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Hydration effects of $Al_2(MoO_4)_3$ and $AlPO_4$ phases in hydrotreating catalysts studied by solid state nuclear magnetic resonance spectroscopy

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Solid state nuclear magnetic resonance spectroscopy of ^{27}Al, ^{31}P, and ^{95}Mo nuclei was used to investigate species on a $NiPMo/Al_2O_3$ hydrotreating catalyst calcined at 750°C before and after rehydration. The $Al_2(MoO_4)_3$ phase disappeared after rehydration in 100% relative humidity at room temperature. However, almost none of the observed crystalline $AlPO_4$ reacted with adsorbed water. The results show that the $Al_2(MoO_4)_3$ phase on an alumina surface reacts easily with moisture unlike $Al_2(MoO_4)_3$ in the bulk phase. It also suggests that the crystalline $AlPO_4$ phase is formed under the $Al_2(MoO_4)_3$ phase or that both species are formed as neighboring islands on the surface of the alumina but have different reactivities toward moisture.

Keywords: NMR studies of $AlPO_4$; NMR studies of $Al_2(MoO_4)_3$

1. Introduction

Catalytic hydrotreating, particularly with regard to hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), has undergone rapid growth in the 1980's and its current capacity approaches 50% of installed crude refining capacity [1,2]. Typical catalysts contain 15–20 wt% MoO_3 promoted with 2.5–3.5 wt% CoO or NiO supported in γ-Al_2O_3. As a practical matter, the Mo precursor is stabilized in solution at low pH using H_3PO_4. Therefore, commercial catalysts in general also contain phosphorus. While hydrotreating catalysts are presulfided to achieve the desired activity and selectivity, both the fresh and regenerated catalysts are sold and transported in the oxidized state which results from calcination, or air oxidation. This process may result in some formation of surface $Al_2(MoO_4)_3$,

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particularly in the burn off of coke in the regeneration of the catalysts [3]. It is generally assumed that this compound is catalytically inactive and stable in subsequent treatment; i.e. formation of $Al_2(MoO_4)_3$ results in irreversible deactivation of the catalyst. However, our results suggest that $Al_2(MoO_4)_3$ is not as inert as has been assumed and that it might be possible to design schemes that would allow regeneration of an active Mo phase from $Al_2(MoO_4)_3$ on alumina supports.

Solid state NMR spectroscopy is one of a few techniques which are sensitive to elements at a surface, and which also give information on its electronic and geometric environment. This method does not necessarily require ultra high vacuum (UHV), single crystals, or synthesis of thin surface layers on the top of a crystal surface as is the case for electron spectroscopies such as X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, electron energy loss spectroscopy (EELS), low electron energy diffraction (LEED), etc. Thus, NMR spectroscopy can be applied to real powdered catalysts and equilibrium adsorption conditions [4–7]. Even though liquid state NMR has been applied to heterogeneous catalysts [8–10], it is necessary to assume that disappearing species in a spectrum are adsorbed in an intact or another form on the catalysts. Solid state NMR spectroscopy is a direct technique for surface species detection on heterogeneous catalysts. However, broader lines in solid state spectra, due to lack of isotropic fast motion, require extra experimental effort, e.g., magic angle spinning (MAS), etc., to increase resolution [11,12].

We report here the investigation of surface species on a commercial $NiPMo/Al_2O_3$ hydrotreating catalyst calcined at 750°C before and after rehydration with solid state nuclear magnetic resonance spectroscopy of ^{27}Al, ^{31}P, and ^{95}Mo nuclei (NiPMo notation means the catalyst is made with the impregnation solution containing Mo, P, and Ni nuclei with γ-alumina as a support, likewise PMo represents the catalyst made with the solution containing Mo and P but no Ni nuclei).

