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Application of the nonstationary state of a catalyst surface for gas purification from toxic impurities

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Abstract

In the present report the results are given of the development of novel catalytic processes based on the forced maintenance of the catalyst in a nonstationary state for deep gas purification from nitrogen oxides (up to 50 mg/m^3), SO_2 (less than 50 ppm) and organic impurities.

Keywords: Gas purification; Nitrogen oxides

Conception of exothermic heterogeneous catalytic processes in the forced unsteady-state regime based on the application of the heat dynamic in a fixed catalyst bed (stated in monograph [1]) has gained a wide dissemination. The process is supposed to perform under the periodic changing of the gas flow filtration through a catalyst bed. As it is presented in the paper by Boreskov and Matros [2] under certain conditions there is no time for the catalyst surface to readjust itself to changing of the gas phase characteristics. In this case the catalyst surface is in a nonstationary state with respect to the gas phase. Using such phenomena one can provide higher efficiency of catalytic processes due to the external influences on the heterogeneous catalyst.

Under selective catalytic reduction (SCR) nitrogen oxide [3] and ammonia may accumulate in various forms on a catalyst surface. Nitrogen oxides react with adsorbed ammonia mainly from the gas phase. At the same time, the SCR process is accompanied by oxidation of adsorbed ammonia. The simplest SCR process mechanism may be presented as:

$$NH_3 + [\ ] \rightleftharpoons [NH_3] \quad (1)$$

$$[NH_3] + NO_x + O_2 \rightarrow N_2 + H_2O + [\ ] \quad (2)$$

$$[NH_3] + O_2 \rightarrow N_2 + H_2O + [\ ] \quad (3)$$

Ammonia surface coverage (Θ) is described in this case by the following equation:

$$a\frac{\partial \Theta}{\partial t} = r_a - r_{NO_x} - r_{NH_3} \quad (4)$$

where $r_a = k_1^+ \cdot C_{NH_3}(1-\Theta) - k_1^- \Theta$ – rate of NH_3

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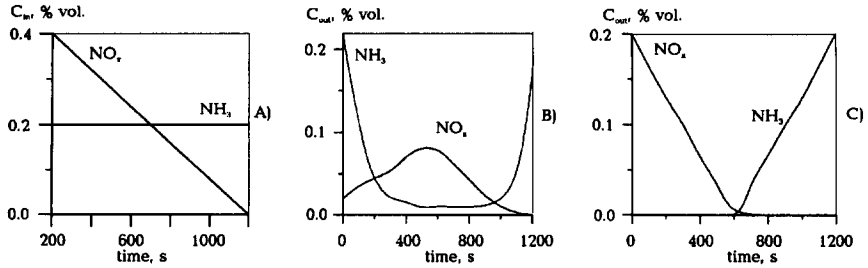

Fig. 1. Nitrogen oxide and ammonia content at the inlet (A) and outlet (B, C) of the catalyst bed under periodical changing of inlet conditions. (B) Calculation via model 1–3; (C) calculation via stationary kinetic model. $T_{in} = 260°C$.

reversible adsorption; $r_{NO_x} = k_2 \cdot C_{NO_x} \cdot \Theta$ – rate of adsorbed ammonia interaction with NO_x; $r_{NH_3} = k_3 \cdot \Theta$ – rate of adsorbed NH_3 oxidation; a = catalyst surface capacity (cm^3 NH_3/cm^3 of the catalyst, for vanadium oxide catalysts $a = 5–10$).

