REDUCTION AND OXIDATION OF VANADIUM CATALYSTS FOR THE NO + NH₃ REACTION

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The reduction of V_2O_5/Al_2O_3 (15 mass % V_2O_5) and V_2O_5 by ammonia, hydrogen, and a NO + NH₃ mixture, and the oxidation of pre-reduced catalysts by oxygen and nitrogen oxide have been investigated. For both catalysts, the reduction rate increases in the sequence $H_2 < < NH_3 < NO + NH_3$. From the character of the temperature and concentration dependences of the oxidation state of vanadium, it has been concluded that in the temperature range 100 to 175°C the catalysts are reduced by the NO + NH₃ mixture within the surface layer only. The reaction of this mixture with oxidized surface of vanadium catalyst is of the same order with respect to NO and NH₃ concentrations.

Vanadium catalysts are used in a number of oxidation and ammoxidation reactions of organic compounds and in oxidation of SO_2. Lately, these catalysts have been widely used in the selective reduction of nitrogen oxides by ammonia. It has been demonstrated that in many cases the activity of the catalyst depends not only on the composition and the method of preparation, but also on the instantaneous oxidation state. Although the main controlling factor for heterogeneous catalysts is the condition of the surface layer, the state of the inner layers is also of importance. The structure of vanadium oxides and the characteristics of the surfaces of V_2O_5, V_6O_{13}, V_2O_4, and V_2O_3 are well known[1−3]. The surface properties of supported catalysts differ significantly, depending on the method of preparation, the kind of support, and the vanadium content. At low vanadium loadings, the support plays a distinct role, whereas the properties of catalysts rich in vanadium approach those of V_2O_5 alone, even when part of the support remains exposed[4,5]. Inomata[4] assumes that both pure V_2O_5 and supported catalysts with low or high vanadium loadings in both the oxidized and reduced states have on their surfaces a large proportion of V=O groups, which act as active sites for the NO + NH₃ reaction and various oxidations. Haber[6] assumes different forms of vanadium oxide on TiO_2 and $γ-Al_2O_3$. When prepared by reaction of $VOCl_3$ in CCl_4 with TiO_2, the catalyst contains monodisperse VO_4 groups, whereas the use of $γ-Al_2O_3$ as the support results in the formation of dimeric V_2O_7 groups.

There has been little systematic investigation into the reduction and oxidation of vanadium catalysts[6-8]. Most papers only note that the reaction under study involves reduction or oxidation of vanadium catalyst and characterize the catalyst used, for example, by temperature-programmed reduction.

In studying the kinetics of the $NO + NH_3$ reaction on a V_2O_5/Al_2O_3 catalyst with the use of EPR, it was established[9,10] that, on admission of the reaction mixture to the fresh catalyst, it took 20 to 60 h, depending on the temperature, before the catalyst attained a steady oxidation state. In the same time, the activity of the catalyst reached a steady level, and the oxidation state remained constant over the temperature range 300 to 450°C and for the ratio of input concentrations $NO : NH_3$ ranging from 0·01 to 100.

The aim of the present work was to determine changes in the oxidation state of vanadium in reduction of a V_2O_5/Al_2O_3 catalyst by ammonia, to ascertain the role of nitrogen oxide in the reaction, and to compare the results with those for pure V_2O_5. Another aim was to determine changes in the oxidation state of vanadium in the oxidation of pre-reduced vanadium catalysts by oxygen and nitrogen oxide.

EXPERIMENTAL

A V_2O_5 catalyst was prepared by calcining vanadyl oxalate at a final temperature of 400°C/48 h. The product was crushed, kneaded with dilute HNO_3, dried, and calcined in the air. Before measurement, the catalyst was recalcined at 450°C in an atmosphere of pure nitrogen. The specific surface area of the catalyst was 10 m^2/g.

A V_2O_5/Al_2O_3 catalyst was prepared by mixing and kneading γ-Al_2O_3 (Condea SC) with a suspension of vanadyl oxalate. The method of catalyst preparation, the apparatus, and the preparation and purification of gases have been described in detail in our previous paper[10].

The oxidation state of vanadium was determined by titration with $KMnO_4$ and a solution of Mohr salt after dissolving the sample in a mixture of concentrated HF and 50% H_2SO_4 in a ratio of 2 : 5 in the absence of air. The end-point in titration with Mohr salt was detected by using a diphenylamine/H_3PO_4 indicator or potentiometrically.