2. Experimental

The catalyst we studied was supplied by American Cyanamid Company with the composition: $MoO_3 = 20$ wt%, $NiO = 3.25$ wt%, and $P_2O_5 = 6.9$ wt% on γ-alumina. γ-alumina was impregnated with the solution containing the heptamolybdate anions, nickel ions, and phosphoric acid. Phosphoric acid was used to lower the pH of the solution to 1.5. After impregnation, the precursor was dried and calcined under an air flow of 25 cc/min at 750°C for 2 h with a 4°C/min rate of temperature increase. After the sample was cooled to room temperature by turning off the oven, it was transferred to a 1 cm diameter NMR tube for ^{95}Mo NMR experiments and to a 5 mm MAS rotor for ^{31}P and ^{27}Al NMR experiments in a dry nitrogen glove bag. For rehydration experiments, the samples were put into the desiccator containing water (100% relative humidity) for 30 h at room temperature. Enrichment of ^{95}Mo has not been used in this study. Therefore, this report would be the first natural abundance ^{95}Mo solid state NMR study on such catalysts [13]. All model and/or reference compounds were purchased ($AlCl_3$, Aldrich; $Na_2MoO_4 \cdot 2H_2O$, Fisher Scientific Company; $Al_2(MoO_4)_3$, $AlPO_4$, and MoO_3, Alfa Products) and used without further purification.

All of the experiments were carried out in a Bruker AM-500 spectrometer with a magnetic field strength of 11.7 T (Larmor frequencies: $^{27}Al = 130.32$, $^{31}P = 200.47$, and $^{95}Mo = 32.59$ MHz). A MAS multinuclear resonance probe (Doty Scientific Inc.) was used for ^{31}P (100% abundance, $I = 1/2$) and ^{27}Al (100% abundance, $I = 5/2$) NMR experiments. Zirconia rotors with 5 mm outer diameter were spun at 2.5–4 kHz. Aqueous 1 M $AlCl_3$ solution and 85% phosphoric acid were used as chemical shift standards for each nucleus. 5 μs solution $\pi/2$ pulse length was obtained for ^{27}Al and 6 μs was obtained for ^{31}P. 0.3 μs and 3 μs pulse lengths with 4 phase pulse cycling were applied to obtain ^{27}Al and ^{31}P MAS spectra, respectively. A number of scans between 100 and 160 was acquired for each ^{27}Al and ^{31}P spectrum. A recycle time of 10 s was used for ^{27}Al spectra and 2 s for ^{31}P spectra.

A high power static probe was home-built for ^{95}Mo (15.72% abundance, $I = 5/2$) NMR experiments. The inner diameter of the coil was 1 cm. Diameter of 1 cm thin-walled NMR tubes with a length of 2–3 cm were used. 11–14 μs solution $\pi/2$ was obtained with 1 M Na_2MoO_4 aqueous solution. A $\pi/2-\tau-\pi$ echo pulse sequence [14,15] was used to acquire ^{95}Mo spectra after pulse lengths were rescaled for the solid by dividing the solution ones by $(1/2 + I)$ [16,17]. Typically 30–50 μs were used for delay interval τ with 3 μs dwell time. Real acquisitions were started several points before the echo maxima to locate the first data point of the echo by left shifting before Fourier transformation. Tens of thousands of scans were required with a recycle time 200 ms or 4 s to get a ^{95}Mo spectrum for the catalyst. A recycle time 16 or 80 s was used for model compounds, MoO_3 and $Al_2(MoO_4)_3$ in bulk, with several hundreds acquisition. The spin echo technique on static samples was applied to take ^{95}Mo spectra instead of MAS to increase signal intensities by taking advantage of a larger volume of sample although MAS might provide improved resolution.

The observed chemical shift at 11.7 T was reported in this work without an external field dependence study unless otherwise stated. The observed chemical shift for quadrupole nuclei with half integer spin number, which is the sum of an isotropic chemical shift and the second order quadrupole shift, depends on external magnetic field strength due to the fact that the second order quadrupole shift is smaller at a higher magnetic field.

