Mendeleev Commun., 1999, 9(2), 78–80

Interactions of adsorbed olefins and benzene with NO and NO_2 on H-ZSM-5 zeolites and Al_2O_3 according to EPR data

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Nitroxyl hydrocarbon complexes formed by the interaction of adsorbed olefin and benzene molecules with NO and NO_2 molecules on H-ZSM-5 zeolite and Al_2O_3 have been detected.

Previously[1,2] it was suggested that nitroxyl hydrocarbon complexes play an important role in the selective catalytic reduction of NO_x by hydrocarbons in an excess of oxygen. However, any nitroxyl species were not detected by EPR spectroscopy under conditions of the reaction on Cu/ZSM-5 zeolite.[3] We attempted to detect these species in the reaction between adsorbed hydrocarbons (C_2H_4, C_3H_6 and C_6H_6) and NO or NO_2 molecules on different oxide systems using EPR spectroscopy. The results obtained are reported in this work.

The experiments were performed using H-ZSM-5 and 0.15–2.85% Cu/ZSM-5 (the ratio $SiO_2/Al_2O_3 = 40$) zeolites and the oxides Al_2O_3 and SiO_2 (analytical grade) with specific surface areas of 70–200 $m^2\,g^{-1}$. The preparation of the zeolites and the EPR technique were described in detail elsewhere.[4] The EPR measurements were performed at room temperature. Concentrations of adsorbed hydrocarbons were determined using temperature-programmed desorption. The O_2 and NO gases used were prepared according to well-known procedures.[5] Chemically pure hydrocarbons (C_2H_4, C_3H_6 and C_6H_6) were additionally purified by twice freezing in a trap cooled with liquid nitrogen under vacuum. The samples (the catalyst weight was 50 mg) were initially evacuated to 10^{-4} Pa at 970 K. Next, they were heated at this temperature in oxygen at $2–5\times10^2$ Pa for 1 h. After this oxygen treatment, the samples were evacuated to 10^{-4} Pa and cooled to room temperature; hydrocarbons were adsorbed at 2×10^2 Pa.

Adsorption of propylene or ethylene and benzene on H-ZSM-5 zeolite was accompanied by the appearance of oligomer ($\mathrm{R}^{+\cdot}$) and benzene ($C_6H_6^{+\cdot}$) radical cations, respectively. These paramagnetic species were studied in detail by EPR spectroscopy.[6,7] Table 1 summarises the concentrations of these radical cations and the *g*-factors and *A* values.

The EPR signal of the $\mathrm{R}^{+\cdot}$ radical cation remained unchanged on evacuation of propylene at room temperature. Adsorption of NO at 2×10^2 Pa resulted in the disappearance of the $\mathrm{R}^{+\cdot}$ radical cations (Figure 1, curves *1* and *2*). After subsequent evacuation of NO, the signal from the $\mathrm{R}^{+\cdot}$ radical cation was not restored, and a new EPR signal with the parameters $g_1 = 2.10$, $g_2 = 2.06$ and $g_3 = 2.018$ was detected (Figure 1, curve *3*). This signal was assigned to the complex formed by the interaction of the strongly adsorbed hydrocarbon and NO (hereinafter, we shall designate this complex as NO–HC), because adsorption of individual NO on the zeolite in the absence of adsorbed hydrocarbons did not produce EPR signals under these conditions. Similar data were also obtained in the reaction of adsorbed ethylene and benzene with NO. Table 1 summarises the results.

The spectra of the radical cations and the complex (NO–HC) disappeared upon treatment of both the zeolite with an adsorbed hydrocarbon and the zeolite with adsorbed hydrocarbon and NO with a mixture of NO + O_2 + NO_2 (prepared from NO and O_2, 1:1, 5×10^2 Pa) for 20–50 min. Subsequent evacuation of the mixture resulted in a new EPR spectrum (Figure 1, curve *4*). This spectrum corresponds to a paramagnetic complex with the nuclear spin $I = 1$ and an anisotropic *g*-tensor. Adsorption of NO or O_2 on the zeolite with an adsorbed hydrocarbon did not produce this spectrum. It was also not detected upon the treatment of the initial zeolite with the gas mixture. Hence it

