

Influence of MoO₃ and WO₃ on the Dispersion and Activity of V₂O₅ in Vanadia-Silica Catalysts

B. MAHIPAL REDDY,¹ K. NARSIMHA, P. KANTA RAO,¹ AND V. M. MASTIKHIN[†]

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India; and [†]Institute of Catalysis, Novosibirsk 630 090, USSR

Received September 2, 1988; revised January 30, 1989

A series of silica-supported vanadia and molybdenum- and tungsten-promoted vanadia catalysts have been prepared and were characterized by means of low temperature oxygen chemisorption, ¹H magic angle spinning nuclear magnetic resonance, X-ray diffraction, and electron spin resonance techniques. Reactivities of these catalysts for partial oxidation of methanol were also determined under atmospheric pressure in a flow microreactor. These results suggest the formation of the "patchy monolayer" phase of V oxide at lower loadings and on top of it bulk V₂O₅ at higher vanadium loadings. The presence of molybdenum increases the activity of the catalyst, whereas tungsten has the opposite effect. The improved activity of molybdena-vanadia catalyst was related to the better dispersion of the V oxide phase in the presence of Mo on silica surface. © 1989 Academic Press, Inc.

INTRODUCTION

Vanadium oxide-based catalysts are extensively used in industry for heterogeneous selective oxidation or ammoxidation of hydrocarbons (1-3). A large part of research activity on these catalysts concerns the role played by the promoter atoms or by the carrier when V₂O₅ is supported (4-17). Despite numerous investigations, there is much yet to be learned about the nature of the active surface phase and in particular the role of promoter atoms on this phase.

To study the supported molybdenum oxide or sulfide catalysts the technique of low temperature oxygen chemisorption (LTOC) has been identified as a powerful tool recently (18-24). The same technique was successfully extended to characterize the supported vanadia catalysts by Nag and co-workers (16, 17). It was also clearly demonstrated that the specific information on the active surface area as well as the nature and the dispersion of the supported vanadia phase could be obtained from

LTOC data. The LTOC when coupled with yet another new technique, the proton (also other nuclei) magic angle spinning (MAS) nuclear magnetic resonance (NMR) (25-27), has been shown to give more meaningful information on the surface structure of Mo/Al₂O₃, Mo/SiO₂, and W/SiO₂ catalysts by Reddy *et al.* (28, 29) more recently. The present investigation was undertaken to see the effect of Mo and W atoms on the dispersion and activity of vanadia in V₂O₅/SiO₂ catalysts. In this study a series of V₂O₅/SiO₂, Mo- and W-promoted V₂O₅/SiO₂ catalysts were systematically investigated by using LTOC, ¹H MAS NMR, X-ray diffraction (XRD), and electron spin resonance (ESR) techniques to obtain some useful information on the surface structure of these catalysts. In order to correlate the physicochemical properties with the catalytic activity, these catalysts were also tested for the partial oxidation of methanol.

EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by wet impregnation of SiO₂ (Ketjen Si-6-5P; surface

¹ Correspondence should be addressed to either of the authors.

area, 597 m² g⁻¹; pore volume, 1.22 cm³ g⁻¹) with aqueous solutions of ammonium metavanadate (Fluka, min 99%). The impregnated samples were air-dried at 110°C for 16 h and then calcined in air at 500°C for 8 h. The 3 wt% MoO₃- and WO₃-promoted catalysts were prepared from the oven-dried 12 wt% V₂O₅/SiO₂ catalyst by impregnation with ammonium heptamolybdate and ammonium metatungstate, respectively, in an identical manner, drying at 110°C followed by calcining at 500°C for 8 h.

LTOC Measurements

A conventional static volumetric high-vacuum system, with the facility for reducing the samples *in situ* by flowing hydrogen, was used for the study of oxygen chemisorption. Details of the setup and the chemisorption procedure have been described elsewhere (16). Chemisorption of oxygen was determined as the difference between two oxygen adsorption isotherms at -78°C. Prior to the first isotherm, the catalyst sample was reduced for 6 h at 500°C in flowing purified hydrogen (35 cm³/min), pumped for 1 h at 500°C, and cooled under vacuum (10⁻⁶ Torr). Between the first and the second oxygen adsorption isotherms the sample was evacuated for 1 h at -78°C. After the chemisorption experiment, the BET surface area of the catalyst was determined by N₂ adsorption at -196°C by taking 0.162 nm² as the area of cross section of N₂.

