

The influence of the operating conditions in ammonia burner on the effectiveness of the catalyst for a nitrous oxide decomposition

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The influence of the ammonia burner operating conditions on PKR-2 catalyst efficiency and structure was investigated. It was found, that the catalyst retains its initial activity even after 13 months of work at 890°C. Only its local overheating can lead to a decrease of its activity or deactivation.

Keywords – nitric acid plant, N₂O emission, greenhouse gas, N₂O abatement technology, catalytic performance, secondary catalyst.

Introduction

Nitrous oxide (N₂O) is a greenhouse gas, whose emission into the atmosphere is subject to increasingly stringent emission standards. One of the significant sources of this gas emission are the nitric acid plants. Nitrous oxide is formed as a by-product in the process of catalytic ammonia oxidation. It does not undergo any chemical transformations in the whole technological line of nitric acid manufacturing and is fully emitted into the atmosphere. Therefore, the use of an effective method of N₂O emission abatement is highly required [1]. One of such methods is the catalytic decomposition of nitrous oxide from a process gas stream at a high temperature. In this case, the layer of deN₂O catalyst is installed in an ammonia burner, directly beneath the catalytic gauzes [2].

The catalyst, which is to be used in ammonia burner, should have a high activity, selectivity and stability under the reaction conditions. A big challenge is to ensure a high mechanical strength and high abrasion resistance of the catalyst extrudates, as well as its long lifetime under the extremely difficult operating conditions (high temperature, possibility of local catalyst overheating, high water vapor pressure in the process gas stream).

New Chemical Syntheses Institute has developed its own Fe₂O₃-Al₂O₃ catalyst (PKR-2), which is active in HT-deN₂O process. The catalyst works stably in many industrial installations and allows to reduce N₂O emission to the desired level. Nevertheless, the investigations on the improvement of the catalyst functional properties are still carried out. They are focused on two practical aspects: modification of the catalyst manufacturing technology and determination of the influence of ammonia burner operating conditions.

The studies, described below are related to the determination of the catalyst resistance to the deactivation (thermal and time-related).

Experimental

The catalyst activity was tested in a pilot ammonia oxidation plant in the flow of a real nitrous gases mixture. Parallel to the studies of PKR-2 catalyst activity and selectivity, the changes in its structure were also investigated. In the adopted research methodology, the activity of the catalyst samples with different “thermal history” was compared with the fresh catalyst sample (reference sample).

All measurements were performed under the identical operating conditions: $p=5$ bar, $T=890^{\circ}\text{C}$, $V_{\text{mix,inlet}}=56$ Nm³/h. The run time of the test in the pilot plant was 120 h. During the measurements, the same volume of deN₂O catalyst bed was used, as well as the same catalytic gauzes package. The diameter of ammonia burner was 100 mm. The catalyst activity was

determined on the basis of the difference of N_2O concentration in nitrous gases stream, measured downstream of Pt-Rh catalytic gauzes and after a secondary catalyst layer, at the outlet of the reactor. For the activity tests, the following PKR-2 catalyst samples were selected: P1 – fresh (reference) catalyst calcined at a temperature of 500°C , P2 – catalyst after 100 days of work in an industrial installation, 3 – catalyst after 400 days of work in an industrial installation, 4 – catalyst overheated at a temperature of 1100°C , 5 – catalyst overheated at a temperature of 1400°C .

In Fig. 1, the activity of tested PKR-2 catalyst samples was compared with the reference sample activity.

