Selective NO Reduction by Propane over Commercial Oxide Catalysts and Their Mechanical Mixture: I. Synergistic Effect

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Abstract—In the reaction of NO reduction by propane in excess oxygen, the activity of a binary mixture of commercial oxide catalysts is higher than should be expected if it were proportional to the activities of separate catalyst components. This synergism reveals itself in the fact that the conversion of NO and C_3H_8 is higher when the catalyst is a mechanical mixture than the sum of conversions over separate catalysts, all other conditions being the same. Based on the kinetic and thermal desorption measurements, the experimental conditions are found under which the synergism is observed. A hypothetical mechanism is proposed.

INTRODUCTION

Considerable attention has recently been paid to the development of new catalysts for selective NO_x reduction by hydrocarbons in excess oxygen [1, 2]. Catalytic systems with synergistic properties are of special interest. Some of such composite catalytic systems are mechanical mixtures [3–6]. Table 1 lists some examples of the catalytic systems based on mechanical mixtures with synergistic properties in selective catalytic NO_x reduction by hydrocarbons.

Previous papers [7, 8] reported selective NO reduction by methane and propane over the commercial oxide catalysts STK, Ni–Cr oxide, and NTK-10-1, which do not contain noble metals. Mechanical binary mixtures of these commercial catalysts have synergistic properties: the catalytic activity of the compound sys-tem is higher than the sum of the activities of separate components in the reactions of NO reduction by alkanes (methane and propane) and the complete oxi-dation of alkanes. It is likely that this synergism is rather common [9], although the mechanism of this phenomenon is poorly understood. Therefore, the goal of this work was to study this phenomenon in more detail using a mixture of STK and NTK-10-1 as sample commercial catalysts.

EXPERIMENTAL

The commercial catalysts STK (TU 113-03-317-86), NTK-10-1 (TU 113-01-31-44-87), and their 1:1 mix-ture MK_2 were used in the experiments. The mixture was prepared by accurate (without grinding and press-

Table 1. Synergism found for several composite catalysts, which are mechanical mixtures

Catalytic system and reaction	Catalyst amount, g		Ref.
	separate component	mechanical mixture, component ratio	
Mn_2O_3 + CeZSM-5,	0.5	0.5, 1 : 1	[3]
CeO_2 + CeZSM-5;	0.5	0.5, 1 : 1	
NO + C_3H_6 + O_2			
Cu/NaZSM-5 + HZSM-5;	0.25	0.25, 1 : 1	[4]
NO + C_3H_6 + O_2			
Ag/Al_2O_3 + Al_2O_3;	0.25	0.25,	[5]
NO + C_3H_6 + O_2		0.23 g Al_2O_3 + 0.022 g Ag/Al_2O_3	
Co/Al_2O_3 + HZSM-5;	0.25	0.5,	[6]
NO + CH_4 + O_2		0.25 g Co/Al_2O_3 + 0.25 g HZSM-5	

ing) mixing of the catalysts taken at 0.5 g each. A fraction of 1–2 mm was chosen for our experiments. In the experiments with individual catalysts, a sample (0.5 g) was mixed with quartz particles of the same size. Quartz was taken to ensure the same volume as in the case of mixed samples. Table 2 specifies the composition and some characteristics of the catalysts.

The catalyst activity was studied in a flow-type reactor at a space velocity of 11 250 h^{-1}. Before measurements, the samples were treated in the flow of an inert gas (nitrogen) at 500–600°C. Nitrogen was not additionally purified before use. Oxygen was the main admixture in nitrogen (up to 0.8 vol %). Therefore, the treatment of catalysts in nitrogen was oxidative. All gases were dried with anhydrone.

The conversions of reactants (NO$_x$ and C$_3$H$_8$) were measured at different temperatures at the following compositions of the reaction mixture (in vol %): NO, 0.1; C$_3$H$_8$, 0.5; O$_2$, 2.5; and N$_2$, 96.9, NO, 0.25; C$_3$H$_8$, 0.3; O$_2$, 2.5, and N$_2$, 96.95, or at a constant temperature and different reactant concentrations. The concentrations of reactants and products were measured using Beckman gas analyzers (NO, NO$_2$, CO, and C$_n$H$_m$).

