^{51}V NMR: A NEW PROBE OF STRUCTURE AND BONDING IN CATALYSTS

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ABSTRACT

Solid State ^{51}V NMR spectra are sensitive to changes in the surface
structure of V_2O_5 dispersed on Al_2O_3 and TiO_2 supports. For V_2O_5 supported on
alumina, wideline and magic-angle spinning experiments at 4.7 and 7.0 T reveal
the presence of two vanadium species with different bonding environments. The
relative proportions of these species change monotonically as a function of the
vanadium concentration. In contrast, supported vanadium oxide on TiO_2
substrates show a much more V_2O_5-like environment. Structural inferences are
discussed in connection with solid state ^{51}V NMR studies on model compounds
with known crystal structures and site symmetries.

INTRODUCTION

Recent studies have shown that V_2O_5 supported on a metal oxide is a superior
catalyst to unsupported crystalline V_2O_5 for the selective oxidation of many
hydrocarbons. For example, the selective oxidation of o-xylene to phthalic
anhydride only proceeds if V_2O_5 is supported on TiO_2 (anatase) [1]. Detailed
studies of the reaction network and the kinetics of this reaction [2,3] have been
complemented by structural investigations using laser Raman spectroscopy [1,3].
Those studies have shown that at low V_2O_5 contents the vanadium oxide species
exist in the form of a monolayer of surface vanadia interacting with the TiO_2
support, whereas vanadia contents in excess of monolayer coverage are present
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. Similar
results have been obtained with other supports such as ZrO_2 and Al_2O_3 [4]. The
complex vanadium oxide structural chemistry prevents a complete structural
determination of the surface vanadium oxide phases solely from Raman
spectroscopy [4]. A need for a complementary technique of structural
characterization also arises from the inherent difficulty to derive quantitative
information from Raman spectra.

Solid state ^{51}V NMR represents a promising approach to these systems.
Owing to a large magnetic moment, high natural abundance (99.76 %) and
favorable relaxation characteristics, this nucleus is very amenable to solid-
state NMR investigation. A number of previous studies have shown that the ^{51}V
chemical shielding tensor is very sensitive to changes in the coordination
environments, and provides a facile means of discrimination between different

vanadates in the solid state [5-11]. The scope of previous ^{51}V NMR applications to catalysts has been extremely limited [11-13], and, to our knowledge, no systematic studies have been carried out. We report here the first application of ^{51}V NMR wideline and magic-angle spinning (MAS) NMR spectroscopy to catalytic systems based on atomically dispersed surface vanadate. In an effort to correlate the spectroscopic information obtained with specific vanadium bonding environments in such systems, we have generated a database of ^{51}V chemical shift tensors of crystalline compounds with known structures. Using this information, we will discuss possible microstructures on catalysts containing pentavalent vanadia supported on alumina, titania, and zirconia substrates.

EXPERIMENTAL

The supported vanadium oxide on TiO_2 catalysts were prepared by the incipient wetness impregnation method with $VO(OC_2H_5)_3$ in ethanol on Degussa P-25 TiO_2 (surface area 50 m^2/g; anatase/rutile ca. 2). The impregnated samples were subsequently dried at room temperature for 16 hrs, dried at 110-120 °C for 16 hrs, and calcined at 450 °C for 2 hrs to form the supported vanadium oxide on TiO_2 catalysts. Vanadia contents were determined by ICP analysis. Raman characterization revealed that samples with up to 7 wt.% V_2O_5 contained only atomically dispersed surface vanadium oxide species, above this limit V_2O_5 crystallites were observed as an additional phase. Thus, a monolayer of surface vanadium oxide corresponds to ca. 7% V_2O_5/TiO_2 for this system.

The supported vanadium oxide on Al_2O_3 catalysts were prepared by the incipient wetness impregnation method with $VO(OC_3H_7)_3$ in methanol on Harshaw Al_2O_3 (surface area 180 m^2/g). The impregnated samples were subsequently dried at room temperature for 16 hrs, dried at 110-120 °C for 16 hrs, and calcined at 500 °C for 16 hrs to form the supported catalysts. Vanadia contents were determined by ICP analysis. Raman characterization of the V_2O_5/Al_2O_3 system revealed that the 1-20% V_2O_5/Al_2O_3 samples contained only atomically dispersed surface vanadium oxide species and that at higher vanadia contents V_2O_5 crystallites are observed in addition to the atomically dispersed species. Thus, a monolayer of surface vanadium oxide corresponds to ca. 20 % V_2O_5/Al_2O_3 for this system. Crystalline vanadates investigated to provide reference data were obtained from commercial sources (Alfa, Aldrich, Strem, Aesar) and their identity was verified by x-ray diffraction and Raman analysis. The sample of $Pb_5(VO_4)_3Cl$ (vanadinite) was taken from the mineral collection of the California Institute of Technology.

