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Radical Cations of Aromatic Molecules with High Ionization Potentials on the Surfaces of Oxide Catalysts: Formation, Properties, and Reactivity

A. F. Bedilo and A. M. Volodin

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: volodin@catalysis.nsk.su

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Abstract—The results obtained by the authors on the formation and properties of the radical cations of benzene and other molecules with high ionization potentials on the surfaces of ZSM-5 zeolites and sulfated zirconium dioxide are analyzed in this paper. It was found that radical cations of aromatic compounds can be obtained both by a thermal process and under illumination with visible light. Radical cations were found to be key intermediates in the low-temperature polycondensation of aromatic compounds on these catalysts. A possible mechanism of the formation of radical cations and the nature of the sites responsible for these processes are discussed.

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INTRODUCTION

Ion–radical reactions are widespread in organic chemistry, and the formation of organic radical cations as intermediate species is assumed for a number of chemical reactions [1–5]. However, the reliable demonstration of such mechanisms is associated with considerable experimental difficulties. At the same time, the formation of radical cations has been observed upon the adsorption of many organic compounds on zeolites and a number of acidic oxide catalysts [1, 6, 7]. As a rule, the resulting radical cations are more stable than their homogeneous analogs. Therefore, they can be detected reliably by optical and EPR spectroscopy and the reaction paths of their chemical transformations can be studied.

On the other hand, it is likely that the ionization of various organic molecules upon their adsorption on acid catalysts is the most surprising property of these materials. At the beginning of this work, the formation of radical cations from molecules with very high ionization potentials, such as benzene ($I_p = 9.24$ eV), on high-silica HZSM-5 zeolites and H-mordenite [6], as well as on sulfated zirconia [8], was found. It is also surprising that considerable concentrations (to 10^{20} g^{-1}) of radical cations were observed after the adsorption of a number of molecules with ionization potentials of ~7 eV on various zeolites and amorphous aluminosilicates [7]. This means that acceptor sites of moderate strength regularly occur even in amorphous systems, and they are not exotic defect structures.

In this context, two principal questions arise: (1) What is the nature of surface sites responsible for the occurrence of these processes and what is the process mechanism? (2) What is the reactivity of the resulting radical cations and do they participate as intermediates in main and side reactions on these catalysts? These questions remain unanswered, although a large body of experimental data has been accumulated in the past five decades and a large number of studies have been performed in this area.

Thus, it seemed very important to us to perform a detailed study of the formation of radical cations using in situ EPR spectroscopy under conditions of reliably controlled states of catalyst surfaces and reaction atmospheres. In this work, we analyze the most important results concerning the formation and reactivity of the radical cations of aromatic compounds on ZSM-5 zeolites and sulfated zirconia.

EXPERIMENTAL

In the experiments on the formation of radical cations on HZSM-5 zeolite, a commercial sample with a Si/Al ratio of 60 was used. To study the effect of copper ions, a series of samples containing from 0 to 3.41 wt % Cu on ZSM-5 zeolite with a Si/Al ratio of 17 was prepared by ion exchange in accordance with a previously developed procedure [9]. All of the samples were calcined in air at 450°C.

Two samples of sulfated zirconia with close specific concentrations of sulfates (2.5 atoms of sulfur per 1 nm^2 of the surface) but with dramatically different catalytic and spectroscopic properties were used in this study. The SZ-1 sample was prepared by a traditional procedure by supporting sulfates onto amorphous hydrated zirconia, and it exhibited high activity in the reaction of butane isomerization [10, 11]. The SZ-2 sample was prepared by supporting sulfates onto crystalline mono-

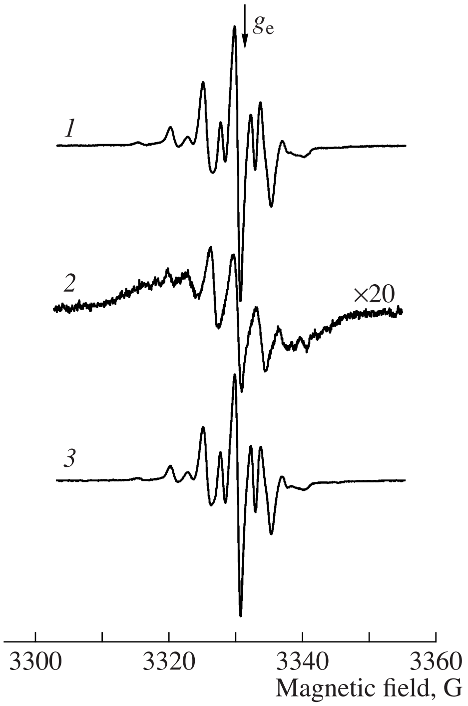

Fig. 1. EPR spectra observed (*1*) after the adsorption of benzene (~1 × 10^{21} molecule/g) onto initial HZSM-5 zeolite, (*2*) after evacuation for 14 h at 295 K, and (*3*) after additional adsorption of benzene (~1 × 10^{21} molecule/g). The temperature of benzene adsorption and measurement of EPR spectra was 253 K.

clinic zirconia, and it did not exhibit detectable catalytic activity. The procedure used for the synthesis of these samples and their physicochemical properties were described in detail previously [12].

The experiments were performed in an in situ EPR system, which was described in detail elsewhere [13, 14]. The samples, which were placed immediately in the resonator of an EPR spectrometer, were activated in oxygen or in a vacuum at 500°C or lower, as specified in the text, and the released gases were frozen in a trap with liquid nitrogen. The samples were irradiated immediately in the resonator with light from a DRSh-1000 mercury lamp with the use of a monochromator.

RESULTS

Formation of Radical Cations on the Adsorption of Aromatic Molecules

The initial sample of ZSM-5 zeolite after training did not exhibit EPR spectra in the region characteristic of the radicals and paramagnetic sites of coke. It exhibited only the EPR spectrum of Fe^{3+} impurity ions with g = 4.27, which is well known [14, 15]. In special experiments performed using ZSM-5 zeolite samples with essentially different iron contents (from 0.003 to 1 wt %), we did not find a relationship between the concentration of iron ions and the amount of radical cations formed.

