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Shape Selectivity Investigation Based on Sorption Data

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A new shape selectivity index, R_{CN}, the ratio of sorption of cyclohexane to that of *n*-hexane, is proposed as a simple and versatile measure to describe the shape selectivity of zeolite catalysts. The C.I. (constraint index) values for 12-membered-ring zeolites are around 1, and hence these are not satisfactory to describe observed discrimination. Another index, S.I. (spaciousness index), is applicable only to 12-membered-ring zeolites, since all the reported values for 10- and 8-membered ring zeolites are again ca. 1. R_{CN} apparently discriminates among 8-, 10-, and 12-membered-ring zeolites, and is a linear function of their aperture size. C.I. and S.I. values for zeolites in their effective range were found to be linearly dependent on R_{CN}. The applicability of R_{CN} to describe shape-selective catalysts was demonstrated for the alkylation of naphthalene and biphenyl compounds.

INTRODUCTION

The first molecular shape-selective reaction was reported about 30 years ago on Ca-exchanged A-type zeolite (LTA), based on discrimination of the shape of the reactant butanols for dehydration. The concept of this molecular shape selection by zeolite pores was further extended by P. B. Weisz and other Mobil researchers (*1*), and by S. M. Csicsery (*2*) to the shapes of reactants, products, and the restricted transition-state complex. All these shapes could determine the reactivity of substrates, the course of the reaction, and the shape specificity of product molecules.

As a numerical measure of the shape selectivity, Mobil scientists (*3, 4*) proposed the constraint index (C.I.), based on the competitive cracking of an equimolar mixture of *n*-hexane (*n*HX) and 3-methylpentane (3MP). The C.I. is calculated as follows:

$$\text{C.I.} = \log(\text{fraction of } n\text{HX remaining}) / \log(\text{fraction of 3MP remaining}).$$

Several indices based on other catalytic test reactions have also been introduced to describe the shape selectivity of zeolites, e.g., the index *R* derived by isomerization of *m*-xylene (*5, 6*) and/or indices derived by disproportionation of alkylaromatics (*7*). The index C.I.* (modified C.I.) is the ratio of 2- to 5-methylnonane at 5% isomerization conversion of *n*-decane (*8, 9*). These indices are effective only for medium pore zeolites.

Weitkamp proposed another index, S.I. (spaciousness index) (*10, 11*). The value is defined as the yield ratio of isobutane to *n*-butane in the hydrocracking of a C_{10} naphthene like butylcyclohexane over zeolites loaded with Pd or other metals with hydrogenation activity. S.I. values reputedly explain the superiority of some of the 12-membered pore zeolites, e.g., MOR, over other zeolites in the selectivity of disproportionation of methylnaphthalenes (MN) or (*trans*)alkylation of alkylnaphthalenes (*11*).

The diffusion constants of a molecule through various zeolites have been measured and shown to be expressed by linear functions of the difference between the sizes of the molecule and the pore diameter (*12*). At 0.06 nm difference in the diameters, more than one order of magnitude in the values of diffusion constants has been reported. This linear dependence is not, how-

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ever, transferable to other molecules directly, since the diffusion constants vary by several orders of magnitude in molecular diameter. Furthermore they are measured in the liquid phase, whereas catalytic applications of zeolites are frequently made in the vapor phase. NMR studies on the motions or states of ^{129}Xe (*13, 14*) or pyrrolidine (*15*) in the zeolite pore have yet to be applied to estimating performance of shape-selective catalysts.

The sorption techniques have been used for the estimation of the pore size of zeolites (*16*). Effective pore size of brand new zeolites with unknown structure was often estimated for patent purposes by sorption of molecules with systematically increasing diameter. In this study, the technique is extended for the evaluation of shape selectivity of the zeolite catalysts. The proposed index, R_{CN}, is defined as the ratio of sorption amount of cyclohexane (CHX, 0.47 × 0.62 × 0.69 nm (*16*)) to that of *n*-hexane (nHX, 0.39 × 0.43 × 0.91 nm (*16*)).