Room temperature wideline and MAS NMR studies were conducted at 4.7 T and 7.0 T. Measurements at the lower field (corresponding to a resonance frequency for ^{51}V of 52.65 MHz) utilized a homebuilt spectrometer system interfaced with a 293 B pulse programmer, Explorer fast digitizer, and Nicolet 1280 computer. ^{51}V NMR wideline experiments were carried out on ca. 100 mg of material, compressed into cylindrical sample tubes of 5 mm outer diameter in a 5 mm homebuilt probe. Magic-angle spinning NMR experiments at 4.7 T were carried out using a modified ^{13}C CPMAS probe from DOTY Scientific. The

powdered materials were spun in sapphire rotors of 7.0mm outer diameter at typical rates of 3-5 kHz.

Measurements at 7.0 T (frequency for ^{51}V: 79.0 MHz) were carried out on a General Electric GN-300 spectrometer, equipped with Henry-Radio amplifiers and a Chem-Magnetics probe. Both wideline and MAS NMR experiments were conducted within KELEF rotors of 9.5mm o.d. which were spun at a number of different speeds up to 3.5 kHz.

All of the spectra at both fields were recorded with pulse lengths between 0.5 and 2 µs (corresponding to solid 90 degree pulses, depending on the pulse power available and the efficiency of the respective probe used). Typical recycle delays were 1-2 seconds, resulting in spectra free from relaxation effects. All ^{51}V NMR chemical shifts were determined with respect to the resonance location of solid vanadinite (which resonates at 514 ppm upfield of VOCl$_3$).

RESULTS AND DISCUSSION

Figures 1 and 2 show ^{51}V MAS NMR spectra of selected model compounds. For all of the samples under investigation, the isotropic shifts were found to be equal within experimental error at both external field strengths, thus confirming that second-order quadrupolar shifts [14] are minimal at the field strengths used, and that the observed spinning sideband patterns are dominated by the chemical shift anisotropy [15]. The isotropic shifts (determined from these spectra) as well the shielding tensor components S_1, S_2, and S_3 (estimated independently from singularities in the corresponding wideline NMR spectra) are shown in Table I. As discussed in more detail below, it is clear from this table that these chemical shift parameters are sensitive to the different vanadium coordination environments in these compounds.

In vanadium pentoxide, the V atoms are coordinated to five oxygen atoms at distances of 154, 188, 188, 202, and 177 pm, whereas the sixth oxygen ligand is further removed (281 pm). The shielding tensor in V_2O_5 is essentially axially symmetric [19], the dominant perpendicular component being located near -250 ppm (giving rise to a peak maximum near 300 ppm). A similar situation obtains in lead metavanadate, where two vanadium sites exist with V-O distances of 193, 192, 206, 167, 165, 273 pm, and 161, 172, 192, 192, 203, 257 pm, respectively. Both wideline and MAS NMR experiments detect only a single species, suggesting that the shielding tensors for both sites must be very similar. The chemical shift anisotropies of the tetrahedrally coordinated vanadates under study are much smaller, and depend on the number of nonbridging oxygen atoms, N_{no} attached to them. For example, N_{no} = 2 in the metavanadates NaVO$_3$ and NH$_4$VO$_3$, the structures of which are based on chains of $VO_2O_{2/2}$ tetrahedra[21,22]. Due to lack of cylindrical symmetry of such microstructures, the spectra of these compounds reveal a non-axially symmetric shielding tensor. In contrast, the compounds Na$_3$VO$_4$, BiVO$_4$, Pb$_5$(VO$_4$)$_3$Cl, and AlVO$_4$ have isolated, more symmetric tetrahedra (N_{no} = 4), thus resulting in only small shift anisotropies [23,24]. In this context, the spectrum of AlVO$_4$ deserves specific comment. Although the structure of this compound remains to be determined, X-ray powder diffraction patterns and infrared spectra [25] suggest an isomorphous

