A study of tin dioxide and antimony tetroxide supported vanadium oxide catalysts by solid-state ^{51}V and ^{1}H NMR techniques

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Abstract

A series of vanadia catalysts with various V_2O_5 loadings supported on SnO_2 and α-Sb_2O_4 are investigated by the application of X-ray diffraction and solid-state ^{51}V and ^{1}H NMR techniques. XRD results show no evidence for the formation of a crystalline vanadia phase on both supports. However, the ^{51}V NMR spectra of the catalysts reveal the existence of two types of vanadia species on the surface of the support: one due to a dispersed vanadia phase at lower vanadia loadings and the other due to a crystalline vanadia phase at higher vanadium content. The quantity of the dispersed vanadia phase, however, depends on the nature of the support material. The ^{1}H NMR results provide evidence for the existence or non-existence of a metal oxide support interaction through the support surface hydroxyl groups.

Keywords: catalysts; vanadium NMR; surface oxide

Introduction

Vanadium oxide-based catalysts are well known for their ability to catalyse a great variety of oxidation and ammoxidation reactions, and have been extensively investigated with various physico-chemical characterization techniques [1–4]. To achieve good activity and selectivity levels, V_2O_5 should be dispersed on a suitable support [4]. Depending on the nature of support material and the extent of loading, the dispersed vanadia phase can simultaneously possess several different molecular states. To study the nature of dispersed vanadia species on the support surface the technique of solid-state ^{51}V NMR has recently

been identified as a powerful tool [5–8]. In general, solid-state NMR methods represent a novel and promising approach to the study of heterogeneous catalyst systems. Since only the local environment of the nucleus under study is probed by the NMR technique, these methods are well suited for the structural analysis of disordered systems, such as the two-dimensional surface oxide phases dispersed on support surfaces. Apart from the structural information provided by NMR methods, the direct proportionality of the signal intensity to the number of contributing nuclei makes NMR a useful technique for quantitative studies. In this communication, the significance of NMR methods over the conventional XRD technique is described and a comparison is made between the solid-state ^{51}V and ^{1}H NMR results of V_2O_5/SnO_2 and V_2O_5/Sb_2O_4 catalyst systems. The SnO_2 and Sb_2O_4 support are interest-

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ing materials [9,10] and have not been exploited fully as support materials to disperse vanadium oxides.

Experimental

Preparation of catalysts

The SnO_2 and α-Sb_2O_4 supports were prepared by precipitating the corresponding hydroxides from stannic chloride (Loba Chemie, AR grade) and antimony trichloride (Loba Chemie, AR grade), respectively, with dilute ammonia solutions. The chloride-free precipitates were dried at 120°C for 16 h and calcined at 600°C (SnO_2) and 500°C (Sb_2O_4) for 6 h in an open air furnace. Ammonium metavanadate (Fluka, AR grade) was used as a source of V_2O_5. A standard wet impregnation method was adopted to prepare the catalysts. The impregnated catalysts were dried at 120°C for 12 h and calcined at 500°C for 6 h in an air circulation furnace. Vanadium contents were expressed in terms of V_2O_5 weight percent and ranged between 0.5 and 6.0%.

XRD measurements

X-ray diffraction patterns of all the samples were recorded on a Philips PW 1051 X-ray diffractometer with nickel filtered CuK_α radiation.

Measurement of NMR spectra

The solid-state [51]V and ^{1}H NMR spectra with using a MAS technique were recorded on a Bruker CXP-300 spectrometer. The [51]V NMR spectra were obtained with a magnetic field of 7.046 T at a frequency of 78.86 MHz in a frequency range of 150 kHz with a radio frequency pulse duration of 1 μs and a pulse repetition rate of 10 Hz. The chemical shifts were measured relative to $VOCl_3$ as the external standard. The ^{1}H NMR spectra were recorded at a frequency of 300.09 MHz in the frequency range of 50 kHz, ($\pi/2$) pulse duration was 5 μs, and the pulse repetition frequency was 1 Hz. The chemical shifts were measured relative to TMS as an external standard. Details of samples preparation for NMR measurements and estimation of surface hydroxyl groups was described elsewhere [11].
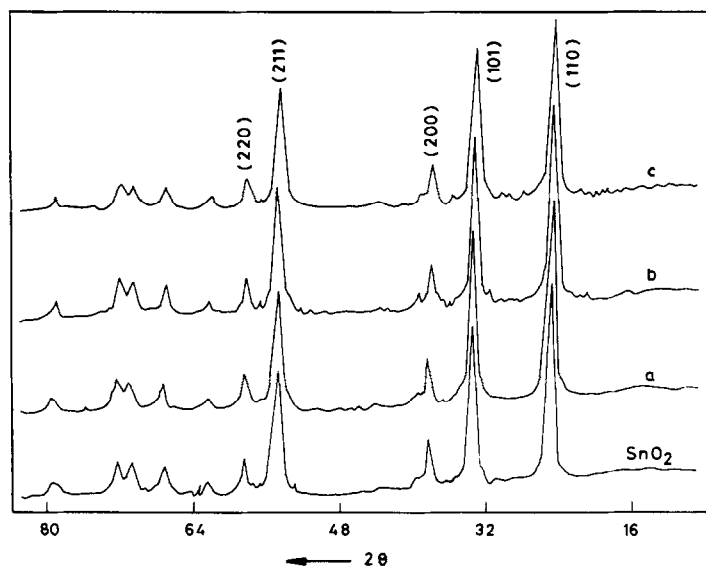

