^{1}H MAS NMR Studies of Alumina-Supported Metal Oxide Catalysts

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The interactions of two-dimensional vanadium oxide and molybdenum oxide overlayers with the surface hydroxyls of an alumina support were examined with ^{1}H MAS NMR spectroscopy. The measurements demonstrated that these surface metal oxide overlayers are homogeneously distributed over the alumina surface and essentially titrate all the accessible surface hydroxyls at monolayer coverage. The investigation also revealed that there are a small number of protons formed near monolayer coverage, suspected of being Bronsted acid sites, which are not titrated by these metal oxide overlayers and are capable of undergoing H/D exchange. In addition, there are protons in blocked pores of the alumina support that neither are accessible to the metal oxide overlayers nor are capable of undergoing H/D exchange. The present ^{1}H MAS NMR results are in excellent agreement with corresponding IR spectroscopy results on the same catalysts.

Introduction

Metal oxides dispersed over high surface area oxide supports represent an important class of heterogeneous catalysts for a variety of applications.[1,2] To better understand the catalytic behavior of these supported metal oxide catalysts, one needs to characterize the two-dimensional surface metal oxide species distributed over the oxide supports. In recent years, a number of characterization techniques have been applied to supported metal oxide catalysts that have provided molecular structural information about these two-dimensional metal oxide overlayers: Raman spectroscopy,[3,4] Fourier transform infrared spectroscopy,[5–7] extended X-ray absorption fine structure (EXAFS), and X-ray absorption near-edge spectroscopy (XANES)[8–10] as well as ^{51}V solid-state NMR for supported vanadium oxide catalysts.[11,12] In addition, it is also important to obtain information about the concentration and properties of surface hydroxyls since they may also influence the dispersion, structure, and reactivity of the supported metal oxide catalysts. Previous studies have used Fourier transform infrared spectroscopy to obtain information about the types of surface hydroxyls on oxide supports and their interactions with the surface metal oxide overlayers.[13,14] Recent ^{1}H MAS NMR high-resolution spectroscopy studies have demonstrated that this characterization technique is a direct method for studying the chemical properties of surface hydroxyls in catalysts.[15] Advantages of the ^{1}H MAS NMR technique are that the hydroxyl concentration can be quantified and that it is element specific (only detects H and, consequently, can be used to discriminate between sites containing H and D).

This article deals with ^{1}H MAS NMR studies on a series of alumina-supported metal oxide catalysts possessing two-dimensional metal oxide overlayers of molybdenum oxide and vanadium oxide. These supported metal oxide catalysts have previously been extensively characterized with *in situ* Raman spectroscopy,[16] Fourier transform infrared spectroscopy,[17] solid-state ^{51}V NMR for the alumina-supported vanadium oxide catalysts,[11] and XANES for the alumina-supported molybdenum oxide catalysts.[18] The objectives of this study are to compare the surface hydroxyl information of the alumina-supported metal oxide catalyst systems obtained by ^{1}H MAS NMR with the earlier IR studies as well as to determine what additional insights can be provided by ^{1}H MAS NMR studies.

Experimental Section

The supported molybdenum/vanadium oxide catalysts were prepared by the incipient-wetness impregnation method with an alumina support (Harshaw, 180 m^{2}/g). Aqueous solutions of ammonium heptamolybdate were used for the preparation of the alumina-supported molybdenum oxide catalysts. After impregnation, the catalysts were initially dried at room temperature overnight, further dried at 120 °C overnight, and finally calcined in dry air at 500 °C overnight. The vanadium oxide catalysts were prepared by impregnation with a vanadium triisopropoxide oxide solution in methanol. Due to the air- and moisture-sensitive nature of the alkoxide precursor, the impregnation and subsequent drying at 350 °C were performed under a nitrogen atmosphere. The vanadium oxide samples were finally calcined in air at 500 °C overnight. The vanadium oxide and molybdenum oxide loadings on the alumina support are expressed in weight percent.

