

REDUCTION OF NITROGEN OXIDE BY AMMONIA. OXIDATION STATE OF V_2O_5/Al_2O_3 CATALYSTS AND REACTION MECHANISM

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Received January 16, 1990

Accepted March 14, 1990

When the ($NO + NH_3 + O_2$) reaction is carried out over V_2O_5/Al_2O_3 , the catalysts are partially reduced, and prereduced catalysts are oxidized by the reaction mixture at a slower rate than by an $O_2 + N_2$ mixture. The degree of catalyst reduction in the ($NO + NH_3 + O_2$) reaction depends on the gas phase composition and particularly on the vanadium loading of the catalyst. The initial oxidation state of catalyst has an effect on the catalyst activity for the reaction. Rate-determining reduction and oxidation steps of the so-called reduction-oxidation mechanism are proposed on the basis of a comparison of the reduction and oxidation of the catalyst by the reaction components.

As is well known, the oxidation state of vanadium catalysts changes already under mild conditions of, say, heating or evacuation, and even more readily during reduction-oxidation reactions such as the oxidation of organic compounds and SO_2 by oxygen or the catalytic reduction of nitrogen oxide by ammonia.

The latter reaction over a vanadium catalyst in the presence of oxygen has frequently been considered to occur by a reduction-oxidation mechanism¹⁻³, sometimes referred to as the Mars-van Krevelen mechanism. In it, the catalyst is reduced by one or more reaction components, and the reduced catalyst is subsequently reoxidized by the other component(s) back to the initial state. The oxidation state during the reaction and in its steady state is therefore one of the basic characteristics of the catalyst and its knowledge may provide an insight into the nature of the reaction and help in developing new catalysts. The basic assumption underlying the reduction-oxidation mechanism of a catalytic reaction is that the rates of oxidation and reduction of the catalyst are equal once a steady-state is attained.

The aim of the present work was to establish what is the oxidation state of V_2O_5/Al_2O_3 catalyst during the reduction of NO by ammonia and which components of the reaction mixture take part in the oxidation and reduction of the catalyst when the reduction of NO by ammonia occurs in the presence of oxygen.

EXPERIMENTAL

V_2O_4 was prepared by reduction of V_2O_5 by 1% ammonia under nitrogen at 350°C for 6 h.

The product was subsequently heated within a closed reactor in an atmosphere of nitrogen at 450°C for 24 h. The specific surface area of the product was 10 m²/g.

V₂O₅/Al₂O₃ catalysts were prepared by mixing and kneading γ -Al₂O₃ (Condea SC) with a suspension of vanadyl oxalate and oxalic acid.

The oxidation state (*Y*) of vanadium was determined by titrating a solution of the sample in a mixture of HF and H₂SO₄ with KMnO₄ and a solution of Mohr's salt. A detailed description of the catalyst preparation and oxidation state determination has been given in our previous paper⁴.

The activity was measured in an integral flow-through glass reactor for a catalyst with 0.5 to 1 mm grain size. The details have been given in our previous paper⁵.

RESULTS

As has been established by kinetic measurements⁵, the activity of V₂O₅/Al₂O₃ catalysts goes to a steady state very slowly, in up to tens of hours depending on the reaction temperature. At the same time, the colour of the catalyst surface changes, both in the absence and in the presence of oxygen, indicating changes in the oxidation state of vanadium. This means that the initially oxidized catalyst is reduced to some degree during the reaction in both cases. The time for the activity of these catalysts to reach a steady state corresponds approximately to that for the catalyst oxidation state to become steady.

Figure 1 shows variations in the oxidation state of vanadium in the initial oxidized as well as reduced V₂O₅/Al₂O₃ catalysts during the (NO + NH₃ + 3% O₂) reaction (curves 1 and 5) with the reaction temperature. The greatest degree of catalyst reduction was found to occur at 200°C. At lower oxygen concentrations in the reaction mixture the catalyst was reduced to an even higher degree over the whole range of reaction temperature (curve 2). When subsequently exposed to an NO + NH₃ +

