

Sorption and Diffusion of Benzene in H-ZSM-5: Effect of Si/Al Ratio, Degree of Cation Exchange and Pretreatment Conditions

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Sorption and desorptive diffusion of benzene in the presence of helium in H-ZSM-5 zeolites (with different Si/Al ratios and degree of H⁺-exchange and pretreated at different conditions) at 523 K have been studied by the dynamic sorption/desorption technique using a gas chromatograph. Influence of the Si/Al ratio, nature of cation and its degree of exchange, pretreatment temperature, and hydrothermal treatment on both the sorption and diffusion has been observed to be very strong. Dehydroxylation of the zeolite has resulted in a very significant decrease in the sorption, indicating the involvement of the hydroxyl groups responsible for the acidity in the sorption process. However, a large increase in the sorption with the decrease in the degree of H⁺ exchange of H-Na-ZSM-5 reveals that benzene interacts more strongly with Na⁺ cations than with protons. For the zeolites having negligibly small Na⁺-content the diffusion increases with the decrease in the protonic acid sites. On the contrary, the diffusion in H · Na-ZSM-5 increases considerably with the increase in the degree of H⁺-exchange, or with the decrease in the Na⁺-content, which causes increase in the protonic acidity. The strong influence of Na⁺-content is mainly due to the stronger interaction of benzene with Na⁺ ions than with the protons and also may be because of a reduction in the effective channel diameter when H⁺ is replaced by Na⁺. Thus the diffusion is strongly influenced by the interaction of the diffusing species with both the protonic acid sites and nonacid sites, and also by the small changes in the channel diameter. © 1986 Academic Press, Inc.

INTRODUCTION

The product distribution (or selectivity) in the catalytic processes occurring in the highly shape-selective ZSM-5 type zeolites is controlled by the diffusion/reaction interactions (1). Thus diffusion in these zeolites plays a very vital role in deciding the product selectivity; hence a sound understanding of the diffusion and factors affecting it is very essential to get an insight into the catalytic processes in the zeolites.

The diffusion in pentasil zeolite has been reviewed by Ruthven (2). Our recent study (3) on the desorptive diffusion of benzene in H-ZSM-5 at catalytic conditions has indicated that the diffusion is highly concentration and temperature dependent. It is interesting to note that the diffusion coefficient for benzene in H-ZSM-5 at 303 K, reported

by Doelle *et al.* (4), is far different from that reported by Wu *et al.* (5).

In ZSM-5 type zeolites the diameter of the intersecting elliptical straight channels (0.51 × 0.55 nm) and near-circular zigzag channels (0.54 × 0.56 nm) (6) is comparable to the size of the molecules of the diffusing species such as benzene (critical diameter: 0.66 nm). Therefore, the diffusing molecules are in very close contact with the zeolite channel walls. Under these circumstances, the diffusion of the species is controlled by its chemical and physical interactions with the structural elements and the cations in the zeolite. The diffusion of a particular species in the zeolite is, therefore, expected to be strongly dependent on the chemical environment of the diffusing species, which in turn depends on the zeolite parameters (*viz.* Si/Al ratio, nature of the cation and its degree of exchange and pretreatment conditions, etc.). These as-

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TABLE 1
H-ZSM-5 Zeolites Used in the Sorption and Diffusion Studies

Zeolite	Si/Al ratio	Degree of H ⁺ exchange (α)	Deammoniation temp. (K)	Steam treatment	Pyridine sorbed irreversibly at 673 K (mmol · g ⁻¹)	Average crystal size (μ m)
H-ZSM-5 (1)	13.6	0.96	773	Nil	0.36	1.20
H-ZSM-5 (1a)	13.6	0.96	773	At 673 K and steam pressure of 95.3 kPa for 4 days	0.14	1.22
H-ZSM-5 (2)	17.2	0.99	773	Nil	0.33	0.77
H-Na-ZSM-5 (2a)	17.2	0.70	773	Nil	0.14	0.79
H-Na-ZSM-5 (2b)	17.2	0.51	773	Nil	0.04	0.80
H-ZSM-5 (2c)	17.2	0.99	1223	Nil	0.006	0.77
H-ZSM-5 (3)	22.0	0.99	773	Nil	0.31	1.44
H-ZSM-5 (4)	31.1	0.99	773	Nil	0.24	2.08
H-ZSM-5 (5)	39.7	0.99	773	Nil	0.19	5.55

pects of diffusion in H-ZSM-5 have not been thoroughly investigated so far.