The alumina-supported metal oxide samples were placed in special glass capsules (7 mm o.d. and 11 mm length glass tubes, which fit precisely inside quartz rotors) that were connected to glass tubes of the same diameter. The tubes were sealed to a vacuum line, and the samples were heated in air at 500 °C for 2 h, evacuated for 1 h, and heated in 200 Torr of oxygen for 30 min. The samples were then cooled to room temperature and evacuated. The tubes were subsequently sealed above the capsule necks, further cooled with liquid nitrogen, and finally sealed under a microtorch flame. The glass sample tubes were then placed in a quartz rotor for the NMR measurements. The sample tube, rotor, and the NMR probe head were dried in flowing hot air to diminish the signal from the traces of water on their outer surface. The H–D exchange of the surface OH groups was performed by exposing the samples to D_2O (13 Torr) at 300 °C for 2 h and evacuating the catalysts at this temperature for 3 h.

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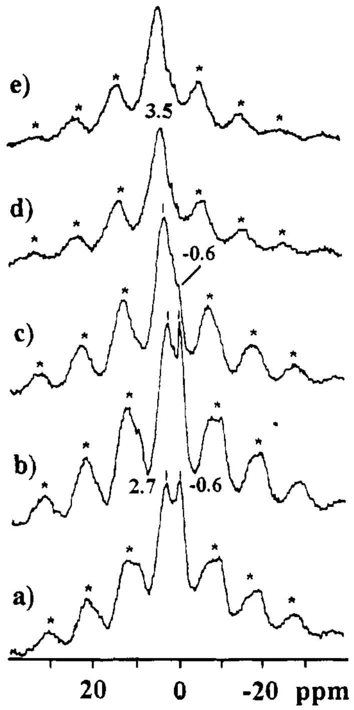

Figure 1. ^{1}H MAS NMR spectra of MoO_3/Al_2O_3 catalysts as a function of molybdenum oxide content: (a) 0%, (b) 1%, (c) 6%, (d) 18%, and (e) 25%.

The ^{1}H MAS NMR spectra were obtained with a Bruker CXP-300 NMR spectrometer at a frequency of 300.063 MHz (magnetic field 7.04 T) at room temperature. Typically 500 scans were collected. The $\pi/2$ pulse duration was 5 μs, and the delay between pulses was 1 s. The rotation frequency was about 3 kHz. Chemical shifts were measured with respect to external tetramethylsilane (TMS). The concentrations of protons were obtained from the integral intensities of the spectra by comparison with the spectrum of a standard Russian sample (KSK SiO_2, 390 m^2/g, evacuated at 300 °C and containing 2×10^{20} OH groups/g). The error in intensity measurements does not exceed 20%, and the background signal was subtracted from the spectra.

Results

Alumina Support. The ^{1}H MAS NMR spectrum of the alumina support, presented in Figure 1a, consists of two overlapping peaks with maxima at −0.6 and 2.7 ppm. The peak at −0.6 ppm was previously attributed to OH groups attached to one aluminum atom in octahedral coordination ($OHAl_o$).[15,19] The high-field shift of the line at −0.6 ppm indicates the basic character of these OH groups. The low-field peak at 2.7 ppm is asymmetric due to overlapping lines from ($OH2Al_o$), ($OH3Al_o$), and ($OHAl_oAl_t$) where Al_t denotes aluminum in tetrahedron coordination.[15,19]