NO adsorption on the catalyst surface was quantitatively studied by temperature-programmed desorption (TPD). The heating rate was 14 K/min, and the carrier gas was nitrogen. In these experiments, the amount of desorbing NO$_x$ molecules was determined with Beckman gas analyzers. To identify other possible desorption products, TPD was coupled with mass spectroscopic analyses.

RESULTS AND DISCUSSION

1. Catalytic Activity Measurements

Figure 1 shows a plot of conversion (X) of nitrogen oxides (Fig. 1a) and propane (Fig. 1b) vs. temperature for the samples under study and the following composition of the mixture (vol %): NO, 0.1; C$_3$H$_8$, 0.5; O$_2$, 2.5; and N$_2$, 96.9. It can be seen that the conversion of NO$_x$ on MK$_2$ becomes noticeable at 350°C.

The data in Fig. 1 show that the sum of NO$_x$ conversions over the separate components is lower than the conversion over the mixture of catalysts. Thus, X_{NO_x}(STK) + X_{NO_x}(NTK-10-1) = 50% at 500°C, while X_{NO_x}(MK$_2$) = 75%. That is, the synergistic effect obviously takes place. Note that a similar effect is observed for propane conversion as well.

Obviously, synergism is due to the difference in the properties of individual catalysts in the reaction under study. Specifically, Yokoyama [3] explained the synergism by a hypothesis according to which one component of the mechanical mixture is favorable for NO$_2$ formation, and the other component converts NO$_2$ into N$_2$ at a higher rate than NO. We tried to identify the differences in the components of individual catalysts using thermal desorption and kinetic studies.

Table 2. Composition and characteristics of commercial catalysts

Catalyst	Composition, wt %		Bulk density, g/cm^3	S_{sp}, m^2/g
STK	Fe$_2$O$_3$	88	1.3–1.6	17.8
	Cr$_2$O$_3$	7		
NTK-10-1	CuO	40		
	ZnO	30	1.3–1.6	9.8
	Al$_2$O$_3$	17		
	NiO	5		
MK$_2$	STK : NTK-10-1 = 1 : 1		–	16.0

Table 3. NO adsorption on the surface of commercial catalysts

Catalyst	NO$_x$ adsorption cm^3/g			
	T_1^{max}	T_2^{max}	T_1^{max}	T_2^{max}
	NO + N$_2$		NO + O$_2$ + N$_2$	
STK	1.2	0	0.93	0
NTK-10-1	1.95	2.7	1.5	1.75
MK$_2$	1.6	1.0	1.16	1.4

2. Temperature-Programmed Desorption

In TPD studies, we paid attention to the interaction of NO with individual catalyst and with their mechanical mixture.

Figure 2 shows the TPD spectra of NO$_x$ for all the samples. Experiments were of two types: after 0.3% NO + N$_2$ adsorption and after 0.3% NO + N$_2$ + 5% O$_2$ adsorption. It can be seen that the TPD spectra for NTK-10-1 and MK$_2$ are characterized by the presence of two peaks (T_1^{max} and T_2^{max}), and the high-temperature peak for NO$_x$ desorption is absent from the spectrum of STK.

These data suggest that adsorbed NO is present in two states on the NTK-10-1 and MK$_2$ surfaces. The maximum of the high-temperature peak is in a temperature region which is characteristic of the selective catalytic reduction of NO by propane (400–450°C).

Upon coadsorption of NO and O$_2$, the overall amount of NO$_x$ molecules desorbed from the surface is the same or somewhat lower than after NO and N$_2$ coadsorption (Table 3). That is, the presence of excess oxygen does not prevent NO adsorption. Therefore, either oxygen weakly adsorbs on the surface or NO and O$_2$ adsorb on different active sites. Note that TPD experiments were carried out with oxidized samples.

