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Zeolite Effects on the Cracking of Long Chain Alkyl Aromatics

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Long chain alkyl aromatic compounds crack by a number of competing reaction pathways including dealkylation, side chain cracking, and self-alkylation. Cracking studies of 1-phenylheptane over zeolites Y, beta, mordenite, and ZSM-5, as well as silica–alumina, show that the catalyst can significantly alter the relative importance of these pathways. For example, large pore zeolites give significant amounts of bicyclic reaction products, whereas the medium pore sieve ZSM-5 gives almost no bicyclic products. Other catalyst properties such as Si/Al ratio, adsorption characteristics, and geometrical factors also affect cracking catalyst performance. © 1994 Academic Press, Inc.

INTRODUCTION

Fluid catalytic cracking (FCC) products are the largest contributor to the U.S. gasoline pool (1). Commercial FCC catalysts are mixtures of zeolite Y and matrix material, typically silica–alumina (3). Aromatic compounds are important components of gasoline from the FCC unit. For example, aromatics have a large impact on the research and motor octane values. However, for environmental reasons, both the benzene content and the total aromatic content of gasoline will be regulated in reformulated gasolines (2). Therefore, the formation of aromatics and the reactions of aromatic compounds in fluid catalytic cracking are important and timely topics for refiners.

In a previous report (4) we have shown that long chain alkyl aromatics (LCAA) such as 1-phenylheptane crack by a variety of pathways over strong acid catalysts containing zeolite Y. These pathways include (1) dealkylation to give benzene and a C7 olefin; (2) side chain cracking to give an alkyl fragment C*n* and a C(7-*n*) alkylbenzene; and (3) formation of bicyclic aromatics by attack of a carbenium ion in the alkyl side chain on the benzene ring (self-alkylation). Self-alkylation is particularly interesting because it produces bicyclic molecules that can lead to coke (5) or to heavy gasoline aromatics.

We expect that the reaction pathways for LCAA cracking can be manipulated by changing catalyst properties such as adsorption, acid strength, acid site density and catalyst architecture. If this is so, then LCAA cracking should be a function of the type of zeolite used in the catalyst. To determine the effect of zeolites on the cracking chemistry of LCAA, the cracking of 1-phenylheptane over zeolites Y, beta, mordenite, and ZSM-5 was investigated. For comparison, cracking over amorphous silica–alumina is reported also.

EXPERIMENTAL

Materials

1-Phenylheptane (>99%) was purchased from Aldrich and used without further purification.

Table 1 lists relevant physical and chemical properties of the catalysts. Zeolite Y was grown in calcined clay microspheres of approximately 70 μm diameter by a procedure described previously (6). Ammonium exchange and zeolite unit cell size reduction to 24.60 Å were done by standard methods (6). This material is designated as USY. Zeolite beta (BEA) was prepared by methods described previously (7). ZSM-5 (MFI) and mordenite (MOR) were synthesized and ion-exchanged to the hydrogen forms by standard methods (8). ZSM-5 was synthesized at Si/Al ratios of 20 (MFI-20) and 50 (MFI-50). Amorphous silica–alumina (13% alumina) was obtained from Crosfield Catalysts. Surface area measurements of the catalysts were made by standard BET methods.

Catalysis

Pure zeolite particles were obtained by pressing the zeolite into a wafer and then crushing and sieving the material to obtain particles of 0.30–0.50 mm diameter.

Catalytic experiments were done in a fixed-bed continuous-flow glass tubular reactor at 773°K and 1 bar as described previously (4). After the reaction was complete, the reactor was stripped with nitrogen at 780°K for 10 min and then the catalyst was regenerated in air flowing at 20 cm^3/min for 5 h at 793°K.

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TABLE 1

Physical and Chemical Properties of the Catalysts

Material	Si/Al	Na_2O	BET surface area m^2/g
USY	3.9	0.41	434[a]
MFI-20	20	<0.1	400
MFI-50	50	<0.1	400
BEA	13	<0.1	450
MOR	14	1.70	419
SiO_2/Al_2O_3	5.7		550

[a] Approximately 41% zeolite Y.