MoO_3/Alumina. Deposition of molybdenum oxide on the alumina support significantly affects the OH groups on alumina as shown in Figure 1. The Mo content of the Mo/alumina catalysts was varied from 0 to 25% MoO_3 and previous Raman studies concluded that a monolayer of surface molybdenum oxide species on this alumina corresponds to approximately 20% MoO_3.[16] Mo oxide loadings in excess of 20% MoO_3 result in the formation of a crystalline MoO_3 phase on top of the surface molybdenum oxide monolayer.[16] Supporting 1% MoO_3 slightly diminishes the intensity of the line at −0.6 ppm and does not appear to affect the line at 2.7 ppm. The total OH intensity is about the same as that found for the alumina support within experimental error (see Figure 2). The 6% MoO_3 loading drastically decreases the intensity of the high-field line at −0.6 ppm, present as a shoulder, and does not appear to alter the shape and intensity of the low-field line at 2.7 ppm. There is a slight decrease in the total OH intensity (see Figure 2). The small narrow lines observed in the Mo oxide/alumina spectra at −0.3 and 1.0 ppm are due to water molecules adsorbed on the outer surface of the sample tube and ambient air humidity, respectively. Further increase in molybdenum oxide content to 18% MoO_3 results in the complete disappearance of the line a −0.6 ppm and a shift of the low-field line to 3.5 ppm. These changes are accompanied by a significant decrease in the total OH intensity (see Figure 2). Higher molybdenum oxide contents on alumina do not change the spectrum and the total intensity decreases only slightly (see Figure 2).

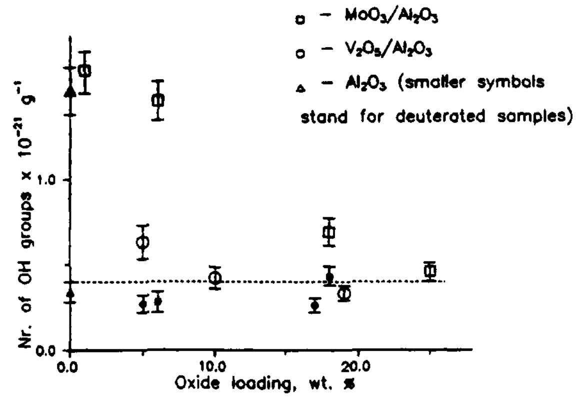

Figure 2. Dependence of the OH group concentration of the alumina supported catalysts on the molybdenum and vanadium oxide loadings.

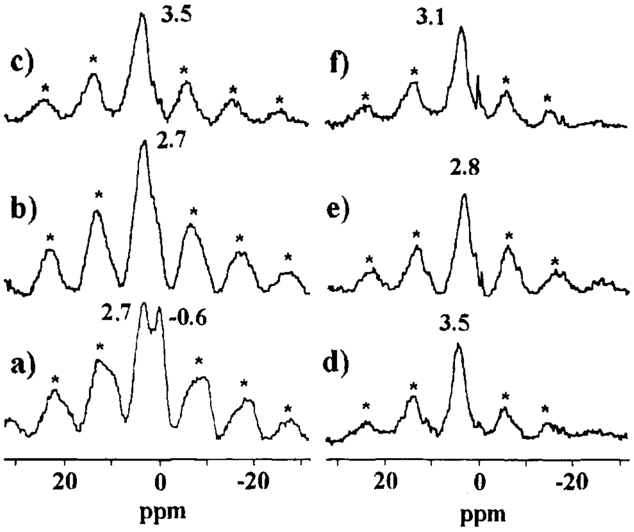

Figure 3. ^{1}H MAS NMR spectra of MoO_3/Al_2O_3 catalysts before H−D exchange (a−c) and after H−D exchange (d−f) as a function of molybdenum oxide content: (a, d) 0%, (b, e) 6%, and (c, f) 18%.

