STUDY OF THE V_2O_5/Al_2O_3 CATALYST OF THE NO + NH_3 REACTION

Pavel STOPKA and Milan ČÍŽEK
Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6

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During the reduction of the catalyst, the maximum intensity in the ESR spectrum does not correspond to the catalyst composition of V_2O_4/Al_2O_3. The feasible explanations of this fact are discussed in relation to the reduction of V^V on the surface and in deeper layers of the catalyst.

Supported vanadium catalysts are frequently used for the oxidation and amooxidation of hydrocarbons and, recently, also for the selective catalytic reduction (SCR) of oxides of nitrogen with ammonia. The redox mechanism is largely assumed to operate in these reactions, implying that the catalyst is reduced by one component and, in the next step, oxidized by the other component giving the reaction products – products of nitrogen and water in the case of SCR. ESR spectroscopy gives us information on some active forms of the catalyst (V^{IV}, VO^{2+}) in a closed reaction vessel. An overview of the extent of reduction and oxidation of supported vanadium catalysts by reaction mixtures and their components has been presented in ref.[1]. A drawback of ESR spectroscopy with respect to the study of the catalysts in question is in the fact that V^{III} and V^V afford no signal in conventional experimental conditions.

EXPERIMENTAL

Preparation of the 15% V_2O_5/Al_2O_3 catalyst has been reported[1]. A flow glass reactor was used for the study. Reduction of the catalyst was accomplished at 150–450°C with hydrogen, ammonia or an NO + NH_3 mixture; oxidation, with oxygen. The ESR spectra of the samples, enclosed in the reactor, were measured on an ERS-220 spectrometer (Academy of Sciences, Berlin, F.R.G.) at 298 and 77 K in the X-band. Magnetic modulation frequency was 100 kHz, microwave power 20 mW, modulation amplitude 1 mT, microwave frequency 9·291 GHz. The magnetic field was measured by means of an ^1H NMR magnetometer (Radiopan, Poland), the microwave frequency, by means of a CZ-S4 frequency counter (C.I.S.). Diphenylpicrylhydrazyl was employed for calibration and checking.

RESULTS

Figure 1 shows typical spectra of the initial oxidized catalyst and of the catalyst reduced with ammonia. The perpendicular splitting line to parallel splitting line intensity ratio is higher for the oxidized samples than for the reduced samples. The spectral line splitting was better at 77 K. Figure 2 shows the dependence of the signal intensity on the average oxidation state of vanadium. The ESR spectral data and average oxidation state values are given in Table I. The maximum of the ESR signal intensity was found for a sample which had been reduced for several hours with the NO + NH_3 mixture at 160°C. The subsequent reduction of the catalyst at higher temperatures resulted in a decrease in the signal intensity.

TABLE I

Spin hamiltonians of the initial oxidized and reduced V_2O_5/Al_2O_3 catalysts

Catalyst modification	x	$g_{\parallel}$	$g_{\perp}$	g_0	$A_{\parallel} . 10^4$ cm^{-1}	$A_{\perp} . 10^4$ cm^{-1}	$A_0 . 10^4$ cm^{-1}	β_2^{*2}
1	4·96	1·9447	1·9726	1·9633	−157·8	−58·3	−91·5	0·852
6	4·10	1·9356	1·9816	1·9663	−164·3	−60·8	−95·3	0·874
5	3·70	1·9322	1·9845	1·9671	−153·7	−61·1	−92·0	0·770
7	3·30	1·9322	1·9827	1·9659	−165·9	−58·9	−94·6	0·902

Catalyst modification numbering as in Fig. 2; x is the average vanadium oxidation state; β_2^{*2} is the MO coeficient giving the degree of delocalization of the unpaired electron at the vanadium atom into the ligands[5]; g_0 and A_0 are isotropic parameters calculated from $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$, $A_{\perp}$, respectively.

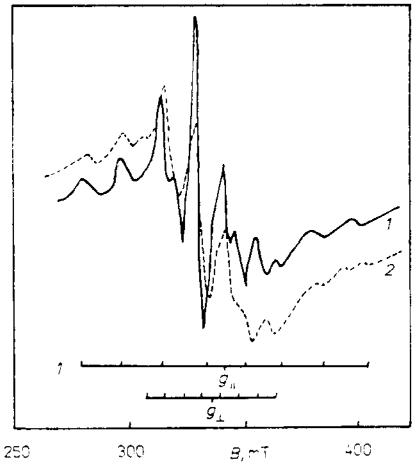

FIG. 1

ESR spectra of the V_2O_5/Al_2O_3 catalyst in the initial oxidized state (*1*) and reduced with 1% ammonia at 450°C (*2*)

As compared to the reduction with the NO + NH_3 mixture, the reduction of the catalyst with the hydrogen–nitrogen mixture sets in at higher temperatures and the ESR intensity maximum is considerably less pronounced. In either case the position of the maximum lies at an average vanadium oxidation state higher than as corresponds to V_2O_4/Al_2O_3. Similar results have been observed for the pure oxides[2].

During the in-depth reduction of the catalyst with the H_2 + N_2 mixture at 450 to 480°C, doublets were observed in the low field region of the spectrum of V_2Ox for $x \leqq 4$ (Fig. 3, doublets indicated with arrows). These doublets were also found for the catalyst reduced with the NO + NH_3 mixture. For the catalyst reduced with pure ammonia the doublets were very weak.

