Letter

Characterization of MoO_3/TiO_2 catalysts by ^1H magic-angle-spinning NMR spectroscopy [1]

K.V.R. Chary [a,*], V. Vijayakumar [a], P. Kanta Rao [a], A.V. Nosov [b], V.M. Mastikhin [b]

[a] Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India
[b] Institute of Catalysis, Novosibirsk, Russia

Abstract

^1H MAS NMR spectra of molybdenum oxide catalysts supported on anatase and rutile polymorphs of TiO_2 reveals the presence of two types of OH groups (acidic and basic) on the surface of TiO_2.

Keywords: Magic angle spinning; Molybdenum; Supported catalysts; Titania

1. Introduction

Supported oxides and sulfides of molybdenum are the subject of extensive investigation because of their significant catalytic role in many industrially important reactions including hydrodesulfurization (HDS), oxidation and metathesis of olefins. It is well documented that the efficiency of supported molybdena catalysts mainly depends on the dispersion of the active component, which in turn can be greatly influenced by the nature of supported oxide and the method of preparation of the catalysts. In the recent past many studies have been made attempting to correlate the structural information of the supported molybdenum oxides/sulfides with their catalytic properties. Among the supported molybdena systems, MoO_3/TiO_2 catalysts have been the subject of recent investigations.

TiO_2 as a support has received much attention in catalysis research over the last decade because of the interaction between group VIII metals and certain reducible oxides. Apart from metal catalysts supported on TiO_2, metal oxides supported on TiO_2 such as the V_2O_5/TiO_2 system is a classical example of support enhancement of the active phase. A considerable amount of research work has been carried out so far to characterize MoO_3/TiO_2 catalysts by various spectroscopic techniques which include the use of ESCA [1–4], laser Raman spectroscopy [1,2,5,6], FT-IR [7], ion scattering spectroscopy (ISS) [7], X-ray diffraction [2,7] and EXAFS [8]. In recent years the development of high resolution solid state NMR spectroscopy provided new possibilities for studying the adsorption and catalysis. 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, sig-

* Corresponding author.
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nals 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. [9] reviewed the application of ^{1}H NMR studies of a variety of heterogeneous catalysts. Enriquez et al. [10] reported the effect of distribution of OH groups on the localization of surface water on anatase. In the present investigation, we report new complementary results of ^{1}H MAS NMR of molybdenum oxide catalysts supported on the anatase and rutile polymorphs of TiO_2.

2. Experimental

A series of MoO_3 catalysts with Mo loadings ranging from 2% to 12% w/w supported on anatase (Ti-oxide UK Ltd., surface area 92 m^2 g^{-1}) and rutile (Ti-oxide UK Ltd., surface area 33 m^2 g^{-1}) were prepared by incipient wetting of the supports using an aqueous solution containing ammonium heptamolybdate at pH 8. The impregnated samples were dried at 383 K for 16 h and then calcined at 773 K for 16 h in air.

The ^{1}H NMR spectra were obtained on a Bruker CXP-300 spectrometer at 300.066 MHz, using a frequency range of 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 tetramethyl silane (TMS) as an external reference.

3. Results and discussion

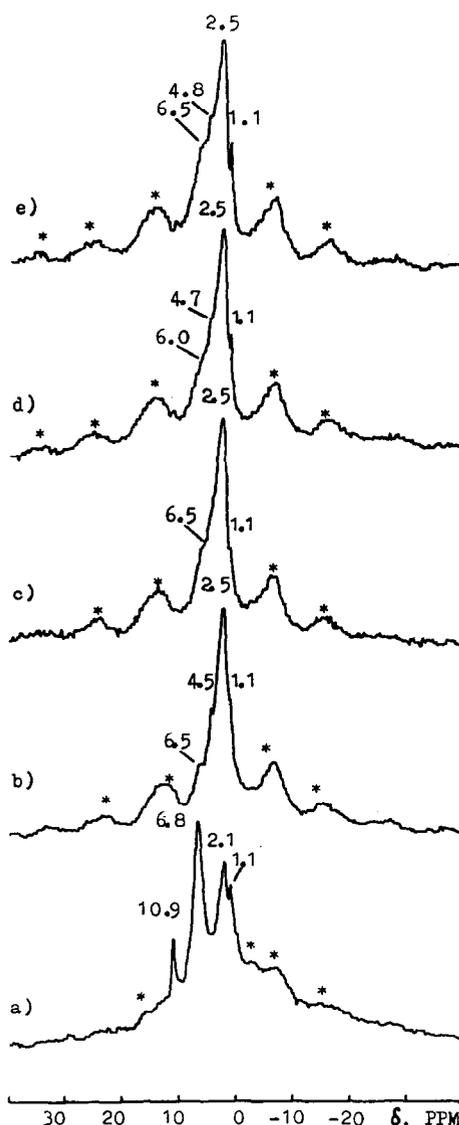The representative ^{1}H NMR spectra of various MoO_3 catalysts supported on anatase and rutile

