Kinetics and Catalysis, Vol. 44, No. 3, 2003, pp. 379–400. Translated from Kinetika i Kataliz, Vol. 44, No. 3, 2003, pp. 412–435.
Original Russian Text Copyright © 2003 by Sadykov, Lunin, Matyshak, Paukshtis, Rozovskii, Bulgakov, Ross.

VI RUSSIAN CONFERENCE ON CATALYTIC REACTION MECHANISMS (Moscow, October 1–5, 2002)

The Reaction Mechanism of Selective Catalytic Reduction of Nitrogen Oxides by Hydrocarbons in Excess Oxygen: Intermediates, Their Reactivity, and Routes of Transformation

V. A. Sadykov*, V. V. Lunin, V. A. Matyshak***, E. A. Paukshtis*,
A. Ya. Rozovskii****, N. N. Bulgakov*, and J. R. H. Ross*******

** Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
*** Department of Chemistry, Moscow State University, Moscow, 117234 Russia*
**** Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117334 Russia*
***** Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 117912 Russia*
****** University of Limerick, Limerick, Ireland*

Received November 12, 2002

Abstract—The main features of the mechanism of selective reduction of nitrogen oxides by hydrocarbons (methane, propane, and propylene) in excess oxygen catalyzed by systems containing transition metal cations are considered. A combination of steady-state and non-steady-state kinetic studies, *in situ* Fourier-transform infrared (FTIR) spectroscopy, temperature-programmed desorption, and theoretical analysis of bond strengths and spectral data for adsorption complexes made it possible to determine reliably that surface nitrate complexes are key intermediates at real temperatures of catalysis. The rate-limiting step in these reactions includes the interaction of these complexes with hydrocarbons or their activated forms. Factors are considered that determine the structure, bond strength, and routes of nitrate complexes transformations under the action of hydrocarbons. Mechanistic schemes are proposed for the reaction of various types of hydrocarbons in which the determining role belongs to the formation of organic nitro compounds in a rate-limiting step. Their further fast transformation with the participation of surface acid sites resulting in the formation of ammonia, which is a highly efficient reducing agent, though not limiting the whole process, but determines nevertheless both the selectivity to the target product, molecular nitrogen, and the selectivity of hydrocarbon consumption for nitrogen oxide reduction.

INTRODUCTION

Currently, the reaction of selective catalytic reduction (SCR) of nitrogen oxides by hydrocarbons, which was discovered independently by Iwamoto *et al.* [1, 2] and Held *et al.* [3, 4] about ten years ago, remains one of the most intensively studied processes worldwide. This interest is due to its potential application for the nitrogen oxide removal from exhaust gases containing excess oxygen (diesel engine exhaust, power plant flue gases, etc.). Various classes of solid catalysts (simple and mixed oxides, including transition metal oxides, zeolites, supported platinum group metals, etc.) and various types of hydrocarbons (alkanes and alkenes) and their derivatives (alcohols, ethers, and others) were tested in these processes. However, the mechanism of these reactions remains debatable despite numerous studies described in hundreds of papers and reviews [5–11].

The main features of the SCR mechanism were proposed already in early papers. These were based on general consideration, analogies with other types of reactions of nitrogen oxide (both homogeneous and heterogeneous), and qualitative IR data. Proceeding from the type of the rate-limiting step, the mechanisms can be divided into three groups.

1. Activated adsorbed hydrocarbons (HC*), including radicals, coke, and oxygen-containing compounds selectively interact with a nitrogen oxide; N_2 is formed via a sequence of intermediate compounds [12–19]:

$$HC + O_2 \text{ (or } NO_x) \longrightarrow HC^* + CO_x + H_2O,$$

$$HC^* + NO_x \longrightarrow N_2 + CO_x + H_2O.$$

2. Nitric oxide is oxidized to nitrogen dioxide and/or surface nitrite–nitrate complexes, which are selectively reduced by hydrocarbons to molecular nitrogen, including the possible formation of organic nitro compounds [20–27]:

$$NO + O_2 \longrightarrow NO_x,$$

$$NO_x + HC \longrightarrow N_2 + CO_x + H_2O.$$

3. Nitric oxide dissociates on reduced surface sites yielding molecular nitrogen and chemisorbed oxygen, which results in the surface reoxidation. A hydrocarbon removes this oxygen and reduces the surface. The

hydrocarbon fragments (coke) chemisorbed on the surface may favor nitrogen oxide dissociation [28–31]:

$$2NO \longrightarrow N_2 + 2O(ads),$$

$$2O(ads) + HC \longrightarrow CO_x + H_2O.$$

The most important problem, which should be reflected in the mechanistic scheme, is the nature of the selective action of catalysts in these reactions. Indeed, when oxygen is in great (more than two orders of magnitude) excess over nitrogen oxides in the reaction mixture, only the high selectivity of the catalysts makes it possible to overcome the unfavorable effect of the high rates of oxygen interaction with hydrocarbons, their activated fragments, and derivatives. It is well known that homogeneous gas-phase reactions in the mixtures of oxygen, hydrocarbon, and nitrogen oxides do not lead to noticeable conversions of nitrogen oxides to molecular nitrogen, although this process is accompanied by the formation of organic nitro compounds. However, usually this problem is not taken into account when constructing a hypothetical mechanism, although this is very important when considering schemes of an oxidation–reduction type.

Another problem is associated with the kinetic justification of hypothetical schemes. Although in a number of cited works, some intermediates were identified (nitrite–nitrate complexes, isocyanates, nitriles, etc.) and corresponding absorption bands were shown to change under the action of gas-phase components, however, the rates of the corresponding surface reactions at real temperatures of catalysis and low concentrations of reactants have not been measured. At the same time, only comparison of the rates of surface reactions with the rate of the catalytic reaction measured under steady-state or non-steady state conditions makes it possible to decide whether the corresponding surface compound is an intermediate, a by-product, or a spectator. Because the schemes proposed were poorly justified, the viewpoint was very popular that several reaction routes may occur on the same catalyst [6, 14].

This paper summarizes the main results of the studies of SCR of nitrogen oxides by light hydrocarbons (methane, propane, and propylene) by a research team consisting of several groups both in Russia and abroad. Original data have been published in periodicals [32–49], generalized in two Cand. Sci. dissertations [50, 51], and reported at international conferences [52–56].

The principal systems used were copper- and cobalt-exchanged ZSM-5 zeolites with an exchange ratio varying broadly [32–40, 47, 50]. Other systems were catalysts based on highly dispersed alumina [36, 42, 48, 49], zirconia in various modifications [41, 43, 51, 56], and pillared clays (nanosized particles of zirconium dioxide fixed between aluminosilicate layers of natural montmorillonite clays), both clean and with active components supported on them, such as copper and cobalt cations, including those promoted with platinum or silver [44, 45, 51, 55].

Details of the sample preparation procedure, their characterization, and steady-state and non-steady-state kinetic experiments (including those with *in situ* IR studies) were reported in [32–49]. We will present them here only when they are needed to illustrate specific results.

Our main idea in developing approaches to elucidate the mechanism of reactions under consideration was based on the assumption that only strongly bound surface complexes containing nitrogen atoms may provide selective conversion of nitrogen oxides to molecular nitrogen in excess oxygen. This assumption is evident from a simple comparison of the number of collisions of nitrogen oxide and oxygen molecules with the surface in the case of great oxygen excess (vide supru). Another favorable argument is the volcano-shaped temperature dependence of the SCR rate, which was observed for the catalysts used in this reaction. This is typical of a reaction with strongly bound surface compounds [57]. Indeed, these compounds should be thermally activated to be reactive, and this results in a drastic increase in the reaction rate with temperature up to a maximum. At high temperatures (above T_{max}), these compounds desorb from the catalyst surface and the route with their participation becomes ineffective. The nitrate–nitrite complexes can play the role of such key complexes in reactions with the participation of nitrogen oxides.

Therefore, the methodology taken as a basis for the determination of the reaction mechanism involved the following stages:

(1) Determination of the route for the formation, composition, bonding strength, and thermal stability of strongly bound nitrate–nitrite complexes using such methods as IR spectroscopy (including experiments with isotopic substitution of oxygen and nitrogen atoms), TPD, and the theoretical analysis of the bonding strengths and vibrational characteristics of nitrate–nitrite complexes for adsorption sites of various types.

(2) The study of the routes of the thermal decomposition of the bound nitrate–nitrite complexes and their transformations under the action of hydrocarbons using the methods of *in situ* IR spectroscopy and pulse titration.

(3) Estimating the rates of separate steps and their comparison to the rate of the catalytic reaction.

(4) Study of the reactivity and routes of transformation of possible products of the nitrite–nitrate complexes reduction containing nitrogen and carbon atoms. Nitromethane [40, 47] and acetonitrile [38] were used as models of intermediate compounds.

RESULTS AND DISCUSSION

1. Identification and Classification of Nitrite–Nitrate Complexes

IR spectroscopy is a direct method for identifying surface complexes, including nitrate–nitrite species.

Table 1. Spectral characteristics of nitrite and nitrate ions in solutions and in the composition of surface complexes [77, 78]

Structure	Frequencies, cm^{-1}				
	ν_1	ν_2	ν_3		ν_4
NO_3^- (aqueous solution)	1047.8	838.5	1372.3		711.7
M–O–NO_2 (monodentate nitrate)	1035–970	–	1530–1480	1290–1250	–
M–O_2NO (bidentate nitrate)	1040–1010	–	1565–1500	1300–1260	–
$(M–O)_2$=NO (bridging nitrate)	1030–1000	–	1650–1600	1225–1170	–
NO_2 (gas)	1355.9	756.8	1665.5		–
NO_2^- (aqueous solution)	750	1182.2	1320		–
$(M–O)_2$=N (bridging nitrite)	–	–	1220–1205		–
M–NO_2 (nitro compounds)	1350–1315	–	1440–1335		–
M–O–NO (monodentate nitrite)	1065–1050	–	1470–1450		–
M–O–N(O)–M (chelating nitro complex)	1260–1180	–	1520–1390		–

Substantial experimental data have been accumulated [58–77], which makes it possible to draw certain conclusions about the nature of such complexes and the specific features of their structure depending on the type of surface sites. The problem of interpretation is complicated by the fact that all types of adsorption NO_x complexes (nitrites, nitrates, nitro complexes, and adsorbed NO_2) may give absorption bands in the 1650–1500 cm^{-1} frequencies range [77]. In many cases, for instance, in the case of zeolites, the inherent absorption of the sample prevents the study of the low-frequency range of the spectrum, which makes the assignment of IR bands difficult.

For the most strongly bound surface complexes of nitrogen oxides (nitrates), the classification of IR bands is based on the scheme proposed in the classical paper by Pozdnyakov and Filimonov [78], which proceeds from the analysis of spectra of nitrate salts and complexes containing these anions. For the free nitrate ion with D_{3h} symmetry, there are four vibrational modes (Table 1). One of them, ν_1, is symmetric and is only observed in Raman spectra. The vibration ν_3 for the surface complexes splits into two components due to symmetry breaking, and the positions of these components depend on the structure of a complex (Table 1). The value of splitting increases when one switches from monodentate to bidentate and bridging complexes. It is assumed that, for the surface nitrate complexes, vibration ν_1 also becomes visible in IR spectra, and its position is believed to depend only slightly on the nature of the complex and adsorption sites. It is also assumed that the positions of low-frequency modes ν_2 and ν_4 for the surface complex remains constant (below 1000 cm^{-1}) and they are superposed/superimposed on the oxide lattice modes and become nonobservable. This scheme makes it possible to identify various types of nitrate complexes for systems that are transparent in the range down to 1000 cm^{-1}. As an example, Fig. 1 shows sample diffuse-reflectance spectra of adsorbed complexes of nitrogen oxides on dispersed tetragonal zirconia [51, 56]. Vibrations in the region 1500–1600 cm^{-1} are assigned to the high-frequency component ν_3 for nitrate complexes of three types (Table 2), whereas wide absorption near 1200 cm^{-1} is assigned to the low-frequency component of this vibration.

However, the range 1500–1600 cm^{-1} may also contain vibrations corresponding to the nitrite ions and adsorbed nitrogen dioxide (Table 1), which complicates absorption band assignment.

Hadjiivanov [58] proposed the use of high-frequency combination modes and overtones as additional criteria for the assignment of absorption bands in the range 1500–1600 cm^{-1} to nitrate complexes of various types. Using these criteria, it was possible to show that absorption bands at 1600 cm^{-1} for the FeZSM-5 system [58] and at 1624 cm^{-1} for the CuZSM-5 system [76] indeed correspond to nitrate rather than nitrite complexes. For zirconia, the composite vibration at 2614 cm^{-1} [58] was assigned to bridging nitrates. Absorption in the region of 1300 cm^{-1}, whose intensity decreases when oxygen is added [51], corresponds to nitrite complexes.