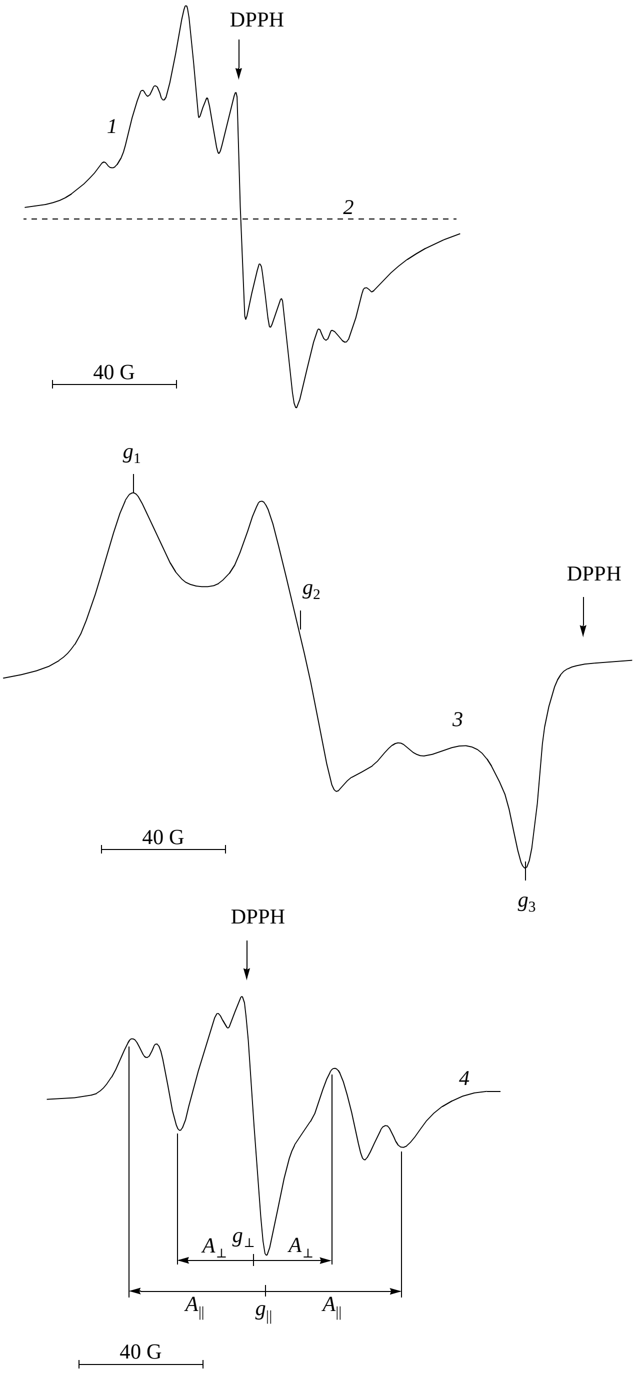

Figure 1 EPR spectra of (*1*) the oligomer radical cation after propylene adsorption on H-ZSM-5 zeolite at $P = 2\times10^2$ Pa and $T = 293$ K in a vacuum and (*2*) in an NO atmosphere at $P = 2\times10^2$ Pa; (*3*) the (NO–HC) complex after evacuation of NO; and (*4*) the (NO_2–HC) complex, formed by the interaction of adsorbed propylene and a mixture of NO + O_2 at $P = 5\times10^2$ Pa and $T = 293$ K for 50 min, in a vacuum.

Table 1 Concentrations of adsorbed molecules and paramagnetic species on H-ZSM-5 zeolite at T = 293 K and P = 2–5×10² Pa.