Post *et al.* (7) studied the effect of Al-content on the diffusion of 2,2-dimethyl butane in H-ZSM-5 (at 373 K) and observed a decrease in the diffusivity with the increase in the Al-content of the zeolite. Wu and Ma (8) observed that the sorption capacity of alkali metal-exchanged ZSM-5 for hydrocarbons depends strongly on the radius of the alkali metal cation, but the effect of cation on the diffusion (at 303 K) is insignificant.

Our earlier studies (9–14) have indicated that the acidity and catalytic properties of ZSM-5 zeolite are strongly affected by the above zeolite parameters. It is, therefore, of great interest to investigate systematically the influence of these parameters on the diffusion of reaction species in the zeolite at conditions close to those typical of catalytic reactions. The present investigation was undertaken with the objective of studying the influence of these parameters on the sorption and desorption diffusion of benzene (which is a reaction species in a number of hydrocarbon conversion processes and which alone does not undergo reaction at high temperatures) in H · Na-

ZSM-5 zeolite at 523 K using the sorption/desorption technique (3).

EXPERIMENTAL

The zeolites used in the present sorption and desorption studies are listed in Table 1, along with their Si/Al ratio; degree of H⁺-exchange [(Al-Na)/Al], the temperature at which the H-ZSM-5 was obtained from its NH₄-form by the deammoniation, the steam treatment conditions, number of strong protonic acid sites (measured in terms of the amount of pyridine irreversibly sorbed at 673 K), and average crystal size. H-ZSM-5 (1 to 5) zeolites were obtained from their NH₄-form by deammoniating them at 773 K for 12 h in air. H-ZSM-5 (2c) was obtained by deammoniating its NH₄-form at 1223 K in air for 12 h. H-ZSM-5 (1a) obtained by treating H-ZSM-5 (1) with steam (at a pressure of 95.3 kPa) at 673 K for a period of 4 days. H-ZSM-5 (2a) and H-ZSM-5 (2b) with different degrees of H⁺-exchange were obtained from H-ZSM-5 (2) by exchanging it with 1 M sodium nitrate solution repeatedly at 353 K. Detailed preparation and characterization of the zeolites have been given elsewhere (9).

All the zeolites were pressed without

binder and crushed to particles of about 0.2 mm in size.

The size and morphology of crystals of the zeolites were determined using a Cambridge Stereoscan Model 150 scanning electron microscope. The shape of the crystals of the zeolites [except that of H-ZSM-5 (4 and 5)] was nearly spherical.

The number of strong protonic acid sites on the zeolites was measured in terms of the amount of pyridine irreversibly sorbed at 673 K; using the GC pulse method (15). The pyridine sorption essentially measures protonic acid sites in H-ZSM-5 zeolite (10). Detailed information on the acid strength distribution on these zeolites has been given earlier (10–13).

The intracrystalline (micro) and intercrystalline (macro) pore volumes of the zeolites were determined by measuring the volumes of *n*-hexane (which penetrates freely both the micro and macro pores) and isooctane (which penetrates the macropores but not the zeolite crystals), respectively, sorbed in the evacuated zeolite particles at 303 K, using the specific gravity bottle method (16, 17). The values of the micro- and macropore volumes of H-ZSM-5 (1 to 5) zeolites were found to be in the range 0.17–0.18 and 0.26–0.28 cm³ · g⁻¹, respectively.