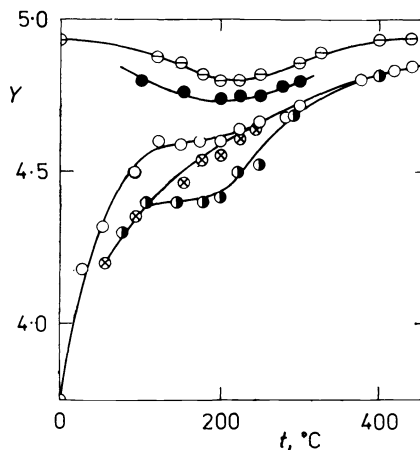


FIG. 1

Temperature dependence of the oxidation state (*Y*) of vanadium in 15% V₂O₅/Al₂O₃ catalyst on 6.25 h exposure to a reaction mixture without pretreatment (○, ●) and with pre-reduction by 1% NH₃ in N₂ at 450°C for 16 h (⊖, ⊕). ⊖, ⊕ 0.4% NO + 0.4% NH₃ + 3% O₂; ● 0.4% NO + 0.4% NH₃ + 0.1% O₂; ○ 1% NO + 1% O₂; ⊖ 1% O₂; ⊕ 1% O₂.

O_2 reaction mixture, the catalyst prereduced by ammonia was oxidized more slowly than on exposure to oxygen or an $NO + O_2$ mixture. The variation in the vanadium oxidation state with time as well as Fig. 1 indicate that the oxidation state found when the reaction over preoxidized catalyst has reached a steady state cannot be attained in reaction over prereduced 15% V_2O_5/Al_2O_3 catalyst at ordinary temperatures, i.e., up to 300°C. At temperatures above 275°C, the ($NO + NH_3 + O_2$) reaction is carried to high conversion (η), the reaction mixture containing 0.4% $NO + 0.4\% NH_3 + 3\% O_2$ is severely depleted of NO and NH_3 on passing through the first layers of the catalyst bed, and further layers of prereduced catalyst are oxidized by excess oxygen to practically the same degree as by an $O_2 + N_2$ mixture. Thus the vanadium oxidation state varies along the catalyst bed, and the determined average oxidation state does not correspond to the composition of the input reaction mixture. The same conclusion applies to the higher-temperature part of curve 1, i.e., the reduction of oxidized catalyst by the same reaction mixture under conditions of high conversion. Subsequent evaluation of the reducibility of V_2O_5/Al_2O_3 catalysts by the reaction mixture was therefore based on measurements carried out at a lower temperature (175°C).

Figure 2 shows variations in the oxidation state with the vanadium loading for the reduction of catalyst by an $NO + NH_3 + O_2$ reaction mixture, an $NO + NH_3$ mixture and by ammonia alone. For comparison, the figure also includes the variation for the initial oxidized catalyst calcined in the air at 575°C (curve 1). In the ($NO + NH_3 + O_2$) reaction at 175°C, the steady-state oxidation state goes through a minimum at a vanadium loading of about 15% (curve 2), i.e., at the catalyst composition which in preliminary measurements showed the highest activity. A similar variation has been found for the oxidation state of catalyst reduced by an $NO + NH_3$ mixture

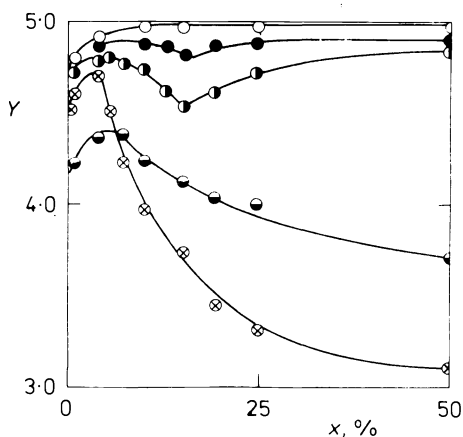


FIG. 2

Variation in the oxidation state (Y) of vanadium in V_2O_5/Al_2O_3 catalysts with the V_2O_5 mass concentration (X) after reduction of 0.5 g of catalyst in a 20 l/h gas mixture stream. \circ Initial catalyst; \bullet 0.4% $NO + 0.4\% NH_3 + 3\% O_2$, 175°C, 6.25 h; \blacksquare 1.8% $NO + 1.2\% NH_3$, 175°C, 6.25 h; \blacktriangle 1.8% $NO + 1.2\% NH_3$, 450°C, 6.25 h; \odot 1% NH_3 , 450°C, 16 h

at the same temperature. Ammonia reduces vanadium catalysts substantially more slowly under the same conditions. Even a 15% V_2O_5/Al_2O_3 catalyst is reduced at this temperature to a higher degree by an $NO + NH_3 + O_2$ mixture than by 1% ammonia. At higher temperatures, catalysts, especially those with higher vanadium loadings, are reduced by ammonia to a higher degree than by an $NO + NH_3$ mixture (curves 4 and 5). Similar concentration dependences of the reduction of V_2O_5/Al_2O_3 catalysts by the reaction mixture and by ammonia have been found for catalysts prepared by impregnation of calcined alumina with a vanadyl oxalate solution.

