Hydrocarbon Radicals and Nitroxy Complexes on the Surface of HZSM-5 and CuZSM-5 Zeolites: An ESR Study

A. N. Il'ichev, V. A. Matyshak, and V. N. Korchak

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117333 Russia

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Abstract—The conditions favorable for the formation of oligomer and benzene cation radicals upon C_2H_4, C_6H_6, and C_3H_6 adsorption on thermally activated HZSM-5 and CuZSM-5 zeolites were studied. In the case of isolated copper ions, the radicals were shown to be formed from C_3H_6 but not from C_2H_4 and C_6H_6. Paramagnetic nitroxy complexes, which were formed as a result of the interaction of adsorbed hydrocarbons C_2H_4, C_6H_6, and C_3H_6 with NO and NO_2, were revealed on HZSM-5 zeolite and Al_2O_3. Hydrocarbon radicals and nitroxy complexes are localized on different zeolite sites. Nitroxy complexes are formed on aluminum cations. The role of radicals and nitroxy complexes in the process of NO_x selective catalytic reduction by hydrocarbons on the zeolites was discussed on the basis of the temperature dependences of the concentrations of these species.

INTRODUCTION

Nowadays, significant attention is given to the mechanistic studies of the reaction of selective NO_x reduction with hydrocarbons on CuZSM-5 catalysts in excess oxygen [1]. Among many viewpoints on this mechanism [2], a hypothesis was put forward considering organonitrogen compounds as species that are essential for the molecular nitrogen formation and play an important role in NO_x reduction. Nitroxy compounds are supposed [3–5] to be formed on copper ions in the ZSM-5 zeolite channels. According to [3], such complexes could be similar to nitromethane, which is formed in the case of the reaction of an activated hydrocarbon with adsorbed NO_2 molecules. The formation of nitroxy complexes is considered in connection with the presence of hydrocarbon oligomers in HZSM-5 and CuZSM-5 zeolites [6]. Indeed, oligomer and benzene radicals were observed upon C_2–C_8 olefin and benzene adsorption on HZSM-5 zeolite [7–10]. These radicals are assumed to be active species in the process of NO_x reduction. Oligomer radicals were found in [11] by ESR spectroscopy after propene adsorption on CuZSM-5 zeolite, but the authors failed to observe any organonitrogen compounds after treating the catalyst with the reaction mixture.

In our works [5, 12], the rate of NO reduction was shown to correlate with the concentration of isolated Cu^{2+} ions. The reaction was considered to proceed on the coordinatively unsaturated copper complex, which is formed because of the interaction of isolated Cu^{2+} ions with NO_2. Such a complex possesses enhanced reactivity. Its interaction with an activated hydrocarbon presumably yields a nitroxy complex. We failed to reveal any nitroxy complexes in the process conditions using *in situ* IR spectroscopy, although such compounds were observed in a sufficiently high concentra-

tion at a lower temperature [12]. This fact could be accounted for by the high rate of transformation of these compounds into reaction products.

Thus, nitroxy complexes are considered in many works to be key intermediates in the reaction of selective catalytic NO_x reduction with hydrocarbons in excess oxygen. However, there are virtually no data on the mechanism of their formation, their thermal stability, localization sites, and the effect of copper ions on this process.

The aim of this paper is to compensate for the lack of knowledge in this field. Therefore, in the first part of this work, we studied radical formation in the course of hydrocarbon (C_2H_4, C_3H_6, and C_6H_6) adsorption on the HZSM-5 and CuZSM-5 zeolites. In the second part, we studied the interaction of these radicals and adsorbed hydrocarbons with NO molecules and a NO + O_2 mixture.

EXPERIMENTAL

The experiments were performed on the HZSM-5 and CuZSM-5 zeolites. The characteristics of HZSM-5 zeolite, Cu^{2+} and Cu^+ distribution in the samples containing 0.15–2.86% Cu in ZSM-5 zeolite and prepared from HZSM-5 zeolite (SiO_2/Al_2O_3 = 40, TsVK type zeolite) by ion exchange, and information on their catalytic activity in the reaction of NO reduction with propane in excess oxygen are described in [5].

The samples were activated in a vacuum. The catalyst (50 mg) was placed in a quartz ampule, and the ampule was sealed to a vacuum setup. After evacuation to $P = 1 \times 10^{-4}$ Pa at 970 K, the sample was heated in either O_2 or H_2 at $P = 2 \times 10^2$ Pa for 1 h at the same temperature. Then, the sample was cooled to room temperature and evacuated to $P = 1 \times 10^{-4}$ Pa. The use of a flex-

ible vacuum connection made it possible to install the ampule with the catalyst in the cavity of an ESR spectrometer under vacuum conditions. After that, the gas under study was admitted to the ampule. The amount of the adsorbed compound was measured using a thermal desorption method (TPD) and a Pirany manometer [13].

The state of adsorbed molecules was studied using an ESR technique. ESR spectra of the samples after thermal vacuum treatment or in the course of gas adsorption were registered at room temperature and at 77 K using an EPR-V (Institute of Chemical Physics) spectrometer equipped with a Diapazon temperature-controlled attachment. $CuSO_4 \cdot 5H_2O$ and Mn^{2+}–MgO were used as standards for determining the concentration of radicals and copper ions in the samples.

The thermal stability of radicals and nitroxy complexes in zeolites was estimated using the thermal vacuum treatment of the sample with a stepwise temperature increase. In the beginning of an experiment, the sample containing radicals was heated at a chosen temperature with further evacuation for 10 min. Desorbed gas was frozen out in the trap with liquid nitrogen. Then, the sample was cooled to room temperature and ESR spectra were measured. The amount of the gas desorbed was determined by measuring the gas pressure after the heating of a trap. Then, the temperature was raised to the next value and the procedure was repeated. Using this method, the data on the radical concentration dependence on the sample treatment temperature were collected.