The significance of this index resides in its linear relationship to *rr* (average diameter of the largest pore) over a wide range of pore sizes of zeolites with 8- to 12-membered rings.

METHODS

The zeolite samples of MTT (Ref. (*17*)), MFI (Ref. (*18*)), MEL (Ref. (*19*)), MCM-22 (Ref. (*20*)), OFF (Ref. (*21*)), MOR (Ref. (*22*)), EMT (Ref. (*23*)), and FAU (Ref. (*24*)) were synthesized following the procedures described in the references as indicated in parenthesis. They were calcined at 540°C to remove organic templates before the sorption measurement. Several other zeolites, which are commercially available from TOSOH Corporation (MAZ, ERI, LTL, FER), G.L. Laboratories, Ltd. (Na-X, LTA), and PQ Corporation (BEA), were also used. Measurements were also made of BEA zeolites which were ion-exchanged by alkali and alkaline earth cations. They were obtained by adding 2 g of H-BEA powder (commercial sample from PQ Corporation) into 1 *M* solution (200 ml) of the corresponding chloride or nitrate and stirring for 8 h at room temperature, followed by filtration, washing, and final calcination at 450°C for 3 h under a dry air flow.

The sorption measurements were made using a conventional vacuum line with 4 sample cells attached by greased glass joints, and a gas container of 2 liters volume. (See Fig. 1.) The vapor of *n*HX or CHX was introduced from the liquid tank into the gas holder after freeze-and-thaw treatment under vacuum for degassing. The sample powder was pressed, crushed to the size of 0.25 to 0.7 mm (24 to 60 mesh JIS) and calcined at 450°C in a dry air flow before it was placed in the cell. After the final evacuation of the sample-containing cell at less than 0.4 Pa (3 × 10^{-3} Torr) pressure and 300°C and weighing, the hydrocarbon vapor was introduced from the gas container. The weight of the zeolite samples ranged from 150 to 600 mg. The sorption measurement was made using a fresh sample at a pressure of 2.6 KPa (20 Torr) at ambient temperature (23 ~ 27°C). The sorption reached equilibrium in about an hour, and sorption amount was determined from the net increase of the

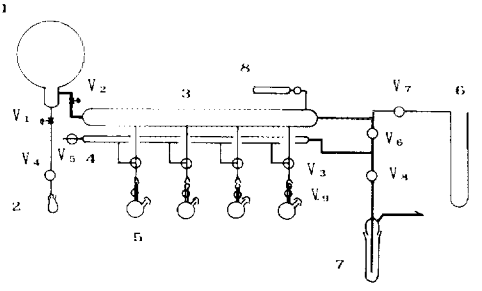

FIG. 1. Schematic view of the apparatus used for the sorption measurement, with four sample cells attached by greased glass joints. (1) Gas container of 2 liters volume. (2) Liquid tank, 10 ml. (3) Gas manifold. (4) Evacuation manifold. (5) Sorption cells, 15 ml in volume including total dead space, with sample inlet. (6) Manometer. (7) Cold trap. (8) Pirani gauge. Valves: (V1, V2) needle valve; (V3) three-way valve; (V4–V9) high-vacuum valve. One of the cells is used without sample to measure the weight of the hydrocarbon gas.