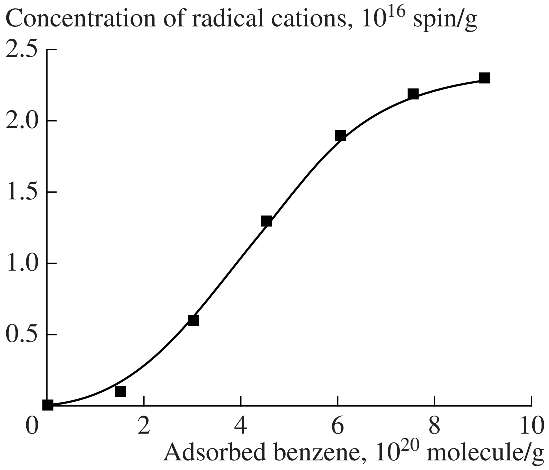

Fig. 2. Dependence of the concentration of benzene radical cations formed on HZSM-5 zeolite on the amount of adsorbed benzene.

The adsorption of benzene at 248–298 K onto this initial zeolite sample was accompanied by the formation of two types of radicals with the hyperfine interaction constants a^H = 0.44 and 0.22 mT (Fig. 1, spectrum *1*). In accordance with published data [16, 17], these constants can be ascribed to the radical cations of benzene monomer and dimer, respectively. These radical cations are sufficiently stable at temperatures lower than 273 K.

Figure 2 shows the dependence of the total concentration of the resulting radical cations on the amount of adsorbed benzene. It can be clearly seen that the maximum concentration of these species (2 × 10^{16} spin/g) was reached upon the adsorption of benzene molecules in an amount of ~10^{21} molecule/g, which corresponds to the complete filling of zeolite channels. Thus, ~5 × 10^4 molecules of benzene are required for the formation of one radical cation. It is believed that adsorbed benzene (more precisely, the liquid phase formed under these conditions) is extremely important for the processes of charge separation and radical cation stabilization.

Note that the formation of radical cations is a reversible process. The evacuation of adsorbed benzene at 295 K resulted in the disappearance of the EPR spectra of these radical cations (Fig. 1, spectrum *2*). In this case, sites responsible for the formation and stabilization of these species were retained and the subsequent adsorption of benzene newly regenerated the initial spectrum (Fig. 1, spectrum *3*). A weak signal with the hyperfine interaction constant a^H of ~0.33 mT (Fig. 1, spectrum *2*), which remained after the evacuation of benzene, can be attributed to the radical cation of biphenyl [18].

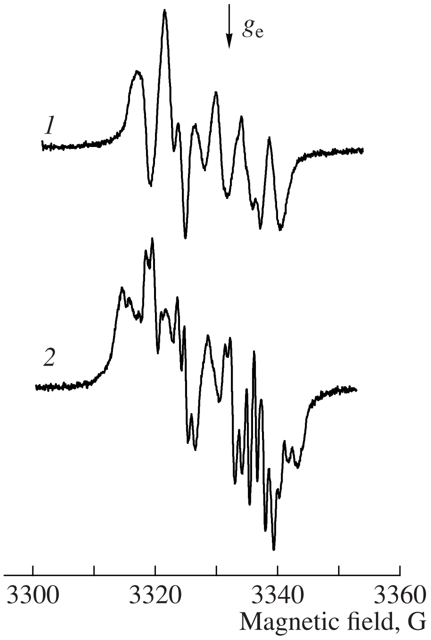

Fig. 3. EPR spectra of phenoxyl radicals obtained after the adsorption of benzene (~10^{18} molecule/g) onto HZSM-5 zeolite at 773 K. The temperature of the measurement of EPR spectra was (*1*) 773 or (*2*) 293 K.

To make a zeolite capable of ionizing adsorbed organic compounds, it should be activated in an oxygen-containing atmosphere at temperatures higher than 600 K. The adsorption of water and ammonia on these activated samples and the high-temperature treatment of these samples in hydrogen eliminated active acceptor sites from the zeolite and, correspondingly, the capability to ionize adsorbed molecules. This means that an acceptor site is a coordinatively unsaturated structure including oxygen as a constituent.

Our experiments on the interaction of hydrogen with the zeolite surface activated in oxygen demonstrated that the interaction of hydrogen at low pressures (~0.1 Torr) even at high temperatures only slightly affected the concentration of the resulting radical cations of benzene. To deactivate the zeolite surface with respect to the formation of these species, high temperatures ($T \geq 773$ K), a hydrogen pressure of ~1 Torr, and a sufficiently long treatment time are required.

The pumping of the benzene–zeolite system at temperatures higher than 473 K resulted in the disappearance of the spectra of all of the species described above: benzene, benzene dimer, and biphenyl radical cations. However, a further increase in the temperature to T = 723–823 K was accompanied by the formation of new paramagnetic species. These hydrocarbon radicals can also be obtained by the adsorption of small amounts of benzene (~10^{18} molecule/g) onto the initial zeolite at 723–823 K (Fig. 3, spectrum *1*). The adsorption of deuterobenzene (C_6D_6) onto a predeuterated zeolite surface under the same conditions and in the same amount resulted in the appearance of a single weakly anisotropic singlet line. This allowed us to conclude that the structure of the EPR spectrum shown in Fig. 3 mainly depends on the hyperfine interaction of an unpaired electron with protons. The radicals detected are accessible to gas phase molecules, as evidenced by the reversible broadening of their spectra by paramagnetic oxygen molecules at a pressure higher than 10 Torr and a lower temperature.

The spectra of the resulting radicals, as well as the dependence of these spectra on detection temperature, can be described assuming the formation of phenoxyl-type radicals stabilized on the zeolite surface. The EPR spectra observed at room temperature (Fig. 3, spectrum *2*) can be adequately described based on the assumption that protons in the *ortho* and *meta* positions of an aromatic ring are pairwise nonequivalent and exhibit the following hyperfine interaction constants: $a_2^H = 0.55$ mT, $a_6^H = 0.33$ mT, $a_3^H = 0.32$ mT, $a_5^H = -0.14$ mT, and $a_4^H = 1.2$ mT. As the temperature was increased, the rotation frequency (exchange rate) of radicals around a bond with the surface increased. In this case, the hyperfine interaction constants with protons in the *ortho* and *meta* positions approached their average values: $a_{2,6}^H =$ 0.44 mT and $a_{3,5}^H = 0.09$ mT.