Molecule	$N_{ad}/10^{-20}$ g^{-1}	Species	$N_s/10^{15}$ g^{-1}	g	A/G
C_2H_4	0.5	($R^{+\cdot}$)	7.0	2.004	8.0
C_3H_6	5.0	($R^{+\cdot}$)	9.0	2.004	8.0
C_6H_6	4.0	($C_6H_6^{+\cdot}$)	7.0	2.004	4.5
NO + C_2H_4	0.4	(NO + C_2H_4)	9.0	$g_1 = 2.09$, $g_2 = 2.07$, $g_3 = 2.018$	
NO + C_3H_6	5.0	(NO + C_3H_6)	10.0	$g_1 = 2.09$, $g_2 = 2.07$, $g_3 = 2.018$	
NO + C_6H_6	3.0	(NO + C_6H_6)	9.0	$g_1 = 2.09$, $g_2 = 2.07$, $g_3 = 2.018$	
NO + O_2 + C_2H_4	1.0	(NO_2 + C_2H_4)	0.5	$g_\perp = 2.006$, $g_\parallel = 2.0035$	$A_\perp = 23$, $A_\perp = 46$
NO + O_2 + C_3H_6	6.0	(NO_2 + C_3H_6)	5.0	$g_\perp = 2.006$, $g_\parallel = 2.0035$	$A_\perp = 25$, $A_\perp = 45$
NO + O_2 + C_6H_6	5.0	(NO_2 + C_3H_6)	10.0	$g_\perp = 2.006$, $g_\parallel = 2.0035$	$A_\perp = 25$, $A_\perp = 45$

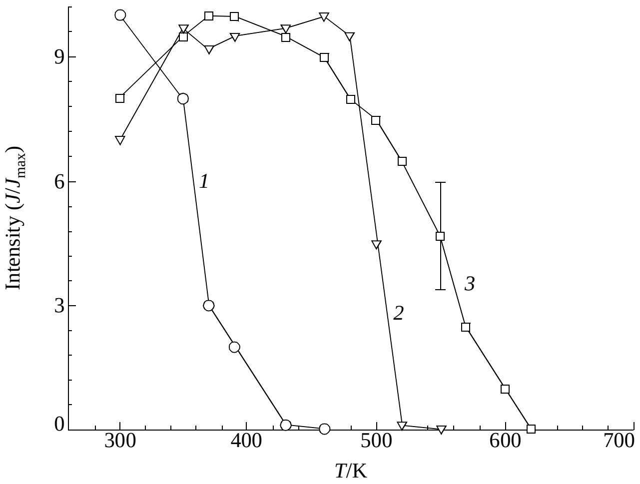

Figure 2 EPR signal intensities for (*1*) the oligomer radical cation, (*2*) the (NO–C_3H_6) complex, and (*3*) the (NO_2–C_3H_6) complex after heating them at different temperatures in a vacuum for 10 min.

follows that the observed spectrum corresponds to the complex that is formed by the interaction of the adsorbed hydrocarbon and an NO_2 molecule. Hereinafter, we shall designate this complex as (NO_2–HC). Similar spectra were also obtained after adsorption of ethylene or benzene and subsequent adsorption of the NO + O_2 + NO_2 mixture. Concentrations of the (NO_2–HC) complexes and the g-factors and A values are given in Table 1. These values are close to the g-factors and A values characteristic of $NO_2\cdot$ radicals in polymer matrices.[8]

The above data allowed us to conclude that spectrum *4* in Figure 1 corresponds to the NO_2 unit of the (NO_2–HC) complex. Three spectral lines are due to the interaction of the unpaired electron with the nitrogen nucleus $I = 1$. The g-tensor values close to $g_e = 2.0023$ can be explained by 'freezing' of the electron orbital moment in (NO_2). In the case of the (NO–HC) complex, the g-factors differ significantly from the g_e value and the g-factors known for nitrogen oxide radicals.[9] At the present time, this difference is difficult to explain, because the structure of this complex is unknown in detail, in particular, the structure of the adsorbed hydrocarbon on which it is formed. These problems call for further investigation.

Table 2 Concentrations, g-factors and A values of the (NO–C_3H_6) and (NO_2–C_3H_6) complexes on different oxide samples.