TABLE 1

Sorption Capacity and Related Properties of Zeolites

M.R.	IZC code	Zeolite name	Shape select. indices			Sorption data			References
			C.I.	C.I.*	S.I.	nHX[a]	CHX[a]	R_{CN}	
8	CHA	Chabazite	50	2.3	—			≦0.1	Mineral
8	LTA	MS-4A	—	2.4	—	0.6	0.1	0.2	This study
8	LTA	MS-5A	—	—	—	9.35	0.37	0.04	This study
8	ERI	Erionite	38	2.5	—	5.9	0.9	0.16	Mineral
10	TON	ZSM-22	4.6–7.3	14.4	ca. 1	4.1	1.1	0.25	Ref. (*25*)
10	MTT	ZSM-23	9.1	10.8	ca. 1	5.4	1.6	0.30	This study and Ref. (*17*)
8,10	FER	ZSM-35	4.5	10.3, 8.1	ca. 1	8.2	2.1	0.26	Ref. (*26*)
8,10	FER	ZSM-21				6.3	3.1	0.49	Ref. (*27*)
8,10	FER	ZSM-38	2.0			7.2	5.2	0.72	Ref. (*28*)
10	MFI	ZSM-5	6–8.3	6.8	ca. 1	10.3	3.92	0.38	Ref. (*18*)
8,10	MFS	ZSM-57	6.3	4.3	—	7.1	4.7	0.66	Ref. (*29*)
10	MEL	ZSM-11	5–8.7	2.7	ca. 1	10.89	5.32	0.49	Ref. (*19*)
10	EUO	ZSM-50	2.1	—	5	9.1	7.3	0.76	Ref. (*30*)
8,10	HEU	Clinoptilolite	3.4	3.6	—	—	—	—	Mineral[c]
uk		MCM-22	1.5	—	—	18.92	4.11	0.83	Ref. (*20*)[d]
10		ZSM-48	3.5	5.2	ca. 1	12.3	4.6	0.37	Ref. (*31*)[e]
8,12	ERI/OFF	ZSM-34	—	—	—	10.5	4.1	0.38	Ref. (*32*)
12	MTW	ZSM-12	2.3	2.2	3	6.8	6.6	0.97	Ref. (*33*)
12	OFF	Offretite	3.7	1.8	5.5	9.54	6.54	0.69	This study
12	MOR	Mordenite	0.4	1.8	7	4.82	3.26	0.68	This study
8,12	GME	Gmelinite	—	—	—	—	7.3	—	Mineral[c]
12	MEI	ZSM-18				15.0	14.7	0.98	Ref. (*34*)
12	MAZ	ZSM-4	0.5	1.2	—	2.23	2.72	1.22	This study
12	LTL	L-type	—	1.0	16.5	8.23	6.63	0.81	This study
12	BEA	Beta	0.6–2.0	1.4	13–19	16.05	19.68	1.23	This study
12	EMT	Hexagonal FAU	0.5	—	20	14.31	15.98	1.12	This study
12	FAU	Y-type	0.4–0.5	1.3	21	16.09	18.06	1.12	This study

[a] In wt%, measured at 2.7 kPa pressure and 25 ± 2°C.

[b] The ratio of sorption amount of CHX to that of nHX.

[c] Sorption in mineral zeolite.

[d] R_{CN} calculated using data in Ref. (*20*).

[e] Data by R. Kumar in Ref. (*41*).

weight of the cell, after subtracting the weight of vapor in the empty cell.

The following analyses of the reaction were made by the R_{CN} values of the present study. They were complemented by the sorption data in the patent literature and other papers. The reaction data of naphthalene and biphenyl derivatives were also taken from the literature, e.g.,

(a) from Ref. (*35*): the data of the reaction of 2-methylnaphthalene (2MN) + methanol (MeOH) to dimethylnaphthalenes (DMN) at a molar feed ratio of 2MN/MeOH/N_2 = 2/1/97, at 673 K and atmospheric pressure, over the catalysts ZSM-35, MTT, MFI, MEL, and MTW.

(b) from Ref. (*36*); the data of the reaction of naphthalene (NL) + methanol (MeOH) to methylnaphthalenes at a molar feed ratio of NL/MeOH/Mesitylene = 1/6.61/3.57, at

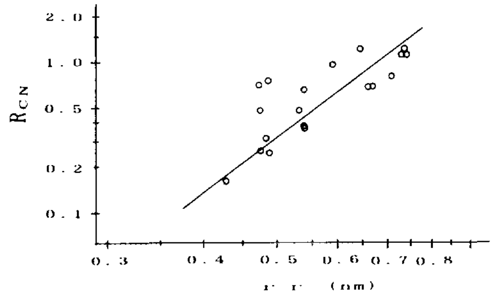

FIG. 2. The R_{CN} values plotted versus rr values, the average aperture diameters in nm of the largest pore of the zeolite.