3. Results and discussion

It has been reported, using ^{27}Al and ^{31}P NMR, that $AlPO_4$ and $Al_2(MoO_4)_3$ phases are formed when the NiPMo or PMo catalyst was calcined above about 700°C [18] and that the $Al_2(MoO_4)_3$ phase disappears after calcination at or above 900°C as molybdena starts to evaporate [19]. The $Al_2(MoO_4)_3$ phase formation was confirmed this time with ^{95}Mo NMR (fig. 3), too. If the $Al_2(MoO_4)_3$ and $AlPO_4$ phases on alumina are formed as a monolayer or isolated molecules, they would likely have different symmetries from the bulk. These symmetry differences will be accompanied by chemical shift and linewidth changes. However, all observed NMR peaks (table 1) correspond with model compunds in the *bulk* with respect to chemical shift and linewidth (all spinning side bands as well as peaks from alumina support, octahedral sites at 8 ppm and tetrahedral sites at 71 ppm, are excluded in this discussion). Therefore, both phases formed on alumina, $Al_2(MoO_4)_3$ and $AlPO_4$, are likely present as islands with more than a couple of layers. The ^{31}P NMR spectra for $AlPO_4$ phases (figs. 2A–2C) with a chemical shift at −29 or −30 ppm seem to be different from our spectrum in fig. 2D taken from $AlPO_4$ in the bulk. However, it is well known that the ^{31}P chemical shift for bulk $AlPO_4$ changes from −25 ppm to −30 ppm depending sensitively on bond length and bond angle [20,21]. Therefore, our spectra do not deviate significantly from bulk $AlPO_4$ spectra. Al signal intensities are linearly proportional to the number of Al in the species when a very short pulse length is applied even though Al in each chemical species has a different quadrupole coupling constant and an asymmetry parameter [22,23]. The mole ratio of $AlPO_4$ and $Al_2(MoO_4)_3$ is approximately 5.4 : 1.0 measured

Table 1

Observed peak positions of the catalyst and model compounds in ^{27}Al, ^{31}P, and ^{95}Mo NMR spectra at 11.7 T

Compound	^{27}Al		^{31}P	^{95}Mo
	δ_{CG} [a]		δ_{CG} [a]	δ_m [b]
catalyst calcined at 750°C	40,	−13	−29	−280
catalyst rehydrated at RT in 100% humidity for 30 h	41,	–	−29	−100
catalyst recalcined at 400°C for 6 h	41,	–	−30	−280
catalyst hydrated at RT in air for years after calcined at 450–550°C for 1 h	–	–	–	−110
bulk $Al_2(MoO_4)_3$	–	−12	–	−300
bulk $AlPO_4$	41.5,	–	−26	–
bulk MoO_3	–	–	–	−60

[a] δ_{CG} is the center of gravity of the main peaks. All spinning side bands are excluded in the table as well as ^{27}Al signal from tetrahedral sites at 71 ppm and octahedral sites at 8 ppm in alumina support. Error range is ±1 ppm unless stated otherwise.

[b] δ_m is the maximum intensity singularity position of the power pattern. Error range is ±20 ppm unless stated otherwise.

from ^{27}Al NMR spectrum obtained with 0.06 of solution $\pi/2$ pulse length. Thus, the observed mole ratio of P and Mo is 1.8 : 1.0 which exhibits a large discrepancy from the calculated value, 0.7 : 1.0, from the impregnation solution composition. This result might mean that Mo forms some species other than the crystalline $Al_2(MoO_4)_3$ phase and that those species are not observed due to very broad linewidth or due to the absence of Al in the species in ^{27}Al NMR spectrum. Some of these species may be shown as the broad components in fig. 3A.

After rehydration, $Al_2(MoO_4)_3$ peaks disappeared in ^{27}Al and ^{95}Mo spectra (figs. 1A and 1B, and 3A and 3B, respectively) but the $AlPO_4$ peaks remained in