Kantcheva and Ciftlikli [66] proposed a somewhat different scheme for interpreting low-intensity high-frequency absorption bands observed upon nitrogen oxide adsorption on zirconia (see also Fig. 1). Thus, the absorption band at ~2240 cm^{-1} was assigned to the composite vibration $\nu_{as}(NO_2) + \nu_s(NO_2)$ for bridging nitrates. Absorption bands at 1980 and 1900–1905 cm^{-1}, which are stable upon evacuation at room temperature and under the action of oxygen, were assigned to the same complexes. They correspond to the composite vibration $\nu_s(NO_2) + \delta(ONO)$. For bidentate nitrate complexes, the absorption band in the region of 2580–2600 cm^{-1} corresponds to the composite vibration $\nu(N{=}O) + \nu_s(NO_2)$, the band at 2430–2470 cm^{-1} corre-

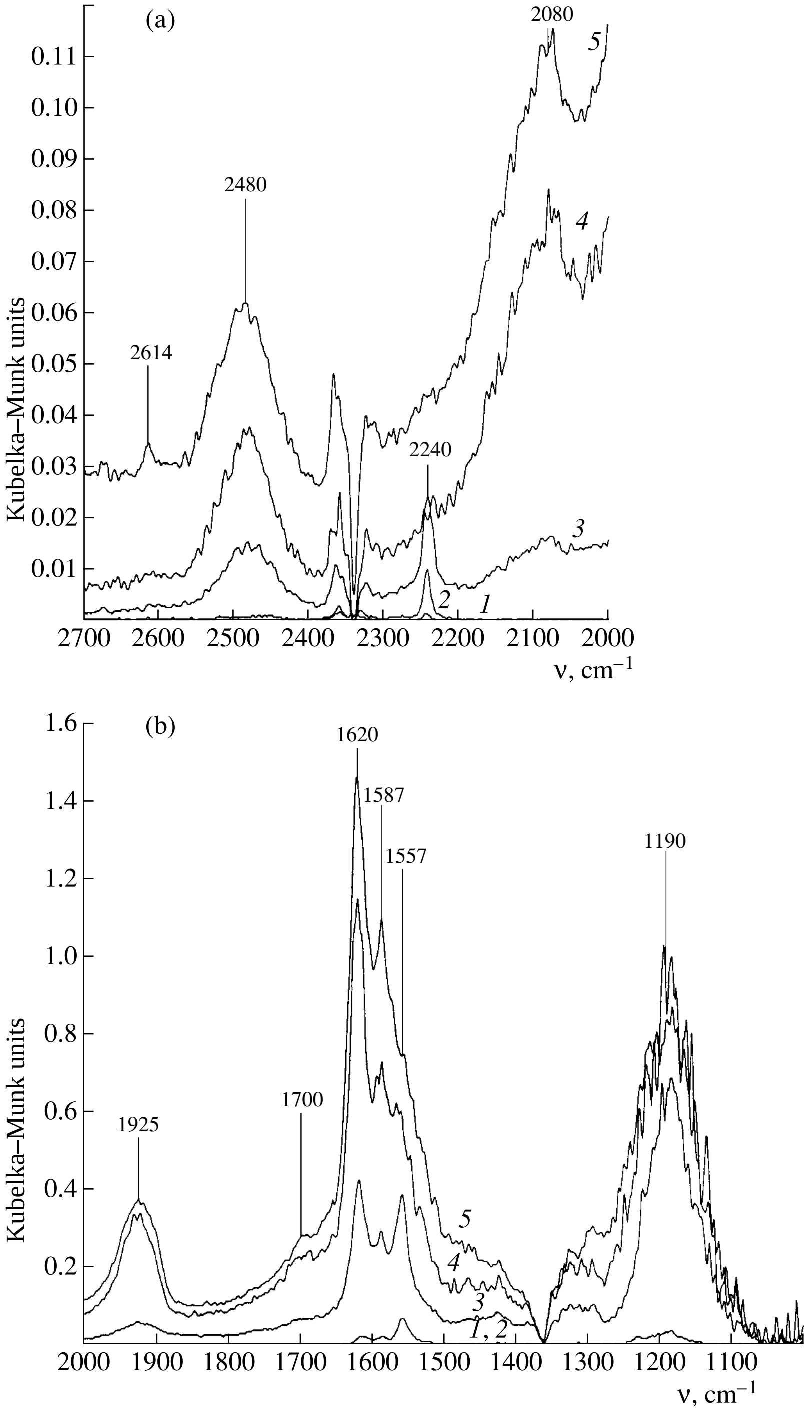

Fig. 1. Diffuse-reflectance IR spectra in the process of interaction of NO from the flow of 0.46% NO/N_2 with ZrO_2 at 20°C for (*1*) 5, (*2*) 7, (*3*) 14, (*4*) 17, and (*5*) 24 min [51]. The temperature of ZrO_2 calculation in air is 500°C with preliminary treatment in N_2 at 500°C for 20 min. The base line is the spectrum of the sample before NO adsorption.

sponds to the overtone $2\nu_{as}(NO_2)$, the bands at 2295 and 2250 cm^{-1} correspond to the composite vibration $\nu_{as}(NO_2) + \nu_s(NO_2)$, and the band at 1755 (1780) cm^{-1} corresponds to the composite vibration $\nu_s(NO_2)$ + δ(OHO). As follows from Fig. 1a, in our experiments, we also observed these low-intensity bands, which points to the formation of bidentate and bridging nitrate complexes on the surface of dispersed zirconia.

A nonsymbate change in the intensity of the components of the spectra in the course of adsorption, evacuation, and oxygen addition usually serves as an addi-

Table 2. Assignment of IR bands in the region of absorption of nitrite–nitrate complexes [35, 51]

System	Position of the absorption band, cm^{-1}	Isotopic shift*, cm^{-1}	Assignment
CuZSM-5 Si/Al = 25, 2.8% Cu [35]	1630	80	Bridging or bidentate nitrate
	1570	70	The same
	1510	60	Nitrite
	1244, 1279 (weak)	–	Nitrite and/or nitrate
CoZSM-5 Si/Al = 12, 2.3% Co [35]	1610	60	Nitrite
	1600	50	Nitrite
	1575, 1450	70	Bridging or bidentate nitrate
	1353, 1265 (weak)	–	Nitrite and/or nitrate
Dispersed ZrO_2 (calcined at 500°C, tetragonal modification) [51]	1600–1612	–	Bridging nitrate
	1590–1584	–	Bidentate nitrate
	1562–1556	–	Monodentate nitrate
	1290–1244	–	Nitrate complexes
	1300–1360	–	Nitrite complexes
	1190	–	Nitrite complexes

* Corresponds to complete substitution of ^{15}N and ^{18}O for all nitrogen and oxygen atoms.

tional criterion for the assignment of bands in the range 1500–1600 cm^{-1} to the nitrate complexes of various types [58–77]. On this basis, the conclusion is drawn that all superimposed components of the complex band in this range of frequencies correspond to different species, and this agrees with the traditional assignment (Table 1). However, it was shown for CuZSM-5 [76] that the intensities of components at 1624 and 1562 cm^{-1} change in parallel. Therefore, these bands belong to a nitrate complex of the same type. This prejudices the assumption that only high-frequency component of the mode ν_3 can be observed in the range 1500–1600 cm^{-1}.

This fact requires theoretical analysis of vibrational spectra of adsorption complexes as a condition of their assignment. Feasibility of such an analysis has been already demonstrated by Dement'ev and Gribov [79] using algorithms based upon purely kinematic approach. We carried out calculations using those algorithms adapted to modern computers for nitrite and nitrate complexes of various types stabilized on small clusters of copper and cobalt cations in zeolite ZSM-5 channels. According to EXAFS data [35] for the systems with a high exchange degree, the coordination of copper was assumed to be square-planar and the coordination of cobalt was assumed to be tetrahedral. Cations in such clusters are believed to be coordinated by the extralattice oxygen atoms. Terminal forms of oxygen are located at the boundary cations of the cluster, whereas the bridging forms of oxygen bind cations in the cluster. As a result of such a difference in the oxygen atoms involved in a cluster, there may be various structures of bidentate and bridging nitrate–nitrite complexes. Thus, for the clusters involving two cations of the transition metal, a nitrogen atom from the N=O fragment of the nitrate complex can bind to two terminal oxygen atoms (type A), one bridging and one terminal atom (type B), and two bridging oxygen atoms (type C).

As follows from the results of calculations (Table 3), upon the formation of a bond with the surface, at least one of the low-frequency vibrational modes shifts to the range above 1000 cm^{-1}. The results of calculations qualitatively agree with the traditional scheme of mode ν_3 splitting for various types of nitrate complexes and with the typical positions of absorption bands for the nitrate complexes. In the general case, the absorption near 1200 cm^{-1} mostly corresponds to nitrate complexes. This agrees well with the conclusions drawn in [77, 78]. The appearance of bridging oxygen atoms in the composition of nitrate complexes leads to an increase in the frequency of the N=O vibration up to the values corresponding to nitrosyl complexes. A physical reason for such a phenomenon may be the formation of relatively weak bonds between nitrogen atoms and bridging oxygen atoms, which results in a slight disturbance of the N=O vibration.

The calculation also showed for the bridging and bidentate nitrate complexes that, when all oxygen and nitrogen atoms are substituted by heavier isotopes, the shift of the highest frequency mode corresponding mostly to the N=O stretching is about 70 cm^{-1}, which is close to the isotopic shift for nitrosyl complexes (80 cm^{-1}) [35]. At the same time, for nitrite complexes, the isotopic shift for the highest-frequency band is usually smaller than 60 cm^{-1}. This result was used in identifying the nature of nitrite–nitrate complexes on cation-exchanged zeolites [34, 35] (Table 2). Judging by from the value of the isotopic shift for a copper-exchanged zeolite, the band at 1630 cm^{-1} was assigned to bidentate or bridging nitrates. For cobalt-exchanged

Table 3. Spectral characteristics of nitrite and nitrate surface complexes calculated in the framework of kinematic approximation for the Cu_2O_6 and Co_2O_7 clusters in zeolite ZSM-5 channels*

Structure	Frequencies, cm^{-1}			
	ν_1	ν_2	ν_3	ν_4
Cu–O–NO_2 (monodentate nitrate)	1096	1325	1392	1429
	(1036)	(1255)	(1332)	(1357)
Co–O–NO_2 (monodentate nitrate)	1096	1280	1392	1429
	(1035)	(1212)	(1330)	(1356)
Cu–O_2NO (bidentate nitrate A)	1050	1248	1410	1472
	(997)	(1186)	(1341)	(1357)
Cu–O_2NO (bridging nitrate B)	1229	1427	1483	1583
	(1165)	(1354)	(1411)	(1507)
Cu–O_2NO (bridging nitrate C)	1202	1238	1625	1785
Co–O_2NO (bidentate nitrate A)	1148	1370	1448	1458
	(1089)	(1292)	(1386)	(1389)
Co–O_2NO (bridging nitrate B)	1240	1361	1454	1896
	(1173)	(1294)	(1380)	(1813)
$(Cu–O)_2$=N (bridging nitrite)	1152	1549	1763	–
	(1087)	(1486)	(1687)	–
Cu–O–NO (monodentate nitrite, ∠180°)	1079	1591	1717	–
	(1032)	(1520)	(1645)	–
Co–O–NO (monodentate nitrite, ∠180°)	1054	1606	1727	–
	(1001)	(1535)	(1655)	–
$(Cu–O)_2$=N (bridging nitrite)	1005	1463	1556	–
	(959)	(1402)	(1490)	–
Cu–O–NO (monodentate nitrite, ∠180°)	978	1513	1530	–
Cu–O–NO (monodentate nitrite, ∠134°30′)	995	1435	1557	–
Cu–O–NO (monodentate nitrite, ∠109°)	1026	1367	1559	–
	(990)	(1306)	(1492)	–
Co–O–NO (monodentate nitrite, ∠109°)	1008	1343	1536	–
	(962)	(1282)	(1470)	–

* The values of frequencies are arranged in increasing order. The values in parentheses correspond to the complexes with the complete substitution of ^{15}N and ^{18}O for all nitrogen and oxygen atoms.

zeolite, this assignment was done for the band at 1575 cm^{-1}.

2. Thermal Stability and Routes of the Nitrite–Nitrate Complexes Decomposition

A combination of the temperature-programmed desorption and *in situ* IR spectroscopy made it possible to show reliably that the thermal stability of nitrite complexes is lower than that of nitrate complexes [35, 50, 51]. Figure 2 shows an example illustrating that, for the dispersed tetragonal zirconia, the TPD peak for NO_x in the range 200–300°C correlates with a decrease in the intensity of the absorption band at ~1200 cm^{-1} corresponding to nitrite complexes, which allows an unequivocal assignment of the indicated maximum. It is noticeable that nitrites decompose yielding mostly NO in this case. The decomposition of nitrites is accompanied by an increase in the intensity of two bands at 1545 and 1240 cm^{-1}, which correspond to monodentate nitrates. Therefore, some nitrite complexes transform into nitrate complexes in the course of thermal activation probably via the disproportionation reaction. The peak of NO evolution at ~500°C most likely corresponds to the decomposition of nitrate complexes, whose absorption band intensities decrease in a given temperature interval. As shown by mass spectrometry [80], in the course of nitrate complex decomposition, the oxygen peak is observed together with the peak of NO and has the same temperature of the maximum. Note that the positions of NO_x TPD peaks for highly dispersed ZrO_2 sample considered here (mostly

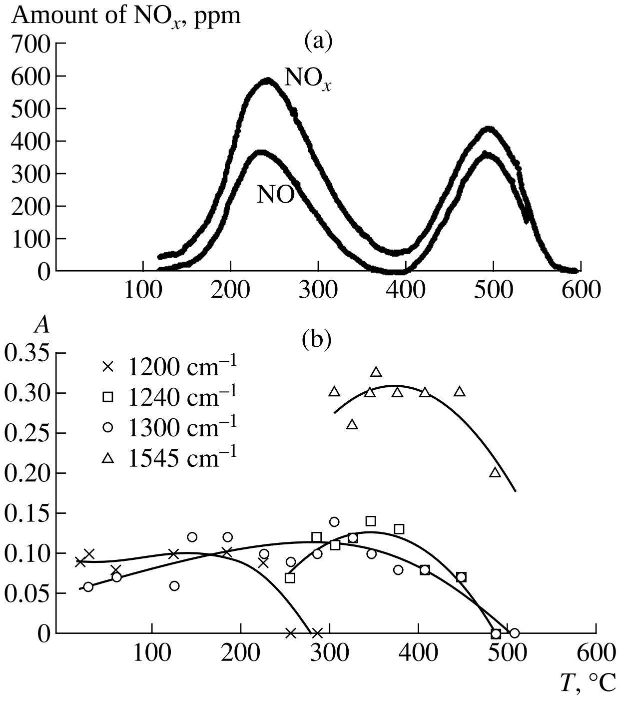

Fig. 2. (a) Thermal desorption spectra of nitrogen oxides on ZrO_2 after NO adsorption at 20°C from a flow of 0.20% NO/N_2. The heating rate was 5 K/min. (b) Changes in the absorption band intensities of the corresponding nitrite–nitrate complexes. Calcination and treatment conditions are indicated in the caption to Fig. 1.

consisting of the tetragonal phase with the monoclinic phase admixed [51]) and the predominant evolution of NO generally correspond to TPD data for dispersed samples of tetragonal ZrO_2 partially stabilized by calcium, strontium, or barium cations [32]. At the same time, for the monoclinic ZrO_2 sample where bridging nitrate complexes dominate, a somewhat different pattern was observed: both nitrite and nitrate complexes decomposed with the formation of mostly NO_2, and the maximum was shifted to the region of lower (by 50 K) temperatures [51]. Moreover, for monoclinic ZrO_2, nitrosyl complexes were also observed (the band at 2020 cm^{-1}), which were absent from the sample with a tetragonal structure. This specific feature probably reflects the effect of the atomic structure of the surface (the coordinative unsaturation of zirconium cations and oxygen anions), which is different for the ZrO_2 samples with different phase compositions [81]. The weaker bond of bridging nitrate complexes (the lower desorption temperature) compared to monodentate complexes detected in [51] is also worth mentioning. This fact and analogous observations for the lanthanum oxide–alumina system [65] led us to conclude that bridging nitrate complexes are not always the most stable. The maximal thermal stability should probably be expected in the case of bridging nitrate complexes only if the characteristics (the coordinative unsaturation) of oxygen atoms of the surface with which a nitrogen atom of

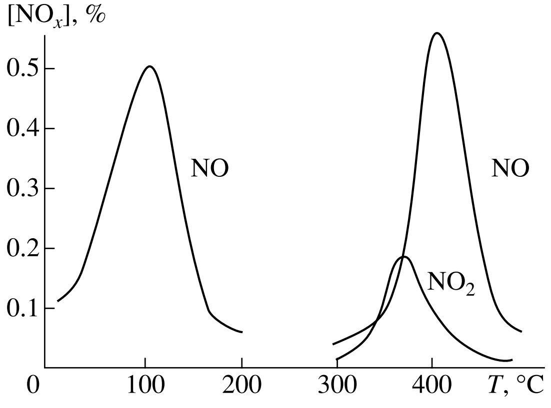

Fig. 3. Thermal desorption spectra of nitrogen oxides on 2.6% CuZSM-5. The heating rate is 15 K/min, NO adsorption is from a flow of 1% NO/He at room temperature. Preliminary treatment was carried out at 400°C in a flow of O_2 [35].

the nitrate complex is bound by one (monodentate complex) or two (bridging or bidentate complex) bonds are identical. As shown in [32], the bonding strength of nitrate complexes (the temperature of the desorption maximum) changes over wide limits depending on the nature of the adsorbent (an oxide or a cation-exchanged zeolite) and on finer parameters: the characteristics of defect (real) structures of the surface, which in turn depends on the modifying additive (e.g., the nature of the stabilizing alkaline-earth cation (Ca, Sr, or Ba) introduced into ZrO_2).

