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Adsorptive Properties of Decationated Zeolite for Some Aromatic Hydrocarbons as Observed by Gas Chromatography

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The adsorptive properties of decationated zeolite for simple aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes were investigated by means of gas chromatography at 270—330°C. The specific retention volumes of these alkylbenzenes increased with the increase in the sodium ion content and the rise in the pretreatment temperature of zeolite. The adsorption heat was substantially independent of the sodium content, but slightly increased with the rise in pretreatment temperature above 550°C. A linear relationship was found between the decrease in the ionization potential of aromatic hydrocarbons and the increase in the heat of adsorption. For comparison, the adsorption of ethylene was also examined. With the rise of pretreatment temperature of zeolite, the retention volume of ethylene decreased. On introduction of water to the system, the retention volume of ethylene reversibly increased, whereas that of aromatic hydrocarbons decreased. In accordance with the decationation process of zeolite proposed by Hall *et al.*, these aromatic hydrocarbons are adsorbed preferably on tricoordinated aluminum site as well as on sodium ion to form the charge transfer complex, while ethylene interacts with hydroxyl group to form the carbonium ion or hydrogen-bonded complex.

In spite of the widespread use of decationated zeolite as a catalyst for the reactions of aromatic hydrocarbons, its adsorptive properties are still open to question. Adsorption measurement at an elevated temperature is improtant in elucidating the kinetics and mechanisms of catalysis. Little information, however, is available on high temperature adsorption of aromatic hydrocarbons on decationated zeolite. Difficulty in experiment seems to arise from the decomposition and poor volatility of the adsorbate. Gas chromatography might be of use to overcome this difficulty.[1,2] In this work, the apparent adsorption constant and apparent adsorption heat of several aromatic hydrocarbons on decationated zeolite were determined using a simple gas chromatographic technique.

Significant advance has been made in understanding the acid property of decationated zeolite by spectroscopic observations, particularly by infrared absorption. Most investigators agree that the acidic sites on this solid consist of the Brönsted and Lewis acids and that the former can be converted into the latter by thermal treatment. The adsorptive properties of decationated zeolite for some aromatic hydrocarbons was discussed in accordance with this concept.

Experimental

Materials. Sodium zeolite used in this work was Linde Y Molecular Sieve (SK-40). The ammonium form was prepared by the ion exchange of sodium zeolite with 0.05—0.5N solution of ammonium acetate at 50°C. The exchange levels of ammonium zeolite, defined as the percentage of the original sodium ion replaced, were determined to be 14, 25, 37, 59, and 67. The zeolite was preliminary dried at 110°C for 4 hr, pelletized, and ground to the size 48—60 mesh. X-ray examination revealed good crystallinity in these materials. Aromatic hydrocarbons (commercial guaranteed grades) were dehydrated with metallic sodium, distilled and passed through a silica gel column before use.

Apparatus and Procedure. The apparatus was similar to that of the usual gas chromatogragh reported by Everly.[1] The unit consisted of a pulse injection system connected in series to a gas chromatographic column packed with 0.2 g of zeolite and a thermal conductivity cell. The column made from stainless steel was settled in an iron block to keep the temperature constant. The maximum temperature variation over the column was less than 1°C. The carrier gas (hydrogen) was passed through a purification train of Pd and 5A Molecular Sieve. No appreciable change in peak width and retention volume of aromatic hydrocarbons was observed with carrier gas (helium, agron, and nitrogen), its flow rate, and

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[1] P. E. Eberly Jr., *J. Phys. Chem.*, **65**, 68 (1961); **66**, 812 (1962).

[2] H. W. Habgood, "The Solid-Gas Interface," Marcel Dekker, New York (1967).

particle size of zeolite.

The weight change of zeolite with thermal treatment was measred by a micro-thermobalance under the condition similar to those in gas chromatography. The effect of water vapor on the retention volume were examined by using a sideline in which the carrier gas passed through a saturator system, consisting of three bubble-vessels filled with water.

Prior to each measurement, fresh zeolite was treated at the desired temperature for 2 hr in a stream of carrier gas. A small amount of argon, as a non-adsorbable gas, was added into a pulse in order to determine the net retention volume of hydrocarbons. The corrected specific retention volume V_r was calculated by means of the equation[3]

$$V_r = (t-t_0)\frac{T}{298}\cdot\frac{3}{2}\cdot\frac{(P_i/P_0)^2-1}{(P_i/P_0)^3-1}\cdot\frac{F}{W}$$

where t and t_0 are the retention times (min) of a hydrocarbon and inert gas, respectively, T is the column temperature (°K), P_i and P_0 are the pressures at the column inlet and outlet, respectively, F is the flow rate of carrier gas (ml/min), and W is the weight of zeolite packed (g).