MAS ¹H NMR Measurements

The solid state proton NMR spectra with MAS technique have been recorded on a Bruker CXP-300 spectrometer at a frequency of 300 MHz with a magnetic field of 7.046 T. The $\pi/2$ pulse width was 5 μ s and pulse repetition rate was 1 Hz. The spectral width was 50 kHz. Chemical shifts were measured relative to tetramethylsilane (TMS) as an external standard. The concentration of OH groups was determined by comparing its signal intensity with that of a known standard sample. Before the measurements, the samples were placed in spe-

cially made glass tubes, evacuated at 500°C for 5 h, and then sealed off under vacuum. The samples thus prepared were placed in a quartz rotor of Beams' type. The rotation frequency of the rotor was 2.5–3.5 kHz.

X-Ray Diffraction

The X-ray diffraction patterns were recorded on a Philips PW 1051 diffractometer by using Ni-filtered CuK α radiation.

ESR Measurements

The ESR spectra were recorded on a Bruker ER 200D-SRC X-band spectrometer with 100 kHz modulation at room temperature.

Activity Measurements

A microreactor, interfaced by a six-way gas sampling valve with a gas chromatograph, was used to study the vapor-phase oxidation of methanol at 225°C under differential conditions. The feed gas consisted of 72, 24, and 4% by volume nitrogen, oxygen, and methanol vapor, respectively. For each run about 0.25 g of catalyst was used and the products were analyzed with a 10% Carbowax 20 M column (2 m long). The major products observed were formaldehyde and dimethyl ether with some traces of methyl formate, CO, and CO₂, respectively.

RESULTS AND DISCUSSION

Oxygen uptake on the reduced catalysts as a function of vanadia loading is shown in Fig. 1. It can be seen from Fig. 1 that oxygen uptake increases as a function of vanadia loading up to about 12 wt% and then decreases rapidly with further increase in vanadia concentration. The loading at which maximum oxygen uptake is observed represents the completion of monolayer coverage of the active support surface by the V oxide phase. (Here the term "monolayer" has not been applied to indicate complete coverage of active support surface; rather it indicates the covering of certain patches of the active support surface,

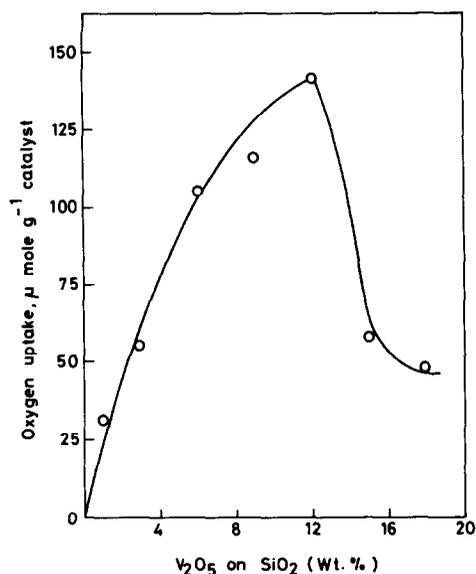


FIG. 1. Oxygen uptake at -78°C plotted as a function of vanadia loading.

as discussed further in the text.) A similar observation was also made earlier when V_2O_5 was supported on an Al_2O_3 surface (16). This is in line with the general obser-

vation that the supported oxides at low loadings do not form three-dimensional crystal phases but rather continuous or patchy monolayers covering the support surface (13, 14). Hence, the 12% concentration of V_2O_5 was chosen for our study to see the effect of MoO_3 and WO_3 on the dispersion and activity of $\text{V}_2\text{O}_5/\text{SiO}_2$ catalysts.