For cation-exchanged zeolites, the exchange level, which determines the degree of cation clustering, affects the bonding strength of nitrite–nitrate complexes and the form of their adsorption. In the general case, nitrate complexes decompose on copper- and cobalt-exchanged zeolites at higher temperatures than on ZrO_2, which correlates with a lower effective charge of cations [32, 46, 50, 51]. Figure 3 shows typical TPD spectra of nitrogen oxides for CuZSM-5 with a high copper loading (2.6 wt %) [35]. The low-temperature peak of NO in this case corresponds to the decomposition of nitrosyl complexes and the high-temperature peak corresponds to the decomposition of nitrate complexes. The low-temperature part of the NO peak at 420°C is superimposed on the peak of nitrogen dioxide (~380°C), which is also observed for cobalt-exchanged zeolites [35, 50]. The fraction of the latter increases with a decrease in the exchange ratio and with a decrease in the degree of copper and cobalt ion clustering [35, 46, 51] and, therefore, with a decrease in the fraction of bridging extra-framework forms of oxygen in the composition of oxide clusters (vide supru). This allows us to assign the evolution of nitrogen dioxide in the high-temperature peak to the decomposition of monodentate nitrate complexes stabilized mostly on isolated transition metal cations. The evolution of NO in the high-temperature peak should be assigned to the

Table 4. Thermal stabilities and the heats of desorption of nitrite–nitrate complexes [32, 35, 46, 50, 51]

System, complex	Temperature of the TPD peak maximum, °C	Activation energy of desorption, kJ/mol	Calculated heat of desorption*, kJ/mol
CuZSM-5			
Nitrate	400	90	110
Nitrite	220	–	80
CoZSM-5			
Nitrate	430	110	150
Nitrite	200	–	60–120
CuO/Al_2O_3			
Nitrate	480	110	–
Nitrite	220	51	–
ZrO_2			
Nitrate	480–590	120–190	–
Nitrite	180–350	40–80	–
Al_2O_3			
Nitrate	500	120	–
Nitrite	220	50	–

* Calculation using the semiempirical interacting bonds method.

Table 5. Comparison of the rates of formation of molecular nitrogen in the steady-state process of nitrogen oxide reduction by propane or methane in excess oxygen, transformation of surface nitrate complexes, and nitrogen formation in pulse titration by the mixtures $C_3H_8 + O_2$ and $CH_4 + O_2$

Sample	Rate $\times10^{-13}$, molecule m^{-2} s^{-1}			Activation energy, kJ/mol	
	catalytic reaction	nitrate transformation (IR spectroscopy)	N_2 formation in a pulse	catalytic reaction	nitrate transformation
0.1% NO + 0.1% C_3H_8 + 1% O_2 in He(1)					
CuZSM-5	0.5	0.5	1.8(2)	80	70
CoZSM-5	0.3	1.0	0.8(2)	80	60
0.1% NO + 0.1% CH_4 + 1% O_2 in He(3)					
CuZSM-5	0.8 (410°C)	0.4	2.0(4)	–	80
CoZSM-5	2.0	14	1.3(4)	70	80

(1) Experimental temperature 210°C.
(2) $C_3H_8 + O_2$ pulses.
(3) Experimental temperature 280°C.
(4) $CH_4 + O_2$.

decomposition of bidentate and bridging nitrate complexes, which have bridging extra-framework oxygen atoms of the oxide cluster in their composition. The lower bond strength (thermal stability) of monodentate nitrates in this case clearly correlates with the lower bonding strength (desorption heat) of terminal oxygen (20 kcal/mol for Cu–O and 53 kcal/mol for Co–O) compared to bridging oxygen (53 and 143 kcal/mol for Cu_2O and Co_2O, respectively) [35].

Experimental [32] and theoretical estimates [35] (Table 4) showed that the heats of adsorption of nitrates and nitrites are in the intervals 90–160 and 60–80 kJ/mol, respectively. Thus, on the one hand, nitrite and nitrate complexes are rather firmly bound to stay at the catalyst surface at real temperatures of SCR (300–600°C). On the other hand, they can be thermally activated in this temperature range, which makes them rather reactive.

From the standpoint of real conditions of catalysis, when reaction mixtures contain high concentrations of water vapor and the temperatures of the efficient catalyst operation at high loads are usually higher than 300°C, nitrate complexes are the most probable intermediate compounds. Therefore, the reactivity of the surface nitrate species was the focus of our studies [33–37, 39, 50, 51, 53, 54, 56]. The adequacy of such an approach was confirmed for various catalytic systems in several studies by other authors, which were carried out simultaneously with ours [25, 26] and later [82–86].

3. *Reactivity of Surface Nitrate Complexes*

3.1. *In situ* IR spectroscopy. The methodology of these studies included the usual stages necessary for the study of reactivity of surface complexes [87]:

(1) Catalyst treatment with a mixture of NO + O_2 at a temperature corresponding to the lower limit of the operating range of this system with subsequent removal of weak forms (nitrosyls and nitrites) by evacuating the gas phase (in a static cell) or purging by a flow of inert gas (flow cell), which provided maximal surface coverage with nitrate complexes.

(2) Admission of a hydrocarbon (switching to the flow of a mixture containing a hydrocarbon) or its mixture with oxygen and analysis of changes in the intensities of absorption bands of nitrate complexes.

(3) Estimating the rate constants of the surface reaction and its temperature dependence (the activation energy).

(4) Calculation of the rate of surface reaction (at a steady-state coverage when possible) and comparison with the steady-state rates of the catalytic reaction.

The scope and limitations of the above approach were considered in a review paper by Matyshak and Krylov [87].

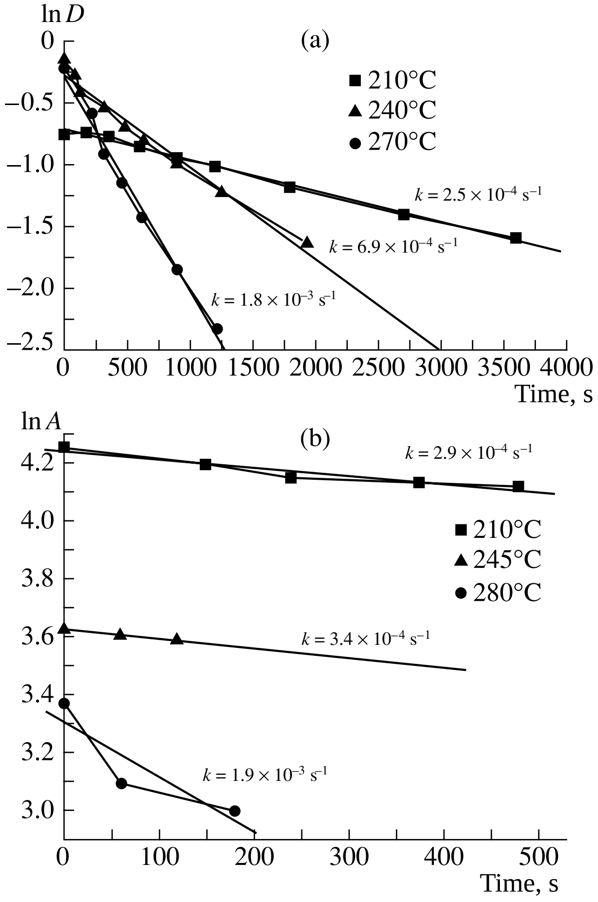

Fig. 4. Typical time dependences of (a) absorbance and (b) integral intensity of absorption bands of surface nitrate complexes stabilized on (a) CuZSM-5 or (b) CoZSm-5 in the course of their interaction with a mixture of (a) C_3H_8 + O_2 or (b) CH_4 + O_2 at different temperatures in a static IR cell [35, 50] in the coordinates of the first-order equation.

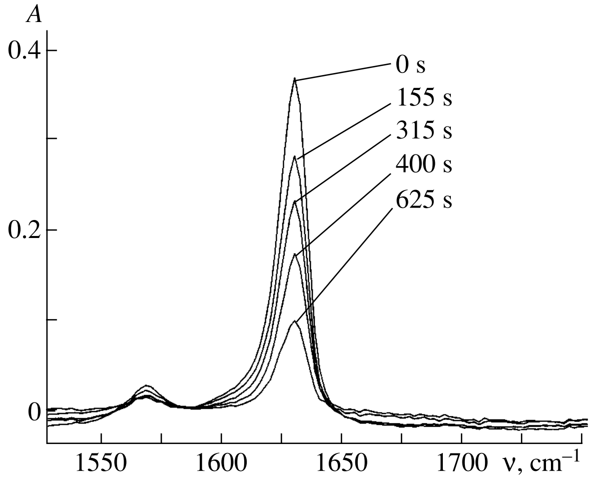

Fig. 5. Changes in the spectra of the sample CuZSM-5 in the process of interaction of preliminarily formed surface nitrate complexes with the reaction mixture containing pure methane at 210°C in a static IR cell [50].

In almost all the experiments on the titration of surface nitrates by propane [33, 35, 36, 46, 50], methane [35, 50], or propylene [51, 56], dynamics of the nitrates band intensity variation is well described by the first-order rate equation, which agrees well with more recent studies of other researchers [82, 83]. Figure 4 shows an example of the typical linearization of time dependences of optical density of nitrate band for copper- and cobalt-exchanged zeolites in the coordinates of the first-order equation. The estimates of the reaction rates and the activation energies of the corresponding surface reactions are listed in Table 5. In contrast to data reported in [25], in our experiments with CuZSM-5, we observed a high rate of the reaction between bridging nitrates and methane or its mixture with oxygen (Fig. 5). Our data were later confirmed for nitrate complexes with similar spectral characteristics stabilized on copper-exchanged zeolite CuZRHMS [64]. To all appearances, in the case of copper-exchanged zeolites, the specific features of oxide clusters determining the bonding strength of nitrate complexes, their reactivity, and the specific features of methane molecule activation play a substantial role in the interaction of methane with nitrate complexes.

By now, the high reactivity of nitrate complexes towards hydrocarbons, including reactions in the presence of oxygen, has been confirmed in a number of papers [25, 26, 82–86] and can be considered a reliably established fact. However, most papers reported only qualitative studies without estimates of the rates of surface reactions. Exceptions are the papers [82, 83], where the reduction of nitrate complexes by hexane over the Ag/Al_2O_3 system was considered.

To prove reliably that the surface nitrate species are true intermediates in the NO_x HC SCR, it is insufficient to demonstrate their rapid disappearance under HC action. It is also necessary to show that the target product (molecular nitrogen) is formed in these reactions, because the reduction of nitrate complexes may be equally effective in NO formation, which was determined in [25, 26, 35]. In our experiments, we used a pulse microcatalytic method for this purpose [35, 50].

3.2. Titration of adsorbed complexes of nitrogen oxides by the pulses of mixtures containing a hydrocarbon. Figures 6 and 7 show typical dependences of the rate of molecular nitrogen formation on the number of pulses containing a hydrocarbon in helium supplied fed to the catalyst. As can be seen from these data, the surface reaction of reductive transformation of nitrate complexes under the action of hydrocarbons does efficiently generate molecular nitrogen even in the absence of NO in a pulse of the initial mixture. This allows us to assume that, in the cases under consideration, the formation of molecular nitrogen (nitrogen atoms pairing) does not require the presence of NO molecules in the gas phase. This conclusion conflicts with the conclusion drawn in [88] that one nitrogen atom in the N_2 mol-

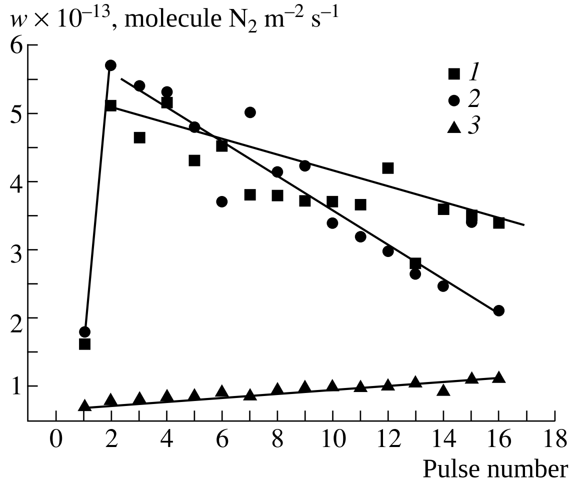

Fig. 6. Dependence of the rate of molecular nitrogen formation in the titration of surface nitrate complexes stabilized on cation-exchanged zeolites (*1, 2)* CuZSM-5 and (*3*) CoZSM-5 by pulses of (*2*) C_3H_8 and (*1, 2*) $C_3H_8 + O_2$ in helium at 210°C on the pulse number [35, 50].

ecule comes from the surface intermediates (acetone oxime for the reaction of SCR of nitrogen oxides by propane) and the other comes from the gas-phase NO molecule. The difference in the conclusions drawn by different authors is due to the considerable difference in the states of the catalyst surface with preadsorbed acetone oxime [88] from the stationary one, for which the concentration of such intermediates is negligibly small.