Blank experiments were done using ground glass in place of the catalyst under reaction conditions. The products obtained from this experiment were assumed to be the result of thermal cracking. The products from the thermal cracking of 1-phenylheptane under our reaction conditions are described in detail in a previous publication (4). In order to analyze acid catalysis, thermal yields over ground glass were subtracted from the yields from the acid catalysts. In some cases, e.g., styrene, negative values result. This is probably due to the saturation of reactive species such as styrene by hydrogen transfer on the catalyst surface.

Yields and Selectivities

Yield is defined as moles of product X obtained per 100 moles of 1-phenylheptane fed. Product selectivity is moles of product X obtained for each mole of phenylheptane converted.

Initial product selectivities were obtained using optimum performance envelope techniques (3). Initial selectivities for each primary product were determined from the initial slope of a plot of (mol%) yield for that product vs 1-phenylheptane conversion. The shape of this plot determines whether the product is primary or secondary, stable or unstable (3).

Analysis

Gaseous and liquid products were analyzed as previously described (4). Product identification was done using gc-mass spectrometry.

RESULTS AND DISCUSSION

Activity

An important property of a cracking catalyst is its ability to convert feed molecules. This is generally termed activity. Typically, amorphous silica—aluminas are less active than zeolites. Among zeolites, Si/Al ratio is an important parameter because acid sites are associated with aluminum atoms in the zeolite framework. Si/Al ratio is related to acid site density and strength, two parameters that have important effects in cracking catalysis (9). Catalyst activity for converting 1-phenylheptane was determined by assuming a pseudo-first order reaction. When a correction is made for the expansion of gases in the cracking reaction, the integrated first order rate equation becomes

$$-(1 - \varepsilon)\ln(1 - X) - \varepsilon X = k/\mathrm{WHSV},$$

where

ε = the expansion factor (no units) determined from the initial selectivities
WHSV = weight hourly space velocity (h^{-1})
X = cumulative mole fraction converted at 51 s TOS
k = cumulative rate constant at 51 s TOS (h^{-1})

A plot (Fig. 1) of the terms on the left side of the equation versus WHSV^{-1} gives a straight line with a slope, k, with units of h^{-1}. Thus k is a measure of the pseudo-first order activity of each catalyst.

The values of k for each catalyst are compiled in Table 2. Since the USY sample contains matrix material as well as zeolite, the values for USY were corrected for the zeolite content of the catalyst.

The activity of the catalysts for cracking 1-phenylheptane decreases in the order USY, ZSM-5, beta, mordenite, and silica–alumina. The observed activity is a function of acid site density, acid site strength, sorption

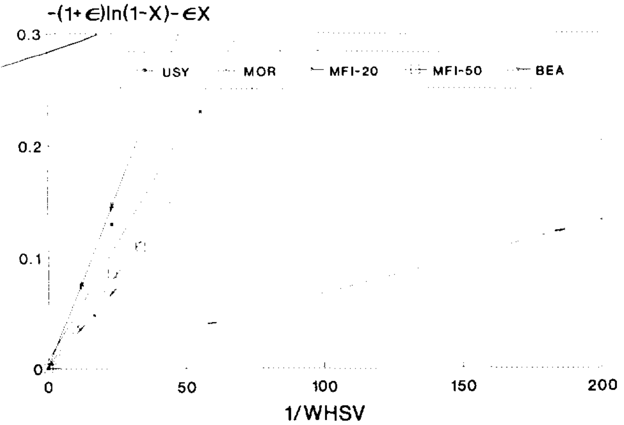


FIG. 1a. Plots for determining k from integrated first order rate equation for cracking of 1-phenylheptane over zeolite catalysts.

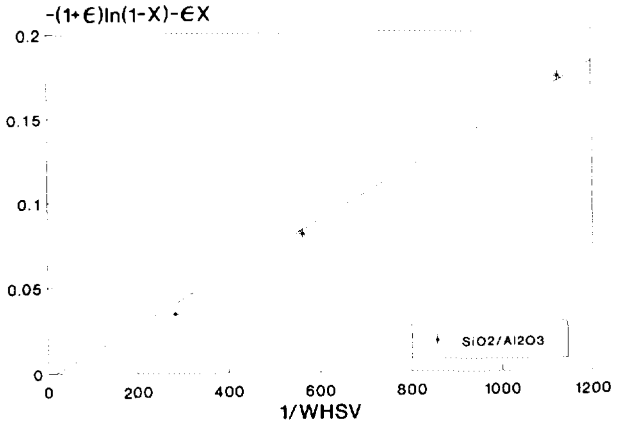


FIG. 1b. Plot for determining k from integrated first order rate equation for cracking of 1-phenylheptane over silica–alumina.