Fig. 1. X-ray diffraction patterns of SnO_2 and V_2O_5/SnO_2 catalysts with various V_2O_5 contents (wt%): a, 1.1; b, 3.2; c, 5.4.

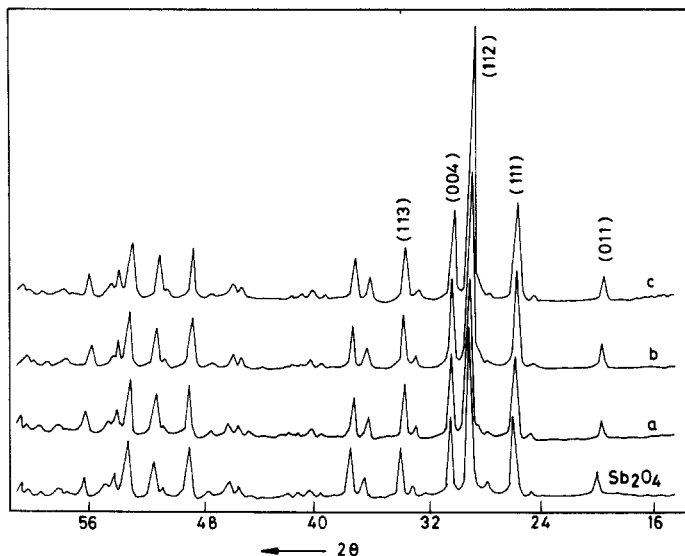Fig. 2. X-ray diffraction patterns of α-Sb$_2$O$_4$ and V$_2$O$_5$/Sb$_2$O$_4$ catalysts with various V$_2$O$_5$ contents (wt%): a, 1.0, b, 3.0; c, 5.0.

Results and discussion

X-ray diffraction patterns of V$_2$O$_5$/SnO$_2$ and V$_2$O$_5$/Sb$_2$O$_4$ catalysts along with the corresponding pure supports are shown in Figs. 1 and 2, respectively. The X-ray diffractograms of V$_2$O$_5$/SnO$_2$ and V$_2$O$_5$/Sb$_2$O$_4$ catalysts show characteristic lines due to SnO$_2$ (ASTM, 21-1250) and α-Sb$_2$O$_4$ (ASTM, 11-694) supports alone. No lines can be seen corresponding either to the V$_2$O$_5$ phase or to a new compound between V$_2$O$_5$ and support. The absence of characteristic peaks due to the V$_2$O$_5$ phase can be taken as an indication of the high dispersion of the V-oxide phase on the support surface or the crystallites formed are less than 4 nm in size, *i.e.*, beyond the detection limit of the XRD technique. Thus, the XRD technique fails to provide further information about the nature of the V-oxide phases on the support surface.

The solid-state [51]V NMR spectra of various V$_2$O$_5$/SnO$_2$ and V$_2$O$_5$/Sb$_2$O$_4$ catalysts are shown in Figs. 3A and B, respectively. It can be noted from this figure, that there are at least two types of distinct signals in the [51]V NMR spectra of the catalysts with varying intensities depending on the vanadium content on the support. Pure and unsupported V$_2$O$_5$ exhibits a line with an axial

anisotropy of the chemical shift tensor ($\delta_\perp = -310$ ppm, $\delta_\parallel = -1270$ ppm) with small peaks due to the first-order quadrupole effects [12]. Accordingly, the species around -310 ppm with
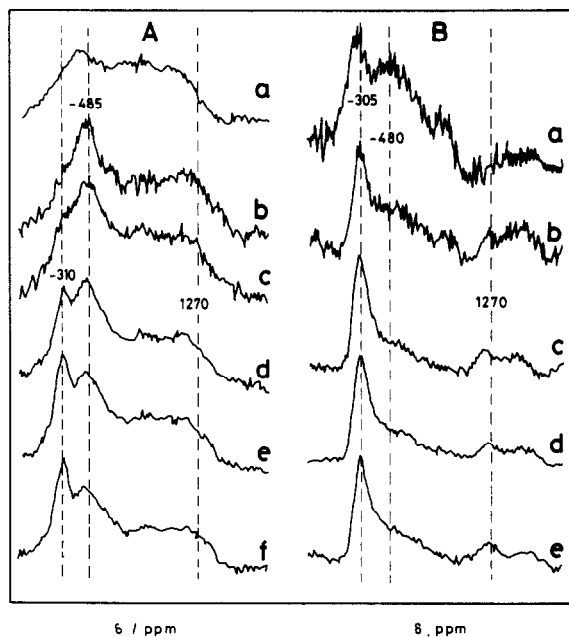

