectra obtained on a series of P–Mo(12)/Al_2O_3 catalysts (where the phosphorus loadings are 1, 2, 4, 6, 10, and 12 wt%), and fig. 3 shows the results of the curve analysis used to obtain the relative amount of observable aluminum present as the species responsible for the resonance at 13 ppm. P(1)Mo(12)/Al_2O_3 exhibits the two resonances at 2 and 13 ppm, as expected. The intensity of the 13 ppm signal decreases with increasing phosphorus loading. At the higher P loadings (6–12 wt%), the decrease in the intensity of the 13 ppm signal is accompanied by an increase of a resonance at 38 ppm which can be assigned to $AlPO_4$. A similar shift in the position of the octahedral surface aluminum resonances is observed, again indicating the presence of a range of surface octahedral sites with differing environments due to bulk salt formation, and adsorption of phosphate and molybdate species. This data shows that the formation of phosphate on the alumina surface prevents the formation of the species giving rise to the 13 ppm resonance.

CP/MAS spectra of the freshly calcined P–Mo/Al_2O_3 samples (discussed

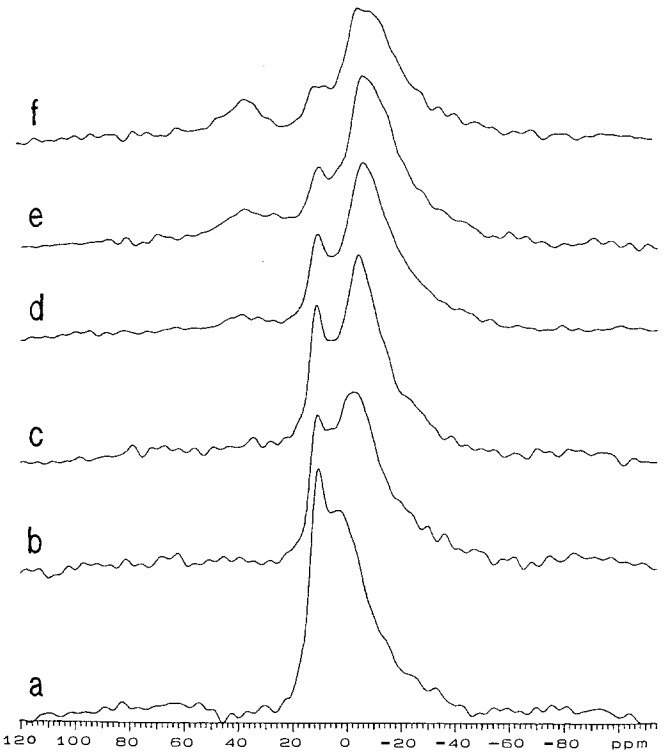

Fig. 2. ^{27}Al CP/MAS spectra of P(x)Mo(12)/Al_2O_3, where (a) $x = 1$ wt%, 8192 transients, (b) $x = 2$ wt%, 10141 transients, (c) $x = 4$ wt%, 5415 transients, (d) $x = 6$ wt%, 32000 transients, (e) 10 wt%, 12795 transients, and (f) 12 wt%, 15393 transients. Recycle delay was 0.5 s, contact times were 250 μs.

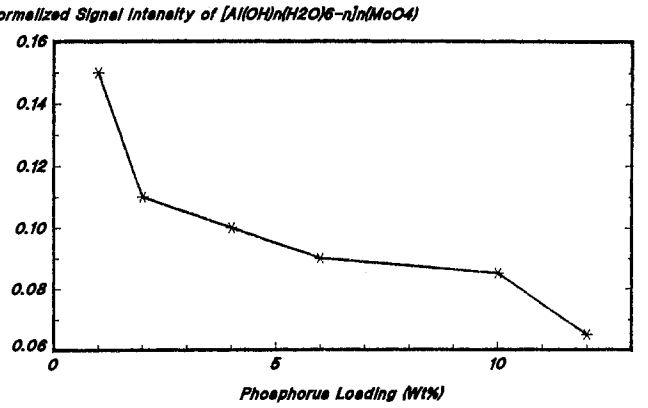

Fig. 3. Plot of observed $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ ($n = 1, 2$) signal intensity versus phosphorus loading for the P(x)Mo(12)/Al_2O_3 catalysts ($x = 1, 2, 4, 6, 10, 12$ wt%).

above) do not exhibit the 13 ppm resonance. This indicates that the 13 ppm resonance is due to a species formed upon rehydration of the catalyst surface. Additionally, the 13 ppm signal is not observed in the CP/MAS spectra of re-hydrated samples of Al_2O_3, or P/Al_2O_3 (P = 1–10 wt%). In our previous work [9], we demonstrated that the presence of phosphorus promotes the formation of bulk phases of $Al_2(MoO_4)_3$ and MoO_3. The formation of $Al_2(MoO_4)_3$ was only observed by SP/MAS NMR for catalysts with molybdenum loadings $\geqslant$ 8 wt%. Our ^{27}Al CP/MAS study of P(0)Mo(x)/Al_2O_3 catalysts with differing molybdenum loadings (x = 2–12 wt%) revealed that the 13 ppm species is observed only at molybdenum loadings $\geqslant$ 8 wt%. This observation suggests that the presence of the resonance at 13 ppm is related to surface conditions being conducive to the formation of a hydrated form of $Al_2(MoO_4)_3$ or MoO_3.

