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Study of the V_2O_5-Al_2O_3 interaction during ultra-high intensity grinding

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Ultrahigh intensity grinding of mechanical mixtures of V_2O_5 with γ-Al_2O_3 at ambient temperature was found to create vanadyl complexes with ESR spectral parameters identical to those of vanadia-alumina samples prepared by impregnation methods.

No interaction was found after intensive grinding of γ-Al_2O_3 with V_2O_4.

Keywords: Vanadia; alumina; grinding; ESR; NMR

1. Introduction

The activity of V_2O_5 based catalysts is significantly improved by the interaction of the active phase with the oxidic support. Recently the treatment by the ultra-high intensity grinding (UHIG) of mixtures of V_2O_5 with alumina or titania has been shown to provide an active and selective catalyst for reduction of nitrogen oxides by ammonia [1,2]. The enhancement of the grinding force was achieved by the combined action of two centrifugal fields. By this treatment, the crystalline V_2O_5 with square-pyramidal environment is transformed into a form of a vanadium oxide layer probably with predominantly tetrahedral V(V) species. This transformation is supposed to be caused by mechanical deformation and consequent temperature elevation at the contact points between particles of the mixture during UHIG. From a thermal treatment, this process differs in some unique properties, such as the increase of temperature occurring at the points of impact only and for a very short time.

One of the important attributes which influence the oxygen mobility of vanadia catalysts is the formation of a V(IV) species [3] which can eventually be stabilized on the vanadia-support interphase. The aim of this work was to answer the question, whether the change of the V(V) coordination by the UHIG treatment is also accompanied by a formation of V(IV) species.

2. Experimental part

UHIG TREATMENT

Mixtures of γ-alumina ($S = 220\ m^2/g$) with 7 wt% of V_2O_5 (Reachim, USSR) or V_2O_4 (Fluka) were treated for up to 30 min in a planetary mill as described previously [2]. Balls and containers from stainless steel or corundum were used in separate experiments.

To distinguish the stage of interaction during the UHIG treatment from the thermal interaction during calcination or catalytic test [2], the V_2O_5/γ-alumina ground mixtures were measured prior calcination.

ESR SPECTROSCOPY

The ESR measurements were performed on an ESR spectrometer (ERS-220, ZWG-Berlin) in air at room temperature and at 77 K in the X-band. The spectra were calibrated with a DPPH standard.

^{51}V-NMR SPECTROSCOPY

The spectra were measured on a Bruker MSL-400 spectrometer as described previously [1]. The ^{51}V chemical shifts were measured relative to external standard $VOCl_3$.

3. Results and discussion

After the intensive grinding, the brownish color of the vanadia-alumina mixtures changes into yellowish. The ESR spectrum of such a sample is shown in fig. 1. It consists of eight fold splitted signal with the lack of line broadening indicating presence of isolated species. The spin Hamiltonian parameters of the ESR signal were obtained by first order analysis and assuming an axial symmetry (see table 1). Because of the similarity of the obtained parameters with those of VO-tartrate complex [4] the signal was as in the case of vanadia-alumina impregnated samples [5] assigned to isolated VO^{2+} species stabilized on the alumina support. This species is supposed to have a distorted octahedral coordination of C_{4v} symmetry with the short vanadyl bond (V=O) directed perpendicularly to the surface. The fact that the ESR signal measured at room

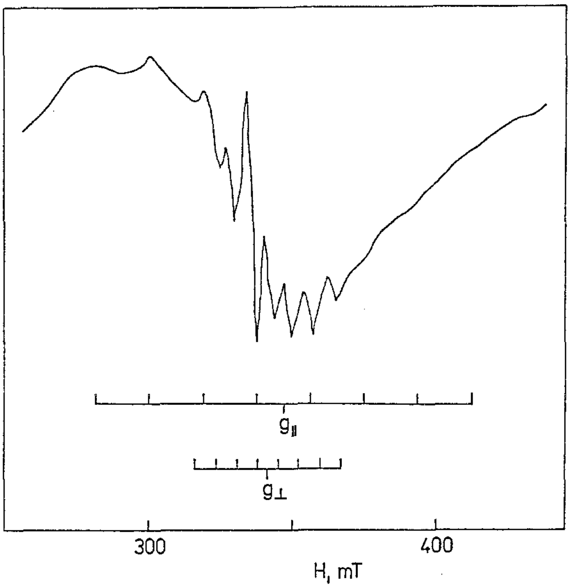

Fig. 1. ESR spectra of V_2O_5-Al_2O_3 mixture (7 wt.% of V_2O_5) after UHIG treatment for 30 min.

temperature did not change by decreasing the temperature to 77 K supported the assignment of the detected signal to VO^{2+} formation during the treatment and ruled out V^{4+}, as some broadening of the lines should be found in such case.