6 / ppm   8 . ppm

Fig. 3. Solid-state [51]V NMR spectra of V$_2$O$_5$/SnO$_2$ (A) and V$_2$O$_5$/Sb$_2$O$_4$ (B) catalysts: (A) a, 0.5; b, 1.1; c, 2.2; d, 3.2; e, 4.3; f, 5.4; (B) a, 1.0; b, 2.0; c, 3.0; d, 4.0; e, 5.0 (loadings of V$_2$O$_5$ in wt%).

a shoulder at -1270 ppm was assigned to the microcrystalline V_2O_5 and the broad spectrum at -485 ppm to the dispersed vanadia species on the support surface with a highly distorted local environment [6,8]. A small change of ±5 ppm in the peak position is due to an error involved in the assignment of the peak maximum (Fig. 3B). It can be noted from Fig. 3 that in the case of V_2O_5/SnO_2 catalysts no crystalline vanadia phase can be seen up to a V_2O_5 loading of ~3.2 wt%, which is close to the theoretical monolayer loading of V_2O_5 on SnO_2 (N_2 BET surface area 29 m^2 g^{-1}) support [13]. However, in the case of V_2O_5/Sb_2O_4 catalysts (Sb_2O_4 surface area 16 m^2 g^{-1}) a small amount of dispersed vanadia phase, in addition to the crystalline phase, exists at the lowest (1 wt%) V_2O_5 loading and at higher vanadia contents a mainly microcrystalline phase can be seen.

The ^1H NMR spectra of representative V_2O_5/SnO_2 and V_2O_5/Sb_2O_4 catalysts along
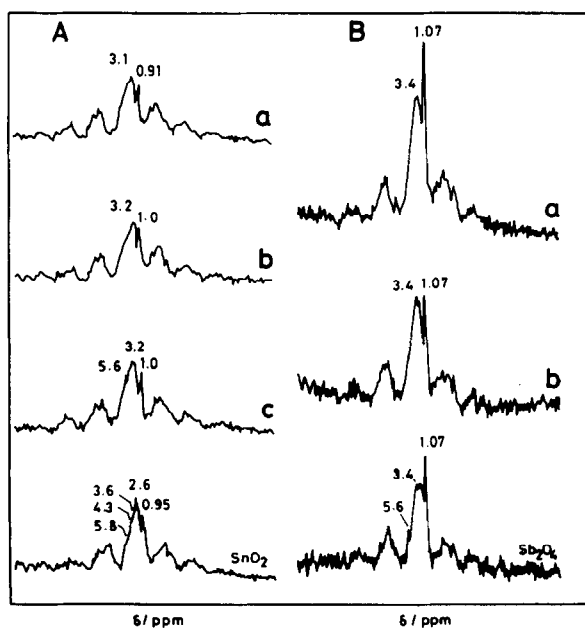
Fig. 5. Total number of hydroxyl groups of V_2O_5/SnO_2 (A) and V_2O_5/Sb_2O_4 (B) catalysts plotted as function of V_2O_5 content.

Fig. 4. Solid-state ^1H NMR spectra of hydroxyl groups of SnO_2 and V_2O_5/SnO_2 (A) and Sb_2O_4 and V_2O_5/Sb_2O_4 (B) catalysts: (A) a, 5.4; b, 3.2; c, 1.1; (B) a, 5.0; b, 2.0 (loadings of V_2O_5 in wt%).
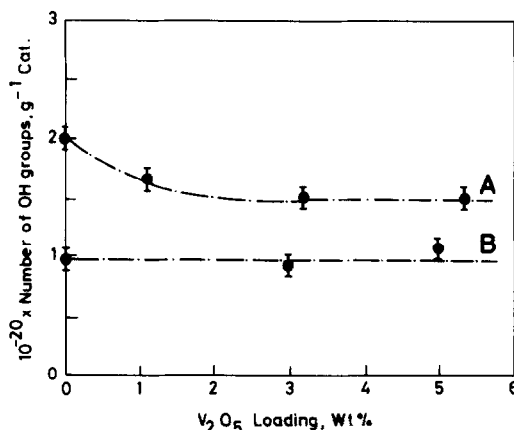
with pure SnO_2 and Sb_2O_4 supports are given in Figs. 4A and B, respectively. The spectra indicate the presence of at least four types of OH groups with chemical shifts from 2.6 to 5.8 ppm in the case of the SnO_2 support and similarly the presence of different types of OH groups with chemical shifts ranging from 3.4 to 5.6 ppm in the case of the Sb_2O_4 support. These are attributed to the support surface hydroxyl groups with different coordination to Sn or Sb atoms, respectively. The narrow line at 0.91–1.07 ppm also seen in the spectra is due to traces of moisture on the outer walls of the sample tubes and the rotor [11].