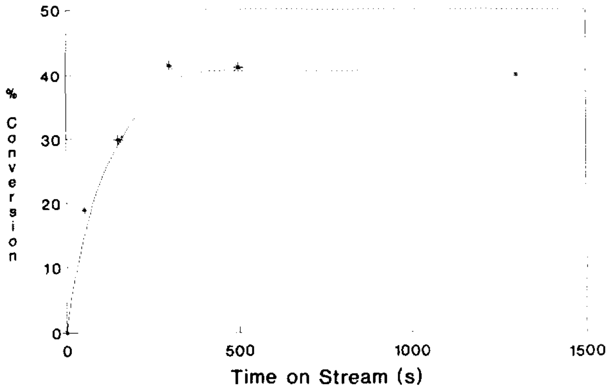


FIG. 2. % Conversion of 1-phenylheptane over USY vs time on stream at constant catalyst/oil ratio (0.0125) illustrating Class II decay.

properties, etc. Not surprisingly, amorphous silica–alumina has the lowest activity and ZSM-5 with Si/Al of 50 is about half as active as ZSM-5 with Si/Al equal to 20.

An important aspect of activity is a catalyst's ability to resist activity decay. Plots of conversion versus time on stream at constant catalyst/oil ratio indicate that phenylheptane cracking gives Class II (10) decay. For Class II decay, a limiting conversion is obtained at a given catalyst/oil ratio and the limiting conversion is determined by the catalyst/oil ratio of the run. This is illustrated for the USY catalyst by Fig. 2.

The rate of decay of the catalysts decreases in the order USY > silica–alumina > beta > ZSM-5. The lower rate of catalyst decay for ZSM-5 contributes to the relatively high activity shown by ZSM-5 relative to the other zeolites at a fixed time on stream.

Initial Selectivities

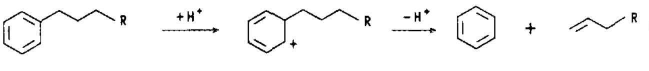
Selectivity is another important characteristic of cracking catalysts. Since there are a number of possible reaction pathways for LCAA cracking, one would expect that the zeolite type would have a profound impact on selectivities. Initial molar selectivities for cracking of 1-phenylheptane over various zeolites and silica alumina are compiled in Table 3. The cracking pattern for these catalysts indicates that two cracking mechanisms are occurring (4). One mechanism is monomolecular, and involves proton attack either on the benzene ring or on a sigma C–C bond in the alkyl chain (protolytic cracking). The first monomolecular pathway is shown in Eq. (1) and involves dealkylation of the benzene ring to give benzene and an olefin. The second pathway is shown in Eq. (2) and involves protolytic cleavage of the alkyl side chain. The resultant products are olefin and an alkyl benzene or a paraffin and an alkenyl benzene.

TABLE 2

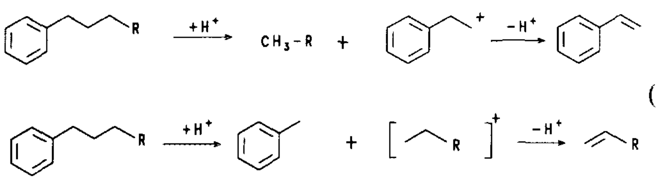
$10^4 \times k[S_0]$ Values for Cracking of 1-Phenylheptane

Catalyst	$10^4 \times k[S_0]$ (h^{-1})
USY	98[a]
MFI-20	64
MFI-50	33
BEA	28
MOR	6.7
SiO_2/Al_2O_3	1.6

[a] Corrected to 100% USY basis. Catalyst contains 41% USY.