The BET surface area, the surface coverage, the active site density, and the activity for partial oxidation of methanol of various catalysts are shown in Table 1. Surface coverages and active site densities are derived from LTOC data according to the procedure described earlier (16). It can be seen from Table 1 that there is a 40% maximum decline in the BET surface area from lower to higher loading levels of V_2O_5 . This large effect indicates blocking of pores by deposited vanadium oxide phase and eventually sintering or agglomeration of silica primary particles. The surface coverages and active site densities also increase as in Fig. 1 in the premonolayer region and decrease in the postmonolayer region as a function of vanadia content. This result is expected, since

TABLE 1

Composition, Oxygen Uptake, Surface Area, Surface Coverage, Active Site Density, CH_3OH Conversion, and Product Selectivities of Various Catalysts

Catalyst	Composition V_2O_5 wt%	Oxygen uptake ($\mu\text{mole g}^{-1}$)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Surface coverage ^b	Active site density ^c (nm^{-2})	CH_3OH conversion (%)	Selectivity (%)	
							HCHO	CH_3OCH_3
VS-1	1	32.4	545	1.8	0.07	2.4	50	46
VS-2	3	55.1	532	3.1	0.12	6.3	31	69
VS-3	6	105.0	470	6.6	0.27	10.8	66	32
VS-4	9	114.8	384	8.8	0.36	18.9	63	30
VS-5	12	142.3	353	12.0	0.49	26.4	60	38
VS-6	15	57.5	323	5.3	0.21	17.9	58	42
VS-7	18	48.6	310	4.6	0.19	15.1	45	52
MoVS-3 ^a	12	102.0	230	13.1	0.53	40.1	73	23
WVS-3 ^a	12	108.1	431	7.4	0.30	17.5	36	43
MoS-3	—	47.2	518	2.8	0.11	3.9	29	69
WS-3	—	56.6	538	— ^d	0.12	2.1	22	75

^a 3 wt% MoO_3 and WO_3 , respectively.

^b Defined as $100 \times (\text{active or effective surface area/BET surface area})$, (Refs. (16) and (18)).

^c This is equal to the number of oxygen atoms chemisorbed per unit area of the catalyst.

^d Conversion factor is not reported so far.

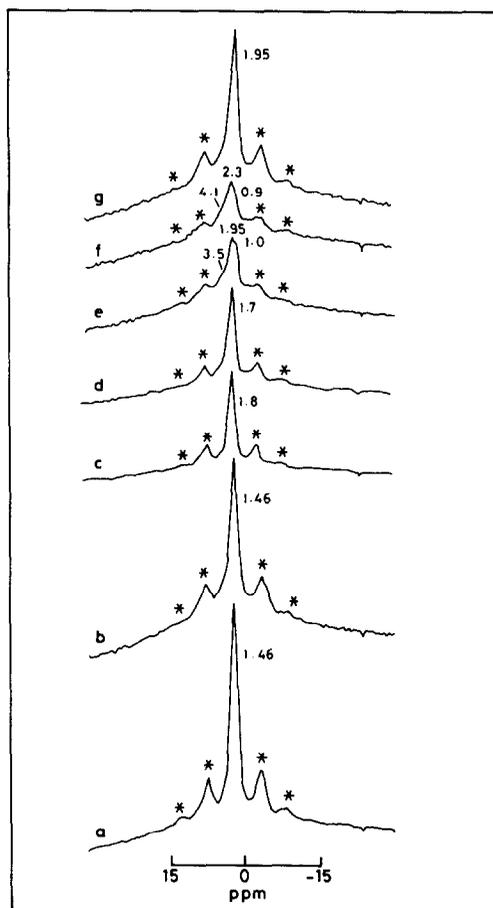


FIG. 2. MAS proton NMR spectra of hydroxyl groups: (a) SiO_2 ; (b) 1% V/SiO_2 ; (c) 3% V/SiO_2 ; (d) 9% V/SiO_2 ; (e) 15% V/SiO_2 ; (f) Mo- V/SiO_2 (3:12); (g) W- V/SiO_2 (3:12) samples. *Spinning sidebands.

the surface coverages and active site densities are derived from LTOC data only. However, an important observation from the surface coverage data is that even at the full monolayer coverage no more than 12% of the total surface is occupied by the active component. A plausible explanation for such a low coverage, as envisaged earlier (16, 17), could be that during the liquid phase preparation step the bulky polyvanadate ions failed to penetrate into some micropores of the support to give a more dispersed phase.