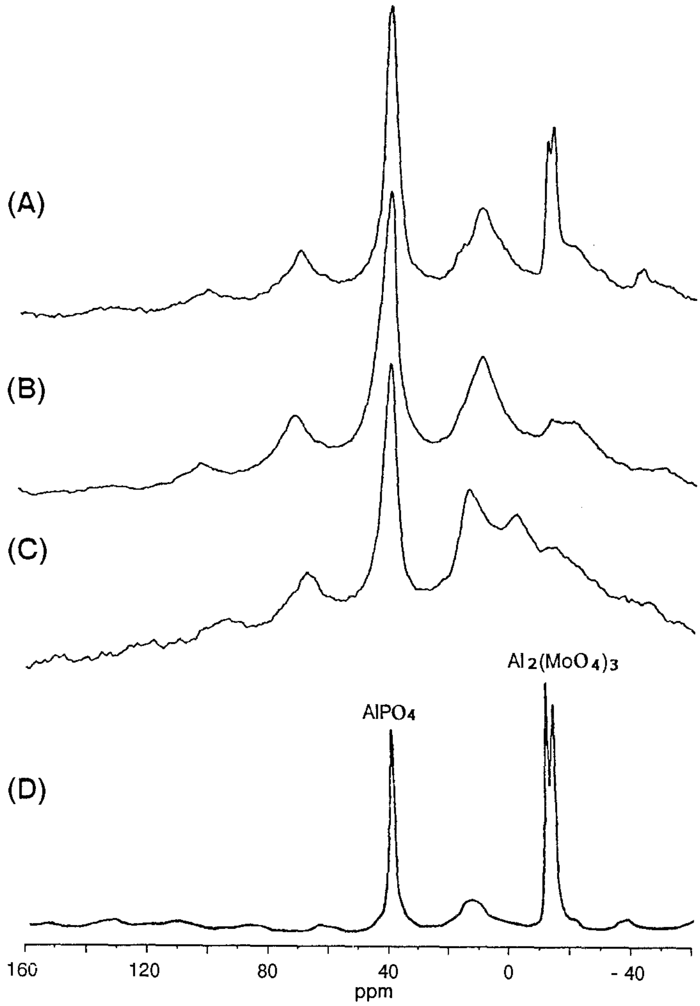

Fig. 1. ^{27}Al MAS spectra of the sample calcined at 750°C, (A) before rehydration, (B) after rehydration at room temperature for 30 h in 100% relative humidity, (C) after recalcination of the rehydrated sample at 400°C for 6 h, (D) ^{27}Al MAS spectrum of a mixture of $AlPO_4$ and $Al_2(MoO_4)_3$ bulk samples.

