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Selective NO Reduction by Propane over Commercial Oxide Catalysts and Their Mechanical Mixture: II. Intermediate Complexes and Reaction Mechanism

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Abstract—Based on a spectrokinetic study (simultaneous measurements of the concentrations of surface complexes and reaction rate using *in situ* IR spectroscopy), a hypothesis is proposed which explains synergism in the reaction of NO reduction by propane on a mechanical mixture of commercial oxide catalysts.

INTRODUCTION

In the preceding paper [1], we reported the effect of synergism in the reaction of NO reduction by propane catalyzed by a mechanical mixture of oxide catalysts NTK-10-1 and STK. To find the cause of this phenomenon, its mechanism should be determined.

To analyze the mechanism of NO reduction by propane, it is important to have information on the surface intermediate species. Information on the vibrational spectra of the species adsorbed on the surface of commercial catalysts such as STK and NTK-10-1 under the conditions of this reaction is unavailable. We showed that individual catalysts have radically different properties with respect to NO adsorption [2]. This difference allowed us to propose two hypotheses that describe the effect of synergism. The first hypothesis is the same as in the literature: one component (NTK-10-1) of the mechanical mixture adsorbs better NO and produces NO_2 more readily. Then, NO_2 is further reduced to nitrogen at a higher rate than NO on the other component (STK).

The other hypothesis suggests that, on the STK catalyst, a hydrocarbon is partially oxidized to form a product which cannot further be oxidized on this component of the mixed catalyst because of the lack of the high-temperature form of NO adsorption. Therefore, this product is further oxidized on NTK-10-1, where this form is available.

In this work, we continue the mechanistic study of synergism. The goal of the study is to elucidate the role of surface complexes formed in the reaction $NO + C_3H_8 + O_2$ on commercial oxide catalysts using the spectrokinetic method.

EXPERIMENTAL

To obtain detailed information on the process mechanism, we carried out spectrokinetic measurements according to the technique described in [3]. This method is based on correlating the spectra of surface species measured *in situ* and the rates of product formation.

In situ spectroscopic study was carried out using a setup with a special cell/reactor, which enabled simultaneous spectral measurements and kinetic studies under nongradient conditions, and an IR spectrophotometer UR-20W modified to register transmission and diffuse-reflectance spectra of the samples at high temperatures.

Before measurements, the samples were treated in the flow of an inert gas (nitrogen) at 500–600°C. All gases were dried with anhydrone and used without additional purification. Reactants and products at the inlet and outlet of the cell were analyzed using Beckman gas analyzers (NO, NO_2, CO, and C_nH_m) and a chromatograph (N_2O, CO_2, and O_2).

Spectrokinetic measurements were carried out with two samples: STK and a 1 : 1 mechanical mixture of STK and NTK-10-1 catalysts (MK_2). A fresh sample was taken for each measurement. Transmission and diffuse-reflectance methods were used. The NTK-10-1 catalyst had a high proper absorbance, which prevented it from spectral measurements.

RESULTS

When the reaction mixture interacts with the surfaces of STK and MK_2 at a high temperature (500°C), these surfaces are reduced to form a metallic phase. This reveals itself in an increase in the background absorbance of the samples observed in IR spectra. Similar changes take place when the surface is reduced in a