The detected radicals are stable in a vacuum up to 823 K. The appearance of O_2 or H_2 molecules in a gas phase at this temperature results in the irreversible decay of all of the observed radical species. In the above phenoxyl radicals, it is most likely that the benzene ring is bound to the surface through surface oxygen. It is likely that these radicals are formed on the surface of zeolite grains by the substitution of phenyl for a hydrogen atom in surface hydroxyl groups.

Treatment with hydrogen and with CO, as well as long-term evacuation at 823 K, inhibited the formation of these radicals. Subsequent treatment with oxygen once again recovered the activity of the zeolite surface toward the test processes. Although the conditions of the appearance of sites capable of generating phenoxyl radicals are close to the conditions of the formation of electron-acceptor sites that cause the appearance of benzene radical cations, a special experiment demonstrated that these two processes occurred independently, that is, at different zeolite sites [19].

The ability of a zeolite to form benzene radical cations can be considerably increased by introducing copper cations into zeolite ion-exchange positions (Fig. 4). The concentration of these sites was proportional to the concentration of introduced copper at low copper concentrations up to $Cu/Al_{at} = 0.35$. It was found that acceptor sites formed upon the introduction of copper into a zeolite were even stronger than the sites of HZSM-5. Thus, the formation of radical-cationic spe-

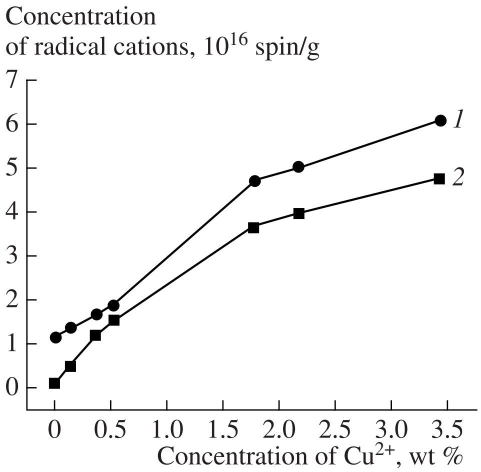

Fig. 4. Dependence of the concentration of radical cations formed from (*1*) benzene and (*2*) chlorobenzene on CuZSM-5 on the amount of copper.

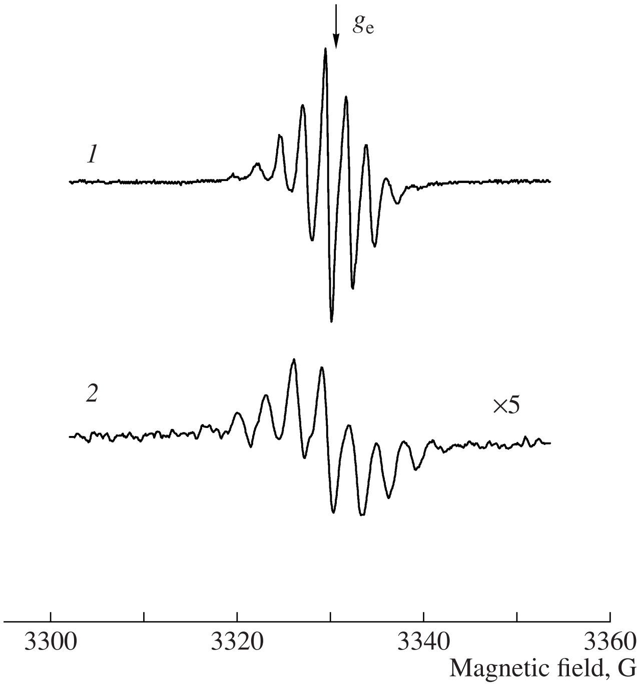

Fig. 5. EPR spectra observed (*1*) after the adsorption of benzene vapor on SZ-1 at 243 K and (*2*) 30 min after heating the system to room temperature.

cies from chlorobenzene, which is not ionized on HZSM-5, was observed on CuZSM-5 zeolites (Fig. 4). In our opinion, this difference in the strengths of sites suggests that the acceptor sites observed on the acidic form of the zeolite are not due to copper impurities. The use of mesitylene molecules, which have a lower ionization potential (I_p = 8.4 eV) but cannot enter zeolite channels, demonstrated that almost all strong acceptor sites in HZSM-5 and CuZSM-5 zeolites are arranged in channels rather than on the outer surface of the zeolites.

Strong acceptor sites were also detected on sulfated zirconia. The in situ adsorption of benzene (0.5 mmol/g) onto the SZ-1 sample at 233 K resulted in the formation of a spectrum of benzene dimer radical cations with the characteristic hyperfine structure constant a = 2.2 G (Fig. 5, spectrum *1*). On heating to room temperature, the benzene dimer radical cations were quantitatively converted into biphenyl radical cations with the hyperfine structure constant a = 3.3 G (Fig. 5, spectrum 2). Of course, these species were observed upon the adsorption of benzene at room temperature [8]. The parameters of the EPR spectra of resulting radical cations were almost identical to the parameters of analogous species produced from benzene on ZSM-5 zeolites.

We observed only secondary radicals upon the adsorption of toluene on SZ-1 even at room temperature. It is well known that the radical cations of toluene are much less stable than the radical cations of benzene. Thus, only the products of their oxidative dimerization (4,4'-dimethylbiphenyl radical cations) were observed upon the adsorption of toluene on mordenite [18]. It is most likely that the observed radicals were formed by the deprotonation of 4,4'-dimethylbiphenyl radical cations [12].

We found that, for sulfated zirconium dioxide, the concentration of radical cations depended on the amount of adsorbed toluene (Fig. 6a). As for ZSM-5 zeolites, the process was completely reversible. Note that only a small portion of adsorbed toluene molecules (<0.2%) underwent ionization. As in the case of HZSM-5 zeolites, the occurrence of a liquid-phase island with certain dimensions is required for charge separation and radical cation formation.