The VO^{2+} species generated by the UHIG treatment seems to be similar to such species which are present in impregnated samples. This is also supported by the similar value of $\Delta g_{\parallel}/\Delta g_{\perp}$ (see tables 1 and 2). As discussed by Nowinska [5] for vanadyl complexes with C_{4v} symmetry the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ depends mainly on tetragonal distortion. With this distortion increasing both the energy levels split ΔE_{xz} and the $\Delta g_{\parallel}/\Delta g_{\perp}$ value increase as well and a shortening of the V=O bond and an increase in the length of the equatorial ligands should be expected.

Similarly the value of the parameter ($\beta_2^{*2} \cong 0.93$; assuming $P = 128 \cdot 10^{-4}$ cm^{-1} [6]) was found to be identical to impregnated and alumina supported

Table 1
Spin Hamiltonian parameters for the vanadia/alumina catalysts

Samples	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ [10^4 cm^{-1}]	$A_{\perp}$	$\Delta g_{\parallel}/\Delta g_{\perp}$	$g_{\perp} - g_{\parallel}$	$A_{\parallel}/A_{\perp}$
VO^{2+} [4]	1.947	1.976	−152	−44	2.1	0.030	3.5
Impregnated catalyst [5]	1.946	1.972	−157	−50	1.9	0.026	3.1
UHIG	1.944	1.973	−170	−58	2.0	0.029	3.0

Table 2

Samples	g_0	A_0 [10^4 cm^{-1}]	β_2^{*2}	K	PK	$A'_{\parallel}$ [10^4 cm^{-1}]	$A'_{\perp}$ [10^4 cm^{-1}]
VO^{2+} [4]	1.967	−80	0.93	0.59	76	−76	31
Impregnated catalyst [5]	1.963	−86	0.92	0.63	81	−76	31
UHIG	1.963	−95	0.93	0.78	100	−70	42

catalysts. With β_2^{*2} nearly equal to 1 the unpaired electron is mostly localized on the metal ion [7], so in both samples the bonds between vanadium ion and the oxygen ligands should be highly ionic.

It is evident that the VO^{2+} signal with hyperfine splitting is superimposed onto a broad background signal with the g value of about 1.97. Similar broad signal corresponds to small amount of V(IV) present in V_2O_5 [8]. No indication of a signal belonging to VO^{2+} was detected under the experimental condition after grinding pure V_2O_5 without alumina.

As it is shown at fig. 2, the intensity of VO^{2+} signal in mixtures of V_2O_5 with alumina is proportional to the duration of UHIG treatment. As we have found the signal line-width is not affected by the treatment duration, so the height of ESR signal has been used to qualify the evolution of the vanadyl ions.

This intensity increase was found to proceed in parallel with the transformation of a vanadia octahedral environment (NMR line with an axial anisotropy of the chemical shift tensor $\delta_{\perp} = -310$ ppm, $\delta_{\parallel} = -1270$ ppm) most probably to a

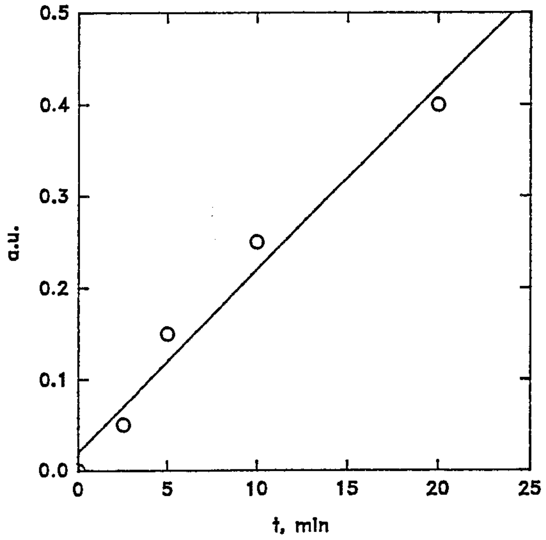

Fig. 2. Intensity of ESR signal of V_2O_5-Al_2O_3 mixtures (7 wt.% of V_2O_5) with increasing time of UHIG treatment.