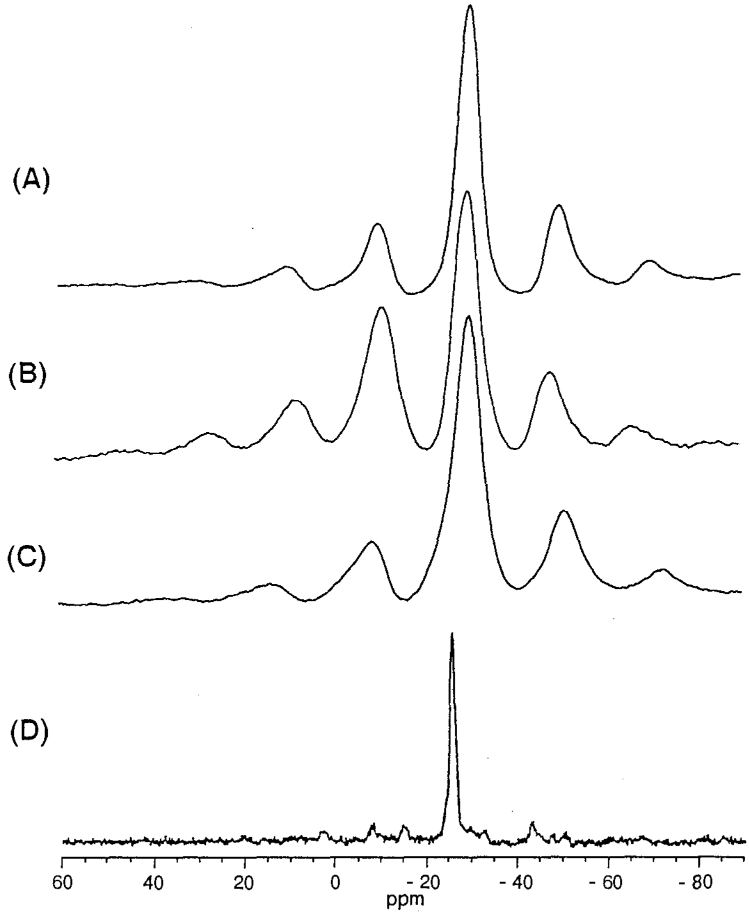

Fig. 2. ^{31}P MAS spectra of the sample calcined at 750°C, (A) before rehydration, (B) after rehydration at room temperature for 30 h in 100% relative humidity, (C) after recalcination of the rehydrated sample at 400°C for 6 h. (D) ^{31}P MAS spectrum of $AlPO_4$ bulk sample.

^{27}Al and ^{31}P spectra (figs. 1B and 2B). A slight increase of peak intensity at -10 ppm in ^{31}P NMR spectra (fig. 2B) might be due to hydration of the top layer of the $AlPO_4$ phase producing a species like polymeric phosphate with a chemical shift of about -10 ppm [24]. Both $Al_2(MoO_4)_3$ and $AlPO_4$ in the bulk are known *not* to be hygroscopic [25,26]. However, spectra in figs. 1B, 2B, and 3B show that the $Al_2(MoO_4)_3$ phase on an alumina surface reacts easily with water molecules. However, almost none of the observed $AlPO_4$ phase on the surface reacted with adsorbed water molecules.

If the disappearance of $Al_2(MoO_4)_3$ peaks is caused by symmetry changes at the sites of the observed nuclei in the top layer due to simple reversible adsorption of water molecules, it should reappear after recalcination. However, after the rehydrated sample was recalcined at 400°C for 6 h, $Al_2(MoO_4)_3$ peaks still did not reappear in the ^{27}Al and ^{95}Mo spectra (figs. 1C and 3C). Therefore,

