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Systematics of Shape Selectivity in Common Zeolites

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A five-component feed comprised of hexane isomers, benzene, and toluene was used as a catalytic probe to compare the behavior of common acid zeolites of widely differing pore structures. It was shown that, among well-characterized, known zeolites, systematic relations exist between sorptive properties, pore structures, and the selectivities for hydrocarbon reactions, including coke formation.

INTRODUCTION

Recognition that, among salts of crystalline aluminosilicate zeolites, the same factors responsible for selective sorptive properties, namely, a regular well-defined intracrystalline pore system, can be advantageously utilized in catalytic reactions occurred early (*1–3*, *28*). By contrasting the behavior of the small pore Na- and Ca-A with that of the corresponding salts of the large pore X, Weisz *et al.* (*2*) demonstrated two simple but general concepts of "molecular-shape selective reactions" over zeolite catalysts, one leading to reactant, the other to product selectivity. Reactant selectivity occurs when access to intracrystalline catalytic sites is afforded to one class of reactant molecules and denied to another, based on molecular shape or dimensions. When, in the cavities of a pore system, a mixture of products occurs not all of which can pass through the ports linking these cavities, product selectivity is observed. Both effects were shown in such diverse reactions as paraffin cracking, dehydration of alcohols, and hydrogenation of olefins (*2*).

Extension of these studies to acid zeolites followed quickly and showed that catalytic behavior could reflect yet another aspect of zeolite structure, stacking faults (*4*). Highly preferential cracking of *n*-hexane (NC6) as compared with 2-methylpentane (2MP) was observed over acid gmelinite, offretite, and chabazite, although the first two are, were it not for their stacking faults, lare-pore structures (*5*). The branched isomer is normally the more reactive in large-pore zeolites.

Similarly, preferential cracking of normal paraffins, in the presence of branched isomers, has been reported for the erionite-T-offretite (*7–11*, *19*) and the ferrierite structures (*12*, *18*), studies generally being conducted in the presence of hydrogen gas. Over erionite, model studies showed ratios of rate constants for NC6 to 2MP conversion (k_{NC6}/k_{2MP}) over 50 at 370°C, but decreasing with increasing temperature (*10*). Silica–alumina or the large-pore faujasite-type zeolites yielded values of 0.3–0.5.

The relationship between zeolite shape-selective properties and coke formation has received little attention in the literature and, indeed, in none of the references cited were coke levels reported. Although the

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TABLE 1

Catalyst Physical Properties

Catalyst designation	Sorption		Pore system[c]
	NC6[a]	CyC6/NC6[b]	
Erionite	4.4	<0.1	**8** 3.6 × 5.2***
Ferrierite	1.4	0.2	**10** 4.3 × 5.5* ↔ **8** 3.4 × 4.8*
TMA Offretite	8.7	0.6	**12** 6.4* ↔ **8** 3.6 × 5.2**
Mordenite	6.4	1.0	**12** 6.7 × 7.0* ↔ **8** 2.9 × 5.7*
Zeolite L	7.4	0.8	**12** 7.1*
Zeolite Y	16.6	1.0	**12** 7.4***
ZSM-4	5.4	1.0	—

[a] Grams per 100 g calcined ammonium zeolite; 20 mm NC6, 25°C.

[b] Ratio of cyclohexane (CyC6) to *n*-hexane (NC6) sorptive capacities, by volume, 25°C.

[c] Bold face numerals are number of tetrahedra defining a channel; light face numbers designate channel dimensions (Å); asterisks indicate whether 1-, 2-, or 3-dimensional (*5*).

polynuclear aromatic nature of coke is well established (*22*, *23*), no attempt has been found in the literature to relate coking tendencies to pore structure for a broad class of zeolites.

In the present work, one objective has been to provide a systematic comparison of the better-defined 8-, 10-, and 12-ring acid zeolites, to include the erionite, ferrierite, offretite, mordenite, L and Y structures.

Paraffin cracking is not the only reaction which can occur when a mixture of hydrocarbons is passed over a zeolite catalyst. When aromatics are present, their alkylation by the olefin fragments of paraffin cracking should theoretically occur. It was the second intent of this work to demonstrate the overwhelming importance of pore structure in determining isomerization/cracking selectivities, aromatics alkylation propensities, and most important, coking tendencies. Data are presented to suggest that coking and aging rates are intrinsic properties of zeolite pore structure.

