Characterization of Vanadium Oxide Catalysts supported on γ-Al_2O_3 by ^{51}V Solid State N.M.R. Spectroscopy

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^{51}V Solid state n.m.r. of V_2O_5/Al_2O_3 catalysts reveals two types of vanadia species on the surface: one due to a dispersed vanadia phase at lower vanadium contents and the other due to crystalline vanadia phase at higher vanadium content.

Vanadium oxide catalysts in combination with various supports and promoters are well known for selective oxidation of hydrocarbons.[1—3] The commonly employed supports are Al_2O_3, SiO_2, and TiO_2 (anatase). Supports are often found to modify the physico-chemical properties of vanadia catalysts. The supported oxides do not form three-dimensional crystal phases but a rather patchy, or continuous, 'monolayer' covering the support. In recent years attention has been focused on the interaction of vanadia species with the supported oxide. Thus, V_2O_5 deposited on various supported

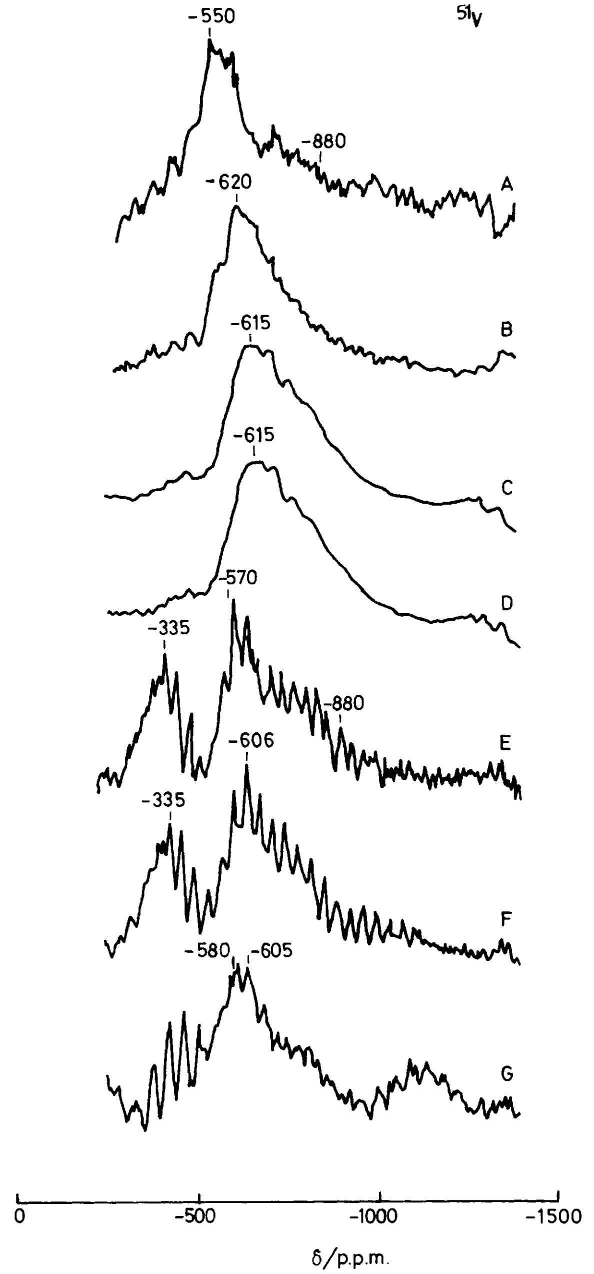

Figure 1. ^{51}V Solid state n.m.r. spectra of various $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts, A = 3.4 wt.% V_2O_5, B = 7%, C = 9.8%, D = 11.9%, E = 14.8%, F = 18.5%, G = 20.1%.

Table 1. Dispersion and crystallite size of various $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts.

Wt.% of V_2O_5 on $\gamma\text{-}Al_2O_3$	B.E.T. Surface area/$m^2\,g^{-1}$	V_2O_5 Crystallite size/nm[a]	% Dispersion[b]
3.4	183.0	—	37.70
7.0	173.0	—	39.90
9.8	172.0	—	36.10
11.9	168	34.5	38.10
14.8	159	74.0	27.40
18.5	167	100.0	17.10
20.1	159	>100.0	8.8

[a] Determined from *X*-ray line broadening method. [b] Calculated from O_2 chemisorption results, ref. 12.

oxides has been studied by several sophisticated techniques such as laser Raman spectroscopy (L.R.S.),[4—6] X.P.S.,[6—8] e.s.r.[9] radial electron distribution (R.E.D.),[10] and E.X.A.F.S.[11] All these studies suggest that the supports were found to modify the properties of the vanadia phase by forming a monolayer of surface vanadia phase as well as the crystalline vanadia phase. The relative amounts of these two kinds of species depends on the vanadia content and the surface area of the supported oxide. In the present investigation we report the results of ^{51}V solid state n.m.r. of V_2O_5 catalysts deposited on Al_2O_3 in order to find the nature of vanadium species on the surface of Al_2O_3.