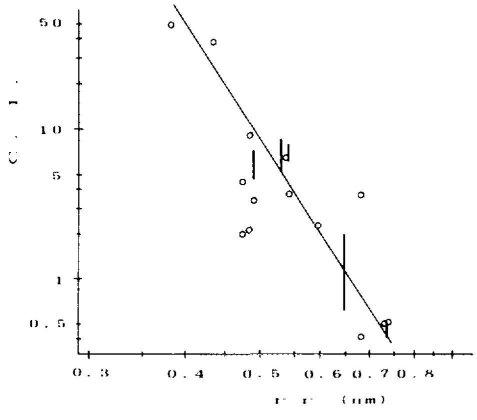

FIG. 3. The C.I. values plotted versus rr values.

673 K and WHSV 1.18 and 3.16, over the catalysts MFI, MOR, and FAU (H-Y).

(c) from Ref. (*37*): the data of the reaction of biphenyl (BIP) + propylene (PPY) to isopropylbiphenyls at a molar feed ratio of BIP/PPY/*trans*-decalin (solvent) = 50 mmol/100 mmol/20 ml, and at a temperature between 180 and 300°C for 4 h over the catalysts MFI, MOR, LTL, and FAU (H-Y).

RESULTS

The sorption data obtained in this study are summarized along with the literature values in the seventh and eighth columns of Table 1. The derived values of R_{CN} are shown in the ninth column. The C.I. values, the C.I.* values and the S.I. values cited in references are shown in the 4–6th columns. The last column indicates the sources of the sorption data, where the term mineral denotes the sorption on natural and nonsynthetic samples.

In Fig. 2, the values of log R_{CN} are plotted versus log rr values, the average diameter of the largest pore in the zeolites. The values of log C.I. are plotted versus log rr values in Fig. 3 (*36*). The plots in both figures are seen to lie around linear plots, although even in the double-logarithmic representation, the plots scatter considerably.

R_{CN} of the larger pore zeolites, however, still shows apparent dependency on rr in Fig. 2. This is not the case in the C.I. vs rr plot in Fig. 3.

The empirical relationships between R_{CN} (Fig. 2), C.I. (Fig. 3), S.I. (plots not shown) values, and the aperture size rr are derived as given by the following equations:

$$\log R_{CN} = (3.778) \log rr + (-3.179);$$

$$\log \text{C.I.} = (-6.120) \log rr + (5.282), \quad 50 > \text{C.I.} > 2;$$

$$\log \text{S.I.} = (9.167) \log rr + (-6.600), \quad \text{S.I.} > 3.$$

The sorption data of cation -exchanged form of BEA zeolite are shown in Table 2. It

TABLE 2

Sorption Properties of Cation-Exchanged BEA Zeolites

Cation	Radius (nm)	Sorption properties[a] nHX	CHX	R_{CN}[b]
H		16.05	19.68	1.23
Li	0.083	15.35	18.72	1.22
Na	0.116	15.53	18.80	1.21
K	0.152	15.31	17.84	1.16
Rb	0.163	14.79	16.72	1.13
Cs	0.184	13.33	15.42	1.16
Ca	0.114	15.60	17.21	1.10
Ba	0.150	14.86	15.53	1.05

[a] In wt%, measured at 2.7 kPa pressure and 25 ± 2°C.

[b] See footnote *b* of Table 1.