EXPERIMENTAL METHODS

Catalysts

Zeolite samples were obtained in a variety of cationic forms, as described below, and were examined by X-ray diffraction techniques for purity. Powder diffraction patterns were obtained both immediately prior to and after catalytic testing and attested to the absence of any inadvertent contamination during catalyst preparation and to the retention of zeolite structural integrity during testing.

Zeolite samples containing alkali and alkaline earth cations were exchanged into the ammonium form by refluxing 3–4 times in 2 *M* $(NH_4)_2SO_4$ or 4 *M* NH_4NO_3, the final exchange lasting overnight. When a zeolite was calcined as, for example, to remove quaternary ammonium cations, the sample was equilibrated with ammonia gas prior to contact with water.

After conversion to the ammonium forms, zeolites were sized to 60/80 mesh, calcined overnight to 500°C, and loaded to the reactor for testing. Individual catalysts are detailed below, with sorptive and structural data listed in Table 1. Crystallite size of the samples was in the range 0.2–2 μm.

Erionite: $SiO_2/Al_2O_3 = 8.0$; $Na_2O/Al_2O_3 = 0.01$; $(K_2O + Ca,MgO) = 0.13$; 0.5 × 4 μm crystallites; prepared from a Jersey Valley, Nevada, erionite ore. The major cation contaminant is the difficultly exchanged potassium, probably locked with the ε-cages of erionite (*6*). In such a location, these cations may reduce overall activity but should not affect reaction selectivities.

Ferrierite: $SiO_2/Al_2O_3 = 10.1$; $Na_2O/Al_2O_3 = 0.04$; $MgO/Al_2O_3 = 0.07$; 1–5 μm crystallites; prepared from a Norton Zeolon 700 sample of ferrierite ore. The major cation contaminant is the difficultly exchanged magnesium, located in the center of the cavities (*6*).

TMA offretite: $SiO_2/Al_2O_3 = 8.1$; $Na_2O/Al_2O_3 < 0.02$; $K_2O/Al_2O_3 = 0.16$; 0.2–1 μm crystallites, prepared from tetramethylammonium (TMA), potassium, and sodium-containing gels (*13*). Again, Breck (*6*) reported that potassium ion is trapped in ε-cages and resists exchange.

Mordenite; $SiO_2/Al_2O_3 = 15$ and 96; $Na_2O/Al_2O_3 < 0.02$; 0.3–1.5 μm crystallites, both obtained from Norton as Zeolon 100 and dealuminized Zeolon 100. Based on the literature (*14*), it is thought that dealuminization was effected by acid-leaching.

Zeolite L: $SiO_2/Al_2O_3 = 6.3$; $Na_2O/Al_2O_3 < 0.01$; $K_2O/Al_2O_3 = 0.17$; 0.3 μm crystallites, obtained from Strem Chemical. Nonexchanged potassium is located in the ε-cages (*6*) and should not affect selectivities.

Zeolite Y: $SiO_2/Al_2O_3 = 5.3$ and 13.2; $Na_2O/Al_2O_3 = 0.02$ and 0.06; 1 μm crystallites, obtained from Strem Chemical (5.3) and dealuminized with EDTA according to techniques developed by Kerr (*15*). Detailed characterization of such dealuminization products has been reported by Jacobs and Uytterhoeven (*25*), Beaumont and Barthomeuf (*26*), and Topchieva and Thanh (*27*).

ZSM-4: $SiO_2/Al_2O_3 = 7.4$; $Na_2O/Al_2O_3 < 0.01$; 1–2 μm crystallites, prepared in the presence of TMA cations (*16*). As reported by Breck (*6*), this zeolite adsorbs cyclohexane indicating large pores. Its X-ray diffraction pattern is similar to that of the mineral, mazzite (*17*).

Catalytic Experiments

Catalytic data were taken with a 5-component feed containing equal weights

TABLE 2

Conversion and Selectivity Comparison of Known Structures[a]

	Erionite	Ferrierite[b]	TMA offretite	Mordenite	L	Y	ZSM-4
Conversion (%)							
2,3-dimethylbutane	1	5	30	61	11.5	32	55
3-methylpentane	0.5	4	8.5	18	4	12	19.5
n-hexane	65	56	24.5	6	0	0	2.5
Relative rates							
k_{NC6}/k_{3NP}	210	20	2.9	0.3	0	0	0.1
k_{23DMB}/k_{3MP}	2	1.2	4.0	2.9	2.9	3.0	3.6
Isomerization selectivity (%)	0	0	53	92	91	94	90
Alkylation efficiency (%)[c]	1	1	12	15	12	11	14
Aromatics k_{A6}/k_{A7}	—[d]	—[d]	0.2	0.1	0.4	0.3	0

[a] 5-Component feed; 316°C; WHSV, 3; 300 psig; H_2:HC, 3.

