

## Characterization of MoO<sub>3</sub>/SiO<sub>2</sub> and WO<sub>3</sub>/SiO<sub>2</sub> Catalysts by Low-Temperature Oxygen Chemisorption, <sup>1</sup>H MAS NMR, and XRD Techniques

### INTRODUCTION

Supported oxides and sulfides of molybdenum and tungsten are well known for catalyzing a great variety of reactions. Therefore, the use of reliable characterization techniques is of great importance in the development of catalysts with greater activity and selectivity. The technique of low-temperature oxygen chemisorption (LTOC) has been identified as a powerful tool for characterizing unsupported and supported molybdenum- (*1-10*) and tungsten- (*11, 12*) based catalysts. Controversial opinions are reported regarding the property measured by oxygen chemisorption on sulfided molybdena catalysts (*13, 14*). However, oxygen chemisorption on reduced catalysts is widely accepted to be a measure of dispersion of molybdenum oxide (*1-10*) or tungsten oxide (*11*) phase on the support.

The importance of the surface hydroxyl groups in catalysis is well-established, and much research activity has also been directed toward the study of the types of hydroxyl groups and their distribution on a number of surfaces and their relevance to catalytic activity (*15, 16*). In recent years, the development of the magic angle spinning (MAS) technique has afforded the high-resolution NMR spectra of interested nuclei in solid samples. Thus, <sup>1</sup>H, <sup>27</sup>Al, and <sup>29</sup>Si MAS NMR techniques have been profitably employed for the structural study of zeolites and aluminas (*17, 18*). However, the applications of the <sup>1</sup>H MAS NMR technique to the characterization of MoO<sub>3</sub>/SiO<sub>2</sub> and WO<sub>3</sub>/SiO<sub>2</sub> catalysts have not been previously reported. In the present study, a

series of MoO<sub>3</sub>/SiO<sub>2</sub> and WO<sub>3</sub>/SiO<sub>2</sub> catalysts was systematically investigated by using LTOC, <sup>1</sup>H MAS NMR, and XRD techniques to obtain some useful information on the surface structure of these catalysts.

### EXPERIMENTAL

Catalysts were prepared by dry impregnation of SiO<sub>2</sub> (Ketjenfine F-5, surface area 672 m<sup>2</sup> g<sup>-1</sup>, pore volume 1.1 cm<sup>3</sup> g<sup>-1</sup>, particle size 0.72 mm) with aqueous solutions of ammonium heptamolybdate and ammonium metatungstate. Dry impregnations were carried out using 1.1 cm<sup>3</sup> solution per gram of carrier. The impregnated samples were dried at 120°C for 16 h and calcined at 540°C for 12 h in dry air.

The LTOC measurements were conducted on a standard static volumetric all-glass high-vacuum system equipped with a mercury diffusion pump and an in-line cold trap. Details of the setup and the chemisorption procedure have been published (*19*). Chemisorption of oxygen was determined as the difference between two oxygen adsorption isotherms at -78°C. Prior to the first isotherm, the catalyst was pre-reduced for 6 h at 500°C in flowing purified hydrogen (35 cm<sup>3</sup>/min), pumped for 1 h at 500°C, and cooled under vacuum (10<sup>-6</sup> Torr). Between the first and the second oxygen adsorption isotherms the sample was evaluated for 1 h at -78°C.

A Bruker CXP-300 NMR spectrometer was used to obtain PMR spectra at a frequency of 300.066 MHz with a magnetic field of 7.05 T. The  $\Pi/2$  pulse width was 5  $\mu$ s and pulse repetition rate was 1 Hz. Chemical shifts were measured relative to

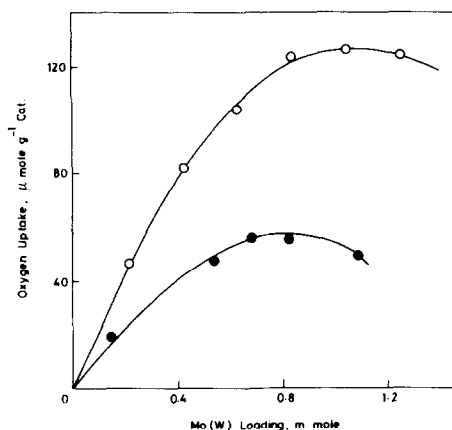


FIG. 1. Oxygen uptake at  $-78^{\circ}\text{C}$  as a function of Mo or W loading: (○) Mo/SiO<sub>2</sub>; (●) W/SiO<sub>2</sub> catalysts. All the data are corrected for the contributions by the support.