The gases used (H_2, O_2, and NO) were prepared in vacuum conditions according to [14]. Before adsorption on the sample, commercial hydrocarbon reagents C_2H_4, C_3H_6, and C_6H_6 were additionally purified by freezing in the trap with liquid nitrogen followed by evacuation.

RESULTS

1. Hydrocarbon Radicals in HZSM-5 Zeolite

The ESR spectrum of the zeolite (preliminarily heated up to 970 K in O_2) after C_3H_6 adsorption at 293 K and $P = 2 \times 10^2$ Pa is presented in Fig. 1 (curve 1). It consists of a single line with $g = 2.004$, $\Delta H = 40$ G and eleven hyperfine structure (hfs) components with a splitting $A_{av} = 8$ G. According to [7], such a spectrum corresponds to the radical fragment $-CH_2-CH^+=CH-CH_2-$ in the oligomer chain. Such cation radicals ($R^{\dot{+}}$) are stable at room temperature and their concentration, which is equal to 8×10^{15} spin/g, does not change after gas evacuation.

As shown in Fig. 2 (curve 1), the step-by-step sample heating is accompanied by a decrease in the intensity of the oligomer radical ESR signal. The intensities of the ESR signal referred to the maximum intensity of the corresponding signal are shown in this figure. The number of desorbed C_3H_6 molecules after sample treatment at

333 K was $N_{des} = 0.6 \times 10^{19}$ molecule/g; at $T = 383$ K, we have $N_{des} = 2.0 \times 10^{19}$ molecule/g; and at $T = 400$ K, $N_{des} = 1.6 \times 10^{19}$ molecule/g. At the same time, the concentration of oligomer radicals $R^{\dot{+}}$ decreased by 2.0×10^{15}, 4.0×10^{15}, and 1.0×10^{15} spin/g, respectively. The analysis of these data testifies that the number of desorbed C_3H_6 molecules is ~10^4 times higher than a decrease in the concentration of oligomer radicals.

Heating of the sample at 470 K in a vacuum results in the complete disappearance of oligomer radicals. Further hydrocarbon adsorption at 293 K does not lead to the formation of radicals. Zeolite ability to form radicals is not recovered even after heating at 970 K in a vacuum.

The same ESR spectrum and ESR signal intensity dependence on the temperature were obtained for C_2H_4 adsorption.

Benzene adsorption at room temperature and $P = 2 \times 10^2$ Pa on HZSM-5 (O_2, 970 K) results in the ESR spectrum shown in Fig. 1 (curve 3). It consists of seven hyperfine structure components with $A_{av} = 4.5$ G and $g = 2.004$. According to [8–10], this spectrum corresponds to the $(C_6H_6)^+$ radical. The concentration of such radicals (7.4×10^{15} spin/g) is close to that of oligomer radicals. Evacuation of the sample for 10 min at 293 K results in a tenfold decrease in the intensity (see Fig. 1, curve 4). This fact indicates the low stability of such radicals in the zeolite under the chosen conditions.

According to [9–12], the formation of radicals $R^{\dot{+}}$ and $(C_6H_6)^+$ depends on the conditions of thermovacuum treatment of the sample. Adsorption of hydrocarbons on the zeolite, which was preliminarily heated in H_2 at 970 K, does not lead to the buildup of radicals. Radicals can be observed only if the samples were heated in oxygen or N_2O at 970 K. Treatment of the zeolite with oxygen at 600 K does not result in complete regeneration of its activity. In this case, the concentration of radicals was 10 times lower.

2. Interaction of Zeolite HZSM-5 Sites Responsible for the Radical Formation with O_2 and NO Molecules

Treatment of the zeolite (O_2, 970 K) with oxygen at $P = 2 \times 10^2$ Pa and 293 K for 10 min does not influence its ability to form radicals from olefins and benzene. Further adsorption of hydrocarbons on this sample is accompanied by the buildup of radicals. Hydrocarbon radicals were not observed if NO was adsorbed first on the zeolite (O_2, 970 K) followed by NO evacuation and admission of a hydrocarbon. Zeolite activity recovers completely after NO desorption at 600 K.

Since NO deactivates the radical-forming sites, it was expedient to compare the concentrations of adsorbed NO molecules and hydrocarbon radicals. Thus, after NO adsorption at 293 K and $P = 2 \times 10^2$ Pa

for 10 min and further gas evacuation at $P = 10^{-4}$ Pa, the number of NO molecules desorbed from the oxidized zeolite (O_2, 970 K) was 3×10^{19} molecule/g, whereas in the case of reduced zeolite (H_2, 970 K), this value was 1.5×10^{19} molecule/g. The number of adsorbed NO molecules corresponds to the concentration of Lewis pairs in the sample [10], but it is approximately three orders of magnitude higher than the number of hydrocarbon radicals formed.

3. Hydrocarbon Radicals on the CuZSM-5 Zeolite

Two types of isolated Cu^{2+} ions were observed in the ESR spectra after heating CuZSM-5 samples in oxygen (O_2, $P = 2 \times 10^2$ Pa, 970 K, 1 h). The first type corresponds to the square pyramid coordination ($g_\| = 2.33$ and $A_\| = 170$ G), and the second type is attributed to the square planar geometry ($g_\| = 2.29$, $A_\| = 180$ G). The ESR spectrum of the sample containing 1.3% Cu in ZSM-5 zeolite is shown in Fig. 3 (curve *1*). The concentration of isolated Cu^{2+} cations is 6×10^{19} ion/g in agreement with the data obtained in [5].

