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Diffusion Controlled Alkylation of Aromatic Compounds in Cation-Exchanged ZSM-5 Zeolites

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Using uniform flat plate-like samples of ZSM-5 zeolites, diffusion coefficients were measured volumetrically for the diffusion of xylene, ethyltoluene and diethylbenzene by direct measurement of sorption rate. Toluene disproportionation over H(100)-, K(72)- and Cs(82)-ZSM-5 at 773 K and toluene methylation, toluene ethylation and ethylbenzene ethylation over Cs(75)-ZSM-5 at 623 K were carried out. The selective formation of para xylene during the toluene disproportionation, presumably due to the increased tortuosity over Cs-ZSM-5, could be explained by smaller diffusion coefficient in Cs-ZSM-5 than in K- and H-ZSM-5. The para selectivity increased in the order; toluene methylation < toluene ethylation < ethylbenzene ethylation. As the chain length of the alkyl substituent in dialkylbenzenes is increased, the para selectivity of the products was improved. It may be attributed to the differences in the ratios of diffusion coefficient of para products to that of ortho ones. Diffusion coefficient of *m*-xylene was about 1 order of magnitude smaller than that of *o*-xylene.

Introduction

When the size and shape of the molecules approach to those of the intracrystalline structure of zeolites, molecular shape selectivity can be observed. Molecular shape selectivity can arise due to large differences in the diffusivities of reactant or product molecules in the intracrystalline channels and to the differences in size and structure of the reaction intermediate. Shape-selective catalysis was first demonstrated by Weisz over CaA zeolite¹. Recent developments in molecular shape-selective catalysis in zeolites have been reviewed by Weisz², Csicsery³ and Derouane⁴. We reported the diffusive properties of cyclohexanes in ZSM-5 zeolites⁵ and para-selectivities in the alkylation of toluene with ethanol over cation exchanged ZSM-5 and ZSM-8 zeolites^{6,7}.

The framework of ZSM-5 type zeolites contains two types of intersecting channels. The straight channels running parallel to the *b*-axis [010] of orthorhombic unit cell have about 5.4 × 5.6 Å free diameter. The sinusoidal channels along *a*-axis [100] interconnected by straight channels have somewhat smaller openings⁸. The typical shape of ZSM-5 crystals is reported to be a platelet shape with the (010) surface being

the plate surface⁹.

Molecular shape selective properties of ZSM-5 type zeolites can be modified by ion exchange. This study involves the investigation of para-selectivities of toluene disproportionation over H-, K- and Cs-exchanged ZSM-5 zeolites and toluene methylation, toluene ethylation and ethylbenzene ethylation over Cs-ZSM-5. Measurement of diffusion coefficient of *o*-, *m*- and *p*-isomers of xylene, ethyltoluene and diethylbenzene made it possible to interpret the para-shape selectivity resulting from diffusional restriction by exchanged cation and the kinetic diameter of aromatics. For measurement of diffusion coefficients, we synthesized the ZSM-5 crystallites of flat plate-like structure.

Experimental

Synthesis of ZSM-5 Zeolites. For the synthesis of Al-free ZSM-5 samples, colloidal silica (29% SiO₂, Snowtex, Nissan Chem.) was added to the aqueous solution of 10% tetrapropylammonium hydroxide (TPAOH, Tokyo Kasei) as organic base, as described in the literature¹⁰. For Na-ZSM-5, sodium aluminate (35% Al₂O₃, Kanto Chem.) was dissolved

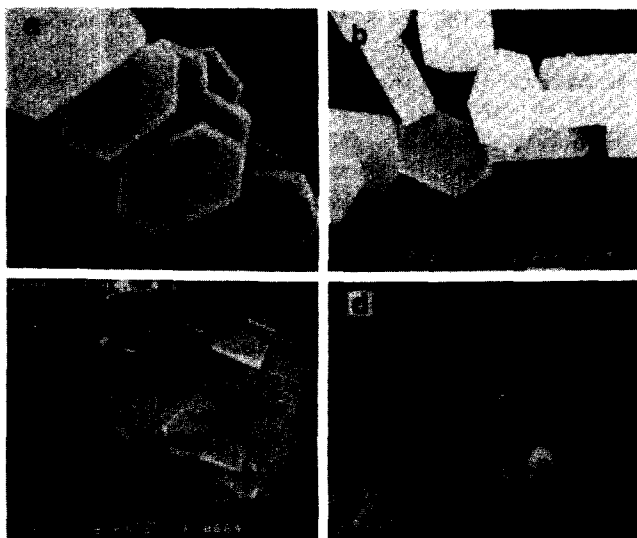


Figure 1. Scanning electron micrographs of (a) *p*-1, (b) *p*-2, (c) *p*-3, and (d) *p*-4.

