

Characterization of MoO₃/TiO₂ (Anatase) Catalysts by ESR, ¹H MAS NMR, and Oxygen Chemisorption[†]

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A series of molybdena catalysts supported on anatase titania with Mo loadings ranging from 2 to 12 wt % were investigated by ¹H MAS NMR, XRD, ESR, and oxygen chemisorption. ¹H MAS NMR spectra reveals the presence of two types of OH groups (acidic and basic) on TiO₂. Dispersion of molybdena was determined by the oxygen chemisorption at 623 K through a static method on the samples prereduced at the same temperature. At low Mo loadings, i.e., below 6% Mo, molybdenum oxide is found to be present in a highly dispersed state. A comparison of the dispersion of molybdena determined by low-temperature oxygen chemisorption (samples reduced at 773 K for 6 h and subsequent oxygen chemisorption at 195 K) with that determined at 623 K shows that the latter method provides a better measure of the dispersion of molybdena. ESR results suggest the presence of Mo⁵⁺ in the reduced catalysts.

Introduction

Supported oxides and sulfides of molybdenum are the subject of extensive investigation because of their importance in many industrially important reactions including hydrodesulfurization (HDS), oxidation, and metathesis of olefins.^{1–13} Molybdenum oxide is also active for the oxidation of alcohols and hydrocarbons.^{6–13} In many reactions catalyzed by molybdenum oxide, the active component is often supported or mixed with oxides such as vanadium. It is well established that the reactivity of supported molybdena catalysts mainly depends on the dispersion of active phase, which in turn can be greatly influenced by the nature of support and the method of preparation of the catalysts. In the recent past, many studies have been focused on relating the structural information of the supported molybdenum oxides/sulfides with their catalytic properties. Considerable efforts have been made to develop methods for determining the dispersion of molybdena in supported catalysts. These include use of electron spectroscopy for chemical analysis (ESCA)^{14,15} and oxygen chemisorption.^{4,11,16–18,35} There has been a plethora of research work published using the latter method which is inexpensive and provides quantitative information about the molybdena dispersion.

Among the supported molybdena systems, MoO₃/TiO₂ catalyst has been the subject of many recent investigations. TiO₂ as a support has received much attention in catalysis research over the past decade because of the interaction between group VIII metals and certain reducible oxides.^{29–31} Apart from metal catalysts supported on TiO₂, metal oxides supported on TiO₂ such as the V₂O₅/TiO₂ system is a classic example of support enhancement of the active phase. In recent years the development of high-resolution solid-state NMR spectroscopy provided new possibilities for studying the structural and adsorption properties of heterogeneous catalysts.³² The use of magic angle spinning (MAS) of the samples for narrowing of NMR lines

makes it possible to obtain high-resolution NMR spectra of solid catalysts and adsorbed molecules. In ¹H NMR MAS spectra of various acidic and basic catalysts, signals from different surface OH groups bound to certain elements are often resolved, and thus allow an accurate measurement of their chemical shifts. Recently, Mastikhin et al.,³² reviewed the application of ¹H NMR studies of a variety of heterogeneous catalysts. Enriquez et al.³³ reported the effect of distribution of OH groups on the localization of surface water on anatase. In the present investigation, we report the characterization of Mo/TiO₂ (anatase) catalysts by XRD, ESR, oxygen chemisorption, and ¹H NMR MAS techniques. The purpose of this work is to estimate the dispersion of molybdena supported on TiO₂ (anatase) and also to identify the changes in the structure of the molybdena phase as a function of the active component loading.

Experimental Section

A series of MoO₃ catalysts with Mo loadings ranging from 2 to 12 wt % supported on anatase TiO₂ (Ti-Oxide UK Ltd., SA 92 m² g⁻¹) were prepared by incipient wetting of the support using aqueous ammonium heptamolybdate solution at pH 8. The catalysts were dried at 383 K for 16 h and subsequently calcined in air at 773 K for 6 h.