Figure 3 (curve *2*) shows that propene adsorption on this sample causes the disappearance of the ESR signal from isolated Cu^{2+} ions and leads to the buildup of the signal from $\overset{\cdot}{R}$ radicals. The concentration of radicals R on this sample is 10 times higher than in the case of HZSM-5 zeolite. Evacuation at room temperature does not change the ESR spectra. The concentrations of radicals and Cu^{2+} cations diminish after the vacuum treatment of the sample. The dependence of the concentration of oligomer radicals on the sample heating temperature in a vacuum is similar to that observed for oligomer radicals on the HZSM-5 zeolite (Fig. 2, curves *1* and *4*).

The dependences of the radical concentration on the copper concentration in the case of propene and benzene adsorption (293 K, $P = 2 \times 10^2$ Pa) on the oxidized zeolites are shown in Fig. 4. Note that the addition of copper to the zeolite influences the buildup of $\overset{\cdot}{R}$ and $(C_6H_6)^+$ radicals in a different manner. The concentration of the $\overset{\cdot}{R}$ radicals formed after propene adsorption increases by an order of magnitude when the copper content in the oxidized zeolite increases from 0.15 to 1.30%. A further increase in the copper loading results in a decrease in the intensity of the ESR signal assigned to $\overset{\cdot}{R}$ radicals, and the hyperfine structure in ESR spectra of these radicals disappears. Therefore, a precise estimate of the concentration of radicals seems to become impossible in the case of the samples containing more than 1.30% Cu. Thus, for the samples with 1.70 and 2.86% Cu, the radical concentrations presented in Fig. 4 were obtained from the spectra without hfs.
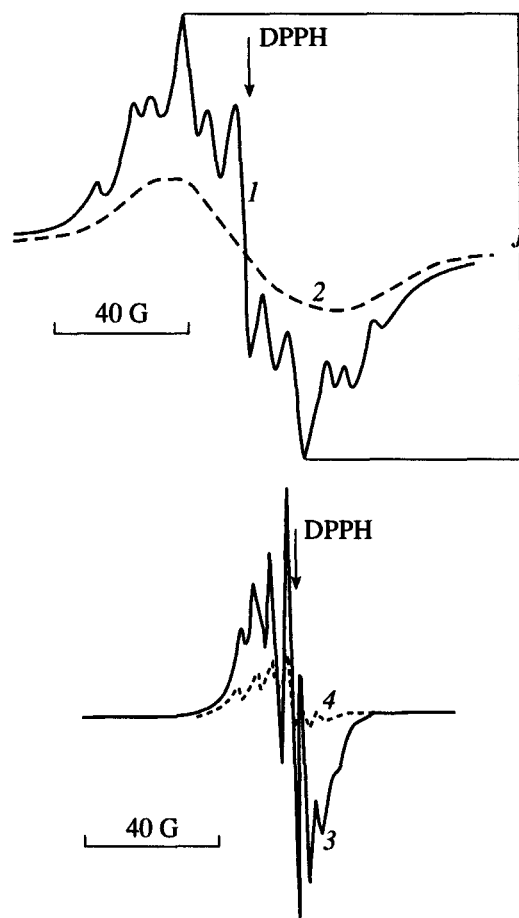

Fig. 1. ESR spectra of the HZSM-5 zeolite preliminarily heated in O_2 at 970 K: (*1*) after propene adsorption ($P = 2 \times 10^2$ Pa, $T = 293$ K), (2) after interaction of sample 1 with oxygen, (*3*) initial sample in the atmosphere of C_6H_6, (*4*) after C_6H_6 evacuation.
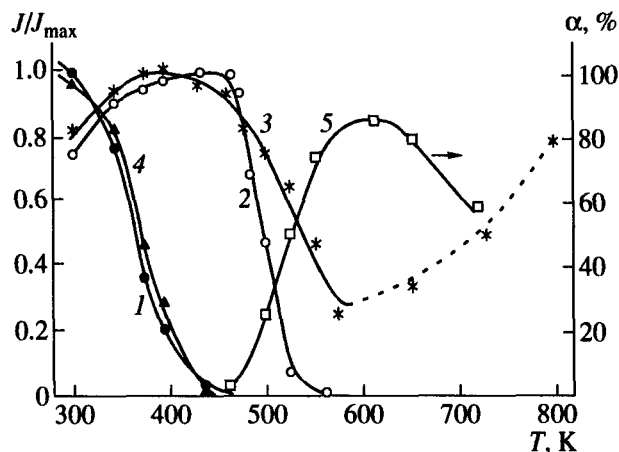

Fig. 2. Temperature dependence of the relative intensity of the signals in the ESR spectra of radicals and complexes, stepwise heating of HZSM-5 zeolite in a vacuum: (*1*) oligomer radical, (*2*) (NO-C_3H_6) complex, (*3*) (NO_2-C_3H_6) complex, (*4*) oligomer radicals on 1.3% CuZSM-5, (*5*) NO_x conversion into N_2 in the process of NO_x reduction on CuZSM-5 [1].
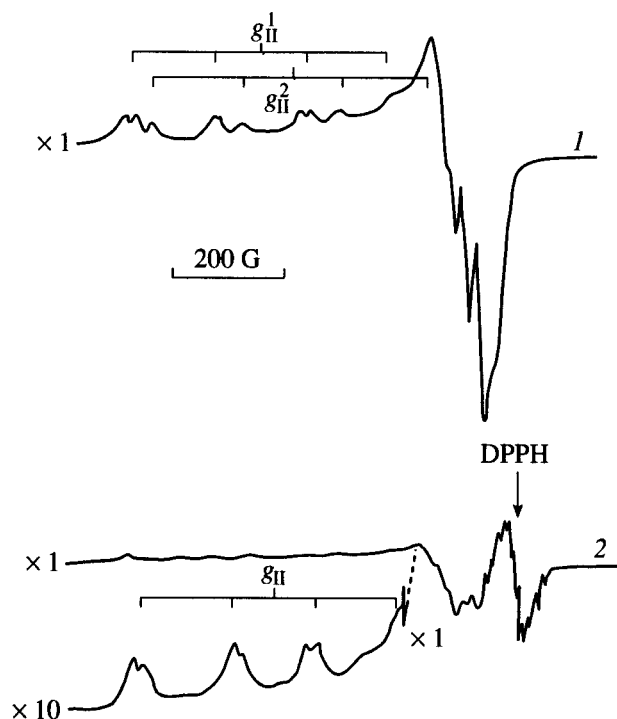
Fig. 3. ESR spectrum of the 1.3% CuZSM-5 zeolite: (1) in a vacuum and (2) after propene adsorption at 293 K and P = 2 × 10² Pa.