Previously, Bolshov and Volodin [20] hypothesized that the acceptor sites of ZSM-5 zeolites include chemisorbed oxygen as a constituent. It was also found that the presence of oxygen increased the apparent strength of acceptor sites in sulfated zirconium dioxide. Oxygen exerted the most significant effect on processes occurring on the adsorption of aromatic molecules onto the SZ-2 sample. Thus, this sample not only exhibited no catalytic activity in butane isomerization but also had much weaker acceptor sites. In the absence of oxygen, the ionization of benzene and toluene molecules was not observed on this sample. The presence of oxygen in the gas phase is required for the ionization of these molecules with the formation of the same radicals as on the SZ-1 sample. The concentration of radicals depends directly on the amount of introduced oxygen (Fig. 6b). In this case, Bedilo et al. [21] managed to detect the appearance of radical cations on this catalyst upon the adsorption of a number of methylbenzenes even in the absence of oxygen.

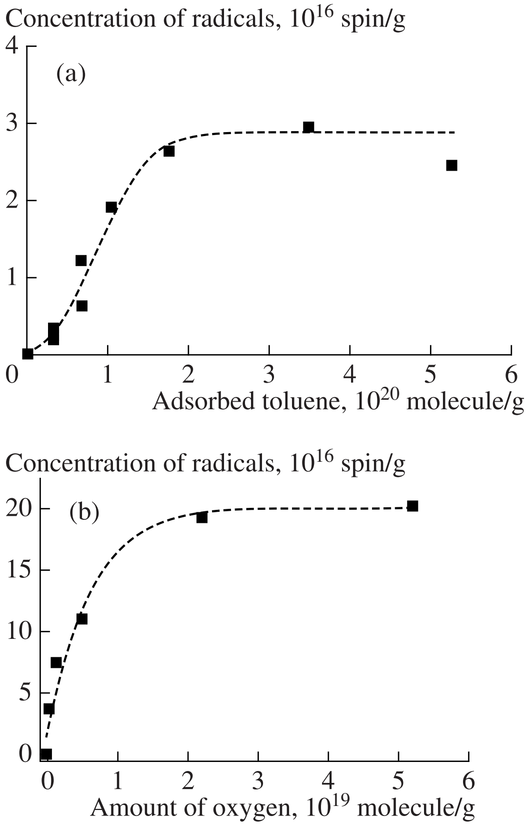

Fig. 6. (a) Dependence of the concentration of radicals on the amount of toluene adsorbed on SZ-1 at 243 K and (b) dependence of the concentration of radicals formed upon the adsorption of toluene onto the SZ-2 sample at 243 K on the amount of oxygen.

In an oxygen-containing atmosphere, the O_2^- radical anions were observed along with primary radical cations and their conversion products in the EPR spectra of catalysts [22]. However, a relationship between the concentrations of oxygen radical anions and aromatic radical cations was not found.

Sulfated zirconium dioxide is of interest as a possible catalyst for light alkane isomerization. Therefore, we attempted to obtain radical cations on it upon the adsorption of alkanes. However, we failed to detect the primary radical cations of alkanes. At the same time, the adsorption of pentane on the SZ-1 sample at room temperature resulted in the appearance of an EPR spectrum with nine narrow lines and a hyperfine structure constant of 16.5 G. This spectrum was attributed to the radical cations of tetramethylethylene [23]. The appearance of these species can be explained by the selective formation of these radical cations because the ionization potential of tetramethylethylene (8.24 eV) is much lower than those of other olefins that can be formed in this system [24]. At room temperature, the above radicals were not highly stable, and their disappearance was not accompanied by the appearance of other radical species [23].

Note that the formation of such radical cations was not observed upon the adsorption of pentane on the SZ-2 sample, which did not exhibit noticeable catalytic activity, although this catalyst also possessed sufficiently strong acceptor sites for the ionization of tetramethylethylene. This was supported in independent experiments upon the adsorption of tetramethylethylene from the gas phase. This fact additionally demonstrates that it is formed as an intermediate in isomerization–disproportionation processes on the adsorption of pentane [23].

A direct comparison between the electron-acceptor properties of a wide range of catalysts based on sulfated zirconia and their catalytic activities revealed a correlation between the amount of acceptor sites, which were tested using the formation of radical cations from chlorobenzene, and the catalytic activity in the reaction of butane isomerization [10, 11]. Samples that did not have these electron-acceptor sites did not exhibit noticeable catalytic activity. In other words, the occurrence of strong electron-acceptor sites on the surface of catalysts based on sulfated zirconium dioxide is a necessary condition for the appearance of catalytic activity, although the particular mechanism of the action of these sites remains unknown, and the contribution of sites of another nature, particularly, Brønsted acid sites, seems very likely.

Low-Temperature Polycondensation Reactions with the Participation of Aromatic Radical Cations

Radical cations formed after the adsorption of benzene on ZSM-5 zeolites were stable for a long time at temperatures lower than 273 K. An increase in the temperature was accompanied by their transformations. Figure 7 shows the EPR spectra measured after the heating of the benzene–zeolite system in the presence of benzene vapor in the gas phase. It can be clearly seen that, after heating to room temperature, the concentration of benzene radical cations decreased (Fig. 7, spectrum *1*) as a consequence of chemical reactions whose primary product is the biphenyl radical cation (Fig. 7, spectrum *2*). Note that the concentration of biphenyl radical cations produced under these conditions was much higher than that under dynamic vacuum conditions. A further heating of the system to 473 K resulted in the conversion of biphenyl radical cations into new radical species whose EPR spectra consisted of a single line with $\Delta H_{av} = 0.55$ mT and $g_{av} = 2.003$ (Fig. 7, spectrum *3*), which is characteristic of coke deposits. In this case, the concentration of spins remained almost unchanged (table).