When a linear isotherm is expected, the apparent equilibrium constant of adsorption K can be obtained by

$$K = \frac{V_r}{\boldsymbol{R}T}$$

where $\boldsymbol{R}$ represents the gas constant.[4] Linearity of an isotherm may be indirectly confirmed by the fact that the specific retention volume is independent of the partial pressure of adsorbate. The result is shown in Fig. 1, in terms of the relation between V_r and the pulse volume of hydrocarbon.

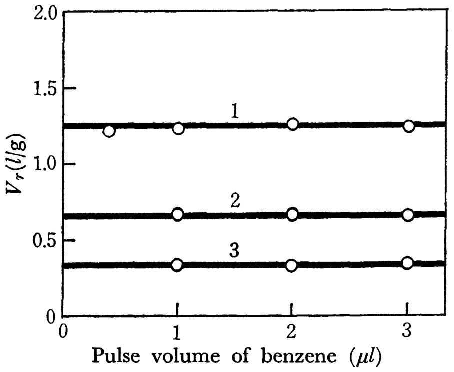

Fig. 1. Effect of injected pulse volume on the specific retention volume.
37% Exchanged zeolite treated at 500°C
Adsorption temperature: 1, 270°C; 2, 300°C; 3, 330°C

Results

Effect of Sodium Ion. Zeolite cation plays an important role for the adsorptive property of zeolite. In the adsorption of aromatic hydrocarbon on decationated zeolite with various degree of ion exchange, the retention volume markedly decreased with the increase of exchange level. The logarithms of $V_r/\boldsymbol{R}T$ for benzene and *o*-xylene are plotted against the reciprocal of the absolute temperature in Figs. 2 and 3, respectively. The data show linear relationships which have practically the same slopes. The apparent heats of adsorption are derived from the tangent of these plots. We see that the apparent adsorption heats of benzene and *o*-xylene are independent of the sodium ion content in the zeolite treated at 500°C, being estimated to be 14.9 and 18.3 kcal/mol, respectively. The former value is rather small in comparison with 15.5 kcal/mol for sodium X zeolite.[1] In similar examinations of other hydrocarbons such as toluene, ethylbenzene and *m*- and *p*-xylene, no appreciable change in the adsorption heat was observed with the change in ex-

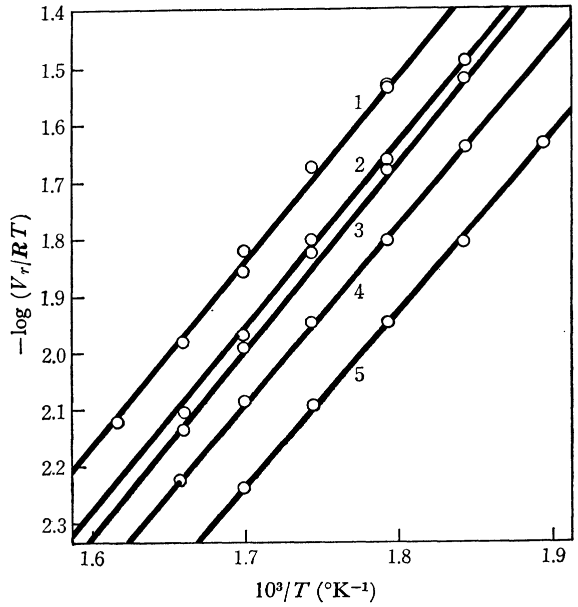

Fig. 2. Temperature dependence of the retention volume of benzene on the zeolites with various degrees of ion exchange.
Pretreatment temperature; 500°C
Ion exchange level: 1, 0 and 14%; 2, 25%; 3, 44%; 4, 59%; 5, 67%