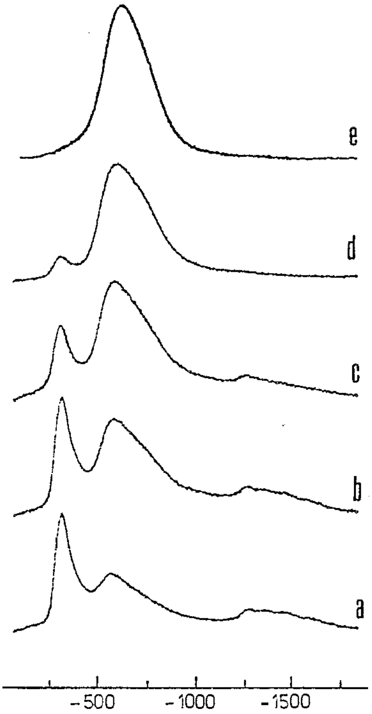

Fig. 3. ^{51}V-NMR spectra of V_2O_5-Al_2O_3 mixtures (7 wt.% of V_2O_5) before (a) and after 2.5 (b), 5 (c), 10 (d) and 20 min (e) of UHIG treatment.

disturbed tetrahedral environment (a signal with a chemical shift in the range of −500 to −750 ppm) (see fig. 3).

With increasing intensity of the energy transferred to the processed material during the UHIG treatment, the contamination of the processed samples by the materials of the grinding tools is increasing as well and it can eventually influence the process of a bulk V_2O_5 transformation. By using stainless steel grinding tools the content of metallic impurities (Fe, Cr and Ni) after about 30 min of treatment was found in a range of 10^{-3} wt.%. and the samples gave a characteristic signal with $g = 4.3$, belonging to Fe(III) complexes in tetrahedral coordination [9]. Nevertheless, no change was observed as regard to both processes accompanying the V_2O_5-alumina interaction, i.e. the change of V(V) environment and VO^{2+} formation, if corundum grinding tools were used instead of metallic ones in the UHIG processing.

We suppose that VO^{2+} species are formed by a solid state reaction of V_2O_5 with alumina which results in a spontaneous reduction of V(V) even in oxidizing conditions. An interaction of the bulk V_2O_4 with alumina during the same UHIG treatment was found to proceed in a very limited extent and after subsequent oxidation, according to the ^{51}V-NMR results, most of the former

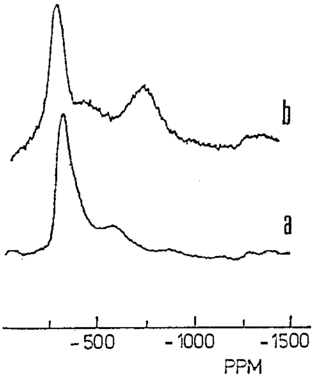

Fig. 4. ^{51}V-NMR spectra of V_2O_5 (a) and V_2O_5-Al_2O_3 (b) mixture (7 wt.% of V_2O_4) after 20 min of UHIG treatment with following oxidation for 30 min at 500°C on air.

V_2O_4 is present in a form of uninteracted bulk V_2O_5 with V(V) in octahedral environment (see fig. 4). His conclusions is supported by the fact that at V_2O_5/Al_2O_3 mixture the coordination sphere of vanadium formed during the UHIG remains mainly unchanged after the following heating on air [1] showing the stability of the structure formed by UHIG treatment.

The difference in V_2O_5 and V_2O_4 behavior seems to reflect much higher stability of the V_2O_4 lattice in agreement with much higher melting point of V_2O_4 (1640 °C) than that of V_2O_5 (658 °C).

Acknowledgments

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