Influence of preparation conditions on activity of bulk Co_3O_4 - based catalysts in the N_2O decomposition

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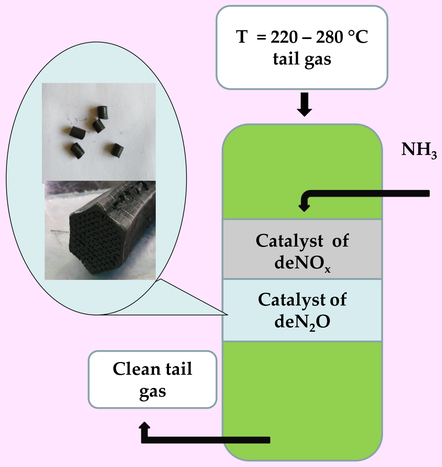
Introduction

Nitrous oxide is a strong greenhouse gas. Nitrous oxide is a contributor to the destruction of ozone in the stratosphere and a strong greenhouse gas. A reduction of N_2O emission from industrial sources is indispensable. To date, there are two EnviNOx® technologies for the combined removal of N_2O and NO_X from tail gases a zeolite catalyst, both technologies require additional energy consumption for tail gas heating up to 300–600°C. A single-reactor scheme for the abatement of NO_X and N_2O under the conditions of a SCR reactor in Russia at 220-280°C can be economically advantageous. For such a scheme, it is preferable to use a low-temperature N_2O decomposition catalyst with the geometry of a honeycomb block or cylindrical granules. The second layer of the N_2O decomposition catalyst must have mechanical strength, uniformity and must not create hydraulic resistance.

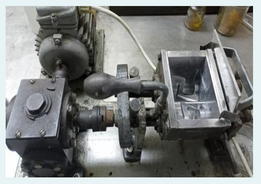


Tail gas treatment technology for UKL-7 units based on the SCR reactor.

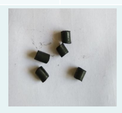
The aim of the work was to obtain a massive granular catalyst, including a honeycomb structure (composition - 2 wt.% Cs/Co_3O_4), for use in the SCR reactor as a second-stage deN_2O catalyst

Experimental

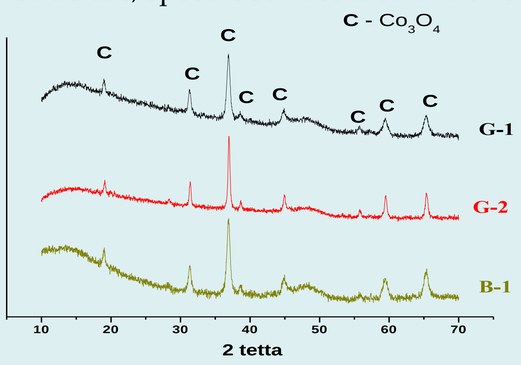
The 2%Cs/Co_3O_4 catalysts were prepared from excellent pastes by extrusion molding through feliers of different geometries. The dried catalysts were calcined in air at 400°C for 2 h. The catalysts were characterized by XRD, TGA, BET, H_2 - TPR.

The Co_3O_4 (S_{bet}~ 100м²/г) was obtained by decomposition of $2Co(OH)_2 \times CoCO_3 \times H_2O$ in a muffle in air at 300 °C for 4 hours	Paste preparation (by mixing at least 20-60 minutes)	Molding (by forcing pastes through a die)
		

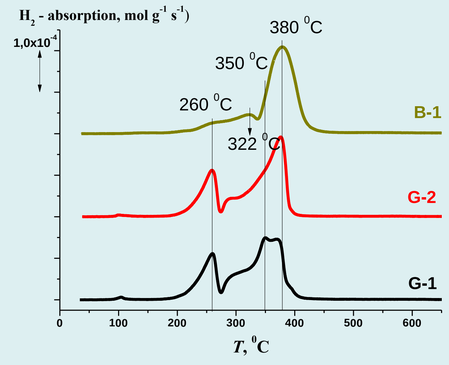
The N_2O decomposition was carried out at 150–450 °C, at atmospheric pressure and space velocity about 9000 h^{-1}, under real conditions (1500 ppm N_2O, 3.6% O_2, 3% H_2O in He).

