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Abstract

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ADSORPTION OF HYDROCARBONS AT ELEVATED TEMPERATURES

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Establishing the mechanism of the contact transformation of hydrocarbons depends, above all, on the possibility of elucidating the elementary act on the catalyst surface. By using adsorption methods to study individual hydrocarbons of different structures, one determines the orientation of their molecules on the catalyst surface and the molecular constants. Therefore, carrying out adsorption measurements at elevated temperatures, under conditions preceding the catalytic decomposition of hydrocarbons, is essential in the study of heterogeneous catalytic processes.

In the present communication we give the results of adsorption from solutions of isopropylbenzene, isopropenylbenzene, propenylbenzene, allylbenzene, and cyclohexene on alumina, which, as is known, catalyzes many important processes, including the isomerization of hydrocarbons. For some of these hydrocarbons—isopropylbenzene, allylbenzene, cyclohexene—catalytic transformations have already been studied both in the vapor and in the liquid phases, and a mechanism of the process has been proposed ([1–4]).

Alkylaromatic hydrocarbons having an unsaturated bond in the side chain (propenylbenzene, isopropenylbenzene) are of particular interest, since they occur as intermediate products in the proposed schemes of catalytic transformations. The adsorption of the listed hydrocarbons is compared by us with the adsorption of *n*-propylbenzene, which has a similar structure and the same number of carbon atoms in the molecule, and also with the adsorption of benzene.

The study of this series of hydrocarbons is important, in our opinion, also because it makes it possible to clarify the question of the influence on adsorption from solutions of a conjugated double bond in the side chain of the aromatic ring (*n*-propylbenzene and propenylbenzene, isopropylbenzene and isopropenylbenzene). The relative adsorbability of hydrocarbons having an unsaturated bond in different positions (allylbenzene—propenylbenzene) is also compared. Adsorption measurements from solutions were carried out interferometrically ([5]). Normal heptane was chosen as the solvent. The adsorbent was industrial (beaded) alumina with a specific surface area of 250 m^2/g ([5]) and a predominant

Fig. 1. Absolute adsorption isotherms of isopropylbenzene (1), benzene (2), isopropenylbenzene (3), n-propylbenzene (4), allylbenzene (5), and propenylbenzene (6) at 20°

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Fig. 2. Adsorption isotherms of n-propylbenzene (1) and allylbenzene (2) at 40°

Figure 2: Fig. 2. Adsorption isotherms of n-propylbenzene (1) and allylbenzene (2) at 40°

pore radius of 40 Å. Adsorption measurements were carried out at 20, 30, and 40°. The adsorption isotherms of the investigated individual hydrocarbons at 20 and 40° are given in Figs. 1 and 2. The molecular constants of the hydrocarbons studied, calculated from the adsorption measurements, are presented in Table 1.

The thickness of the adsorption layer of benzene molecules on the surface of alumina coincides with the theoretically calculated thickness of the benzene ring, equal to 3.7 Å (^{7}). Consequently, the benzene molecules are oriented flat, parallel to the catalyst surface.

Similar values of the quantity τ are also found for the other alkyl aromatic hydrocarbons studied: isopropylbenzene, propenylbenzene, and isopropenylbenzene. Evidently, their molecules are arranged on the surface in the same way as benzene molecules, i.e., with the plane of the benzene ring parallel to the surface of aluminum oxide. Thus, the presence of a double conjugated bond in the side chain of an alkyl aromatic molecule does not change its plane-parallel orientation in the monolayer during adsorption on the catalyst surface. The molecules of allylbenzene are probably arranged less flatly. The decrease in the value of τ for *n*-propylbenzene is apparently associated with the lower density of its monolayer compared with the other hydrocarbons studied. The arrangement of the molecules of the hydrocarbons studied parallel to the surface on aluminum oxide is likewise retained as the temperature increases.

Fig. 1. Absolute adsorption isotherms of isopropylbenzene (1), benzene (2), isopropenylbenzene (3), *n*-propylbenzene (4), allylbenzene (5), and propenylbenzene (6) at 20°

Fig. 2. Adsorption isotherms of *n*-propylbenzene (1) and allylbenzene (2) at 40°

Analysis of the data in Table 1 shows that, on going from an aromatic hydrocarbon with a saturated alkyl radical to a radical bearing a double bond, a considerable decrease is observed in the molecular area w_0 occupied by the molecule in a dense monolayer (*n*-propylbenzene-propenylbenzene, isopropylbenzene-isopropenylbenzene).

The value of the molecular area occupied by a benzene molecule at 20° in a dense monolayer on aluminum oxide, $w_0 = 44$ $\mathring{A}^2$, is close to the value determined for adsorption from its solutions in *n*-heptane on silica gel (8).

As the temperature is raised, the fraction of surface accounted for by each adsorbed molecule increases, while the thickness of the adsorption layer decreases somewhat. This "dilution" of the adsorbed layer is probably connected with the fact that the adsorbed molecules of the hydrocarbons studied are not fixed on the surface and, with increasing temperature, acquire greater mobility. This conclusion is of interest for catalysis.