Activity of the catalyst for methanol partial oxidation also increases like LTOC

with vanadia loading up to the 12% saturation monolayer loading level and then declines with further loading (Table 1). In fact LTOC correlates directly with the partial oxidation activity of methanol when no promoter was added to V_2O_5/SnO_2 catalyst (30). However, no definite trend in the product selectivities could be seen as a function of loading. An important observation from Table 1 is that the addition of 3 wt% MoO_3 to the 12% V_2O_5 catalyst shows a tremendous increase in the activity and also in the formaldehyde selectivity of the catalyst. In contrast the addition of WO_3 to the 12% V_2O_5 catalyst shows an opposite effect, i.e., decrease in the activity and selectivity. Corresponding effects also could be seen in the surface coverages and active site densities with the respective promoted catalysts in Table 1.

The proton NMR spectra of SiO_2 and selected V_2O_5/SiO_2 catalysts which give sharp features due to the relatively isolated hydroxyl groups, under the conditions employed for recording the spectra, are shown in Fig. 2. The spectra of Mo- and W-promoted catalysts are also shown in this figure. The spectrum of Si-OH groups consists of a single sharp line having the chemical shift at 1.46 from external TMS. The intensity of this sharp line decreases depending upon the concentration of V_2O_5 in V_2O_5/SiO_2 catalysts. A small increase in the chemical shift can also be seen in the impregnated catalysts with respect to pure SiO_2 . This change in chemical shift can be attributed to the Si-OH groups perturbed by the dispersed vanadium oxide units. For the sample with V_2O_5 concentration of 15% and Mo promoter of 12%, two additional lines at different chemical shifts can be seen in the spectra. The lines at 1.95 and 2.3 ppm can be attributed to the Si-OH groups while those at 3.5, 1.0, 4.1, and 0.9 ppm can be tentatively ascribed to the OH groups bonded with surface vanadium and/or molybdenum oxide phases, respectively.

The total number of OH groups observable under the conditions employed for re-

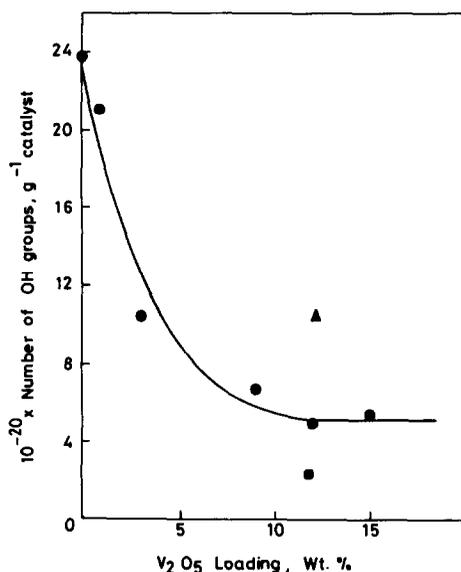


FIG. 3. Number of OH groups plotted as a function of vanadia loading: ●, V/SiO₂; ■, Mo-V/SiO₂; ▲, W-V/SiO₂ catalysts.

cording the spectrum, as a function of vanadia loading, is shown in Fig. 3. The effect of MoO₃ and WO₃ on the number of OH groups when added to the 12% V₂O₅ catalyst is also shown in this figure. The concentration of isolated OH groups decreases as a function of the V₂O₅ loading up to about 12 wt% and then almost levels off with further loading. This is an important observation from the proton NMR. This observation clearly shows that a large support surface is left unoccupied by the V oxide phase in agreement with results of LTOC. Therefore, one can depict the monolayer as isolated patches or islands of V oxide units attached to the support surface through Si-OH groups by a strong chemical reaction. This chemical interaction via the elimination of Si-OH groups is limited to a small fraction of the total surface of the support. The completion of the monolayer occurs when this active surface is covered completely by V oxide. Any further addition of the active component leads to multilayer growth on the monolayer and eventual formation of bulky crystallites, while a large

fraction of the support surface still remains bare (17, 29). This concept clearly accounts for the LTOC and ¹H NMR results. Another important observation to be noted from Fig. 3 is that the behaviors of the promoted catalysts are drastically different. The addition of WO₃ to the 12% V₂O₅ has increased the intensity of the spectrum implying an increased number of OH groups. Addition of MoO₃ decreases the number of Si-OH groups with respect to the bare 12% V₂O₅/SiO₂ catalyst. These results, therefore, indicate that the role of Mo oxide is quite opposite to that of W oxide on the dispersion of the V oxide phase on the support. Hence, one can even conclude at this stage that Mo oxide fairly increases the dispersion of V oxide on the support whereas W oxide shows a reverse effect. This observation is in line with the results presented in Table 1.