Usually, the rate of molecular nitrogen formation versus the pulse number passes through a maximum (Figs. 6, 7) pointing to the accumulation of intermediates containing nitrogen, carbon, and oxygen atoms in the course of titration [35, 71].

For copper-containing systems, the rate of nitrogen formation is usually independent of the presence of oxygen in the mixture with propane (Fig. 6). This fact implies that oxygen does not participate in the steps where intermediate species are converted. Since the rate of propane conversion weakly depends on the presence of oxygen in the gas phase [35, 50], we can assume that the specifics of the copper-containing system are determined by the low bonding strength (high reactivity) of the oxygen in oxide–copper clusters (vide supru).

For a cobalt-containing system, the evolution of molecular nitrogen is substantially retarded if oxygen is absent in the pulse of propane in helium [35, 50]. This fact suggests that molecular oxygen is directly involved in the transformations of intermediate species in this system. From the standpoint of the surface chemistry of the given system, this specific feature is due to the higher bonding strength and the low reactivity of oxygen in cobalt oxide clusters.

In the course of nitrate titration with the pulses of pure methane or its mixture with oxygen, the formation of nitrogen is observed at comparable rates in the systems containing either copper or cobalt cations (Fig. 7). This result is unexpected from the standpoint of the steady-state catalytic properties of these systems in SCR of nitrogen oxides by methane. Indeed, CoZSM-5 is an active and selective catalyst in this reaction, whereas only deep oxidation of methane is observed on CuZSM-5 and the selectivity to molecular nitrogen is low [35, 88]. However, IR spectroscopic data on the rate of interaction of surface nitrate complexes with methane (vide supru) also point to the fact that, under non-steady-state conditions, the behavior of two systems is indeed similar. The difference in the behavior of the systems under steady-state conditions is primarily due to the different reactivities of intermediates containing nitrogen, carbon, and oxygen atoms (vide infra) rather than to the low reactivity of nitrate complexes on CuZSM-5 towards methane, as was suggested in [88]. Indeed, for both systems, the rates of methane con-

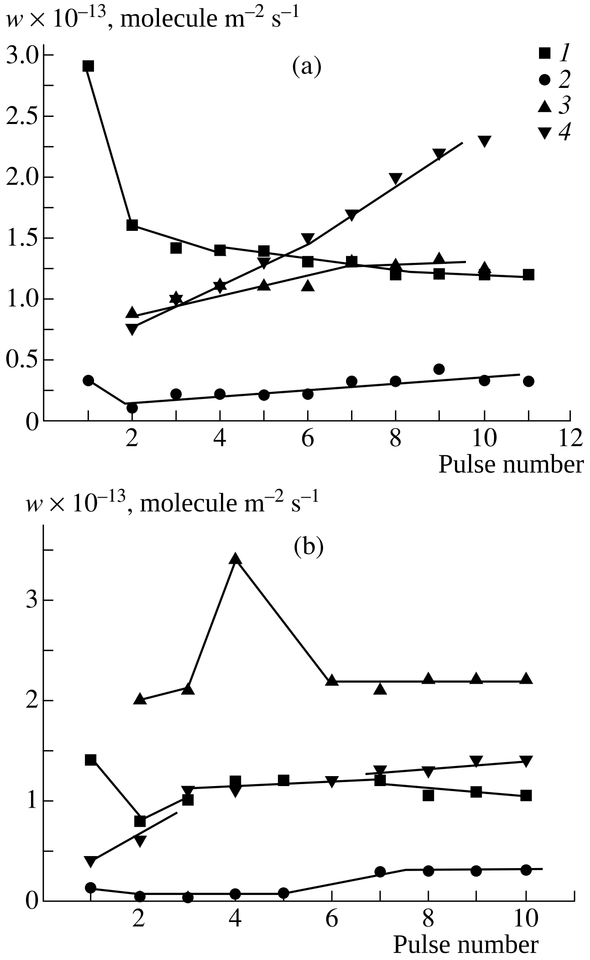

Fig. 7. Dependence of the rates of (*1, 3*) molecular nitrogen formation and (*2, 4*) methane conversion in the titration of surface nitrate complexes stabilized on cation-exchanged zeolites (a) CoZSM-5 and (b) CuZSM-5 by the pulses of the mixture (*1, 2*) CH_4 and (*3, 4*) $CH_4 + O_2$ in helium at 210°C on the pulse number.

sumption are rather close when the pulses of the $CH_4 + O_2$ mixture are supplied onto the preadsorbed nitrate complexes (Fig. 7), whereas the rates of nitrogen formation are higher for the copper-containing system.

In addition to molecular nitrogen in the process of pulse titration of surface nitrate complexes, NO formation was noticed (Fig. 8). The amount of NO formed was much higher in the case of the cobalt-containing system. This means that a part of nitrate complexes is unselectively reduced by hydrocarbons to form NO. The presence of oxygen in the gas phase containing methane substantially reduces the formation of NO, probably due to its reoxidation by oxygen back to the nitrate complexes. The elevated rate of nitrogen formation in the first pulses of methane onto the surface with preadsorbed nitrate complexes (Fig. 7a) clearly correlates with the intensive evolution of NO into the gas phase (Fig. 8). Some portion of molecular nitrogen can probably be generated by a reaction between C,N-containing intermediates with NO molecules from the gas phase or nitrosyl complexes.

For platinum-containing catalysts (PtZrPILC and (Pt+Cu)/ZrPILC), the titration of strongly bound nitrogen oxides by propylene or its mixture with oxygen also resulted in the formation of molecular nitrogen [55, 89]. Nitrous oxide was also observed, but the selectivity was low (several percent).

Studies by other researchers carried out at the same time as ours or later also demonstrated the formation of molecular nitrogen in the reaction of hydrocarbons with surface nitrate complexes for a number of very different systems [25, 86], although the rates of the reaction have not been estimated in almost all cases.

3.3. The nature of the rate-determining step and key intermediates. Comparison of the rates of target product formation (molecular nitrogen in the pulse titration of surface nitrate complexes), the rate of nitrate complex transformation under about the same conditions according to *in situ* IR data, and the steady-state rate of the NO_x HC SCR shows that, when propane is used as a reducing agent, all the three rates are close for both copper- and cobalt-exchanged zeolites if oxygen is present in the reaction mixture (Table 5). The activation energies of separate steps and the overall catalytic reaction are also close. These results provide direct evidence for the participation of strongly bound nitrate complexes as key intermediates in the rate-limiting step of SCR of nitrogen oxides by propane. Drastic retardation of molecular nitrogen evolution for cobalt-containing systems in the absence of oxygen in the gas phase assumes that, in this case, the step of C,N-containing intermediates becomes the rate-limiting step [35].

Recent data for the Ag/Al_2O_3 system [82, 83] demonstrating that the rate of SCR of nitrogen oxides by hexane in the excess of oxygen and the rate of nitrate complex transformation under the action of hexane measured independently are close make it possible to assume that nitrate complexes are key intermediates when the reducing agents are C_2–C_6 paraffins regardless of the type of active components—Co, Cu, Ag, or other cations.

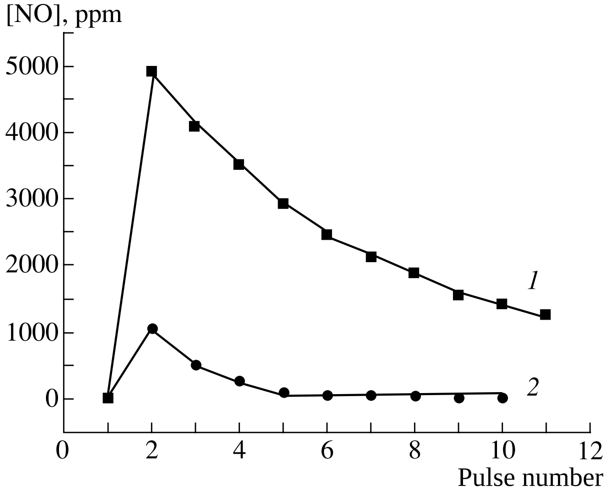

Fig. 8. The concentration of NO in helium at the outlet of the reactor in the process of nitrate complex titration on CoZSM-5 by the pulses of (*1*) CH_4 or (*2*) $CH_4 + O_2$ in helium at 280°C.

For SCR of NO by methane, the same conclusion about the nature of the rate-limiting step and key intermediates is undoubtedly applicable to the CoZSM-5 system (Table 5). It agrees well with the conclusion drawn by Cowan *et al*. about the nature of the rate-limiting step of this reaction, which is associated with the cleavage of the C–H bond in the methane molecule with the participation of nitrite–nitrate complexes [90, 91].

For the CuZSM-5 system, the stationary rate of SCR of NO by methane is much lower than the rates of separate steps (Table 5). This allows us to conclude that, under non-steady-state conditions with high concentrations of intermediate complexes on the surface of the given system, the route of selective reduction of nitrogen oxides is rather efficient (vide infra). Under steady-state conditions, the rate of formation of intermediates responsible for this route is most likely lower than the rate of their oxidation by oxygen with the predominant formation of NO molecules.

In our papers, for SCR of nitrogen oxide by propylene over zirconium dioxide at 300–450°C, we also showed that the rates of the steady-state catalytic reaction and the step of conversion of surface nitrate complexes under the action of propylene are close [51, 56]. For the Cu/Al_2O_3 system, the high reactivity of nitrate complexes toward propylene or its activated, partially oxidized forms (probably, acetates) in a similar temperature range was demonstrated in [92].

For platinum-containing systems (platinum supported on clays pillared with zirconium dioxide, including systems modified by copper cations) in the low-temperature range (150–250°C), pulse titration also

Table 6. Effect of NO addition to the mixtures with oxygen on the kinetic parameters of hydrocarbon oxidation

Catalyst	Reaction mixture	Activation energy, kJ/mol	Hydrocarbon oxidation rate*, molecule m^{-2} s^{-1}
CoZSM-5	$NO + CH_4 + O_2$	113	1.1×10^{14}
	$CH_4 + O_2$	80	4.2×10^{13}
	$NO + C_3H_8 + O_2$	100	6.0×10^{11}
	$C_3H_8 + O_2$	100	2.0×10^{11}
CuZSM-5	$NO + CH_4 + O_2$	134	2.6×10^{14}
	$CH_4 + O_2$	80	1.5×10^{14}
	$NO + C_3H_8 + O_2$	100	9.0×10^{10}
	$C_3H_8 + O_2$	100	1.6×10^{12}

* Reaction temperature: 210°C for C_3H_8 and 400°C for CH_4.

showed that the rates of nitrogen formation are close in the case of $C_3H_6 + NO + O_2$ pulse supply on a clean oxidized surface and in the case of mixtures without NO on the surface with preadsorbed nitrogen oxides. At the same time, the rates of molecular nitrogen formation under pulses of NO on a reduced surface of these platinum-containing systems with preadsorbed propylene were much lower than the rate of catalysis [55]. We do not exclude that, in the latter case, the reaction route of SCR includes the interactions of both nitrite and nitrate surface complexes with hydrocarbons due to low operating temperatures, at which the surface coverage by nitrite complexes is rather high. The low rates of molecular nitrogen formation under of NO pulses on a reduced surface of platinum-containing catalysts with preadsorbed propylene suggest that, in contrast to the scheme proposed in [29–31], at least in these systems, SCR of nitrogen oxides by olefins does not include the step of NO decomposition on a reduced platinum surface covered by coke.

4. Routes of Hydrocarbon Activation in SCR of Nitrogen Oxides

Although the above results showed that, for a number of catalytic systems and reducing agents, the step of nitrate complex reduction with hydrocarbons is rate-limiting in the SCR process, it is obvious that this step is not elementary. This primarily concerns the routes of activation of hydrocarbons, which can be activated with the direct participation of nitrite–nitrate complexes [25, 26, 90, 91] or independently of them with the participation of various surface sites: Brønsted acid sites [19, 93], reactive oxygen [94], and coordinatively unsaturated cations [51, 95, 96]. Comparison of the rates of hydrocarbon oxidation in the mixtures with oxygen with and without nitrogen oxide addition allows to clarify these problems.

Typical results of such experiments are shown in Table 6 for cation-exchanged zeolites. These data show that an increase in the rate of propane oxidation on CoZSM-5 is observed if NO is added to the mixture. Therefore, for zeolites containing cobalt cations, the activation of propane occurs with the direct participation of ad-NO_x species. This is explained by the high degree of coordinative unsaturation of cobalt cations shielded by nitro groups (according to EXAFS data [35], the coordination number Co–O practically does not change upon the adsorption of nitrogen oxides) and by the higher strength of oxygen bonding in oxidic cobalt clusters and, therefore, by the relatively low reactivity (vide supru).

For CuZSM-5, the addition of NO to the mixture leads to a decrease in the rate of propane transformation. This means that some of the sites for propane activation are blocked due to the formation of nitrate complexes. Because the formation of nitrate complexes implies the inclusion of oxygen atoms from oxide clusters in their composition, we may conclude that propane activation occurs most readily in the case of direct participation of such oxygen, most likely with the formation of such intermediate compounds as carboxylates [87]. A relatively low bonding strength (vide supru) and, therefore, a relatively high reactivity of both terminal and bridging oxygens of copper oxidic clusters favors this route. According to IR spectroscopic data of adsorbed CO [35], nitrogen oxide adsorption with the formation of nitrite–nitrate complexes leads to an increase in the concentrations of coordinatively unsaturated Cu^+ sites. In agreement with these conclusions, EXAFS data for copper-exchanged zeolite point to a noticeable decrease in the coordination number Cu–O and an increase in the coordination number Cu–Cu in NO adsorption [35]. The Cu^+ sites are well known for their ability to activate the C–H bond in hydrocarbons in their selective oxidation. We do not exclude that propane activation with the participation of such Lewis sites leads to the formation of alkyl radicals and/or propylene. This conclusion about the routes of propane activation in the presence of nitrogen oxides on CuZSM-5 agrees well with results obtained in [93]. Our data do not confirm the hypothesis that propane is directly activated on adsorbed NO_2 [23] or nitrate groups stabilized on copper cations [25, 26].