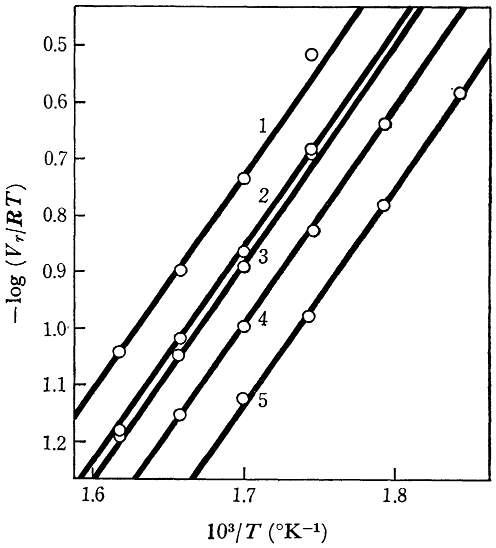

Fig. 3. Temperature dependence of the retention volume of *o*-xylene on the zeolites with various degrees of ion exchange.
Pretreatment temperature: 500°C
Ion exchange level: 1, 0 and 14%; 2, 25%; 3, 44%; 4, 59%; 5, 67%

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[3] A. J. M. Keulemans, "Gas Chromatography," Reinhold, New York (1959).

[4] J. J. Yan Deemter, F. J. Zwiderweg, and A. Klinkenberg, *Chem. Eng. Sci.*, **5**, 271 (1956).

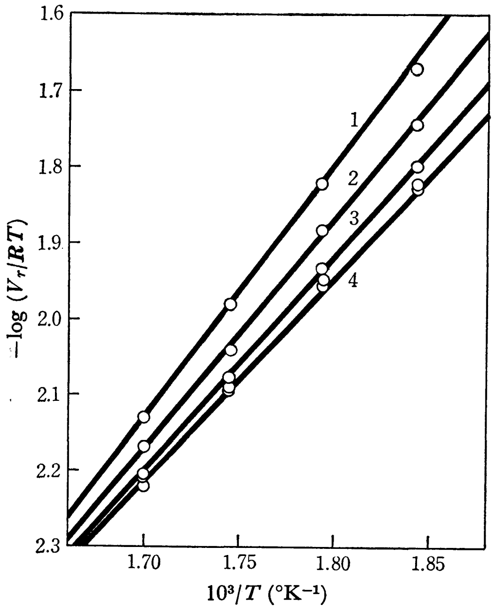

Fig. 4. Temperature dependence of the retention volume of benzene on the zeolite treated at various temperatures.
Ion exchange level: 67%
Pretreatment temperature: 1, 650°C; 2, 600°C; 3, 550°C; 4, 500, 450, 400, and 350°C

change level of zeolite. Thus, it might be expected that ion exchange influences not the strength but the number of the adsorptive sites on zeolite surface.

Effect of Thermal Treatment. Thermal treatment also influences adsorptive properties of decationated zeolite. Figure 4 shows the temperature dependence of benzene adsorption on 67% exchanged zeolite treated at various temperatures. Hardly any variation was observed in adsorptive properties of the zeolite subjected to the treatment at 350—500°C. In the higher temperature range of the treatment, both the specific retention volume and the apparent adsorption heat increased with the rise in the pretreatment temperature. This might indicate that the thermal treatment at a higher temperature changes the adsorption sites on decationated zeolite.

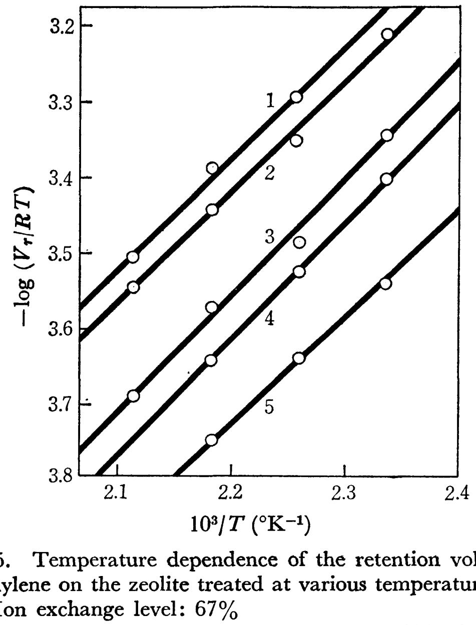

Fig. 5. Temperature dependence of the retention volume of ethylene on the zeolite treated at various temperatures.
Ion exchange level: 67%
Pretreatment temperature: 1, 400°C; 2, 350°C; 3, 450°C; 4, 500°C; 5, 600°C

For comparison, similar examinations were carried out for ethylene adsorption. The results are shown in Fig. 5. There is a marked difference between the adsorption of ethylene and that of benzene. With the rise of temperature of heat treatment, the specific retention volume of ethylene decreased, whereas that of benzene increased. The apparent adsorption heat of ethylene is amlost independent of the pretreatment temperature, while that of benzene depends on the pretreatment temperature above 550°C. It seems that benzene and ethylene are adsorbed on different sites.

