

## Catalytic Action of Natural Iron–Manganese Ores on the Process of Ammonia Removal from Producer Gas

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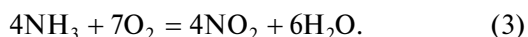
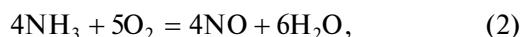
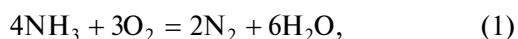
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**Abstract**—The applicability of iron–manganese catalysts (ores of natural origin) with different ratios between iron and manganese to the decomposition of ammonia in producer gas from coal gasification is considered. The results of experimental studies in this area are presented. It was established that all of the test ores were the catalysts of ammonia decomposition at 400–750°C with a total degree of 0.92–0.995 or higher. The best result of 0.997 was obtained on the catalyst containing 50.5 wt % manganese and 1.3 wt % iron. However, a specific regularity in the effect of the iron and manganese content of the ores on the degree of ammonia removal was not revealed. It was hypothesized that the textural and structural characteristics of the catalyst affect the efficiency of ammonia removal.

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Ammonia (NH<sub>3</sub>) is contained in producer gases, which are obtained upon the gasification of coal and mainly used at combined-cycle plants. This is a toxic component (its maximum permissible concentration in workplace air is 20 mg/m<sup>3</sup>), although it is one of the most important products of chemical industry, which is primarily used for the manufacture of nitrogen fertilizers. As applied to combined-cycle plants, ammonia is converted into nitrogen and nitrogen oxides (primarily, NO) on combustion in a gas turbine burner according to the following reactions:



A noticeable amount of NO is formed already at 300°C, and the degree of ammonia oxidation to nitrogen oxides increases with temperature to reach a maximum (of about 98%) at 800–900°C. This reaction is purposefully used in the technology of inorganic substances for the production of nitric acid [1].

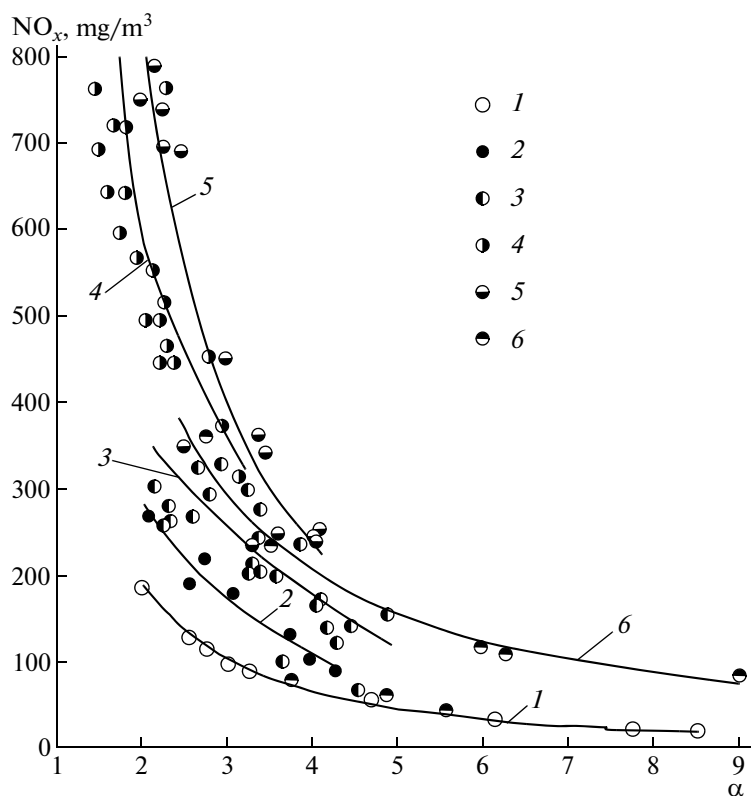
On the combustion of producer gas, nitrogen oxides formed according to reactions (2) and (3) are added to the nitrogen oxides formed due to the oxidation of molecular nitrogen by atmospheric oxygen. As a result of this, special measures should be taken for the neutralization of NO<sub>x</sub> to regulatory values according to GOST [State Standard] R 50831-95 (no higher than 350 mg/m<sup>3</sup> under standard conditions of 0°C, 101.3 kPa, and α = 1.4).

Figure 1 shows the results of the measurements of NO<sub>x</sub> concentrations in the combustion products of natural gas and also producer gas generated from different coals by a furnace method [2] with the use of air blast as the function  $C_{\text{NO}_x} = f(\alpha)$ , where  $C_{\text{NO}_x}$  is the concentration of nitrogen oxides in flue gases, mg/nm<sup>3</sup>, and α is the excess coefficient of air supplied to a gas turbine burner.

