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Decalin and Tetralin as Probe Molecules for Cracking and Hydrotreating the Light Cycle Oil

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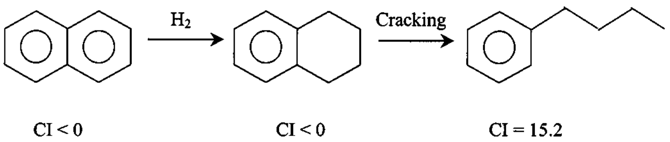
Cracking of tetralin and decalin was carried out over several zeolites to establish the effect of the pore topology of the catalyst on product distribution. These molecules were chosen as probe molecules, because they indicate which catalyst is the best for cracking or hydrotreating the light cycle oil (LCO) fraction, which is obtained directly from fluid catalytic cracking units. A set of zeolites with medium-sized (ZSM-5, MCM-22, ITQ-2), large (USY, Beta), and ultralarge pores (UTD-1), as well as a mesoporous MCM-41, were used as catalysts at 723 K. The results demonstrate that pore size and topology have a strong influence on diffusion, and consequently, on activity and selectivity in reactions such as ring opening, dealkylation, transalkylation, hydride transfer, and coke formation. UTD-1 generally has the highest activity per framework Al owing to the pore size and topology of this zeolite that enables flat molecules to diffuse easily inside the pores. According to the results, zeolites with medium-sized pores are adequate in combination with large-pore zeolites to crack naphthenes and fused aromatic–naphthenic rings, of the type present in LCO, to produce propene. Large-pore zeolites show good selectivity for naphthenic ring opening and appear to be better suited for hydrotreating LCO. Beta zeolite is a catalyst that is especially suitable for both processes.

Key Words: **decalin cracking; tetralin cracking; light cycle oil cracking**

INTRODUCTION

Vacuum gasoil and residual oil are cracked in fluid catalytic cracking (FCC) units to liquid fuels (gasoline and light cycle oil, LCO) for automotive fuels and short-chain olefins that are used as feed stocks in petrochemistry. While FCC gasoline has acceptable research octane (RON) and motor octane numbers (MON), the LCO produced has a low cetane index (∼20) and a high content of aromatics and sulfur. The ability of diesel fuel to burn with the proper characteristics is described by its cetane number, a measure of ignition delay. Excessively long ignition delays (low cetane number) cause rough engine operation, misfiring, incomplete combustion, and poor startability. Cetane (*n*-hexadecane) has a short delay period during ignition and is assigned a cetane number of 100; heptamethylnonane has a long delay period and has a cetane number of 15. Just as the octane number is meaningful for automobile fuels, the cetane number is a means of determining the ignition quality of diesel fuels and is equivalent to the percentage by volume of cetane, in the blend with heptamethylnonane, that matches the ignition quality of the test fuel. Therefore, the direct introduction of LCO into the diesel fuel lowers the overall quality and can limit its use unless LCO is previously hydrotreated. Therefore, the trend in LCO hydrotreating is not only to decrease the sulfur content, but also to partially hydrogenate the polyaromatic compounds to form aromatic–naphthenic molecules that can then be cracked to alkylaromatic compounds. In this way, the cetane number increases, as can be deduced from the cetane index (CI) of the compounds produced.



In this process, a moderate amount of H_2 is consumed, while the cetane index increases. On the other hand, when the demand for LCO is not large, as opposed to that for C_3 and C_4 olefins, LCO can be reintroduced into the FCC unit to crack the naphthenes, aromatic naphthenes, and the alkyl chains in the alkylaromatic molecules.

Therefore, regardless of whether hydrotreating or recracking of LCO is chosen, the cracking of naphthenes and aromatic naphthenes must be carried out. However, depending on the method chosen, the naphthene ring can be opened or the cracking process can be used to produce a large amount of small olefinic molecules.

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We have studied the two methods by selecting two molecules, decalin and tetralin, as model reactants. Once the catalytic cracking pattern for both molecules has been determined, one can rationalize the influence of the pore topology of the zeolite on product distribution and, in this way, select the catalyst that is most suitable for performing naphthenic ring opening or deeper cracking to short-chain olefins.

