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Ion-radical Mechanism of Low-temperature Benzene Polycondensation on ZSM-5 Zeolites

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Benzene cation-radicals are shown to be the key intermediates in benzene low-temperature (T < 400 K) polycondensation on ZSM-5 zeolites.

In certain cases the interaction of benzene molecules with the surface of zeolite catalysts is known to be accompanied, even at room temperature, by the formation of cation-radicals of other aromatic compounds, including biphenyl.[1–3] Thus, chemical reactions with benzene molecules are quite possible at the temperature mentioned.

On the other hand, formation of condensed organic structures (coke deposits) on a catalyst surface is usually supposed to proceed *via* a carbocationic mechanism.[4] However, the results of our work show that the cation-radical mechanism should also be considered for a detailed analysis of the problem.

Previously we studied the mechanisms of thermal[5] and photostimulated[6] formation of benzene cation-radicals on ZSM-5 zeolites. Here we investigate chemical reactions of these cation-radicals with benzene molecules.

The experimental procedure and zeolite samples were the same as in ref. 5. The system benzene–zeolite was heated at a benzene pressure of *ca.* 60 Torr.

Benzene adsorption on ZSM-5 zeolite at 248–298 K is accompanied by formation of monomeric and dimeric benzene cation-radicals. Their EPR spectra are characterized by hyperfine interaction constants $a_1^{\mathrm{H}} = 0.44$ and $a_2^{\mathrm{H}} = 0.22$ mT (Fig. 1, spectrum 1),[5] respectively. These cation-radicals are rather stable when $T < 273$ K. Increase in the temperature in a dynamic vacuum results in a decrease in their concentration *via* reaction (1) and is reversible.[5]

$$\mathrm{C_6H_6} + \mathrm{A_s} \rightleftarrows [\mathrm{C_6H_6} \cdot \mathrm{A_s}] \rightleftarrows \mathrm{C_6H_6^{+\cdot}} + \mathrm{A_s^{-\cdot}} \qquad (1)$$

Heating in a benzene atmosphere at $T > 273$ K is accompanied by chemical transformations of benzene cation-radicals. Fig. 1 shows the EPR spectra that result from such heating at various temperatures. Heating to room temperature decreases the concentration of benzene cation-radicals and provides biphenyl cation-radicals (Fig. 1, spectra 2 and 3). Further heating of the system to 363 K (Fig. 1, spectrum 4) and to 473 K (Fig. 1, spectrum 5) results in a decrease in the concentration of biphenyl cation-radicals and the appearance of an EPR spectrum that displays a single line with $\Delta H = 0.55$ mT and $g_{\mathrm{av}} = 2.0029$, typical of coke deposit spectra.

From Fig. 1, heating of the zeolite does not influence the total number of paramagnetic particles, which is approximately equal to the initial number of benzene cation-radicals. This shows the formation of all the paramagnetic products to result, under the conditions mentioned, from the interaction of benzene molecules with cation-radicals.

Thus, it is interesting to compare the thermodynamics in reactions of condensation of neutral aromatic molecules with those of reactions in which cation-radicals are involved in the reaction.

There are no data on the interaction of the products with the catalyst surface. Therefore, we shall consider the simplest case of condensation in the gas phase. Let us compare the equilibrium constants in reactions producing polyaromatic compounds (PAC) from neutral benzene molecules and from $\mathrm{C_6H_6}$ cation-radicals, reactions (2) and (3).

$$(n-1)\mathrm{C_6H_6} + \mathrm{C_6H_6^{+\cdot}} \rightleftarrows \mathrm{PAC^{+\cdot}} + m\mathrm{H_2} \qquad (2)$$

$$n\mathrm{C_6H_6} \rightleftarrows \mathrm{PAC} + m\mathrm{H_2} \quad n \geqslant 2 \qquad (3)$$