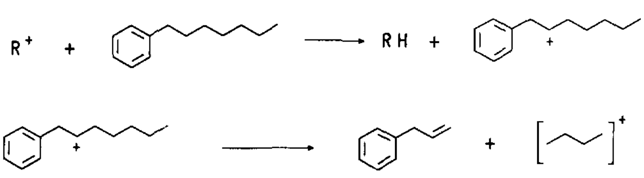


(1)



(2)

The other mechanism is a bimolecular reaction involving carbenium ions, chain transfer via hydride transfer, and β-scission (11) (Eq. (3)). Short chain paraffins and olefins as well as substituted benzenes result.



(3)

TABLE 3

Initial Molar Selectivities for Cracking of 1-Phenylheptane over Zeolite Catalysts

	USY[a]	BEA	Si/Al	MFI20	MFI50	MOR
Methane	—	0.066	0.005	0.011	0.050	0.020
Ethane	0.023	0.071	0.050	0.056	0.109	0.039
Ethene	0.026	0.165	0.026	0.118	0.200	0.015
Propane	0.117	0.044	0.050	0.040	0.039	0.064
Propene	0.293	0.447	0.520	0.810	0.773	0.885
Isobutane	0.150	0.097	0.099	0.024	0.017	0.044
n-Butane	0.046	0.016	0.013	0.011	0.011	0.047
Butenes	0.128	0.362	0.253	0.638	0.577	0.636
Isopentane	0.023	0.002	0.007	0.001	0.002	0.002
n-Pentane	0.001	0.009	0.003	0.004	0.005	0.002
Pentenes	0.006	0.089	0.020	0.119	0.030	0.056
n-Hexane	0.008	0.020	0.012	0.011	0.020	0.018
Branched C6s	0.075	0.030	0.031	0.007	0.004	0.004
Monobranched C7s	0.141	0.037	0.081	0.004	0.004	0.011
Dibranched C7s	0.031	0.008	0.016	0.002	0.001	—
Heptenes	0.007	0.012	0.020	0.004	0.004	0.018
Benzene	0.503	0.744	0.790	1.000	0.895	0.854
Toluene	0.090	0.122	0.049	0.012	0.205	0.091
C2 Benzenes	0.055	0.073	0.017	0.041	0.125	0.196
ethylbenzene	0.092	0.178	0.085	0.008	0.017	0.097
styrene	−0.037	−0.045	−0.069	0.034	0.108	0.098
C3 Benzenes	0.113	0.064	0.076	0.024	0.025	0.015
saturated	0.026	0.043	0.011	0.021	0.023	0.010
unsaturated	0.085	0.021	0.066	0.003	0.001	0.005
C4 Benzenes	0.161	0.050	0.064	—	0.010	0.041
butylbenzenes	0.010	0.008	0.003	0.011	0.005	—
butenylbenzenes	0.022	0.010	0.007	—	0.005	0.026
tetralin	0.024	0.007	0.016	—	—	0.005
naphthalene	0.086	0.006	0.010	−0.010	—	0.003
methylindan	0.019	0.019	0.029	—	—	0.007
C5 Benzenes	0.051	0.042	0.076	0.001	0.001	0.005
pentenylbenzenes	0.003	—	0.004	—	—	—
methylnaphthalene	0.034	0.013	0.006	—	—	0.005
1,3 dimethylindan	0.016	0.029	0.066	0.001	0.001	—
C6 Benzenes	—	−0.003	0.005	−0.016	—	−0.009
C7 Benzenes	0.026	0.035	0.061	—	0.002	0.008
2-heptenylbenzene	−0.002	−0.007	−0.040	—	—	—
2-phenylbicyclo-[2.2.1]hept-2-ene	0.012	0.028	0.035	—	0.002	0.006
1,4,6-trimethyl-naphthalene	0.016	0.014	0.030	—	—	0.002
C8 Benzenes	0.006	−0.011	0.002	—	—	—
C10 Benzenes	0.021	0.003	0.007	—	—	0.022

[a] Initial Selectivities for USY previously published in Ref. (4).

From inspection of the initial selectivities it is apparent that products expected from each of the reaction mechanisms are observed.

