Characterization of vanadium oxide catalysts supported on SnO2 by 51V and 1H solid-state NMR spectroscopy

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lumnar conduction discussed in ref 5).

On the other hand, the rise of $\epsilon'_{\parallel}$ from the isotropic–discotic transition temperature to its maximum value observed at 407 K could be attributed to a gradual "arrangement" of the columnar phase; i.e., the lengths of the columns increase with decreasing temperature. Such a gradual increase in the columnar and orientational order with decreasing temperature has already been observed by Vilfan et al.[19] in their study of hexapentoxytriphenylene. Below this temperature (407 K), $\epsilon'_{\parallel}$ decreases down to the discotic–solid transition. This behavior may be explained by the decrease of the thermally activated charge carriers concentration and their mobility. On the contrary, the slight variation of $\epsilon'_{\perp}$ indicates that the induced dipolar contribution in the molecular plane is much lower and independent of temperature (hence, of charge carriers concentration) but it depends only on the electronic polarizability of the molecules in their planes.

(19) Vilfan, M.; Lahajnar, G.; Rutar, V.; Blinc, R.; Topic, B.; Zann, A.; Dubois, J. C. *J. Chem. Phys.* **1981,** *75,* 5250. Rutar, V.; Blinc, R.; Vilfan, M.; Zann, A.; Dubois, J. C. *J. Phys.* **1982,** *43,* 761.

Conclusion

We have measured the dielectric constant and conductivity of $[(C_{12}O)_8Pc]_2Lu$ in the homeotropic and homogeneous orientation obtained with a relatively low magnetic field. The dielectric anisotropy is positive and its value may be compared to that found for nematic liquid crystals. We have proposed an explanation based on the intracolumnar conduction which generates an important induced dipolar moment along the columnar axis. We may thus conclude that the columnar phase possesses a negative diamagnetic anisotropy. These results are in agreement with what is actually observed: the major contribution to the conduction occurs along the columnar axis. The validity of such an argument is to be tested by further dc and ac investigations under magnetic and/or electric fields, which are in progress and will be reported in a future publication.

Characterization of Vanadium Oxide Catalysts Supported on SnO2 by 51V and 1H Solid-State NMR Spectroscopy

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The solid-state 51V and 1H NMR spectra of V_2O_5/SnO_2 catalysts reveal the existence of two types of vanadia species on the surface: one due to a dispersed vanadia phase at lower vanadium loadings and the other due to crystalline vanadia phase at higher vanadium contents.

Vanadia-based catalysts are well-known for catalyzing a great variety of industrial reactions.[1] Recent studies have shown that V_2O_5 supported on a metal oxide support such as Al_2O_3, SiO_2, and TiO_2 is a superior catalyst to unsupported crystalline V_2O_5 for the selective oxidation and ammoxidation of many hydrocarbons.[2] Thus the support metal oxide plays a major role in determining the dispersion and activity of the V_2O_5 when supported. In recent years attention has been focused mainly on the study of the dispersion as well as the interaction of vanadia species with the supported oxides. The availability of new surface sensitive techniques such as XPS,[3-5] EXAFS,[6] ESR,[7] and Raman spectroscopy[5,8] have made possible a number of recent careful scientific studies. The technique of solid-state 51V NMR represents a promising approach to these systems. Owing to a large magnetic moment, high natural abundance (99.76%), and favorable relaxation characteristic, this nucleus is very amenable to solid-state NMR investigation.[9] In addition, the recent development of the magic angle spinning (MAS) technique has afforded the high-resolution NMR spectra of 1H nuclei in solid samples.[10] However, the applications of the 51V and 1H MAS NMR techniques to the characterization of V_2O_5/SnO_2 catalysts have not been previously reported. It is only recently that the importance of tin oxide-based catalytic systems has begun to be recognized.[11]

In this study the SnO_2-supported catalysts containing 0.5–5.5 wt % V_2O_5 were prepared by the standard wet impregnation technique with the required amounts of aqueous ammonium

metavanadate solutions. The impregnated catalysts were dried at 120 °C for 12 h and calcined at 500 °C for 6 h. The SnO_2 support (N_2 BET surface area 30 $m^2 g^{-1}$) was prepared by precipitating stannic hydroxide from stannic chloride with dilute ammonia solution. The chloride free precipitate was dried at 120 °C for 16 h and calcined at 600 °C for 6 h in air. The solid-state 51V and 1H NMR spectra with MAS technique have been recorded on a Bruker CXP-300 spectrometer. 51V NMR spectra were recorded at a frequency of 78–86 MHz in the frequency range of 150 kHz, using 1-μs radio frequency pulses with repetition rate of 10 Hz. Chemical shifts were measured relative to external $VOCl_3$. The 1H NMR spectra were recorded at a frequency of 300.090 MHz. The frequency range was 50 kHz, ($\pi/2$) pulse