Bolshov et al. [25] calculated that the formation of biphenyl from two neutral benzene molecules is a thermodynamically unfavorable process; correspondingly, the equilibrium constant of this process is low. At the same time, the equilibrium constant of the reaction of the benzene radical cation with the neutral benzene molecule is higher than that for the reaction between the neutral molecules by 16 orders of magnitude. The ionization potentials of biphenyl and benzene differ by approximately 1 eV; because of this, reaction (I) of the benzene molecule with the benzene radical cation is thermodynamically favorable, unlike the reaction with the neutral benzene molecule.

$$C_6H_6^{\dot{+}} + C_6H_6 \rightleftarrows C_{12}H_{10}^{\dot{+}} + H_2; \qquad (I)$$

$$C_{12}H_{10}^{\dot{+}} + C_6H_6 \rightleftarrows C_{18}H_{14}^{\dot{+}} + H_2. \qquad (II)$$

It is believed that the subsequent interaction of benzene with biphenyl radical cations on the heating of the sample resulted in the formation of more complicated aromatic radical cations (terphenyls, etc.) according to reaction (II), although the EPR spectrum shown in Fig. 7 (spectrum *3*) is difficult to interpret because of the absence of a resolved hyperfine structure. A computer simulation of the EPR spectra of the radical cations of *para*-terphenyl, which can be formed on the addition of the benzene molecule to biphenyl radical cations in accordance with the proposed mechanism, demonstrated a qualitative agreement between theoretical and experimental spectra [25]. Note that the assignment of these spectra to aromatic radical cation–acceptor site radical anion radical pairs according to Marquis et al. [26] seems unlikely in the context of the above results.

Timoshok et al. [27] obtained analogous results for sulfated zirconia. The table summarizes the results of the measurement of the total concentration of radical species after a number of consecutive heatings of the catalyst with adsorbed benzene and toluene under various conditions. An analysis of these data and the resulting EPR spectra demonstrated that the following two temperature regions of the formation of radical species can be reliably distinguished:

(1) Low-temperature region to 473 K. It is characterized by transformations of the initial radical cations because of polycondensation processes. In this region, the concentration of paramagnetic species remained almost unchanged. It is believed that this concentration depends on the concentration of acceptor sites on the catalyst surface, which are capable of ionizing adsorbed molecules.

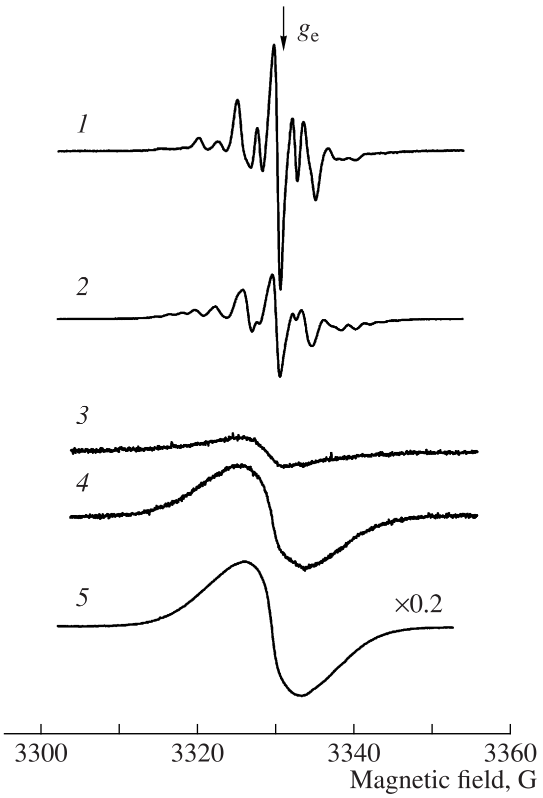

Fig. 7. EPR spectra of ZSM-5 zeolite after (*1*) the adsorption of saturated benzene vapor at 253 K, (*2*) exposure at 295 K for 2 h, and additional heating for 1 h at (*3*) 473, (*4*) 773, and (*5*) 873 K. The temperatures of the measurement of spectrum *1* and spectra *2–5* were 253 and 295 K, respectively.

(2) High-temperature region above 573 K. In this temperature region, a new channel of the generation of paramagnetic sites comes into play and all of the polycondensation processes with the participation of gas phase molecules are strongly intensified.

Note that the above processes in the high-temperature region occur with the participation of gas phase molecules. In the absence of the gas phase, that is, on heating the system under dynamic vacuum conditions, the concentration of the resulting paramagnetic species was low (table).

Because the oligomerization of aromatic compounds by a radical cation mechanism results in the for-

Dependence of the total concentration of paramagnetic species ($\times 10^{-16}$ spin/g) on the temperature of catalyst heating

Catalyst	Conditions	*T*, K						
		293	373	473	573	673	773	873
HZSM-5	Benzene, saturated vapor	1.5	1.5	1.1	1.1	1.6	3.8	20.4
SZ-1	Benzene, saturated vapor	2.5	1.4	1.5	1.5	3.4	33	–
SZ-1	Toluene, *P* = 10 Torr	0.9	0.8	1.5	3.0	40	–	–
SZ-1	Toluene, evacuation	0.6	0.4	0.7	1.1	0.7	–	–

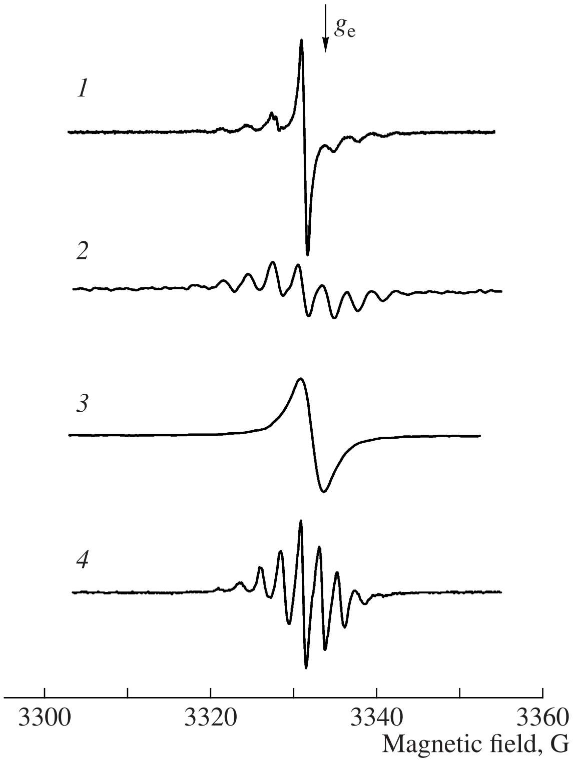

Fig. 8. EPR spectra observed on the SZ-1 sample activated at 500°C (*1*) 5 or (*2*) 30 min after the adsorption of benzene (10 Torr) and on the SZ-1 sample activated at 300°C (*3*) 5 min after the adsorption of benzene (1 Torr) and (*4*) the subsequent evacuation for 30 min. The temperature of the measurement of the EPR spectra was 295 K.

mation of polycondensed structures, which are coke precursors, it seemed important to study whether this oligomerization can be suppressed by varying experimental conditions with the retention of strong acceptor sites.