Oxygen chemisorption was measured by a static method using an all-Pyrex glass system capable of attaining a vacuum of 10⁻⁶ Torr. The details of experimental setup are given elsewhere.³⁴ Two different methods of oxygen chemisorption were employed to determine the dispersion of molybdena on titania. In the first method, the samples were prereduced in a flow of hydrogen (40 mL/min) at 623 K for 2 h and evacuated at the same temperature for 1 h. Oxygen chemisorption uptakes were determined as the difference of two successive adsorption isotherms measured at 623 K. The surface area of the catalysts was determined by the BET method using nitrogen physisorption at 77 K. In the second method, the catalyst sample was reduced at 773 K for 6 h, and oxygen chemisorption was determined at 195 K using the method employed by Parekh and Weller.³⁵

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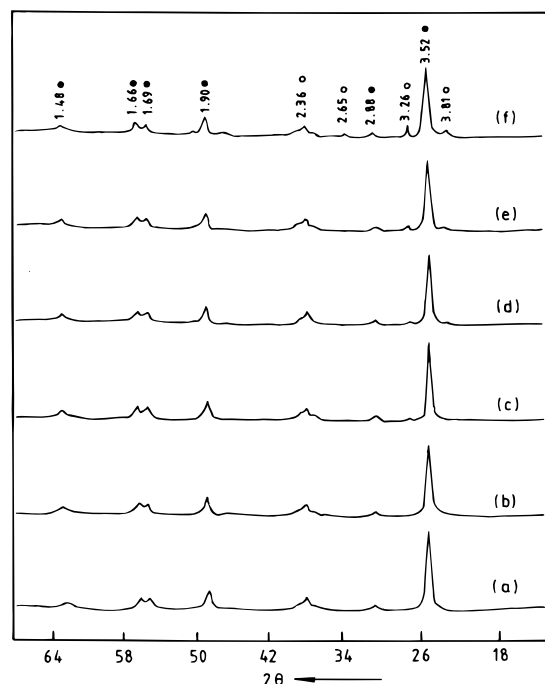


Figure 1. X-ray diffractograms of MoO₃/TiO₂ (anatase) catalysts: (a) 2% Mo/TiO₂, (b) 4% Mo/TiO₂, (c) 6% Mo/TiO₂, (d) 8% Mo/TiO₂, (e) 10% Mo/TiO₂, (f) 12% Mo/TiO₂. ○, XRD lines due to MoO₃; ●, XRD lines due to anatase TiO₂.

¹H MAS NMR spectra were obtained on a Bruker CXP-300 spectrometer at 300.066 MHz, using 50 kHz. The $\pi/2$ radiation in pulse was 5 ms and the pulse repetition frequency 0.2 Hz. Prior to NMR experiments the samples were placed in special NMR tubes of 7 mm o.d. and 12 mm length and then evacuated at 523 K at 10^{-3} Pa for 24 h. The spinning of the samples was performed in quartz rotors at frequency 3–3.5 kHz using a probe with minimal background signal. The probe head, rotor, and the sample tubes were dried to remove the traces of water from their outside surfaces. Chemical shifts were measured relative to tetramethylsilane (TMS) as an external reference.

ESR measurements were recorded at ambient temperature on a Bruker ER-200D-SRC X-band spectrometer with 100 kHz modulation. The reduced catalysts for the ESR study were prepared in quartz tubes (25 cm long, 4 mm diameter). The samples were prereduced at 623 K for 2 h in a continuous flow (40 mL/min) of purified hydrogen. The setup was subsequently evacuated for 1 h at 10^{-6} Torr. The catalysts thus prepared was transferred to the ESR tube and sealed off under vacuum. X-ray diffraction studies of the calcined catalysts were recorded on a Philips diffractometer using Ni-filtered Cu K α radiation.