RESULTS

The determination of the oxidation state of vanadium revealed that the dissolution rate of a catalyst sample depends largely on the degree of its reduction. The dissolution rate of strongly reduced samples was substantially lower than that for oxidized samples, and also lower than the rate of the reaction of $V^{5+} + V^{3+}$ to V^{4+} in solution, as verified by potentiometric measurements. For these reasons, it was not possible to obtain the proportions of tri-, tetra-, and pentavalent vanadium in a dissolved sample as described by Niwa[11], and only the average oxidation state Y was determined.

An average oxidation state of 4·93 in the fresh V_2O_5/Al_2O_3 catalyst decreased to 4·86 by prolonged calcination in an atmosphere of pure nitrogen. Variations in the

oxidation state of vanadium with time during reduction by $1\% NH_3$ at various temperatures (Fig. 1) indicate that the catalyst is reduced at a measurable rate starting from 200°C, the reduction curves showing no maxima or minima or flat portions. Different kinetics are observed for the reduction of the catalyst by a mixture of NO and NH_3 (Fig. 2). The reduction starts at lower temperatures and occurs in two different stages. At temperatures between 100 and 200°C, a very rapid reduction, to a degree depending on the temperature, occurs within the first 15 min. This is accompanied by a colour change of the catalyst surface from yellow-green to grey. Thereafter, the reduction continues very slowly. At 450°C, an oxidation state of 4·10 is attained in 25 h. The same oxidation state is reached on prolonged oxidation of a pre-reduced catalyst by a NO + NH_3 mixture, and this state is that for which the kinetics of the NO + NH_3 reaction were studied under steady-state conditions in our previous work[10].

Fig. 3 shows variations in the oxidation state of vanadium with NH_3 concentration and with the composition of the reaction mixture, $x \% NO + 1\% NH_3$ and $1\% NO + x \% NH_3$, for a constant overall reduction time.

The temperature dependence of the oxidation state of vanadium in V_2O_5/Al_2O_3 catalyst represented in Fig. 4 is qualitatively similar to that for pure V_2O_5 shown
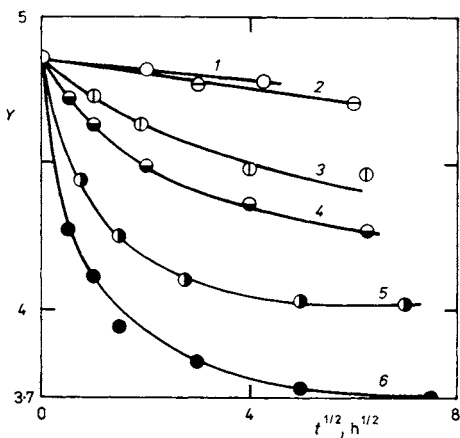

FIG. 1

Oxidation state of vanadium, Y, in $V_2O_5/$ /Al_2O_3 catalyst vs time for reduction by ammonia (0·3 g of catalyst, $1\% NH_3$, 10 l/h). *1* 200°C, *2* 250°C, *3* 300°C, *4* 325°C, *5* 375°C, *6* 450°C
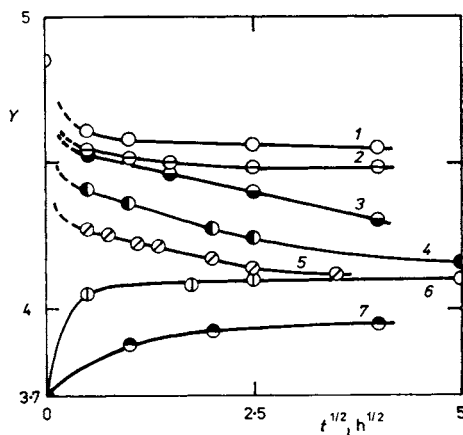
FIG. 2