Complex	Sample	SiO_2/Al_2O_3	$N_s/10^{-15}$ g^{-1}	g	A/G
NO + C_3H_6	H-ZSM-5	40	10	$g_1 = 2.10$, $g_2 = 2.06$, $g_3 = 2.018$	
NO + C_3H_6	H-ZSM-5	50	5	$g_1 = 2.104$, $g_2 = 2.07$, $g_3 = 2.018$	
NO + C_3H_6	H-ZSM-5	80	1	$g_1 = 2.10$, $g_2 = 2.065$, $g_3 = 2.019$	
NO + C_3H_6	$Al_2O_3^a$		<0.5	$g_1 = 2.11$, $g_2 = 2.06$, $g_3 = 2.018$	
NO + C_3H_6	SiO_2^b		0		
NO_2 + C_3H_6	H-ZSM-5	40	7	$g_\parallel = 2.005$, $g_\perp = 2.008$	$A_\parallel = 45$, $A_\perp = 27$
NO_2 + C_3H_6	H-ZSM-5	50	8	$g_\parallel = 2.003$, $g_\perp = 2.007$	$A_\parallel = 52$, $A_\perp = 29$
NO_2 + C_3H_6	H-ZSM-5	80	3	$g_\parallel = 2.005$, $g_\perp = 2.008$	$A_\parallel = 50$, $A_\perp = 30$
NO_2 + C_3H_6	$Al_2O_3^a$		60–30	$g_\parallel = 2.003$, $g_\perp = 2.006$	$A_\parallel = 48$, $A_\perp = 28$
NO_2 + C_3H_6	SiO_2^b		0		

[a] The Al_2O_3 surface areas varied from 70 to 200 m² g^{-1}. [b] The SiO_2 surface area was 70 m² g^{-1}.

We failed to obtain additional information on the (NO–C_3H_6) and (NO_2–C_3H_6) complexes from the spectra measured at 77 K and with C_3D_6 in place of C_3H_6.

Note that oligomer radicals and coke take no part in the formation of the complexes under study. Indeed, the complexes were formed upon NO or NO_2 adsorption on the zeolite with adsorbed propylene after heating of the zeolite at 450 K for 15 min, *i.e.*, when the oligomer radicals were just absent at the surface. On the other hand, coke was formed on the zeolite as a result of decomposition of the (NO_2–C_3H_6) complex at T > 570 K. It was detected using the EPR signal with g = 2.004 in accordance with data given in ref. 3. With the advent of coke on the zeolite, the complexes were not formed.

It can be seen in Table 1 that concentrations of (NO–HC) complexes were approximately equal to 10^{16} g^{-1} at different concentrations of the adsorbed hydrocarbons, whereas concentrations of (NO_2–HC) complexes depended on concentrations of the adsorbed hydrocarbons. These facts suggest that the (NO–HC) complex is no intermediate in the formation of the (NO_2–HC) complex.

Table 2 summarises the data on the (NO–C_3H_6) and (NO_2–C_3H_6) complexes on various oxide systems. It can be seen that the complexes were formed on H-ZSM-5 zeolites (DuPont, SiO_2/Al_2O_3 = 50, 80) and Al_2O_3 with different specific surface areas, and they were not detected on SiO_2. Consequently, specific cations Al^{3+} are responsible for the formation of the (NO_2–C_3H_6) complex on the oxide systems examined.

Figure 2 demonstrates the relative intensities of EPR signals (J/J_{max}) against the temperature of heating the zeolite with different complexes in a vacuum for 10 min. It can be seen that the (NO–C_3H_6) and (NO_2–C_3H_6) complexes exhibit higher thermal stability that the oligomer radical cation $R^{+\cdot}$. They were detected even after heating the zeolite at 540 K. Reactions of NO_x reduction by hydrocarbons on H-ZSM-5 and Cu/ZSM-5 zeolites proceed at this temperature.[10] This fact suggests that these complexes can participate in the reaction of NO_x reduction.

We failed to detect the (NO–HC) and (NO_2–HC) complexes on Cu/ZSM-5 zeolite; however, we believe that, according to refs. 1 and 4, they can also occur on copper-containing zeolites. In this case, it is likely that the paramagnetic complexes and Cu^{2+} cations interact with each other to form species that are EPR-silent.

This work was supported by the Russian Foundation for Basic Research (grant no. 97-03-32012a).

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Received: 28th September 1998; Com. 8/07882C