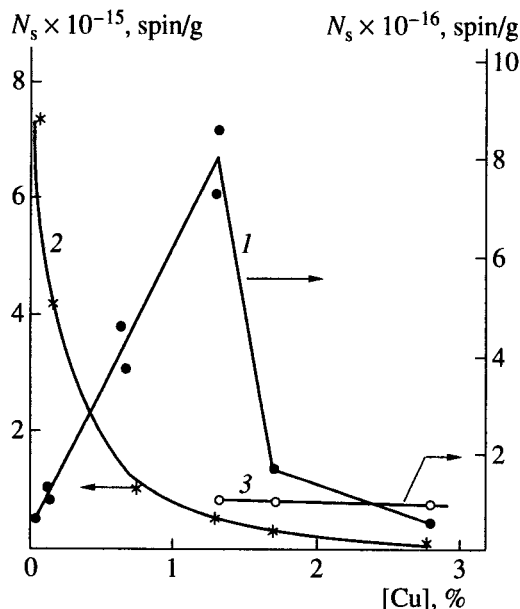Fig. 4. Dependence of the concentration of (1) R⁺ and (2) (C₆H₆)⁺ radicals on the oxidized samples and (3) R⁺ radicals on the reduced samples on the copper concentration in zeolite; R⁺ species are formed after propene adsorption.

In the case of benzene adsorption, an increase in the copper content is followed by a monotonic decrease in the concentration of benzene radicals. Seven hfs components in the spectra of $(C_6H_6)^+$ were registered only for the samples containing 0.15–0.25% Cu, but no hfs

was revealed when the copper concentration reached 1.30–2.86%.

Thus, copper addition to the HZSM-5 zeolite with a Cu loading of 0.15–1.30% results in an increase in the concentration of oligomer radicals in the case of propene adsorption, while the benzene radicals concentration diminishes.

Furthermore, in the presence of copper, the formation of oligomer radicals can be observed even on the samples that were reduced in hydrogen at 970 K. According to Fig. 4 (curve 3), propene adsorption on the reduced samples leads to the radical formation in the concentration ~8 × 10¹⁵ spin/g. For the samples with 1.70 and 2.86% Cu, ESR spectra of the oligomer radicals consist of eleven well-resolved lines in contrast to the spectra registered for the oxidized catalysts.

It should be noted that the concentration of oligomer radicals after ethylene adsorption on the oxidized copper-containing samples diminishes with an increase in the copper content, as in the case of $(C_6H_6)^+$ radicals.

4. Interaction of Hydrocarbon Radicals with O₂ and NO Molecules and the Formation of Hydrocarbon Complexes with NO on the HZSM-5 Zeolite

The interaction of hydrocarbon radicals with various molecules in zeolites changes the ESR spectra of these radicals. Thus, O₂ adsorption (T = 293 K and P = 2 × 10² Pa) leads to the irreversible loss of hfs (Fig. 1, spectrum 2). No spectra attributed to oxygen radicals were observed. The spectra of hydrocarbon radicals disappear completely after NO adsorption and do not recover after gas evacuation. This fact indicates the accessibility of hydrocarbon radicals for the reaction with NO molecules in zeolite channels.

Moreover, a new ESR signal appears after NO evacuation. The parameters of this signal are independent of the structure of the initial adsorbed hydrocarbon (C₂H₄, C₃H₆, or C₆H₆). The ESR spectrum of the sample after propene and NO adsorption is shown in Fig. 5 (curve 1). According to [15], such a line shape in the spectra is characteristic for a paramagnetic complex with the anisotropic g-factor. Its components are $g_1 = 2.090$, $g_2 = 2.070$, and $g_3 = 2.018$. This complex will be henceforth denoted as (NO–HC), where HC means a preliminarily adsorbed hydrocarbon. The concentrations of these complexes for the hydrocarbons under study were close to 1 × 10¹⁶ spin/g. This concentration does not change with an increase in the NO pressure from 2 × 10² to 5 × 10³ Pa during adsorption. The (NO–C₃H₆) complex exhibits higher thermal stability as compared to the oligomer radical. It can be registered after the stepwise thermovacuum treatment of the sample from 293 to 530 K (Fig. 2, curve 2).

The (NO–HC) complex formation is not related to R⁺ radicals, because this complex is formed upon NO adsorption on the sample even after removal of oligomer radicals by heating in a vacuum at 460–530 K.

No ESR signals were observed after NO adsorption on the zeolite that had been preliminarily treated in oxygen or hydrogen at 970 K. The (NO–HC) complex was not registered on the reduced zeolite.