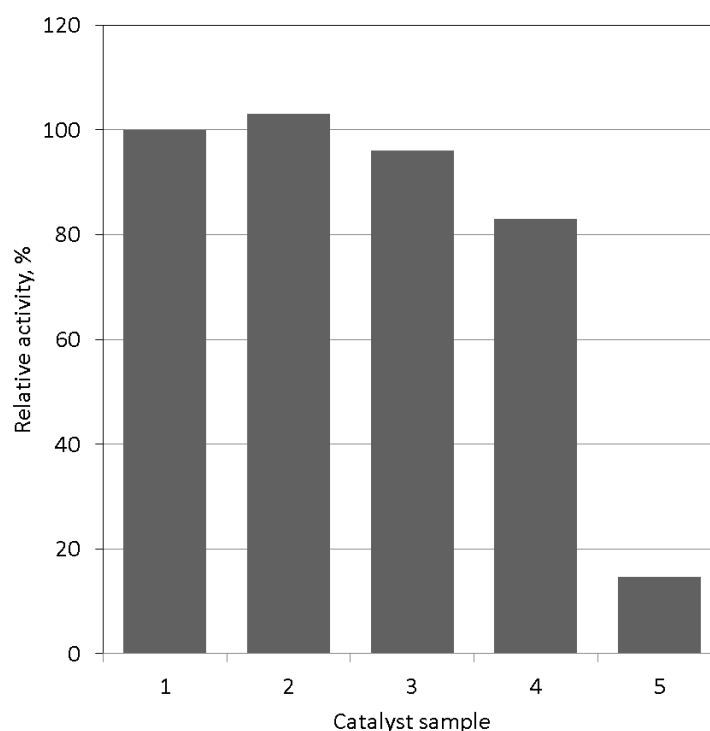


Fig.1. The comparison of PKR-2 catalyst samples activity, tested in a pilot plant.

The PKR-2 catalyst after shaping and calcination at a temperature of 500°C (P0) is a mesoporous material with an average pore diameter of 20 nm and specific surface area of $50 \text{ m}^2/\text{g}$. In case of the catalyst, subjected to a high temperature of 890°C (P1), the sintering process is observed. In the catalyst structure disappear the mesopores and increases the average pore diameter, while a total pore volume does not change. Moreover, a thermal shrinkage of the catalyst extrudates, 6-percent weight loss of the catalyst bed and lowering of a specific surface area is observed. Longer operation of the catalyst in ammonia burner does not cause any further changes in its structure (samples P2 and P3).

Exposure of the extrudates to a temperature higher than the operating temperature in ammonia burner (1100°C (P4) and 1400°C (P5), e.g. due to the local catalyst overheating, causes further changes in the catalyst structure, due to the greater progress of sintering process. In Table 1, the physicochemical parameters for different PKR-2 catalyst samples are given.

Table 1. The basic physicochemical parameters of PKR-2 catalyst samples, tested in a pilot plant

Sample	S , m^2/g	V , g/cm^3	$V_{mesop.}$, g/cm^3	d_{pore} , nm	P , %	Comments
P0	50	0.27	0.26	22	53	The fresh sample
P1	9	0.27	0.01	115	56	Sample P0 after test in the pilot plant
P2	2.2	0.19	0.00	350	49	After work in the industrial plant (100 days)
P3	1.8	0.22	0.00	490	51	After work in the industrial plant (400 days)
P4	2.1	0.16	0.00	216	44	Overheated at 1100°C
P5	<0.1	<0.01	-	-	<4	Overheated at 1400°C

where: S - surface area, V – total pore volume, $V_{mesop.}$ – volume of mesopores, d_{pore} – average pore diameter, P - porosity.

Conclusion

The significant changes in the PKR-2 catalyst structure are observed in the initial period of its operation in the ammonia burner. The sintering of the catalyst extrudates causes the decrease of catalyst specific surface area, as well as disappearance of mesopores and appearance of macropores in its structure. Calcination of the catalyst at a temperature of 500°C does not allow for the complete stabilization of its structure. Exposure of the catalyst to a higher temperature results in a weight loss of the catalyst bed and leads to a reduction of the catalyst bed volume.

During the catalyst work, its gradual sintering is observed, accompanied by an increase in the pore diameter. Despite the changes in the catalyst structure, its operation at a temperature of 890°C in the ammonia burner does not cause any negative changes in its activity. The catalyst retains its initial activity, even after 13 months of work in the industrial plant.

Overheating of the catalyst (1100°C) causes further sintering of the extrudates. At a higher temperature, the porosity and a total pore volume of the catalyst are decreased, but despite this, only a slight lowering of its activity is observed. Its significant overheating above this temperature (1400°C) causes the complete destruction of the catalyst structure and leads to its permanent deactivation.

References

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