Results and Discussion

Powder X-ray diffraction patterns of MoO₃ catalysts supported on anatase TiO₂ are shown in Figure 1. The diffractograms indicate the absence of characteristic peaks of MoO₃ at lower Mo loadings. However, XRD lines at $d = 3.81$, 3.26 , and 2.36 Å appeared due to crystalline MoO₃ phase at higher Mo loadings. The most intense XRD line due to MoO₃, corresponding to the (021) plane at $d = 3.26$ Å, was observed only at 6 wt % of Mo and higher on anatase support (Figure 1c–1f). The intensity of this peak increases with increase of Mo loading in the catalyst. The XRD patterns also indicate that no characteristic peaks were found due to a mixed oxide phase of MoO₃ and TiO₂ even at the highest loading of Mo in the catalyst. The absence of XRD peaks due to MoO₃ at lower

TABLE 1: Results of Oxygen Uptake, Dispersion, Oxygen Atom Site Density, and Surface Area of Various MoO₃/TiO₂ Catalysts

cat. compn, wt % Mo	SA, ^b m ² g ⁻¹	O ₂ uptake, μ mol g ⁻¹	O site density, 10 ¹⁸ m ⁻²	dispersion O/Mo ^c
0	92			
2	48	111.5	2.78	0.99
4	52	223.0	4.26	1.00
6	51	303.4	5.90	0.97
8	46	331.0	7.17	0.79
10	49	346.0	8.51	0.66
12	40	342.8	10.29	0.54

^a $T_{\text{reduction}} = T_{\text{adsorption}} = 623$ K. ^b BET surface area determined after oxygen chemisorption. ^c Dispersion = fraction of molybdenum atoms at the surface assuming $O_{\text{ads}}/Mo_{\text{surf}} = 1$.

TABLE 2: Results of Oxygen Uptake, Dispersion, Oxygen Atom Site Density, and Surface Area of Various MoO₃/TiO₂ Catalysts

cat. compn, wt % Mo	SA, ^b m ² g ⁻¹	O ₂ uptake, ^a μ mol g ⁻¹	O site density, 10 ¹⁸ m ⁻²	dispersion ^c O/Mo
2	57	85.0	1.80	0.41
4	53	134.8	3.87	0.32
6	51	170.4	4.02	0.27
8	46	194.8	5.10	0.23
10	47	197.6	5.06	0.19
12	38	199.2	6.31	0.16

^a $T_{\text{reduction}} = 773$ K, $T_{\text{adsorption}} = 195$ K. ^b BET surface area determined after oxygen chemisorption. ^c Dispersion = fraction of molybdenum atoms at the surface assuming $O_{\text{ads}}/Mo_{\text{surf}} = 1$.

concentration of the catalysts indicates that the MoO₃ phase is present as a highly dispersed or amorphous state on the surface of TiO₂. However, the possibility cannot be ruled out of the existence of MoO₃ crystallites having size less than 40 Å in the lower loadings of the catalysts, which is beyond the detection capacity of the powder X-ray diffraction technique.

As mentioned earlier in the Experimental Section, two methods of oxygen chemisorption were employed to determine the dispersion of molybdenum oxide on titania (anatase). In the first method, the procedure described by Oyama et al.¹⁶ was followed for the estimation of dispersion of molybdenum oxide. In this method, the catalysts were prereduced at 623 K for 2 h, and subsequent oxygen chemisorption was carried out at the same temperature. The amount of oxygen chemisorbed was calculated using the double-isotherm method described elsewhere.³⁵ Pure TiO₂ support did not chemisorb oxygen under similar experimental conditions employed for MoO₃/TiO₂ catalysts. The O₂ uptake determined at 623 K by various MoO₃/TiO₂ catalysts are given in Table 1. At low Mo loadings the oxygen uptake approached a stoichiometry of one oxygen atom per one molybdenum atom. Using this stoichiometry, Oyama et al.,^{16,17} defined the dispersion of molybdena as a fraction of total O atoms (determined from oxygen chemisorption) to total Mo atoms in the sample. The changes in the dispersion of molybdena and the oxygen atom site density as a function of Mo loading are also reported in Table 1. In the second method of oxygen chemisorption, the catalysts were reduced at 773 K for 6 h, and oxygen chemisorption was measured at 195 K. The results of Table 2 represent the oxygen uptake measured at 195 K for various MoO₃/TiO₂ catalysts. The oxygen chemisorption capacities are found to increase with molybdenum loading up to 6 wt % of Mo and levels off at higher loadings. The leveling off is attributed to the formation of monolayer of molybdenum oxide on titania. At high molybdenum loadings no further increase of oxygen chemisorption was noticed. This might be due to the presence of the crystalline molybdena phase