Options	G-1	G-2	B-1
Humidity of pasts we. %	34	22	5
Plasticzer, we. %	4 (sol. 1% polyethylene oxide)	7 (sol .1% polyethylene oxide)	25 (molasses)
Catalyst geometry	 Granules 0.4 × 0.4 cm		 Blok Chanells ≥ 20 pcs/cm²

XRD data reveals: the composition of the pastes does not affect the phase parameters of the samples (**a =8.084 Å, CSR: 150-160 Å**), but affects the porous structure, specific surface area and strength.



H_2-TPR results: two peaks observed for bulk catalysts are due to subsequent reduction of $Co^{3+} \rightarrow Co^{2+} \rightarrow Co^0$



TG data: the polyethylene oxide plasticizer burnouts up to 400 °C, but the molasses - up to 600 °C.

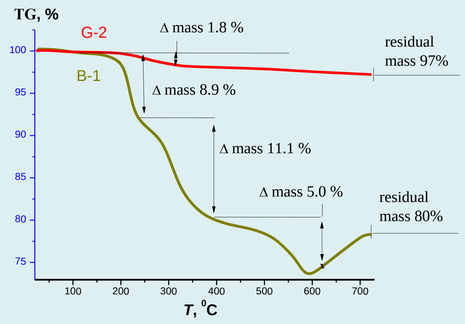
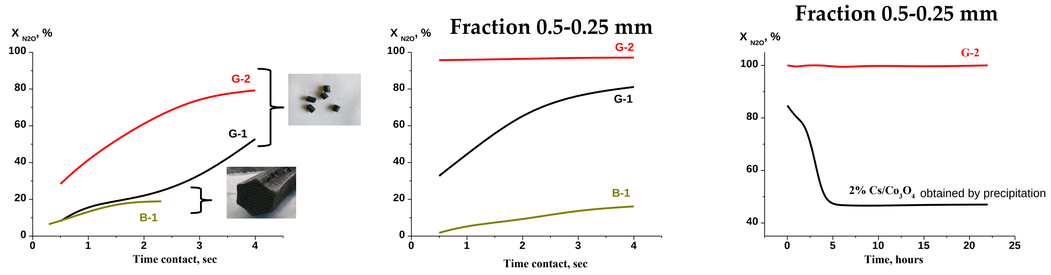


Table 1 Physicochemical characteristics of the samples

Samples	Strength granules, kg/cm²	S_{bet}, m²/g	V_{por}, cm³/g	D_{por}, Å	H_2 -TPR $\Sigma H_2 \times 10^{-2}$, mol/g	
					T_1 - 260 °C $Co^{3+} \rightarrow Co^2$	T_2 - 380 °C $Co^{2+} \rightarrow Co^0$
G-1	18.40	22.7	0.41	700	0.39	1.15
G-2	36.13	25.7	0.35	430	0.38	1.12
B-1	27.33	18.9	0.21	390	0.37	1.22

Samples G-1 and G-2 - the theoretical ratio of hydrogen absorption values in the peaks as 1:3 for normal spinel is practically observed.
In Sample B-1, only a part of the Co^{+3} cations is restored. Undecomposed molasses prevents the complete reduction of Co^{+3} cations to Co^{+2} at low temperatures.

Decomposition of N_2O under conditions close to the SCR reactor $0.15\%N_2O+3.6\%O_2+3\%H_2O$ in He (280 °C)



The activity of fractions G-1 and G-2 is higher than that of granular samples G-1 and G-2 ⇒ diffusion inhibition (incomplete degree of use of granules).

The activities of fraction and block fragment B-1 are almost the same ⇒ the best using of the inner surface of the block walls.

G-2 is highly resistant to O_2 and H_2O inhibitors for up to 22 hours.

2% Cs/Co_3O_4 sample obtained by precipitation was deactivated during the first 5 hours even at a higher temperature (300 °C).

Conclusion

For the first time, using a waste-free technology, by extrusion molding a paste from cobalt oxide powder and a solution of cesium nitrate with the addition of polyethylene oxide, a highly active, durable granular massive catalyst for low-temperature decomposition of nitrous oxide was obtained for use in a one-reactor scheme for purification from NO_x and N_2O.

The activity of the prepared catalysts depends on the composition of the pastes. Optimization of the paste composition will make it possible to form an active block catalyst with a honeycomb structure, providing a minimum pressure drop in the catalyst bed