Immediately after the adsorption of benzene at room temperature onto the SZ-1 sample, which was activated at 500°C, the EPR spectrum exhibited a superposition of the signal due to the biphenyl radical cation, which consisted of nine lines with the hyperfine interaction constant $a = 3.3$ G, and a narrow ($\Delta H \sim 1$ G) intense signal with $g = 2.0026$ (Fig. 8, spectrum *1*). The intensity of the latter signal rapidly decreased until the complete disappearance approximately 20 min after adsorption. The signal intensity of biphenyl radical cations gradually increased for a time when a singlet signal was observed. Figure 8 shows the spectrum measured 30 min after adsorption (spectrum *2*). Subsequently, these species slowly underwent further polycondensation.

In the case of benzene adsorption at negative temperatures, the singlet signal was observed at the instant the system was heated, when the conversion of benzene dimer radical cations into biphenyl radical cations came into play, rather than after benzene adsorption, when only benzene dimer radical cations were observed (Fig. 5, spectrum *1*). This experiment unambiguously demonstrated that the singlet signal did not correspond to free electrons removed from aromatic molecules, as assumed previously by Chen et al. [8], because in this case it would be observed on the formation of radical cations at low temperatures.

The true nature of this signal was determined only from the experiments performed by Bedilo and Volodin [28] on the catalyst activated at 300°C. The adsorption of benzene at 1 Torr onto this catalyst at room temperature in the absence of oxygen resulted in the appearance of a Lorentzian singlet line with $g = 2.0026$ and $\Delta H = 2.5$ G in the EPR spectrum (Fig. 8, spectrum *3*). This spectrum remained stable for at least 30 min. In this case, neither biphenyl radical cations nor benzene dimer or monomer radical cations were observed.

Sample evacuation for half an hour at room temperature resulted in the appearance of a spectrum of benzene dimer radical cations with lines from 12 equivalent protons with the hyperfine interaction constant $a =$ 2.2 H (Fig. 8, spectrum *4*) with no changes in the integral intensity of the spectrum. The repeated adsorption of benzene onto this sample resulted in the repeated formation of a singlet with the complete reversible disappearance of the signal from benzene dimer radical cations.

All the above allowed us to suggest that the singlet EPR signal was also due to the formation of benzene radical cations, and it was due to the delocalization of spin density over a few benzene rings. Undoubtedly, electron exchange between charged and neutral molecules should be involved in this process; this exchange is very typical of aromatic radical cations in solutions [4]. Thus, the singlet is due to a quasi-free positive charge localized in the adsorption layer of the liquid rather than to free electrons in the near-surface layer of the catalyst.

The above results indicate that, after catalyst activation at 300°C, strong acceptor sites capable of removing an electron from benzene molecules appeared on the surface. At the same time, further oligomerization with the formation of biphenyl radical cations and heavier products was suppressed under these conditions. It is very likely that the formation of biphenyl radical cations requires the participation of other catalytic sites, which are formed at a higher temperature as a result of the removal of surface hydroxyl groups.

Formation of Radical Cations under Illumination

In the previous section, it was demonstrated that HZSM-5 zeolite treated in oxygen in accordance with a standard procedure afforded a set of radical cations after the adsorption of benzene on it. After zeolite evacuation at 295 K, the disappearance of spectra due to benzene radical cations was observed, although the amount of adsorbed benzene remaining after evacuation was sufficiently large (~3 wt % or ~2×10^{20} molecule/g), and it was much higher than the maximum concentration of the resulting benzene radical cations (~2×10^{16} spin/g). In this context, it was of interest to consider the photostimulated formation of benzene radical cations on ZSM-5 zeolites at small amounts of adsorbed benzene, when charge separation was hindered and the concentration of thermally formed radical cations was insignificant.

In these experiments, benzene adsorption was performed at 373 K followed by evacuation at the same temperature for 30 min. The amount of adsorbed benzene remaining on the zeolite thus treated was ~0.4 wt % (~3×10^{19} molecule/g). The illumination of the initial sample starting with a photon energy of 2.8 eV was accompanied by the formation of benzene radical cations, whose EPR spectrum consisted of seven lines with $g_{av} = 2.0026$ and the hyperfine interaction constant $a^H = 0.45$ mT [13].

Figure 9 shows the experimental spectra of the initial rates of formation of benzene radical cations on the test zeolite. A considerable increase in the initial rate was observed under irradiation with light at the wavelength $\lambda = 365$ nm ($h\nu = 3.4$ eV); however, the formation of radical cations was reliably detected up to $\lambda = 436$ nm ($h\nu = 2.8$ eV) (Fig. 9, curve *1*).

As noted previously, high-temperature treatment with hydrogen inhibited the formation of benzene radical cations. Heating in hydrogen ($T = 823$ K; $P_{H_2} = 2$ Torr; $t = 2$ h) immediately before benzene adsorption completely suppressed the activity of the test zeolites toward photostimulated processes (Fig. 9, curve *2*). To regenerate the initial activity, high-temperature treatment of the zeolite in oxygen was required in all cases. The dependence of the rate of formation of benzene radical cations on the incident light flux intensity was nearly linear. This suggests that the photoionization of benzene on the surface of the test HZSM-5 zeolites is a single-photon process.

The photoinduced radical cations of benzene were stable at 173 K. As the temperature was increased, the decay of the radicals was observed without the formation of any paramagnetic products. Bolshov et al. [13] found that the kinetics was adequately described by a straight line on logarithmic coordinates with a slope of –1. This fact suggests that the rate-limiting step in the decay of the radical cations over the tested concentration range was a bimolecular reaction and the initial concentrations of reactants were equal to each other. It seems unlikely that other reaction species with a concentration very close to the concentration of benzene radical cations occurred on the surface in addition to the radical cations and their counterions. Thus, it is most likely that the above process is a recombination of the radical cation and its counterion.