The data of TPD coupled with mass spectrometry of the products show that, along with NO desorption, N$_2$ desorbs into the gas phase from the reduced surface of STK by contrast to the oxidized surface. This is evident
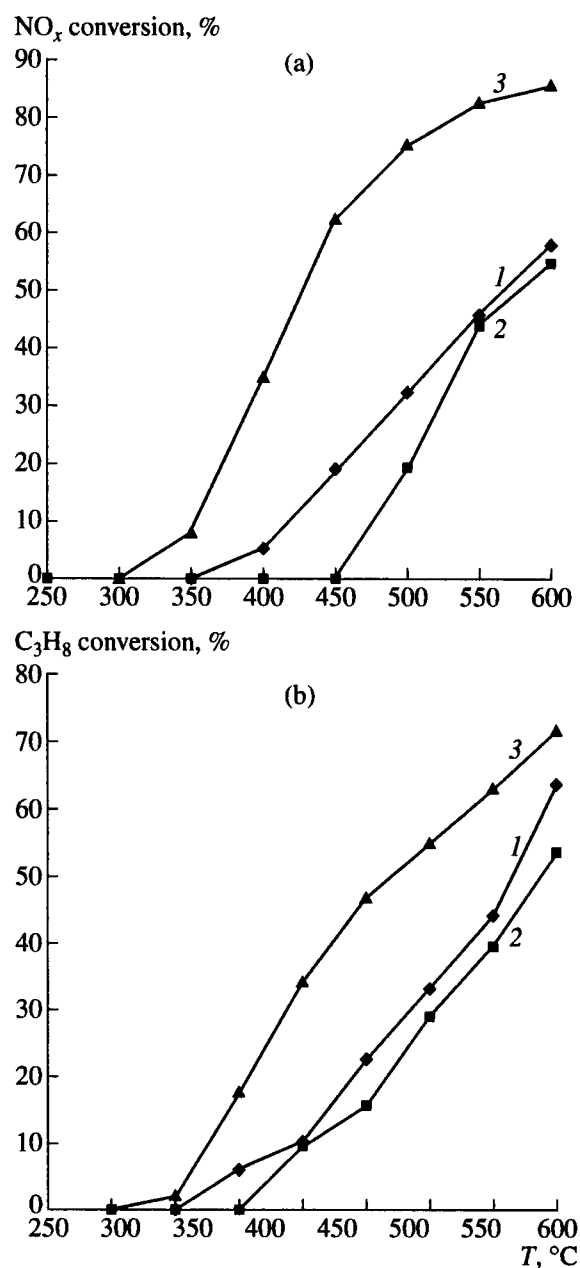
Fig. 1. Conversions of (a) NO_x and (b) C_3H_8 vs. temperature in the reaction $NO + C_3H_8 + O_2$ on (*1*) STK, (*2*) NTK-10-1, and (*3*) MK_2 ($v = 11250$ h^{-1}; [NO] = 0.1 vol %; [C_3H_8] = 0.5 vol %; [O_2] = 2.5 vol %; [N_2] = 96.9%).

from an additional peak in the spectra at 200–400°C (Fig. 3). Oxygen does not desorb from the surface at these temperatures.

3. Dependence of the Rate of NO_x + C_3H_8 + O_2 Reaction on the Composition of the Reactive Flow

The activity of MK_2 depends on the ratio between the concentrations of oxidants ($NO_x + O_2$) and a reducing agent (propane) in the reactive flow. If the reactive