Pb$_5$(VO$_4$)$_3$Cl

BiVO$_4$

NH$_4$VO$_3$

PbV$_2$O$_6$
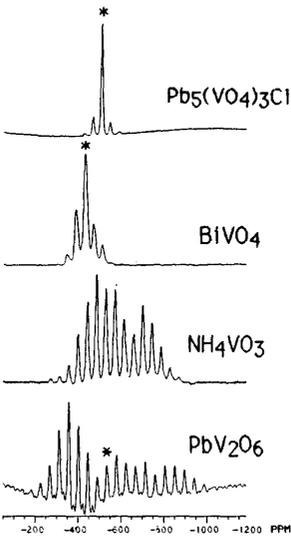
Figure 1: 79.00 MHz ^{51}V MAS–NMR spectra of model compounds. Central bands are indicated by asterisks.

Figure 2:

52.65 MHz ^{51}V MAS–NMR spectrum of AlVO$_4$.

20 wt.% (1.0)

15 wt.% (0.75)

10 wt.% (0.50)

5 wt.% (0.25)

4 wt.% (0.20)

Figure 3: 52.65 MHz wideline ^{51}V NMR spectra of V$_2$O$_5$ supported on Al$_2$O$_3$ catalysts. Vanadia contents and surface coverages are indicated.

AlVO$_4$

5% V$_2$O$_5$/Al$_2$O$_3$ (0.25)

4% V$_2$O$_5$/TiO$_2$ (0.6)

8% V$_2$O$_5$/TiO$_2$ (1.1)

7% V$_2$O$_5$/ZrO$_2$ (3.5)

V$_2$O$_5$
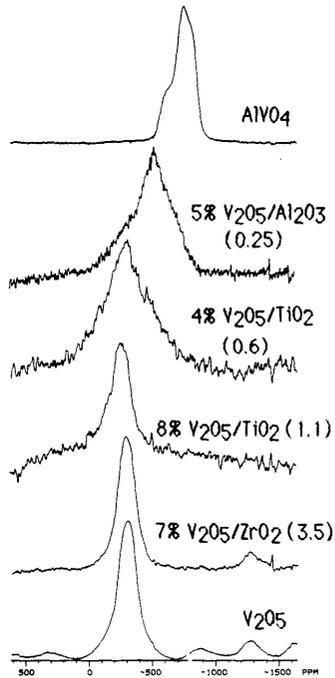
Figure 4: 52.65 MHz wideline ^{51}V NMR spectra of several catalysts and model compounds. Surface coverages in parentheses.

Table I: NMR chemical shift parameters for reference
compounds under study (in ppm vs. $VOCl_3$)

| Compound | S_1 | S_2 | S_3 | ∂_{iso} | Structure ref. |
	(± 10 ppm)			(±1 ppm)	
V_2O_5	-250	-250	-1300	-614	[16,17]
PbV_2O_6	-310	-320	-1000	-538	[18]
$NaVO_3$	-360	-530	-840	-584	[21]
NH_4VO_3	-370	-530	-830	-578	[22]
Na_3VO_4	*	*	*	-550	
$BiVO_4$	-365	-415	-520	-439	[23]
$Pb_5(VO_4)_3Cl$	*	*	*	-514	[24]
$AlVO_4$	*	*	*	-678	[25,26]
	*	*	*	-753	
	*	*	*	-786	

* not determined

relation with $FeVO_4$, which crystallizes in the space group $P\bar{1}$ and shows three
crystallographically inequivalent vanadium sites [26]. The MAS- NMR spectrum
(Figure 2) confirms this interpretation. Overall, Table I suggests that the
anisotropic shielding information is more valuable than the isotropic chemical
shift in discriminating between different vanadium environments.

Figure 3 shows the wideline NMR spectra of five V_2O_5/Al_2O_3 catalyst
samples, where the vanadium oxide is present as an atomically dispersed surface
phase. Up to concentrations of 5 wt.% V_2O_5, a broad resonance around -540 ppm
is observed. Linewidth, shape and chemical shift location of this resonance are
consistent with an assignment to a tetrahedral vanadate species, most likely
with $N_{no}=2$. However, magic-angle spinning experiments (5 kHz) do not result in
any line-narrowing, hence indicating a broad distribution of isotropic chemical
shifts. This result is suggestive of a distribution of vanadate tetrahedral
environments, possibly involving different numbers of non-bridging oxygen
atoms, within the surface layer. In addition, the NMR results give no evidence for
the formation of a bulk crystalline or amorphous $AlVO_4$ phase. Upon increasing
the vanadia content beyond 5 wt.%, a new downfield signal component around
-330 ppm emerges. The contribution of this signal increases monotonically with
increasing vanadia content, suggesting the appearance of a distinct species with
a different V(V) coordination. Both wideline and magic-angle spinning spectra
suggest that the short range order structure for this species is similar to that of
V_2O_5. Figure 4 illustrates, along with the wideline NMR spectra of some model
compounds, the influence of the support on the nature of the surface vanadia
species. In the TiO_2 supported catalysts studied, the V_2O_5 like species seems
more prominent in comparison to Al_2O_3 supported catalysts with comparable