as seen in the XRD results and which upon prereduction with hydrogen does not appreciably chemisorb oxygen. Other information such as oxygen atom site density, dispersion, etc., derived from oxygen uptake is given in Table 2. The oxygen atom site density values reported in Tables 1 and 2 suggest that the oxygen chemisorption in the plateau region is indeed titrating surface molybdenum atoms. These findings are in excellent agreement with Oyama et al.¹⁶ A comparison of dispersion of molybdenum oxide supported on titania (Tables 1 and 2) reveals that the prereduction of catalysts at 623 K and subsequent oxygen chemisorption at the same temperature provides a better measure of the dispersion of molybdena (Table 1) than the samples reduced at 773 K followed by oxygen chemisorption at 195 K. The reduction behavior of supported molybdena catalysts prior to oxygen chemisorption is an interesting topic. Many authors reported using the reduction of molybdena at 773 K followed by oxygen chemisorption at 195 K or 77 K for determining dispersion of molybdena.^{11,35–39} These conditions were evaluated by Rodrigo et al.,⁴⁰ who concluded that oxygen chemisorption at these conditions does not provide a quantitative determination of Mo dispersion because a fraction of the reduced Mo is in the bulk. It has been shown recently that oxygen chemisorption sites are easily generated at very mild reduction conditions.^{16,17,41} Our results of oxygen chemisorptions are in excellent agreement with Oyama et al.,¹⁷ on $\text{MoO}_3/\text{TiO}_2$ (anatase). Similar to our findings, they have also obtained higher dispersion of MoO_3 at low loadings on titania (anatase).

The findings of oxygen chemisorption by the two methods are supported by XRD results (Figure 1). The most intense X-ray diffraction line ($d = 3.26 \text{ \AA}$) due to MoO_3 corresponds to the (021) plane and the peaks observed from 6 wt % of Mo on anatase. We have calculated the theoretical monolayer capacity of MoO_3 supported on anatase TiO_2 as described by Van Hengstum et al.,²⁷ taking 0.16 wt % of MoO_3 per m^2 of surface. Accordingly, the theoretical monolayer capacity of MoO_3 supported on titania employed in the present study having a BET surface area (SA) of $92 \text{ m}^2 \text{ g}^{-1}$ corresponds to 14.72% MoO_3 or 9.85% Mo. However, XRD results of the present work show the presence of MoO_3 crystallites appearing from 6% Mo (Figure 1c) that is about 60% of a theoretical monolayer based on the structure of MoO_3 and agrees very well with those reported in the literature. We have therefore denoted this loading representing the experimentally found monolayer capacity. Several authors reported the structure of monolayer MoO_3 on TiO_2 .^{19–21,42–45} For example, Ng and Gulari⁴² reported that as the coverage of TiO_2 by molybdenum approaches one monolayer of tetrahedrally coordinated molybdates, extensive polymerization occurs and octahedrally coordinated polymeric surface species are formed. Bond et al.⁴³ have reported that the monolayer capacity of MoO_3 supported on TiO_2 (Degussa P-25, SA $52 \text{ m}^2 \text{ g}^{-1}$) was found to be 4.1 wt % MoO_3 . Recently, Matralis et al.⁴⁴ reported that the monolayer capacity for MoO_3 supported on TiO_2 (Sakai, SA $74 \text{ m}^2 \text{ g}^{-1}$) corresponds to 6.1 wt % MoO_3 . Liu et al., found that, for $\text{MoO}_3/\text{TiO}_2$ catalysts prepared by impregnation, the saturation coverage with MoO_3 corresponds to a density of 4×10^{14} Mo atoms per cm^2 of TiO_2 . This concentration of MoO_3 amounts to half of the theoretical monolayer capacity, and it was explained by the structure of the MoO_3 monolayer in which each Mo cation shares two bridging O anions with its two nearest Ti cations. In present study the leveling off of oxygen chemisorption beyond the monolayer composition (above 6% Mo loading) might be due to the presence of the larger crystallites of MoO_3 as evidenced from the X-ray diffraction results (Figure 1c–1f). These larger