Figure 3 shows variations in the conversion with temperature when steady-state has been established in the $(NO + NH_3 + O_2)$ reaction over fully oxidized 15% V_2O_5/Al_2O_3 (curve 1) and the same catalyst strongly reduced by ammonia (curve 2). It is seen that the activity of preoxidized catalyst is markedly higher than that of prerduced catalyst, especially at the intermediate temperature of 200°C. After measurement of the activity of the reduced catalyst, the activity of oxidized catalyst was not attained until long-term oxidation in pure oxygen at 450°C was carried out.

DISCUSSION

The observations of partial reduction of preoxidized catalysts and partial oxidation of prerduced catalysts in the $(NO + NH_3 + O_2)$ reaction, as well as the influence of the oxidation state on the catalyst activity support the concept of a reduction-oxidation mechanism of the reaction over vanadium catalysts.

For all the catalysts investigated, the reduction rate of oxidized catalysts at temperatures up to 300°C is substantially higher when an $NO + NH_3$ mixture instead of ammonia alone is used as the reducing agent. The curve for the partial reduction

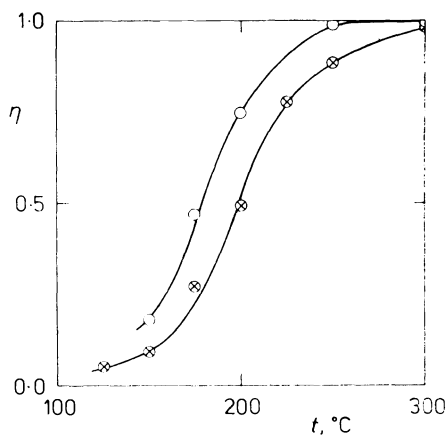


FIG. 3

Temperature dependence of the conversion (η) in the reaction of 0.4% $NO + 0.4\% NH_3 + 3\% O_2$ over oxidized (○) and reduced (×) catalysts. Conditions: 1 g of 15 mass % V_2O_5/Al_2O_3 catalyst; 30 l/h; catalyst oxidation by 1% O_2 at 450°C for 16 h; catalyst reduction by 1% NH_3 at 450°C for 16 h; reaction: 0.4% $NO + 0.4\% NH_3 + 3\% O_2$, 6 h

of catalysts by the $\text{NO} + \text{NH}_3 + \text{O}_2$ reaction mixture is similar in shape to that for the reduction by the $\text{NO} + \text{NH}_3$ mixture. 15% $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ catalyst, which is not reduced at 200°C by a mixture containing 1% of ammonia, undergoes reduction during the reaction of NO with ammonia preadsorbed on the catalyst. It has even been found that catalysts with low vanadium loadings reduced at 450°C by ammonia are further reduced on cooling to 175°C by interaction with an $\text{NO} + \text{NH}_3$ mixture. For these reasons, it may be assumed that the rate-determining step in the mechanism of the $(\text{NO} + \text{NH}_3 + \text{O}_2)$ reaction is the reduction of oxidized catalyst surface by the $\text{NO} + \text{NH}_3$ mixture.

With the exception of very low vanadium loadings, the oxidation of reduced catalysts is substantially faster on exposure to an $\text{NO} + \text{O}_2$ mixture than to oxygen alone. This is documented by curves 3 and 4 in Fig. 1. As shown by EPR and IR spectroscopy measurements⁶, the oxidation state of vanadium in the $(\text{NO} + \text{NH}_3)$ reaction over V_2O_5 in the absence of oxygen is close to 4. Using V_2O_4 samples prepared by us and obtained commercially (from Fluka), we found that the oxidation of both samples by an $\text{NO} + \text{O}_2$ mixture started at temperatures 100 to 150°C lower than the temperature of the onset of V_2O_4 oxidation by oxygen. The results obtained for catalysts with higher vanadium loadings, i.e., the catalysts used in the selective reduction of NO by ammonia, indicate that the rate-determining step is the oxidation of reduced catalyst by the $\text{NO} + \text{O}_2$ mixture.

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Translated by M. Škubalová.