Table 1. Effect of water addition on the retention volume of benzene and ethylene

Condition	V_r of benzene at 225°C (l/g)	V_r of ethylene at 155°C (ml/g)
After calcination at 600°C[a]	3.41	9.80
On introduction of water	2.22[b]	14.4[c]
After calcination at 600°C	3.45	9.00
On reintroduction of water	2.08[b]	12.0[c]

a) 67% exchanged zeolite
b) 18.9 mmHg of water pressure
c) 4.6 mmHg of water pressure

Effect of Water Vapor. The effect of thermal treatment on adsorptive properties is presumably due to the water content in zeolite, since a major portion of ammonia seems to evolve below 300°C.[5] The effect of water was examined by introducing water vapor to the system. The results are shown in Table 1. For 67% exchanged zeolite calcined at 600°C, the specific retention volumes of benzene and ethylene are 3.41 l/g at 225°C and 9.8 ml/g at 155°C, respectively. On introduction of water to the system, the retention volume of benzene decreased and reached the stationary value of 2.22 l/g under 18.9 mmHg of water pressure, whereas that of ethylene increased to the level of 14.4 ml/g under 4.6 mmHg of water pressure. When addition

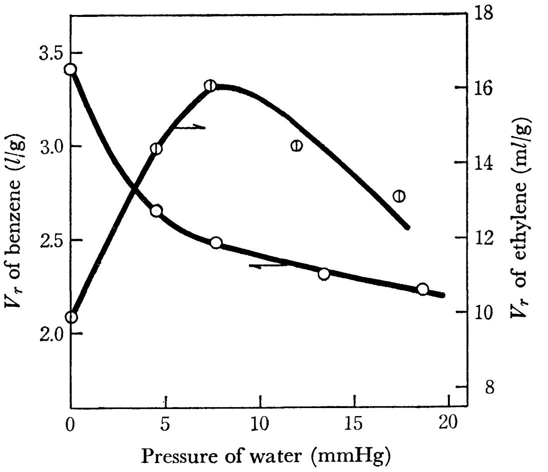

Fig. 6. Retention volume of benzene and ethylene under various pressures of water.

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5) J. W. Ward, *J. Catal.*, **9**, 225 (1967).

of water was stopped and the zeolite was treated at 600°C, the original levels of the retention volumes were restored. Again on further introduction of the same pressure of water, each retention volume showed almost the same value as that on the first introduction.

For the adsorption of benzene and ethylene, poisoning and promotive effects of water vapor increased with the increase of its vapor pressure in carrier gas as shown in Fig. 6. A low retention volume of ethylene under a high pressure of water seems to be due to poisoning by the adsorption of excessive water on the surface.

TABLE 2. THE RETENTION VOLUME AND THE ADSORPTION HEAT OF SEVERAL AROMATIC HYDROCARBONS

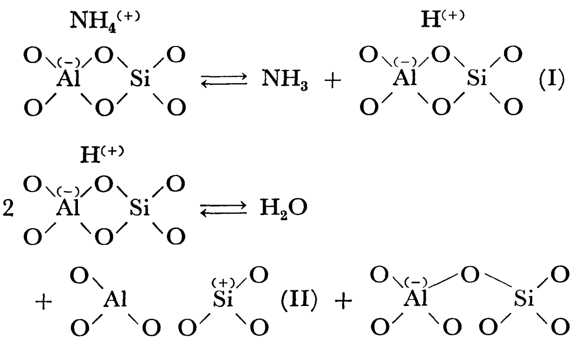
Hydrocarbons	V_r at 330°C (l/g)	Q (kcal/mol)
Benzene	0.267	14.9
Toluene	0.947	16.1
Ethylbenzene	2.40	17.4
o-Xylene	3.74	19.1
m-Xylene	2.47	17.8
p-Xylene	2.80	19.2

Sample: 67% exchanged zeolite treated at 600°C

Effect of Alkyl Substituent. Similar measurements were carried out for several alkylbenzenes such as toluene, ethylbenzene, and xylenes in order to confirm the influence of alkyl groups. No chemical reaction of these compounds occurred. The specific retention volume and apparent heat of these hydrocarbons are shown in Table 2. The retention volume increased with the number of alkyl substituents. It can be seen that the larger the retention volume, the larger the heat of adsorption. In the case of cumene and higher alkylbenzene, dealkylation and disproportionation occurred under similar conditions. Adsorption of these alkylbenzenes was not examined, since sorption mechanism might be influenced by the adsorption of reaction products.