A series of V_2O_5 catalysts with V_2O_5 loadings of *ca.* 3—20 wt.% supported on $\gamma\text{-}Al_2O_3$ were prepared by impregnating the support material with an aqueous solution containing NH_4VO_3. The catalysts were subsequently dried and calcined in air at 500 °C for 6 h. The vanadium contents in the catalysts were analysed using atomic absorption spectrometry. The details of catalyst preparation have been given elsewhere.[12]

^{51}V N.m.r. magic angle spinning spectra were measured on a CXP-300 Bruker spectrometer (magnetic field = 7.046 T) at 78.87 MHz in the frequency range 125 kHz. 1 μs Radiofrequency pulses were used to excite the $-1/2 \longleftrightarrow +1/2$ transition. The pulse repetition rate was 10 Hz. Chemical shifts were measured relative to external $VOCl_3$. P.M.M.A. rotors with a rotation speed of 4 kHz were used.

The spectra of various V_2O_5 catalysts are shown in Figure 1. At least three types of spectra can be distinguished depending on the vanadium concentration on the Al_2O_3 surface. At the lowest concentration of *ca.* 3 wt.% V_2O_5 a rather broad and complicated spectrum with a peak at about −550 p.p.m. is observed (spectrum A). Increasing the V_2O_5 content on the Al_2O_3 surface changes the shape of the spectrum to a rather intense peak at about −620 p.p.m. with a shoulder at about −1200 p.p.m. (spectrum B). The shape of spectrum B does not change significantly on increasing the V_2O_5 content up to *ca.* 15 wt.% V_2O_5 (spectrum E). This can be interpreted as an indication of the same type of local environment of vanadium nuclei present in the region of 5—15 wt.% V_2O_5. Most probably the shapes of the A and B spectra are determined by the combined effect of chemical shift anisotropy and the second order quadrupole effect with asymmetry parameter $\eta \simeq 1$.

The inspection of the spectra of the samples having 3.4 wt.-% and 7 wt.% V_2O_5 shows that the sample with a higher vanadium content has a superposition of the spectrum A over spectrum B. The characteristic feature of spectra A and B is that they do not change their shapes on magic angle spinning probably because the line width is large compared with the spinning rate.

A large line width is typical for ^{51}V nuclei in a highly distorted local environment and is caused by second order quadrupole effects. The line shapes of spectrum A and spectrum B do not have distinct characteristic points for the determination of quadrupole parameters. But the different positions of the peaks indicate the differences of the spectral parameters for both cases and therefore the spectra A and B are observed due to different local environments of vanadium nuclei.

At 14.8 wt.% V_2O_5 and a higher vanadium content a new spectrum with a series of side bands appears. Thus at low vanadium concentration two types of vanadium surface complexes are formed with highly distorted oxygen environment. The first type of complexes existing up to 3—5 wt.% V_2O_5 can be tentatively attributed to the distorted surface vanadium–oxygen structures surrounded by a distorted tetrahedron of oxygen atoms. The increase of vanadium content (*ca.* 5—15 wt.% V_2O_5) on the surface leads to the formation of the surface vanadium–oxygen clusters with a highly distorted structure different from that of V_2O_5. The increase of V_2O_5 content beyond 15 wt.% leads to the formation of a crystalline V_2O_5 phase.

These findings are in agreement with the results of low temperature oxygen chemisorption (L.T.O.C.) and *X*-ray diffraction studies of these catalyst samples reported earlier.[12] No *X*-ray diffraction lines due to V_2O_5 were observed below 11.9 wt.% V_2O_5. However, at higher V_2O_5 contents the intensity of vanadia peaks increases as a function of V_2O_5 loading. The crystallite size of V_2O_5 determined by *X*-ray line broadening, and the percentage of vanadia dispersion determined from oxygen chemisorption studies, are reported in Table 1. From the L.T.O.C. results it was found that a monolayer of V_2O_5 was formed at 11.9 wt.% with high degree of dispersion of vanadia on the alumina surface. The dispersion of vanadia remained constant within the monolayer region, but it decreased beyond the monolayer region. This could be due to the formation of a bulky crystalline vanadia phase at higher loadings as evidenced from the *X*-ray diffraction and ^{51}V solid state n.m.r. results. Thus, the findings of ^{51}V solid state n.m.r. further supports the observations made from L.T.O.C. and X.R.D. results.

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