Sorption and kinetics of desorption of benzene on the zeolites were measured by the dynamic sorption/desorption technique (3, 18) using a Perkin–Elmer Sigma 3B gas chromatograph with a flame ionization detector with helium as a carrier gas. A shallow bed (4 mm o.d. × 3 mm length) zeolite column (made of stainless steel) containing 50 mg zeolite particles was used in the sorption/desorption measurements. The zeolite in the column was calcined *in situ* by heating in a flow of helium (50 cm³ · min⁻¹) at 673 K for 4 h. The sorption of benzene in the zeolite at 523 K was determined by saturating it with the sorbate at a known concentration by passing a mixture of the sorbate and helium through the zeolite for a sufficiently long period of time (about 30 min) so that sorption equilibrium is estab-

lished, and measuring the extent of sorption by determining the amount of sorbate desorbed in the inert gas (He) stream (flow rate: 200 cm³ · min⁻¹). During the first few minutes, when the desorption was rapid, it was allowed to occur isothermally. This was followed by the temperature-programmed desorption (TPD) of the sorbate still remaining in the zeolite. The detector sensitivity and chart speed were changed from time to time so as to obtain more accurate desorption data.

The extent of sorption (q_a) and desorption kinetic data were estimated from the desorption chromatogram using the relations:

$$q_a = q_d = A/sm \quad (1)$$

and

$$Q_t/Q_\infty = A_t/A \quad (2)$$

where, q_d is the amount desorbed; A , the total area (normalized) under the desorption chromatogram; s , the molar response of the detector; m , the mass of the zeolite; Q_t , the amount desorbed at time t ; Q_∞ , the total amount desorbed; and A_t , the area (normalized) under the desorption chromatogram from time $t = 0$ to $t = t$.

In order to be sure that the desorption rate is controlled only by the intracrystalline (micropore) mass transfer and not influenced by the intercrystalline (macropore) and film diffusional mass transfer resistances, a few experiments were performed by changing the particle size of the zeolites from 0.2 to 0.1 mm and also varying the carrier gas flow rate from 100 to 200 cm³ · min⁻¹.

The detailed experimental procedures for obtaining data on the sorption and the kinetics of the desorption on the zeolite are given elsewhere (3, 18).

RESULTS

Representative Q_t/Q_∞ vs \sqrt{t} plots for the desorption of benzene from H-ZSM-5 (1) at 523 K are shown in Fig. 1. It can be noted that the plots are linear in the initial short

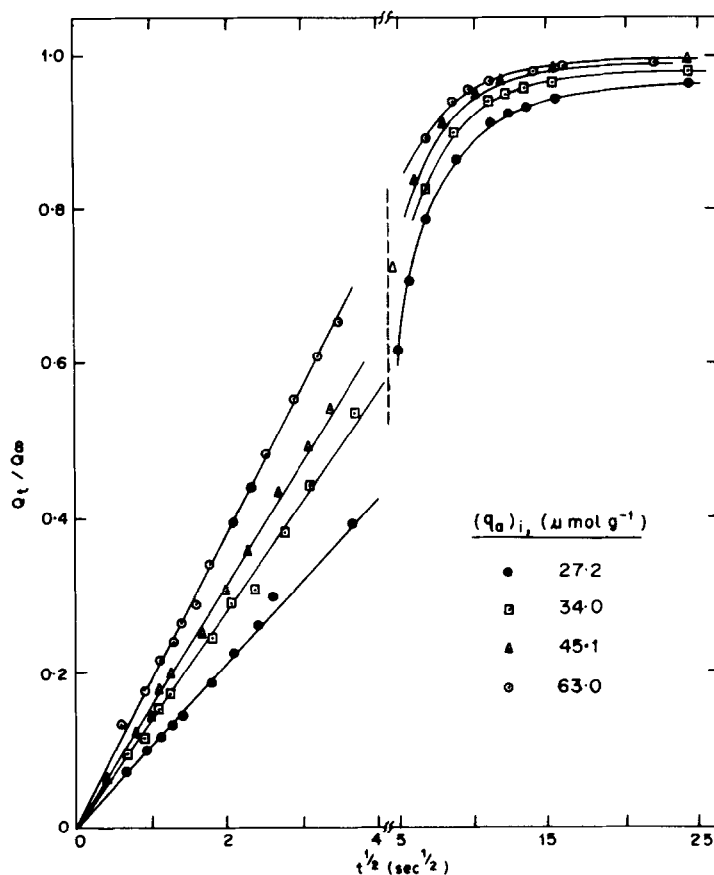


FIG. 1. Q_t/Q_∞ vs $t^{1/2}$ plots for the desorption of benzene from H-ZSM-5 (I) at 523 K.

