JOURNAL OF CATALYSIS 154, 65–68 (1995)

Quantitative ^{1}H MAS NMR Studies of Structurally Different OH Surface Groups on η-Al_2O_3 and Mo/η-Al_2O_3 Catalysts

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Received August 24, 1994; revised January 4, 1995

Quantitative results for the coverage of surface hydroxyl groups on η-Al_2O_3 and calcined molybdenum catalysts supported on η-Al_2O_3 have been obtained by ^{1}H MAS NMR spectroscopy. By studying catalysts with different molybdenum concentrations, information on the nature of the reaction of molybdate ions with the structurally different hydroxyl species of the support could be obtained. The present studies show that a preferential interaction of molybdenum with the most basic hydroxyl groups of η-Al_2O_3 takes place and that monolayer structures dominate up to approximately 12 wt% Mo corresponding to 4.0 Mo atoms per nm^2.

INTRODUCTION

Infrared spectroscopy has been extensively used over the years for the characterization of aluminas and the nature of their surface interactions with metal oxides (1). Quantitative FTIR studies of calcined molybdenum catalysts have recently been reported (2). These studies show that the more basic OH groups are the most reactive toward molybdenum and that the monolayer structures are restricted to the hydroxylic part of the surface. However, due to the possible differences in extinction coefficients for the different types of OH groups, it is difficult to quantitatively determine the distribution of OH groups. This difficulty may be overcome by ^{1}H MAS NMR which should be capable of providing such information. The major requirements are that the interactions causing line-broadening of the ^{1}H resonances (i.e., the proton–proton dipolar couplings and chemical shift anisotropies) can be sufficiently suppressed in order to resolve signals from the different surface sites. Furthermore, due to the dependence of the ^{1}H chemical shifts on the acidity of the OH groups, as assignment of the OH group resonances according to this property could possibly be more directly established.

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Previously, Mastikhin *et al.* (3) have reported a characterization of both η-Al_2O_3 and Mo/η-Al_2O_3 by ^{1}H MAS NMR. However, the conclusions from these experiments are generally not in agreement with the FTIR studies (2, 4). This discrepancy may be caused by lack of resolution in the ^{1}H spectra resulting from the rather slow MAS rotation frequencies employed ($\omega_r/2\pi$ = 4 kHz) and from insufficient pretreatment of the samples such that the signals from the OH sites are masked by the signal from physisorbed water. Recently, it has been demonstrated that by application of faster MAS rotation frequencies more information can be obtained from ^{1}H MAS NMR spectra of alumina and modified aluminas (5). In the present work improved ^{1}H MAS NMR spectroscopy has been used to investigate how the distribution of surface OH groups depends on calcination temperature and on the molybdenum concentration for a series of carefully prepared samples of η-Al_2O_3 and Mo/η-Al_2O_3, respectively. The results from the ^{1}H MAS NMR experiments are compared with those obtained from previous FTIR studies on similar samples.

EXPERIMENTAL

Preparation of support samples. The support used was pure η-Al_2O_3 (η-Al_2O_3: $Fd3m$, a_0 = 7.91 Å). The alumina had a surface area of 230 m^2/g and a pore volume of 0.70 ml/g and was calcined at 550°C for 2 h in a stream of air. After calcination and exposure to the ambient, samples of the support were evacuated at 200, 300, 400, and 500°C for 18 h at 10^{-5} bar in Pyrex tubes.

Preparation of catalyst samples. Samples containing 2, 4, 8, and 10 wt% Mo/η-Al_2O_3 were prepared by impregnating the η-Al_2O_3 support with ammoniacal aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ using the incipient wetness technique. The samples were dried at room temperature for 24 h and calcined in a stream of air at 500°C for 2 h before they were transfered to Pyrex tubes and evacuated to 10^{-5} bar at 500°C for 18 h.