Discussion

In the adsorption of π-base such as aromatic hydrocarbons, there is no doubt that the adsorptive sites of decationated zeolite are acidic. It is, however, still obscure whether such sites are the Brönsted acid or Lewis acid. Following Uytterhoeven, Christner, and Hall,[6] decationation process of zeolite can be visualized as follows



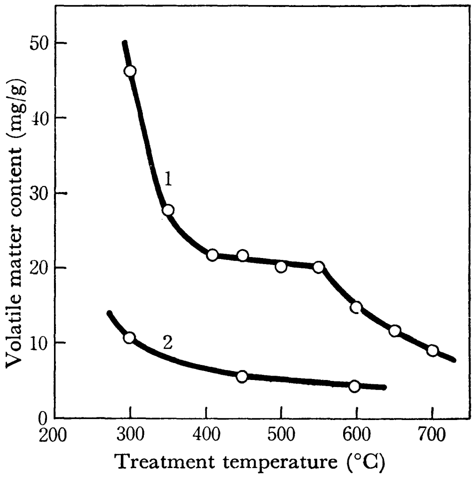


Fig. 7. Weight changes of decationated and sodium zeolite as a function of temperature.
1, Decationated zeolite (67% exchanged)
2, Sodium zeolite

The Brönsted acid site is given by I and the Lewis acid site by II.

Figure 7 shows weight changes of 67% decationated and the original sodium zeolite as a function of the temperature of heat treatment. The results are expressed in terms of the amount of volatile component (water and ammonia) of the samples after each calcination, assuming that the zeolite treated at 1000°C contains no volatile matter. For the decationated zeolite, a marked weight loss takes place below 400 and above 550°C. Effluent gas analysis shows that the initial weight decrease is due to the evolution of ammonia and of water (probably physically adsorbed water). Although the evolution is still continued little by little until 550°C, only that of water is observed above 550°C. It might be that below 400°C the greater part of ammonium ions has been decomposed to ammonia and proton to produce the Brönsted acid sites, and that the removal of the protons as water to generate the Lewis acid sites starts around 550°C. On the other hand, no appreciable weight change of sodium zeolite is detected above 400°C.

It might be considered that aromatic hydrocarbon is adsorbed more preferably on the Lewis acid site than on the Brönsted acid site, since the specific retention volume markedly increased by the treatment above 550°C (Fig. 8). The retention volume of ethylene decreased with the rise of temperature of heat treatment of decationated zeolite. This trend is similar to that of catalytic activity in the reactions *via* carbonium ion intermediate.[7,8] Ethylene seems to be adsorbed on the Brönsted acid site to form carbonium ion or strong hydrogen-bonded complex as a precursor to carbonium ion.[6] Ward[5] and Hattori *et al.*[9] have recognized in infrared measurements of adsorbed pyridine on decationated zeolite that the strong Lewis acid site can be

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[6] J. B. Uytterhoeven, J. B. Christner, and W. K. Hall, *J. Phys. Chem.*, **69**, 2117 (1965).

[7] P. B. Venuto, L. A. Hamilton, and P. S. Landis, *J. Catal.*, **5**, 484 (1966).

[8] J. Turkevich, Japan-U. S. A. Seminer on Catalytic Sci. (Tokyo, 1968).

[9] H. Hattori and T. Shiba, *J. Catal.*, **12**, 111 (1968).

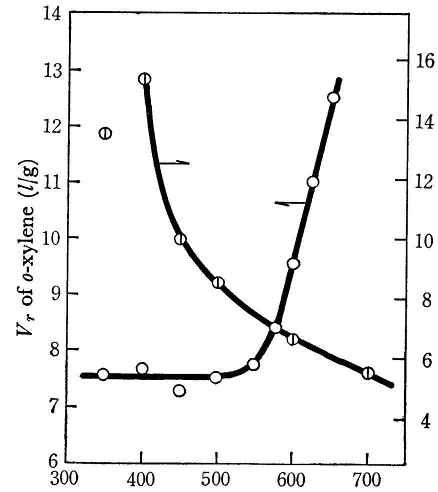

Fig. 8. The retention volume of *o*-xylene and ethylene as a function of pretreatment temperature of zeolite.
Ion exchange level: 67%
Adsorption temperature: *o*-xylene, 285°C; ethylene, 185°C