period of the desorption, which indicates that the simple \sqrt{t} - law (19) can be applied for estimating the desorptive diffusion of benzene from the desorption data. The diffusion coefficients were estimated from the slopes of the linear plots according to the \sqrt{t} - law expression

$$Q_t/Q_\infty = 6[D/(\pi r^2)]^{1/2} \cdot t^{1/2} \quad (3)$$

where, D is the desorptive diffusion coefficient; r , the radius of zeolite crystal; and t , the period of desorption. The change in the particle size of the zeolites (from 0.2 to 0.1 mm) showed no effect on the desorption rates. Also, the variation in the carrier gas flow rate (from 100 to 200 $\text{cm}^3 \cdot \text{min}^{-1}$) resulted no significant change in the desorption rate data. All these facts indicated that the desorption rate data were free from the

effects of the macropore and film diffusional mass transfer resistances. The desorptive diffusion coefficients could, therefore, be estimated from the desorption rate data using Eq. (3).

Figures 2 and 3 show the influence of the Si/Al ratio on the sorption and the diffusion of benzene in H-ZSM-5 zeolite at 523 K, respectively.

It is evident from the results that the sorption increases with the decrease in the Si/Al ratio of the zeolite. The diffusion on the contrary, increases with the increase in the Si/Al ratio.

Figures 4 and 5 show a very strong influence of the degree of H^+ -exchange in H · Na-ZSM-5 zeolite on both the sorption and the diffusion of benzene. While there is a pronounced decrease in the sorption, there

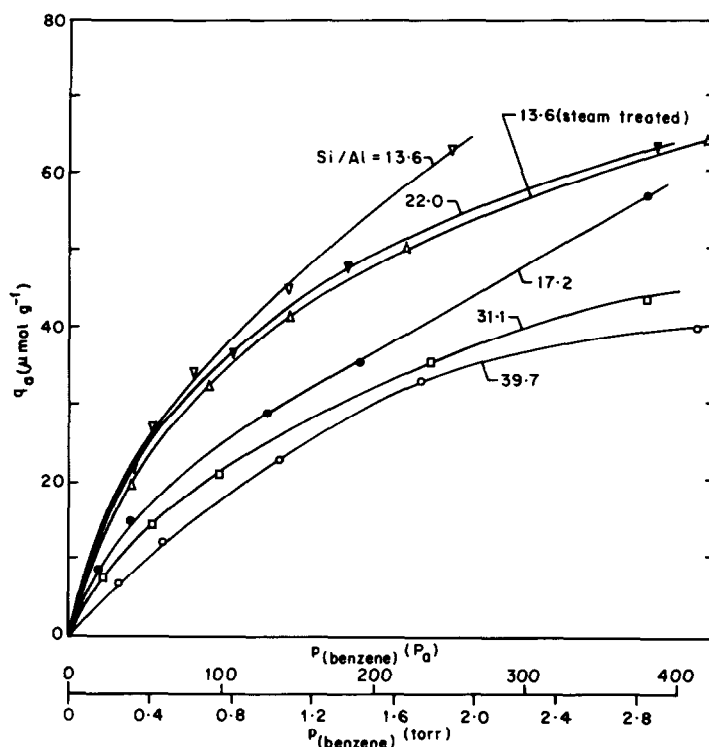


FIG. 2. Influence of Si/Al ratio and steam treatment on the sorption of benzene in H-ZSM-5 at 523 K.

is a drastic increase in diffusion when the H^+ -exchange increases from 0.51 to 0.99.

The results showing the effect of the

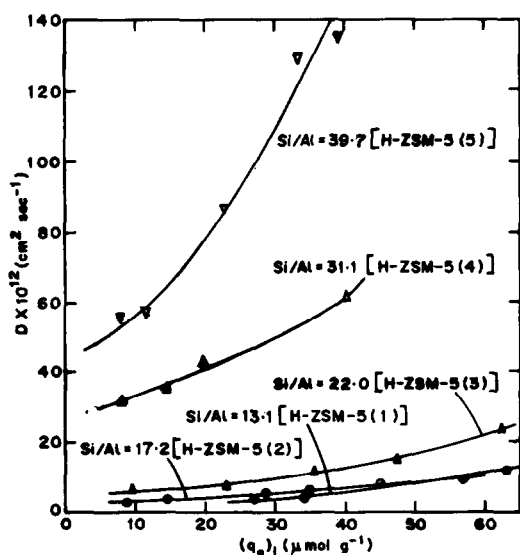


FIG. 3. Effect of Si/Al ratio on the diffusion of benzene in H-ZSM-5.