The X-ray diffractograms of the unreduced V₂O₅/SiO₂, MoO₃-V₂O₅/SiO₂, and WO₃-V₂O₅/SiO₂ catalysts are shown in Fig. 4. The pure SiO₂ support pattern is also shown in this figure for comparison. In the X-ray diffractograms of silica-based catalysts, a broadband can be seen at approximately $2\theta = 22^\circ$, which is due to the amorphous carrier itself. No characteristic XRD peak of V₂O₅ could be seen up to a loading of 12 wt%, while the samples with higher vanadia content show the V₂O₅ XRD patterns which grew in intensity as the amount of vanadia increases. The absence of characteristic V₂O₅ peaks at the lower concentration region can be taken as the indication of high dispersion of V oxide on the support surface. Otherwise, if the crystallites are formed, they are less than 4 nm and are beyond the detection capability of the technique. This observation agrees with earlier published works (14-16). An important observation to be noted from Fig. 4 is the formation of the crystalline V₂O₅ phase in the WO₃-promoted catalysts. However, no such crystalline phase formation can be observed in the case of the MoO₃-promoted catalyst. This observation is in good agree-

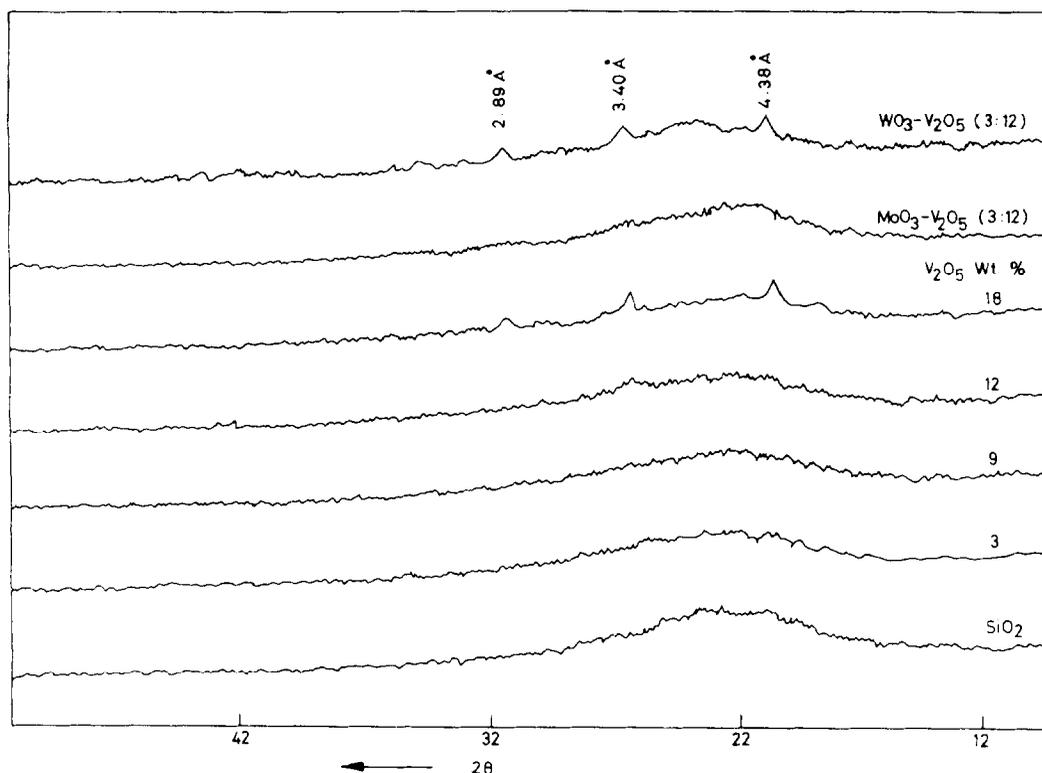


FIG. 4. X-ray diffraction patterns of V/SiO_2 , $Mo-V/SiO_2$, and $W-V/SiO_2$ catalysts.

ment with the preceding discussion and in line with the results of LTOC and 1H NMR. Thus, the WO_3 addition increases the size of V_2O_5 crystallites thereby decreasing its dispersion. On the other hand, under the influence of MoO_3 the vanadia phase spreads more and covers more support surface. However, the exact mechanism is not clearly known at present. An important point to mention here is that no compound formation could be seen between $MoO_3-V_2O_5$ and $WO_3-V_2O_5$ oxides from XRD data. However, the formation of compounds between these oxides cannot be ruled out.