tetramethylsilane (TMS) as an external standard. Before the measurements, the samples were placed in specially made glass tubes, evacuated at  $400^{\circ}\text{C}$  for 4 h, and then sealed off under vacuum. The samples thus prepared were placed in an Andrew-type quartz rotor. The rotation frequency of the rotor was 3.5 kHz.

The X-ray diffraction patterns have been recorded on a Philips PW 1051 diffractometer by using Ni-filtered  $\text{CuK}\alpha$  radiation.

#### RESULTS AND DISCUSSION

Oxygen-uptake values of the reduced MoO<sub>3</sub>/SiO<sub>2</sub> and WO<sub>3</sub>/SiO<sub>2</sub> catalysts as a function of Mo or W loading are presented in Fig. 1. For the purpose of better comparison Mo and W loadings are expressed in terms of millimoles per gram catalyst. It is observed in Fig. 1 that for both series, oxygen uptake per gram of catalyst increases linearly as a function of Mo or W loading up to a certain level and then levels off or declines with further loading. These saturation levels indicate the completion of a "monolayer" coverage of the active SiO<sub>2</sub> support surface by Mo (W) oxide. (Here the term "monolayer" has not been applied to

indicate complete coverage of the active support surface; rather it indicates the covering of certain patches of the active support surface, as discussed further in the text.) The saturation loadings correspond to about 8 and 12.5 wt% Mo and W, respectively. These levels correspond to an Mo or W loading that is generally reported to give the classical monolayer coverage (20) of the active support surface. The maximum oxygen uptake per gram of catalyst by Mo/SiO<sub>2</sub> catalysts is found to be about 127  $\mu\text{mol}$  compared to 56  $\mu\text{mol}$  for W/SiO<sub>2</sub> catalysts. These results, therefore, indicate that the Mo oxide is dispersed better than W oxide on the same SiO<sub>2</sub> support surface.

The MAS PMR spectra of SiO<sub>2</sub> and selected Mo/SiO<sub>2</sub> and W/SiO<sub>2</sub> catalyst samples are shown in Fig. 2. The spectrum

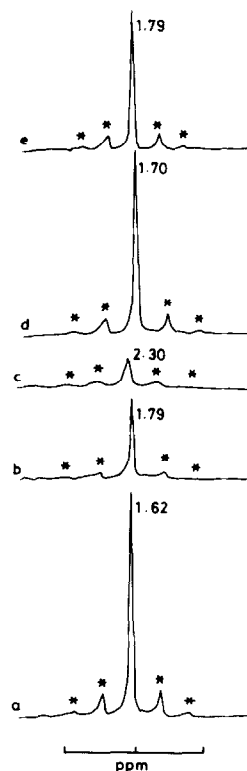


FIG. 2. MAS PMR spectra of hydroxyl groups: (a) SiO<sub>2</sub>; (b) 4% Mo/SiO<sub>2</sub>; (c) 10% Mo/SiO<sub>2</sub>; (d) 5% W/SiO<sub>2</sub>; (e) 25% W/SiO<sub>2</sub> samples. \* Spinning of sidebands.

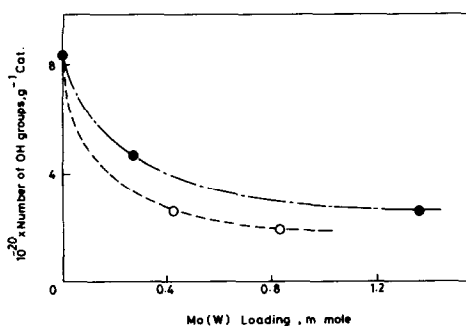


FIG. 3. Number of hydroxyl groups plotted as a function of Mo(W) loading: (○) Mo/SiO<sub>2</sub>; (●) W/SiO<sub>2</sub> catalysts.