[b] Low conversion at 316°C; data are at 427°C.

[c] Percentage paraffin cracked which is found as aromatics side chains.

[d] Conversion too low for accurate comparison.

of 2,3-dimethylbutane (23-DMB), 3-MP, NC6, benzene (A6) and toluene (A7), 1–4 days on stream, 316–528°C. Reaction conditions were 200 psig, 3 moles H_2/mole hydrocarbon, and WHSV = 3 g feed/g catalyst/hr, unless otherwise stated. Hydrocarbons were Phillips 99^+ grade. No attempt, other than exhaustive NH_4^+ exchange, was made to optimize catalyst activity.

Complete product analyses were performed on a 3-hr balance period, using both mass spectral and glc techniques. Glc columns required were a 150 ft PMPE capillary for the liquids, a 100 ft Squalane SCOT column for hexane isomers, and a 6 ft Porapak Q column for C_2–C_4 olefins and paraffins.

On completion of a 4-day series of tests, the reactor was cooled (in flowing hydrogen), the catalyst was removed, and coke was determined by weight loss on calcination to 500°C, just as had been done prior to catalyst loading into the reactor.

RESULTS

Sorption and Structure

Structural information on the catalysts tested is listed in Table 1 and shows the relationship between sorptive properties and, for those materials of established structure, pore dimensions.

Small-pore structures such as erionite effectively exclude branched or cyclic hydrocarbons, the ratio of cyclohexane (CyC6) to NC6 sorptive capacities being less than about 0.1. The 10-ring ferrierite channel is similarly restrictive with respect to branched and cyclic hydrocarbons exhibiting a CyC6/NC6 ratio of 0.2 and a capacity for NC6 of 1.4 g/100 g. Since synthetic ferrierites exhibiting NC6 capacities as high as 4.1 g/100 g have been reported (*12*), it is concluded that a portion of the channels in the present sample are blocked and inaccessible for percent catalytic purposes.

TMA offretite represents a unique case within this group of known structures in that it contains two channel systems accessible to NC6, only one of which accommodates the larger CyC6. A measured CyC6/NC6 ratio of 0.6 reflects this dual channel distinction and is identical with the calculated ratio of Breck and Grose (*20*).

Little distinction is drawn between NC6 and CyC6 in the case of mordenite, L, Y, and ZSM-4, both hydrocarbons being permitted entry to the large, 12-ring pores. With mordenite, as was the case with ferrierite, the smaller 8-ring channels appear inaccessible to NC6. No explanation of the lower CyC6/NC6 ratio for L is available (*20*), but, as with ZSM-4, the substantial access by CyC6 would nonetheless indicate a large-pore system.

Catalytic Behavior

Under the conditions of the present test, the important reactions are isomerization and cracking of the hexanes, aromatics alkylation by the light olefinic products of cracking, and coking. Selectivity in the conversion of the various hexane isomers is given by the ratios $k_{NC6}/k_{3\text{-MP}}$ and $k_{2,3\text{-DMB}}/k_{3\text{-MP}}$, the first-order rate constants for disappearance of the respective feed components. In addition, an isomerization selectivity must be specified which is defined as the grams of 2,2-DMB and 2-MP produced per 100 g feed hexanes converted. Interconversion of feed hexanes is ignored in this 5-component test, but its importance is examined with single isomer feeds below.

Benzene/toluene selectivities are similarly represented by k_{A6}/k_{A7}, reflecting both the differing reactivities and differing alkylation propensities of the two compounds. Coke yields are cumulative in the initial survey of zeolite structures and are reported as grams of coke produced per 100 g charge converted. Based on this survey, actual coking and aging rates are compared with selected catalysts in isothermal, single component feed tests.

Conversion and selectivity data for the zeolites tested are presented in Table 2 and show the striking control of relative rates of reaction by pore dimensions. With the erionite sample, 65% NC6 conversion was effected with less than 1% reaction of 3-MP, none of the products appearing as isomerized hexanes but rather as light gases, predominantly propane. Conversion of 2,3-DMB (excluded by the pores) was attributed to external surface. The external surface area of these 0.5 × 4 μm lath-shaped crystallites is calculated to be about 6 m^2/g, about 2% of the measured total BET surface area of 280 m^2/g. Both benzene and toluene are effectively excluded from the erionite pore system and aromatics alkylation was correspondingly minimal.