in a demineralized water and added to silica sol containing TPAOH. Initial composition of the sols for the samples were $(\text{TPA})_2\text{O}\cdot 5\text{SiO}_2\cdot 700\text{H}_2\text{O}$ for *p*-1, $14(\text{TPA})_2\text{O}\cdot \text{NaAlO}_2\cdot 200\text{SiO}_2\cdot 10900\text{H}_2\text{O}$ for *p*-2, $13(\text{TPA})_2\text{O}\cdot \text{NaAlO}_2\cdot 33\text{SiO}_2\cdot 3110\text{H}_2\text{O}$ for *p*-3 and $5(\text{TPA})_2\text{O}\cdot 2\text{NaAlO}_2\cdot 95\text{SiO}_2\cdot 4000\text{H}_2\text{O}$ for *p*-4. The sols were transferred to a stirred reactor (Parr Instrument, No. 4542) of 2000 ml and crystallized at autogenous pressure at 453–473 K for 2 days with vigorous stirring. After completion of the reaction, the reactor was cooled in atmosphere, and the products were filtered, dried overnight at 373 K, and calcined at 773 K for 15 hr. The crystallites were characterized by X-ray diffractometry, scanning electron microscopy and N_2 adsorption. Figure 1 showed the SEM's of ZSM-5 zeolites. The crystallites of *p*-1, *p*-2 and *p*-3 had flat plate-like shapes and the thicknesses were 0.3, 0.8, and 0.8 μm , respectively. The crystallites of *p*-4 sample had elliptical shapes and the sizes were about 0.6 μm . The silica/alumina ratios of *p*-1, *p*-2 and *p*-3 for the measurement of diffusion coefficients were 498, 333, and 43, respectively, and that of *p*-4 for catalytic reactions were 43. *P*-3 and *p*-4 samples were exchanged to K(I) and Cs(I) by conventional method¹¹.

Sorption Measurement. In order to minimize the external bed diffusion resistance and maximize the heat transfer rate, a very small adsorbents, about 0.05 g, was used. The uptake curves of ortho-, meta- and para-isomers of xylene, ethyltoluene and diethylbenzene, respectively on ZSM-5 zeolites were determined volumetrically. The G.R. grade aromatic compounds for sorption measurements were purchased from Poly Science Corporation. The pressure was monitored by a Datametric capacitance manometer system (Model 5310, 1173). A schematic diagram of adsorption unit is shown in Figure 2. The temperature of the whole unit was controlled within ± 1 K. Before each run, the sample was activated under vacuum at 623 K. The diffusion equation in a plane sheet was applied to obtain the diffusion coefficients. When the surface concentration of the diffusing molecules is uniform and the diffusion coefficient is constant, one-dimensional diffusion in a plane-sheet of thickness $2L$ may be expressed¹² as

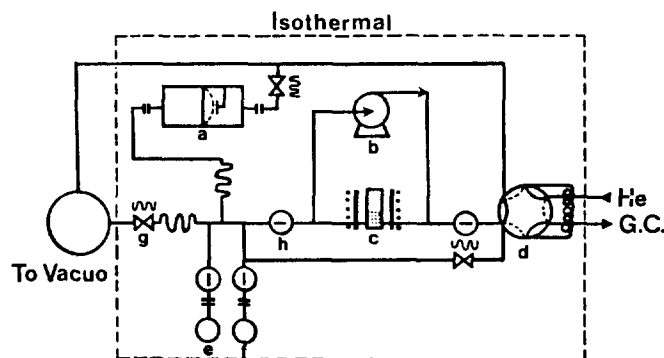


Figure 2. Schematic diagram of adsorption unit: a, capacitance manometer sensor; b, magnetic circulator; c, reaction furnace; d, six-port; e, adsorbent; f, adsorbate; g, flexible on-off valve; and h, teflon stopcock.

