REMOVING NITRIC OXIDE FROM FLUE GASES BY CATALYTIC REDUCTION

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A Ti–W–V catalyst has been proposed for removing NO by means of ammonia reduction from flue gases from power stations and boiler systems operating with natural gas; it contains 10% WO_3 and 5% V_2O_5 deposited on anatase. The optimum NH_3/NO ration is 0.8. oxygen at levels of 0.1-7.8 vol. % does not affect the reduction of the NO. Industrial tests in flue gas from a power station show that the reduction of the NO is 96% at 240-270°C. The basic technological parameters have been determined.

Considerable amounts of oxides of nitrogen are discharged into the atmosphere from the combustion of fuel to produce energy, which produces unfavorable ecological settings. Oxides of nitrogen are formed in flue gases by the thermal reaction of atmospheric nitrogen and nitrogen compounds in the fuel as well as the oxidation of nitrogen-bearing combustion products.

Engineering methods to improve the ecological setting are subdivided into primary and secondary. A primary method involves using various engineering facilities in the combustion and altering the thermodynamic parameters there. The specifications in various countries for denitrifying gases vary from 60 to 80% removal. When primary methods do not provide the necessary reduction, some countries (Japan and the Federal German Republic) specify secondary methods: gas treatment after combustion. It is assumed that natural fuels will continue to be used to produce energy in the near future, so research on reducing the discharge of pollutants is of primary importance.

We have examined the catalyst composition and the removal of nitric oxide in application to flue gases from power stations and boilers.

We used selective catalytic reduction of nitrogen oxides, which gives harmless products. The reducing agent was ammonia, as it has high selectivity by comparison with other reducting agents (CO, CH_4, H_2, and hydrocarbons) when the gas contains oxygen.

The reactions are

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O, \quad (1)$$

$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O. \quad (2)$$

The selectivity is determined by

$$4NH_3 + 5O_2 = 4NO + 6H_2O, \quad (3)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O, \quad (4)$$

$$4NH_3 + 7O_2 = 4NO_2 + 6H_2O. \quad (5)$$

The predominant is (1), since the flue gas after combustion has 96-98 vol. % nitric oxide in the total NO_x.

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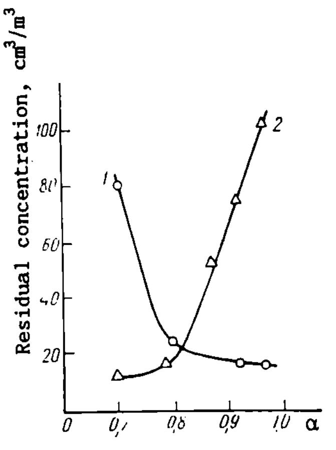

Fig. 1

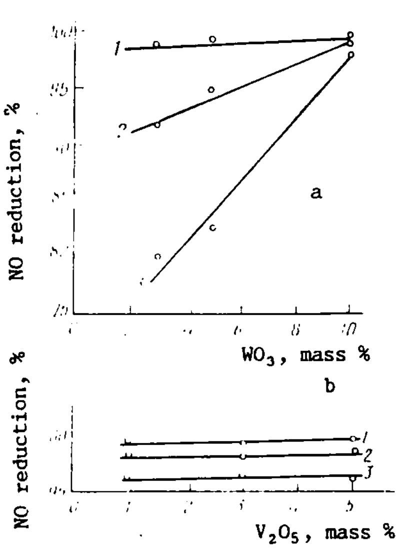

Fig. 2

Fig. 1. α-dependence of the NO (1) and NH_3 (2) concentrations in the treated gas.

Fig. 2. Degree of NO reduction as a function of WO_3 content (a) and V_2O_5 content (b): 1) $\alpha = 1.0$; 2) $\alpha = 0.8$; 3) $\alpha = 0.7$.

The reduction is restricted by various requirements: exact ammonia dispensing, careful mixing, temperature maintenance (not less than 200°C) to avoid the formation of ammonium nitrite and nitrate, which are deposited, and maintaining conditions that rule out (3)-(5). Published data indicate that various catalyst systems have been used for the purpose, whose choice is determined by the type of fuel, the power level, the design features, and other parameters.