H−D exchange experiments were undertaken to obtain additional information about the accessibility of the remaining OH groups of the Mo oxide/alumina catalysts. Alumina surface OH groups are known to readily exchange with D_2O giving OD groups which do not contribute to the ^{1}H MAS NMR signal intensity.[15] The spectra of the aluminum support, prior to and after being subjected to H−D exchange, are shown in Figure 3. The ^{1}H MAS NMR intensity of the H−D exchanged alumina is about one-fifth of that for the unexchanged alumina (see Figure 2), and the exchanged sample exhibits a line at 3.5 ppm. The ^{1}H MAS NMR spectra of the higher loaded Mo oxide/alumina catalysts which primarily contain the low-field line, however, are only slightly affected by the H−D exchange (see

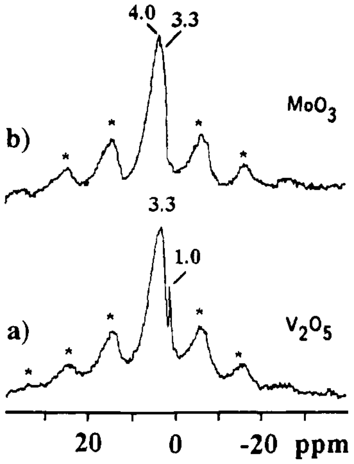

Figure 4. ^1H MAS NMR spectra of bulk MoO_3 and V_2O_5, evacuated at 250 °C.

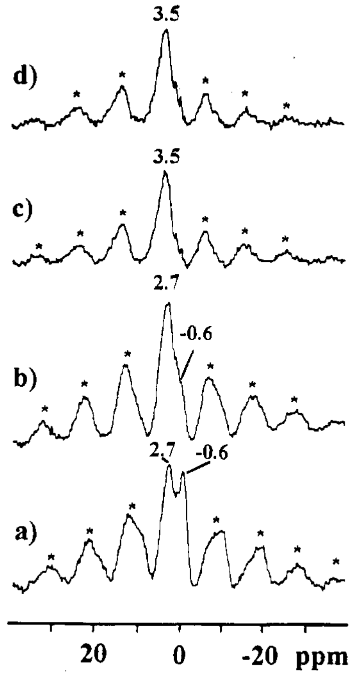

Figure 5. ^1H MAS NMR spectra of V_2O_5/Al_2O_3 catalysts as a function of vanadium oxide content: (a) 0%, (b) 5%, (c) 17%, and (d) 19%.

Figures 2 and 3). This means that most of the remaining OH groups for these high-loaded Mo oxide samples are not accessible for H−D exchange and, therefore, are not located on the outer surface of the alumina support. Thus, Mo oxide cannot titrate these remaining OH groups since they are not accessible and may exist in closed pores. Furthermore, the spectra of the Mo oxide/alumina samples with high Mo oxide loadings have chemical shifts and linewidths which are slightly different from those of the H−D exchanged samples. Integration of the ^1H NMR signals for the 18% MoO_3/Al_2O_3 sample reveals approximately a 30% drop in signal upon deuteration (see Figure 2). This suggests the presence of protons associated with the low-field line that are capable of H−D exchange. These protons give ^1H MAS NMR features similar to that observed for Mo−OH (see Figure 4) and Al−OH and, consequently, their location cannot be discriminated on the basis of ^1H MAS NMR measurements.

V_2O_5/Alumina. Deposition of vanadium oxide on the alumina support also significantly affected the alumina support hydroxyls as shown in Figure 5. The V oxide content of the catalysts was varied from 0 to 19% V_2O_5, and previous Raman studies concluded that on this alumina support approximately 20% V_2O_5 corresponds to a monolayer of surface vanadium oxide species.[16] At low surface vanadium oxide coverages on alumina, there is a decrease in the intensity of the high-field line at −0.6 ppm. At high surface vanadium oxide coverages on alumina, there is a complete disappearance of the high-field line at −0.6 ppm and a decrease in intensity as well as shift of the low-field line to 3.5 ppm. The H−D exchange experiments presented in Figure 6 for the V oxide/alumina catalysts reveal that at high surface vanadium oxide coverages the remaining OH groups are not accessible and, consequently, are not located on the outer surface of the alumina support. The slight shift in the positions and widths of the high-field line upon H−D exchange reveal that some of these protons are capable of H−D exchange. Integration of the ^1H NMR signals for the 17% V_2O_5/Al_2O_3 sample reveals approximately a 20% drop in signal upon deuteration. These protons give similar ^1H NMR features for V−OH (see Figure 4) and Al−OH and their location cannot be discriminated with ^1H MAS NMR measurements.