EXPERIMENTAL

Materials

The USY zeolite was prepared from a partially ammonium-exchanged NaY zeolite (SK-40) by repeated steam calcination and ammonium exchange. The unit cell size of the resultant sample was 24.34 Å. A UTD-1 zeolite was synthesized from a borosilicate, which was prepared in the Al form according to the procedure described elsewhere (1), by substituting boron for aluminum. The ITQ-2 zeolite was obtained by swelling an MCM-22 ($\mathrm{Si/Al} = 15$) precursor with hexadecyltrimethylammonium bromide followed by delamination. Details of this procedure are described elsewhere (2).

Beta, MCM-22 (3), and ZSM-5 (4) were synthesized according to the procedures reported in the literature. An MCM-41 sample with an Si/Al ratio of 17 was synthesized according to the procedure described in Ref. (5) using a hexadecyltrimethylammonium (Panreac 98 wt%) cation as a template and silica (Aerosil Degussa), pseudoboehmite (Catapal B, Vista), and sodium aluminate (Carlo Erba) as the aluminum sources. The sample was activated at 813 K.

The size of the crystallites in the zeolite was determined from the SEM results. Surface area and pore volume were measured by nitrogen adsorption according to the BET method.

Catalytic Experiments

Catalytic experiments were performed at 723 K and atmospheric pressure in a fixed-bed glass tubular reactor (300 mm × 16 mm i.d.) with an independently controlled three-zone heater. The catalyst-to-oil ratio, defined as the amount of catalyst divided by the total amount of reactant (tetralin or decalin) fed in each experiment, was varied from 0.005 to 0.100 $\mathrm{g \cdot g^{-1}}$, depending on the catalyst or reactant used, in order to keep the same range of conversion. The different catalyst-to-oil ratios were obtained by changing the amount of catalyst and feeding a constant weight of reactant (2 g). In order to obtain different conversion levels for a fixed catalyst-to-oil ratio, the final time on stream (TOS), i.e., the time the catalyst has been working, was varied by changing the reactant feed rate with a positive displacement pump. The times of the reaction were 49, 121, 243, 487, and 1214 s for decalin cracking and 45, 112, 224, 449, and 1120 s for tetralin cracking. Zeolites were pelletized and crushed, and the selected particle size was 0.50 to 0.75 mm, for which no control of internal diffusion was observed. The experimental procedure used in this work has been described previously (6).

Reaction products were analyzed by gas chromatography (GC) in a Hewlett Packard 6890 Series chromatograph using an HP-1 capillary column (100 m long) connected to a thermal conductivity detector and to a flame ionization detector in series.

Cumulative average conversion (X) is defined as the total number of carbon atoms of outlet hydrocarbons, other than the feed, divided by the number of carbon atoms in the reactant fed. The product yield is defined as the moles of product per mole of reactant fed.

Thermal cracking experiments were carried out with both reactants. All the reaction conditions were the same as those in the presence of the catalyst. The conversions due to thermal cracking at the longest TOS were practically negligible, i.e., 1.0% for tetralin and 0.3% for decalin. In any case, these thermal results were taken into account when determining conversion and product yields.

RESULTS AND DISCUSSION

The dimensions of decalin and tetralin as determined by the Cerius 2 Molecular Simulations Inc. program are given in Fig. 1. The distances are given in angstroms, and the van der Waals diameter of hydrogen should be added. Even with the approximations made, it can be seen that these molecules will easily penetrate the 12-member-ring (MR) zeolite pores, but the diffusion will be hindered in the case of 10 MR zeolites. The same was assumed for molecules formed by three condensed rings. A series of zeolites with 10, 12, and 14 MR pores as well as a mesoporous Al-MCM-41 were then prepared. The physicochemical characteristics are given in Table 1. We selected two 10 MR pore zeolites, which perform well in the production of short-chain olefins (MCM-22 (3) and ZSM-5 (7)), as potential catalysts together with ITQ-2 (3), two zeolites with large pores (USY, Beta), and a zeolite with ultralarge pores (UTD-1).