Oxidation state of vanadium, Y, in $V_2O_5/$ /Al_2O_3 catalyst vs time for reduction and oxidation by a NO + NH_3 mixture (0·3 g of catalyst, $1\cdot8\% NO + 1\cdot2\% NH_3$, 20 l/h). Reduction: *1* 100°C, *2* 200°C, *3* 225°C, *4* 300°C, *5* 450°C; oxidation: *6* 450°C, *7* 300°C

in Fig. 5. For both catalysts, we see a marked increase in the reduction rate in the sequence $H_2 < NH_3 < NO + NH_3$, and a completely different shape of the curve for the reduction by the $NO + NH_3$ mixture. After an initial rapid reduction starting from 100°C, the curve becomes flat, rising again only at temperatures above 175°C.
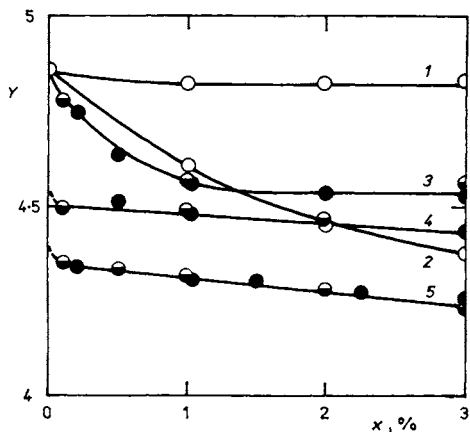

FIG. 3

Oxidation state of vanadium, Y, in $V_2O_5/$ $/Al_2O_3$ catalyst vs concentrations of ammonia and $NO + NH_3$ mixture (0·3 g of catalyst, 20 l/h, 6·25 h). Reduction by NH_3 (○): *1* 200°C, *2* 300°C; reduction by $NO + NH_3$ (●, x % $NO + 1$% NH_3; ◐, 1% $NO + x$% NH_3): *3* 150°C, *4* 200°C, *5* 300°C
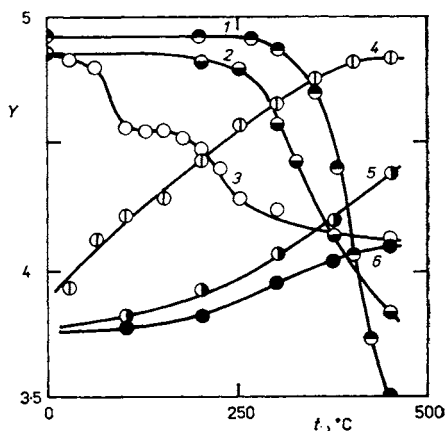

FIG. 4

Oxidation state of vanadium, Y, in $V_2O_5/$ $/Al_2O_3$ catalyst vs temperature of reduction and oxidation (0·3 g of catalyst, 20 l/h). Reduction (6·25 h): *1* 1% H_2, *2* 1% NH_3, *3* 1·8% $NO + 1·2$% NH_3; oxidation ($Y^0 =$ $= 3·75$): *4* 1% O_2, 1 h, *5* 1% NO, 1 h, *6* 1·8% $NO + 1·2$% NH_3, 6·25 h
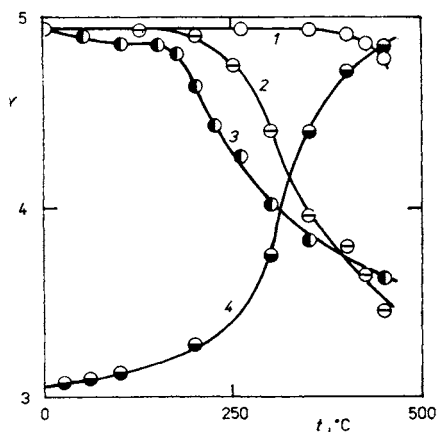

FIG. 5

Oxidation state, Y, of pure V_2O_5 vs temperature of reduction and oxidation (0·05 g of catalyst, 10 l/h). Reduction (6·25 h): *1* 1% H_2, *2* 1% NH_3, *3* 1·8% $NO + 1·2$% NH_3; oxidation ($Y^0 = 3·00$, 1 h): *4* 1% O_2

The variations in the oxidation state of vanadium with temperature for the reduction of V_2O_5 and V_2O_5/Al_2O_3 by hydrogen are in accordance with results of GTA measurements[12], and the observation for the reduction of V_2O_5 by ammonia agrees essentially with the results of Malecki[7].

The reduced catalysts were also used in a study of oxidation by O_2, NO and NO + NH_3 diluted with nitrogen (Figs 4 and 5). Before the oxidation, the V_2O_5/Al_2O_3 and V_2O_5 catalysts were subjected to prolonged reduction by dilute ammonia to initial oxidation states Y^0 of 3·75 and 3·00, respectively.

