# Reduction of nitrogen oxides with ammonia over complex vanadium and chromium oxides

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Catalytic properties of $\gamma$-$Al_2O_3$-supported complex vanadium and chromium oxides $V_{2-x}Cr_xO_{5-\delta}$ ($0 < x \le 1.3$), amorphous to X-rays, in the reduction of nitrogen oxides with ammonia were studied. Vanadium exists in these catalysts mostly in a pentavalent state and chromium exists as $Cr^{3+}$ and $Cr^{6+}$. As the content of chromium in the catalysts increases, the optimal temperature of the process decreases, and the degree of conversion of nitrogen oxides increases.

**Key words**: complex oxides, vanadium, chromium; catalytic properties; nitrogen oxides, ammonia, reduction.

Selective catalytic reduction of nitrogen oxides with ammonia is the most promising method for the purification of various industrial exhaust gases.[1,2] The process is carried out in the 250—400 °C temperature range, usually in the presence of vanadium-containing catalysts, whose activity depends on the method used for their preparation and on the support. Therefore, all the studies dealing with the synthesis and study of properties of supported catalysts are of practical interest. The purpose of this work is preparation and investigation of the properties of vanadium- and chromium-containing catalysts, amorphous to X-rays, in the reduction of nitrogen oxides with ammonia.

## Experimental

Vanadium(v) oxide, chromium(vi) oxide, and a 30 % solution of hydrogen peroxide of "pure for analysis" grade were used as the starting substances. Samples of the general formula $V_{2-x}Cr_xO_{5\pm\delta}$, where $0 < x < 1.3$, were prepared for the studies. Vanadium(v) oxide was dissolved in hydrogen peroxide, the required amount of $CrO_3$ was added, and $\gamma$-$Al_2O_3$ serving as the support was added to the resulting solution. Then the catalyst was dried at 50—60 °C and calcined for 5 h at 300 °C. Samples for the physicochemical studies were synthesized in the same way, except that no support was added. The compositions (mass. %) of the catalysts on $\gamma$-$Al_2O_3$ were determined using an Inductively Coupled Plasma Spectrometer after dissolving them in aqua regia:

| Catalyst | V | Cr | Al |
|---|---|---|---|
| **A** | 3.02 | 1.92 | 45.3 |
| **B** | 6.01 | 5.74 | 40.3 |
| **C** | 2.38 | 5.97 | 41.3 |

The variation of the chemical compositions of the catalysts on going deep into the support from its surface was determined using an EDAX-707B X-ray microanalyzer. For all of the samples, the active shell containing the maximum amounts of chromium and vanadium was 150—200 μm thick (Fig. 1).

Morphological characteristics of the catalysts were determined from adsorption and desorption isotherms of nitrogen using an ASAP 2000 instrument (the Micrometrics Company). The size of the micropores was found to vary in the 4—20 nm range. The specific surface areas were determined by using the Langmuir equation for monomolecular adsorption. According to the results obtained (Table 1), the active adsorbing surface areas of the catalysts differed from their overall surface areas.

Diffractograms of the samples were recorded on a DRON-UM1 unit (Cu-Kα-radiation). The results obtained indicate the absence of long-range order in the active mass of $V_{2-x}Cr_xO_{5\pm\delta}$ (*i.e.*, that it is amorphous to X-rays). In the case of supported catalysts, only peaks typical of $\gamma$-$Al_2O_3$ were recorded.

The IR spectra of the catalysts were recorded on a Specord 75 IR spectrometer as pastes with Vaseline oil. Analysis of the results obtained (Table 2) made it possible to distinguish vanadium-oxygen and chromium-oxygen groups typical of $V_2O_5$ and chromium orthovanadate. The variations of the frequencies of the IR absorption maxima indicate that the lengths of the Cr—O—V and V—O bonds increase as the content of crhomium in the samples increases. The V—O—V bond lengths remain

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 339—342, February, 1996.