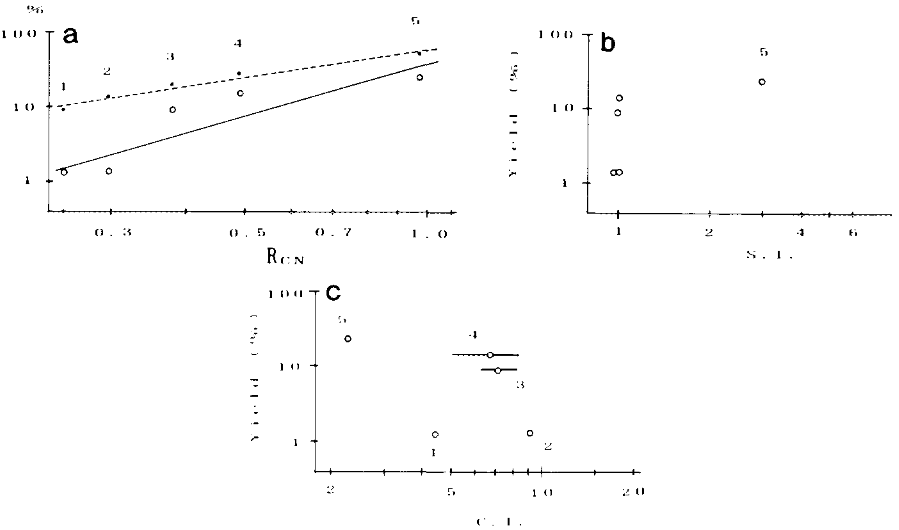

FIG. 4. Conversion of 2-methylnaphthalene (dotted line) and the yield of dimethylnaphthalenes (solid line) by the alkylation with methanol over ZSM-35 (1), MTT (2), MFI (3), MEL (4), and MTW (5) as plotted against (a) the R_{CN} values, (b) S.I. values, and (c) C.I. values of zeolites listed in Table 1. The reaction data are from Ref. (*35*).

is clearly seen that R_{CN} of this 12-membered-ring zeolite can be slightly modified by the kind of cations, the effect being larger by larger cations and by divalent alkaline earth metal cations.

The usefulness of R_{CN} for zeolite catalysis was examined in the transformation reactions of bulky aromatic hydrocarbons.

In Fig. 4, the conversion (dotted line) and the yield of DMN (solid line) by the alkylation of 2MN with MeOH over ZSM-35, MTT, MFI, MEL, and MTW were plotted against the R_{CN}, S.I., and C.I. values. The tendency that the conversion and DMN yield are higher for the reaction over zeolites having larger pore size was best reflected by the plot against the R_{CN} values. Poor linearity was observed in the plot vs S.I. and C.I.

For the alkylation of NL with MeOH over FAU, MOR, and MFI zeolites, the yields of methyl-, dimethyl-, trimethyl-, and tetramethyl-NLs were plotted against. S.I. values (Fig. 5a). The yields of methyl- (line 1) and dimethyl-NLs (line 2) are seen to be independent of S.I. values, whereas the yields of trimethyl- (line 3) and tetramethyl-NLs (line 4) increase when the zeolites with larger S.I. values (larger aperture size) were used. The plots of the latter yields against R_{CN} values are shown in Fig. 5b, and again a linear relation is observed. The plot against C.I. (open circle) or C.I.* (filled circle) values given in Fig. 5c shows no such tendency. For the reaction of PPY with BIP to mono-isopropylbiphenyls (MIPB), the selectivity to the byproducts (products other than MIPB), S_B, is plotted against the S.I. and R_{CN} values in Figs. 6a and 6b, respectively. Here S_B is defined as

$$S_B = 2 - \log (S_{MIPB}),$$
$$S_{MIPB} = \text{selectivity (\%) to MIPB},$$

and is meant to enlarge in the logarithmic scale the difference in selectivities among the zeolite catalysts. The linear dependence is seen in both plots, although the scattering of data points is much less in Fig. 6b.

DISCUSSION

Since the theoretical maximum free diameters of zeolite rings are 0.28 nm(6), 0.43