Let us consider how the storage capacity of ammonia on a catalyst surface affects the efficiency of the SCR process under distorting the ratio of nitrogen oxides and ammonia. In Fig. 1 there are given NO_x and ammonia concentrations (calculated by stationary (C) and non-stationary (B) models) at the outlet of the catalyst bed under cyclic changes of nitrogen oxides at the inlet (see Fig. 1A). For a half of a cycle NO_x exceeds ammonia concentration and the SCR process proceeds at a reducer deficiency. For another half of a cycle ammonia is fed with a large excess. The calculated behavior of the outlet concentrations of NO_x and NH_3 over the whole period is shown in Fig. 1B and C. If the adsorption catalyst capacity is taken into account (model 1–4) in the first half of a period the increased ammonia content (Fig. 1B) is observed in the outlet, flow notwithstanding its deficiency. The reason is the desorption of some amount of ammonia accumulated in the cycle above. Adsorbed ammonia comes into reaction at the increased nitrogen oxides content in the gas flow. Since the content of NH_3 adsorbed is particularly high on the inlet part of a catalyst nitrogen oxides reduction proceeds mainly over them. The gas mixture depleted in NO_x passes to the outlet end. As adsorbed ammonia utilized, the degree of gas purification from nitrogen oxides and ammonia slip are reduced. In the middle of the period the situation changes due to the appearance of excessive ammonia in a gas phase at the inlet of the catalyst bed. Being dependent on the catalyst adsorption capacity the ammonia content begins to increase at the outlet, whereas NO_x concentration starts to decrease from the middle of the period. Simulation of the SCR process with stationary kinetic model has shown that the output NO_x and NH_3 concentrations change with the input ones (Fig. 1C). In the first half of the period all ammonia is consumed and only nitrogen oxides are observed at the outlet. Then the excess of ammonia is registered.

By this means taking into account the catalyst adsorption capacity with respect to ammonia via model 1–4 one can demonstrate that the efficiency of gas purification from NO_x remains at the high level with the nitrogen oxides content varying in a gas phase. An excess ammonia accumulates on a catalyst surface and is consumed at NH_3 deficiency in the gas phase in accordance to reaction 2.

Previously, the authors have developed an unsteady-state SCR process performed under periodic changing of the direction of reaction mixture filtration through a catalyst bed (reverse-NO_x process) [3]. The process mathematical modelling based on the stationary kinetic model does not show the concordance of the design data with the observed high efficiency of the industrial unit in the purification from nitrogen oxides and the absence of residual ammonia. In the present report on the basis of mechanism 1–3 there is considered the effect of a nonstationary state of the catalyst surface described by equation 4 on reverse-NO_x characteristics. Some calculated results are given in Fig. 2. One can see that at the same input characteristics a periodic reverse of a gas flow filtration

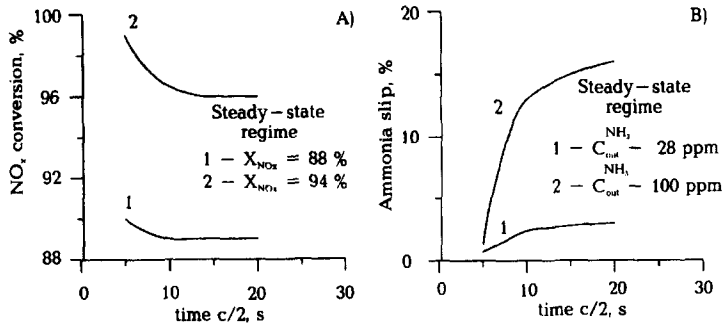

Fig. 2. Dependence of the degree of gas purification from nitrogen oxides (A) and residual NH_3 concentration (B) under periodic reverse-flow operation in a catalyst bed on the time between switchings ($t_{c/2}$). Inlet conditions: T_{in} = 260°C; $C_{NO_x}^{in}$ = 0.20 vol.%; $C_{NH_3}^{in}$ = 0.18 vol.% (1) and $C_{NH_3}^{in}$ = 0.20 vol.% (2).

through a catalyst bed allows one to increase the nitrogen oxides conversion as compared to a conventional process with the permanent flow direction (steady-state regime). Under reducing the time between the gas flow reversals ($t_{c/2}$) the reaction heat accumulated in a catalyst bed causes a rise of the maximum temperature. An increase of the quantity of ammonia adsorbed on the catalyst surface occurs as well. A simultaneous effect of these two factors results in an increase of both the reaction 2 rate and, therefore, in NO_x conversion degree (Fig. 2A). A quantity of nonconverted ammonia in a gas phase after passing through a catalyst bed is also reduced (Fig. 2B). Flow reverse more strongly affects the process characteristics at stoichiometric ratio NO_x/NH_3 (curve 2, Fig. 2A and B). It is possible to provide the residual ammonia content less than 5 ppm at the efficiency of nitrogen oxides removal of about 99% (ratio $NO_x/NH_3 = 1$). Under steady-state conditions these characteristics are $C_{NH_3}^{out} = 100$ ppm and $X_{NO_x} = 94\%$, correspondingly. Industrial realization of reverse-NO_x process has proved both stability of its characteristics at NO_x inlet concentration oscillations and high purification efficiency (98–99%). For the inlet nitrogen oxides concentration (2–10 g/m^3) their residual content does not exceed 30–70 mg/m^3 with the practical ammonia absence at the outlet.