coverages. The spectrum of V_2O_5 supported on ZrO_2 with a low surface area closely resembles that of crystalline V_2O_5 (Figure 4, bottom).

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REFERENCES:

[1] I.E. Wachs, R.Y. Saleh, S.S. Chan, and C.C. Chersich, Appl. Catal. 15, 339 (1985) and references therein.
[2] R.Y. Saleh and I.E. Wachs, Appl. Catal. 31, 87 (1987)
[3] R.Y. Saleh, I.E. Wachs, S.S. Chan, and C.C. Chersich, J. Catal. 98, 102 (1986).
[4] I.E. Wachs, S. D. Hardcastle, and S.S. Chan, this volume
[5] V.A. Gubanov, N.I. Lazukova, and R. N. Pletnev, Zh. Neorg. Khim. 23, 655 (1978) [Russ. J. Inorg. Chem. 23, 362 (1978)]
[6] R.N. Pletnev, N.I.Lazukova, and V.A. Gubanov, Zh. Fiz. Khim. 51, 2359 (1977) [Russ. J. Phys. Chem. 51, 1382 (1977)]
[7] V.A. Gubanov, R.N. Pletnev, V.N. Lisson, and A.K. Chirkov, Spectrosc. Lett. 10, 527 (1977).
[8] S. Ganapathy, S. Schramm, and E. Oldfield, J. Chem. Phys. 77, 4360 (1982).
[9] E. Oldfield, R.A. Kinsey, B. Montez, T. Ray, and K.A. Smith, J. Chem. Soc. Chem. Comm. 1982, 254
[10] S.L. Segel and R.B. Creel, Can. J. Phys. 48, 2673 (1970)
[11] V.M. Mastikhin, O.B. Lapina, V.N. Krasilnikov, and A.A. Ivakin, React. Kinet. Catal. Lett. 24, 119 (1984).
[12] V.M. Mastikin, O.B. Lapina, and L.G. Simonova, React. Kinet. Catal. Lett. 24, 127 (1984).
[13] T.P. Gorshkova, R.I. Maksimovskaya, D.V. Tarasova, N.N. Chumachenko, and T.A. Nikoro, React. Kinet. Catal. Lett. 24, 107 (1984).
[14] M.H. Cohen and F. Reif, in Solid State Physics, edited by F. Seitz and D. Turnbull, Vol. 5 (Academic Press, New York, 1957), p. 321.
[15] J.F. Baugher, P.C. Taylor, T. Oja, and P.J. Bray, J. Chem. Phys. 50, 4914 (1969).
[16] A. Bystrom, K.A. Wilhelmi, and A. Brotzen, Acta Chem. Scand. 4, 1119 (1950).
[17] H.G. Bachmann, F.R. Ahmed, and W.H. Barnes, Z. Krist. 115, 110 (1961)
[18] B.D. Jordan and C. Calvo, Can. J. Chem. 52, 2701 (1974).
[19] S.D. Gornostansky and C.V. Stager, J. Chem. Phys. 46, 4959 (1967).
[20] H. Eckert and I.E. Wachs, to be published.
[21] F. Maruma, M. Isobe, and S. Iwai, Acta Crystallogr. B30, 1628 (1974).
[22] H.T. Evans, Jr., Z. Krist. 114, 257 (1960).
[23] A.W. Sleight, H.Y. Chen, and A.Ferretti, Mat. Res. Bull 14, 1571 (1979).
[24] J. Trotter and H.W. Barnes, Can Miner. 6, 161 (1957-61).
[25] E.J. Baran and I.L.Botto, Monatsh. Chem. 108, 311 (1977).
[26] B.Robertson and E. Kostiner, J. Solid State Chem. 4, 29 (1972).