Fig. 1. ^{1}H NMR MAS spectra of TiO_2 (anatase) and MoO_3/TiO_2 (anatase) samples at various 'Mo' levels. (a) TiO_2 (anatase) ; (b) 2% Mo ; (c) 4% Mo ; (d) 8% Mo ; (e) 12% Mo.

modifications of TiO_2 are shown in Figs. 1 and 2. The dependence of the total signal intensity measured relative to the standard sample (SiO_2 evacuated at 573 K for 4 h contained 5×10^{19} OH groups) as a function of MoO_3 content for both anatase and rutile supported catalysts, are illustrated in Fig. 3.

According to previous work [11–16] the anatase surface consists predominantly of the most dense (001) plane, with admixture of (010) and
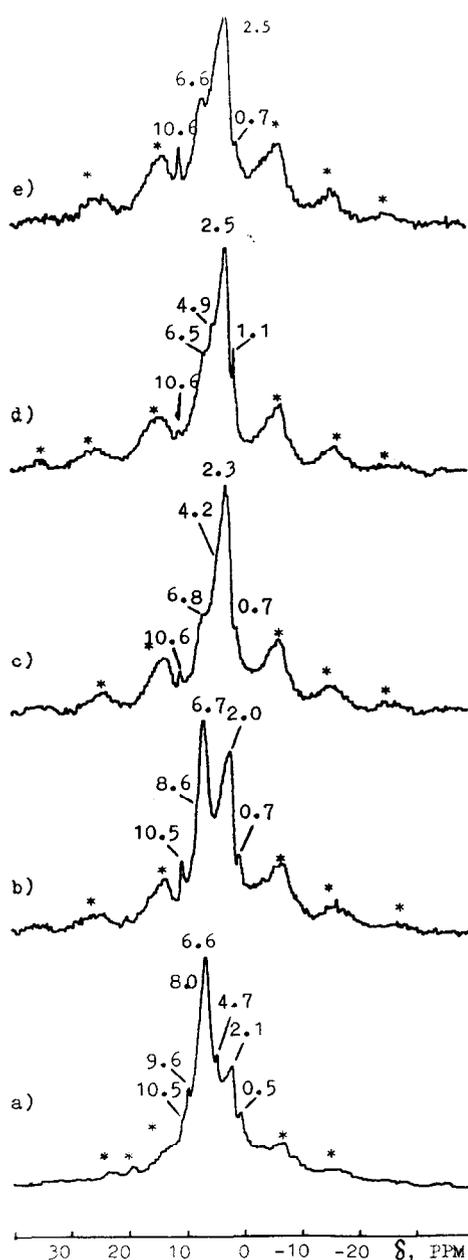
Fig. 2. ¹H NMR MAS spectra of TiO₂ (rutile) and MoO₃/TiO₂ (rutile) samples at various 'Mo' levels. (a) TiO₂ (rutile); (b) 2% Mo ; (b) 4% Mo ; (c) 8% Mo ; (d) 10% Mo.

(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 (001),(010) and (100) planes of TiO₂ surface. Oxygen atoms of the first type are coordinated to Ti atoms and have a formal