DISCUSSION

The results presented above confirm the conclusion drawn from EPR measurements[9] that, in the NO + NH_3 reaction occurring under steady-state conditions, the oxidation state of vanadium in V_2O_5/Al_2O_3 catalyst remains constant over wide temperature and concentration ranges, corresponding to the formula $V_2O_{4.10}/Al_2O_3$. In accord with results for the activity of the catalyst[10], the time it takes to attain this constant state depends on the starting oxidation state of vanadium, and primarily on the temperature.

The flat portions of the curves for the reduction of the catalyst by the mixture NO + NH_3 (Figs 4 and 5), and the existence of two different parts of the catalyst reduction at temperatures above 200°C indicate that the reduction of vanadium catalysts consists of two consecutive processes.

The low-temperature reduction in the range 100 to 175°C probably involves just a superficial reduction through reaction between the NO + NH_3 mixture and oxygen atoms of the active sites which, according to Miyamoto[13], consist of V=O groups. The linear dependence of the average oxidation state of vanadium on the square root of time for the reduction by NO + NH_3 mixture at temperatures above 200°C (Fig. 2) suggests that diffusion of oxygen ions from lower V---O layers may take place. This idea is in accord with results obtained by Kakioka[14] for oxygen diffusion within V_2O_5, and was also used by Miyamoto[13] to explain the shape of a record from pulse measurements on the reaction between NO + NH_3 and oxidized vanadium catalysts at temperatures above 200°C.

According to Miyamoto[13] and Shikada[15], it may be assumed that the surface of a catalyst reduced by a NO + NH_3 mixture has vanadium in an oxidation state close to 4. The subsequent slower reduction at temperatures above 200°C could involve, besides the diffusion of oxygen ions, an incipient deeper reduction of tetravalent vanadium on the catalyst surface to V^{3+}.

From the identical linear dependences of the oxidation state of vanadium in V_2O_5/Al_2O_3 catalyst on the composition of the reduction mixtures 1% NO + x % NH_3 and x % NO + 1% NH_3 at 200 and 300°C (Fig. 3), it may be concluded that the reaction between the gaseous mixture and the oxidized surface of the catalyst

is of the same order with respect to NO and NH_3 concentrations. This is in contradiction to results of Inomata[16], who found the catalyst reduction to be first order in NO and zero order in NH_3.

A more detailed study of the relation between the oxidation state of vanadium and the activity of the catalyst for NO + NH_3 and NO + NH_3 + O_2 reactions will be the subject of our next paper.

REFERENCES

1. Byström A., Wilhelmi K., Brotzen O.: Acta Chem. Scand. 4, 1119 (1950).
2. Andersson A.: J. Solid State Chem. 42, 263 (1982).
3. Gray M. L., Kershaw R., Croft W., Dwight K., Wold A.: J. Solid State Chem. 62, 57 (1986).
4. Inomata M., Mori K., Miyamoto A., Murakami Y.: J. Phys. Chem. 87, 761 (1983).
5. Roozeboom F., van Dillen A. J., Geus J. W., Gellings P. J.: Ind. Eng. Chem., Prod. Res. Dev. 20, 304 (1981).
6. Haber J., Kozlowska A., Kozlowski R.: J. Catal. 102, 52 (1986).
7. Malecki A., Gajerski R., Komornicki S.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. 29, 461 (1981).
8. Malecki A., Prochowska-Klisch B.: Bull. Acad. Pol. Sci., Ser. Sci. Chim. 33, 517 (1985).
9. Čížek M.: Thesis. Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague 1985.
10. Čížek M., Pour V.: Collect. Czech. Chem. Commun. 51, 2528 (1986).
11. Niwa M., Murakami Y.: J. Catal. 76, 9 (1982).
12. Štěpánková V.: Unpublished results.
13. Miyamoto A., Yamazaki Y., Inomata M., Murakami Y.: Chem. Lett. 1978, 1355.
14. Kakioka K., Ducarme V., Teichner S. J.: J. Chim. Phys. Physicochim. Biol. 68, 1715 (1971).
15. Shikada T., Ogawa H., Fujimoto K.: Nippon Kagaku Kaishi 1983, 141.
16. Inomata M., Miyamoto A., Murakami Y.: J. Catal. 62, 140 (1980).

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