We examined mounted and oxide catalysts for the reduction of NO to nitrogen and water and found that their activities fall in the sequence

$$\begin{gathered}Pd-Al_2O_3 < TiO_2 \\ < TiO_2-WO_3 < Ru-Al_2O_3 < CuO-MgO \simeq Cu-Cr_2O_3 < \\ < V_2O_5-Al_2O_3 < TiO_2-V_2O_5 < TiO_2-WO_3-V_2O_5.\end{gathered}$$

We subsequently used Ti–W–V catalysts, which have shown the highest activity in this reaction. The carrier was titanium dioxide in anatase form made by hydrolysis from titanium tetrachloride; the active components were tungsten and vanadium oxides.

The tests were done with a laboratory dynamic system having an immobile catalyst bed at 0.1 MPa with an artificial gas mixture containing the following trace components in nitrogen: O_2 0.1-7.8 vol. %, NO about 500 cm^3/m^3, and NH_3 350-500 cm^3/m^3. Tightening standards for atmospheric discharges of pollutants led us to assume that the nitric oxide content should not exceed 20 cm^3/m^3 and ammonia 10-15 cm^3/m^3. The experiments were done at 160-420°C with volume flow rates of 10^4 h^{-1}. The NO, NO_2, and O_2 concentrations in the initial and treated gases were determined by means of a TESTO-33 gas analyzer (Testoterm, Germany), while ammonia was analyzed colorimetrically.

In the first stage, we examined how the ammonia concentration in the treated gas affected the reduction. We varied the ration of ammonia to nitric oxide α from 0.7 to 1.0 (Fig. 1). The optimum α was 0.8. This produced the required levels of nitric oxide and ammonia in the products. Larger amounts of ammonia increased the performance in removing the nitric oxide but led to ammonia breaking through.

The next step was to determine the optimum catalyst composition, for which we prepared specimens with various tungsten and vanadium oxide contents (Fig. 2). 98.5-99.5% NO reduction was obtained in the working range of α with a maximal tungsten oxide content of 10 mass %. The degree of NO reduction exceeded the requirement (96%), and only with α of 0.7-0.8 did the ammonia concentration in the products not exceed the permissible level.

TABLE 1. Temperature Ranges for Ti—W—V Catalyst Operation with a Volume Flow Rate of 10^4 h^{-1} and $\alpha = 0.8$

Catalyst composition, mass %			t, °C	Δt, °C	NO reduction, %
TiO_2	WO_3	V_2O_5			
89	10	1	300—350	50	95
87	10	3	270—330	60	99
85	10	5	240—340	100	~100

TABLE 2. Tests Results with Catalysts on an Artificial Gas Mixture and with Flue Gas, 240-270°C, 10^4 h^{-1}, α 0.8

% active components in catalyst	NO reduction, %	
	artificial mixture	flue gas
5 % WO_3+1 % V_2O_5	84,5	63,0
10 % WO_3+3 % V_2O_5	97,5	90,0
10 % WO_3+5 % V_2O_5	99,5	96,5

Varying the vanadium oxide content from 1 to 5 mass % had no marked effect on the NO reduction. The catalyst composition may affect the working temperature, so we prepared Ti—W—V catalysts containing 10 mass % WO_3 and 1, 3, and 5 mass % V_2O_5. Table 1 shows that increasing the vanadium oxide content enables one to operate at lower temperatures and over a wider temperature range.

We also examined how oxygen affected the working characteristics. The oxygen concentration in the gas mixture passing to the catalyst was varied from 0.1 to 7.8 vol. %. Within that range, it had no effect on the nitric oxide reduction.

We examined the scope for (3)-(5) to occur with the Ti—W—V catalysts as they influence the selectivity. The supply of nitric oxide was cut off from the mixture and experiments were made at 25-300°C with a flow rate of 10^4 h^{-1}. There was a slight reduction in the ammonia concentration relative to the initial gas, while oxides of nitrogen were not observed. The data indicate that the process is selective.

Further tests on the catalysts were performed with the gas from a power station working with natural gas. The composition of the flue gas a regards the major components and the nitric oxide was close to that of the artificial gas mixture. A mixture of 5% ammonia in air was dispensed from a cylinder into the flue gas before passage to the catalyst. Table 2 gives the results obtained with flue gases, together with the reduction in NO with the artificial mixture.

These tests showed that the degree of conversion for the NO was high on specimens in which the tungsten and vanadium oxide contents were correspondingly 10 and 5%. We thus propose a Ti—W—V catalyst for treating flue gases from power stations and boilers working with natural gas that consists of an 85:10:5% metal oxide mixture. The major technological parameters have been determined, which provide the necessary removal of the NO and the permissible ammonia concentration in the treated gas.