Table 1

Hydrocarbon	v_m, cm^3/mol	τ, Å	ω_0, Å^2	$\Gamma_{\max}$, μmol/m^2	Adsorb. potential, cal/mol
I. 20°					
Benzene	88.8	3.7	44		
n-Propylbenzene	139.4	2.8	81	1.47	1550
Isopropylbenzene	139.5	3.9	60	1.75	1100
Allylbenzene	132.4	4.1	52	2.05	1190
Propenylbenzene	129.3	3.8	54	2.37	1760
Isopropenylbenzene	129.7	3.8	56	2.37	1860
II. 40°					
n-Propylbenzene	141.5	2.3	99	1.17	1970
Allylbenzene	134.4	3.6	63	1.75	1610

The data from adsorption measurements at 20° make it possible to establish that propenylbenzene, isopropenylbenzene, and allylbenzene, which contain a double bond in the side chain, are adsorbed better than aromatic molecules having a saturated alkyl radical with the same number of carbon atoms. The adsorption maxima of propenylbenzene and isopropenylbenzene are shifted toward lower concentrations in comparison with the adsorption maxima of allylbenzene, isopropylbenzene, and *n*-propylbenzene.

This shift of the adsorption maxima cannot be associated with their smaller molecular volumes v_m (see Table 1); it is explained by an increase in the adsorption potential ([9,10]) when a conjugated double bond appears in the side chain of the aromatic molecule. The decrease in the molecular area ω_0 for these hydrocarbons also testifies to this.

The intensifying adsorption action of the double bond in the side chain of the aromatic ring corresponds to its high reactivity on aluminum oxide. It is known from the literature (1,2) that the active centers of aluminum oxide catalyze isomerization associated with migration of the double bond in the side chain.

The migration of an unsaturated bond in the side chain of an aromatic molecule into the conjugated position in going from allylbenzene to propenylbenzene, as calculation shows, also significantly increases the adsorption potential, although the magnitude of the maximum adsorption increases only slightly. The greater adsorbability of propenylbenzene in comparison with allylbenzene confirms the validity of applying, in processing the results of the catalytic isomerization of allylbenzene to propenylbenzene, a kinetic equation which assumes that the reaction products are adsorbed more strongly than the starting substances.

Analysis of the results obtained at 40° shows that, for both hydrocarbons studied, an increase in temperature is accompanied by a decrease in adsorption. At the same time, the maxima of the adsorption isotherms of allylbenzene and *n*-propylbenzene shift toward lower concentrations in comparison with their position at 20°, which corresponds to an increase in the adsorption potential by about 400 cal/mol.

Consideration of adsorption from solutions of the studied series of individual hydrocarbons leads to the conclusion that a conjugated double bond behaves specifically on the surface of aluminum oxide. In terms of these studies, it was of interest to compare the adsorption of cyclic hydrocarbons containing different numbers of double bonds in the ring.

It is known that the chemical nature of adsorbents exerts a great influence on the adsorption of hydrocarbons having an unsaturated bond. Thus, on silica gel benzene is adsorbed more strongly than cyclohexene (11,12); however, transition to aluminosilicate catalysts and aluminum oxide, as shown by K. V. Topchieva (13), changes the adsorption picture. In the adsorption of cyclohexene vapors, a compaction of the cyclohexene monolayer was found, explained

with orientation of its molecules by the double bond toward the catalyst surface. This assumption and the irreversibility of the adsorption isotherm of cyclohexene vapor make it possible to speak of chemisorption of the latter, which is essential for catalysis. The adsorption isotherms of cyclohexene from solutions in *n*-heptane on industrial aluminum oxide at 20 and 30° are given in Fig. 3. Unlike the isotherms presented by us earlier, they have an inflection point, after which adsorption increases sharply and, after passing through a maximum, decreases linearly. The form of the isotherms indicates a reorientation of cyclohexene molecules in the concentration region above the inflection point. A calculation, in the first approximation (6), of the absolute adsorption isotherms shows that the area occupied by a cyclohexene molecule in a dense monolayer is approximately 27 Å^2. At the inflection point of the isotherm, the area occupied on average by a molecule on the aluminum oxide surface is about 60 Å^2.

Fig. 3. Adsorption isotherms of cyclohexene: **1** –at 30°, **2** –at 20°

Fig. 3. Adsorption isotherms of cyclohexene: 1 –at 30°, 2 –at 20°

Figure 3: Fig. 3. Adsorption isotherms of cyclohexene: 1 –at 30°, 2 –at 20°

Consequently, cyclohexene molecules are at first adsorbed flat on the surface of aluminum oxide, similarly to benzene molecules, but then, as the concentration increases, they reorient, standing on edge, with the double bond toward the catalyst surface.

As the temperature is raised, the maximum of the adsorption isotherm shifts into the region of lower concentrations, i.e., at 30° a greater part of the adsorbed cyclohexene molecules has an edgewise orientation on the catalyst surface. Since at 40°, under the experimental conditions, isomerization of cyclohexene on aluminum oxide begins, apparently such an orientation of it precedes the catalytic transformation.

Thus, the presence of one double bond in the molecule of a cyclic hydrocarbon adsorbed on a catalyst introduces its own specific features into the adsorption process.

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Note: Figure translations are in progress. See original paper for figures.