The activation of a stronger C–H bond in methane should clearly be less efficient on such coordinatively unsaturated copper oxidic clusters. This probably explains why the formation of surface nitrates, which are highly reactive in the reaction with methane (vide supru), also leads to an increase in the steady-state rate of methane conversion in the copper-containing system, almost exclusively via the route of deep oxidation.

Using similar criteria, it was shown that propylene activation on the surface sites of zirconia in SCR occurs without the participation of nitrite–nitrate complexes, which retard the oxidation of propylene due to the blocking of coordinatively unsaturated sites on the surface [51, 56].

5. Routes of Nitrate–Nitrite Complex Conversion to Molecular Nitrogen

Although for most systems and for most reactions of SCR by hydrocarbons studied by us, the steps of conversion of products of interaction of nitrite–nitrate complexes and hydrocarbons are not rate limiting, it is these steps that determine the routes of nitrogen atom coupling leading to the formation of molecular nitrogen, which is the target product. Moreover, they are important for an understanding of the routes for the formation of nitrous oxide, which is an undesirable product, as well as a number of other by-products, such as HCN, aldehydes, amines, and others. The selectivity of reducing agent (hydrocarbon) consumption in the target route also depends on these steps.

Currently, the hypothesis that strongly bound intermediates containing nitrogen, oxygen, and carbons participate in these steps has been further corroborated [49, 70, 71, 82–84, 92–94, 96–107]. Some researchers [97, 104] prefer to refer to such intermediates using the rather broad term condensation products containing carbon and nitrogen. Nevertheless, a more detailed description of these intermediates was given in other papers [68, 70, 71, 82–86, 92, 99, 101, 102, 106] based on IR spectroscopic studies coupled with non-steady-state kinetic experiments. The identification of surface compounds using their absorption bands is more reliable when one uses isotopically substituted NO molecules with labels on nitrogen and oxygen [35, 62, 92, 96, 108]. Of course, some of the observed surface compounds may be dead ends in the routes or by-products. The criterion used to judge that the species is an intermediate is the required stability, reactivity, and selectivity of their conversion into the target products.

As follows from data in Table 7, in our experiments with propane and propylene as reducing agents, we observed the formation of such compounds as nitropropane, nitrile, isocyanate, and organic carbonyl-containing compounds (ketene, acrolein). Nitropropane is the most important intermediate among these compounds. It is observed under both steady-state and non-steady-state conditions. Nitropropane is not necessarily the primary product of propane or propylene interaction with nitro groups. Thus, for SCR of NO by propylene on platinum-containing pillared clays under contact with the reaction mixture at a moderate temperature (150°C) [51], acrolein, which is the product of propylene oxidative conversion, is first formed (absorption bands at 1675 and 1638 cm^{-1}) followed by a subsequent of the intensities of bands at 1575 and 1385 cm^{-1} corresponding to organic nitro compounds (Fig. 9). We do not exclude that an organic nitro compound may be formed due to the interaction with nitrite–nitrate complexes of allyl complexes, which are concurrently oxidized to acrolein, and due to the interaction of acrolein with NO$_x$, as proposed in [86].

Currently, the formation of nitropropane in SCR by propane or propylene can be considered a reliably

Table 7. Main types of C,N,O-containing intermediate species in the reaction of SCR of nitrogen oxide by propane and propylene found using IR spectroscopy

Absorption band*, cm^{-1}	Compound	Type of vibration	Catalyst	Reducing agent, reference
2155 (2155, 2107)	Ketene C=C=O	ν(C=O)	CuZSM-5	Propane [35, 50]
1575 (1550) 1380 (1361)	Nitropropane	$\nu_{as}(NO_2)$, $\nu_s(NO_2)$	Cu, CoZSM-5 (Pt + Cu)/ZrPILC ZrO_2	Propane [35, 50] Propylene [51] Propylene [51]
1565 (1530) 1380	Nitropropane	$\nu_{as}(NO_2)$, $\nu_s(NO_2)$	Pt/SiO_2	Propylene [96]
1593 1328	Nitropropane	$\nu_{as}(NO_2)$, $\nu_s(NO_2)$	CuO/Al_2O_3	Propylene [92]
2180 (2140)	Nitrile	ν(CN)	CoZSM-5	Propane [35, 50]
2260 (2240)	Isocyanate	ν(NCO)	CoZSM-5	Propane [35, 50]
1655 (1615)	Nitritopropane	–	Pt/SiO_2	Propylene [96]
1662	Nitritopropane	–	CuO/Al_2O_3	Propylene [92]
2237	Cu^+–NCO	ν(NCO)	CuO/Al_2O_3	Propylene [92]
2156	Cu^0–CN	ν(CN)	CuO/Al_2O_3	Propylene [92]
1675, 1638	Acrolein	ν(C=O), ν(C=C)	(Pt + Cu)/ZrPILC	Propylene [51]

* Positions of absorption bands for intermediate compounds observed when isotope-substituted $^{15}N^{18}O$ molecules (in parentheses) are used.

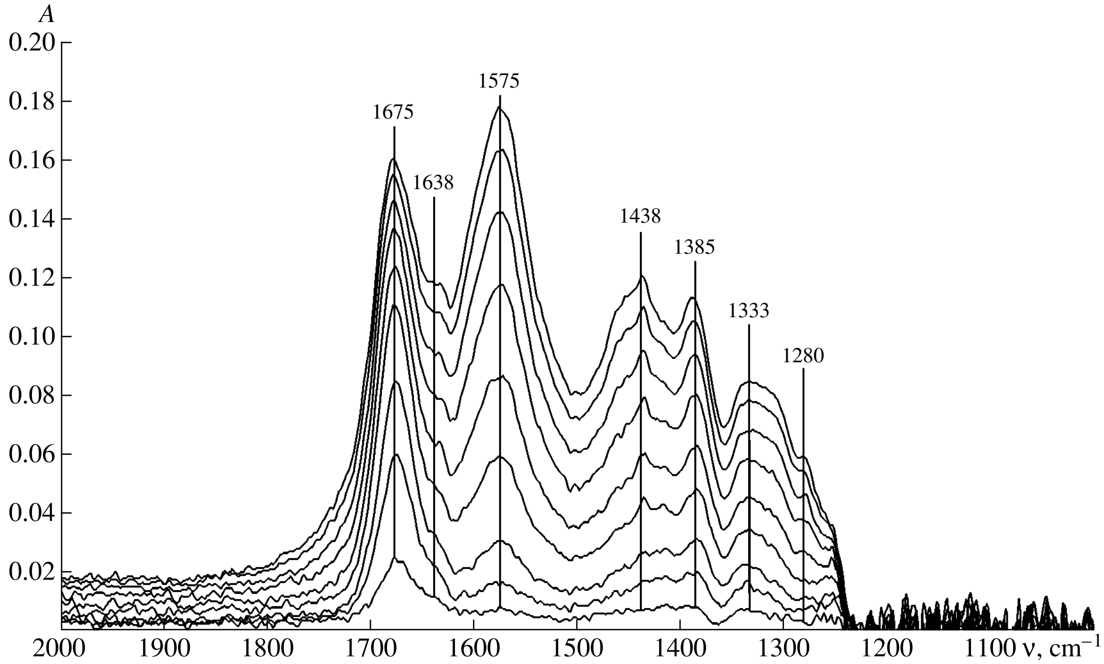

Fig. 9. IR transmittance spectra obtained in the process of interaction of (Pt + Cu)ZrPILC with a mixture of 0.2% NO + 0.2% C_3H_6 + 2.5% O_2/N_2 at 150°C. Spectra were recorded after 1, 2, 3, 5, 7, 10, 14, and 20 min, respectively.

established fact, which was reproduced independently for various systems in a number of studies [35, 49, 51, 82, 83, 92, 96]. A pioneering work by Tanaka and coworkers [96] demonstrated the formation of nitropropane in SCR by propylene for the Pt/SiO_2 system using *in situ* IR spectroscopy combined with isotopic substitution of nitrogen atoms. In this work, as in [92] for the CuO/Al_2O_3 system, the formation of organic nitrites R–O–NO (the band at 1660 cm^{-1}) was observed together with organic nitrates (bands at 1565–1593 cm^{-1} and 1330–1380 cm^{-1}).

Direct evidence for the formation of various C,N,O-containing compounds in SCR by propylene was obtained recently using GC–MS technique for the Ga_2O_3/Al_2O_3, In_2O_3/Al_2O_3 [84, 86], and Pt/Al_2O_3 systems [100]. In addition to nitro compounds and nitriles, including acrylonitrile, the formation of ketones, acids and even benzene is also observed. This points to the deep fragmentation of propylene molecules, including the formation of highly reactive species, that are capable of undergoing oligomerization.

To determine whether the surface species observed are intermediates, spectators, or by-products, we studied the dynamics of their accumulation and consumption using *in situ* IR spectroscopy [34–38, 50].

For CuZSM-5 and CoZSM-5, the transformation of bridging nitrates (1630 and 1505 cm^{-1}, respectively) in the process of their titration by a mixture of propane and oxygen is accompanied by the accumulation of nitropropane (1575 and 1550 cm^{-1}, respectively) at a comparable rate and with the first order with respect to the concentration of nitrates (Fig. 10). Nitropropane possesses the necessary thermal stability (up to 250–300°C) in a vacuum. Moreover, it adsorbs on tetrahedrally coordinated cobalt cations more strongly than on copper cations in the square planar coordination [35]. The interaction of nitropropane with oxygen and NO in the working range of SCR temperatures leads to its fast removal (Fig. 10). Therefore, nitropropane meets all the criteria, allowing one to classify it as the intermediate product in the reduction of nitrate complexes.

The routes for nitromethane conversion can be determined from the analysis of dynamics of transformation of other surface compounds, which are also observed in the process of titration. Thus, for CuZSM-5, we observe the accumulation of such an intermediate as ketene (2156 cm^{-1}) (Fig. 10, Table 7), which is described well by the second-order equation with respect to the concentration of nitrate complexes [35]. This allows us to assume that, for this system, relatively mobile nitropropane is capable of interacting with surface nitrate groups to form nitrogen and the product of selective oxidation of the hydrocarbon part, ketene [35]. Ketene is rapidly removed by oxygen at these temperatures.

For CoZSM-5, the accumulation of nitriles and isocyanates is observed along with nitropropane (Table 7).These complexes are thermally stable up to 400°C, but they rapidly interact with oxygen and NO at 250–350°C [35]. These data assume that nitropropane further transforms into nitriles and/or isocyanates on CoZSM-5. This conclusion agrees with more recent results [84, 86], showing that, in SCR of nitrogen oxides by propylene over the Ga_2O_3/Al_2O_3 system, nitriles and isocyanates are only observed under conditions of a non-steady-state process of titration of nitrite–nitrate complexes by propylene at 350°C. The concentration of such complexes passes through a maximum in the course of titration as expected for an intermediate species. These complexes are formed by the thermal transformation of organic nitrates and are rapidly consumed by hydrolysis yielding ammonia [84, 86].

The situation with intermediates in SCR of NO by methane is more complex; they cannot be detected under steady-state conditions. Aylor *et al.* [109, 110] proposed a scheme for this reaction, which involves the activation of methane by nitrite–nitrate complexes with intermediate formation of nitriles, whose interaction with gas-phase NO (NO_2) in the rate-limiting step of the reaction produces molecular nitrogen. Although these researchers estimated using *in situ* IR spectroscopy the turnover frequencies for the rate-limiting steps, which are rather close (within an order of magnitude) to the turnover frequency of the catalytic reaction, it should be noted that the authors managed to create high surface coverages by nitriles only in the absence of O_2 in the reaction mixture at high temperatures and reactant concentrations. We do not exclude that under these conditions the state of the surface active sites also changed (in any case, their reduction is very probable), and this makes dubious any comparison of the rates of separate stages with the steady-state rate of catalysis occurring on the oxidized surface.

To determine the routes of transformations of possible intermediates in this reaction, reactions of specially synthesized compounds (organic nitro compounds, hydrocyanic acid, etc.) [103–107, 111] over different types of catalysts used to be studied. We carried out an IR spectroscopic study of nitromethane [40, 47] and acetonitrile [38] transformation on cation-exchanged zeolites, as well as nitromethane and tertiary butyl nitrite on alumina-containing systems [49].

A typical change in the intensities of various bands in the process of nitromethane adsorption on CuZSM-5 is shown in Fig. 11. Even in the course of adsorption at 280°C, nitromethane (the absorption band at 1580 cm^{-1}) rapidly transforms into isocyanates (2205 cm^{-1} for Cu^+–NCO; 2276 cm^{-1} for Cu^{2+}–NCO) and into such polymerization products as melamine ($CN(NH_2)_3$, 1665 cm^{-1}) and cyanuric acid, a cyclic trimer of isocyanic acid (1720 cm^{-1}). The same picture is observed for the CoZSM-5 system with the only exception that the absorption band corresponding to nitrosyls Co^{2+} is also observed (1801 cm^{-1}) [47]. In the general case, the results obtained agree with schemes proposed in [103–107], where very fast steps of nitromethane transformation are described by the following equations:

$$CH_3NO_2 \longrightarrow CO_2 + NH_3;$$

$$CH_3NO_2 \longrightarrow HNCO + H_2O;$$

$$3HNCO + 3NH_3 \longrightarrow C_3N_6H_6 + 3H_2O.$$

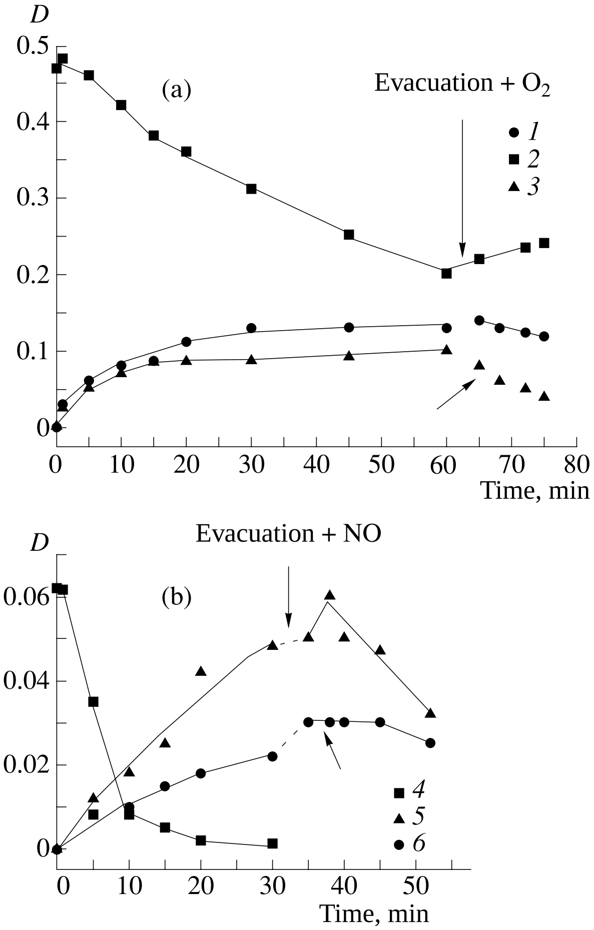

Fig. 10. Time changes of the intensities of the absorption bands (cm^{-1}) corresponding to the surface nitrate complexes and the products of their interaction with a mixture of propane + oxygen at 210°C on (a) CuZSM-5 and (b) CoZSM-5: (*1*) 1575, (*2*) 1630, (*3*) 2156, (*4*) 1505, (*5*) 1550, and (*6*) 2240. The arrow points to the moment of evacuation and further admission of (a) O_2 and (b) NO. The nitrate complexes were formed using NO of (a) the natural composition and (b) $^{15}N^{18}O$.