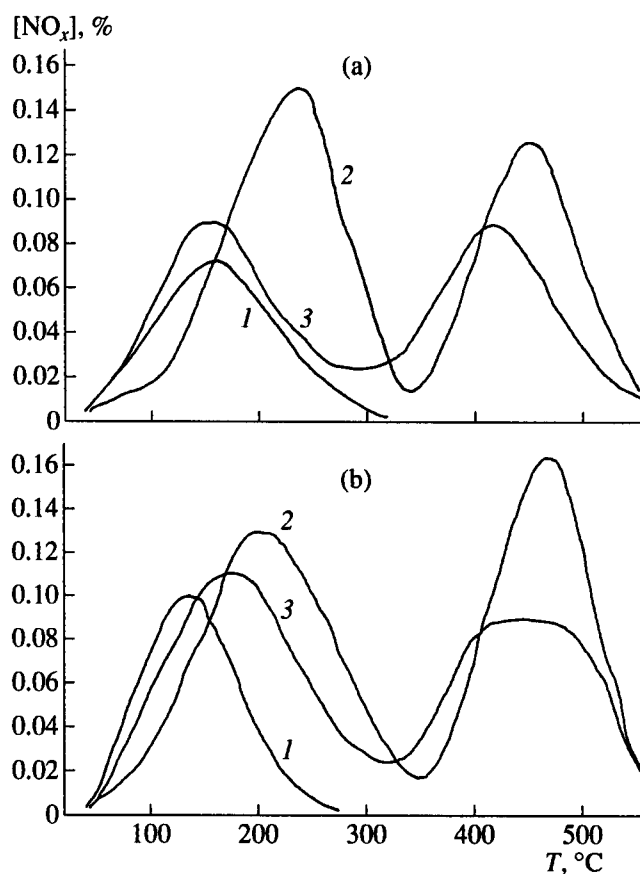**Fig. 2.** TPD spectra of NO_x for (*1*) STK, (*2*) NTK-10-1, and (*3*) MK_2 after the adsorption of the mixture (a) 0.3 vol % NO + N_2 and (b) 0.3 vol % NO + 5 vol % O_2 + N_2.

flow contains excessive oxidants, the concentration of propane becomes a critical factor. Thus, for the 0.25 NO + 0.3 C_3H_8 + 2.5 O_2 mixture (vol %), the activity of MK_2 toward NO_x reduction is zero at 300–600°C, whereas there is some activity at 550°C if the composition is 0.25 NO + 0.4 C_3H_8 + 2.5 O_2. The fact that the activity is very sensitive to the concentration of propane in the reactive flow containing 2.5–3.0 vol % O_2 is supported by the measurements of the reactant conversions for different compositions of the reaction mixture.

3.1. Effect of NO_x concentration. Figure 4 describes the NO_x conversion as a function of the concentration of nitrogen oxides in the reaction mixture, containing 0.5 C_3H_8 + 2.5 O_2 (vol %) at 500°C for STK, NTK-10-1, and MK_2. It can be seen that, for all samples, the conversion of NO_x is insensitive to an increase in the NO concentration in the reactive flow from 0.02 to 0.37 vol %.

3.2. Effect of C_3H_8 concentration. With a decrease in the propane concentration, the conversion of NO_x decreases at any temperature on all the samples, including MK_2. This is observed for the mixtures containing 0.1 NO + 2.5 O_2 (vol %) and 0.25 NO + 2.5 O_2 (vol %).

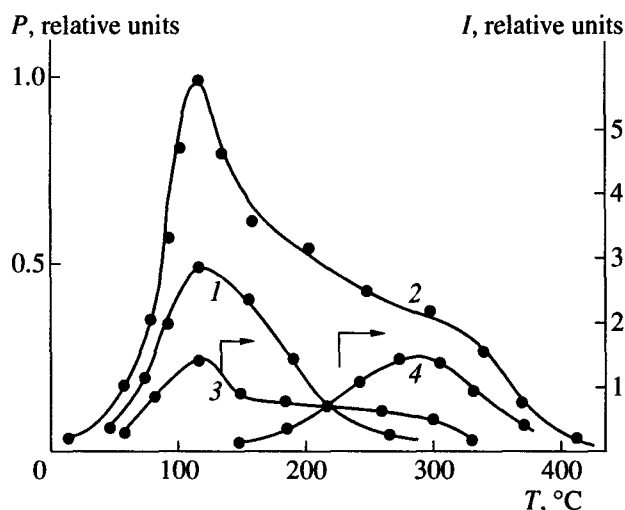P, relative units   I, relative units

Fig. 3. TPD spectra of NO_x for (*1*) oxidized and (*2*) reduced STK with mass spectrometric analysis of the products: (*3*) NO ($m_e = 30$) and (*4*) N_2 ($m_e = 28$) for the reduced sample (*P* is the total pressure in the desorption chamber and *I* is the intensity of a signal from a mass spectrometer).