deammoniation temperature on the sorption are included in Fig. 4 and those on the diffusion are presented in Fig. 6. These results indicate a very strong effect of the dehydroxylation of the zeolite on the sorption, which decreases due to dehydroxylation caused by the deammoniation at the higher temperature, and on the diffusion which increases due to the dehydroxylation of the zeolite.

A comparison between the sorption in the H-ZSM-5 (Si/Al = 13.6) with and without steam treatment (Fig. 2) shows that the steam treatment causes a decrease in the sorption. On the other hand, it leads to an increase in the diffusion in the zeolite (Fig. 7).

It is interesting to note from the sorption isotherms (Figs. 2 and 4) that they are non-linear even at very low partial pressures of benzene. It may also be noted that the desorptive diffusion of benzene in all the zeolites is highly concentration dependent; it

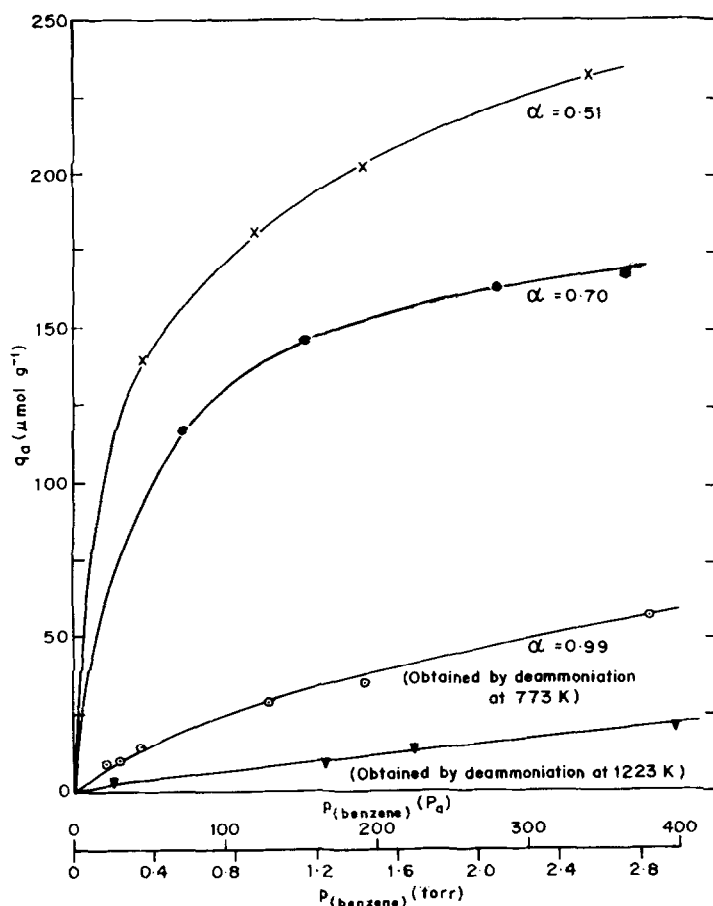


FIG. 4. Influence of degree of H^+ -exchange (α) and deammoniation temperature on the sorption of benzene in H-ZSM-5 (Si/Al = 17.2) at 523 K.

increases almost exponentially with the increase in the initial sorbate loading $[(q_a)_i]$. This is consistent with our earlier observation on the desorption diffusion of benzene in H-ZSM-5 at 523–673 K (3).