The plots given in Fig. 1 show that the concentrations of NO<sub>x</sub> upon the combustion of producer gas are higher than analogous values for natural gas by a factor of 3–4. As a rule, the curves are shifted relative to each other in accordance with the nitrogen content of the initial fuel on a dry ash-free basis (N<sup>daf</sup>).

According to experimental data [3], upon the gasification of anthracite with N<sup>daf</sup> = 0.8%, the ammonia content of the resulting gas was 875–990 mg/m<sup>3</sup> under standard conditions or 2.28–2.46 g/m<sup>3</sup> under standard conditions for Kuznetsk lean coal with N<sup>daf</sup> = 1.9%.

Coals from the Kuznetsk Basin, which contain to 2.9% nitrogen on a dry ash-free basis (N<sup>daf</sup>), are most commonly used in the Russian Federation [4]; therefore, the calculated ammonia content of these gases in the selected method of gasification will be 2500–3700 mg/m<sup>3</sup> under standard conditions. Considering that 50–90% nitrogen is converted into nitrogen oxide upon the combustion of ammonia and the volume of flue gas is greater than the volume of the initial producer gas by a factor of about 4.2 (experimental data), an increase in nitrogen oxides in the flue gases due to ammonia will be



**Fig. 1.** Dependence of the measured concentrations of  $\text{NO}_x$  on the excess air ratio ( $\alpha$ ) in the combustion of natural gas and producer gas from different coals: (1) natural gas; (2) agglomerated anthracite culm,  $N^{daf} = 0.8\%$ ; (3) anthracite,  $N^{daf} = 0.8\%$ ,  $\text{NH}_3 = 0.88\text{--}0.99 \text{ g/m}^3$ ; (4) Kuznetsk lean coal,  $N^{daf} = 1.9\%$ ,  $\text{NH}_3 = 2.28\text{--}2.46 \text{ g/m}^3$ ; (5) Tarbagatai coal,  $N^{daf} = 1.8\%$ ; and (6) Berezovso brown coal,  $N^{daf} = 0.7\%$ .

about  $950\text{--}1400 \text{ mg/m}^3$  under standard conditions. In this case, the normative concentrations of nitrogen oxides converted to  $\alpha = 3.2\text{--}3.5$  are  $140\text{--}150 \text{ mg/m}^3$  under standard conditions.

The concentration of  $\text{NO}_x$  is decreased by the following two methods: the stepwise combustion of producer gas and the installation of systems for flue gas denitrification. The former method is suitable for coals with moderate initial nitrogen contents, and the latter method is used for Kuznetsk coal with an especially high nitrogen content. The flue gas denitrification is performed with the use of a reagent (ammonia or expensive carbamide) to obtain nitrogen at  $300\text{--}400^\circ\text{C}$  on industrial synthetic catalysts with a honeycomb structure (SCR method) or at higher temperatures without the use of a catalyst (SNCR method).

The high-temperature catalytic method of the decomposition of ammonia in producer gas into nitrogen and hydrogen is more preferable in comparison with methods for the reagent removal of nitrogen oxides. This method does not require reagent consumption, and the products obtained occur in the producer gas. Because the producer gas is hot (its temperature is higher than  $400^\circ\text{C}$ ), its heat is retained as a

result of the application of this method. The reversibility of the reaction of ammonia decomposition is a disadvantage of this method.

The decomposition of ammonia is accomplished at high temperatures and low pressures in accordance with the Le Chatelier principle. Catalysts are required for decreasing the process temperature; in this case, palladium, iridium, copper with nickel on aluminum oxide, etc., are commonly used.

In this work, we experimentally studied the capability of natural iron–manganese ores from the Porozhinskoe deposit (Krasnoyarsk krai) to catalyze the decomposition of ammonia. This catalyst was chosen because it is inexpensive and does not require special synthesis from chemical reagents; moreover, the above ores at temperatures higher than  $750^\circ\text{C}$  catalyze the reaction of methane decomposition with the production of hydrogen and tubular type nanocarbon [5]; that is, they possess necessary active centers for the occurrence of catalysis.