Discussion

Comparison of the above ^1H MAS NMR results with the previous infrared spectroscopy findings[17] on these alumina-supported metal oxide catalysts reveals the similarities as well as subtle differences between these two spectroscopic techniques. Both ^1H MAS NMR and IR demonstrate that the basic surface hydroxyls are preferentially titrated by the deposition of the two-dimensional molybdenum/vanadium oxide overlayers. The IR information is much richer in the hydroxyl region because as many as five different surface hydroxyls are detected, but only two major surface hydroxyl signals are detected in the ^1H MAS NMR spectra (at −0.6 ppm, basic, and approximately 3.0 ppm, acidic). The IR measurements show that the surface hydroxyls are sequentially titrated from the most basic to the most acidic hydroxyl with increasing metal oxide loading. The ^1H MAS NMR measurements employing deuterated water show that there are also unreacted alumina hydroxyls present in the catalysts that are not accessible and apparently present in closed pores of the alumina support. These hydroxyls are typically not detectable in IR because of vibrational broadening due to hydrogen bonding but can also be clearly revealed in IR after exchange with deuterated water because of the significant vibrational shift of deuterium. Furthermore, the quantitative ^1H MAS NMR studies with the deuterated water also reveal that essentially all the accessible surface hydroxyls are titrated at monolayer coverages of vanadium/molybdenum oxide on the alumina support (see Figure 2) and that these surface metal oxides are homogeneously distributed over the entire exposed support surface rather than concentrated as islands. This conclusions is also supported by CO_2 chemisorption experiments which show that the exposed basic alumina surface hydroxyls are essentially absent at monolayer coverage and not available for CO_2 chemisorption.[13,17]

The ^1H MAS NMR deuteration studies also imply the presence of some accessible protons, at approximately 3.0 ppm, that are only present at high surface metal oxide coverages. The presence of these additional protons is suggested by the slight changes in line width and peak positions of the ^1H MAS NMR signals upon deuteration and a 20−30% decrease in the ^1H NMR signal upon deuteration. These protons are typically not detectable in the IR hydroxyl region, probably due to their low concentrations or to vibrational broadening as a result of hydrogen bonding, but should be observable by IR upon deuteration. These protons are thought to be indirectly detected as Bronsted acid sites via IR pyridine adsorption experiments.[17]

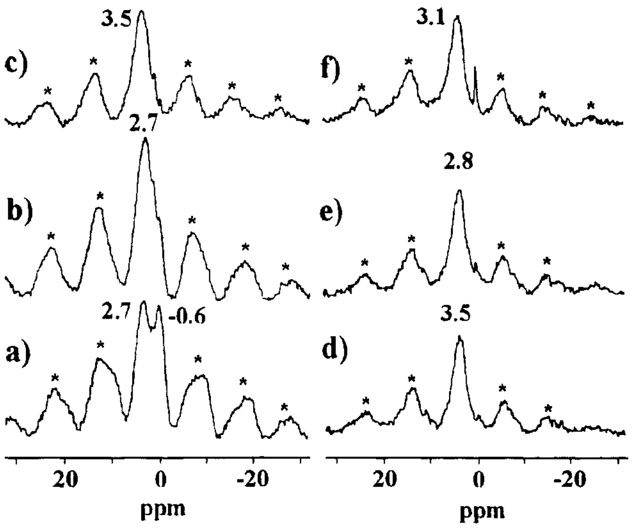

Figure 6. ^1H MAS NMR spectra of V_2O_5/Al_2O_3 catalysts before H−D exchange (a−c) and after H−D exchange (d−f) as a function of vanadium oxide content: (a, d) 0%, (b, e) 5%, and (c, f) 17%.