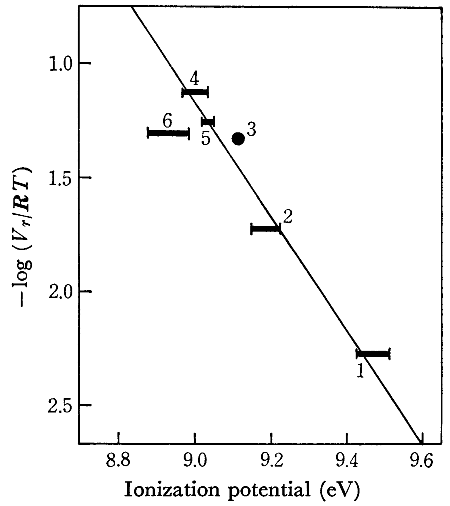

Fig. 9. Relation between the apparent adsorption constant and the ionization potential of aromatic hydrocarbons.
1, benzene; 2, toluene; 3, ehtylbenzene; 4, *o*-xylene; 5, *m*-xylene; 6, *p*-xylene

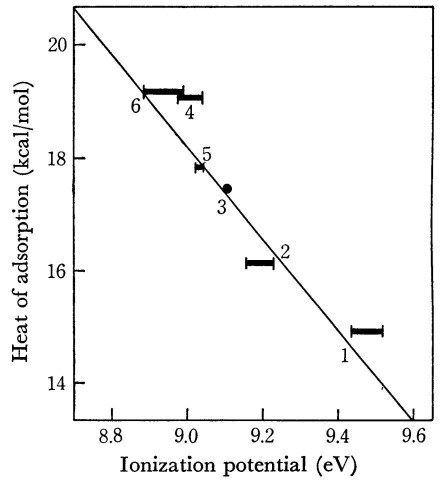

Fig. 10. Relation between the apparent adsorption heat and the ionization potential of aromatic hydrocarbons.
1, benzene; 2, toluene; 3, ethylbenzene; 4, *o*-xylene; 5, *m*-xylene; 6, *p*-xylene

converted into the Brönsted acid site by the addition of water. We see in Table 1 and Fig. 6 that the specific retention volume of ethylene increased and that of benzene decreased by the introduction of water. Thus, the adsorptive sites of decationated zeolite available for ethylene and benzene seem to be the Brönsted acid and the Lewis acid, respectively.

Alkylbenzene are probably adsorbed not only on tricoordinated aluminum atoms (the Lewis acid) but also on sodium cations, since the sodium ions on the zeolite are almost exposed by heat treatment above 400°C (Fig. 7) and the specific retention volume increases with the increase in the sodium ion content (Figs. 2 and 3). The apparent adsorption heat of benzene is practically independent of the sodium ion content. The adsorptive strength of sodium sites, therefore, does not appear to be affected by a change in the concentration. On the other hand, the adsorption heat of benzene increased with the rise of the temperature of heat treatment above 550°C. This probably indicates that tricoordinated aluminum sites are stronger than sodium sites for the adsorption of benzene.

The interaction between π-base and electrophilic site would be due to charge transfer. It can be seen that both the retention volume and the adsorption heat of benzene derivatives increased with the extent of alkyl substitution (Table 2). The electron-releasing alkyl groups increase the electron density of aromatic ring, making it more susceptible to interact with tricoordinated aluminum atom or sodium ion. This might be confirmed quantitatively with the ionization potential sequence of adsorbates. Figures 9 and 10 show the linear correlations of logarithmic adsorption constant and adsorption heat, respectively, with the ionization potential of aromatic hydrocarbons. The values of the ionization potential (measured by the electron impacting method) are taken from literature,[10] thick lines indicating the variations of these values. It can be seen that the higher the ionization potential, the smaller the adsorption constant and adsorption heat. These correlations suggest the charge transfer interaction between aromatic hydrocarbon and decationated zeolite.

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[10] P. E. Honing, *J. Chem. Phys.*, **16**, 105 (1948); J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952); F. H. Field and J. L. Franklin, *ibid.*, **22**, 1895 (1954); I. Omura, H. Baba, and K. Higashi, *J. Phys. Soc. Japan*, **10**, 317 (1955); G. F. Grable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).