The high Si/Al zeolites (MFI, BEA, MOR) have relatively high selectivity to methane and C2s. The C2s are particularly high and cannot be accounted for by simply cracking phenylheptane into stable C2 and C5Ph fragments since the initial molar selectivities for C2s are much higher than those for the corresponding C5Ph species. This suggests that C5Ph recracks to give C2 and C3 products (4). In addition, there are precedents for high yields of C2 cracking products from high Si/Al zeolites. For example, Abbot has reported (12) that the initial molar selectivities for C2s from cracking of C6 paraffins at 500°C are much higher for MFI than for HY zeolites. One potential explanation for the trend is that high Si/Al zeolites tend to give more cracking at the end of the chain (13).

TABLE 4

Lumped Selectivities for Cracking of 1-Phenylheptane

Catalyst	Dealkylation cracking	Olefin paraffin	Cyclization
USY	0.97	0.73	0.178
BEA	2.15	2.99	0.074
MOR	2.53	4.82	0.020
MFI-20	13.72	9.93	0.001
MFI-50	4.94	6.09	0.001
SiO_2/Al_2O_3	2.76	2.21	0.130

There are also other significant differences among the catalysts. These can most easily be seen by lumping products into classes and comparing ratios of classes of products. Table 4 contains data on olefin/paraffins; dealkylation/side chain cracking; and selectivity to bicyclic products that arise from self-alkylation of the benzene ring.

The olefin/paraffin ratio for products is generally used as a measure of the hydride transfer ability of cracking catalysts (14). As shown in Eq. (3) the net effect of the hydride transfer reaction is to convert olefins into paraffins. However, in the case of 1-phenylheptane cracking the olefin/paraffin ratio will also depend on the ratio of dealkylation to cracking in the side chain. This can be seen in Fig. 3, where the paraffin/olefin ratio for alkanes and alkenes is plotted vs the logarithm of the dealkylation to cracking ratio. The result is a straight line. Thus as dealkylation relative to side chain cracking increases the ratio of olefins to paraffins increases as well. This occurs because dealkylation (Eq. (1)) gives a C7 olefin and benzene. Further cracking of this product olefin gives two olefins. On the other hand, protolytic cracking (Eq. (2)) of the side chain can give a paraffin and an alkenylbenzene or a alkylbenzene and a relatively hard to crack (compared

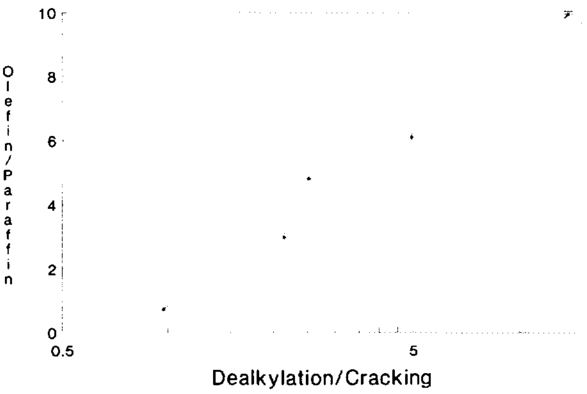


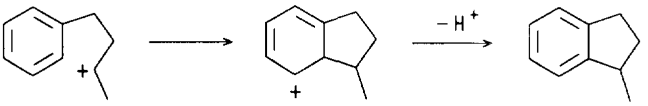
FIG. 3. Olefin/paraffin ratio for alkyl chain fragments vs logarithm of dealkylation/cracking for cracking of 1-phenylheptane.

to larger olefins) short chain olefin. Therefore, the olefin/paraffin ratio depends not only on the intrinsic hydrogen transfer capabilities of the catalyst but also on the ratio of dealkylation to cracking. For these reasons, catalysts which have intrinsically low hydrogen transfer and also high ratios of dealkylation to side-chain cracking should have the highest olefin/paraffin ratios. Medium pore zeolites such as MFI have reduced activity as a result of steric inhibition of the bulky bimolecular transition state (see Eq. (3)) (15). In addition, MFI has a high dealkylation to side-chain cracking ratio. Therefore, in phenylheptane cracking, MFI zeolites have high olefin to paraffin ratios, as can be seen in Table 4. In contrast, MOR and BEA are large pore zeolites with more room to accomodate the bulky hydride transfer reaction and their olefin/paraffin ratios are lower.