We studied the iron–manganese ores from the Porozhinskoe deposit different in sampling sites and manganese and iron concentrations in them. In this work, they are referred to as  $P_1\text{--}P_4$ . Table 1 summa-

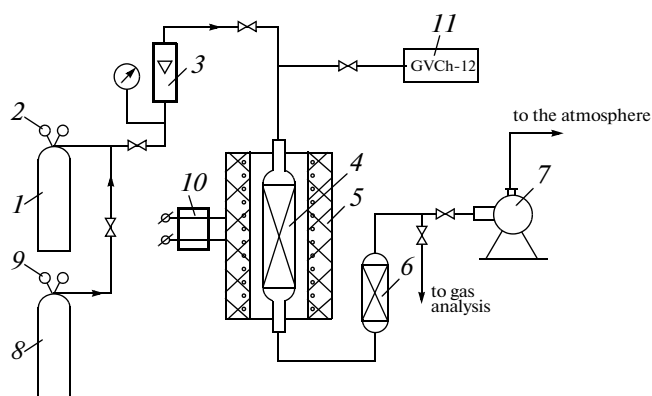
**Table 1.** Chemical composition of ores from the Porozhinskoe deposit used as catalysts for the decomposition of ammonia

| Ore            | Component concentration, wt % |      |                                |                  |                               |        |                  |      |                  |            |                                |       |
|----------------|-------------------------------|------|--------------------------------|------------------|-------------------------------|--------|------------------|------|------------------|------------|--------------------------------|-------|
|                | Na <sub>2</sub> O             | MgO  | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | S      | K <sub>2</sub> O | CaO  | TiO <sub>2</sub> | Mn (total) | Fe <sub>2</sub> O <sub>3</sub> | Ba    |
| P <sub>1</sub> | 0.02                          | 1.25 | 3.74                           | 6.7              | 0.17                          | 0.0042 | 0.75             | 0.26 | 0.15             | 50.5       | 1.30                           | 0.67  |
| P <sub>2</sub> | 0.02                          | 2.10 | 2.50                           | 4.8              | 0.44                          | 0.0043 | 0.47             | 6.21 | 0.10             | 42.1       | 3.52                           | 0.009 |
| P <sub>3</sub> | 0.04                          | 1.48 | 10.28                          | 19.6             | 0.19                          | 0.0058 | 0.59             | 1.56 | 0.57             | 31.1       | 9.04                           | 0.028 |
| P <sub>4</sub> | 0.02                          | 1.26 | 8.82                           | 17.2             | 0.36                          | 0.0038 | 0.70             | 0.54 | 0.48             | 16.6       | 21.3                           | 0.047 |

izes the chemical composition of these ores determined by X-ray spectrometry analysis (in terms of the basic components).

The corresponding experimental studies were performed on a laboratory setup, which is shown in Fig. 2, under a pressure of 0.1 MPa. The setup consisted of a reactor (position 4) placed in a furnace (position 5), cylinders with a model gas (position 1) and nitrogen (position 8), a hydrogen generation system (position 11), and systems for measuring gas flow rate, composition, pressure, and temperature.

The model gas mixture of NH<sub>3</sub>–N<sub>2</sub> with an ammonia concentration of 0.35 vol % (or 2656 mg/m<sup>3</sup> under standard conditions) from a cylinder (position 1) was supplied through a reducer (position 2) to the reactor (position 4) filled with the test material and placed in an electric furnace (position 5) connected to a laboratory transformer (position 10). The gas from the reactor passed through a filter (position 6), and it was vented into the exhaust system. A portion of the waste gas was sampled for analysis to determine ammonia by



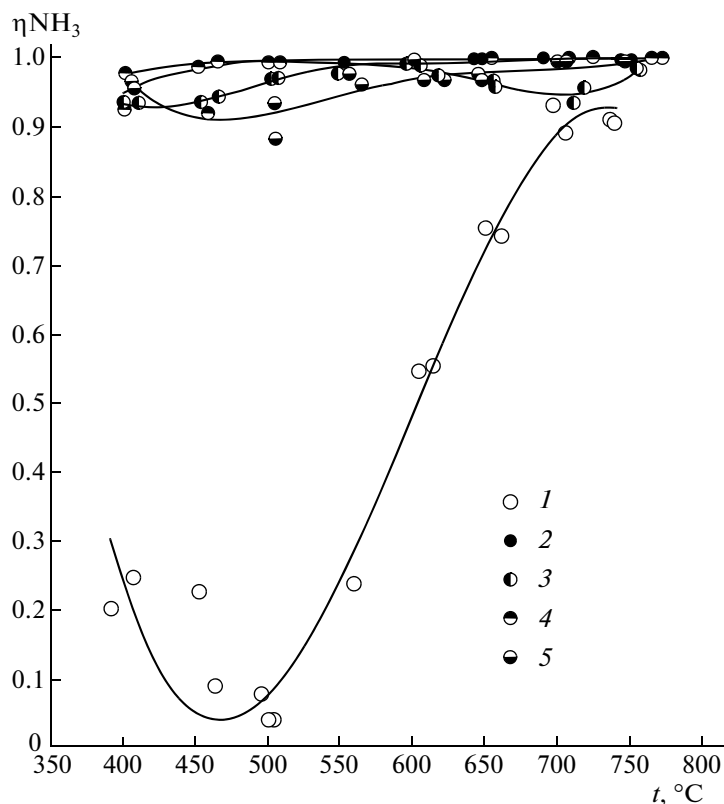
**Fig. 2.** Schematic diagram of the laboratory setup for studying the decomposition of ammonia on the natural catalysts from the Porozhinskoe deposit: (1) cylinder with a model gas mixture; (2, 9) reducers; (3) electronic gas flow meter; (4) reactor; (5) electric furnace; (6) filter; (7) gas meter; (8) cylinder with nitrogen; (10) laboratory transformer; and (11) hydrogen generation system.