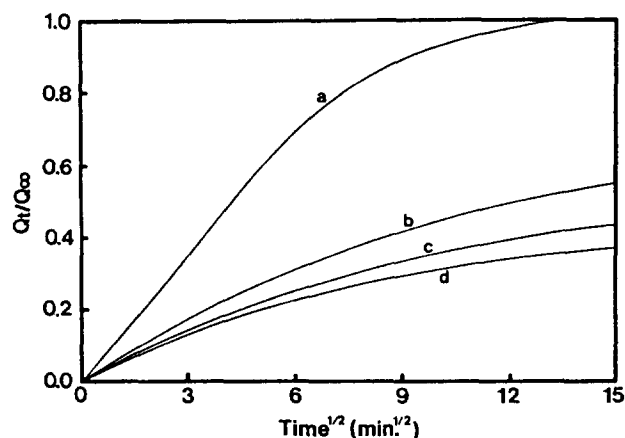


Figure 3. Sorption kinetics of *o*-xylene in (a) 0.3 μm -silicalite, (b) 0.8 μm -HZSM-5, (c) 0.8 μm -KZSM-5, and (d) 0.8 μm -CsZSM-5 at 383 K.

$$Q_t/Q_\infty = 2(Dt/L^2)^{1/2} \left\{ \left[\pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \text{ierfc}(nL/\sqrt{Dt}) \right] \right\} \quad (1)$$

where Q_∞ is the amount taken up at infinite time and Q_t is that at time t .

Catalytic Reaction. A fixed-bed continuous-flow micro-reactor was used with 0.4 g of powder sample and was made from 3/8 inch O.D. and 35 cm long stainless steel tubing. The reactor was equipped with electrical resistance heater and proportional temperature controller. The calcination was carried out in nitrogen stream for 5 hours at 773 K. Reactants were fed into the catalytic bed with the help of a syringe liquid pump Nitrogen was used as a carrier gas and the preheater was maintained at 473 K. The vapor stream produced from the reactor was passed successively through a sampling 6-port valve, and analyzed by an on-lined TCD-gas chromatograph with Porapak Q column. The liquid products were collected periodically and analyzed by a FID-gas chromatograph with a chromosorb *W*(80/100) column containing 5% Benton-34 and 5% dinonylphthalate.

Results

Diffusion of Dialkylaromatic Compounds in ZSM-5. Using a uniform flat plate-like sample of ZSM-5 zeolites,

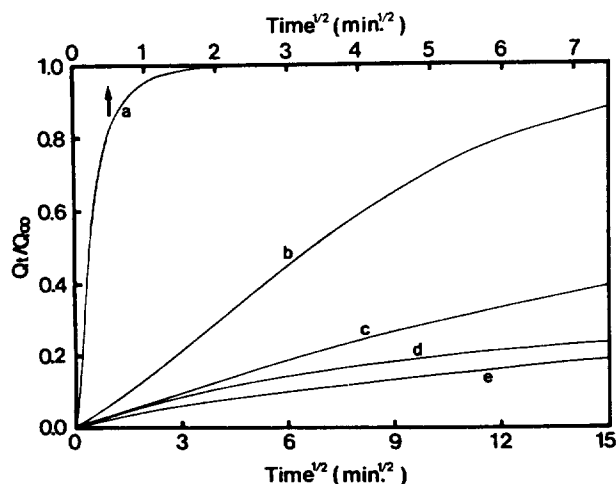
Table 1. Diffusion Coefficients of Dialkylaromatics in Ion-Exchanged ZSM-5 Zeolites

Zeolite	Adsorbate	Thickness (μm)	Diff. Coeff. (cm^2/sec)	Temp. (K)
H-ZSM-5	<i>o</i> -Xylene	0.3	4.6×10^{-14}	383
H-ZSM-5	<i>o</i> -Xylene	0.8	4.5×10^{-14}	383
K-ZSM-5	<i>o</i> -Xylene	0.8	3.1×10^{-14}	383
Cs-ZSM-5	<i>o</i> -Xylene	0.8	2.2×10^{-14}	383
H-ZSM-5	<i>p</i> -Xylene	0.8	$\text{ca. } 1 \times 10^{-10}$	373
H-ZSM-5	<i>m</i> -Xylene	0.3	9.6×10^{-16}	373
H-ZSM-5	<i>o</i> -Xylene	0.3	2.2×10^{-14}	373
H-ZSM-5	<i>p</i> -Ethyltoluene	0.8	$\text{ca. } 1 \times 10^{-10}$	373
H-ZSM-5	<i>o</i> -Ethyltoluene	0.3	2.4×10^{-15}	373
H-ZSM-5	<i>p</i> -Diethylbenzene	0.8	$\text{ca. } 1 \times 10^{-10}$	373
H-ZSM-5	<i>o</i> -Diethylbenzene	0.3	3.8×10^{-16}	373