DISCUSSION

Sorption of Benzene

The very significant decrease in the sorption occurring as a result of the dehydroxylation during deammoniation at higher temperatures clearly shows that the hydroxyl groups responsible for the protonic acidity in the zeolite are involved in the sorption process. This is consistent with the increase in the sorption with the decrease in the Si/Al ratio (i.e., with the increase in the

number of protonic acid sites) (except for the zeolite with Si/Al = 17.2) and also with the observation on the sorption of benzene in pyridine poisoned H-ZSM-5 carried out earlier (20), which showed that the poisoning of the stronger protonic acid sites on H-ZSM-5 causes a very significant decrease in the sorption of benzene. The decrease in the sorption due to the steam treatment is also expected to be mainly because of the decrease in the acidity of the zeolite. However, a large increase in the sorption with the decrease in the degree of H^+ -exchange or with the increase in the Na^+ -content leads to the conclusion that benzene interacts more strongly with Na^+ ions than with H^+ ions. Earlier studies (20, 21) on the tem-

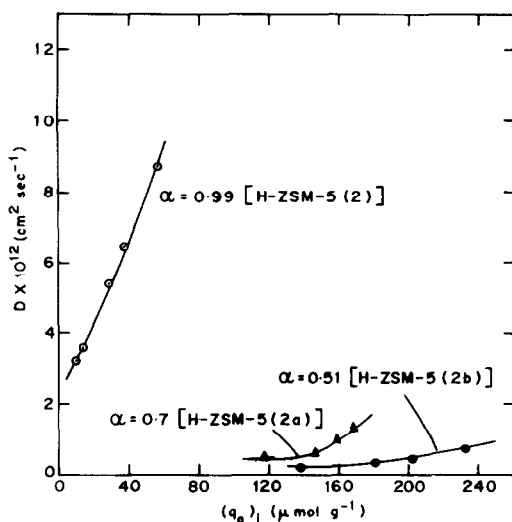


Fig. 5. Effect of degree of H^+ -exchange on the diffusion of benzene in $H \cdot Na$ -ZSM-5 ($Si/Al = 17.2$).

perature-programmed desorption of benzene from NaY , $CeNaY$ (with different degrees of Ce^{3+} -exchange) and HY zeolites showed that the heat of sorption increases with the Na^+ -content of the zeolite. This has indicated that benzene also interacts more strongly with the Na^+ ions than with the protonic acid sites of Y type zeolites. This is probably because of the fact that

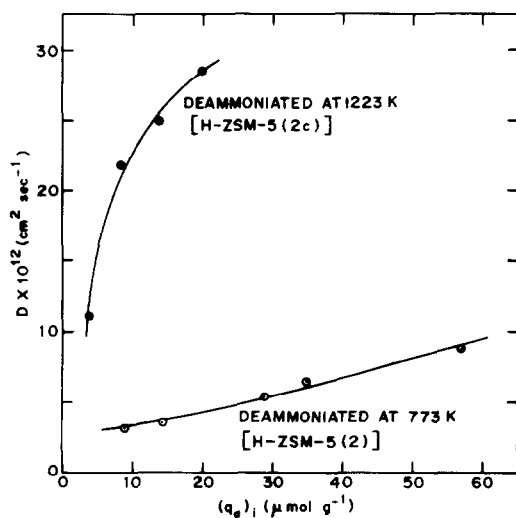


Fig. 6. Effect of deammoniation temperature on the diffusion of benzene in H -ZSM-5 ($Si/Al = 17.2$).

benzene is a very weak base and, therefore, its interaction with protons is weak as compared to the interaction of π -electrons of benzene ring with Na^+ ions.

Our studies (18, 20) on the sorption of benzene in H -ZSM-5 ($Si/Al = 22$) at 373–673 K (benzene partial pressure: 0 to 58 Torr) carried out by the dynamic sorption/desorption technique have shown that the sorption at ≤ 523 K occurs by the volume filling mechanism, satisfying the Dubinin–Polanyi equation. The maximum sorption at 373 K was found to be $1.3 \text{ mmol} \cdot \text{g}^{-1}$. The isosteric heat of sorption has been found to be strongly dependent on the sorbate loading, particularly in the lower region, indicating the presence of site energy distribution in the zeolite. The maximum sorption of benzene was found to be close to the one obtained from the static sorption measurement. This indicates that the presence of helium has no effect on the sorption. The present investigation shows that the sorption of benzene in ZSM-5 zeolites is not specific as it can result from the interaction of the sorbate with both the acidic and nonacidic (e.g., Na^+) sites. Benzene may also be physically sorbed at temperatures below its critical temperature and the physical sorption may form a very significant