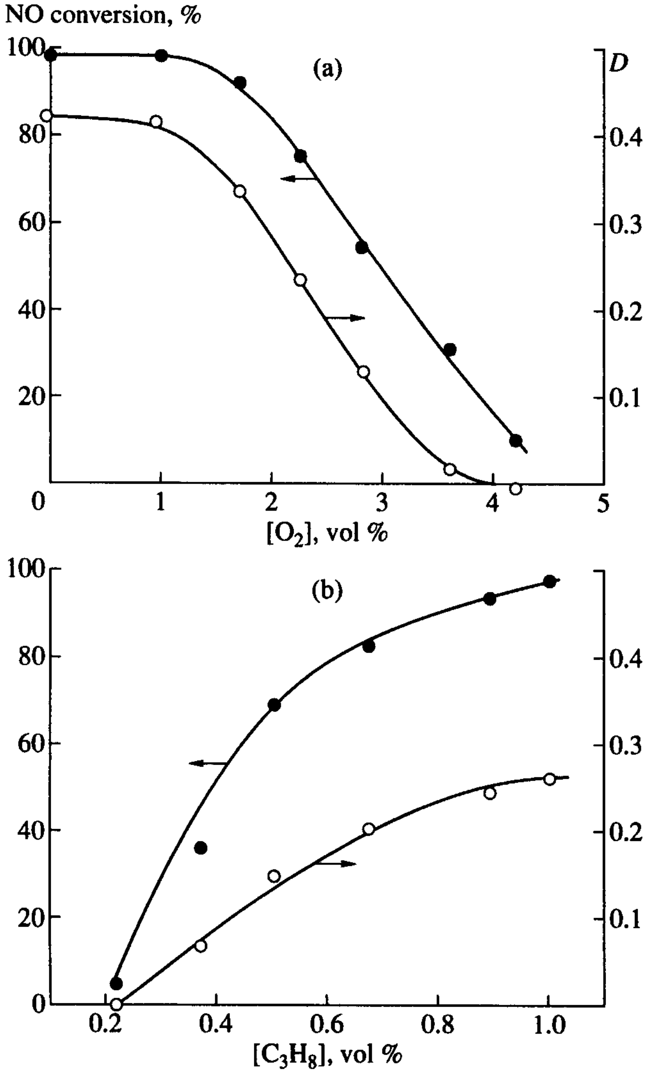

Fig. 1. Absorbance (D) at $\nu = 1900$ cm^{-1} and NO$_x$ conversion vs. (a) O_2 concentration and (b) propane concentration for the STK catalyst at 500°C ([NO] = 0.1 vol %; (a) [C_3H_8] = 0.5 vol %; and (b) [O_2] = 2.5 vol %).

hydrogen flow. Also, it is known that oxide surfaces are reducible in the presence of a reducing agent even if an oxidant is in excess. The fact that a metallic phase is formed is further supported by the existence of N_2 in the products of NO thermal desorption from the reduced STK catalyst. The degree of sample reduction was estimated from a change in absorbance at 1900 cm^{-1}.

Figure 1 shows a plot of NO$_x$ conversion and absorbance D at 1900 cm^{-1} for STK versus oxygen and propane concentrations. It can be seen that, with an increase in the concentration of propane and with a decrease in the concentration of oxygen in the reaction mixture, the conversion of NO$_x$ and absorbance at 1900 cm^{-1} increase. That is, an increase in the degree of STK surface reduction is accompanied by an increase in NO conversion. The same ratio of parameters was obtained from the changes in NO$_x$ conversion depending on temperature. An increase in the concentration of NO in the reaction flow only slightly affects the conversion of NO$_x$. The degree of surface reduction also remains almost unchanged.

The following data suggest that the reduction of surface is important for the effective reaction. For MK$_2$ in the gaseous mixture with a composition 0.24 NO + 0.3 C_3H_8 + 2.5 O_2 + 96.96 N_2 (vol %), the conversion of NO$_x$ is low (~5.5%) at 500–600°C. Under these conditions, the sample surface is not reduced. In the reactive flow with the same concentrations of NO and O_2, but with 0.5 vol % of C_3H_8 the catalytic system MK$_2$ is very active at the same temperatures (the conversion of NO is ~90%). Under these conditions, the sample is reduced.

To elucidate the role of oxide catalyst surface reduction in the reaction NO + C_3H_8 + O_2 and the nature of synergism observed in the MK$_2$ system, we studied surface complexes formed under the reaction conditions. The spectrokinetic measurements were carried out with the mixtures of the following composition (vol %): [NO] = 0.25, [C_3H_8] = 0.25, [O_2] = 5.0, and [N_2] = 94.5. The space velocity was 11250 h^{-1}. Figure 2 shows typical spectra of surface species recorded under the reaction conditions for STK and MK$_2$.

STK Catalyst

In the spectra of the STK catalyst, absorption bands at 1400–1550 cm^{-1} are observed. Figure 3a shows the plots of absorbance at $\nu = 1540$ cm^{-1} and NO and C_3H_8 conversions versus temperature. Note that the beginning of the reaction of propane oxidation is accompanied by a decrease in the absorbance at 1400–1550 cm^{-1}. With an increase in temperature from 100 to 450°C, the absorbance drops to almost zero, the conversion of propane increases, and the conversion of NO$_x$ is virtually equal to zero. At these temperatures, TPD [2] failed to find adsorbed NO molecules on the surface of the STK catalyst. Figure 4 shows the dependence of NO$_x$ and propane conversions and changes in the absorbance at 1450 and 1540 cm^{-1} on the concentrations of reactants.