0021-9517/95 $6.00

Following these pretreatments of the samples the Pyrex tubes were sealed under vacuum. Weighed amounts of the samples were transferred to airtight MAS rotors in a glove box under a high-purity nitrogen atmosphere and rigorously moisture-free conditions. The effect of water adsorption by exposing the samples to the ambient atmosphere was determined in separate experiments.

^{1}H MAS NMR spectroscopy. ^{1}H MAS NMR experiments were performed at 300 MHz on a Varian XL-300 (7.1 T) spectrometer employing a homebuilt MAS probe (6) with a stator produced from Kel-F. A 7-mm o.d. PSZ (partially stabilized zirconia) rotor equipped with a Kel-F endcap having two Viton (a fluoroelastomer) O-rings was employed. The volume of the sample chamber was 225 μl. All spectra were recorded using a rf-field strength of $\omega_{1H}/2\pi$ = 40 kHz, a pulse width of 3 μs, a repetition delay of 1 s, and MAS rotation frequencies in the range of $\omega_r/2\pi$ = 7.0–7.2 kHz. These spinning frequencies were sufficient to significantly suppress the homonuclear dipole and chemical shift anisotropy interactions for all samples and resulted in relatively narrow ^{1}H resonances. No attempts were made to determine the ^{1}H spin-lattice relaxation times for the OH resonances. However, an experiment of arrayed recycle delays indicates that all OH sites were completely relaxed within a repetition delay significantly shorter than 1 s. Therefore, all experiments can be considered quantitatively reliable. The ^{1}H intensity observed for the ^{1}H MAS NMR spectrum of a weighed sample of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ formed the basis for the determination of quantitative results for all other samples.

The ^{1}H MAS NMR spectra were interpreted on the assumption that no water from the atmosphere penetrates the rotor into the highly hygroscopic samples. In order to justify this assumption, ^{1}H MAS NMR spectra of a η-Al_2O_3 sample calcined at 500°C were recorded immediately after and several days after being transferred to the rotor. As these two spectra turned out to be identical and very different from samples exposed to moisture, the possibility of water penetrating through the O-rings into the sample can be neglected. Rotor and endcap materials were chosen so as to minimize any ^{1}H background signal. The ^{1}H background resonance from the probe itself, identified by recording a ^{1}H MAS NMR spectrum of an empty rotor, consisted of a broad and very low-intensity resonance (apparently a static resonance). All ^{1}H MAS NMR spectra employed and shown in this paper have been corrected for this background resonance by subtracting the "empty-rotor" spectrum. ^{1}H chemical shifts are in ppm and are reported relative to TMS using an external sample of neat dioxane as a secondary reference.

The quantitative evaluation of the observed resonances in the experimental spectra was performed by computer deconvolution. All spectral deconvolutions were carried out by iterative lineshape fitting on the spectrometer system (SUN 3/150) using Lorentzian lineshapes.

FTIR spectroscopy. Details of the FTIR spectroscopic measurements and data analysis can be found in Ref. (2).

RESULTS

^{1}H MAS NMR spectra obtained for the pure precalcined η-alumina (identified as such by X-ray powder diffraction) as a function of pretreatment temperature are illustrated in Fig. 1. As is apparent from this figure, the spectra change significantly upon an increase in the evacuation temperature from 200 to 300 and 400°C. The most conspicuous feature is the disappearance of the broad resonance observed as a shoulder at ca. 4 ppm. This observation is ascribed to the desorption of physisorbed water. By further increasing the temperature from 400 to 500°C only a slight change in the spectral appearance is observed. From the total intensity for the spectrum of pure η-Al_2O_3, pretreated at 500°C for 18 h, a total H content of 0.18 wt% is determined. This corresponds to 4.7 OH/nm^2 or 21 Å^2/OH which is very close to values obtained by using other techniques (7, 8). Thus, the average distance between the OH groups is ca. 4.6 Å.