Under deep oxidation of alkylaromatic compounds (styrene, cumene and others) the presence of the following stages has been experimentally established (up to the temperature of 320°C) [4]:

- hydrocarbons chemisorption over an oxide catalyst surface;
- oxidation of the chemisorption products by oxygen.

The oxidation process at temperatures 200–300°C is characterized by a prolonged time (of the order of 1 h) for setting of a steady-state rate.

The chemical essence of the reaction may be presented in a following way:

$$C_nH_m + [\ ] \rightarrow [P] \quad (5)$$

$$[P] + O_2 \rightarrow CO_2 + H_2O + [\ ] \quad (6)$$

where [P] represents intermediate surface compound. Analysis of the experimental data has made it possible to determine the kinetic equations and the activation energy: $W_5 = k_1 C^{0.5}(1-\Theta)$, $E_1 = 8.9$ kcal/mol – chemisorption stage; $W_6 = k_2 C_{ox} \Theta$, $E_2 = 18.1$ kcal/mol – stage of chemisorption products oxidation, where C, C_{ox} = concentration of the alkylaromatic compound (cumene) and oxygen, respectively; Θ = surface fraction, occupied by the products of chemisorption.

The chemisorption capacity of the CuO–Cr_2O_3–Al_2O_3 catalyst surface was found to be equal to $3.5 \cdot 10^{-6}$ mol/m^2.

As an example of application of the above description we can give the data on the reaction rate relaxation at the termination of feeding of one of the reagents into a lab ideal mixing reactor (Fig. 3). The rate of CO_2 formation at the termination of oxygen feeding (curve 1, Fig. 3) drops rapidly to zero and this fact confirms the suppo-

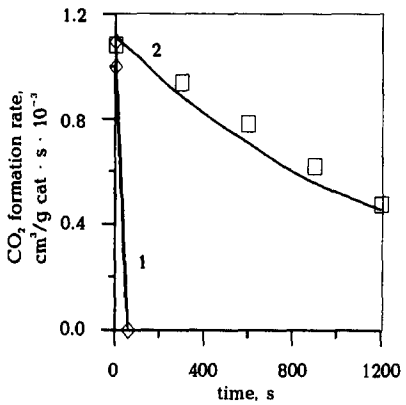

Fig. 3. Change of CO_2 rate formation at the termination of feeding of one of reagents into a reactor. (1) Termination of oxygen supply, (2) cumene. □,◇ = Experimental values, — = calculated.

sition that carbon dioxide in this temperature range (250°C) is produced only by oxidation of chemisorption products by oxygen from a gas phase. At the same time the termination of cumene feeding results in a slow reduction of CO_2 rate evolution (curve 2, Fig. 3), since a considerable capacity of the catalyst surface provides a considerable system inertness. It should be noted that the experimental and calculated data correlated satisfactorily.

For the purification of low concentrated gas wastes from alkylaromatic compounds vapors the following stages consequence might be proposed. At relatively low temperatures gas is passed through a catalyst bed. This is accompanied by chemisorption and accumulation of alkylaromatic compounds in a catalyst bed. Over a definite period of time the temperature rise is performed in a reverse-flow operation mode in a catalyst bed. This induces oxidation of chemisorbed compounds to CO_2 and simultaneous bed autoheating by oxidation reaction heat.

Fig. 4 shows the calculated rate of CO_2 formation under the oxidation of preliminary chemisorbed cumene and programmed temperature rise. It should be noted that catalyst heating depends on the rate of temperature rise. At a slow temperature rise (1°/min) no dramatic increase of temperature occurs. This is explained by the fact that a considerable portion of chemisorbed substance is oxidized at moderate temperatures. The calculations allow one to estimate a characteristic time of the protective effect of an oxide catalyst bed (the contact time is 1 s) under passing the air, contaminated by isopropylbenzene vapors (50 mg/m^3), up to 75 h. The regeneration process is performed within 1–1.5 h. As a whole, the purification efficiency of such process is higher than 99%.