Note that a decrease in the absorbance at 1400–1550 cm^{-1} and an increase in propane conversion with increasing temperature is accompanied by an increase in the degree of surface reduction. Reduction is probably associated with the reaction of propane oxidation.

MK$_2$ Catalyst

Figure 2b shows typical spectra for the surface compounds formed under the reaction conditions on the MK$_2$ catalyst at different temperatures.

It is seen that a change in the absorbance at 1550–1470 cm^{-1} with a change in temperature is not as pronounced as in the case of the STK catalyst. Note the presence of the absorption band at 1800 cm^{-1}, which is assigned to vibrations in an NO molecule adsorbed on transition metal ions. Figure 3b shows a change in the absorbance D_{1800} together with a change in NO_x and propane conversions with temperature. It is seen that a decrease in D_{1800} is accompanied by an increase in the conversion of NO_x. Note that the propane conversion is low, and the changes at 1550–1470 cm^{-1} in the spectra are less pronounced than for the STK catalyst.

DISCUSSION

Identification of the Surface Complex

Absorption bands at 1540 and 1450 cm^{-1} appear in the spectra after treating the STK and MK_2 samples in the gaseous flow containing propane. At 300°C, the respective absorbance increases with an increase in the propane concentration in the gas, does not depend on the concentration of NO, and passes through a maximum with an increase in the concentration of O_2 (Fig. 4). Figure 3a shows that a decrease in the absorbance of these bands with an increase in temperature is associated with the propane conversion and accompanied by an increase in the degree of surface reduction.

The above facts allow us to assign the absorption bands at 1470–1550 cm^{-1} to C–H bond vibrations in the fragment of adsorbed propane formed on the surface of the STK catalyst. This is supported by the presence of chromate groups capable of efficiently activating the C–H bond on the surface of the oxidized iron–chromium STK catalyst, chromium oxide surface, and copper–chromium spinel [4].

The absorption band at 1800 cm^{-1} appears after NO adsorption and can be assigned to the vibration in the nitrosyl complex, which is probably bound to transition metal ions [5]. The detailed structure of the absorption site is not discussed. In the presence of NO in the gas phase, the nitrosyl complex exists on the surface when heating it to 420°C [6].

Figure 2 shows that the absorption band at 1800 cm^{-1} is absent from the spectrum of the STK catalyst in the case of the above-mentioned composition of the reaction mixture, whereas it is present in the spectrum of the MK_2 catalyst. This absorption band is probably due to the NTK-10-1 catalyst. As shown in [2], the high-temperature form of NO adsorption is present on the surface of NTK-10-1. This form of adsorption is associated with the formation of nitrate–nitrite complexes on the surface of oxide catalysts [7], and these complexes play the main role in selective NO_x reduction. On the NTK-10-1 catalyst with copper oxide is a principal phase, and nitrate–nitrite complexes are readily formed upon NO adsorption. As this takes place, the presence of strongly bound nitrate complexes retards propane activation on copper-containing systems because these complexes block reactive oxygen forms on the surface [8]. In our case, the separation of contributions from nitrosyl and nitrate–nitrite complexes to the overall reaction of selective NO_x reduction is impossible because precise spectral measurements cannot be performed in the region of nitrate–nitrite complex absorption. In this region, the proper absorbance of MK_2 is high. However, for the MK_2 system, which is a mechanical mixture of STK and NTK-10-1, the activated form of NO is localized on NTK-10-1.