Conversion plots obtained for decalin and tetralin at different contact times, at a fixed time on stream (45 s for decalin and 49 s for tetralin), are given in Fig. 2. The slopes in the conversion vs contact time curves, when the contact time is close to zero, were obtained. They represent the initial reaction rates (Table 2). From the initial reaction rates and the turnover numbers (TON) (calculated by dividing the initial reaction rates by the number of micromoles of pyridine per gram of catalyst which are still adsorbed at 400°C desorption temperature and which correspond to the number of strongest acid sites), it is clear that those values are higher for large-pore than for medium-pore zeolites. Consequently, we conclude that decalin and tetralin can penetrate some of the pores of the 10 MR zeolites,

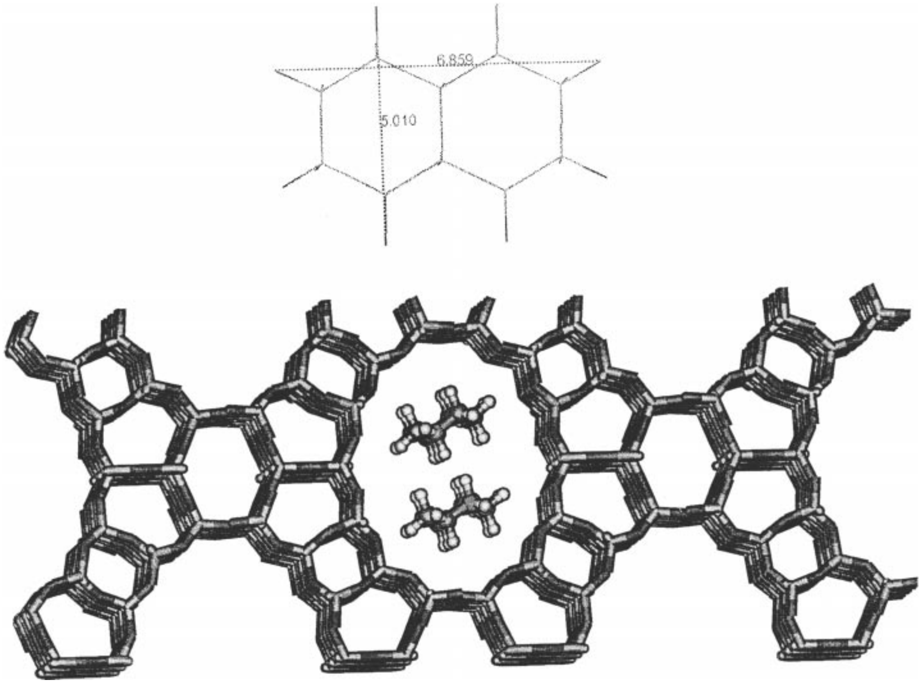


FIG. 1. Dimensions of decalin and tetralin molecules and the fitting of two molecules in the channels of UTD-1.

but they do not reach all the acid sites. It is remarkable that, when the MCM-22 was delaminated to give the corresponding ITQ-2 sample, the accessibility of the acid sites to the reactants improved considerably, the TON increasing by about 25 for the reaction of decalin and tetralin.

However, even more surprising are the large differences in the intrinsic activity of the 12 MR zeolites. Despite being crystallized with small crystallites (0.2 μm), Beta gives the lowest conversion. This is due to the fact that the Beta zeolite has two channels 7.2 × 6.2 Å in diameter, and a third channel that is only 5.5 × 5.5 Å wide, so that decalin and tetralin probably cannot diffuse in that direction. On the other hand, UTD-1, which has a unidirectional pore topology, gives the highest TON owing to the shape of the pores (7.5 × 10 Å), which probably enables a fast diffusion of the relatively flat decalin and tetralin molecules. The results of this study agree with those obtained during the catalytic cracking of another flat molecule (triisopropylbenzene) in several 12 MR zeolites and UTD-1 (1). In that study, it was shown that UTD-1 has a higher intrinsic activity. It was hypothesized that this zeolite is a very adequate catalyst in reactions with larger flat molecules.

In order to gain further insight into the interactions between the zeolite and the reactants, docking of decalin in Beta, USY, and UTD-1 zeolites was carried out with

TABLE 1

Properties of Catalysts Used in This Work

					Acidity[a] (μmol Py/g)					
					Brønsted (1545 cm^{-1})			Lewis (1450 cm^{-1})		
Catalyst	Si/Al ratio	Area BET (m^2/g)	Crystal size (μm)	Micropore volume (cm^3/g)	250°C	350°C	400°C	250°C	350°C	400°C
ZSM-5	15	380	1.5–2.5	0.12	44	26	12	9	6	5
MCM-22	15	400	0.38	0.17	42	33	24	21	20	18
ITQ-2	15	600			16	5	1	16	17	—
Beta	16	600	<0.2	0.24	22	9	5	37	35	33
USY	15[b]		0.6	0.161	44	16	5	19	13	9
UTD-1	80	305	0.2–0.3	0.091	8	3	1	7	5	5
A1-MCM-41	17				12	6	3	47	34	24

[a] Acidity measured by pyridine adsorbed and desorbed at different temperatures according to Emeis *et al.* (17).