5. Hydrocarbon Complex with NO_2 on the HZSM-5 Zeolite

Treatment of the zeolite (preactivated in O_2, 970 K) in an $NO + O_2$ mixture (1 : 1) at $P = 4 \times 10^2$ Pa, $T = 293$ K, and $t = 50$ min does not result in the appearance of any ESR signals. If C_3H_6 was preliminarily adsorbed on the zeolite (10 min, $P = 4 \times 10^2$ Pa, $T = 293$ K) and the sample was then evacuated for 20 min the $NO + O_2$ mixture was further adsorbed for 20–50 min then the new ESR spectrum shown in Fig. 5 (curve 2) was registered after the evacuation of the $NO + O_2$ mixture at 293 K. The same spectrum was registered in the case of C_6H_6 and C_2H_4 preliminary adsorption. In the case of C_2H_4, the ESR signal intensity was 10 times lower in comparison with the cases of benzene or propene adsorption. Using this procedure, we failed to observe any ESR spectra for the zeolite pretreated in H_2 at 970 K.

The ESR spectra of the complex under discussion consist of three lines and, according to [15], correspond to the spectrum of a paramagnetic complex with the nuclear spin $I = 1$ and an anisotropic g-tensor. The triplet is probably connected in this case with the nuclear spin of nitrogen in the nitrogen-containing hydrocarbon complex formed. Since separate NO and O_2 adsorption on the zeolite with a preadsorbed hydrocarbon does not result in the ESR spectrum 2 (Fig. 5), one can suppose that this complex is formed in the adsorbed hydrocarbon reaction with NO_2 molecules. By analogy with the (NO–HC) complex, this complex will be denoted as (NO_2–HC). Assuming the axial symmetry of the g- and A-tensors, their values were determined for (NO_2–C_3H_6) and (NO_2–C_6H_6) complexes: $g_\perp = 2.0060$, $g_\parallel = 2.0035$, $A_\perp = 25$ G, $A_\parallel = 45$ G. It should be emphasized that these values are similar for different hydrocarbons.

The presence of $NO + O_2$ in the gas phase influences the shape of the spectrum, attributed to the (NO_2–HC) complex. As it is seen from Fig. 6, the ESR spectrum of the sample with adsorbed benzene after treatment by the $NO + O_2$ mixture for 40 min at room temperature and $P = 5 \times 10^2$ Pa represents a singlet (curve 1). After evacuation to 10^{-4} Pa, a characteristic triplet appears (curve 2) and the intensity of the signal increases, presumably as a result of decomposition of unstable compounds, which yields NO or O_2 in the reaction with the (NO_2–HC) complex.

The data on the thermal stability of the (NO_2–C_3H_6) complex are presented in Fig. 2 (curve 3). The signal intensity in the spectrum increases as the temperature of the sample treatment grows from 293 to 400 K. The spin concentration 5×10^{15} spin/g corresponds to the spectrum with the maximum intensity. The signal
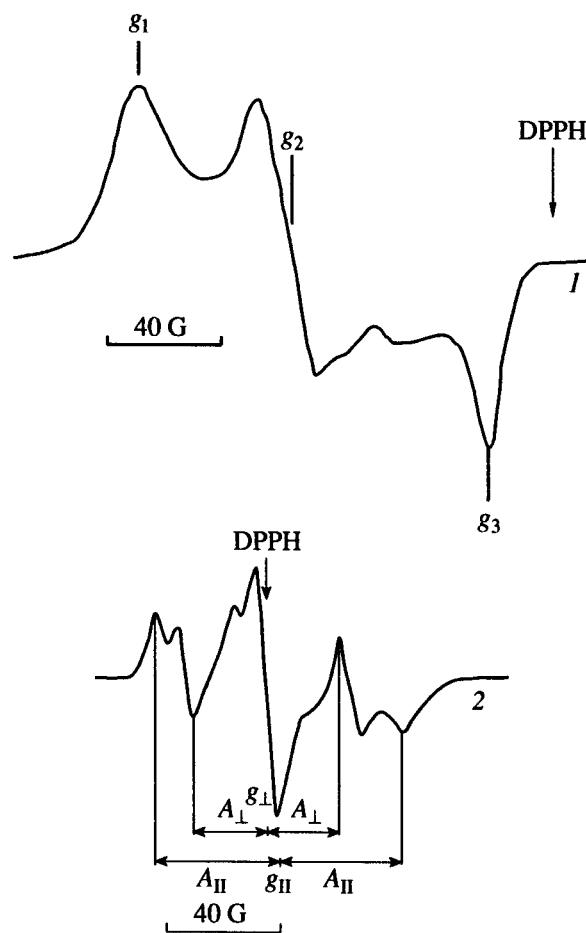

Fig. 5. ESR spectra after propene adsorption on the oxidized HZSM-5 zeolite and further (1) NO and (2) NO + O_2 adsorption, the spectra were registered after evacuation at 293 K.

intensity diminishes at $T > 420$ K and the signal vanishes at 560 K. A further temperature increase leads to the appearance and growth of a new signal with $g = 2.004$ and $\Delta H = 40$ G. This signal corresponds to the carbon deposit (coke) [11]. The coke formation is also observed in the case of decomposition of (NO_2–C_2H_4) and (NO_2–C_6H_6) complexes. This process occurs more readily in the case of benzene adsorption. Spectrum 4 shown in Fig. 6 was registered after (NO_2–C_6H_6) complex decomposition at 500 K in a vacuum for 10 min. It consists mainly of the signal attributed to coke ($N_s = 2 \times 10^{16}$ spin/g) and features assigned to residual (NO_2–C_6H_6) complexes. Overlapping of these signals makes the analysis of the temperature dependences of their intensities almost impossible. Spectra 2 and 3 in Fig. 6 likely represent a superposition of the singlet of coke and one triplet line of the (NO_2–C_6H_6) complex. It should be noted that no coke formation was observed in the case of (NO–HC) complex decomposition.