For cation-exchanged zeolites in dry reaction mixtures of nitromethane with oxygen, the initial activity in the reaction of nitromethane decomposition at 285°C is high for both copper- and cobalt-exchanged zeolites [90, 91, 98, 103–106]. However, although in the case of CuZSM-5 the main product is molecular nitrogen and the other products are traces of ammonia, hydrogen cyanide, and isocyanic acid, the main product is ammonia in the case of CoZSM-5. Thus, for the copper-containing system, the rate of intermediate product transformation is substantially higher than for the cobalt-based system, and this agrees with our data for pulse titration (vide supru). For the systems of both types at a relatively low temperature, the activity rapidly decreases with time, and this is associated with the accumulation of condensation products, cyanuric acid and melamine, which block zeolite pores. In the pres-

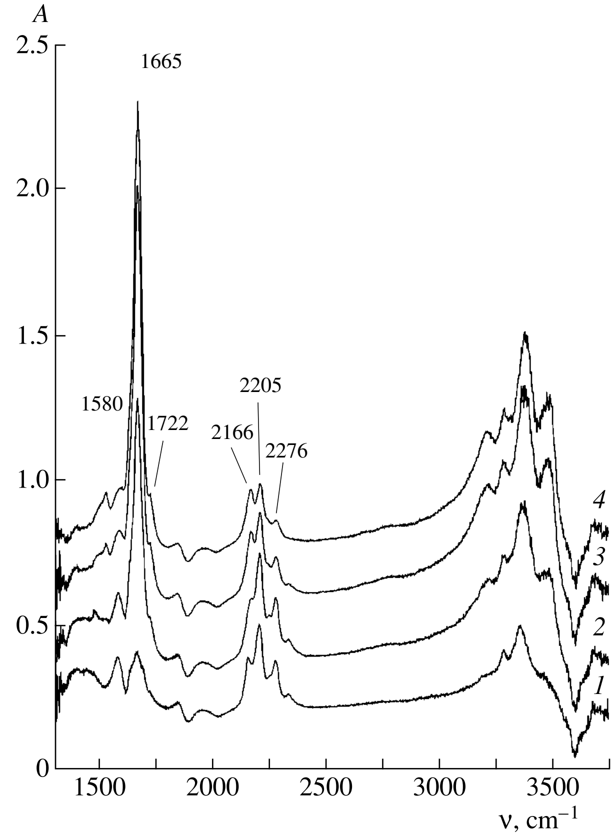

Fig. 11. Change of the spectrum in the course of nitromethane adsorption on CuZSM-5 at 280°C after (*1*) 0, (*2*) 120, and (*3*) 360 s and after (*4*) further evacuation at the same temperature.

ence of oxygen at high temperatures (400°C), rapid oxidation of condensation products provides stable activity. The addition of water to the mixture suppresses deactivation by accelerating hydrolysis reactions. For pure alumina and alumina with a small amount of supported silver or cobalt, deactivation was not observed even at low temperatures (150–200°C), and ammonia was the main reaction product. In this case, IR spectroscopy did not detect the formation of the condensation products observed in zeolite systems. In addition to the absorption bands assigned to isocyanates and adsorbed ammonia, bands assigned to such products of nitromethane transformation as formhydroxamic acid CHO–N(H)OH and carbamic acid NH_2COOH were observed [49]. Hydrolysis of these compounds on acid surface sites generates ammonia, which is an efficient reducing agent for surface nitrite–nitrate complexes and NO_x molecules in the gas phase.

Unlike organic nitrates, organic nitrites are predominantly converted by oxygen into nitrogen dioxide and the products of complete oxidation of their organic part [49]. This result explains the overequilibrium concentration of NO_2 in the products, which was noted for a number of catalysts based on oxide systems [48, 49]. Hence, the selectivity of SCR is largely determined by the difference in the structure of similar C,N,O-containing intermediate species.

In addition to the specific features of structures, the coordinative unsaturation of surface sites plays an important role. Thus, acetonitrile is not transformed in the course of adsorption on CuZSM-5 followed by desorption, which can be explained by weak binding in the axial position of copper cations in the square planar coordination [38].

For CoZSM-5, in the course of sample evacuation after acetonitrile adsorption, the bands at 1660, 1580, and 1460 cm^{-1} are observed, whose intensity increases with an increase in the temperature of evacuation. The positions of absorption bands allow one to assign them to the vibrations of the surface compounds CH_3–CO–NH_2 (acetamide) formed by the addition of a water molecule to acetonitrile [38]. Thus, the stronger binding of acetonitrile in the coordination sphere of cobalt cations leads to its hydrolysis.

Analysis of published data shows that currently most researchers agree on the relatively high reactivity of organic nitro compounds. They rapidly transform into molecular nitrogen under the action of oxygen due to intermediate formation of ammonia, which is a highly efficient reducing agent. This was first demonstrated in 1994 [96] for the reduction of nitrogen oxides by propylene on Pt/SiO_2. It was shown that the rate of molecular nitrogen formation from organic nitrates under the action of O_2 was comparable with the rates of its formation under the action of NO_2. Therefore, in contrast to schemes proposed in [25, 26], nitrogen atom coupling is rather efficient in the absence of NO_x in the gas phase. At the same time, the formation of nitrous oxide occurs with a much higher selectivity under the action of nitrogen dioxide [96]. We do not exclude that, the routes of nitrous oxide formation may include the interaction of organic nitro and nitrite compounds with molecular NO or NO_2.

As we showed in [40], even polymerized products of nitromethane conversion, such as melamine, readily transform into isocyanates and then to molecular nitrogen under the action of oxygen. Figure 12 shows changes in the corresponding absorption bands for cation-exchanged zeolites. For the copper-containing system, a high rate of isocyanate and melamine transformation was achieved even at 280°C, whereas for CoZSM-5 these intermediates practically did not react with oxygen at this temperature. At the same time, an increase in the temperature to 350°C provides the same rate of transformation of these intermediates for the cobalt-containing system as well. These results point to the high reactivity of intermediate compounds, which are bound to copper cations less strongly than to cobalt cations (vide supru). Comparison of the rate constants of intermediate transformations with the rate constants of transformation of surface nitrate complexes [40, 50] showed that isocyanates and even the products of their trimerization can be intermediates in SCR of nitrogen oxides by methane.

Pulse titration of nitromethane transformation products by oxygen and NO over the CuZSM-5 system confirmed that molecular nitrogen is formed under the action of both reactants [40, 50]. Therefore, parallel routes of nitrogen atom coupling are possible and have comparable efficiencies. Because the rates of molecular nitrogen formation were much higher than the rate of the steady-state catalytic reaction over both copper- and cobalt-containing systems, we concluded that these steps cannot be rate limiting. This finding agrees well with the conclusion drawn in [90, 91] on the cleavage of the C–H bond in the methane molecule as a rate-determining step in this process.

Figure 13 shows the generalized scheme of the reaction mechanism of SCR of nitrogen oxides by alkanes for copper- and cobalt-exchanged zeolites. The key intermediates are shown in this scheme by Roman numerals. The key step that limits the process is the formation of organic nitro compound **I**.

Because the catalytic chemistry of nitro derivatives of methane and propane differ substantially, it is reasonable to comment on the proposed mechanism separately for these two reducing agents.

The routes of 2-nitropropane transformations differ depending on the type of transition metal cation, which we explained by the specificity of the square-planar coordination of copper cations. As a consequence, weakly bound nitropropane molecules easily migrate through zeolite channels and may react with either Brønsted acid sites of the surface to undergo hydrolysis reactions or with nitrite–nitrate (NO/NO_2) complexes to be oxidized with the formation of molecular nitrogen. For the copper-containing system, these steps are complex and fast, because in our non-steady-state experiments we and other researchers [9, 93] failed to detect any intermediates like oxime. The study of acetonitrile transformation over this system [38] made it possible to exclude the participation of this intermediate from the route of possible nitropropane transformations. It is also clear that, for the copper-containing system, the interaction of nitropropane transformation products with nitrite–nitrate complexes is more efficient and does not require the presence of oxygen or nitrogen oxide in the gas phase.

According to [97], two routes of nitropropane transformation are possible on CuZSM-5: (1) via tautomerization of 2-nitropropane to the acynitro form $(CH_3)_2C{=}N(O)(OH)$, whose hydrolysis leads to the formation of a carbonyl compound like $(CH_3)_2C{=}O$(**II**) and NH_2OH. The latter can readily react with nitrite–nitrate complexes to form molecular nitrogen and water; (2) nitropropane may transform into nitrosopropane via the reoxidation of reduced surface sites. Nitrosopropane may readily isomerize into oxime $(CH_3)_2C{=}N{-}OH$. The simplest route of oxime transformation involves either hydrolysis (which is clearly catalyzed by acid sites) with the formation of acetone and hydroxylamine (the latter readily interacts with nitrite–nitrate complexes to form molecular nitrogen) or Beckmann rearrangement into N-methyl-acetamide, $CH_3C(O){-}N(H){-}CH_3$, which readily hydrolyzes to methylamine and acetic acid. Amine readily interacts with nitrite–nitrate complexes to form molecular nitrogen via a diazo compound.

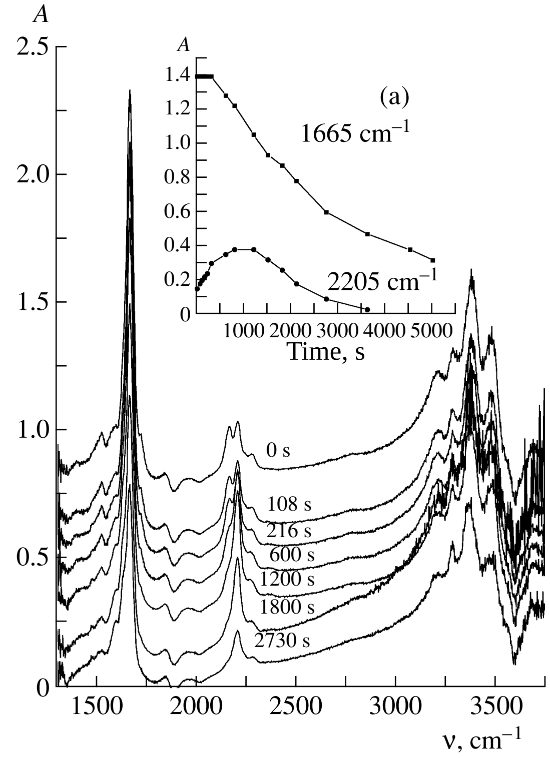

Fig. 12. Time changes of the spectrum of nitromethane adsorbed on CuZSM-5 under the action of oxygen (280°C); (a) time change of the intensities of absorption bands 1665 and 2205 cm^{-1}.

These routes are very plausible from the standpoint of our findings, because the formation of carbonyl compounds **II** was observed in the process of interaction of nitrite–nitrate complexes with propane (vide supru).

For the CoZSM-5 system, the route with the formation of nitriles and isocyanates (**III**) plays the important role. The acid hydrolysis of these compounds leads to the formation of the corresponding amines (**IV**) and ammonia, which is an efficient reducing agent. When propane is used as a reducing agent, the formation of molecular nitrogen is drastically retarded in the absence of gas-phase oxygen, which we explained by the need to oxidize the long hydrocarbon “tail” with the formation of the water molecule required for hydrolysis. An alternative explanation was given in [97], where it was noted that acetonitrile may be formed via the oxidative fragmentation of oxime $(CH_3)_2C{=}N{-}OH + 1/2O_2 = CH_3CN + CH_2O + H_2O$. We do not exclude that oxygen

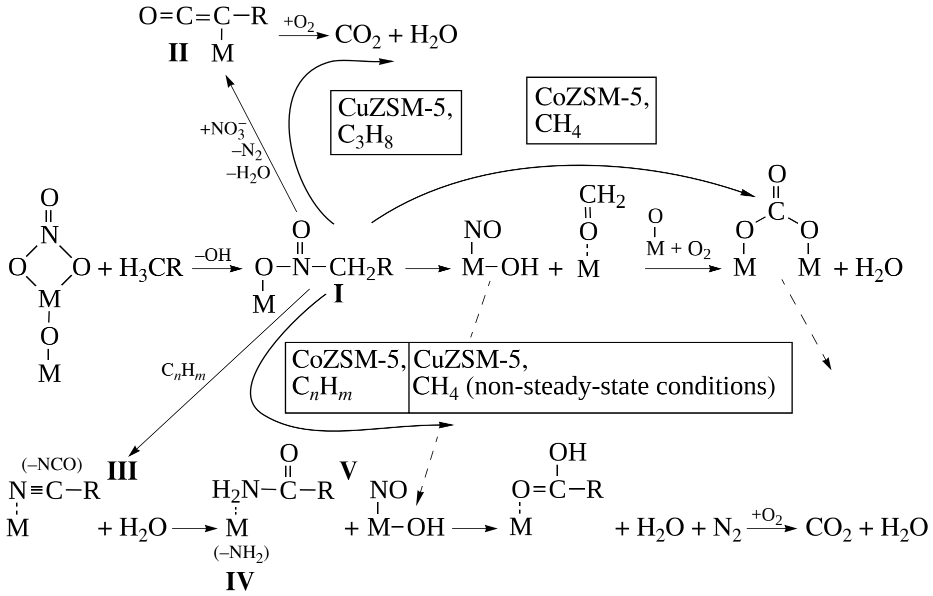

Fig. 13. Mechanistic scheme of the selective reduction of nitrogen oxides by alkanes [35, 50].

also favors the transformation of nitriles into isocyanates, which are readily hydrolyzed to form ammonia.