**Table 1**. Morphological characteristics of the catalysts

| Parameter | Catalyst A | Catalyst B | Catalyst C |
|---|---|---|---|
| BET specific surface area/m$^2$ g$^{-1}$ | 170 | 165 | 160 |
| Langmuir specific surface area/m$^2$ g$^{-1}$ | 256 | 236 | 221 |
| Volume of pores/cm$^3$ g$^{-1}$ | 0.196 | 0.185 | 0.190 |
| Characteristic size of micropores/nm | 8.2 | 6.3 | 8.0 |
| Characteristic size of macropores/nm | 1190 | 1250 | 1050 |

**Table 2**. Frequencies ($\nu$/cm$^{-1}$) of the absorption maxima in IR spectra of the active mass of the catalysts and $CrVO_4$

| $V_{1.7}Cr_{0.3}O_{5-\delta}$ | $V_{1.3}Cr_{0.7}O_{5-\delta}$ | $VCrO_{5-\delta}$ | $Cr_xVO_4$ | Assignment |
|---|---|---|---|---|
| 1614 | — | — | — | $\delta$ (H—O—H) |
| 1010 | 1015 | — | — | $\nu_s$ (V=O) |
| 881 | 878 | 872 | 870 | $\nu_{as}$ (Cr—O—V) |
| 800 | 800 | 800 | 800 | $\nu_{as}$ (V—O—V) |
| 650 | 655 | 680 | 650 | $\nu_s$ (Cr—O) |
| 560 | 550 | 530 | 550 | $\delta_s$ (V—O) |

virtually the same, and the Cr—O distances decrease as the concentration of vanadium decreases.

According to the ESR spectra, the main contribution to the paramagnetic properties of the samples is made by the atoms of trivalent chromium with a *g*-factor of 1.968, which determines the value of the effective magnetic moment of $Cr^{3+}$. The proportion of chromium(III) ions in the samples dramatically increases in the $0.3 < x \le 0.5$ range, and then decreases to a composition of $V_{1.3}Cr_{0.7}O_{5\pm\delta}$ (Fig. 2). The decrease in the concentration of $Cr^{3+}$ ions is due to an increase in the concentration of chromium(VI). $Cr^{3+}$ ions are known[3] to be oxidized on heating in the presence of $V_2O_5$ to $Cr^{4+}$ and $Cr^{6+}$, the yield of various products depending substantially on the composition of the mixture of vanadium and chromium oxides.

Catalytic properties were determined for three samples with the initial composition $V_{2-x}Cr_xO_{5\pm\delta}$, where $x = 0.7$, 1.0, or 1.3, at the following parameters: the volume velocity of the gas mixture was 65000 h$^{-1}$; the amount of the catalyst was 30 cm$^3$; the grain size of the catalyst was 3—4 mm; the initial concentration of $NO_x$ in the gas was 0.44 % (v/v); the initial $NO_x$/NO molar ratio was 1—0.9; the ratio of the actual quantity of $NH_3$ to the theoretical quantity was 0.5—1.3; and the quantities of nitrogen, carbon dioxide, and water vapor in the initial gas mixture were the same as those in air ($CO_2$, 0.5 %; $H_2O$, 1.0 %).

The theoretical amount of ammonia $(NH_3)_{theor}$ was determined from the reaction:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O.$$

## Results and Discussion

Figure 3 shows the main results of the study of the conversion of nitrogen oxides in the presence of complex

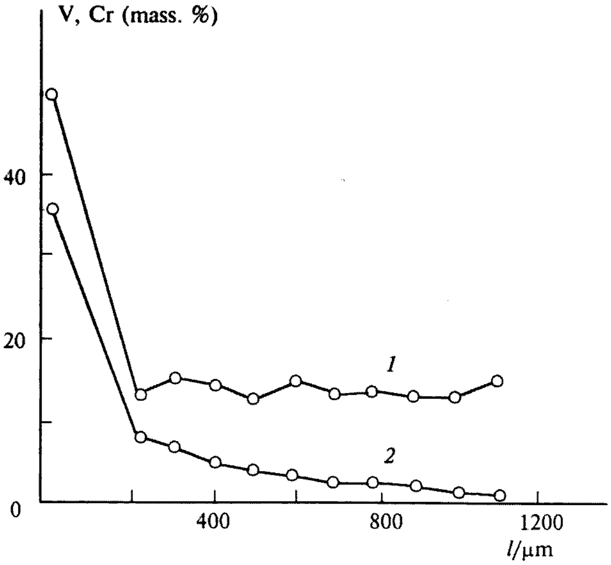

**Fig. 1**. Dependences of the contents of chromium (*1*) and vanadium (*2*) in catalyst **B** on the distance between surface and center of the support grain.