of Si-OH groups consists of a single sharp line having the chemical shift at 1.62 ppm from external TMS. Upon impregnation with MoO<sub>3</sub> or WO<sub>3</sub> the intensity of the sharp line due to Si-OH groups has been decreased and at the same time a small increase in the chemical shift was also observed. The change in chemical shift can be attributed to the Si-OH groups perturbed by Mo or W atoms. The total numbers of OH groups as a function of Mo or W loading are shown in Fig. 3. The concentration of OH groups decreases with an increase in the loading of the metal oxide. However, an

important point to note from Fig. 3 is that even at the highest loading of Mo or W a considerable number of OH groups are left free, uncondensed by Mo (W) oxide. This is an important observation in this study, since the monolayer model (20) especially for Mo/Al catalysts has recently been found to be inadequate (10). This is true from the present PMR results, since much of the support surface is left free, unoccupied by the active component even at much higher loadings.

X-ray diffractograms of the unreduced MoO<sub>3</sub>/SiO<sub>2</sub> and WO<sub>3</sub>/SiO<sub>2</sub> catalysts are given in Figs. 4 and 5, respectively. In the XRD patterns of the silica-based catalysts a broadband is observed at approximately  $2\theta = 22^\circ$ , which is due to the amorphous carrier itself. Pure SiO<sub>2</sub> support pattern is also shown in Fig. 4 for a better understanding. In the XRD patterns of MoO<sub>3</sub>/SiO<sub>2</sub> catalysts with Mo contents of 6 wt% and above, sharp diffraction bands are present at  $2\theta = 22.3^\circ$ ,  $26^\circ$ , and  $27.2^\circ$ . The intensity of these peaks increases with an increase in the Mo loading. The positions of the lines are in good agreement with orthorhombic MoO<sub>3</sub>. However, the intensities of the various lines do not agree. Apparently, the structure of the crystals on the support surface

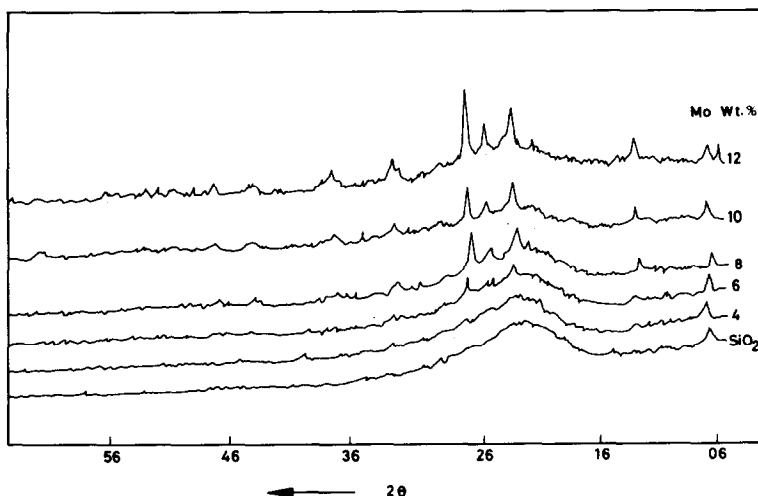


FIG. 4. X-ray diffraction patterns of MoO<sub>3</sub>/SiO<sub>2</sub> catalysts.

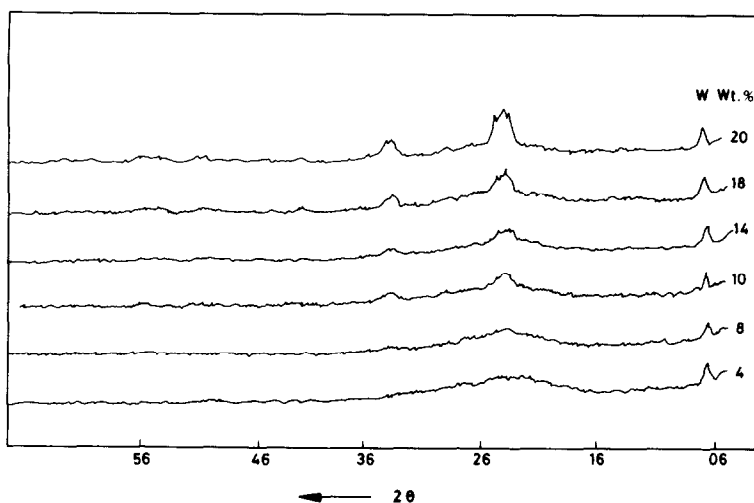


FIG. 5. X-ray diffraction patterns of  $\text{WO}_3/\text{SiO}_2$  catalysts.