When considering the mechanism of SCR of nitrogen oxides by methane on CoZSM-5, it is interesting to compare with the scheme of catalytic transformation of nitromethane proposed on the basis of the study of nitromethane decomposition in the presence of oxygen [98, 103–107]:

(1) $CH_3NO_2 \Leftrightarrow CH_2{=}N(O)OH$ (isomerization into acynitro species),

(2) $CH_2{=}N(O)OH \longrightarrow CHO{-}N(H)OH$ (formation of formhydroxamic acid),

(3) $CHO{-}N(H)OH \longrightarrow HNCO + H_2O$,

(4) $HNCO + H_2O \longrightarrow NH_3 + CO_2$,

(5) $2NH_3 + 2NO\ (+ 1/2O_2) \longrightarrow 2N_2 + 3H_2O$,

(6) $CHO{-}N(H)OH + H_2O$

$\longrightarrow HCOOH + NH_2OH\ (\longrightarrow N_2)$,

(7) $NH_3 + HCOOH \xrightarrow[(-H_2O)]{} NH_2CHO \xrightarrow[(-H_2O)]{} HCN$.

Comparison of this scheme with our data on the mechanism of nitromethane transformation shows that they agree in the main details of hydrolysis leading to the formation of intermediates, which contain nitrogen in reduced forms (formamide **V** in our case, ammonia and hydroxylamine in the scheme of Cowan *et al.*). As shown above, in our experiments on the decomposition of nitromethane, we also observed the formation of isocyanates, and the estimates of their reactivities shows that they can be intermediates in the routes of reductive transformation of nitromethane. Our scheme also takes into account the unselective transformation of nitromethane leading to the formation of the products of complete oxidation and NO.

The most important difference of our scheme from the scheme of Cowan [98, 103–107] is that we consider the formation of nitrile complexes **III** as a direct consequence of the reductive transformation of nitromethane under the action of the hydrocarbon (or, more likely, radicals formed by hydrocarbon activation). The fast formation of nitrile complexes in the process of titration of nitrite–nitrate complexes by propane on CoZSM-5 observed in our experiments [35] supports this conclusion. At the same time, the mechanistic scheme of Cowan *et al.* considers the formation of nitrile complexes as a consequence of formamide dehydration. This difference may be associated with different experimental conditions, specifically, with the absence of methyl radicals in the process of nitromethane decomposition studied by Cowan *et al.* Indeed, in our experiments on the decomposition of nitromethane, we also observed the formation of nitriles.

The scheme proposed in [109, 110] should also be commented on. In this scheme, the main route of molecular nitrogen formation involves direct interaction of nitrile and NO. As noted in [107], the dominating role of this route is only possible in a rather unrealistic case of absolutely dry reaction mixtures, where hydrolysis of the CN group does not occur.

Thus, the mechanistic schemes proposed by us for SCR of nitrogen oxides by alkanes agree well with the known regularities of chemical transformations of nitro compounds, which are the main intermediates in SCR of nitrogen oxides by hydrocarbons in excess oxygen. At the same time, they supplement the known schemes

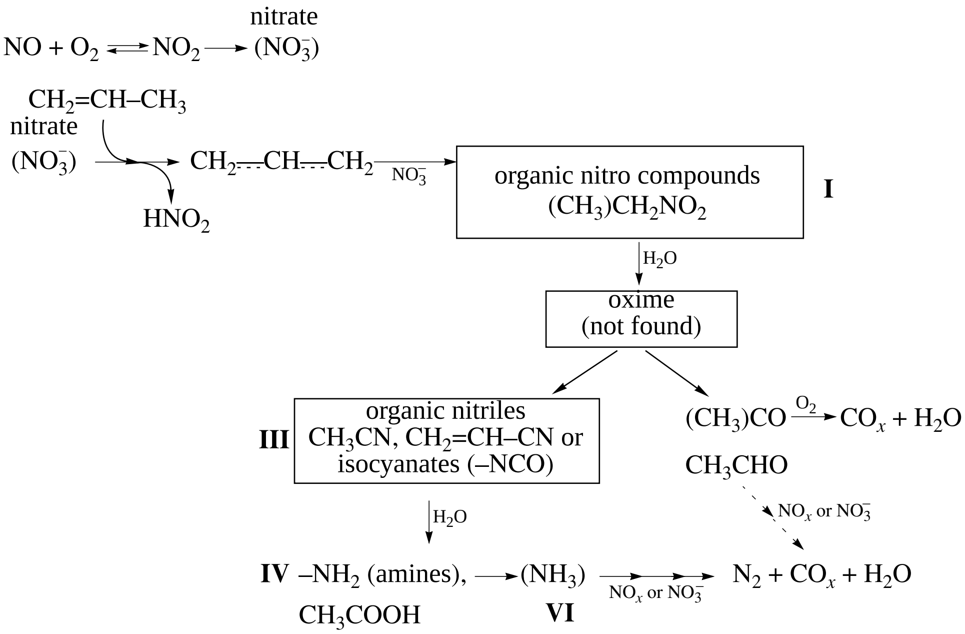

Fig. 14. Mechanistic scheme of the selective reduction of nitrogen oxides by propylene [51, 84].

and provide a better understanding of the mechanism of the reactions under study.

For SCR of nitrogen oxides by propylene, we obtained data that agree well with schemes proposed in [84, 86, 92] (Fig. 14). The key step is the formation of organic nitro compounds (most likely, 2-nitropropane). They transform into nitriles and/or isocyanates **III** via a route that probably involves the formation of oxime. Hydrolysis of nitriles and isocyanates produces amines **IV**, which generate ammonia (**VI**) in further hydrolysis. The latter is a highly efficient reducing agent. The interaction of ammonia with gas-phase nitrogen oxides or surface nitrate groups gives the target product, molecular nitrogen.

CONCLUSIONS

Our studies suggest that, for the reactions of selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen catalyzed by oxide systems, including those promoted by platinum, the key intermediates are surface nitrate complexes. The rate-limiting step in the reaction is the interaction with hydrocarbons or their activated fragments with the formation of nitro derivatives. Although further steps of thermal decomposition, acid hydrolysis, and oxidation of C,N,O-containing intermediates are fast, they critically depend on the chemical nature of a catalyst, which determines both the reaction route and the selectivities to by-products. The thermal stability of nitrate complexes, their high reactivity toward hydrocarbons, and the rich chemistry of organic nitro compounds, which provides the formation of ammonia under reaction conditions, make it possible to realize the process of selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen.

ACKNOWLEDGMENTS

We thank S.A. Belopashkin, G.A. Konin, T.G. Kuznetsova, R.V. Bunina, G.M. Alikina, S.A. Ven’yaminov, D.I. Kochubei, A.N. Kharlanov, V.F. Tret’yakov, T.N. Burdeinaya and other coauthors of original publications for their experimental studies and fruitful discussions. This work was supported by the Russian Foundation for Basic Research (grant nos. 95-03-09675 and 95-03-09622) and INTAS (grant no. 97-11720).

REFERENCES

1. Iwamoto, M., Yahiro, H., Shundo, S., Yu-u, Y., and Mizuno, N., *Shokubai*, 1990, vol. 32, p. 430.
2. Iwamoto, M., *Proc. Meeting of Catalytic Technology for Removal of Nitrogen Monoxide*, Tokyo, 1990, p. 1.
3. Held, W. and Koenig, A., *Ger. Offen.*, DE 3642018, 1987.
4. Held, W., Koenig, A., Richter, T., and Puppe, L., *SAE Paper*, 1990, 900496.
5. Iwamoto, M., Mizuno, N., and Yahiro, H., *Proc. 10th Int. Congr. Catalysis*, Budapest: Akademiai Kiado, 1993, part B, p. 1285.
6. Iwamoto, M., *Proc. 10th Int. Zeolite Conf.*, Weitkamp, J., Karge, H.G., Pfeifer, H., and Holderich, H.P., Eds., 1994, p. 1395.
7. Iwamoto, M., *Catal. Today*, 1996, vol. 29, nos. 1–4, p. 29.

8. Amiridis, M.D., Zhang, T., and Farrauto, R.J., *Appl. Catal., B*, 1996, vol. 10, p. 203.
9. Centi, G. and Perathoner, S., *Appl. Catal., A*, 1995, vol. 132, p. 179.
10. Walker, A.P., *Catal. Today*, 1995, vol. 26, p. 107.
11. Burch, R., *Catal. Today*, 1997, vol. 35, p. 27.
12. Ansell, G.P., Diwell, A.F., Goloinski, S.F., Hayes, J.W., Rajaram, R.R., Truex, T.J., and Walker, A.P., *Appl. Catal. B*, 1993, vol. 2, p. 81.
13. Kintaichi, Y., Hamada, M., Tabata, M., Sasaki, M., and Ito, T., *Catal. Lett.*, 1990, vol. 6, p. 239.
14. Smits, R.H.H. and Iwasawa, Y., *Appl. Catal., B*, 1995, vol. 6, p. L201.
15. Lukyanov, D.B., Lombardo, E.A., and Sill, G.A., d'Itri J.L., Hall W.K, *J. Catal.*, 1996, vol. 163, no. 2, p. 447.
16. Sun, T., Fokema, M.D., and Ying, J.Y., *Catal. Today*, 1997, vol. 33, p. 251.
17. Otsuka, K., Zhang, Q., Yamanaka, I., Tono, H., Hatano, M., and Kinoshita, H., *Bull. Chem. Soc. Jpn.*, 1996, vol. 69, p. 3367.
18. Jen, H.W. and Gandhi, H.S., *ACS Symp. Ser.*, 1995, vol. 552, p. 53.
19. Shelef, M., *Chem. Rev.*, 1994, vol. 95, p. 209.
20. Centi, G. and Perathoner, S., *Catal. Today*, 1996, vol. 29, nos. 1–4, p. 117.
21. Sasaki, M., Hamada, H., Kintaichi, Y., and Ito, T., *Catal. Lett.*, 1992, vol. 15, p. 297.
22. Hamada, H., Kintaichi, Y., Sasaki, M., and Tabata, M., *Appl. Catal.*, 1991, vol. 70, p. L15.
23. Bethke, K.A., Li, C., Kung, M.C., Yang, B., and Kung, H.H., *Catal. Lett.*, 1995, vol. 31, p. 287.
24. Stakheev, A.Yu., Lee, C.W., Park, S.J., and Chong, P.J., *Catal. Lett.*, 1996, vol. 38, p. 271.
25. Adelman, B.J., Beutel, T., and Lei, G.-D., and Sachtler, W.M.H., *J. Catal.*, 1996, vol. 158, p. 327.
26. Beutel, T., Adelman, B.J., Lei, G.-D., and Sachtler, W.M.H., *Catal. Lett.*, 1995, vol. 32, p. 83.
27. Bamwenda, G.R., Ogata, A., Obuchi, A., Takahashi, H., and Mizuno, K., *React. Kinet. Catal. Lett.*, 1995, vol. 56, no. 2, p. 311.
28. Cho, B.K., Yie, J.E., and Rahmoeller, K.M., *J. Catal.*, 1995, vol. 157, p. 14.
29. Burch, R., Millington, P.J., and Walker, A.P., *Appl. Catal., B*, 1994, vol. 4, no. 1, p. 65.
30. Burch, R. and Watling, T.C., *Catal. Lett.*, 1996, vol. 37, p. 51.
31. Burch, R. and Watling, T.C., *Catal. Lett.*, 1997, vol. 43, p. 19.
32. Sadykov, V.A., Baron, S.L., Matyshak, V.A., Alikina, G.M., Bunina, R.V., Rozovskii, A.Ya., Lunin, V.V., Lunina, E.V., Kharlanov, A.N., Ivanova, A.S., and Veniaminov, S.A., *Catal. Lett.*, 1996, vol. 37, p. 157.
33. Matyshak, V.A., Baron, S.L., Ukharskii, A.A., Il'ichev, A.N., Sadykov, V.A., and Korchak, V.N., *Kinet. Katal.*, 1996, vol. 37, no. 4, p. 585.
34. Sadykov, V.A., Paukshtis, E.A., Beloshapkin, S.A., Alikina, G.M., Veniaminov, S.A., Bunina, R.V., Lununa, E.V., Kharlanov, A.N., Lunin, V.V., Matyshak, V.A., and Rozovskii, A.Ya., *Proc. 8th Int. Symp. on Heterogeneous Catalysis*, Varna, 1996, vol. 1, p. 347.
35. Sadykov, V.A., Beloshapkin, S.A., Paukshtis, E.A., Alikina, G.M., Kochubei, D.I., Degtyarev, S.P., Bulgakov, N.N., Veniaminov, S.A., Bunina, R.V., Kharlanov, A.N., Lunina, E.V., Lunin, V.V., Matyshak, V.A., and Rozovskii, A.Ya., *Pol. J. Environ. Stud.*, 1997, vol. 1, p. 21.
36. Sadykov, V.A., Beloshapkin, S.A., Paukshtis, E.A., Alikina, G.M., Kochubei, D.I., Degtyarev, S.P., Bulgakov, N.N., Veniaminov, S.A., Netyaga, E.V., Bunina, R.V., Kharlanov, A.N., Lunina, E.V., Lunin, V.V., Matyshak, V.A., and Rozovskii, A.Ya., *React. Kinet. Catal. Lett.*, 1998, vol. 64, p. 185.
37. Sadykov, V.A., Rozovskii, A.Ya., Lunin, V.V., Lin, G.I., Alikina, G.M., Buchtiyarova, G.A., Zolotovskii, B.P., and Beloshapkin, S.A., *React. Kinet. Catal. Lett.*, 1999, vol. 66, p. 337.
38. Beloshapkin, S.A., Matyshak, V.A., Paukshtis, E.A., Sadykov, V.A., Ilyichev, A.N., Ukharskii, A.A., and Lunin, V.V., *React. Kinet. Catal. Lett.*, 1999, vol. 66, p. 297.
39. Matyshak, V.A., Ukharskii, A.A., Il'ichev, A.N., Sadykov, V.A., and Korchak, V.N., *Kinet. Katal.*, 1999, vol. 40, no. 1, p. 116.
40. Beloshapkin, S.A., Paukshtis, E.A., and Sadykov, V.A., *J. Mol. Catal. A: Chem.*, 2000, vol. 158, p. 355.
41. Sadykov, V.A., Bunina, R.V., Alikina, G.M., Ivanova, A.S., Kuznetsova, T.G., Beloshapkin, S.A., Matyshak, V.A., Konin, G.A., Rozovskii, A.Ya., Tretyakov, V.F., Burdeynaya, T.N., Davydova, M.N., Ross, J.R.H., and Breen, J.P., *J. Catal.*, 2001, vol. 199, p. 131.
42. Metelkina, O.V., Lunin, V.V., Sadykov, V.A., Beloshapkin, S.A., Alikina, G.M., Lunina, E.V., and Kharlanov, A.N., *Neftekhimiya*, 2000, vol. 40, p. 108.
43. Metelkina, O.V., Lunin, V.V., Sadykov, V.A., Alikina, G.M., Bunina, R.V., Paukshtis, E.A., Fenelonov, V.B., Derevyankin, A.Yu., Zaikovskii, V.I., Schubert, U., and Ross, J.R.H., *Catal. Lett.*, 2002, vol. 78, p. 111.
44. Konin, G.A., Il'ichev, A.N., Matyshak, V.A., Khomenko, T.I., Korchak, V.N., Sadykov, V.A., Doronin, V.P., Bunina, R.V., Alikina, G.M., Kuznetsova, T.G., Paukshtis, E.A., Fenelonov, V.B., Zaikovskii, V.I., Ivanova, A.S., Beloshapkin, S.A., Rozovskii, A.Ya., Tretyakov, V.F., Ross, J.R.H., and Breen, J.P., *Top. Catal.*, 2001, vol. 17, no. 17, p. 193.
45. Konin, G.A., Il'ichev, A.N., Matyshak, V.A., Khomenko, T.I., Korchak, V.N., Sadykov, V.A., Doronin, V.P., Bunina, R.V., Alikina, G.M., Kuznetsova, T.G., Paukshtis, E.A., Fenelonov, V.B., Zaikovskii, V.I., Ivanova, A.S., Beloshapkin, S.A., Rozovskii, A.Ya., Tretyakov, V.F., Ross, J.R.H., and Breen, J.P., *Proc. CAPOC-5*, Brussels, 2000, vol. 2, p. 97.
46. Matyshak, V.A., Il'ichev, A.N., Ukharsky, A.A., and Korchak, V.N., *J. Catal.*, 1997, vol. 171, p. 245.
47. Il'ichev, A.N., Matyshak, V.A., Korchak, V.N., and Yan, Yu.B., *Kinet. Katal.*, 2001, vol. 42, no. 1, p. 108.
48. Meunier, F.C., Breen, J.P., Zuzannik, V., Olsson, M., and Ross, J.R.H., *J. Catal.*, 1999, vol. 187, p. 493.
49. Zuzaniuk, V., Meunier, F.C., and Ross, J.R.H., *J. Catal.*, 2001, vol. 202, p. 340.
50. Beloshapkin, S.A., *Cand. Sci. Dissertation*, Novosibirsk: Inst. of Catal., 2000.