the back titration of an absorbing acid solution with an alkali solution [6].

The gas flow rates at the reactor inlet and outlet were determined with the aid of an electronic gas flow meter (position 3) and a GSB-400 gas meter (position 7), respectively. The furnace temperature in a range of  $T$  was measured with a Chromel–Alumel thermocouple and recorded with a secondary instrument (it is not shown). The preliminary reduction of ore for the conversion of manganese and iron oxides into the lowest valence state (up to the formation of the corresponding metals) was carried out with the use of a GVCh-12 hydrogen generator (position 11) with an increase in the temperature from 300 to 600°C at a heating rate of 10 K/min.

Before and after operations, the system was blown with nitrogen. In the course of operation, the weights of the initial ore and ore reduced with hydrogen were measured and the degree of ammonia decomposition ( $\eta_{\text{NH}_3}$ ) was determined; it was calculated as a ratio of the molar amount of ammonia decomposed as a result of the experiment to its initial molar amount. Figure 3 shows the results of studies on the decomposition of ammonia for the P<sub>1</sub>–P<sub>4</sub> ores and also the results of so-called blank experiments, in which a gas containing ammonia was passed through the reactor with no catalyst.

An analysis of the data given in Fig. 3 showed that the value of  $\eta_{\text{NH}_3}$  increased with temperature for the P<sub>1</sub> ore catalyst with the smallest concentration of trivalent iron oxide (1.3 wt %) and with the highest manganese content (50.5 wt %) and for the P<sub>3</sub> ore catalyst. The capability of the P<sub>2</sub> catalyst to decompose ammonia was the lowest, and the dependence was nonlinear and had three extremums: two minimums at 450 and 700°C and a maximum at 575°C (the degree of ammonia decomposition was 0.99). For the P<sub>4</sub> ore with the greatest trivalent iron oxide content (21.3 wt %), a minimum at 450–500°C was observed in the test temperature range with a decrease in the value of  $\eta_{\text{NH}_3}$  to 0.91; then, the value of  $\eta_{\text{NH}_3}$  smoothly increased to 0.995% at 750°C.



**Fig. 3.** Dependence of the degree of decomposition of ammonia from the model gas on temperature for different catalysts in comparison with a blank experiment: (1) experiment without a catalyst, (2) experiment on the  $P_1$  catalyst, (3) experiment on the  $P_2$  catalyst, (4) experiment on the  $P_3$  catalyst, and (5) experiment on the  $P_4$  catalyst.

Experimental data on the decomposition of ammonia without the participation of catalysts showed that, at temperatures higher than  $700^\circ\text{C}$ , ammonia is decomposed to a value of 0.93, whereas the degree of decomposition at  $400\text{--}550^\circ\text{C}$  did not exceed 0.3.

Table 2 summarizes averaged data on the degree of decomposition of ammonia from a model gas depending on the concentrations of total manganese and iron(III) oxide in the test natural catalysts.

An analysis of the data given in Table 2 showed that no dependence of the effect of the manganese and iron content of the test catalysts on the degree of ammonia

decomposition was observed. It is likely that the textural and structural properties of each particular ore exert an effect on the efficiency of ammonia removal. However, the best result of 0.997 under a pressure of 0.1 MPa was obtained on the  $P_1$  catalyst, which possessed the highest total manganese content of 50.5 wt % and the lowest iron(III) oxide content of 1.3 wt %.

As the pressure was increased to 2.0–3.0 MPa, which is characteristic of the overwhelming majority of combined-cycle plant gasification systems, the degree of ammonia decomposition decreased in accordance with the Le Chatelier principle; nevertheless, it remained sufficiently high.