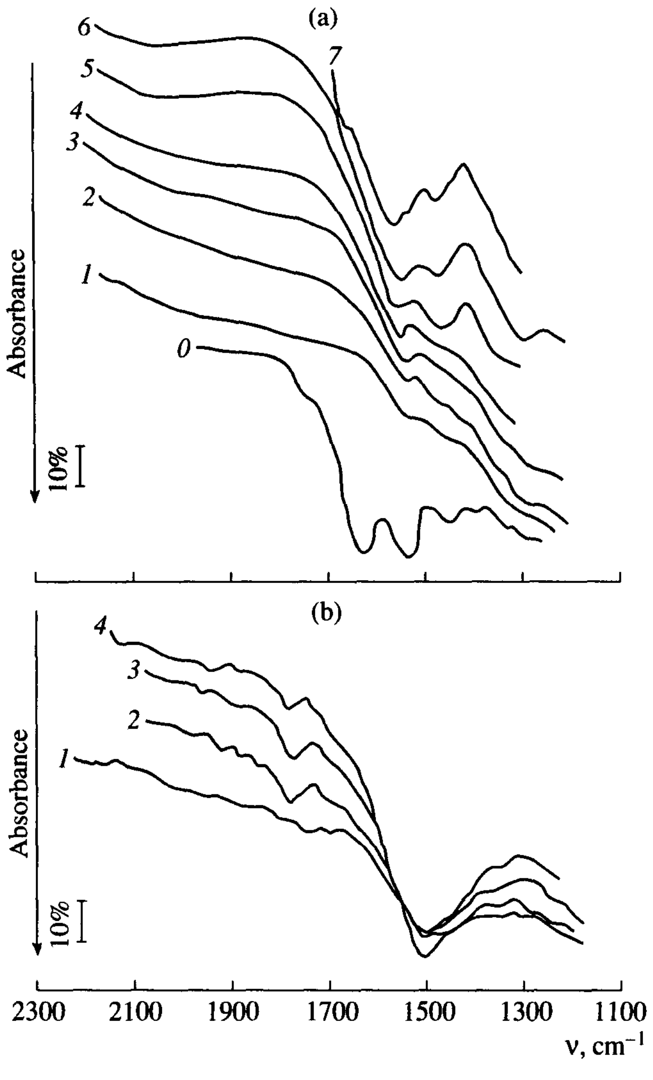

Fig. 2. IR spectra of the (a) STK and (b) MK_2 catalysts under the conditions of the reaction NO + C_3H_8 + O_2 ([NO] = 0.25 vol %; [C_3H_8] = 0.25 vol %; [O_2] = 5.0 vol %): (a) in the reaction mixture at (*1*) 420, (*2*) 340, (*3*) 290, (*4*) 220, (*5*) 160, and (*6*) 130°C; (*7*) in N_2 at 60°C; (*0*) initial sample; (b) (*1*) in N_2 at 420°C and in the reaction mixture at (2) 420, (*3*) 270, (*4*) 160°C.

Reactivity of Surface Complexes and Possible Mechanism of Synergism

Complexes found on the surface are highly reactive. Their concentration depends on the experimental temperature and the composition of the reactive flow. A decrease in the intensity of the corresponding absorption bands in the spectra is accompanied by an increase in the reactant conversion (Fig. 3). This fact

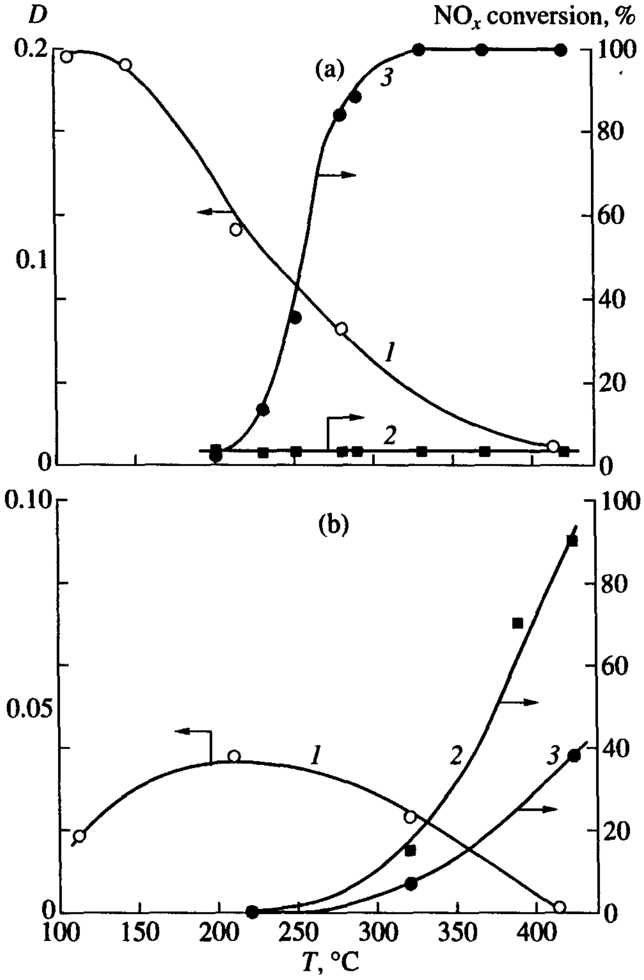

Fig. 3. (*1*) Absorbance (D) at (a) 1540 and (b) 1800 cm^{-1}, (*2*) NO$_x$ conversion, and (*3*) propane conversion vs. temperature for the (a) STK and (b) MK$_2$ catalysts.

suggests that these complexes can be intermediates in the complex process of NO reduction.