Apparently the resonances in the spectrum of pure η-Al_2O_3, following pretreatment at 500°C, can be roughly divided into two groups centered at about 2 and −0.5 ppm. Each of the groups most probably consists of a superposition of several resonances. These two groups of proton resonances may be characterized by different acidities (3, 5) and hereafter the resonances at 2 and −0.5 ppm will be referred to as the acidic and basic protons of η-Al_2O_3, respectively.

Spectra of the η-Al_2O_3 (pretreated at 500°C) were also recorded after the sample was exposed to the ambient atmosphere for 1 and 30 min. After an exposure time of only 1 min, a shoulder at ca. 4 ppm could easily be detected whereas after 30 min the spectrum is completely dominated by this resonance. This supports the assignment of this resonance to physisorbed water and also

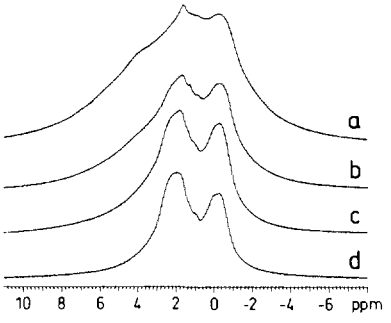

FIG. 1. 300 MHz ^{1}H MAS NMR spectra ($\omega_r/2\pi$ = 7 kHz) of η-Al_2O_3 dehydrated at 10^{-5} bar for 18 h at (a) 200, (b) 300, (c) 400, and (d) 500°C.

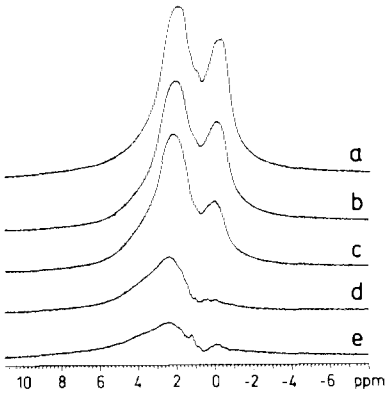

FIG. 2. 300 MHz ^{1}H MAS NMR spectra ($\omega_r/2\pi$ = 7 kHz) of Mo/η-Al_2O_3 containing (a) 0, (b) 2, (c) 4, (d) 8, and (e) 10% molybdenum after evacuation to 10^{-5} bar at 500°C for 18 h.

confirms the absence of physisorbed water in the Mo/η-Al_2O_3 samples described below since no resonance is visible at 4 ppm in their ^{1}H MAS spectra.

Figure 2 shows the ^{1}H MAS NMR spectra for the Mo/η-Al_2O_3 catalysts with molybdenum loadings corresponding to 0, 2, 4, 8, and 10 wt% Mo/η-Al_2O_3 and following evacuation at 500°C. It is apparent from these spectra that the total ^{1}H signal intensity decreases upon increasing molybdenum loading and that the resonance at −0.5 ppm is preferentially removed compared to that at 2 ppm (see also Fig. 5 below).

Thus, for a molybdenum loading of 10 wt% only a weak signal centered at 2.4 ppm remains. Quantitative information about the relative and total signal intensities of the −0.5 and 2 ppm signals were extracted from the spectra shown in Figs. 2a–2e by spectral deconvolution. In the deconvolution procedure all spectra were resolved into a number of Lorentzian components. No attempts were made to assign the individual resolved components. Instead, the components were classified into two groups, one contributing to the signal intensity of the −0.5 ppm resonance and the other contributing to the signal intensity of the 2 ppm resonance. The total signal intensity of a spectrum was calculated as the sum of all components and normalized by dividing this sum by the total signal intensity of the pure alumina sample (Fig. 2a). The signal intensities of the −0.5 ppm resonances in the spectra of Figs. 2a–2e were calculated as the sum of all components contributing to the −0.5 ppm resonance and normalized by dividing the sum by the signal intensity of the −0.5 ppm resonance of the pure alumina sample. Signal intensities of the 2 ppm resonance were calculated by a method analogous to the one described above (see also Figs. 4 and 5).