The ferrierite sample was relatively inactive, consistent with its somewhat low NC6 sorptive capacity (Table 1). In the absence of pore blockage, the main channels of the ferrierite structure should have a capacity of 4–5 g NC6/100 g zeolite (*12*). Catalytic data are presented at 427°C and show preferential cracking of NC6, as well as the essential absence of isomerization or of reactions of aromatics. [The ratio k_{NC6}/k_{3MP} is of course temperature dependent and, among most small-pore zeolites, decreases with increasing temperature (*10*).]

Contrasting the erionite and ferrierite behavior is that of the simple 12-ring structures, mordenite, L, Y, and ZSM-4. In all four cases preferential conversion of 2,3-DMB occurred and isomerization became an important reaction. Of those paraffins cracked, 10–15% of the fragments were found as aromatics side chains with toluene conversion exceeding that of benzene. That these results were not simply an artifact of toluene disproportionation was demonstrated by replacing toluene with benzene in the feed. Alkylation again occurred, this time with an efficiency of 7–10%. Activity and selectivities were otherwise comparable.

TABLE 3

Effect of SiO_2/Al_2O_3 Ratio on Catalyst Selectivity[a]

	Y		Mordenite	
SiO_2/Al_2O_3	5.3	13.2	15	96
Conversion (%)				
2,3-dimethylbutane	32	24.5	61	69
3-methylpentane	12	8.5	18	22
n-hexane	0	0	6	7
Relative rates				
k_{NC6}/k_{3MP}	0	0	0.3	0.3
k_{23DMB}/k_{3MP}	3.0	3.0	4.7	4.7
Isomerization selectivity (%)	94	93	92	79
Alkylation efficiency (%)	11	11	15	18
Aromatics k_{A6}/k_{A7}	0.3	0.3	0.1	0

[a] 5-Component feed.

Isomerization selectivity data are rendered qualitative by the possible interconversion of feed hexane isomers, and a detailed analysis of this problem is beyond the scope of the present study. Nevertheless, an experiment was conducted wherein a Y catalyst was subjected at 427°C to, in one case, the standard 5-component mixture and, in another, pure 3-MP. Paraffin partial pressure in both cases was made equal. Isomerization selectivity was 59% with the mixture as compared with 65% for 3-MP alone, comparison being made at a constant isomer conversion of about 20%.

TMA offretite contains both 8- and 12-ring channels, both accessible to NC6. Branched hexanes should be excluded from the former, however, The catalytic behavior of TMA offretite reveals the duality of the channel system in that substantial conversion of both NC6 and 2,3-DMB occurred relative to that of 3-MP. Isomerization assumed an intermediate importance between that observed with the simple

TABLE 4

Coke Selectivities[a]

Catalyst	Selectivity	
	Coke[b]	Normalized[c]
Erionite	0.14	0.16
Ferrierite	0.03	0.04
TMA offretite	0.7	0.8
Mordenite	0.3	0.4
Zeolite L	0.4	0.5
ZSM-4	0.4	0.5
Zeolite Y	2.2	2.9

[a] 5-Component feed; 3.3 days on stream. All catalysts treated under a standard cycle with WHSV, 3; temperature, 316–538°C; 200 psig: $H_2/HC = 3$.

[b] Grams/100 g conversion, observed.

[c] Grams/100 g conversion, normalized to 50% conversion using first-order approximation.

8- and with the 12-ring catalysts. The reactions of aromatics observed with simple 12-ring structures were again evident. In this regard it is noted that the 8-ring pores define a distinct pore *volume* and are not simply 2-dimensional apertures between 12-ring channels. Breck and Grose (*20*) calculated a volume of 13 cm^3/100 g for the 12-ring channels and an additional 8 cm^3/100 g when the 8-ring pore system is included.

One aspect of these materials deserves special examination, their SiO_2/Al_2O_3 ratio. The examples cited in Table 2 were taken with materials of silica/alumina ratio between 5.3 (Y) and 15 (mordenite). As shown in Table 3 little or no effect on reaction selectivities was observed when a Y sample was carefully dealuminized from $SiO_2/Al_2O_3 = 5.3$ to 13.2. A similar lack of effect was observed on comparison of mordenite ($SiO_2/Al_2O_3 = 15$) and dealuminized (acid-leached) mordenite ($SiO_2/Al_2O_3 = 96$). These results militate against any large effect of SiO_2/Al_2O_3 ratio on reaction selectivities and indicate, as originally proposed (*1*), that these selectivity effects must originate in the zeolite pore structure.