It is important that the presence of oxygen in large amounts does not prevent NO from adsorption. The reduction of samples in the mixture containing 0.1 NO, 0.5 C_3H_8, and 2.5 O_2 (vol %) (Fig. 1) suggests that oxygen binding to the surface is weak. The weaker this binding, the higher the degree of surface reduction.

Based on the experimental data and taking into account the difference in the spectral and adsorption properties of STK and NTK-10-1, we propose the following mechanism for synergism.

The oxidation of propane on the STK catalyst passes through the intermediate compounds characterized by the absorption bands at 1450 and 1540 cm^{-1} with the participation of lattice oxygen. The reduction of a sample during selective NO reduction by propane and the appearance of nitrogen in the products of thermal desorption from the catalyst surface provides evidence for this conclusion. If the surface of STK is dosed by propane only, propane conversion is observed

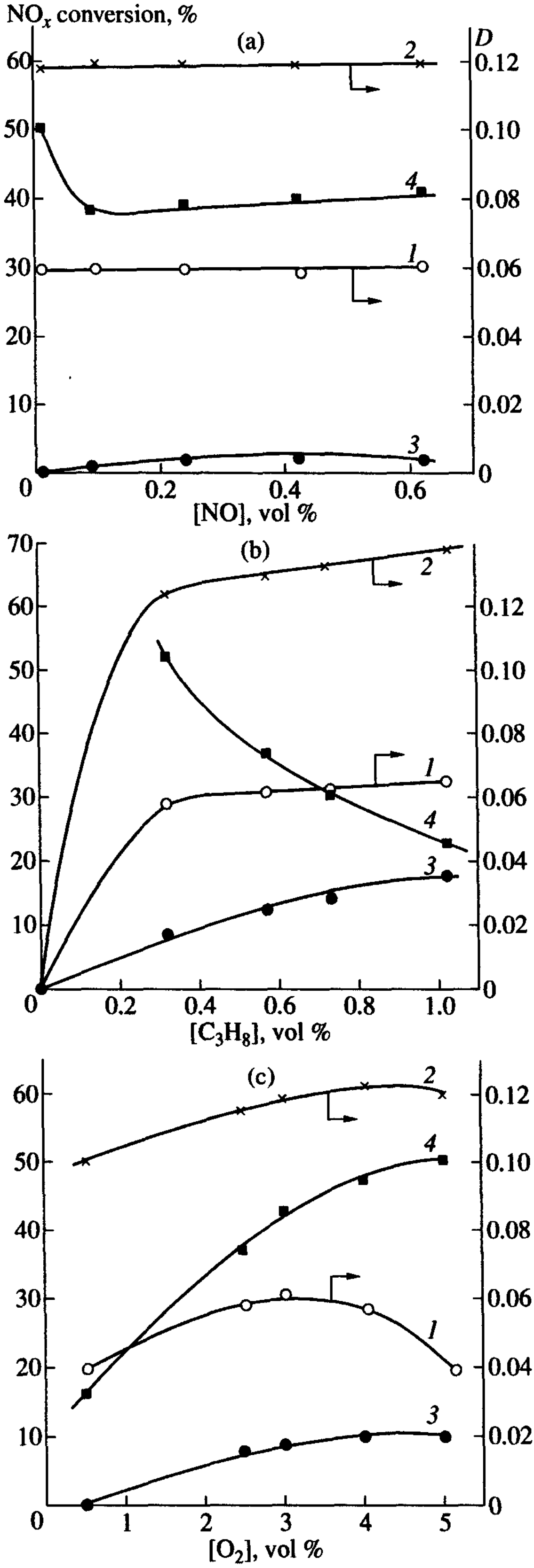

Fig. 4. Absorbance (D) at (*1*) 1450 and (2) 1540 cm^{-1}, (*3*) NO$_x$ conversion, and (*4*) propane conversion vs. (a) NO concentration, (b) propane concentration, and (c) O_2 concentration for the STK catalyst at 300°C.

for a certain period. Therefore, propane can be oxidized by oxygen. The reduction of a sample is not a necessary condition for the reaction of NO reduction and propane oxidation. Rather, this is a consequence of the efficient oxidation of propane.