3.3. Effect of O_2 concentration. Figure 5 and Table 4 illustrate the dependence of reactant conversions on the concentration of O_2 in reacting flows with different NO : C_3H_8 ratios.
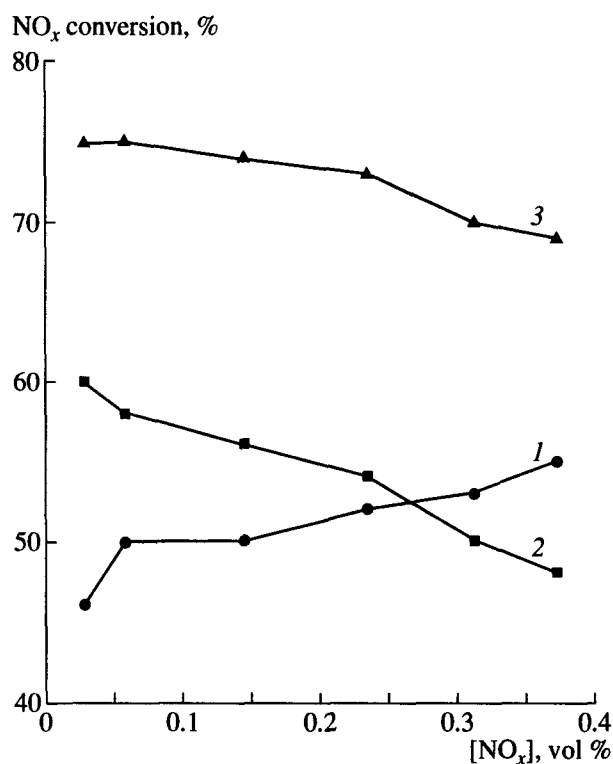
A decrease in X_{NO_x} and an increase in $X_{C_3H_8}$ with an increase in the oxygen concentration in the mixture is common. This is observed at all temperatures at which the catalysts are active. Note that the conversion of NO in a flow with the NO : C_3H_8 ratio lower than 1 is substantially higher than in a flow where this ratio is higher than 1 (Table 4). In the former case, at [O_2] = 4.2 vol % and 500°C, the conversion of NO_x is 48%. In the latter case, there is no conversion even at [O_2] = 2.8 vol % and 550°C.

Thus, the conversion of NO_x is virtually independent of NO concentration in a flow. This means that the rate of NO reduction linearly increases with an increase in the NO concentration in the reaction mixture. An increase in the concentration of propane in a flow leads to a higher NO conversion, whereas an increase in the O_2 concentration lowers it.

Our study showed that, at all changes in the compositions of the reacting flow (Figs. 4 and 5), the conversion of NO_x on MK_2 is always higher than on individual components of this mixture. At the same time, we can see that reactant conversions on individual catalysts are substantially higher in these experiments than in the experiments where we studied the dependence on temperature (Fig. 1), all other conditions being the same. It
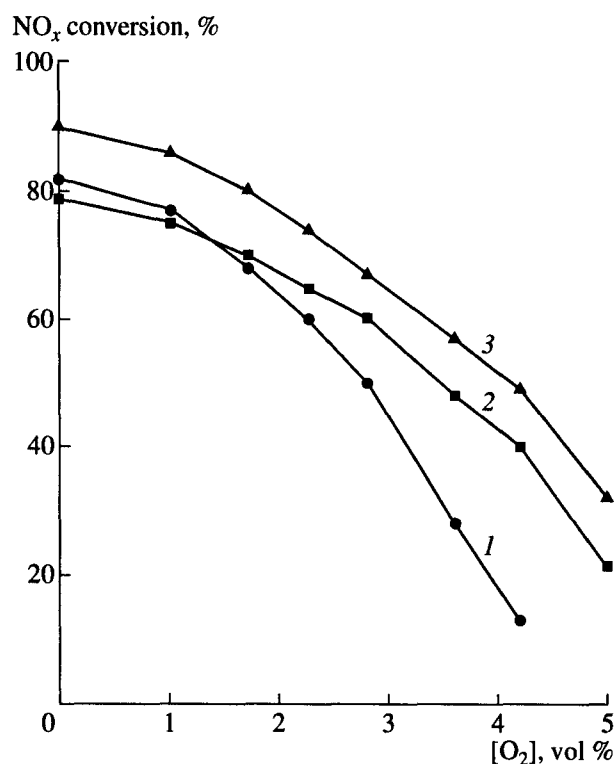