differs from that of the reference  $\text{MoO}_3$ . A similar effect has also been described by Thomas (21). In the case of  $\text{WO}_3/\text{SiO}_2$  catalysts no sharp reflections due to the  $\text{WO}_3$  phase are observed in the spectra. However, the formation of crystalline  $\text{WO}_3$  phase can be manifested at much higher W loadings. As proposed by Thomas (21), these catalysts can be described as a mixture of crystalline bulk oxide and surface compounds. The ratio of these species is a function of metal oxide content and the nature of transition metal. The nature of these surface compounds has been the object of several investigations.

The initial increase and subsequent leveling off or decline in oxygen uptake capacity of the catalysts as a function of Mo loading, as presented in Fig. 1, were also reported on  $\text{Mo}/\text{Al}_2\text{O}_3$  and C (22),  $\text{Mo}/\text{TiO}_2$  (23), and  $\text{Mo}/\text{ZrO}_2$  (24) catalyst systems by Reddy and co-workers in their recent study. Those results were interpreted in terms of Hall's (25) "patchy monolayer" model of the Mo oxide phase on the support surface. Based on this model, it is proposed that the coordinatively unsaturated Mo sites (CUS) of  $\text{MoO}_2$  patches, generated upon reduction in

hydrogen, are considered to be the exact locations for dissociative  $\text{O}_2$  chemisorption at low temperatures (10). As the Mo loading increases, the number of these  $\text{MoO}_2$  patches increases with an attendant increase in the number of CUS up to the monolayer level. Hence, oxygen uptake increases linearly with loading up to the monolayer level. Beyond the monolayer level, these patches grow three-dimensionally, thus decreasing the dispersion of Mo oxide. On the basis of these concepts, the present LTOC results can also be interpreted in those lines. The overall reduction behavior of the supported metal oxide catalyst is strongly dependent on the distribution of the type species, nature of the oxide precursor, and also the metal oxide support interaction strength (21). Their reduction behaviors are expected to have an important bearing on the oxygen chemisorption (10). This is because LTOC is possible only on prereduced catalysts that contain the CUS generated by the removal of oxygen from Mo or W oxide as  $\text{H}_2\text{O}$  by  $\text{H}_2$  reduction.

Also recalling the fact that the patchy monolayer phase is formed by a strong

chemical interaction between the active OH groups of the support surface and the oligomeric molybdate or tungstate ions present in the impregnating solution, it can be concluded (from Fig. 3) that the drop in the surface concentration of active OH groups with Mo is higher than that of W. In other words, the extent of chemical reaction via the condensation of OH groups of silica and molybdate ions is much higher than that between tungstate and silica. This may well be the reason why molybdate is more dispersed than tungstate on silica. Because of the strong interaction between molybdena and silica, the CUS that are generated during reduction are more stable, which can hold chemisorbed oxygen at  $-78^{\circ}\text{C}$  (10). Hence, an higher dispersion of Mo oxide on silica surface is observed. Although  $\text{WO}_3$  has a higher reduction than  $\text{MoO}_3$  (21), it appears that the CUS that are generated by reduction of  $\text{WO}_3$  probably do not hold chemisorbed oxygen.

#### ACKNOWLEDGMENTS

We thank Professor K. I. Zamaraev, Director, Institute of Catalysis, Novosibirsk, USSR, for providing the NMR facility, DST, India, and the Academy of Sciences, USSR, for arranging B.M.R.'s visit to USSR. Thanks are also due to Dr. B. Rama Rao, Head, Inorganic and Physical Chemistry Division, RRL, Hyderabad, for his help in obtaining XRD data.

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*Received November 30, 1987; revised March 29,  
1988*

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