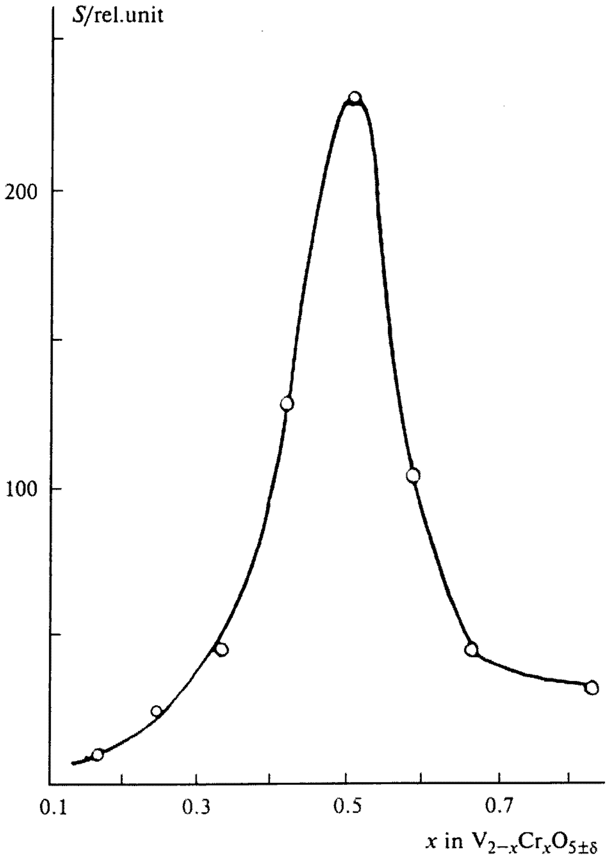

**Fig. 2**. Dependence of the relative surface area (*S*) under the ESR line on the chromium content.

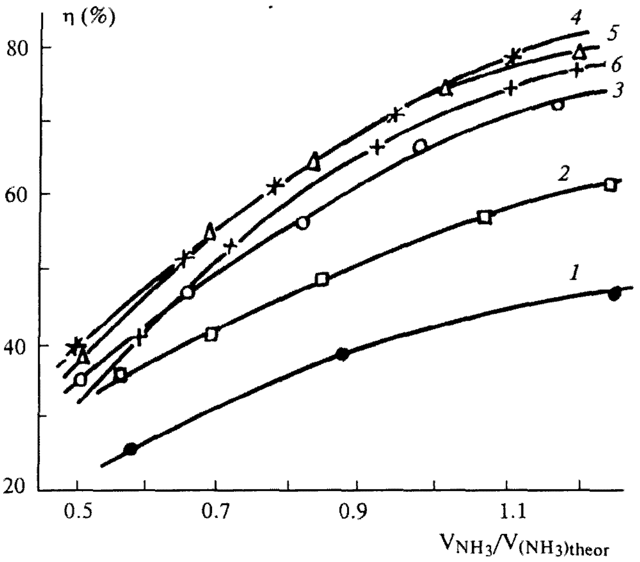

**Fig. 3**. Dependence of the degree of reduction of nitrogen oxides (η) over catalyst **B** on the $V_{NH_3}/V_{(NH_3)theor}$ molar ratio at the temperatures/°C: 236 (*1*); 267 (*2*); 307 (*3*); 352 (*4*); 386 (*5*); 422 (*6*).

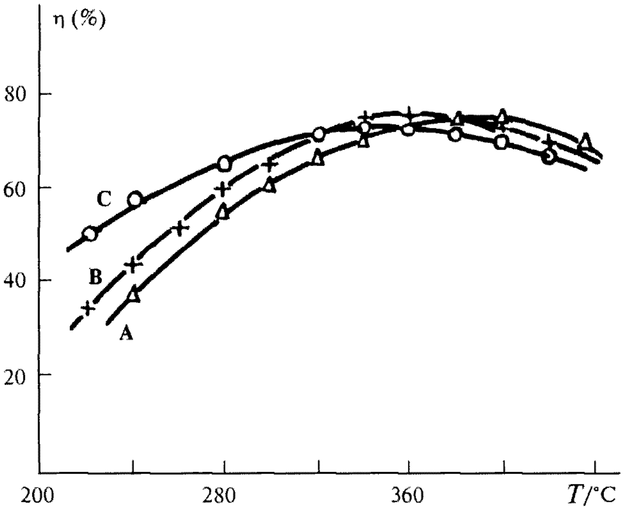

**Fig. 4**. Dependence of the degree of reduction of nitrogen oxides (η) over catalysts **A**, **B**, and **C** on the temperature of the process at $V_{NH_3}/V_{(NH_3)theor}$ = 1.00.