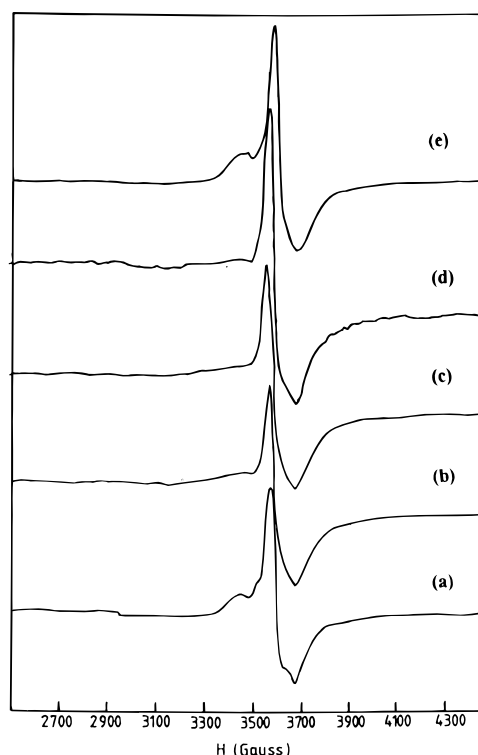


Figure 2. ESR spectra of reduced (at 623 K for 2 h) MoO_3 catalysts supported on TiO_2 (anatase) at 300 K: (a) 2% Mo/TiO_2 , (b) 4% Mo/TiO_2 , (c) 6% Mo/TiO_2 , (d) 8% Mo/TiO_2 , (e) 10% Mo/TiO_2 , (f) 12% Mo/TiO_2 .

crystallites of molybdenum oxide are preventing reduction of the catalyst with hydrogen gas; therefore, no appreciable change in oxygen uptake is observed for the catalysts beyond the monolayer composition. It is generally believed that oxygen selectively chemisorbs dissociatively at low temperature (195 K) on the coordinatively unsaturated sites (CUS) generated upon reduction.¹⁸ Most of the CUS sites are located on the MoO_2 phase as a patchy monolayer on the TiO_2 surface. Based on the “patch” model of Hall,⁴⁵ the nature of the oxygen chemisorption sites on $\text{Mo}-\text{Al}_2\text{O}_3$ catalysts has been discussed by Nag.¹⁸ It has been envisaged that at lower Mo loadings small patches of Mo oxide, two layers thick and with Mo in an octahedral coordination, are formed on the support surface. Upon reduction, coordinatively unsaturated sites (CUS) of MoO_2 are generated by the removal of oxygen from the edge and corner sites of the patches.⁴⁵ These are the sites upon which oxygen chemisorption take place. It has also been proposed that as the Mo loading increases, the number of these patches increases with attendant increase in the number of CUS up to the monolayer level. Beyond the monolayer level the patches grow three-dimensionally, thus decreasing the dispersion of Mo oxide. It is proposed that a similar mechanism operates in the $\text{Mo}-\text{TiO}_2$ system, and the present results can be explained with the help of the above concepts. Thus, the initial increase and subsequent leveling off in the oxygen uptake capacity of the catalysts as a function of Mo loading are due to generation of new CUS up to monolayer level and a subsequent decrease in the edge and corner growth. The ESR results of the hydrogen reduced catalysts further supports the findings of oxygen chemisorption. The spectra of reduced catalysts recorded at 300 K are represented in Figure 2. In all the catalysts an axially symmetric spectrum appears at the center of the pattern with $g_{\parallel} = 1.917$. The intensity of the anisotropic spectrum increased with Mo loading. The spectral features of hydrogen reduced