DISCUSSION

ESR spectroscopy is a very convenient method for the examination of V_2O_5/Al_2O_3 catalysts of the reaction of NO + NH_3 + O_2. Whereas ions of V^V and V^{III} are inactive in ESR, ions of V^{IV} exhibit a very well-developed spectrum with a hyperfine

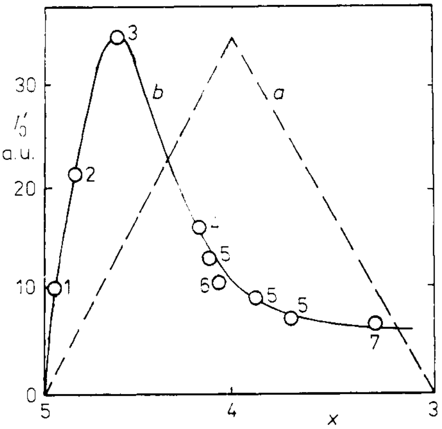

FIG. 2

Dependence of the ESR spectral intensity on the average vanadium oxidation state x (for V_2Ox/Al_2O_3). Curves: *a* expected curve shape, *b* experimental dependence. Catalyst treatment: 1 initial state, 2 N_2 at 450°C, 3 NO + NH_3 mixture at 160°C, 4 NO + NH_3 mixture at 450°C, then 25°C in dry air, 5 NH_3 at 450°C, time dependence, 6 NO + NH_3 mixture at 450°C, 7 H_2 at 450°C

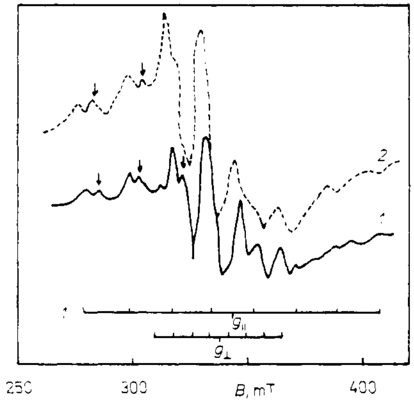

FIG. 3

ESR spectra of deeply reduced V_2O_5/Al_2O_3 catalysts. Reduction: *1* H_2 at 450°C, *2* NO + NH_3 mixture at 450°C structure. It was reasonable to assume that during the catalyst reduction the ESR intensity curve (curve *a* in Fig. 2) would pass through a maximum as V^{IV} appears and vanishes in the $V^{V} \rightarrow V^{IV} \rightarrow V^{III}$ sequence. The results of chemical analysis[1] of samples reduced for a long period of time gave evidence that the concentration of ions of V^{IV} can be expected to be highest at 300°C. However, for the same samples reduced with $NO + NH_3$ the maximum ESR intensity was observed at a temperature as low as 160°C. The character and intensity of the ESR spectrum across a wide region about this temperature do not vary during a long-run reduction. We assume that under such conditions the reduction of surface layers of the catalyst is considerably faster than the reduction of deeper layers. This assumption is corroborated by chemical analysis and by DTA as well as by the examination of a temperature programmed reaction[3].

In the reduction of the catalyst with ammonia or hydrogen the situation is different. The V_2O_5/Al_2O_3 catalyst starts to be reduced by them at higher temperatures, above 250°C. We assume that the reduction of the surface and of deeper vanadium layers occurs simultaneously, and gradually proceeds across the bulk. This is also borne out by the fact that the intensity maxima are less expressive and the catalyst reduction gives rise to lower HFS splitting than samples "surface-reduced" with the $NO + NH_3$ mixture.

The appearance of doublets during the catalyst reduction with hydrogen in the low field region can be due:

a) to a symmetry lowering of the V^{IV} structure in the complex from the octahedral (axial) symmetry to the tetrahedral symmetry – a similar interpretation of the spectra has been suggested[4];

b) to the formation of two different types of V^{IV} complexes, probably V^{IV} and VO^{2+}, on the catalyst surface. However, as in ref.[4], these doublets were not observed in the high field region of the spectrum in the parallel part.

As mentioned above, the ESR spectral maximum should pass through a maximum during the gradual reduction of the vanadium catalyst. There exist four explanations of the shift or suppression of the spectral intensity maximum (the first three have been partly discussed in ref.[5]):

1) The ions of V^{V} are reduced at low temperatures in parallel to ions of V^{IV} and V^{III}; the feasibility of this is indicated by the broadening of the spectrum of V^{IV} due to the $V^{IV} \cdots V^{IV}$ interaction.

2) During the reduction of the multicomponent V_2O_5/Al_2O_3 catalyst, ESR-inactive or, in the conditions applied, low-active $V^{IV} \cdots V^{IV}$ pairs can form. This possibility is indicated by the very low intensity of the ESR spectrum of V_2O_4.

3) Decrease in the sensitivity of the ESR measurement due to the presence of electrons in the conductivity band of the partly reduced ions of V^{IV}.

4) In the 15% V_2O_5 catalyst used, preliminary measurements suggested the occurrence of several vanadium layers on the support. During its gradual reduction from the surface into the bulk, the ESR intensity maximum can be expected to be attained sooner, which implies its shift to an average vanadium oxidation state higher than 4.

Based on the analysis of ESR spectra of V_2O_5, V_2O_4 and reduced as well as oxidized vanadium catalysts of various compositions and prepared by various procedures we suggest that the shift of the ESR signal intensity maximum during the catalyst reduction, from the assumed vanadium oxidation state 4 to a value about 4·5, is primarily related with the gradual appearance of ESR-inactive vanadium pairs. The opportunity for such ESR-inactive pairs to form increases with increasing number of vanadium layers on the support, i.e., with increasing vanadium content of the catalyst.

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