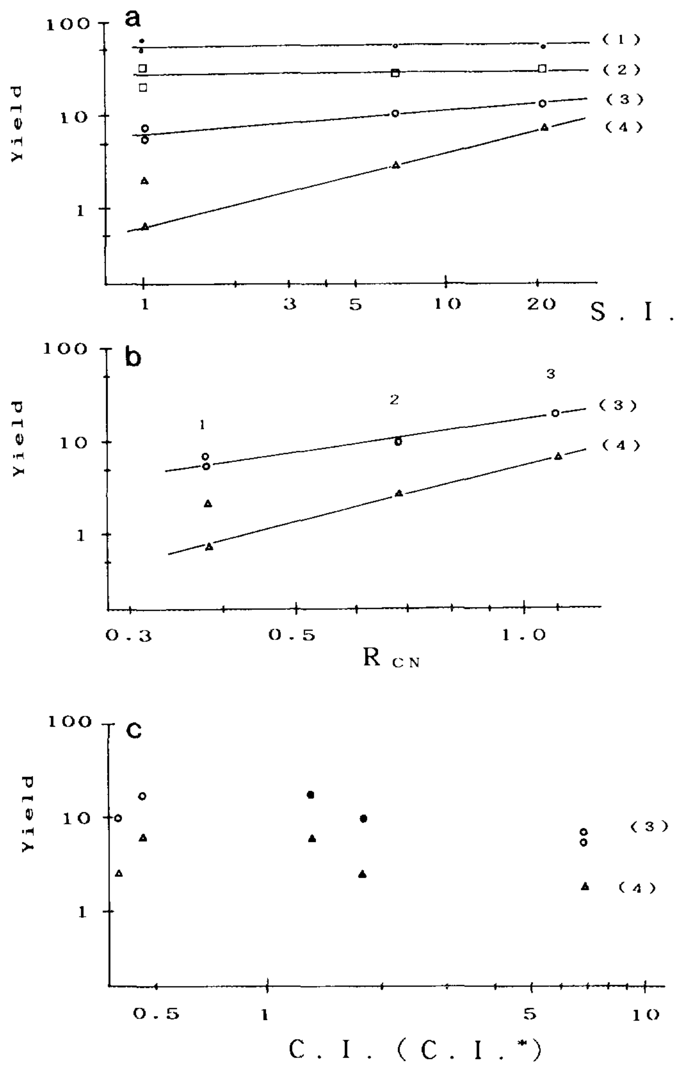

FIG. 5. Yields of monomethyl-NL (line 1), dimethyl-NL (line 2), trimethyl-NL (line 3), and tetramethyl-NL (line 4) by the alkylation of naphthalene (NL) with methanol as plotted against (a) the S.I. values, (b) R_{CN} values, and (c) C.I. values of zeolites listed in Table 1. The zeolite catalysts are MFI (1), MOR (2), and FAU (3), and the reaction data are from Ref. (*36*).

nm(8), 0.63 nm(10), 0.80 nm(12) and 1.5 nm(18), where the numbers in parenthesis are the number of SiO_4 or AlO_4 tetrahedra in a ring (*2*), the discrimination of the two hexanes is expected in the 8-, 10-, and 12-ring systems. *n*-HX can be sorbed by almost all of these systems, whereas CHX can be sorbed by circular 10- and 12-ring systems.

The amount of sorption depends on the density of pores on the zeolite surface and of channels in the bulk, which differs from one zeolite to another. The index R_{CN}, the ratio of the sorption amounts of two different molecules, eliminates this dependence and is expected to reflect only the size and shape of the zeolite pore. Several zeolites, like MFS (ZSM-57) and HEU (clinoptilolite), have both 8 and 10 rings. In such cases,

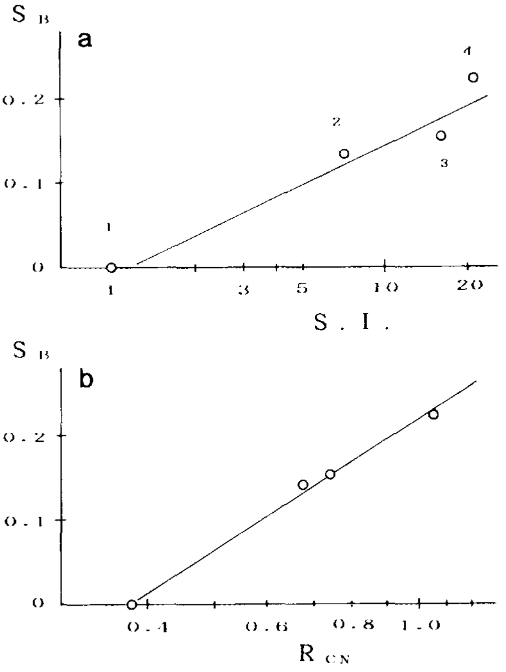

FIG. 6. Selectivity to byproducts, S_B, in the alkylation of biphenyl with propylene as plotted against (a) the S.I. values and (b) R_{CN} values of zeolites listed in Table 1. The zeolites are MFI (1), MOR (2), LTL (3), and FAU (4), and the reaction data are from Ref. (*37*).

the ratio may be lower than that of the usual 10-ring system zeolites.