[b] Framework Si/Al ratio from XRD data and Fichtner–Schmittler's equation (18); Si/Al ratio of other zeolites based on chemical analysis.

TABLE 2

Rates and TON in Decalin and Tetralin Cracking over Different Catalysts Measured at 49 and 45 s of TOS for Tetralin and Decalin respectively at 723 K

	Rates (g · g^{-1} · h^{-1})		TON$_{400^\circ C}$ (g · μmol Py^{-1} · h^{-1})	
Catalyst	Tetralin	Decalin	Tetralin	Decalin
ZSM-5	106	103	8.8	8.6
MCM-22	39	60	1.6	2.5
ITQ-2	41	58	41.4	58.0
Beta	395	454	79	90.8
USY	561	899	112	180
UTD-1	410	714	410	714
Al-MCM-41	10	14	3.3	4.7

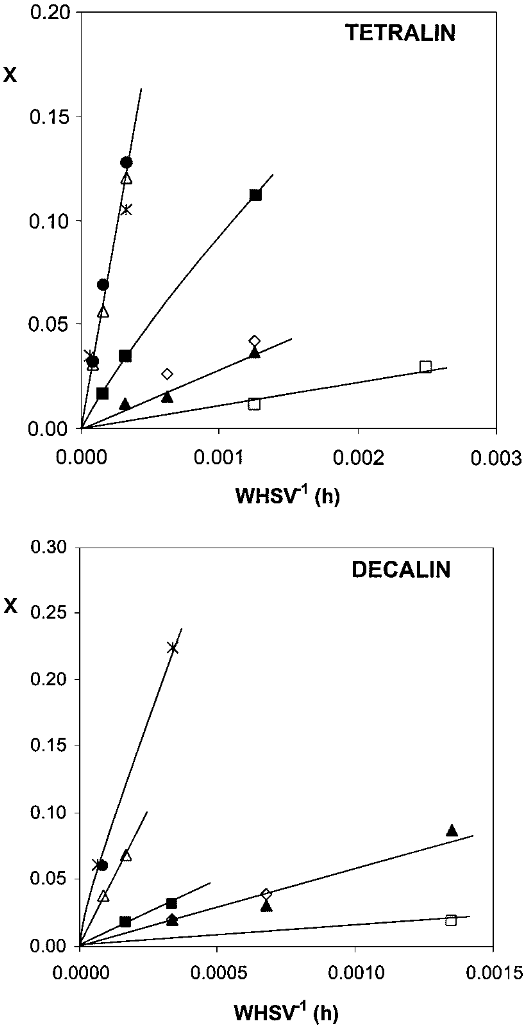


FIG. 2. Cumulative conversion versus contact time (weight hourly space velocity^{-1}) for different catalysts in tetralin and decalin cracking. Experimental points: (●) UTD-1, ($*$) USY, (△) Beta, (▲) MCM-22, (◇) ITQ-2, (■) ZSM-5, and (□) Al-MCM-41 catalysts.

the Cerius program. The results indicate that decalin and tetralin diffuse within the pores of the three zeolites, but they diffuse much better in the pores of UTD-1. It is remarkable that, in the case of the 14 MR zeolite, two molecules fit together in the channel (see Fig. 1). It is thus concluded from the theoretical as well as from the experimental work that UTD-1 reacts especially well with flat molecules that can diffuse through its pore structure. This zeolite is, thus, better than the others with a tridirectional large-pore network system.

The mesoporous MCM-41 material with a pore diameter of 35 Å is almost inactive due to the small number of acid sites that are strong enough for the cracking of the naphthenic ring. A similar conclusion was reached after cracking *n*-alkanes with MCM-41 (8).