Table 2. Toluene Disproportionation over Ion-Exchanged ZSM-5 Zeolites at 773 K

Catalyst	H-ZSM-5	K-ZSM-5	Cs-ZSM-5
Degree of exchange	100	72	82
Toluene WHSV ^a	6.5	6.5	6.5
Conversion (mole %)	20.2	1.60	0.93
Products (mole %)			
Benzene	10.1	0.8	0.5
Toluene	79.8	98.4	99.1
Xylenes	9.9	0.8	0.5
Others	0.2	—	—
Xylene isomer (%)			
para (24.1) ^b	25.3	26.3	44.0
meta (55.5)	51.5	51.2	44.3
ortho (20.3)	23.2	22.5	11.7

^aWeight hourly space velocity (hr^{-1}). ^bEquilibrium composition at 773 K¹³.

**Figure 4.** Sorption kinetics of (a) *p*-xylene, (b) *o*-xylene, (c) *o*-ethyltoluene, (d) *m*-xylene, and (e) *o*-diethylbenzene in 0.3 μm -silicalite at 373 K.

diffusion coefficients were measured for the diffusion of xylene, ethyltoluene and diethylbenzene. Figure 3 shows the uptake curves of *o*-xylene in H-ZSM-5, K-ZSM-5 and Cs-ZSM-5 of the thickness of 0.8 μm at 383 K. As shown in Table 1, diffusion coefficients of *o*-xylene are $4.5 \times 10^{-14} \text{ cm}^2/\text{sec}$ for H-ZSM-5, $3.1 \times 10^{-14} \text{ cm}^2/\text{sec}$ for K-ZSM-5 and $2.2 \times 10^{-14} \text{ cm}^2/\text{sec}$ for Cs-ZSM-5. Figure 3a and b illustrate the uptake curves of *o*-xylene in 0.3 μm ZSM-5 zeolite free of aluminum and 0.8 μm H-ZSM-5 zeolite. The diffusion coefficients of *o*-xylene in the two samples are nearly the same. These are $4.5 \times 10^{-14} \text{ cm}^2/\text{sec}$ and $4.6 \times 10^{-14} \text{ cm}^2/\text{sec}$ respectively as illustrated in Table 1.

The diffusion coefficients and uptake curves of dialkylaromatic isomers in H-ZSM-5 zeolites at 373 K are given in Table 1 and Figure 4, assuming that the adsorbed amounts of *o*-ethyltoluene and *o*-diethylbenzene at infinite time are the same as that of *o*-xylene (3.9 molec./U.C.). Diffusion coefficients decreased in the sequence; *o*-xylene > *o*-ethyltoluene > *o*-diethylbenzene. The diffusion coefficients of *o*-xylene, *o*-ethyltoluene and *o*-diethylbenzene are $2.2 \times 10^{-14} \text{ cm}^2/\text{sec}$, $2.4 \times 10^{-15} \text{ cm}^2/\text{sec}$ and $3.8 \times 10^{-16} \text{ cm}^2/\text{sec}$, respectively. The

diffusion coefficient of *m*-xylene turned out to be about 1 order of magnitude smaller than that of *o*-xylene. The adsorption of *m*-ethyltoluene and *m*-diethylbenzene at this temperature is negligible. The diffusion coefficients of *p*-xylene, *p*-ethyltoluene and *p*-diethylbenzene are nearly the same, about $1 \times 10^{-11} \text{ cm}^2/\text{sec}$ at 373 K.

Diffusion Controlled Reaction in Ion-Exchanged ZSM-5. Cs(I) and K(I), respectively, was introduced into $\text{NH}_4\text{-ZSM-5}$ by ion exchange, then, dried, calcined and tested for the para selectivity in toluene disproportionation, toluene methylation, toluene ethylation and ethylbenzene ethylation. The results of toluene disproportionation are summarized in Table 2. The product distribution was designated as mole percents. At a constant reaction condition, the conversion of *m*-xylene over H(100)-, K(72)- and Cs(82)-ZSM-5 was 20.2, 1.60 and 0.93, respectively. The catalytic activity of H-ZSM-5 for the reactions was high, while those of K- and Cs-ZSM-5 were low. This is due primarily to reduced acid sites, *i.e.*, exchanged cations could kill the acid sites or weaken the acid strength of H-ZSM-5. The selectivity of para-isomer was defined as follows; $S_p = x_p / (x_o + x_m + x_p) \times 100$, wherein x_o , x_m and x_p is the percent yield of *o*-, *m*- and *p*-isomer, respectively. In the case of toluene disproportionation, only Cs-ZSM-5 zeolite shows the para-selectivity while the distribution of xylene isomers over H- and K-ZSM-5 zeolites corresponds to near thermodynamic equilibrium composition. Table 3 shows the distribution of xylene isomers from the products of toluene methylation, toluene ethylation and ethylbenzene ethylation over Cs(75)-ZSM-5 at 623 K. The xylene selectivity among aromatic products was 89.1%, ethyltoluene selectivity, 97.6% and diethylbenzene selectivity, 84.8%. The distribution of *p*-isomers in above reactions was 66.1%, 78.9% and 85.6%, respectively. The para-selectivity increased in the order; toluene methylation > toluene ethylation > ethylbenzene ethylation. Pore modification by ion exchange was confirmed especially in Cs-ZSM-5 zeolite showing highly enhanced para-selectivities in the formation of dialkylbenzenes.