The total number of OH groups as a function of V_2O_5 loading are shown in Fig. 5. The concentration of OH groups on V_2O_5/SnO_2 catalysts decreases with increase in the loading of V_2O_5 up to ~3.2 wt% and then levels off with further loading (Fig. 5A). However, in the case of V_2O_5/Sb_2O_4 catalysts the total number of OH groups of Sb_2O_4 support does not change (within experimental limitations) upon impregnation with vanadium oxide (Fig. 5B). A considerable decrease in the concentration of support surface OH groups upon impregnation with an active component is an indication of strong interaction between the support and the active component [14,15]. The support surface hydroxyl groups of a

particular nature are normally eliminated during the calcination step after impregnating with an active component. No appreciable change in the concentration of OH groups on Sb_2O_4 support, in line with ^{51}V NMR results, may presumably be due to the inertness of antimony tetraoxide support as proposed by Schuit and Gates [16].

Well-studied supports such as Al_2O_3, SiO_2 and TiO_2 are known to modify the physico-chemical properties of vanadia catalysts. It is also well established that at low vanadium contents the V-oxide phase exists in the form of a highly dispersed monolayer, a patchy monolayer or surface vanadium-oxide species, whereas, at higher vanadia contents in excess of monolayer coverage, the vanadia species exists preferentially as microcrystalline V_2O_5 [2–4]. The maximum amount of vanadium oxide that can be formed in the two-dimensional vanadium oxide over layer, monolayer coverage, depends on the support area, nature and concentration of reactive surface hydroxyl groups. The present ^{51}V and ^1H NMR results on V_2O_5/SnO_2 and V_2O_5/Sb_2O_4 catalysts also supports these concepts.

Acknowledgements

References

1 D.J. Hucknall, Selective Oxidation of Hydrocarbons, Academic Press, London, 1974.
2 G.C. Bond and S.F. Tahir, Appl. Catal., 71 (1991) 1.
3 I.E. Wachs, Chem. Eng. Sci., 45 (1990) 2561.
4 G. Busca, Materials Chem. Phys., 19 (1988) 157, and references therein.
5 H. Eckert and I.E. Wachs, J. Phys. Chem., 93 (1989) 6796, and references therein.
6 L.R. Le Coustumer, B. Taouk, M. Le Meur, E. Payen, M. Guelton and J. Grimblot, J. Phys. Chem., 92 (1988) 1230.
7 V.M. Mastikhin and K.I. Zamaraev, Z. Phys. Chem. N.F., 152 (1987) 59.
8 K. Narsimha, B.M. Reddy, P.K. Rao and V.M. Mastikhin, J. Phys. Chem., 94 (1990) 7336.
9 K. Tanaka, M. Sasaki and I. Toyashima, J. Phys. Chem., 92 (1988) 4730.
10 B. Shou, B. Doumain, B. Yasse, P. Ruiz and B. Delmon, in M.J. Phillips and M. Ternan (Eds.), Proc. 9th Intern. Congr. Catal., Vol. 4, Chemical Institute of Canada, Ottawa, 1988, p. 1850.
11 B.M. Reddy and V.M. Mastikhin, in M.J. Phillips and M. Ternan (Eds.), Proc. 9th Intern. Congr. Catal., Vol. 4, Chemical Institute of Canada, Ottawa, 1988, p. 1850.
12 Z. Sobalik, O.B. Lapina, O.N. Novgorodova and V.M. Mastikhin, Appl. Catal., 63 (1990) 191.
13 G.C. Bond, J.P. Zurita, S. Flamerz, P.J. Gellings, H. Bosch, J.G. Van Ommen and B.J. Kip, Appl. Catal., 22 (1986) 361.
14 B.M. Reddy, K.S.P. Rao and V.M. Mastikhin, J. Catal., 113 (1988) 556.
15 B.M. Reddy, K. Narsimha, P.K. Rao and V.M. Mastikhin, J. Catal., 118 (1989) 22.
16 G.C.A. Schuit and B.C. Gates, Chemtech., 1988, 693.