DISCUSSION

The reaction between molybdate ions and surface hydroxyl groups resulting from the drying and calcination procedures has often been qualitatively described by the reaction scheme (9) illustrated in Fig. 3. As is seen from this scheme, on increasing the molybdenum loading the number of surface hydroxyl groups (and thereby the number of OH protons) decreases as a result of the condensation reaction. To obtain a better understanding of this reaction we have quantitatively determined the total amount of protons for the surface hydroxyl groups by ^{1}H MAS NMR and compared the results with those obtained by FTIR spectroscopy. In Fig. 4 these results are plotted separately as a function of the molybdenum concentration and a very good correlation between the two data sets is apparent.

The linear correlation between the total number of hydroxyl groups and molybdenum loading shows that on average the Mo/OH ratio is nearly constant regardless of the molybdenum concentration. From the intersection of the straight line (Fig. 4) with the x-axis at 12 wt% Mo, the maximum number of molybdenum atoms that may be bonded per unit surface area is calculated to be 4.0 Mo/nm^2 or 1 Mo/25 Å^2. Comparing this value with the total number of OH groups for the unloaded η-Al_2O_3 surface, a Mo/OH ratio of 0.86 is obtained, which corresponds to about six Mo per seven OH groups. As mentioned above, a preferential interaction of the molybdate with the basic hydroxyl groups has been demonstrated by FTIR spectroscopy and the same behavior can be deduced from the ^{1}H MAS NMR spectra as illustrated in Fig. 5.

Masthikin *et al.* (3) recently performed a ^{1}H MAS NMR study for a similar series of catalysts. However, these authors did not observe a linear correlation between the concentrations of the OH surface groups and molybdenum but rather a nonlinear decrease from 4.7×10^{20} to 2.5×10^{20} OH/g upon increasing the molybdenum concentration from 0 to 8 wt% (Fig. 17 in Ref. 3). Above 8 wt% Mo a constant concentration of OH was observed and this was taken as evidence for the inadequacy of the so-called monolayer model. This is contrary to the results of the present study and we believe the discrepancy arises for two reasons. The first and probably most important reason can be observed from the spectrum recorded by Mastikhin *et al.* for their sample of pure η-alumina (see Fig. 5 in Ref. 3). This clearly indicates the presence of physisorbed water as a shoulder at ca. 4.3 ppm which accounts for approximately 25% of the total signal inten-

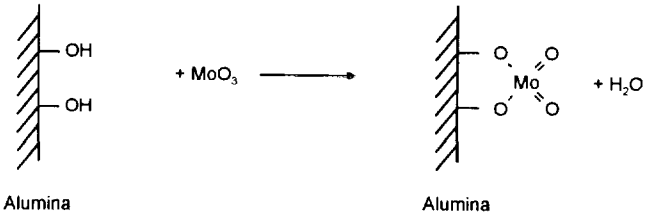

FIG. 3. Reaction between molybdate and η-Al_2O_3 surface hydroxyls as a result of drying and calcination.