Product Distribution

Tetralin cracking. A large number of products is obtained after reacting tetralin; 40 major products were detected and quantified. The yield of each product was plotted against total conversion, and an example of the curves obtained for some products with the ZSM-5 catalyst are given in Fig. 3. From these curves, the initial selectivities were calculated, and the results are given in Table 3. When reacting tetralin, C1 to C4 fraction, naphthalene, benzene, and C10 olefin/naphthene aromatics (O/N-AC10) (mainly methylindanes) account for close to 85% of the total conversion, and their relative initial selectivity changes from one zeolite to another.

It is quite clear that, to form the above products from tetralin, reactions such as ring opening, dealkylation, transalkylation, and hydrogen transfer must be involved. It has been reported in the literature (9) that the reaction of tetralin can be initiated by two different mechanisms: a bimolecular mechanism, which is responsible for the formation of species related to phenylbutyl tetralin (PBT), and a unimolecular mechanism. Under our reaction conditions and a relatively high temperature, the amount of PBT was negligible and, consequently, the unimolecular initiation step (Scheme 1), involving the attack of a Brønsted site either on the aromatic ring (10) or on the naphthenic ring (11, 12), dominates. β-Scission and protolytic cracking of the resultant carbenium and carbonium ions can explain the opening of the naphthenic ring, forming alkenyl and alkylbenzenes respectively (Scheme 1). On the other hand, an isomerization reaction can occur by means of a PCP mechanism (13), which may be responsible for the contraction of the ring and the formation of methylindanes and methylindenes.

Dealkylation reactions (14) produce gaseous molecules and aromatics with fewer than 10 carbon atoms (Tables 3 and 4), while disproportionation reactions between carbenium ions and aliphatic species (15) or between aromatics and olefins can explain the formation of aliphatic and