Hydration of $Al_2(MoO_4)_3$ may lead to a species such as $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ where n can be either 1 or 2. In order to confirm this we have prepared a sample which appears to have this formulation. XRD patterns of the synthesized, hydrated model compound are shown in fig. 4. The dried sample produces signals at 2-theta = 9.3, 18.5, 27.4, 31.7, 45.5 and 51.9° (fig. 4a). This pattern indicates the presence of amorphous material as well as crystalline NaCl (31.7, 45.5°). The elemental analysis of this wet sample gives and Al : Mo ratio as 1.5 : 1 as would be expected for a mixture of $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ where n is either 1 or 2. After calcination of the model compound at 500°C, the powder diffraction spectrum reveals the presence of a high concentration of crystalline aluminum molybdate (fig. 4b), as well as NaCl. Thus, our XRD and elemental analysis results suggest very strongly that the model compound is an amorphous hydrated form of aluminum molybdate containing a small amount of NaCl which was not removed by washing of the filtrate during synthesis.

In fig. 5 we show the CP/MAS spectra obtained for P(3)Mo(8)/Al_2O_3 (fig. 5a), and the synthesized model compound ($[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$) (fig. 5b). The

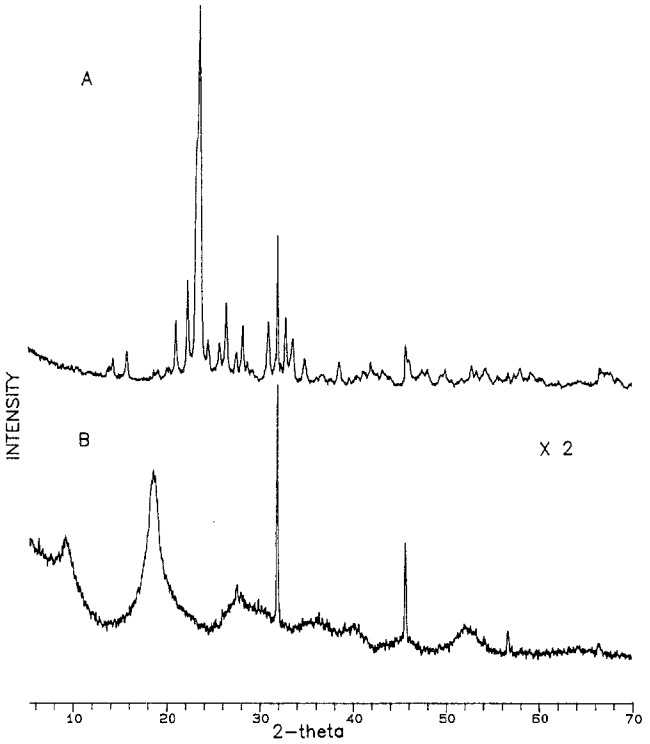

Fig. 4. X-ray powder diffraction patterns of (a) the model compound dried at 25°C, and (b) the model compound calcined at 500°C.

^{27}Al CP/MAS spectrum of the synthesized compound reveals a narrow resonance at 13 ppm and at least two broader signals observed as shoulders on the upfield edge of the 13 ppm resonance. (The calcined model compound does not give a resonance at 13 ppm as the sample has been converted to crystalline aluminum molybdate which does not give rise to a CP/MAS signal due to the absence of hydroxyl and water protons.) As observed previously, the P(3)–Mo(8)/Al_2O_3 produces resonances at 13 and −2 ppm (due to the octahedral surface aluminum). The presence of the 13 ppm resonance in both P(3)–Mo(8)/Al_2O_3 and the synthesized compound suggests that the resonance is due to a similar species. The chemical shift of the resonance suggests octahedral symmetry [20] while the narrowness of the lineshape indicates that the species has a small quadrupole interaction as one might find in a highly octahedral aluminum environment such as axially hydroxylated $[Al(OH)_2(H_2O)_4]_2(MoO_4)$. The broader signals appearing upfield from the resonance may be due to further H_2O/OH coordination possibilities present in a mixture of $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ phases, where n can be 1 or 2.