R_{CN} has been found to be linearly dependent on *rr* values of 8-, 10-, and 12-membered-ring zeolites and this makes it more versatile than the formerly adopted indices like C.I., S.I., C.I.*, and *R* which are based on the result of chemical test reactions. Furthermore, their applicability is limited to small to medium pore (C.I.), medium pore (C.I.*, *R*) or larger pores (S.I.) zeolites, respectively.

It should be kept in mind that the pore structure of zeolites has hitherto been estimated from the C.I. values. From the present R_{CN} measurements, several of them seem to rquire reinvestigation. For example, zeolites of the reportedly FER structure show very different R_{CN} values; 0.26, 0.49, and 0.72 for ZSM-35, ZSM-21, and ZSM-38, respectively. The sorption result in the present study for another FER (TSZ-700K0A, TOSOH Co.) was the following: *n*HX 4.08%, CHX 0.85%, and R_{CN} = 0.21, a value slightly less than that for ZSM-35. The C.I. value of ZSM-35 is 4.5, while the value is 2.0 for ZSM-38 (*26*). The C.I. value of ZSM-21 is not reported. The reason for this large difference in R_{CN} values of the same FER group zeolite is not clear at present. These zeolites differ in the sorption of 2-methyl-pentane, too (*26*, *39*). There is also a slight difference in the XRD data. The identity or purity of crystals should be reinvestigated. As has been proved for C.I. values, the sorption characteristics of MFI with different synthetic conditions showed only a weak dependency on the crystallite sizes (*40*).

The C.I. values of cation-exchanged zeolites have not been reported to the author's knowledge, although their importance in shape-selective catalysis is frequently documented. This may be due to the reduced solid acidity and cracking activity of zeolites exchanged by alkali cations. The results of the sorption measurement of cation-exchanged zeolites are shown in Table 2, and the values will be helpful in understanding the change in shape selectivity by this kind of cations.

The linear dependency of R_{CN} on *rr* and C.I. values should mean that this parameter directly reflects the kinetics and shape-selective catalysis for aliphatic hydrocarbons and hydrocarbons with a naphthenic or a benzene ring. R_{CN} could be applied further to the reactions of naphthalene and biphenyl derivatives. One example is the alkylation of 2MN with MeOH to DMNs studied by Neuber *et al.* (Fig. 4). The alkylation is normally accompanied by isomerization to 1MN. They proposed that the hindered diffusion of the bulky molecules within zeolite pores limited their conversion, thus the conversion (dotted line) and the yield of DMN (solid line) decrease with decreasing pore size. This tendency is best reflected by the plot made against the R_{CN} values in Fig. 4a. Rather poor linearity is seen in the plot made against S.I. values in Fig. 4b.

As is obvious from Fig. 5a, the yields of methyl- and dimethyl-NL produced by the alkylation of NL with MeOH are apparently independent of S.I. values as seen from lines 1 and 2, respectively, whereas the yields of trimethyl-NL (line 3) and tetra-methyl-NL (line 4) increased when zeolites with larger S.I. values were used. The yield of the latter two species are plotted against R_{CN} values in Fig. 5b, and we see the linear dependency as in Fig. 5a. In Fig. 5c, which is the plot made against the values C.I. (open circle) or the C.I.* (filled circle) values, no such correlation is observed. In the case of the alkylation of BIP with PPY, the reduction of polyalkylated products together with the selective formation of 4-isopropyl or 4,4′-diisopropyl derivative would be expected. The selectivity of the byproducts, S_B, is plotted versus R_{CN} and S.I. values in Figs. 6a and 6b, respectively. It was found that larger pore zeolites tended to promote formation of the dialkylates, and that both plots are linear, but the scattering of the data points in Fig. 6b is apparently much smaller than that in Fig. 6a.

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