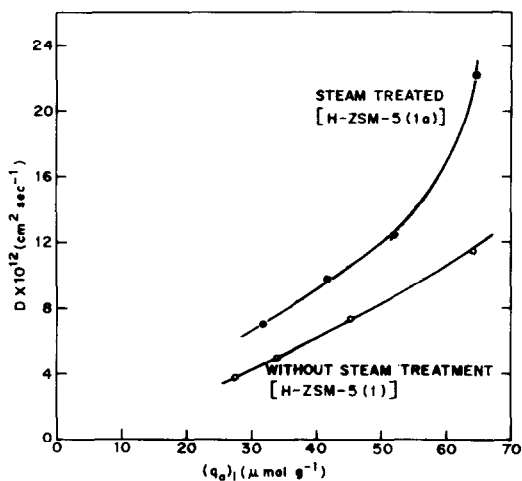


Fig. 7. Effect of steam treatment on the diffusion of benzene in H -ZSM-5 ($Si/Al = 13.6$).

part of the total sorption in the zeolite at lower temperatures.

Diffusion of Benzene

In order to obtain reliable values of desorption diffusion coefficient from the desorption data, it is very essential to ensure that the desorption rate is controlled only by the intracrystalline diffusion and not at all contaminated by the macropore and film diffusional mass transfer effects. In the present case, the absence of these mass transfer effects (and also the film and inter-crystalline heat transfer resistances) on the desorption rates was confirmed by changing the zeolite particle size and the carrier gas flow rate. As compared to the static sorption/desorption system, the present dynamic system has an advantage that both the interparticle heat and mass transfer resistances are completely eliminated as the carrier gas flows through the zeolite particles.

Heat effects resulting in nonisothermal desorption may also affect the desorption rates (22–24). In the present system, the maximum fall in the temperature of the zeolite due to desorption of $50 \mu\text{mol} \cdot \text{g}^{-1}$ benzene under static adiabatic conditions is estimated to be about 4 K (the heat of sorption of benzene and heat capacity of the zeolite assumed to be $15 \text{ kcal} \cdot \text{mol}^{-1}$ and $0.2 \text{ cal} \cdot \text{g}^{-1}$, respectively). Thus even the adiabatic temperature changes in static systems are very small. These are eliminated or largely minimized under the present experimental conditions [viz. the small diameter (6 mm o.d.) desorption tube containing 50 mg zeolite particles kept in a well mixed GC oven and the carrier gas, preheated to the desorption temperature, passed through the zeolite particles at high velocity] because the heat transfer rate between the zeolite and the gas phase is expected to be very high. Doelle and Riekert (22, 23) observed that the initial rates of sorption or desorption of *n*-butane in NaX, even in the static system, are not affected significantly by the heat effects, but the

heat transfer is rate limiting in the final approach to equilibrium in unsteady sorption or desorption. The above discussion leads to the conclusion that the desorption coefficients (estimated from the initial desorption rate data) are not contaminated by both the heat and mass transfer (macropore and film diffusional) effects. This is further supported by the fact that the changes in the initial sorbate loading and in the degree of H⁺-exchange, Si/Al ratio and pretreatment conditions of the zeolite produced marked changes in the observed desorption diffusion rates.

The results (Figs. 3, 5, 6, and 7) show that the diffusion of benzene in H-ZSM-5 increases when (i) the Si/Al ratio is increased, (ii) the deammoniation of NH₄-ZSM-5 to get the zeolite in the H-form is carried out at high temperatures, and (iii) the zeolite is treated with steam. The increase in the diffusivity with the increase in the Si/Al ratio is consistent with the observation of Post *et al.* (7) for 2,2-dimethyl butane in H-ZSM-5. It may be noted that the increase in Si/Al ratio, the deammoniation at higher temperatures and the steam pretreatment cause a substantial decrease in the protonic acidity of the zeolite (Table 1). These facts bring out the dependence of the diffusion on the acidity; it increases with the decrease in the protonic acid sites in the zeolite. It can therefore be concluded that the diffusion of benzene is strongly influenced by the interactions between the diffusing species and the hydroxyl groups responsible for the protonic acid sites.

Deammoniation at higher temperatures (10) and steam treatment (11) cause a significant dealumination of the zeolite, which, in turn, results in a small change in the protonic acidity and may also cause a small change in the effective channel diameter. This may also have some effect on the diffusion.