The ESR spectra of V_2O_5/SiO_2 and of MoO_3 - and WO_3 -promoted V_2O_5/SiO_2 catalysts recorded at room temperature and under identical conditions are shown in Fig. 5. The ESR spectra of these unreduced catalysts are recorded with the aim of gaining more information which can substantiate

the LTOC and 1H NMR results. However, a good account of work has already been published on the application of ESR to characterize vanadia-silica catalysts (31-34). A well-resolved spectra with hyperfine splitting due to ^{51}V ($I = 7/2$) could be seen from Fig. 5. The intensity of the spectra increases with increase in vanadia loading again up to 12%. The addition of WO_3 does not cause any appreciable change in the shape of the V oxide spectrum. However, the intensity of spectra is decreased. On the other hand, the addition of MoO_3 causes an appreciable increase in the intensity of the spectrum. The parameters of the hyperfine signal of $MoO_3-V_2O_5/SiO_2$ are rather similar to those of covalent V^{4+} units on the V_2O_5/SiO_2 sample. A further interaction of the unpaired electron with Mo nuclei seems unlikely because of the relatively slight perturbation of the principle g values found. The absence of signals due to Mo^{5+} may be

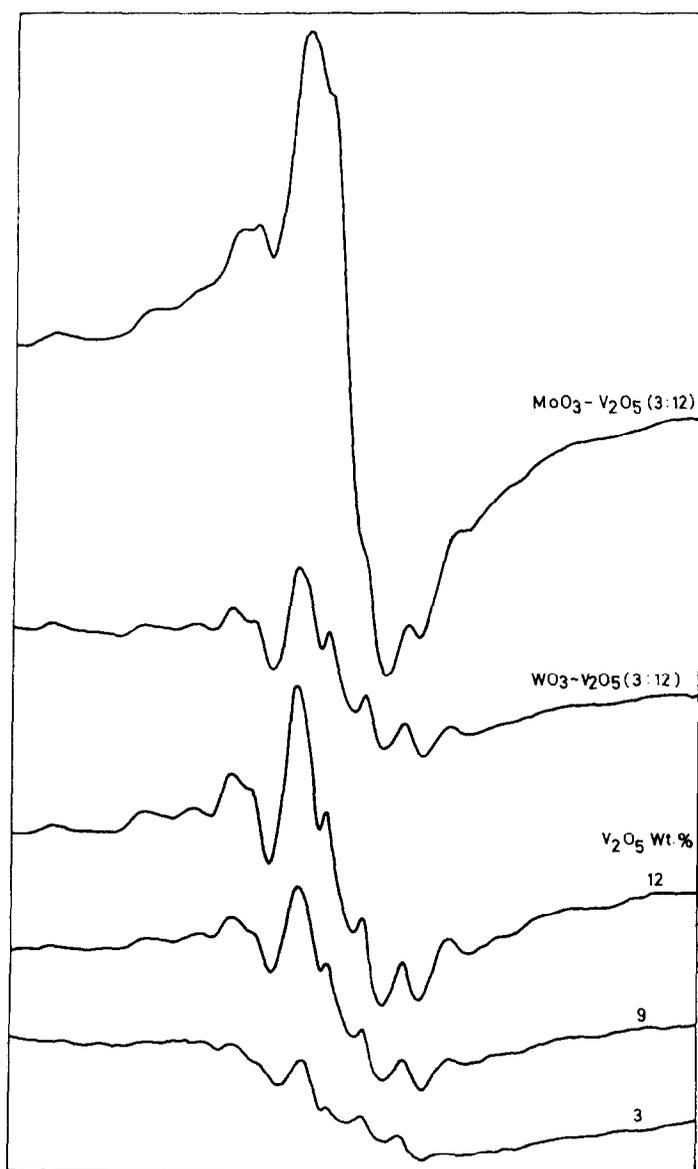


FIG. 5. ESR spectra of unreduced V/SiO₂, W-V/SiO₂, and Mo-V/SiO₂ catalysts.

interpreted according to the literature (35, 36) as an evidence for a stabilization of V⁴⁺ by Mo⁶⁺ on the surface-mixed oxide phase.