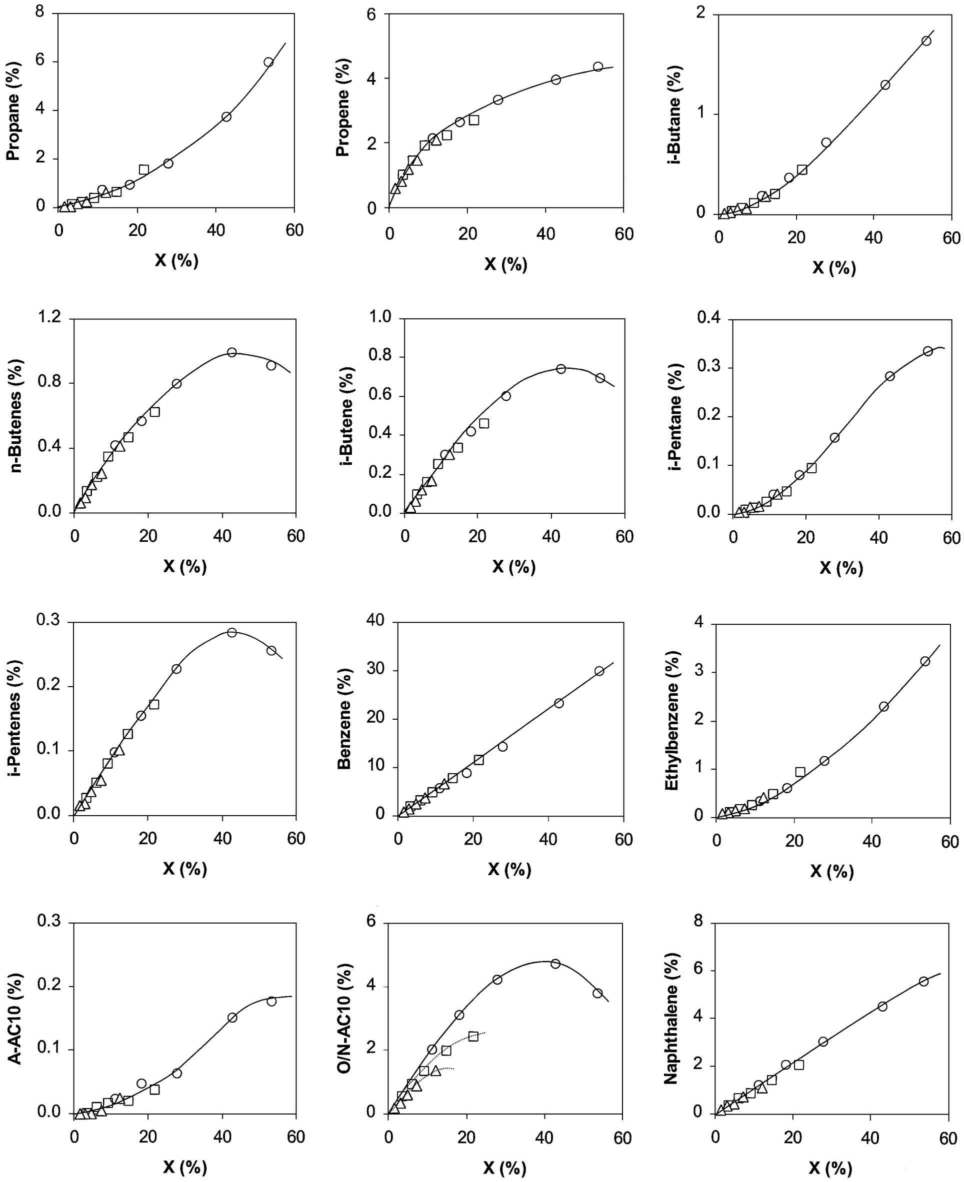


FIG. 3. Yield (mol%) versus conversion of primary products in tetralin cracking over ZSM-5 zeolite. Experimental points: (△) 0.0125, (□) 0.0250, and (○) 0.1000 catalyst/oil ratios. Unbroken lines represent catalyst behavior without deactivation.

aromatic compounds with more than 4 and 10 carbon atoms respectively. Scheme 2 shows, for example, transalkylation reactions between several aromatic species and the butane and butene obtained from tetralin by ring opening (10).

The formation of naphthalene as a primary product is explained by fast hydrogen transfer between tetralin and the adsorbed carbenium ions formed during the isomerization and ring opening of tetralin. Saturation of the benzene ring of tetralin was detectable only with zeolite USY and to a much lesser extent than the amount of naphthalene that was formed. The extent of the bimolecular hydrogen transfer reactions can also be evaluated by means of the paraffin/olefin (P/O) ratio in the reaction products (Table 4). Scheme 1 shows the main reactions that occur during the cracking of tetralin and the products involved. The fact that both unimolecular and bimolecular reactions take place and that intermediates and final products of different dimensions are formed precludes the pore dimensions of the zeolite affecting the initial selectivities.

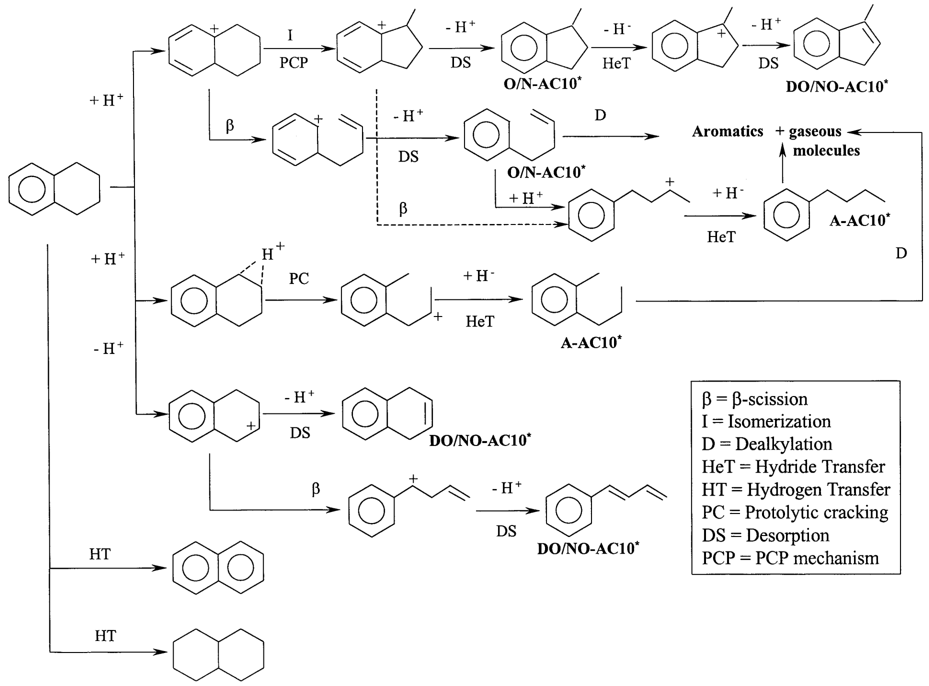
The results in Tables 3 and 4 clearly show that bimolecular hydrogen transfer (naphthalene and P/O ratio) occurs to a much smaller extent with the 10 MR ZSM-5 zeolite than with the other molecular sieves; hydrogen transfer probably occurs mainly on the outer surface of the crystals of ZSM-5. MCM-22 results in greater hydrogen transfer than does ZSM-5, probably due to the larger external surface of the