The dealkylation to chain cracking ratio is estimated by the ratio of benzene to the sum of substituted benzene products. Benzene results primarily from protonation of the benzene ring of phenylheptane (Eq. (1)) or C(7-*n*)Ph products. Alkyl benzenes arise from side-chain cracking via protolytic (Eq. (2)) and hydride transfer (Eq. (3)) mechanisms. The dealkylation to side-chain cracking ratio varies by over an order of magnitude from USY at the low end to ZSM-5 at the high end.

A number of catalyst properties may influence this ratio. Increasing acid strength should result in increased side chain cracking since protolytic cracking is a more demanding reaction (16). Increasing Si/Al for a particular zeolite increases initial adsorption of the side chain relative to the aromatic ring (4). This increases the chances for side-chain cracking. On the other hand, dealkylation is a unimolecular reaction, whereas side-chain cracking can be either a unimolecular or a bimolecular process. For steric reasons, zeolites with relatively narrow pores, such as MFI (5–6 Å), restrict the space-demanding bimolecular process. This is consistent with relatively high dealkylation/side-chain cracking ratios for MFI compared to large pore zeolites such as USY, BEA, or MOR. Another potential reason for high dealkylation resulting from MFI zeolites involves adsorption. If, for steric reasons, adsorption occurs with the benzene ring leading the alkyl chain, then protonation of the benzene ring, which leads to dealkylation, is more likely to occur than side-chain cracking. On the other hand, if the alkyl chain leads the benzene ring into the zeolite pore, then alkyl chain cracking predominates. For medium pore zeolites like MFI, adsorption of alkyl aromatics is favored when the benzene ring leads the alkyl chain (17). Thus MFI cracking of long chain alkyl aromatics gives relatively high yields of benzene.

The selectivity to bicyclic products should also be dependent on steric constraints dictated by the catalyst architecture. Bicyclic products result from self-alkylation of the benzene ring by a pendant carbenium ion in the side chain:



(4)

One would expect that materials with large internal cavities, such as USY with supercages of about 13 Å diameter, or amorphous silica–alumina with relatively large pores, would give more bicyclic products than MFI. Zeolites with large straight pores would be intermediate between the two extremes. Indeed, this is the case, as shown in Table 4. For MFI, steric constraints for cyclization, as well as high dealkylation to side-chain cracking ratios, which mean few alkyl chain carbenium ions are generated, combine to give a very low yield of cyclization products.

Previous investigators (5) have shown that bicyclic aromatics tend to make coke. Then catalysts and molecular sieves that give significant yields of bicyclic reaction products may deactivate more rapidly due to coke formation that blocks catalyst acid sites and pores.

Those bicyclic aromatics that do not form coke contribute to the aromatics-rich higher boiling FCC gasoline fraction, the so-called heavy gasoline. Heavy gasoline aromatics are one of the primary factors causing automobile engine deposits (18). Engine deposits result in more unwanted engine emissions and higher octane requirements (18).

CONCLUSIONS

Catalytic cracking of long chain alkyl aromatics is a complex process that occurs by a number of reaction pathways. Cracking catalyst composition can significantly alter the relative importance of those pathways and therefore affect product selectivities.

For example, molecular sieve catalysts with large pores and/or large internal cavities have sufficient space to accomodate the transition states for hydride transfer and self-alkylation. Hydride transfer promotes cracking in the alkyl chain, which leads to substituted benzenes and bicyclic aromatic products. In contrast, medium pore sieves with steric constraints, e.g., ZSM-5, facilitate monomolecular processes such as dealkylation (benzene) and protolytic cracking in the side chain. Although protolytic cracking can result in carbenium ions which could lead to self-alkylation, there are almost no bicyclic products due to steric constraints. Other catalyst properties such as Si/Al ratio of the zeolite, adsorption properties, and zeolite geometrical factors also affect cracking catalyst performance.

Therefore, it becomes apparent that zeolite and catalyst properties have a profound effect on the activity, selectivity, and stability of catalysts for 1-phenylheptane cracking, and by extension, on the cracking of long chain alkylaromatics. As a result, long chain alkyl aromatics cracking can be manipulated by an informed choice of catalyst properties and components.

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