Several suggestions concerning the structure of vanadium species on silica support can be found in the literature. For example, Vorobev *et al.* (37) suggest that isolated or associated (VO₄)³⁻ units share one corner with the (SiO₄) chain. With increasing vanadium concentration the partition between

various species is shifted towards associated species and agglomerated finally to form V₂O₅. On the other hand, Yoshida *et al.* (33) have deduced formation of (VO₄) units accompanied by distorted square pyramidal coordinated V⁴⁺ and V₂O₅ at higher loadings. Ohlman and co-workers (38) propose various different vanadia phases on silica. Narayana *et al.* (34) suggest the existence of four-coordinated V⁴⁺ on the re-

duced V/SiO₂. Horvath *et al.* (39), Kazansky and co-workers (40), and Jonson *et al.* (14) have proposed tetrahedral vanadium surface complexes. Nag and co-workers (17) suggest two types of species, isolated (VO₄)⁴⁻ and a dimeric V⁵⁺, both in tetrahedral coordination in the lower vanadia loading region, while at higher loadings beyond the so-called monolayer coverage only one V⁵⁺ oxide phase in square pyramidal or octahedral surroundings. This difference of opinion might stem from the method of preparation, starting materials, and characterization techniques which are drastically different. As regards the role of MoO₃ in the bulk V₂O₅ catalysts there were also several theories with respect to a particular catalytic reaction (35, 41). However, from the present study it appears that the MoO₃ increases the activity of the vanadia catalyst for methanol oxidation by increasing its dispersion on the support. The WO₃ shows a negative effect on the dispersion of vanadia and accordingly on its activity.

ACKNOWLEDGMENTS

We thank Professor K. I. Zamaraev, Director, Institute of Catalysis, Novosibirsk, USSR, for NMR facility and Dr. B. Rama Rao, Head, I & PC Division, ICT, Hyderabad, India, for XRD and ESR facilities. Thanks also to Council of Scientific and Industrial Research, India, for the research fellowship to K.N.