Discussion

Table 3. Alkylation of Alkylbenzene over Cs(75)-ZSM-5 at 623 K

Alkylbenzene/Alcohols (mole ratio); 5, LHSV ^a ; 0.75					
Toluene methylation		Toluene ethylation		Ethylbenzene ethylation	
Products (mole %)					
Methanol	1.4	Ethanol	4.9	Ethanol	4.6
Toluene	93.1	Toluene	91.7	Ethylbenzene	90.7
Xylene	4.9	Ethyltoluene	3.3	Diethylbenzene	3.9
Others	0.6	Others	0.1	Others	0.7
Xylene Selectivity; 89.1%		Ethyltoluene Selectivity; 97.1%		Diethylbenzene Selectivity; 84.8%	
Isomers(%)					
para	66.1		78.9		85.6
meta	14.0		21.1		14.4
ortho	19.9		—		—

^aLiquid hourly space velocity (hr⁻¹).

Molecular shape-selective properties of ZSM-5 type zeolites can be modified by ion-exchange. The modification alters the diffusional characteristics by reducing the channel dimensions and available space at the channel intersections. The cations in channels of ZSM-5 are believed to be located at channel intersection¹⁴.

Scanning electron micrographs of the sample crystallites for the measurement of diffusion coefficient of the dialkylaromatic isomers revealed the typical flat plate-like shape of our samples. The straight channels are perpendicular to the (010) surface. The pore diameter of the sinusoidal channel is somewhat smaller than that of the straight channel and it would be more difficult for *o*- and *m*-isomers of dialkylaromatic compounds to diffuse into the sinusoidal channel than into the straight one. It therefore seems reasonable to assume that the uptake curves represent primarily the diffusion of dialkylaromatic compounds into the straight channel. The results that the nearly same diffusion coefficient of *o*-xylene was obtained from the measurements using the crystallites of different thickness support our assumption in Eq. (1).

The determination of diffusion coefficients of dialkylaromatic isomers by direct adsorption measurement made possible to interpret the para-selectivities of toluene disproportionation, toluene methylation, toluene ethylation and ethylbenzene ethylation. Enhanced para-selectivity over Cs-ZSM-5 than H- and K-ZSM-5 in toluene disproportionation is due to the decreased diffusion rate of *o*- and *m*-isomers in Cs-ZSM-5 resulting from the larger ionic diameter of Cs(1.69Å) than K(1.33Å). Diffusion coefficient of *o*-xylene in Cs-ZSM-5 was smaller than those in K-ZSM-5 and H-ZSM-5. That is, the difference in para selectivity arises due to the channel tortuosity by the exchanged cation. Because the adsorbed amounts of *o*-ethyltoluene and *o*-diethylbenzene in Cs-ZSM-5 are negligible and the diffusion through it is too much slow, the measurement of diffusion coefficient carried out in H-ZSM-5 instead of Cs-ZSM-5 used as a catalyst in these reactions. The order of para selectivity in toluene methylation, toluene ethylation and ethylbenzene ethylation can be attributed to the increased diffusional restriction imposed on *o*- and *m*-isomers with varying the kinetic diameter of dialkylaromatics. The ratio of diffusion coefficient of para isomer to ortho one was about 10³ for xylene, 10⁴ for ethylto-

luene and 10⁵ for diethylbenzene as shown in Table 1. The amount of *m*-isomer produced was generally larger than *o*-isomer, although the diffusivity of *o*-xylene was found to be nearly one order of magnitude larger than that of *m*-xylene. It may be that the formation of *p*-isomer is sterically favored and isomerization of *p*-isomer to *o*-isomer proceeds through *m*-isomer¹⁵ and that for the equilibrium composition of dialkylaromatics, the ratio of *m*-isomer is higher than that of *o*-one.

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