After the removal of the NO_2–HC complex from the zeolite surface at 560 K the sample was repeatedly treated with the $NO + O_2$ mixture at 293 K without preliminary hydrocarbon adsorption.
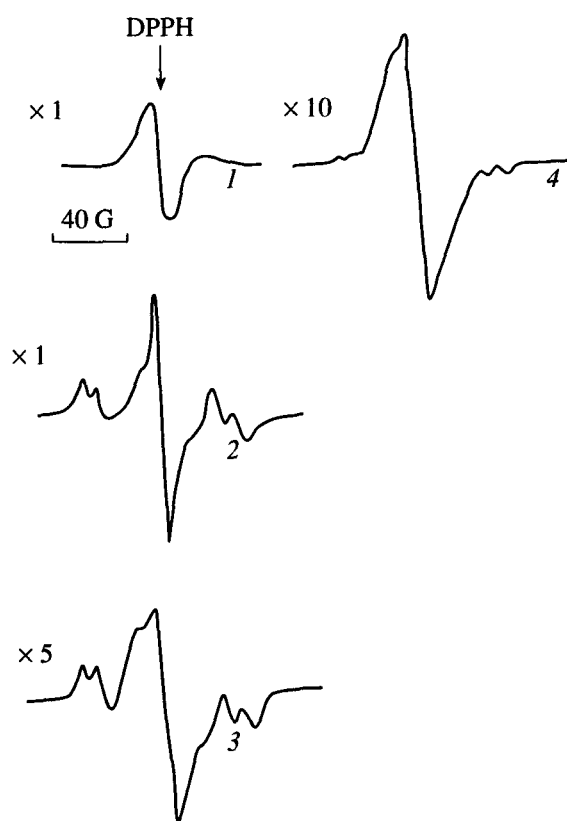
Fig. 6. ESR spectra of the $(NO_2-C_3H_6)$ complex on the HZSM-5 zeolite at different conditions: (1) in an $NO + O_2$ gas mixture, (2) after evacuation, (3) after heating in a vacuum at 400 K for 10 min, (4) after heating in a vacuum at 500 K for 10 min.

This treatment resulted in the formation of the NO_2–HC complex. After the decomposition of the NO_2–HC complex at $T > 560$ K, the signal from coke with $g = 2.004$ is observed. In this case, the $(NO_2$–HC) complex was not formed during the adsorption of the $NO + O_2$ mixture. This means that coke does not participate in the nitroxy complex formation.

DISCUSSION

1. Radical-Forming Sites in the HZSM-5 Zeolite

According to the available literature data, the reactions of oligomerization and cracking on HZSM-5 zeolite start with hydrocarbon adsorption on Brönsted acid sites (BAS) [16]. This is supported by the correlation between the number of adsorbed hydrocarbon molecules and the concentration of BAS. Indeed, the number of propene or benzene molecules desorbed from the HZSM-5 zeolite in the temperature range 293–800 K $(5 \times 10^{20}$ and 4×10^{20} molecule/g, respectively) is close to the number of BAS $(3 \times 10^{20}$ g$^{-1})$ in HZSM-5 zeolite (Table 1). The BAS concentration was measured using ammonia TPD according to [16].

The number of desorbed ethylene molecules (5 × 10^{19} molecule/g) is ten times lower than the BAS concentration, but it is approximately equal to the concentration of Lewis acid sites (LAS) $(1.5-3.0 \times 10^{19}$ g$^{-1})$, which was determined by NO thermal desorption. It is impossible to determine the amount of ethylene adsorbed on each type of active sites. Therefore, ethylene adsorption on BAS requires special investigation. In agreement with the literature data [16, 17], we can deduce that ethylene adsorption on BAS is weaker than propene adsorption at room temperature.

However, the formation of benzene and oligomer radicals is not directly connected with the presence of BAS or LAS, because these sites are present in HZSM-5 zeolite heated both in O_2 and in H_2 at 970 K, whereas the radicals were observed only on the oxidized zeolite. Moreover, the radical concentration is 10^3–10^4 times lower than the LAS and BAS concentrations. Such a correlation between the concentrations of acid sites, adsorbed species and radicals, as well as the effect of blocking of the radical-forming sites by NO molecules, suggests that radicals are formed on a part of Lewis sites. According to [18], the Si–O and Al–O acid–base pairs can play the role of such sites.

Active Si–O and Al–O pairs are formed in the course of zeolite HZSM-5 heating in oxygen or N_2O. Therefore, the buildup of active oxygen species on these sites or near them, which participate in the cation radical formation, can be considered. Strongly adsorbed oxygen in zeolite, which is evolved upon zeolite heating [19], could possibly play this role.

The authors of [10] supposed that cation radical formation from benzene was connected with the presence of uncontrolled Fe^{2+} ions. We failed to find any influence of Fe cations on the formation of oligomer or benzene radicals after introducing iron cations into HZSM-5 zeolite via ion exchange in the concentration 0.05 and 0.5 wt % Fe. In this connection, paper [19] should be mentioned. In this connection, formation of cation radicals on both zeolites, containing iron ions and samples without iron was observed. Iron ions may participate in the cation radicals formation, but their role in this process is probably unimportant.

2. The Formation of Hydrocarbon Radicals on the CuZSM-5 Zeolite

The intensity of the ESR signals from the radicals formed after hydrocarbon adsorption changes with an increase in the copper content in the samples (Fig. 4). Thus, the intensity of the ESR signal and, hence, the concentration of cation radicals decrease after benzene or ethylene adsorption. Propene adsorption, in contrast, results in the radical concentration dependence on the copper content with a maximum.