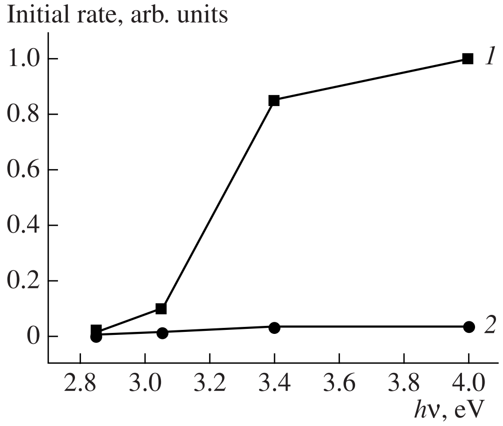

Fig. 9. Relative initial rate of formation of benzene radical cations under irradiation with light with various energies at 173 K depending on pretreatment conditions: (*1*) initial sample, (*2*) zeolite treated in hydrogen (823 K, 2 Torr, 2 h) followed by benzene adsorption in accordance with the standard procedure.

Illumination with visible light was also found to be an efficient technique for the production of aromatic radical cations on sulfated zirconia. Previously, it was found that the adsorption of benzene on the SZ-2 sample in the absence of oxygen did not result in the formation of radical cations. Because we failed to observe benzene monomer radical cations at considerable amounts of adsorbed benzene, we evacuated a sample with adsorbed benzene (which was adsorbed at room temperature) at 0°C in order to detect these radical cations. Then, the system was cooled to 103 K and illuminated with visible light.

After illumination with green light (546 nm) for 5 min, we observed a weak EPR spectrum of benzene monomer radical cations (Fig. 10, spectrum *1*). Their concentration can be increased by one order of magnitude under the action of prolonged irradiation with light at the wavelength $\lambda = 365$ nm (Fig. 10, spectrum *2*). The model spectrum shown in Fig. 9 (spectrum *3*) was simulated for splitting by six equivalent protons with $g_\perp = 2.0029$, $g_\parallel = 2.0024$, $a_\perp = 4.2$, and $a_\parallel = 5.0$.

The addition of oxygen at a low concentration of adsorbed benzene did not result in the appearance of thermal radicals. Nevertheless, the introduction of oxygen resulted in a shift in the spectral characteristics of the photoprocess. Figure 11 shows the dependence of the concentration of benzene radical cations formed under the action of light at various wavelengths on the pressure of oxygen. It was found that the concentration of radical cations increased as the pressure of oxygen was increased to several Torr. It is also of interest that we managed to generate noticeable concentrations of radicals under the action of yellow light (579 nm) only in the presence of oxygen. This additionally demonstrates that oxygen enhanced acceptor sites on the surface. This resulted not only in the thermal ionization of benzene and toluene on the SZ-2 sample, which was not observed in the absence of oxygen, but also in a

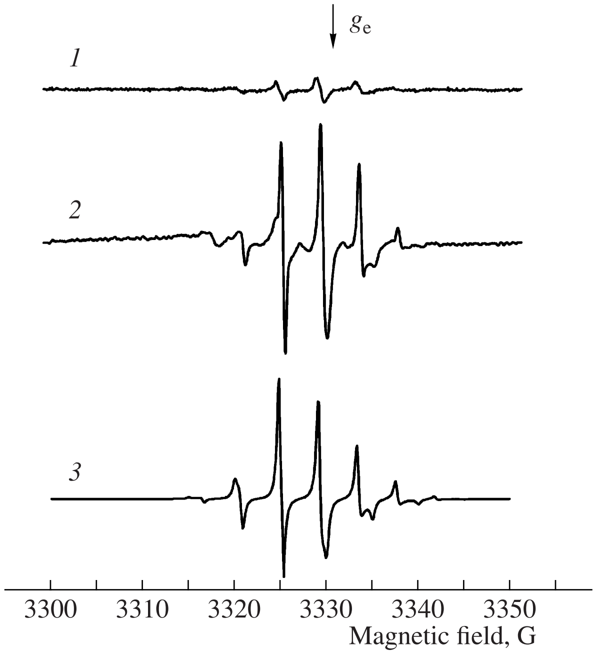

Fig. 10. EPR spectra observed after the adsorption of benzene on the SZ-2 sample at room temperature, evacuation for 30 min at 273 K, and illumination at 103 K with light (*1*) at λ = 546 nm for 5 min and (*2*) at λ = 365 nm for 30 min and (*3*) a model spectrum of benzene radical cations.

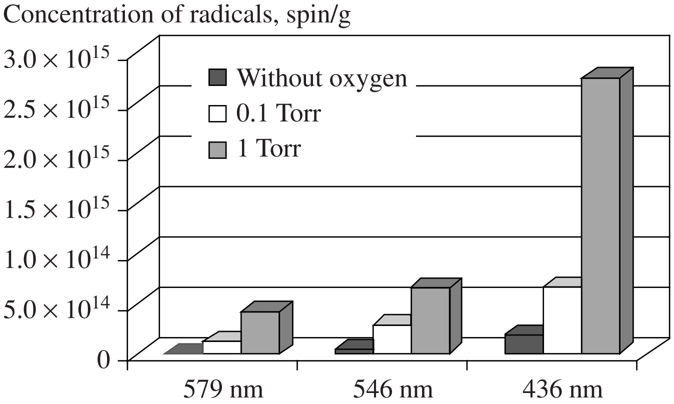

Fig. 11. Concentration of benzene radical cations formed after the adsorption of benzene on the SZ-2 sample at room temperature followed by evacuation for 30 min at 273 K and illumination with light at the chosen wavelength for 1 min at 103 K in the absence of oxygen and in the presence of 0.1 and 1 Torr of oxygen.

shift of the absorption band of donor–acceptor complexes to the region of longer wavelengths.

It was also possible to efficiently generate radical cations on the SZ-1 sample under the action of visible light [12]. In this case, we failed to create a situation in which radical cations were not observed after benzene adsorption. However, it was possible to increase considerably (several times) the concentration of these radical cations under the action of light. In this case, illumination with visible light resulted in the formation of the same benzene dimer radical cations ($a = 2.2$ G) as those in the thermal process and the concentration of radicals generated by light in this sample was much higher than on the SZ-2 sample.