REFERENCES

- Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, New York, 1974.
- Haber, J., in "Surface Properties and Catalysis by Non-Metals" (J. P. Bonnelle, B. Delmon, and E. Derouane, Eds.), p. 19. Reidel, Dordrecht, Netherlands, 1983.
- Pomonis, P. J., and Vickerman, J. C., *Faraday Discuss. Chem. Soc.* **71**, 247 (1981).
- Kozlowski, R., Pettifer, R. F., and Thomas, J. M., *J. Phys. Chem.* **87**, 5172 (1983).
- Wachs, I. E., Salem, R. Y., Chan, S. S., and Chersich, C. C., *Appl. Catal.* **15**, 339 (1985).
- Bond, G. C., Zurita, J. P., Flamerz, S., Gellings, P. J., Bosch, H., Van Ommen, J. G., and Kip, B. J., *Appl. Catal.* **22**, 361 (1986).
- Roozeboom, F., Mittelmeijer-Hazeleger, M. C., Moulijn, J. A., Medema, J., de Beer, V. H. J., and Gellings, P., *J. Phys. Chem.* **84**, 2783 (1980).
- Gil-Llambias, F. J., Escudey, A. M., Fierro, J. L. G., and Agudo, A. L., *J. Catal.* **95**, 520 (1985).
- Miyata, H., Fujii, K., Ono, T., Kubokawa, Y., Ohno, T., and Hatayama, F., *J. Chem. Soc. Faraday Trans. 1* **83**, 675 (1987).
- Niwa, M., Matsuoka, Y., and Murakami, Y., *J. Phys. Chem.* **91**, 4519 (1987).
- Tanaka, T., Tsuchitani, R., Ooe, M., Funabiki, T., and Yoshida, S., *J. Phys. Chem.* **90**, 4905 (1986).
- Le Coustumer, L. R., Taouk, B., Le Meur, M., Payen, E., Guelton, M., and Grimbolt, J., *J. Phys. Chem.* **92**, 1230 (1988).
- Bergeret, G., Gallezot, P., Chary, K. V. R., Rao, B. R., and Subrahmanyam, V. S., *Appl. Catal.* **40**, 191 (1988).
- Jonson, B., Rebenstorf, B., Larsson, R., and Andersson, S. L. T., *J. Chem. Soc. Faraday Trans. 1* **84**, 1897 (1988).
- Vogt, E. T. C., de Beer, M., Van Dillen, A. J., and Geus, J. W., *Appl. Catal.* **40**, 225 (1988).
- Nag, N. K., Chary, K. V. R., Reddy, B. M., Rao, B. R., and Subrahmanyam, V. S., *Appl. Catal.* **9**, 225 (1984).
- Nag, N. K., Chary, K. V. R., Rao, B. R., and Subrahmanyam, V. S., *Appl. Catal.* **31**, 73 (1987).
- Weller, S. W., *Acc. Chem. Res.* **16**, 101 (1983), and references therein.
- Chung, K. S., and Massoth, F. E., *J. Catal.* **64**, 101 (1983).
- Hall, W. K., and Millman, W. S., in "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 1304. Elsevier, Amsterdam, 1981.
- Muralidhar, G., Concha, B. E., Bartholomew, G. L., and Bartholomew, C. H., *J. Catal.* **89**, 274 (1984).
- Nag, N. K., *J. Catal.* **92**, 432 (1985).
- Reddy, B. M., Chary, K. V. R., Subrahmanyam, V. S., and Nag, N. K., *J. Chem. Soc. Faraday Trans. 1* **81**, 1655 (1985), and references therein.
- Reddy, B. M., and Subrahmanyam, V. S., *Appl. Catal.* **27**, 1 (1986).
- Clague, A. D. H., in "Catalysis," Vol. 7 p. 61. Specialist Periodic Report, Royal Society, London, 1984.
- Thomas, J. M., and Klinowsky, J., in *Advances in Catalysis* (D. D. Eley, P. W. Sellwood, and P. B. Weisz, Eds.), Vol. 33, p. 199. Academic Press, San Diego, CA, 1985.
- Mastikhin, V. M., and Zamaraev, K. I., *Z. Phys. Chem. (Munich)* **152**, 59 (1987), and references therein.
- Reddy, B. M., and Mastikhin, V. M., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), p. 82. The Chemical Institute of Canada, Ottawa, 1988. [Preprints]
- Reddy, B. M., Rao, K. S. P., and Mastikhin, V. M., *J. Catal.* **113**, 556 (1988).

30. Reddy, B. M., Narsimha, K., Sivaraj, Ch., and Rao, P. K., *J. Chem. Soc. Chem. Commun.*, submitted for publication.
31. Sharma, V. K. Wokaun, A., and Baiker, A., *J. Phys. Chem.* **90**, 2715 (1986).
32. Che, M., Canosa, B., and Gonzalez-Elipe, A. R., *J. Phys. Chem.* **90**, 618 (1986).
33. Yoshida, S., Iguchi, T., Ishida, S., and Tarama, K., *Bull. Chem. Soc. Japan* **45**, 376 (1972).
34. Narayana, M., Narasimhan, C. S., and Kevan, L., *J. Catal.* **79**, 237 (1983).
35. Dyrek, E., and Labanowska, M., *Appl. Catal.* **23**, 63 (1986).
36. Busca, G., and Marchetti, L., *J. Chem. Res. (S)*, 174 (1986).
37. Vorobev, L. N., Badalova, I. K., and Razikov, K. Kh., *Kinet. Catal.* **23**, 119 (1982).
38. Richter, M., Heise, K., and Ohlman, G., *React. Kinet. Catal. Lett.* **27**, 109 (1985).
39. Horvath, B., Strutz, J., Geyer-Lippmann, J., and Horvath, E. G., *Z. Anorg. Allg. Chem.* **483**, 193 (1981).
40. Gritscov, A. M., Shvets, V. A., and Kazansky, V. B., *Chem. Phys. Lett.* **35**, 511 (1975).
41. Najbar, M., and Stadnicka, K., *J. Chem. Soc. Faraday Trans. 1* **79**, 27 (1983).