This means that the addition of copper changes the activity of the zeolite sites responsible for the radical formation in the reaction with hydrocarbons. At the

Table 1. Concentrations of molecules and paramagnetic species on the HZSM-5 zeolite after adsorption of gases at 293 K and $P = 2$–5×10^2 Pa and parameters of their ESR spectra

Adsorbed gas	$N_{ad} \times 10^{-20}$, molecule/g	Paramagnetic particle	$N_s \times 10^{-15}$, spin/g	Parameters of ESR spectra	
				g-factor	A, G
C_2H_4	0.5	$R^{\pm}$	7.0	2.004	8.0
C_3H_6	5.0	$R^{\pm}$	8.7	2.004	8.0
C_6H_6	4.0	$(C_6H_6)^+$	7.4	2.004	4.5
$NO + C_2H_4$	0.4	$(NO + C_2H_4)$	9.0	$g_1 = 2.090, g_2 = 2.070, g_3 = 2.018$	–
$NO + C_3H_6$	5.0	$(NO + C_3H_6)$	10.0	$g_1 = 2.090, g_2 = 2.070, g_3 = 2.018$	–
$NO + C_6H_6$	3.0	$(NO + C_6H_6)$	9.0	$g_1 = 2.090, g_2 = 2.070, g_3 = 2.018$	–
$NO_2 + C_2H_4$	1.0	$(NO_2 + C_2H_4)$	0.5	$g_\perp = 2.006, g_\parallel = 2.0035$	$A_\perp = 23, A_\parallel = 46$
$NO_2 + C_3H_6$	6.0	$(NO_2 + C_3H_6)$	5.0	$g_\perp = 2.006, g_\parallel = 2.0035$	$A_\perp = 25, A_\parallel = 45$
$NO_2 + C_6H_6$	5.0	$(NO_2 + C_6H_6)$	10.0	$g_\perp = 2.006, g_\parallel = 2.0035$	$A_\perp = 25, A_\parallel = 45$

same time, copper ions introduced by ion exchange are known [20] to be localized near the aluminum ions. Therefore, radical formation on the HZSM-5 zeolites may be connected with aluminum ions. This hypothesis is in agreement with the concept of participation of Si–O and Al–O pairs in this process.

Cation radical formation from hydrocarbons depends not only on the nature of active sites but also on the ionization potential of a hydrocarbon [18, 19]. The ionization potentials of benzene and ethylene are higher than that of propene [21]. Therefore, the formation of radicals from propene, unlike benzene and ethylene, on the copper-containing zeolites indicates a lower activity of copper ions as compared to the Si–O and Al–O pairs.

In the case of propene, an increase in the concentration of oligomer radicals with increasing copper content correlates with the growth of the concentration of isolated copper ions in oxidized CuZSM-5 zeolites containing 0.15–1.30% Cu. It is shown in [5] that the concentration of isolated copper cations and the concentration of oligomer radicals increase linearly with the copper content increase. The formation of $R^{\pm}$ radicals after propene adsorption on the copper-containing reduced catalysts seems to be connected with isolated Cu^{2+} ions, which are present in the CuZSM-5 samples (1.70–2.86% Cu) in the concentration 1×10^{19} ion/g [5] even after prolonged sample treatment in hydrogen at 970 K.

Nevertheless, not all of the observed isolated copper ions are involved in the formation of oligomer radicals upon propene adsorption, because the ratio of the number of oligomer radicals to that of isolated Cu^{2+} ions does not exceed 2×10^{-3} in both cases of the oxidized or reduced CuZSM-5 zeolites containing 0.15–2.86% Cu. Such a low ratio can be explained by fast transformation of the main part of oligomer radicals formed on the isolated copper ions.

Similar temperature dependences of the intensity of the oligomer signal for the zeolites containing copper and without copper (Fig. 2, curves *1* and *4*), as well as the same shape of the spectra for these samples, enable us to suppose that oligomer radicals in the sample with copper are stabilized near Cu^{2+} cations in the zeolite cavity.

A decrease in the concentration of $R^{\pm}$ radicals with a growth of the copper content from 1.30 to 2.86% (Fig. 4, curve *1*) could be explained by the formation of new complexes which are not registered by the ESR technique and which are probably formed as a result of interaction of Cu^{2+} cations with $R^{\pm}$ radicals.

3. Nitroxy Complexes in HZSM-5 Zeolite

The (NO–HC) complex has an anisotropic g-factor, and its components are $g_1 = 2.090$, $g_2 = 2.070$, $g_3 = 2.018$. These values are considerably higher than the corresponding parameters for the NO molecule adsorbed on oxides [15]. The spectrum of the (NO–HC) complex (Fig. 5, curve *1*) differs from the ESR spectra of all known hydrocarbon nitroxy radicals. This spectrum represents the spectrum of paramagnetic species with $S = 1/2$, nuclear spin $I = 1$, and g-factor which differs from g_e-factor of electrons only by a few hundredths [22]. The considerably higher values of the g-factor components for the signal of the (NO–HC) complex as compared with those for adsorbed NO molecules and nitroxy radicals indicate their different natures. Additional experiments are needed to clarify this difference.