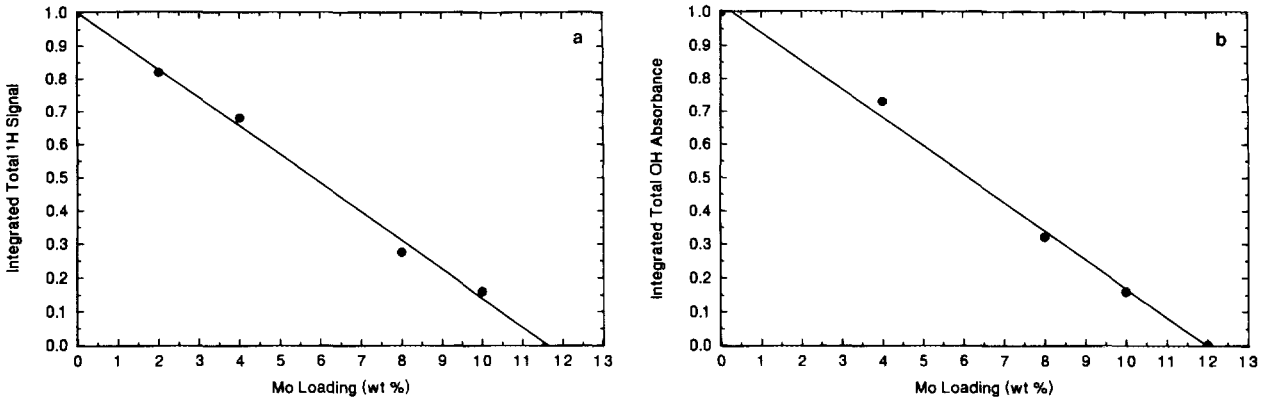

FIG. 4. (a) Normalized integral of total ^{1}H MAS NMR signal versus molybdenum loading and (b) normalized total OH band IR absorbance versus molybdenum loading.

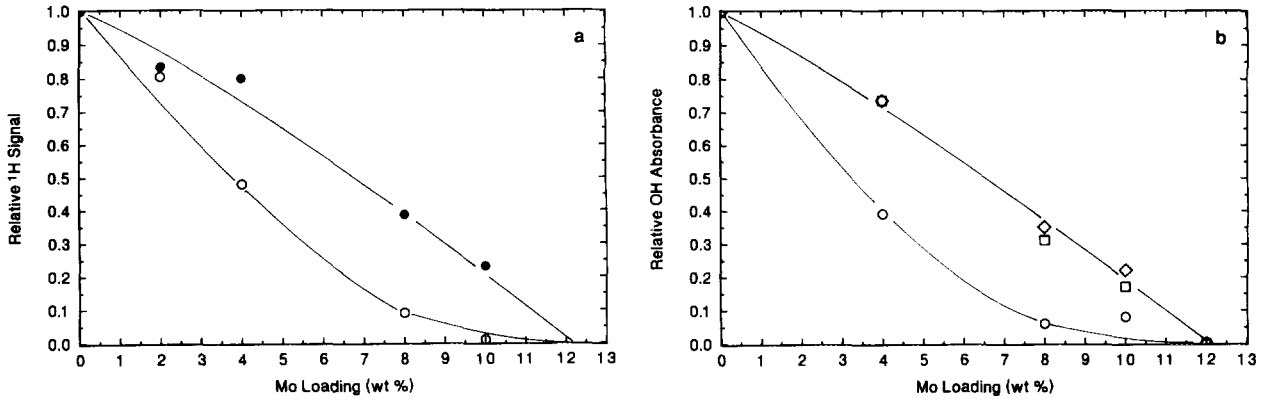

FIG. 5. (a) Normalized integral of ^{1}H MAS NMR signal versus molybdenum loading (● and ○ represent the signals at 2 and −0.5 ppm, respectively) and (b) normalized OH band IR absorbance versus molybdenum loading (○, □, and ◇ representing 3771, 3730, and 3680 cm^{-1}, respectively.

sity. Secondly, the slower MAS rotation speed applied in their experiments (ca 4 kHz) causes partial overlap between the center band signals (isotropic peaks) and the spinning side bands which may lead to determination of less accurate signal intensities and poorer spectral resolution.

Despite the fact that MAS NMR is a bulk technique, the excellent agreement between the ^{1}H MAS NMR and the FTIR measurements of the present study indicates that the vast majority of the OH groups for η-Al_2O_3 are positioned at surface sites accessible to the molybdate ions. Furthermore, the similarity of the intensity ratios for the ^{1}H MAS NMR and IR intensities of the basic and acidic OH groups suggests that IR extinction coefficients of the different OH groups are quite similar. This suggests that both the relative distribution of different OH groups and their absolute concentration may also be determined with quite good accuracy by the use of IR spectroscopy.

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