51. Konin, G.A., *Cand. Sci. Dissertation*, Moscow: Inst. Chem. Phys., 2001.
52. Sadykov, V.A., Rozovskii, A.Ya., Lunin, V.V., and Matyshak, V.A., *U.S.-Russia Workshop on Environmental Catalysis*, Wilmington, 1994, p. 20.
53. Sadykov, V.A., Alikina, G.M., Bunina, R.V., Baron, S.L., Veniaminov, S.A., Romannikov, V.N., Doronin, V.P., Rozovskii, A.Ya., Tretyakov, V.F., Lunin, V.V., Lunina, E.V., Kharlanov, A.N., and Matyshak, V.A., *Environmental Catalysis for a Better World and Life* (Proc. 1st World Congr. on Environmental Catalysis, Pisa), Centi, G., Cristiani, C., Forzatti, P., and Perathoners, S., Eds., Roma: Societa Chimica Italiana, 1995, p. 315.
54. Sadykov, V.A., Alikuna, G.M., Baron, S.L., Veniaminov, S.A., Bunina, R.V., Paukshtis, E.A., Lunina, E.V., Kharlanov, A.N., Lunin, V.V., Matyshak, V.A., and Rozovskii, A.Ya., *Abstracts of 11th Int. Congr. on Catalysis*, Baltimore, 1996, Po-202.
55. Sadykov, V.A., Kuznetsova, T.G., Alikina, G.M., Doronin, V.P., Sorokina, T.P., Bunina, R.V., Kochubei, D.I., Novgorodov, B.N., Paukshtis, E.A., Fenelonov, V.B., Derevyankin, A.Yu., Zaikovskii, V.I., Beloshapkin, S.A., Kolomiichuk, V.N., Anufrienko, V.F., Vasenin, N.T., Rozovskii, A.Ya., Tretyakov, V.F., Burdeynaya, T.N., Davydova, M.N., Matyshak, V.A., Konin, G.A., Ross, J.R.H., and Breen, J.P., *Europacat-V*, Limerick, 2001, Abstracts, Book 3, 7-O-03.
56. Konin, G.A., Il'chev, A.N., Matyshak, V.A., Khomenko, T.I., Korchak, V.N., Papakhin, D.M., Kuritsyn, D.Yu., Ivanova, A.S., Sadykov, V.A., Rozovskii, A.Ya., and Ross, J.R.H., *Europacat-V*, Limerick, 2001, Abstracts, Book 2, 21-O-10.
57. Rozovskii, A.Ya., *Katalizator i reaktsionnaya sreda* (The Catalyst and the Reaction Medium), Moscow: Nauka, 1988.
58. Hadjiivanov, K., *Catal. Lett.*, 2000, vol. 68, p. 157.
59. Davydov, A.A., Lokhov, Yu.A., and Shchekochikhin, Yu.M., *Kinet. Katal.*, 1978, vol. 19, no. 3, p. 673.
60. Schraml-Marth, M., Wokaun, A., and Baiker, A., *J. Catal.*, 1992, vol. 138, p. 306.
61. Centi, G., Perathoner, S., Biglino, D., and Giamello, E., *J. Catal.*, 1995, vol. 151, no. 1, p. 75.
62. Eng, J. and Bartolomew, C.H., *J. Catal.*, 1997, vol. 171, no. 1, pp. 14, 27.
63. Kijlstra, W.S., Brands, D.S., Poels, E.K., and Bliek, A., *J. Catal.*, 1997, vol. 171, no. 1, p. 208.
64. Hadjiivanov, K. and Dimitrov, L., *Microp. Mesopor. Mater.*, 1999, vol. 27, p. 49.
65. Huang, S.-J., Walters, A.B., and Vannice, M.A., *Appl. Catal., B*, 2000, vol. 26, p. 101.
66. Kantcheva, M. and Ciftlikli, E.Z., *J. Phys. Chem.*, 2002, vol. 106, p. 3941.
67. Hadjiivanov, K., Knozinger, H., Tsyntsarski, B., and Dimitrov, L., *Catal. Lett.*, 1999, vol. 62, p. 35.
68. Chi, Y. and Chuang, S.S.C., *J. Phys. Chem.*, 2000, vol. 104, p. 4673.
69. Klingenberg, B. and Vannice, M.A., *Appl. Catal., B*, 1999, vol. 21, p. 19.
70. Haneda, M., Kintaichi, Y., Inaba, M., and Hamada, H., *Catal. Today*, 1998, vol. 42, p. 127.
71. Haneda, M., Bion, N., Daturi, M., Saussey, J., Lavalley, J.-C., Duprez, D., and Hamada, H., *J. Catal.*, 2002, vol. 206, p. 114.
72. Chen, H.-Y., El-Makli, E.-M., Wang, X., van Santen, R.A., and Sachtler, W.M.H., *J. Mol. Catal., A: Chem.*, 2000, vol. 162, p. 159.
73. Ivanova, E., Hadjiivanov, K., Klissurski, D., Bevilacqua, M., Armaroli, T., and Busca, G., *Micropor. Mesopor. Mater.*, 2001, vol. 46, p. 299.
74. Beutel, T., Adelman, B.J., and Sachtler, W.M.H., *Appl. Catal., B*, 1996, vol. 9, p. L1.
75. Huang, S.-J., Walters, A.B., and Vannice, M.A., *Appl. Catal., B*, 2000, vol. 26, p. 101.
76. Fanson, P.T., Stradt, M.W., Delgass, W.N., and Lauterbach, J., *Catal. Lett.*, 2001, vol. 77, p. 15.
77. Hadjiivanov, K., *Catal. Rev.–Sci. Eng.*, 2000, vol. 42, p. 71.
78. Pozdnyakov, D.V. and Filimonov, V.N., *Kinet. Katal.*, 1973, vol. 14, p. 760.
79. Gribov, L.A. and Dement'ev, B.A., *Metody i algoritmy vychislenii v teorii kolebatel'nykh spektrov molekul* (Methods and Algorithms of Calculations in the Theory of Vibrational Spectra of Molecules), Moscow: Nauka, 1981.
80. Wang, T., Sklyarov, A.V., and Keulks, G.W., *Catal. Today*, 1997, vol. 33, p. 291.
81. Jung, K.T. and Bell, A.T., *J. Mol. Catal., A: Chem.*, 2000, vol. 163, p. 27.
82. Shimizu, K., Satsuma, A., and Hattori, T., *Catal. Surv. Jpn.*, 2000, vol. 4, p. 115.
83. Shimizu, K., Shibata, J., Yoshida, H., Satsuma, A., and Hattori, T., *Appl. Catal., B*, 2001, vol. 30, p. 151.
84. Haneda, M., Joubert, E., Menezo, J.-Ch., Duprez, D., Barbier, J., Bion, N., Daturi, M., Saussey, J., Lavalley, J.-C., and Hamada, H., *J. Mol. Catal., A: Chem.*, 2001, vol. 175, p. 179.
85. Shi, Ch., Cheng, M., Qu, Zh., Yang, X., and Bao, X., *Appl. Catal., B*, 2002, vol. 36, p. 173.
86. Haneda, M., Bion, N., Daturi, M., Saussey, J., Lavalley, J.-C., Duprez, D., and Hamada, H., *J. Catal.*, 2002, vol. 206, p. 114.
87. Matyshak, V.A. and Krylov, O.V., *Catal. Today*, 1995, vol. 25, p. 1.
88. Adelman, B.J., Beutel, T., Lei, G.-D., and Sachtler, W.M.H., *Appl. Catal., B*, 1996, vol. 11, p. L1.
89. Kuznetsova, T.G., Sadykov, V.A., Paukshtis, E.A., Matyshak, V.A., Konin, G.A., Rogov, V.A., Doronin, V.P., Sorokina, T.P., and Ross, Dzh. R. Kh., *Tez. dokl. VI Ross. konf. "Mekhanizmy kataliticheskikh reaktsii"* (Proc. VI Ross. Conf on the Mechanisms of Catalytic Reactions), Moscow, 2002, vol. 2, p. 197.
90. Cowan, A.D., Dumpelmann, R., and Cant, N.W., *J. Catal.*, 1995, vol. 151, p. 356.
91. Cant, N.W. and Cowan, A.D., *Catal. Today*, 1997, vol. 35, p. 89.
92. Chi, Y. and Chuang, S.S.C., *J. Catal.*, 2000, vol. 190, p. 75.
93. Poignant, F., Freysh, J.L., Daturi, M., and Saussey, J., *Catal. Today*, 2001, vol. 70, p. 197.

94. Fokema, M.D. and Ying, J.Y., *Catal. Rev.–Sci. Eng.*, 2001, vol. 43, p. 1.
95. Sadykov, V.A., Ivanova, A.S., Ivanov, V.P., Alikina, G.M., Kharlanov, A.N., Linina, E.V., Lunin, V.V., Matyshak, A., Zubareva, N.A., and Rozovskii, A.Ya., *Mater. Res. Soc. Symp. Ser.*, 1997, vol. 454, p. 199.
96. Tanaka, T., Okuhara, T., and Misono, M., *Appl. Catal., B*, 1994, vol. 4, p. L1.
97. Chen, H.-Y., Voskoboinikov, T., and Sachtler, W.M.H., *Catal. Today*, 1999, vol. 54, p. 483.
98. Cant, N.W. and Liu, I.O.Y., *Catal. Today*, 2000, vol. 63, p. 133.
99. Schiesser, W., Vinek, H., and Jentys, A., *Appl. Catal. B*, 2001, vol. 33, p. 263.
100. Joubert, E., Menezo, J.C., Duprez, D., and Barbier, J., *Top. Catal.*, 2001, vols. 16/17, p. 225.
101. Kameoka, S., Chafik, T., Ukisu, Y., and Miyadera, T., *Catal. Lett.*, 1998, vol. 55, p. 211.
102. Haneda, M., Kintaichi, Y., Inaba, M., and Hamada, H., *Catal. Today*, 1998, vol. 42, p. 127.
103. Satsuma, A., Cowan, A.D., Cant, N.W., and Trimm, D.L., *J. Catal.*, 1999, vol. 181, p. 165.
104. Cant, N.W., Cowan, A.D., Liu, I.O.Y., and Satsuma, A., *Catal. Today*, 1999, vol. 54, p. 473.
105. Lombardo, E.A., Sill, G.A., d'Itri J.L., and Hall, W.K., *J. Catal.*, 1998, vol. 173, p. 440.
106. Cant, N.W., Chambers, D.C., Cowan, A.D., Liu, I.O.Y., and Satsuma, A., *Top. Catal.*, 2000, vol. 10, p. 13.
107. Cowan, A.D., Cant, N.W., Haynes, B.S., and Nelson, P.F., *J. Catal.*, 1998, vol. 176, p. 329.
108. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1963.
109. Aylor, A.W., Lobree, L.J., Reimer, J.A., and Bell, A.T., *Stud. Surf. Sci. Catal.*, 1996, vol. 101A, p. 661.
110. Aylor, A.W., Lobree, L.J., Reimer, J.A., and Bell, A.T., *J. Catal.*, 1997, vol. 170, p. 390.
111. Haj, K.O., Ziyade, S., Ziyad, M., and Garin, F., *Appl. Catal., B*, 2002, vol. 37, p. 49.