The spectrum of the (NO$_2$–HC) complex corresponds to the spectrum of paramagnetic species with $S = 1/2$, nuclear spin $I = 1$, and anisotropic A- and g-tensors ($g_\perp = 2.0060$, $g_\parallel = 2.0035$, $A_\perp = 25$ G, $A_\parallel = 45$ G). This complex is formed in the reaction of an adsorbed hydrocarbon with NO$_2$. The above-discussed compo-

Table 2. Parameters of ESR spectra of nitroxy (NO–C_3H_6) and (NO_2–C_3H_6) complexes on different oxide systems pretreated in oxygen at 970 K

Complex	Sample	SiO_2/Al_2O_3	$N_s \times 10^{-15}$, spin/g	g-factor	A, G
NO–HC	HZSM-5	40	10	$g_1 = 2.090, g_2 = 2.070, g_3 = 2.018$	–
NO–HC	HZSM-5	50	5	$g_1 = 2.104, g_2 = 2.070, g_3 = 2.018$	–
NO–HC	HZSM-5	80	1	$g_1 = 2.100, g_2 = 2.065, g_3 = 2.019$	–
NO–HC	$Al_2O_3^{*}$	–	<0.5	$g_1 = 2.110, g_2 = 2.060, g_3 = 2.018$	–
NO–HC	SiO_2^{**}	–	0	–	–
NO_2–HC	HZSM-5	40	5	$g_{\parallel} = 2.0035, g_{\perp} = 2.006$	$A_{\parallel} = 45, A_{\perp} = 25$
NO_2–HC	HZSM-5	50	8	$g_{\parallel} = 2.003, g_{\perp} = 2.007$	$A_{\parallel} = 52, A_{\perp} = 29$
NO_2–HC	HZSM-5	80	3	$g_{\parallel} = 2.005, g_{\perp} = 2.008$	$A_{\parallel} = 50, A_{\perp} = 30$
NO_2–HC	$Al_2O_3^{*}$	–	60–30	$g_{\parallel} = 2.003, g_{\perp} = 2.006$	$A_{\parallel} = 48, A_{\perp} = 28$
NO_2–HC	SiO_2^{**}	–	0	–	–

* The specific surface area of Al_2O_3 (analytical grade) varied from 70 to 200 m^2/g.
** The specific surface area of SiO_2 (analytical grade) is 70 m^2/g.

nents of g-factor for this complex are close to the values corresponding to stable imino-oxyl radicals or isolated NO_2 molecules in molecular sieves and polymers. The value and anisotropy of g-factor and hfs components indicate the formation of a sufficiently strong bond and restricted mobility of the NO_2 molecule in the complex, similar to the NO_2 molecule in a rigid polymer matrix [23]. It should be noted that, according to the available spectral data [24], the same anisotropy is observed in the case of nitroxy radicals adsorbed in the ZSM-5 zeolite channels as a result of restricted >NO⁺ group mobility in the zeolite channels.

The data on the structure of adsorbed hydrocarbons in such complexes are scarce. ESR spectra obtained at 77 K provide no information about their structure. If C_3H_6 is used instead of C_3D_6, the spectra of the complex remain unchanged. The adsorption of different hydrocarbons probably leads to the formation of the same hydrocarbon structure. This structure seems to participate in further complex formation after NO or NO_2 adsorption and has nothing in common with R⁺ and $C_6H_6^+$ radicals, because nitroxy complexes are formed even after elimination of R⁺ radicals by thermovacuum treatment. At the same time, it cannot be similar to carbon species because coke does not participate in the formation of complexes and radicals. The data given in Table 1 indicate that the (NO_2–HC) complex concentration after propene or benzene adsorption is 10 times higher than after ethylene adsorption. This difference seems to be connected with stronger propene and benzene adsorption by the zeolite in contrast to ethylene adsorption, other conditions being the same.

According to Table 1, the (NO–HC) complex concentration (10^{16} spin/g) is almost independent of the nature of an adsorbed hydrocarbon. Consequently, the (NO–HC) complex cannot be an intermediate in the (NO_2–HC) complex formation. This means that these complexes are probably formed via different hydrocarbon structures.

Similar complexes were experimentally observed in the same conditions on the HZSM-5 zeolites obtained from Du Pont with the SiO_2/Al_2O_3 ratios 50 and 80 and on Al_2O_3 samples with a specific surface area varying within 70–200 m^2/g. The results obtained using the ESR technique for the (NO–C_3H_6) and (NO_2–C_3H_6) complexes are presented in Table 2. Note that the samples containing aluminum are active in the formation of nitroxy complexes. A decrease in the aluminum content in zeolites is accompanied by a decrease in the concentration of nitroxy complexes. No complexes are formed in the case of SiO_2 ($S_{sp} = 70$ m^2/g). This result lends support for the hypothesis that certain surface aluminum cations are responsible for the complex formation.

4. Participation of Oligomer Radicals and Nitroxy Complexes in the Reaction of Catalytic Selective NO Reduction by Hydrocarbons

It was found in this work that the oligomer radicals R⁺ and nitroxy complexes (NO–HC) and (NO_2–HC) are formed on HZSM-5 zeolites. This fact confirms the hypothesis made in [3] that nitroxy compounds are formed from adsorbed hydrocarbons.

The comparison of the data on the thermal stability of radicals and complexes (Fig. 2, curves 1–4) with the temperature dependence of NO_x conversion into N_2

(curve 5) in the course of NO_x reduction by propene in excess oxygen on HZSM-5 and CuZSM-5 zeolites [1] indicates that oligomer radicals are decomposed completely at the temperatures of the reaction onset. The (NO–HC) and (NO_2–HC) complexes are more stable, and the temperature range of their existence considerably overlaps with the temperature range of the reaction. This fact allows us to consider these complexes as possible intermediates in the reaction of NO_x reduction on HZSM-5 zeolite.

Because of the limitations of the ESR technique, we failed to obtain any ESR data on the formation of (NO–HC) and (NO_2–HC) complexes on copper-containing zeolites. Nevertheless, in our previous study of the process of NO_x reduction by propene using *in situ* IR spectroscopy [12], we registered a organonitrogen compound existing in the same temperature interval as those found on HZSM-5 zeolites. Therefore, we can suppose that organonitrogen compounds can play an important role in the process of NO_x reduction on copper-containing ZSM-5 zeolites. The final conclusion on the role of organonitrogen compounds in the reaction of NO_x reduction can be made by comparing the rate of NO_x conversion and the rate of the reaction.

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