

SnO₂-Cr₂O₃ as a Catalyst for the Low-temperature Reduction of Nitric Oxide

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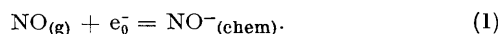
Summary SnO₂ containing a small amount of Cr₂O₃ is a very active catalyst for the adsorption and reduction of NO with CO, H₂, and C₂H₄ at low temperatures.

A CATALYST consisting of SnO₂ doped with Cr₂O₃ was prepared by adding Cr₂O₃ to an aqueous suspension of SnO₂. The homogeneous suspension was dried at 110 °C, heated at 350 °C for 5 h, and finally sintered at 900 °C for 5 h in air. This treatment resulted in a catalyst containing a higher-valent chromium ion (the average valency of the chromium in SnO₂ + 1% Cr₂O₃ is 3.85) stabilized in the surface layer of SnO₂. The average valency of chromium was calculated on the basis of the active oxygen content of the catalysts determined by Bunsen's method.

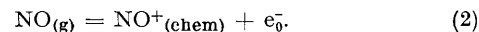
Adsorption isotherms and adsorption rates for NO on pure SnO₂ were measured in the temperature range 25–100 °C and gave isotherms of the Freundlich type in the pressure range 8–50 torr. The amount of NO required for monolayer is $q_m = 7.46 \mu\text{mol g}^{-1}$. The evaluation of the NO chemisorption rate with the Elovich equation yielded two linear segments with a distinct break between them. The rate of the chemisorption on both segment sites increases with temperature. On the partially reduced catalysts (with CO at 400 °C for 60 min) the in-

stantaneous uptake of NO was almost six times larger than that of an unreduced sample. In addition, the rate of adsorption of NO at 100 °C was almost ten times higher. A very large increase in the amount of NO adsorbed and in the rate of chemisorption occurred as a result of incorporating Cr₂O₃ (0.1–1 mole %) into the surface layer of SnO₂.

The study of the electronic interaction between SnO₂ and NO indicated at least two kinds of adsorbed NO. Up to about 250 °C NO significantly decreases the electric conductivity of pure and Cr₂O₃-doped SnO₂, which can be explained by equation (1). However, on evacuation of



the NO from the reaction cell at the same temperature the electric conductivity of the sample further decreased. This indicates that, besides the above mode of adsorption, part of the NO is chemisorbed by giving its unpaired electron to the oxide surface, forming an apparently positive chemisorbed ion [equation (2)]. This kind of NO adsorption partly compensates the result of the electron acceptor



adsorption of NO [equation (1)]. This adsorption is much weaker than the former, so that on evacuation of the sample

TABLE. Kinetic data for the catalytic reduction of NO.

Reactions	SnO ₂ (5.81 m ² g ⁻¹) 10 ³ k _{spec} /min ⁻¹ m ⁻² at 400 °C		SnO ₂ + 1 mol % Cr ₂ O ₃ (11.87 m ² g ⁻¹) 10 ³ k _{spec} /min ⁻¹ m ⁻² at 200 °C	
		E/kcal mol ⁻¹		E/kcal mol ⁻¹
NO + CO	2.4	36.6	5.3	18.2
NO + H ₂ ^a	2.7	15.2	0.45	15.2
NO + C ₂ H ₄	1.62	19.6	0.21	14.1

^a At NO:H₂ = 1:2.

NO⁺ is desorbed from the surface [equation (3)] and as a



result the electric conductivity of the SnO₂ decreases.

According to kinetic measurements the reduction of NO with CO, H₂, and C₂H₄ on pure SnO₂ at a measurable rate proceeded only above 360 °C. A marked increase in the efficiency of the catalyst was experienced, however, when a small amount of Cr₂O₃ was incorporated into the surface layer of the SnO₂. The reduction of NO with all three fuels

occurred with well measurable rates at 150—220 °C. The reactions were of zero order with respect to CO and H₂ and first order with respect to NO. Some kinetic data are shown in the Table.

The high activity of SnO₂ + 0.1—1% Cr₂O₃ catalyst can be attributed to the presence of "active" chromium centres which can easily be reduced by fuels and rapidly reoxidized by NO.

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