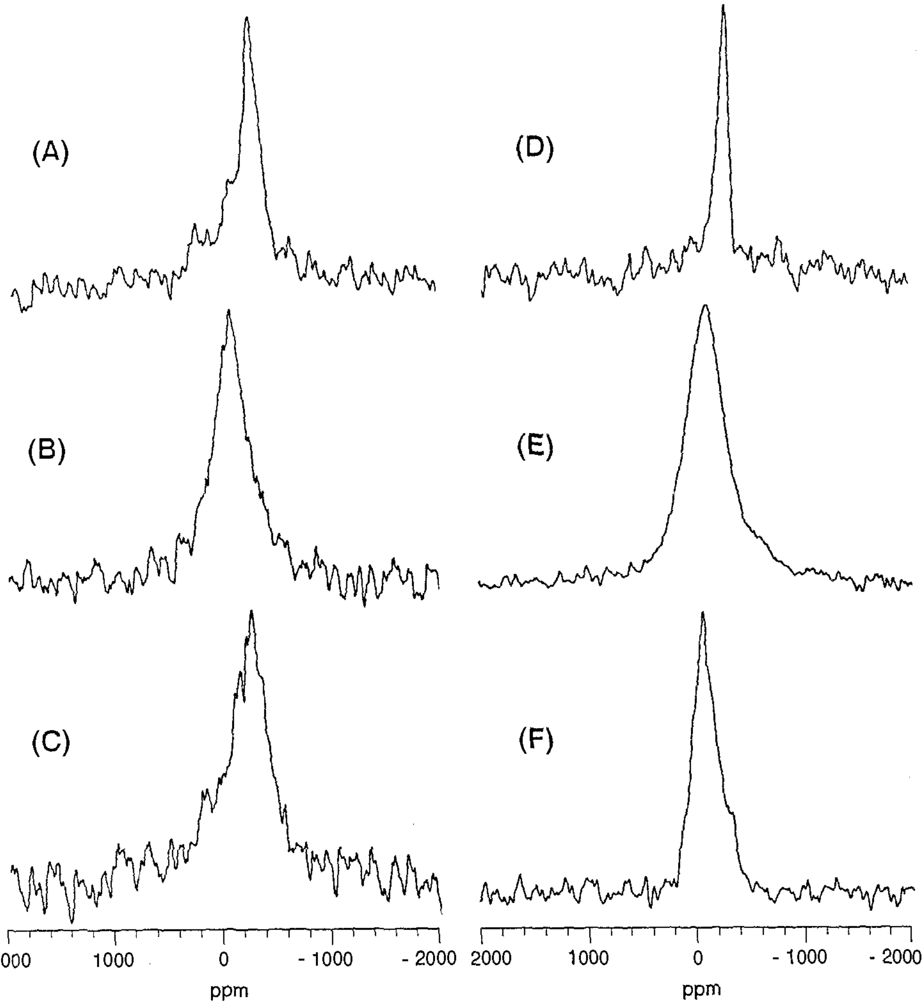

Fig. 3. ^{95}Mo static echo spectra of the sample calcined at 750°C, (A) before rehydration, (B) after rehydration at room temperature for 30 h in 100% relative humidity, (C) after recalcination of the rehydrated sample at 400°C for 6 h. (D) ^{95}Mo static echo spectrum of $Al_2(MoO_4)_3$ bulk. (E) ^{95}Mo static echo spectrum of a commercial NiPMo catalyst sample untreated (the catalyst was hydrated for years in air after calcination at 450–550°C for 1 h). (F) ^{95}Mo static echo spectrum of MoO_3 bulk sample.

disappearance of $Al_2(MoO_4)_3$ peaks is not due to a simple reversible adsorption of water molecules on the surface of the $Al_2(MoO_4)_3$ phase. The identity of a new peak near -1 ppm in fig. 1C is not certain by itself, but may have something to do with an amorphous $Al_2(MoO_4)_3$ phase in fig. 3C as described below. The ^{95}Mo spectrum in fig. 3B shows that the rehydration of the $Al_2(MoO_4)_3$ phase produces a hydrated amorphous MoO_3 phase. This hydrated amorphous MoO_3 phase is the same as the one observed (fig. 3E) from the untreated catalyst (the untreated catalyst was hydrated for years in air after calcination at 450–550°C for 1 h). The ^{95}Mo spectrum in fig. 3C has a very similar powder pattern and a chemical shift to those for crystalline $Al_2(MoO_4)_3$, although it has a wider line-broadening overall. This broadening could be due to a distribution of quadrupole coupling constants and asymmetry parameters caused by deviation from crystallinity, i.e. amorphism of the material. Thus, the fig. 3C spectrum suggests that the rehydrated amorphous MoO_3 phase becomes an amorphous $Al_2(MoO_4)_3$ phase rather than a crystalline $Al_2(MoO_4)_3$ phase when the sample was recalcined at 400°C for 6 h. Further calcination at 750°C for 2 h recreated crystalline $Al_2(MoO_4)_3$ as confirmed by ^{27}Al NMR (the spectrum is not shown but is exactly the same as fig. 1A). The catalyst sample calcined at 850°C (the spectra are not shown) produced the same results upon rehydration and recalcination.

In conclusion, our results shows that the $Al_2(MoO_4)_3$ phase on an alumina surface reacts readily with water molecules producing a hydrated amorphous MoO_3 phase. This observation is quite different from what is expected from $Al_2(MoO_4)_3$ in the bulk. Therefore, it may allow regeneration of an active Mo phase from the $Al_2(MoO_4)_3$ phase on an alumina surface. On the other hand, almost none of the observed crystalline $AlPO_4$ phase was reactive toward water. Another possible interpretation of the observed different tendency of the $AlPO_4$ and $Al_2(MoO_4)_3$ phases toward moisture is that the $AlPO_4$ phase is formed under the $Al_2(MoO_4)_3$ phase or that both species are formed as neighboring islands on the surface of the alumina but with different reactivities toward moisture when the compounds are formed on the surface of γ-Al_2O_3 during calcination.

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