**Table 2.** Dependence of the degree of decomposition of ammonia from a model gas on the manganese and iron content of the test ores

| Ore   | Concentration in ore, wt % |            | Experimental temperature, $^\circ\text{C}$ |       |       |       |       |       |       |       |
|-------|----------------------------|------------|--|-------|-------|-------|-------|-------|-------|-------|
|       | $\text{Fe}_2\text{O}_3$    | Mn (total) | 400  | 450   | 500   | 550   | 600   | 650   | 700   | 750   |
| $P_1$ | 1.30                       | 50.5       | 0.983                                      | 0.992 | 0.995 | 0.997 | 0.997 | 0.997 | 0.997 | 0.997 |
| $P_2$ | 3.52                       | 42.1       | 0.936                                      | 0.946 | 0.977 | 0.989 | 0.993 | 0.967 | 0.950 | 0.988 |
| $P_3$ | 9.04                       | 31.1       | 0.937                                      | 0.988 | 0.995 | 0.986 | 0.993 | 0.996 | 0.996 | 0.996 |
| $P_4$ | 21.3                       | 16.6       | 0.960                                      | 0.920 | 0.924 | 0.973 | 0.979 | 0.984 | 0.995 | 0.995 |

Earlier, Epikhin et al. [7] found that the test iron–manganese ores from the Porozhinskoe deposit in a producer gas atmosphere supported a number of side reactions, which changed the composition of gas, such as the oxidation of hydrogen and carbon monoxide, the disproportionation of carbon monoxide, and the decomposition of methane. This fact does not allow one to use them directly in the combined-cycle plant systems with gasification. The preliminary reduction of ore excludes the oxidation reactions of producer gas components; the decomposition of methane occurs at temperatures higher than 750°C, whereas the disproportionation of CO, which occurs at 500–700°C, is important. Therefore, data on the decomposition of ammonia obtained at 400–500°C, when the above side reactions do not occur, are most interesting.

As noted above, the P<sub>1</sub> high-manganese ore ( $\eta_{\text{NH}_3} = 0.983\text{--}0.995\%$ ) is an optimum catalyst; however, the P<sub>3</sub> ore containing 9.04 wt % iron(III) oxide is also not bad, for which the degree of ammonia decomposition was 0.988% at 450°C. At this temperature, the uncatalyzed decomposition of ammonia was 0.21 (see Fig. 3); therefore, according to the calculations, the contribution of catalysis on the P<sub>3</sub> ore catalyst at 450°C gave  $\eta_{\text{NH}_3} = 0.985$ .

To reach a normative value of 140 mg/m<sup>3</sup> for nitrogen oxides under standard conditions, the concentration of ammonia in the test gas with the initial ammonia concentration of 2656 mg/m<sup>3</sup> should be decreased to a value of no higher than 368 mg/m<sup>3</sup> under standard conditions, that is, by 86.1%. This purification efficiency can be ensured with the use of any of the test catalysts or by an increase in the gas temperature to 700°C or higher. However, the producer gas obtained by the furnace gasification of coals in a dense layer with the use of air blast has a temperature of no higher than 500–600°C, and the normative values of nitrogen oxides are established for the entire sum of them including nitrogen oxides formed upon the interaction of nitrogen and oxygen. In this context, the degree of ammonia removal from producer gas under the above conditions should be knowingly higher than 86%.

Thus, all of the tested ores from the Porozhinskoe deposit, which differ in iron and manganese contents, are catalysts for the decomposition of ammonia at

400–750°C, and the best results were achieved on the ore with the smallest iron content. Difference in the efficiency of the other catalysts is small, although it can be of importance with specific requirements imposed on them. The degrees of ammonia decomposition on these catalysts differ by 1–2%; in the general case, they are 0.920–0.997, having a tendency to increase with temperature.

In the general case, we failed to reveal the effects of iron and manganese contents of the catalysts on the degree of ammonia decomposition; this is likely related to the textural and structural properties of the catalysts.

All of the test catalysts for the decomposition of ammonia ensure the degree of its decomposition of no less than 0.924 at 400–500°C. In this case, the ammonia concentration in the purified gas is no higher than 201 mg/m<sup>3</sup> under standard conditions; under the specified conditions, this corresponds to an NO<sub>x</sub> concentration of 76 mg/m<sup>3</sup> in the flue gases under standard conditions. In the same temperature range, it is possible to ensure a higher degree of ammonia decomposition, which will lead to even smaller nitrogen oxide emissions.

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