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(1) Gellings, P. J. *Catalysis;* Royal Society of Chemistry: London, 1985; Vol. 7, p 165.
(2) Bond, G. C.; Flamerz, S.; Shukri, R. *Faraday Discuss. Chem. Soc.* **1989,** *87,* 225 and references therein.
(3) Anderson, S. L. T. *J. Chem. Soc., Faraday Trans. 1* **1979,** *75,* 1357.
(4) Bond, G. C.; Zurita, J. P.; Flamerz, S. *Appl. Catal.* **1986,** *27,* 353.
(5) Saleh, R. Y.; Wachs, I. E.; Chan, S. S.; Chersich, C. C. *J. Catal.* **1986,** *98,* 102.
(6) Kozlowski, R.; Pettifer, R. F.; Thomas, J. M. *J. Phys. Chem.* **1983,** *87,* 5176.
(7) Chary, K. V. R.; Reddy, B. M.; Nag, N. K.; Sunandana, C. S.; Subrahmanyam, V. S. *J. Phys. Chem.* **1984,** *88,* 2622.
(8) Oyama, S. T.; Went, G. T.; Lewis, K. B.; Bell, A. T.; Somorjai, G. A. *J. Phys. Chem.* **1989,** *93,* 6786.
(9) Zamaraev, K. I.; Mastikhin, V. M. *Colloids Surf.* **1984,** *12,* 401.
(10) Clague, A. D. H. *Catalysis;* Royal Society of Chemistry: London, 1985; Vol. 7, p 61.
(11) Tanaka, K.; Sasaki, M.; Toyoshima, I. *J. Phys. Chem.* **1988,** *92,* 4730.

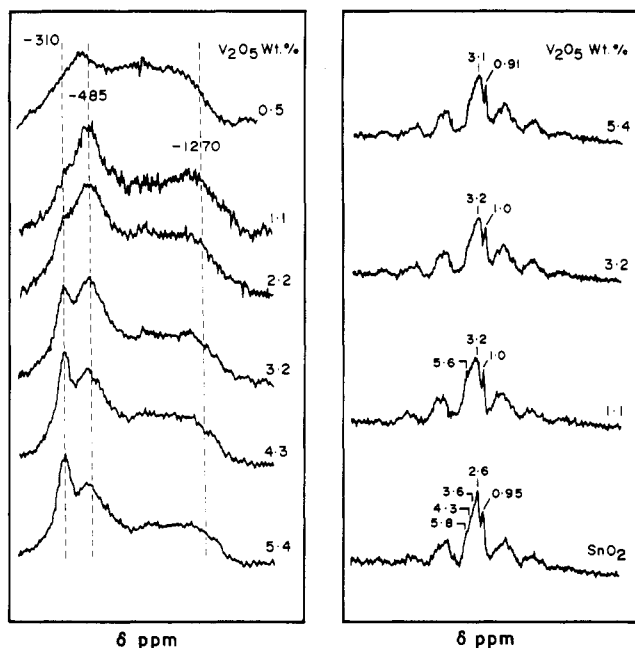**Figure 1.** (a, left) Solid-state ^{51}V NMR spectra of V_2O_5/SnO_2 catalysts. (b, right) Solid-state ^1H NMR spectra of hydroxyl groups of SnO_2 and V_2O_5/SnO_2 catalysts.

Figure 2. Total number of hydroxyl groups plotted as a function of V_2O_5 loading.

duration was 5 μs, and the pulse repetition frequency was 1 Hz. The chemical shifts were measured relative to TMS as an external standard. Surface OH groups were quantitatively estimated by measuring the area under the peak with reference to a known standard sample.[12] Before the measurements, the samples were placed in specially made glass tubes, evacuated (10^{-5} Torr) at 500 °C for 4 h and sealed under vacuum. The samples thus prepared were placed in quartz rotors. The rotation frequency of the rotor was 3.0–3.5 kHz.