vanadium and chromium oxides amorphous to X-rays. It was found that as the proportion of ammonia in the starting gas mixture increases, the degree of reduction of nitrogen oxides monotonically increases. The degree of $NO_x$ reduction also depends on the composition of the catalyst (Fig. 4). At temperatures below 340 °C, the catalytic activity of the samples increases with increase in the proportion of chromium, and in the high-temperature region ($t$ > 380 °C), an opposite dependence is observed. Simultaneously, the degree of conversion of nitrogen oxides decreases due to oxidation of ammonia.

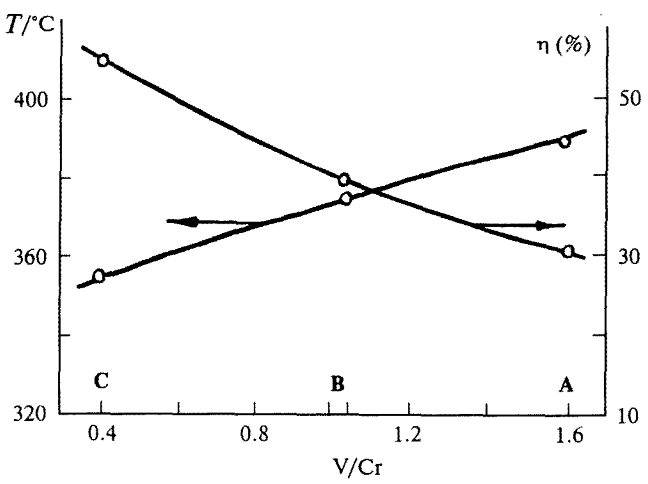

**Fig. 5** Dependence of the degree of reduction of nitrogen oxides (η) at 230 °C and dependence of the optimal temperature of the process on the V/Cr molar ratio at $V_{NH_3}/V_{(NH_3)theor}$ = 1.00.

According to the results of thermal analysis of a $VCrO_{5\pm\delta}$ sample, a considerable decrease in its mass associated with oxygen evolution ($\delta$ = 0.7) starts above 360 °C; it ends at ~650 °C with the formation of a complex oxide of pentavalent vanadium and $Cr^{III}$. The DTA curve exhibits an exothermic effect with a maximum at 535 °C corresponding to the transition of the active mass amorphous to X-rays into a crystalline state. Therefore, the oxidation of ammonia at high temperatures is a consequence of loosening of the linkage of some of the oxygen in vanadium and chromium complex oxides. As the content of chromium in the samples increases, the temperature at which the highest degrees of nitrogen oxide reduction and ammonia oxidation are attained decreases. This is due to increase in the content of chromium(VI), which promotes oxidation of ammonia at high temperatures (above 350 °C).

Analysis of the data obtained implies that the optimal temperature of the process and the degree of reduction of nitrogen oxides depend on the vanadium : chromium ratio in the catalysts (Fig. 5). At low temperatures (220—350 °C), catalyst **C** containing the highest proportion of chromium exhibits the highest activity. In the 330—350 °C and 350—420 °C temperature ranges, catalysts **B** and **A**, respectively, are the most active.

Thus, the catalysts containing γ-$Al_2O_3$-supported complex vanadium and chromium oxides amorphous to X-rays can be used to purify exhaust gases, flowing at a high rate (650 $h^{-1}$), from nitrogen oxides by reducing them with ammonia. The optimal temperature of the process that ensures a degree of $NO_x$ conversion of more than 80 % is 350 °C. At the volume velocities of gases normally used in industry (10000—30000 $h^{-1}$), the catalysts under consideration are highly reactive in the 280—330 °C temperature range at a $V_{NH_3}/V_{(NH_3)theor}$ ratio of 1. The degree of reduction of nitrogen oxides under these conditions is more than 90 %.

The catalyst under study are obtained by an ecologically beneficial technology, *i.e.*, no toxic exhaust gases or waste water are produced. They are efficient at high (more than 15000 $h^{-1}$) velocities of gas flows; and when excess ammonia is present, it is oxidized over these catalysts. These advantages make the catalysts under consideration competitive with the currently used vanadium-titania catalysts.

## References

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*Received May 22, 1995;*
*in revised form July 14, 1995*