The ^1H MAS NMR measurements reveal that these minority accessible protons cannot be titrated by the surface metal oxide overlayers. The exact location of these Bronsted protons are not known because their NMR peak position coincides with the NMR peak positions for M−OH (M = V, Mo, Al). In a previous publication it was proposed that these protons may be located at bridging M−OH−Al bonds (M = V or Mo).[17] However, no direct information about the location of these Bronsted acid protons have been obtained by any spectroscopic technique to date.

Comparison of ^1H MAS NMR data for the alumina-supported vanadium oxide and molybdenum oxide catalysts (Figures 1, 3, 5, and 6) reveals a very similar trend with regard to the interaction of these two surface metal oxide overlayers with the alumina hydroxyls. Structural characterization studies, however, have shown that both of these surface metal oxide overlayers prefer different coordinations: surface molybdenum oxide species on alumina possess both 4- and 6-fold coordination[18] and surface vanadium oxide species on alumina primarily possess 4-fold coordination.[11] Similar observations were also made for other metal oxides (rhenium oxide, chromium oxide, tungsten oxide, and niobium oxide) supported on alumina.[17,20] Thus, it appears that the interaction of certain metal oxides, those metal oxides possessing high oxidation states, with the surface hydroxyls of oxide supports is not dependent on the specific structure of the surface metal oxide overlayer.

Quantitative comparison of the decrease in the number of surface OH groups for the alumina supported vanadium oxide and molybdenum oxide catalysts (see Figure 2) suggests that there may be some differences since the number of OH groups decreases more rapidly with vanadium oxide loading than with molybdenum oxide loading. However, when the weight loading is converted to molar loading, this difference is essentially absent since vanadium oxide has approximately half the mass of molybdenum oxide and both catalysts possess essentially the same surface areas. There is still a difference between monolayer coverage for alumina-supported vanadium oxide (20% V_2O_5) and molybdenum oxide (20% MoO_3) since surface vanadium oxide has twice the surface density of surface molybdenum oxide. This suggests that the surface vanadium oxide species are able to pack twice as many oxide units per unit surface area as the surface molybdenum oxide species. It is not clear from any spectroscopic studies how the surface vanadium oxide overlayer is achieving this packing of higher surface density. It is possible that the surface vanadium oxide overlayer is actually a bilayer, but no direct evidence is currently available. This higher surface density of the vanadium oxide overlayer may also be related to the much higher number of surface Bronsted acid sites detected for the alumina-supported vanadium oxide monolayer relative to the alumina-supported molybdenum oxide monolayer.[17]

Conclusions

The interactions of surface vanadium oxide and molybdenum oxide overlayers with the surface hydroxyls of an alumina support were examined with ^1H MAS NMR spectroscopy. The measurements demonstrated that the metal oxide overlayers are homogeneously distributed over the alumina surface and essentially titrate all the accessible surface hydroxyl at monolayer coverage. The ^1H MAS NMR investigation also revealed that there are additional minority protons formed at monolayer coverage, suspected of being Bronsted acid sites, which are not titrated by the vanadium/molybdenum oxide overlayers and are capable of undergoing H−D exchange. In addition, the ^1H MAS NMR investigation revealed that there are also protons that are not accessible to the vanadium/molybdenum oxide overlayers or undergo H−D exchange. These protons are thought to be present inside closed pores of the alumina support that are inaccessible. The present ^1H MAS NMR results are in excellent agreement with corresponding IR spectroscopy results on the same catalysts. The different structures of the metal oxide overlayers do not appear to affect the overall interaction of the metal oxide overlayers with the alumina surface hydroxyls. However, the different packing densities of the vanadium oxide and molybdenum oxide overlayers are thought to affect the number of surface Bronsted acid sites at higher surface coverages.

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