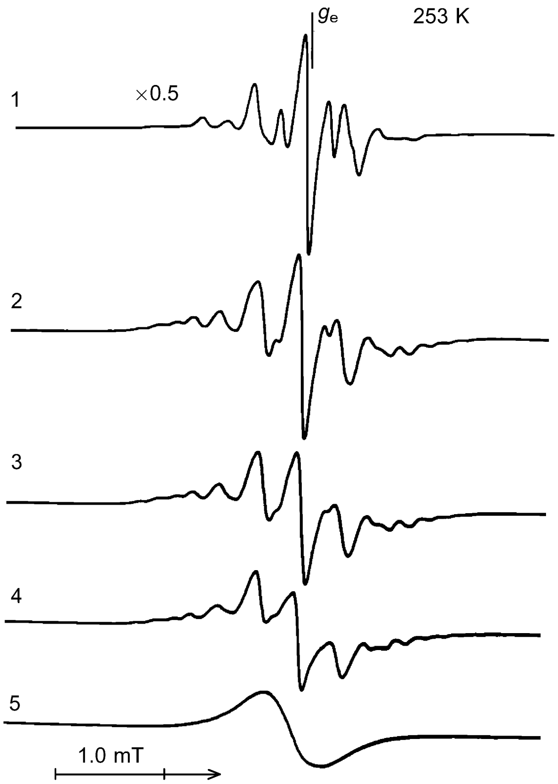

Fig. 1 EPR spectra observed upon benzene adsorption on H-ZSM-5 zeolite: 1, immediately after adsorption [spin concentration $N = (10.5 \pm 0.5) \times 10^{15}$ spin g^{-1}]; 2, after 2 h at 293 K [$N = (11.5 \pm 0.5) \times 10^{15}$ spin g^{-1}]; 3, after 19 h at 293 K [$N = (11.8 \pm 0.3) \times 10^{15}$ spin g^{-1}]; 4, after an additional 1 h heating up to 363 K [$N = (11.7 \pm 0.3) \times 10^{15}$ spin g^{-1}]; 5, after an additional 1 h heating to 473 K [$N = (8.1 \pm 0.2) \times 10^{15}$ spin g^{-1}]. The temperature of benzene adsorption and EPR spectrum recording is 253 K.

The equilibrium constant values obtained (Table 1) prove the cation-radical mechanism of PAC formation in the gas phase to be thermodynamically favourable as compared to that of polycondensation of neutral benzene species. The distinctions between the equilibrium constants for reactions (2) and (3) are determined, at least in the first stages of polycondensation, by the ionization potential of the intermediates (see Table 1).

It should be noted that the kinetic peculiarities of the reactions and the interaction of species in the adlayer can influence the progress of polycondensation. However, it is believed that these factors are unlikely to produce a pronounced effect.

Thus, experiments show benzene polycondensation on ZSM-5 zeolites to proceed at low temperatures *via* a cation-radical mechanism. Thermodynamic calculations do not contradict the above assumption and point to a possible energetic source for this process.

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Table 1 Changes in Gibbs free energies (G^0_{298}) and equilibrium constants (K) for reactions (2) and (3). Gibbs free energies of the formation of compounds (G_f^{298}) were determined *via* correlation methods: Thinh[9a] and Benson.[9b] The change of Gibbs free energy (ΔG) upon ionization of a molecule in the gas phase is equal to its adiabatic ionization potential (I_{ad}).

PAC formula	G_f^{298} /kcal mol^{-1}	I_{ad}/eV[7]	G^0_{298} /kcal mol^{-1}		lg K		Ref.
			2	**3**	**2**	**3**	
$C_{12}H_{10}$ biphenyl	66.94	8.23	−18.45	4.96	13.57	−3.65	8
m-$C_{18}H_{14}$	102.65	8.01	−18.80	9.68	13.83	−7.12	9*a*
m-terphenyl	101.93		−19.52	8.96	14.36	−6.59	9*b*
o-$C_{18}H_{14}$	103.42	7.99	−18.49	10.45	13.60	−7.69	9*a*
o-terphenyl	102.98		−18.93	10.01	13.93	−7.36	9*b*
p-$C_{18}H_{14}$	103.20	7.78	−23.55	10.23	17.33	−7.53	9*a*
p-terphenyl	102.34		−24.41	9.37	17.96	−6.89	9*b*
$C_{18}H_{12}$	95.93	7.84	−29.44	2.96	21.66	−2.18	9*a*
triphenylene	93.72		−31.65	0.75	23.28	−0.55	9*b*

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