For both the $[Al(OH)_2(H_2O)_4]_2(MoO_4)$ model and some P–Mo/Al_2O_3 catalyst samples, we have obtained the CP relaxation parameters which are given in table 1. The T_{Al-H} cross-relaxation time is related to the size and location of the ^{1}H spin reservoir with respect to the ^{27}Al spins in the bulk phase [21,22]. An increase in the

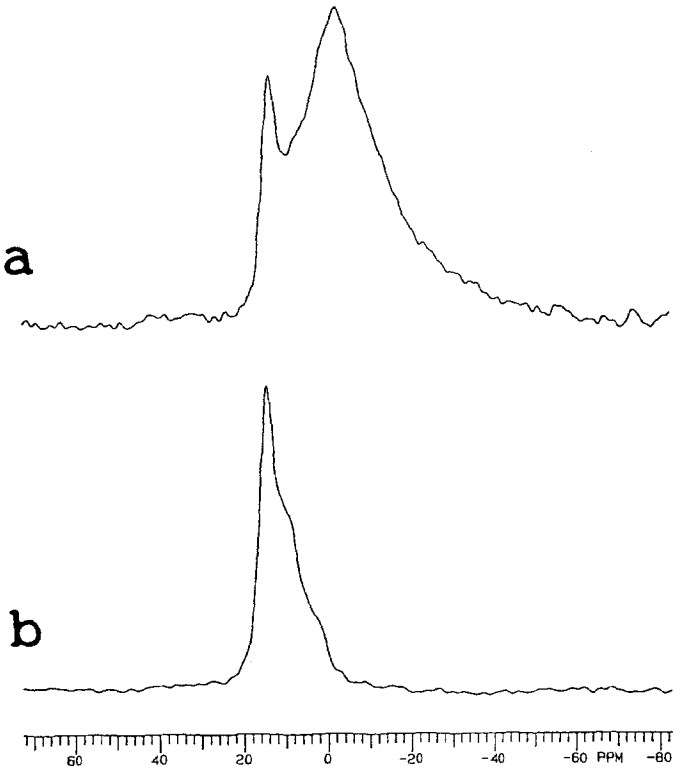

Fig. 5. ^{27}Al CP/MAS spectra of (a) P(3)Mo(8)/Al_2O_3, 2 s recycle delay, 16384 transients, and (b)$[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ ($n = 1, 2$) model compound, 16384 transients, recycle delay 1 s.

^{27}Al–^{1}H internuclear distance, or a decrease in the number of ^{1}H in close proximity to ^{27}Al, results in an increase in the value T_{Al-H}. Highly dispersed amorphous hydrated aluminum molybdate domains would give rise to higher T_{Al-H} values than larger crystalline domains. Thus, T_{Al-H} values yield information on the size of the bulk phases, many of which are too small to be detected by conventional techniques such as XRD.

The T_{Al-H} value for the pure model compound is 67 μs, the T_{Al-H} value for the P(1)Mo(8)/Al_2O_3 surface $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ species is 190 μs (table 1). However, the T_{Al-H} values for the P(3)Mo(12)/Al_2O_3 surface $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ species is identical to that for the model compound. This shows that the $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ species is not present as large crystallites on the surface of P(1)–Mo(8)/Al_2O_3, but as small isolated amorphous phases, so that the aluminum center is not in dipolar contact with a great many surrounding protons associated with neighboring $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ molecules. In the 12 wt% Mo catalyst, however, it appears that the $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ is present in larger crystalline domains giving rise to a very similar relaxation behavior of the surface and model compounds. Also, in the case of 8 wt% Mo catalyst, the $T_{1\rho}^{H}$

Table 1
Cross-polarization relaxation parameters

Sample	T_{Al-H} (μs)	$T_{1\rho}^{H}$ (ms)
model compound		
$[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$	67	1.72
P(1)Mo(8)/Al_2O_3		
$[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ surface species	190	1.44
surface O_h Al site	99	1.24
P(3)Mo(12)/Al_2O_3		
$[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ surface species	74	1.80
surface O_h Al site	48	1.42

value for the surface species is shorter than that observed for the model compound. This could be due to the closer proximity of the alumina surface to the $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$ aluminum centers providing a relaxation route for the spin-locked protons.

4. Conclusion

In conclusion, the 13 ppm resonance can be assigned to hydrated forms of aluminum molybdate, possibly $[Al(OH)_n(H_2O)_{6-n}]_n(MoO_4)$. Variable relaxation time experiments provide information about the relative sizes of the phases, consistent with the findings of other researchers, the size of the phase is dependent on the molybdenum loading. Additionally, the NMR data obtained for P–Mo(8)/Al_2O_3 and P–Mo(12)/Al_2O_3 shows that the presence of surface phosphates prevent the formation of the hydrated phases (perhaps because phosphate promotes the formation bulk aluminum molybdate and molybdenum trioxide [9]). This shows that one of the roles of phosphorus is to stabilize the molybdenum oxide phases on the calcined catalyst.

Acknowledgement

The authors thank Texaco, Inc. for permission to publish this work, and Tom Scalzo for sample preparation and XRD analysis.

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