The solid-state ^{51}V and ^1H NMR spectra of various V_2O_5/SnO_2 catalysts are shown in Figure 1, a and b, respectively. As can be noted from Figure 1a, there are at least two types of distinct signals in the ^{51}V NMR spectra of catalysts with varying intensities depending on the vanadium content on SnO_2 surface. At the lowest concentration of about 0.5 wt % V_2O_5, a rather broad resonance around −440 ppm with a much broader shoulder around −1000 ppm is observed. As the V_2O_5 concentration increases, a small shift in the peak maximum to $\delta = -485$ ppm with a shoulder developing at −1230 ppm can be seen (1.1 wt %). The shape of this signal does not change significantly on increasing V_2O_5 content upto about 5.4%. This can be interpreted as an indication of the same local environment of vanadium nuclei present in the region 0.5–5.4 wt % V_2O_5. Upon increasing the vanadium content from 0.5 to 3.2 wt % a new downfield signal component around −310 ppm emerges. The intensity of this signal increases monotonically with increasing vanadia content, suggesting the appearance of a different distinct species with a different V(V) coordination. A comparison of the spectra with the spectra of unsupported V_2O_5 and also from known vanadium compounds shows that this species is similar to that of V_2O_5.[13,14]
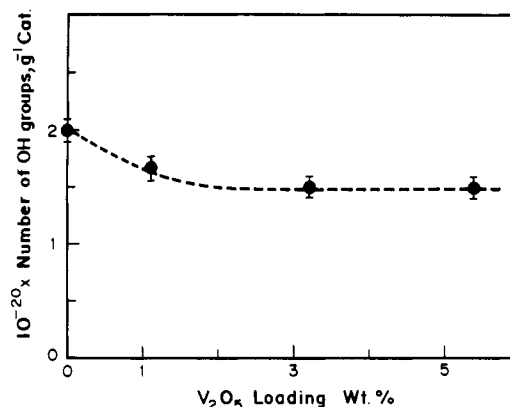
The ^1H NMR spectra of representative catalysts and SnO_2 (Figure 1b) show several features. For SnO_2 support the spectra indicate the presence of at least four types of OH groups with chemical shifts from 2.6 to 5.8 ppm, respectively. These can be attributed to Sn–OH groups with different coordination to Sn atoms.[15] The narrow line at 1.0 ppm belongs to the traces of H_2O on the outer walls of the sample tubes and the rotor.[12] Upon impregnation with V_2O_5 the intensity of the spectra due to Sn–OH groups has been decreased and the peaks have slightly broadened.

The total number of OH groups as a function of V_2O_5 loading are shown in Figure 2. The concentration of OH groups decreases with an increase in the loading again upto 3.2 wt % and levels off with further loading. This loading is close to the theoretical monolayer coverage of V_2O_5 on SnO_2 support.[2] The behavior of leveling off at a certain loading level is very similar to that found previously on MoO_3/SiO_2[16] and V_2O_5/SiO_2[17] catalyst systems, indicating an evidence for the interaction of surface OH groups with the supported species. However, the considerably smaller extent of decrease in NMR signal intensity due to Sn–OH groups for V_2O_5/SnO_2 catalysts may be due to the nonavailability of all Sn–OH groups to the interacting vanadia phase. It appears from these results that the majority of the hydroxyls in SnO_2 are not at the exposed surface, but rather in the interior of the structure. This observation is in agreement with the dispersion of vanadia phase on SnO_2 support obtained via low-temperature oxygen chemisorption technique as reported earlier.[18]

Thus the present ^{51}V and ^1H solid-state NMR studies show that at low V_2O_5 contents the vanadium oxide species exists in the form of a dispersed monolayer of surface vanadia interacting with the SnO_2 support, whereas at higher vanadia contents in excess of monolayer coverage the vanadia species exists preferably as microcrystalline V_2O_5. The amount of V_2O_5 necessary to form a monolayer depends on the specific surface area of the system under consideration.

(12) Reddy, B. M.; Mastikhin, V. M. In *Proceedings of the 9th International Congress on Catalysis*; Phillips, M. J., Ternan, M., Eds.; Chemical Institutes of Canada: Ottawa, 1988; Vol. 1, p 82.

(13) Eckert, H.; Wachs, I. E. *Mater. Res. Soc. Symp.* **1988**, *3*, 459.

(14) Le Coustumer, L. R.; Taouk, B.; Le Meur, M.; Payen, E.; Guelton, M.; Grimblot, J. *J. Phys. Chem.* **1988**, *92*, 1230.

(15) Hoflund, G. B., NASA Conference Publication 2456, NASA, 1987; p 179.

(16) Reddy, B. M.; Rao, K. S. P.; Mastikhin, V. M. *J. Catal.* **1988**, *113*, 556.

(17) Reddy, B. M.; Narsimha, K.; Rao, P. K.; Mastikhin, V. M. *J. Catal.* **1989**, *118*, 22.

(18) Reddy, B. M.; Narsimha, K.; Sivaraj, Ch.; Rao, P. K. *Appl. Catal.* **1989**, *55*, L1.