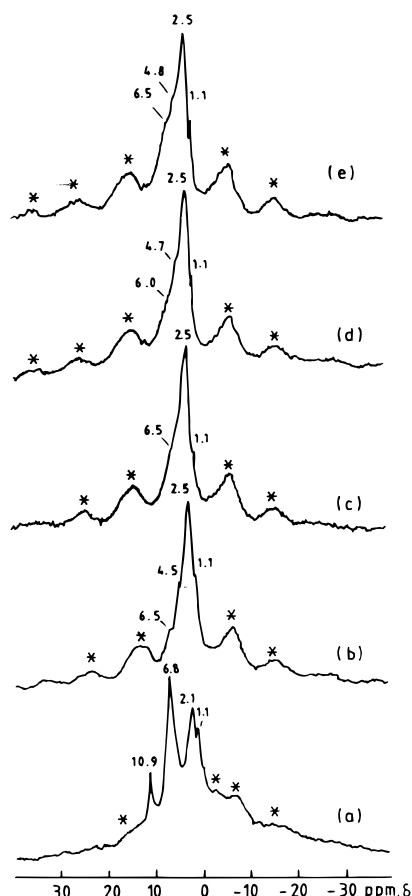


Figure 3. ^1H NMR MAS spectra of TiO_2 (anatase) and $\text{MoO}_3/\text{TiO}_2$ (anatase) samples at various "Mo" levels: (a) TiO_2 (anatase), (b) 2% Mo/TiO_2 , (c) 4% Mo/TiO_2 , (d) 8% Mo/TiO_2 , (e) 12% Mo/TiO_2 . Asterisks represent spinning sidebands.

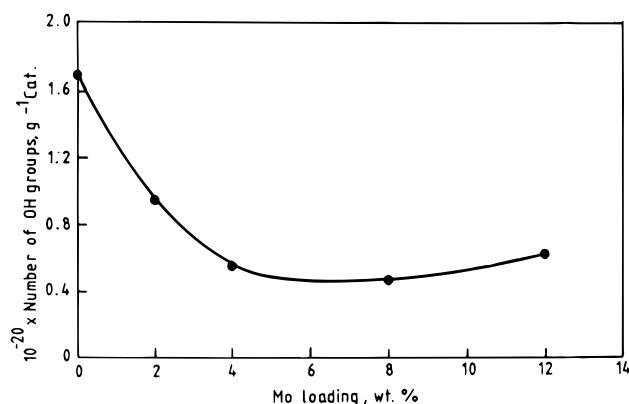


Figure 4. Concentration of the surface OH groups as a function of Mo content on various $\text{MoO}_3/\text{TiO}_2$ (anatase) catalysts.

samples suggest the presence of Mo^{5+} and are in good agreement with earlier works.⁴⁶

The representative ^1H NMR spectra of various MoO_3 catalysts supported on anatase modification of TiO_2 are shown in Figure 3. The dependence of the total signal intensity measured relative to a standard sample of SiO_2 evacuated at 573 K for 4 h which contained 5×10^{19} OH groups as a function of MoO_3 content for anatase supported catalysts is illustrated in Figure 4.