Coking and Aging Behavior

After 3 days of testing, catalyst performance under the initial reaction conditions was again examined. Paraffin conversion with all large-pore structures except TMA offretite was found to be 1% or less, indicating essentially complete deactivation. In this group were the catalysts mordenite, L, Y, and ZSM-4.

The two-shape selective materials substantially retained their activity. Losses in conversion (treated as first-order rate constants) ranged from 70% in the case of erionite to 20% for the ferrierite sample, but in neither case was the complete deactivation observed which had been found with the large-pore catalysts. The shape selective properties of these materials were retained on aging.

On completion of testing, coke on catalyst was determined. Using conversion data taken during the run, coke selectivities (grams of coke/100 g conversion) were calculated (Table 4) and showed a striking correlation between shape selective properties and low coking tendencies. Selectivities of ≤ 0.1 g coke/100 g conversion were observed with the shape selective erionite and ferrierite catalysts. Large-pore materials averaged 1.0 g/100 g with a high of 2.2 for the 3-dimensional 12-ring Y.

Coke yields in these catalysts are not, of course, directly proportional to conversion but increase nonlinearly as conversion increases (*21*). If, for the purposes of illustration, coke yields are assumed proportional to − log (1-fraction converted) and the coke selectivities are accordingly normalized to 50% conversion, the distinctions between large-pore and shape selective catalysts are even more pronounced (Table 4).

Actual aging rates have been determined in 1-week tests on two zeolites of similar pore class. Comparison was made between ferrierite and mordenite, both possessing one-dimensional channels, the former a

10-ring, the latter a 12-ring structure. Experiments were conducted at 427°C, 300 psig, H_2:HC = 7.

Plots of log (conversion) vs log (time on stream) were linear (6–78 hr on stream) with slopes given by the *n*-values in Table 5, according to the Voorhies relationship (*21*),

$$\text{conversion} = k \cdot (\text{time on stream})^n.$$

The more closely n approaches zero, the slower the aging. In agreement with the coking selectivities, the aging rate (slope) of the ferrierite catalyst with NC6 was at least an order of magnitude lower than that of the mordenite samples. The ferrierite pore system is accessible to NC6 such that conversion occurs predominantly within the pore channels. On the other hand, ferrierite should exclude 3-MP from its intracrystalline pore system and permit conversion of this isomer only on its external surface (or on large-pore contaminants). Conversion of 3-MP on ferrierite was found to age much more rapidly than that of NC6 (Table 5) and at a rate similar to that of mordenite.

The large-pore mordenite structure shows aging rates 1–2 orders of magnitude larger than that of the shape selective catalyst. That this is not an artifact of data treatment, due to the presence of isomerization reactions, was shown by comparing *n*-values for total conversion with those for cracking-only conversion. With the dealuminized mordenite, for example, a value of $n = -0.21$ was found for total paraffin conversion and $n = -0.24$ for cracking only. It is again noted that the aging distinction between catalyst groups cannot be explained by differences in SiO_2/Al_2O_3 ratio. Acid leaching of mordenite did not greatly affect its aging rate.

DISCUSSION

These present studies with a five-component feed have attempted to probe the behavior of zeolite catalysts in a variety of simultaneous reactions, including selective paraffin cracking, paraffin isomerization, aromatics alkylation, and coking. Where ambiguities arose, single-component feeds were employed as well. From these various reactions, a direct correlation between zeolite sorptive properties and catalytic behavior has been developed.

Three classes of zeolites are distinguished in Table 1 according to sorptive properties, with CyC6/NC6 ratios of ≤ 0.2, ~ 0.6, and ≥ 0.8. Zeolite Y is singled out by its very high NC6 sorptive capacity, the result of a high porosity, 3-dimensional, 12-ring structure. This distinction of zeolites by sorptive

TABLE 5

Aging Rates[a]

	SiO_2/Al_2O_3	WHSV	Initial conversion[b]	Isom. selectivity	*n*-Values[c]	
					3-MP	NC6
Ferrierite	10	1.5	96.5[d]	0[d]	−0.20	−0.008
Mordenite	15	1.5	38	28	−0.11	−0.18[e]
	96	1.6	22	36	−0.21	—

[a] Single-component feeds; 300 psig; H_2/HC = 7; 427°C.