The diffusion of benzene in H · Na-ZSM-5 decreases considerably with the increase in the Na⁺-content of the zeolite. The marked influence of Na⁺-content on the dif-

fusion is expected to be mostly due to the stronger interaction of benzene with Na^+ cations than with the protons in the zeolite. It may also be due to a reduction in the effective channel diameter as H^+ (with negligibly small ionic diameter) is replaced by Na^+ (ionic diameter: 0.19 nm). According to Anderson *et al.* (25), "the size of the Na^+ cations influences the apparent 'free,' channel size in a manner that is superimposed on a constant basic skeletal channel geometry."

In the conversion of methanol and ethanol to aromatics on $\text{H} \cdot \text{Na-ZSM-5}$ ($\text{Si/Al} = 17.2$), the para-selectivity of the zeolite was found to increase markedly with the increase in its Na^+ -content (26). This is attributed mostly to the increase in the diffusional resistance of the zeolite due to increase in its Na^+ -content.

For $\text{H} \cdot \text{Na-ZSM-5}$ with different degrees of H^+ -exchange, the diffusion does not decrease with the increase in the protonic acidity, but increases. On the contrary for $\text{H} \cdot \text{ZSM-5}$, whose Na^+ -content is negligibly small, the diffusion increases with the decrease in the protonic acidity.

From the above discussion it is clear that the diffusion of benzene in $\text{H} \cdot \text{ZSM-5}$ is strongly influenced by the interaction of the diffusing species with both the protonic acid sites and nonacid sites (e.g., Na^+ ions). Thus all the factors which cause changes in the chemical environment of the diffusing species and in the effective channel size are expected to play a vital role in controlling diffusion in ZSM-5 type zeolites.

CONCLUSIONS

The sorption and desorption diffusion of benzene in H-ZSM-5 at 523 K depend strongly on its Si/Al ratio, degree of cation exchange and pretreatment conditions. The desorptive diffusion in all the cases is strongly concentration dependent. The experimentally measured diffusion coefficients are free from the interparticle, film diffu-

sional, and intercrystalline mass transfer effects and also free from the heat effects.

The very large decrease in the benzene sorption due to the dehydroxylation occurring during deammoniation at higher temperature has clearly shown that hydroxyl groups responsible for the protonic acidity in the zeolite are involved in the sorption process. However, the large increase in the sorption with the decrease in the degree of H^+ -exchange (or with the increase in the Na^+ -content) reveals that benzene interacts more strongly with Na^+ cations than with H^+ cations. Thus the sorption of benzene in $\text{H} \cdot \text{Na-ZSM-5}$ is not specific.

The increase in the Si/Al ratio, the deammoniation at higher temperatures, and the steam pretreatment to the zeolite cause a substantial decrease in the protonic acidity of the zeolite, but significant increase in the diffusion in the zeolite. These findings lead to the conclusion that the diffusion depends on the protonic acidity, it increases with the decrease in the protonic acid sites.

The diffusion of benzene in $\text{H} \cdot \text{Na-ZSM-5}$ increases considerably with the increase in the degree of H^+ -exchange (or with the decrease in the Na^+ -content). The strong influence of Na^+ -content on the diffusion is expected to be mostly due to the stronger interaction of benzene with Na^+ cations than with the protons in the zeolite. It may also be due to a reduction in the effective channel diameter, when H^+ (with negligible ionic diameter) is replaced by larger diameter Na^+ . In this case ($\text{H} \cdot \text{Na-ZSM-5}$ with different amounts of Na^+ -content) the diffusion does not decrease with the increase in the protonic acidity, but increases. These contradictory observations lead to the conclusion that diffusion of benzene in ZSM-5 is strongly influenced by the interaction of the diffusing species with both the protonic acid sites and nonacid sites (such as Na^+ ions). Thus all the factors which cause changes in the chemical environment of the diffusing species and in the effective channel size play a vital role in controlling the diffusion in ZSM-5 zeolites. These factors

include the Si/Al ratio, the cation and its degree of exchange and the various pre-treatments which cause changes in the protonic acidity and the effective channel diameter.

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