An analogous effect of radical cation formation under illumination was also found in other aromatic test molecules (toluene and xylene). The long-wavelength threshold of the described photoinduced processes is far beyond the characteristic absorption bands of both the catalyst and adsorbates, which occur in the UV region of the spectrum. In fact, in this system, the light energies (up to λ = 579 nm) required were lower than those for analogous processes on ZSM-5 zeolites, where radical cations can be generated only under the action of blue light (λ = 436 nm).

DISCUSSION

To summarize, we note the most important properties of the formation of radical cations on the test catalysts. Very strong one-electron acceptor sites, which are capable of removing an electron from benzene molecules (*IP* = 9.2 eV), occur on the surfaces of HZSM-5 zeolites and sulfated zirconium dioxide. High-temperature activation in oxygen or air is required for the formation of these sites. In this case, the deactivation of these sites by hydrogen was observed only at sufficiently high temperatures. The presence of oxygen in the gas phase enhanced acceptor sites on the surface of sulfated zirconia, whereas the effect of oxygen was not detected in the case of zeolite.

The found dependence of the concentration of detected radical cations on the concentration of adsorbed aromatic molecules is an important result. The formation and decay of radical cations were completely reversible with respect to the evacuation of an adsorbate, although only one of several tens of thousands of molecules underwent ionization. It is likely that a large amount of adsorbed molecules is required for the formation of a liquid phase and for hole transfer from the point of formation near an acceptor site to the site of stabilization. This reversibility unambiguously indicates that radical cations are formed by an elementary event of electron transfer rather than the products of a complex chain of chemical reactions.

It was found that benzene radical cations formed on sulfated zirconia can undergo rapid electron exchange with neutral benzene molecules to result in the appearance of a singlet Lorentzian line in the EPR spectrum. We believe that even the temporary stabilization sites of a positive charge should be associated with surface sites. Hence, it follows that the concentration of these sites is much higher than the observed concentration of radical cations.

A study of benzene oligomerization demonstrated that it mainly occurred by a radical cation mechanism at low temperatures. In this case, the total concentration of paramagnetic species remained almost unchanged up to a certain critical temperature, at which other polycondensation mechanisms came into play. It was found that radical cation oligomerization processes on sulfated zirconia can be considerably inhibited by performing catalyst activation at lower temperatures (about 300°C). Under these activation conditions, which are nearly optimal for the butane isomerization process [29], a considerable amount of Brønsted acid sites occurred on the catalyst surface. It is likely that these acid sites suppressed sites responsible for oligomerization processes.

The introduction of copper ions into ZSM-5 zeolites resulted in the appearance of new stronger acceptor sites. In this case, the concentration of the resulting benzene radical cations can increase by a factor of several tens. Undoubtedly, these sites will have a considerable effect on the occurrence of catalytic processes on CuZSM-5. Further study of the effects of various metals on the electron-acceptor properties of catalysts and the role of these sites in catalysis is of deep interest from both fundamental and applied points of view.

The observed reversibility of the formation of radical cations and the photostimulated formation of these species suggest that the process occurs with the participation of electron donor–acceptor complexes, and it can be described by the following reaction scheme:

$$C_6H_6 + A_S \rightleftarrows [C_6H_6 \cdot A_S]; \qquad \text{(III)}$$

$$[C_6H_6 \cdot A_S] \overset{kT,\, h\nu}{\rightleftarrows} [C_6H_6^+ \cdot A_S^-]^*; \qquad \text{(IV)}$$

$$[C_6H_6^- \cdot A_S] \longrightarrow C_6H_6^+ + A_S^- (?). \qquad \text{(V)}$$

In the above scheme, step (III) corresponds to the formation of the electron donor–acceptor complex of an adsorbed benzene molecule with an acceptor site of the zeolite surface (As); step (IV) is the thermal or photoinduced excitation of this complex; step (V) is the relaxation of this excited state accompanied by charge separation and formation of stabilized radical cations. It is important that all of these processes occurred at large amounts of adsorbed benzene, corresponding to the formation of the liquid phase. Note that we failed to detect the As^- counterion, which is formed in the course of step (V), using EPR spectroscopy.

Stamires and Turkevich [30] ascribed electron-acceptor sites to Lewis acid sites (LAS's), which act as the acceptors of a single electron rather than an electron pair in this process. Slinkin et al. [31] and Shih [32] ascribed the electron-acceptor sites to radical species like O^- formed upon the thermal treatment of the catalyst, whereas Vishnetskaya et al. [33] ascribed them to singlet oxygen and Zholobenko et al. [34] and Richardson [35] ascribed them to the impurity ions of transition metals. However, none of these models has been reliably supported by experiments.

We found that the participation of the impurity ions of transition metals in the formation of radical cations on the acid forms of zeolites is improbable. Although, in principle, the participation of LAS's as an acceptor does not contradict experimental data, a reasonable model of LAS's with the electron affinity required for the ionization of not only benzene but also organic molecules with lower ionization potentials is currently unavailable. Thus, in our opinion, the model proposed by Shih [32] for acceptor sites of radical nature formed by the removal of a hydrogen atom from a Brønsted acid site is most probable.

Our quantum-chemical simulation of these sites (the results of which will be published elsewhere) demonstrated that the electron affinity of these sites is a few electron volts. These single sites will be formed on any aluminosilicate system, and they can be responsible for the formation of radical cations from molecules with low ionization potentials, for example, anthracene or perylene. At the same time, it is most likely that stronger sites are formed by the interaction of several different sites and they are sensitive to the structure of zeolites.

Note that charge-transfer complexes are formed upon the adsorption of various organic molecules at these acceptor sites. In organic chemistry, complexes of this kind with partial charge transfer exhibit a number of unique properties [36]. The chemical properties of these surface complexes, which remain unstudied so far, can be similar to the properties of radical cations. By analogy with complexes formed upon the adsorption of organic reagents at surface acid sites, these complexes with acceptor sites can initiate reactions in a cage (i.e., with no spatial charge separation) by radical cation mechanisms, which have been hypothesized previously [4, 37]. In this case, the concentration of these complexes can be much higher than the observed concentration of radical cations.

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