Fig. 4. Conversion of NO_x vs. NO_x concentration in the reaction NO + C_3H_8 + O_2 on (*1*) STK, (*2*) NTK-10-1, and (*3*) MK_2 (v = 11250 h^{-1}; T = 500°C; [C_3H_8] = 0.5 vol %, [O_2] = 2.5 vol %, and N_2 completes the overall concentration to 100%).

Fig. 5. Conversion of NO_x vs. O_2 concentration in the reaction NO + C_3H_8 + O_2 on (*1*) STK, (*2*) NTK-10-1, and (*3*) MK_2 (v = 11250 h^{-1}; T = 500°C; [NO] = 0.1 vol %, [C_3H_8] = 0.5 vol %, and N_2 completes the overall concentration to 100%).

Table 4. Conversions of NO_x and propane in the reaction $NO + C_3H_8 + O_2$ on MK_2 depending on the concentration of O_2 in the reaction mixtures with different [NO] : [C_3H_8] ratios at $v = 11250$ h^{-1}

T, °C	O_2 concentration, vol %						
	0	1.0	1.7	2.3	2.8	3.6	4.2
[NO] = 0.1 vol %, [C_3H_8] = 0.5 vol %							
NO conversion, vol %							
300	0	5	7	5	5	5	5
400	37	24	12	0	0	0	0
500	89	86	81	76	65	55	48
C_3H_8 conversion, vol %							
300	5	7	7	10	10	10	10
400	13	16	30	38	45	54	56
500	24	23	36	47	57	65	73
[NO] = 0.25 vol %, [C_3H_8] = 0.25 vol %							
NO conversion, vol %							
350	7	5	2	0	0	0	0
450	58	40	16	2	0	0	0
550	85	65	21	6	0	0	0
C_3H_8 conversion, vol %							
350	7	17	31	38	45	51	51
450	27	38	62	77	83	88	88
550	46	52	67	77	78	78	78

is clear that at high reactant conversions on individual catalysts, we cannot draw any conclusions on the existence of synergism in the MK_2 system. Therefore, a question arises as to the reason for the high activities of individual catalysts under certain experimental conditions.

In our opinion, this can be explained if we assume that kinetic data were obtained for the fresh reduced samples. Special measurements show that a sample is indeed reduced for ~15 min in a flow containing only NO and propane. Let us consider as an example the dependence of reactant conversions on the concentrations of oxygen in the flow (Fig. 5, Table 4). Even if a sample is preoxidized, first values of conversion are measured when oxygen is absent from the flow. The time of measurement is ~15 min. Therefore, measurements correspond to a reduced sample. The same reasoning is true of all of the kinetic runs.

Thus, the samples in the reduced state are more active than in the oxidized state, and we should not expect synergism in the case of reduced samples. The effect of synergism found for the mechanical mixture of commercial catalysts is most probable for the oxidized samples. The behavior of individual catalysts in NO adsorption is radically different. This difference allows us to propose two hypotheses, which describe the effect of synergism.

The first hypothesis is the same as in the literature: one component (NTK-10-1) of the mechanical mixture, which is more capable of NO adsorption (Table 3), readily produces NO_2, which 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 is either rapidly oxidized by molecular oxygen on the same component or migrates to the second component (NTK-10-1) via the gas phase to undergo further oxidation by NO molecules. In this case, synergism should be determined by the ratio of the rates of the further oxidation of the activated hydrocarbon fragment and its migration onto NTK-10-1.

It is clear that the detailed mechanism of synergism can be determined in the studies of surface species, which are formed under the reaction conditions and the pathways for species transformations.

ACKNOWLEDGMENTS

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