charge $-2/3$, assuming all the bonds in TiO₂ are pure ionic. They are located 0.41 Å above the (001) plane. The oxygen atoms of second type, located 0.41 Å below (001) plane, are three-coordinated to Ti atoms are neutral. For (010) and (100) planes, all oxygen atoms are located in the plane. Dissociation of H₂O molecules over a TiO₂ surface results in the formation of OH groups with the formal charges of $-1/3$ and $1/3$ on the protons respectively. Yates [16] found the existence of two types OH groups on the anatase surface and was confirmed by the infra-red 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 White [17] reported similar types of OH groups are also characteristic for rutile TiO₂. The observation of two main peaks in the ¹H MAS NMR spectra of the molybdenum oxide catalysts supported on anatase and rutile samples of the present study are in agreement with this model. The downfield peak at $\delta \approx 6.5$ ppm can be attributed to 'acidic' OH groups co-ordinated to two Ti atoms, while the signal with $\delta \approx 2.1$–2.5 ppm is more likely to belong to 'basic' OH groups co-ordinated 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 with adjacent to
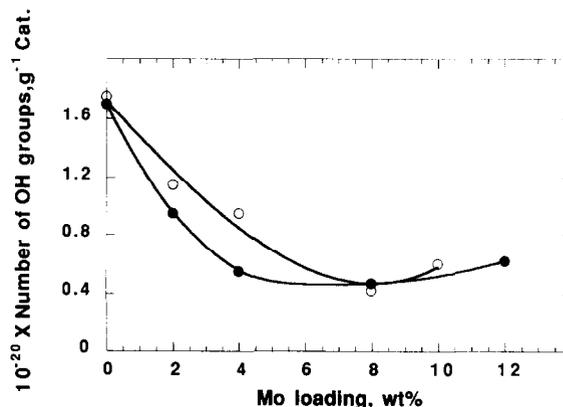

Fig. 3. The concentration of the surface OH groups as function of Mo content on various MoO₃/TiO₂ catalysts. ● Mo/anatase ; ○ Mo/rutile.

oxygen atoms. While the high field peak was ascribed to the more basic OH groups, where hydrogen atoms are bound with terminal oxygen atoms. The unidentified sharp line at $\delta \approx 10.9$ ppm most probably belongs to some OH groups associated with impurities present in the samples under study.

The results presented in Figs. 1 and 2 unambiguously show that the selective interaction of Mo atoms with the 'acidic' Ti–OH groups while the 'basic' OH groups are remain unperturbed when MoO_3 is supported on the TiO_2 surface. The impurity OH group also decreases in the sample with supported MoO_3. The decrease of the NMR signal intensity proceeds rapidly at the lowest concentration (2% Mo w/w on TiO_2) studied, there after the decrease in intensity becomes much less pronounced (Fig. 3). This is the case for both anatase and rutile supported molybdena catalyst samples. It should be noted that the largest Mo concentration (12% Mo w/w on TiO_2), is larger than the formal 'monolayer' amount of MoO_3. This observation indicates that there is a non uniform distribution of MoO_3 on the TiO_2 surface in agreement with the 'patchy-monolayer' model of Mo/Al_2O_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% Mo w/w 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

in the catalyst monomeric isolated Mo species are formed, while at the larger concentrations of Mo in the catalysts 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 and rutile polymorphs 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.

References

[1] Y. Okamoto, A. Maezawa and T. Imanaka, J. Catal., 120 (1989) 29

[2] D.S. Kim, Y. Kurusu, I.E. Wachs, F.D. Hardcastle and K. Segawa, J. Catal., 120 (1989) 325

[3] R.B. Quincy, M. Houalla and D.M. Hercules, J. Phys. Chem., 106 (1990) 85

[4] N.K. Nag, J. Phys. Chem., 91 (1987) 2324

[5] R.B. Quincy, M. Houalla and D.M. Hercules, J. Catal., 106 (1987) 85

[6] K.Y.S. Ng and E. Gulari, J. Catal., 92 (1985) 340

[7] T. Machej, B. Doumain, B. Yasse and B. Delmon, J. Chem. Soc. Faraday Trans 1, 84 (1988) 3905

[8] G.U. Kulkarni and C.N.R. Rao, Catal. Lett., 11(1991) 63

[9] V.M. Mastikhin, I.L. Mudrakovsky and A.V. Nosov, Progr. NMR Spectrosc., 23 (1991) 259

[10] M.A. Enriquez, C. Doremeux-Morin and J. Fraissard, J. Solid State Chem., 40 (1981) 233

[11] H.P. Boehm. Adv. Catal., 16 (1966) 179

[12] H. Knozinger. Adv. Catal., 25, (1982) 184

[13] M. Primet, P. Pichat and M.V. Mathieu, J. Phys. Chem., 75 (1971) 1216

[14] M. Primet, P. Pichat and M.V. Mathieu, J. Phys. Chem, 75 (1971) 1221

[15] M. Primet, P. Pichat and M.V. Mathieu, CR Acad. Sci. Ser. B, 267 (1968) 799

[16] D.J.C. Yates, J. Phys. Chem., 65 (1961) 746

[17] K. Tanaka and J.M. White, J. Phys. Chem., 86 (1982) 4708

[18] N.K. Nag, J. Catal., 92 (1985) 432