[b] Six hours on stream, percent.

[c] Based on total conversion (isomerization and cracking), using the equation, conversion = $k \cdot (\text{time on stream})^n$, minutes.

[d] NC6.

[e] Based on cracking only.

characteristics correlates remarkably with catalytic properties.

Reactant selectivity is demonstrated by the erionite and ferrierite samples which exclude branched paraffins and even aromatics. Thus paraffin conversion is effectively restricted to the linear isomer and little or no aromatics alkylation is observed (Table 2).

Product selectivity is reflected in the absence of hexane isomerization activity with erionite and ferrierite. As discussed below, however, the most significant evidence of product selectivity lies in coking. It is suggested that cyclo-paraffin coke precursors cannot readily form in the restrictive pore system of these shape selective catalysts, with the result of substantially reduced catalyst aging rates (Table 4).

Such low aging rates contrast, as do the other shape selective phenomena, with the behavior of the large-pore structures, mordenite, L, ZSM-4, and Y. Preferential cracking of branched paraffins occurs in these latter materials accompanied at these low temperatures by substantial isomerization. Aromatics alkylation is present but with toluene conversion predominating. Finally, little restriction on coke formation is afforded by the large-diameter pores and aging becomes significant.

Coking and aging are of course distinct phenomena. Where coking occurs within the pores of a zeolite, loss in catalyst activity must certainly result. Several papers present evidence for the aromatic, or polycyclic aromatic, nature of coke [(*22, 23*), for example]. That the formation of such structures, and particularly that of the cyclo-paraffin precursors to coke, is inhibited by the restrictive pore system of the shape selective catalysts is consistent with their exceptional retention of activity.

It is recognized of course that not all coke is formed in the intracrystalline pore system, nor would all zeolites be expected to have the same sensitivity to coke. The more rapid deactivation of mordenite, as compared with Y, in the transalkylation of alkylbenzenes was attributed, for example, to the one-dimensional nature of the mordenite pores (*24*). Zeolite Y has a 3-dimensional pore system.

Under present test conditions, however, it is suggested that pore-mouth plugging of mordenite may not be an important cause of deactivation. The data in Table 5 for dealuminized mordenite can serve to illustrate this contention. Over the test period in Table 5, 3-MP conversion declined from 22 to 13%. Recovered catalyst contained 7.0% carbon. Based on the sorptive properties in Table 1 and assuming a coke density of 1.5 g/cm^3, about 48% of the pore volume would be filled if all the coke were inside the catalyst crystallite, a value quite similar to the loss in activity (45%).

Finally, recognition is given to the nonuniform dimensions of many zeolite pore systems. With Y, for example, distinction may be drawn by intersection of the pores. Such a distinction is particularly pertinent to the aging of erionite samples. Although the 8-ring pores have dimensions of only 4.2 Å, the intersections of these pores result in the ϵ-cages having free dimensions of $\sim 7 \times 14$ Å. The higher coke selectivity of erionite in Table 4, as compared with ferrierite, is attributed to just such a feature of pore structure.

CONCLUSIONS

The catalytic behavior of a series of acid zeolites of well-established structure was examined with a mixture of hexane isomers, benzene, and toluene. Structures included erionite, ferrierite, offretite, mordenite, L, ZSM-4, and Y.

In agreement with their selective sorptive properties, the zeolites erionite and ferrierite exhibited preferential cracking of NC6, to the virtual exclusion of such reactions as paraffin isomerization and aromatics alkylation. Both zeolites gave coke selectivities <0.2 g coke/100 g conversion.

Those zeolites showing minimal distinction between NC6 and CyC6 in their sorptive properties were mordenite, L, ZSM-4, and Y. Common to all was the preferential cracking of branched paraffins, the importance of paraffin isomerization, and aromatics alkylation, preferably that of toluene. Coke selectivities were 0.4–0.5 for the one-dimensional mordenite and L pore systems and for ZSM-4 and 2.9 for the three-dimensional Y. The unusual dual pore system of TMA offretite was evidenced by a unique cracking selectivity but with properties otherwise more similar to the large-pore materials.

The relationship between coking rates and aging rates in the cracking of hexanes was examined with catalysts of each structural group. It was shown that those catalysts exhibiting shape selective activity also exhibited low coking and aging rates, and it was proposed that intracrystalline coking (aging) is a shape selective reaction directly related to zeolite pore structure.

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