The process is also characterized by an extremely low energy consumption averaged per adsorption–oxidation cycles (below 0.8 kcal per m^3 of waste gases).

Under SO_2 oxidation to SO_3 over the vanadium catalysts the reaction proceeds via a stage of SO_2 and O_2 dissolving in an active component liquid film. In work [5] an unsteady-state kinetic model, allowing for both a catalyst reversible deactivation (formation of four-valence vanadium, V_2^{4+}) possible in the course of the reaction, and an inertia of SO_2 and SO_3 concentration change in the melt. The availability of the absorption capacity of the vanadium catalysts with respect to SO_2 makes it possible to suggest a novel process of SO_2 oxidation into SO_3. The process contains two consecutive stages: (i) SO_2 absorption (dissolving) and oxidation to SO_3 in the liquid film; (ii) removal of absorbed SO_3 by air, upon which a simultaneous catalyst activation proceeds as well.

Such consequence of the operations allows one to maintain the catalyst in a more active state and

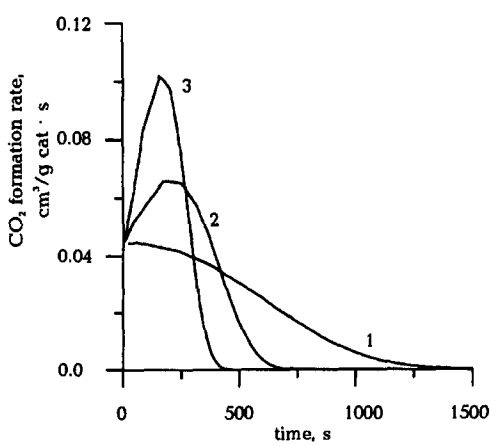

Fig. 4. Dependence of the rate of chemisorbed cumene oxidation (CO_2 evolution) on the rate of catalyst temperature rise (1–1°/min; 2–10°/min; 3–20°/min).

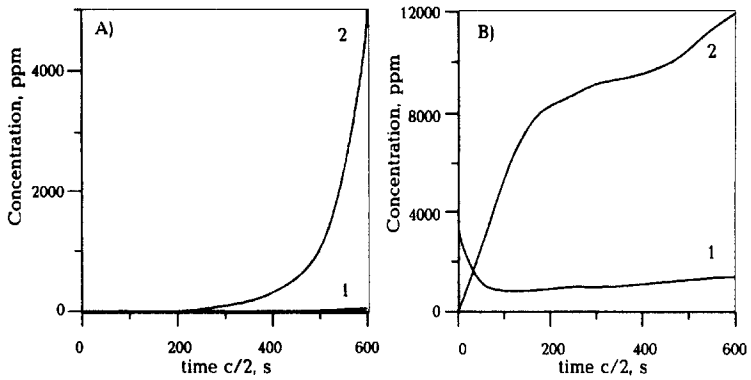

Fig. 5. Concentration dependence at the reactor outlet during semicycle ($C^{in}_{SO_2}$ = 1 vol.%; $C^{in}_{O_3}$ = 4 vol.%). C_{SO_2} (1); C_{SO_3} (2), (A) at the stage "reaction-absorption"; (B) at the stage "desorption-activation".

provide the conditions favorable for the equilibrium shift to SO_3 formation. The catalyst capacity with respect to SO_2 and SO_3 causes the absorption of SO_2 in a melt and its content at a bed outlet will be extremely low. From the calculated dependencies given in Fig. 5A it may be noted that SO_2 concentration at the outlet of "reaction-absorption" stage is very low and SO_3 appears with a considerable delay. After a given time a catalyst bed is blown up by a hot air. During such treatment absorbed SO_2 and SO_3 are removed from the catalyst and it becomes more active. The change of SO_2 and SO_3 concentrations at the bed outlet during stage "desorption-activation" is given in Fig. 5B. A certain combination of "reaction-absorption" and "desorption-activation" stages makes it possible to create the process providing the residual SO_2 content lower than 50 ppm without application of chemical purification cleanup system. The application of the proposed process at the second stage of DC/DA system allows to increase SO_2 conversion up to 99.995%.

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