According to previous work,^{47–52} the anatase surface consists predominantly of the most dense (001) plane, with admixture of (010) and (100) planes having about the same structure. Ti atoms in these planes are pentacoordinated with respect to oxygen. There are two types of oxygen atoms on each of the

(001), (010), and (100) planes of TiO_2 surface. Oxygen atoms of the first type are coordinated to Ti atoms and have a formal charge $-2/3$, assuming all the bonds are purely ionic. They are located 0.41 Å above the (001) plane. The oxygen atom of second type, located 0.41 Å below (001) plane, are three-coordinated to Ti atoms and are neutral. For (010) and (100) planes, all oxygen atoms are located in the plane. Dissociation of H_2O molecules over a TiO_2 surface results in the formation of OH groups with the formal charges of $-1/3$ and $1/3$ on the protons, respectively. Yates⁵² found the existence of two types OH groups on the anatase surface, and this was confirmed by the infrared studies (two stretching infrared absorption bands at 3715 and 3675 cm^{-1}). The band at 3675 cm^{-1} corresponds to the adjacent OH groups interacting via weak hydrogen bonds, while the band at 3715 cm^{-1} can be attributed to OH groups attached to Ti atoms. Tanaka and White⁵³ reported that similar types of OH groups are also characteristic for rutile TiO_2 . The observation of two main peaks in the ^1H MAS NMR spectra of the anatase samples of the present study is in agreement with this model. The downfield peak at $\delta = 6.5$ ppm can be attributed to acidic OH groups coordinated to two Ti atoms, while the signal with $\delta = 2.1$ – 2.5 ppm is more likely to belong to basic OH groups coordinated to one Ti atom. The low field peak most probably can be ascribed to the more acidic OH groups localized on bridging oxygen atoms and forming weak hydrogen bonds adjacent to oxygen atoms, while the high field peak was ascribed to the more basic OH groups, where hydrogen atoms are bound to terminal oxygen atoms. The unidentified sharp line at $\delta = 10.9$ ppm most probably belongs to some OH groups associated with impurities present in the samples under study.

The results presented in Figure 4 unambiguously show the selective interaction of Mo atoms with the acidic Ti–OH groups while the basic OH groups remain unperturbed when MoO_3 is supported on the TiO_2 surface. The impurity OH groups also decrease in the sample with supported MoO_3 . The decrease of the NMR signal intensity proceeds rapidly at the lowest concentration (2 wt % Mo on TiO_2) studied; thereafter, the decrease in intensity becomes much less pronounced (Figure 4). This is the case for anatase supported molybdena catalyst samples. It should be noted that the largest Mo concentration (12 wt % on TiO_2) is larger than the formal monolayer amount of MoO_3 . This observation indicates that there is a nonuniform distribution of MoO_3 on the TiO_2 surface in agreement with the patchy-monolayer model of $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts discussed elsewhere.¹⁸

A comparison of the quantity of reacted OH groups with the quantity of adsorbed Mo atoms reveals that, at the lowest content of molybdenum (2 wt % Mo on TiO_2), each Mo atom reacts with approximately one OH group. However, at the higher Mo contents several Mo atoms are required for the interaction with one OH group. Therefore, most probably at the low Mo (2%) concentration the catalytic monomeric isolated Mo species are formed, while at the larger concentrations of Mo most probably the clusters containing several Mo atoms are created on the TiO_2 surface. Thus, ^1H magic-angle-spinning NMR spectra of MoO_3 catalysts supported on anatase polymorph reveal the presence of two types of OH groups on the surface: one ascribed to OH groups of acidic nature and other to basic OH groups. The nature of interaction of surface molybdenum oxide with TiO_2 and other supported oxides has been discussed by Desikan et al.¹⁷ using Raman spectroscopy. They concluded that molybdenum oxide strongly interacts with titania, moderately with alumina, and weakly with silica, and it is primarily of an acid–

base nature. The present ^1H NMR results also reveals that the interaction of the MoO_3 with TiO_2 is of acid–base nature.

Conclusions

^1H MAS NMR spectra of MoO_3 catalysts supported on anatase titania reveal the presence of two types of OH groups on the surface: one ascribed to OH groups of acidic nature and other to basic OH groups. Oxygen chemisorption measured at 623 K on the catalysts reduced at the same temperature provides a better measure of dispersion of molybdenum oxide supported on titania as these results are supported by the XRD findings.

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