According to the literature data [9, pp. 137–175], the oxidation of hydrocarbons on oxide catalysts occurs via two routes: complete and partial oxidation. Complete oxidation is usually stipulated by the presence of weakly bound oxygen on the surface. Partial oxidation is usually associated with lattice oxygen. The product of complete oxidation (CO_2) cannot be a reducing agent for NO. It is likely that the product of partial oxidation is formed on the surface of the STK catalyst due to the presence of lattice oxygen. This product is efficient as a reducing agent for NO. According to [10], the absorption bands in the region under discussion appear when acrolein is adsorbed on the CuO, Cr_2O_3, and ZnO surfaces. These oxides are the components of catalysts studied in this work.

Adsorbed NO may react with the product of propane partial oxidation to form N_2 and CO_2. Because the amount of adsorbed NO on the STK surface is small, the excessive product of propane partial oxidation desorbs from STK. Then, this product can adsorb on the NTK-10-1 surface. The concentration of NO adsorbed on this catalyst is high. NO is reduced in the reaction by the product of propane partial oxidation. In other words, the cause of synergism is the reaction of propane with O_2 to form a partial product on one component (STK) of the mechanical binary mixture of the catalysts and the diffusion [11] of this product, which is an efficient reducing agent, from one phase onto another (NTK-10-1) whose surface is covered with activated NO molecules.

In addition to the above-mentioned reactions, the product of propane partial oxidation can further be oxidized by oxygen on both components of the catalytic system. It is clear that synergism is determined by the ratio between the rates of further oxidation on STK and NTK-10-1, diffusion between phases, and the reaction of the partial oxidation product with NO_{ads} on NTK-10-1.

The concentration of propane plays an important role in the process. The conversion of NO and the degree of surface reduction become higher with an increase in the concentration of propane in the reaction flow. This is characteristic of the individual catalysts and of their mechanical mixture.

An increase in the degree of surface reduction of the STK and MK_2 samples is accompanied by an increase in the activity (Fig. 1). An increase in the catalyst activity is probably due to the stronger adsorption of NO on the reduced surface of STK than on the oxidized surface. Indeed, the TPD and mass spectrometric data for the reaction products [2] show that a reduced sample adsorbs much more NO than the oxidized sample. The desorption products contain nitrogen.

These facts enable us to propose the following scheme of the process on the reduced sample. Propane reacts with the catalyst surface and reduces it. The metallic phase of a reduced sample efficiently adsorbs NO, which further dissociates there. Nitrogen molecules are formed by the recombinative desorption of nitrogen atoms. Oxygen atoms participate in the reaction of propane oxidation to form CO_2 in the gas phase. This scheme may be true of both the components of the mixed catalyst as confirmed by the high stationary conversion of NO at 500°C if the reduced catalyst is dosed with the mixture of NO and propane without oxygen.

This scheme explains the high activity of reduced samples and the absence of synergism.

In the general case, both schemes are probably operative. However, under oxidative conditions (the concentration of propane is low, the degree of catalyst surface reduction is low, NO is not adsorbed on the STK catalyst, and a low selectivity to the product of partial oxidation), the activity toward NO reduction is low. In this case, synergism is observed. The reason for that is discussed above.

Under reductive conditions (the concentration of propane is high, the degree of surface reduction is high, NO is adsorbed on STK at high temperatures, selectivity to the partial oxidation product), the activity is high and there is no synergism.

The above conclusions allow us to explain all experimental data:

(1) An increase in the oxygen concentration in the reacting flow results in a change in the selectivity of propane oxidation to CO_2. The activity decreases together with the degree of surface reduction. Phenomena associated with synergism dominate. With a decrease in the concentration of oxygen in the reacting flow, the fraction of weakly bound oxygen responsible for the complete oxidation of propane decreases. The selectivity to the product of partial oxidation increases probably due to this fact.

(2) An increase in the concentration of propane in the reacting flow results in an increase in the concentration of the partial oxidation product. The degree of surface reduction and NO adsorption increase. Therefore, the activity increases and synergism is not observed.

(3) An increase in the concentration of NO in the reacting flow does not influence the process of propane oxidation. Therefore, the conversion of propane and the degree of surface reduction remain unchanged. In this case, the number of converted NO molecules increases in proportion to the NO pressure in the gas phase.

Thus, we proposed the scheme that explains synergism in the system under study and its absence when the conditions for NO reduction change. Further progress in the study of this phenomenon can be achieved by obtaining detailed information on the forms of reactant adsorption, intermediate species, and the pathways for their transformations into the products. The study of the structure of the product of propane partial oxidation is also of interest.

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