TABLE 3

Initial Molar Selectivities of Products in Tetralin Cracking at 723 K

Product	Catalyst							
	ZSM-5	MCM-22	ITQ-2	Beta	USY	USY-24.26	UTD-1	Al-MCM-41
C1 + C2 Fractions	0.0017	0.0000	0.0049	0.0092	0.0024	0.0000	0.0000	0.0016
Propane	0.0209	0.0498	0.0400	0.0398	0.0453	0.0454	0.0412	0.0000
Propene	0.3534	0.1520	0.1089	0.1639	0.0663	0.0830	0.0310	0.0370
C4 Fraction	0.0690	0.0612	0.1225	0.0668	0.1286	0.1363	0.0934	0.0283
C5 Fraction	0.0120	0.0058	0.0167	0.0093	0.0266	0.0160	0.0138	0.0047
C6 Aliphatics	0.0040	0.0000	0.0059	0.0033	0.0074	0.0048	0.0059	0.0051
C6 Naphthenics	0.0059	0.0046	0.0088	0.0043	0.0164	0.0166	0.0203	0.0185
AC6^a	0.5130	0.1567	0.1951	0.1753	0.0933	0.1076	0.0807	0.0670
C7 Aliphatics	0.0035	0.0000	0.0019	0.0000	0.0173	0.0208	0.0054	0.0000
C7 Naphthenics	0.0007	0.0035	0.0033	0.0010	0.0013	0.0042	0.0042	0.0000
AC7^a + AC8^a	0.0721	0.0457	0.0592	0.0610	0.0522	0.0758	0.0201	0.0000
A-AC9^a	0.0000	0.0033	0.0000	0.0150	0.0125	0.0000	0.0000	0.0000
O/N-AC9^a	0.0243	0.0141	0.0216	0.0484	0.0316	0.0000	0.0109	0.0155
A-AC10^a	0.0000	0.0079	0.0276	0.0162	0.0635	0.1084	0.1586	0.0145
O/N-AC10^a	0.1498	0.3373	0.3247	0.3153	0.1119	0.1710	0.2338	0.4563
DO/NO-AC10^a	0.1118	0.0415	0.0112	0.0225	0.0123	0.0090	0.0062	0.0968
c-Decalin	0.0000	0.0000	0.0000	0.0000	0.0219	0.0000	0.0000	0.0000
Naphthalene	0.1008	0.2003	0.2417	0.1722	0.4332	0.3503	0.3461	0.1845
O/N-AC11^a	0.0550	0.0649	0.0431	0.0942	0.0371	0.0575	0.0319	0.0331
Methylnaphthalenes	0.0089	0.0000	0.0114	0.0252	0.0134	0.0118	0.0088	0.0110
O/N-AC12^a	0.0037	0.0034	0.0037	0.0063	0.0035	0.0015	0.0012	0.0007
Coke	0.0206	0.0170	0.0350	0.0290	0.0369	0.0267	0.0459	0.1053

[a] AC6, C6 aromatic (C_6H_6); AC7, C7 aromatic (C_7H_8); AC8, C8 aromatic (C_8H_{10}); A-AC9, C9 alkyl aromatics (C_9H_{12}); O/N-AC9, C9 olefin or naphtheno aromatics (C_9H_{10}); A-AC10, C10 alkyl aromatics ($C_{10}H_{14}$); O/N-AC10, C10 olefin or naphtheno aromatics ($C_{10}H_{12}$); DO/NO-AC10, C10 diolefin or naphtheno-olefinic aromatics ($C_{10}H_{10}$); O/N-AC11, C11 olefin or naphtheno aromatics ($C_{11}H_{14}$); O/N-AC12, C12 olefin or naphtheno aromatic ($C_{12}H_{16}$). Examples of these molecules are shown in Schemes 1–4.



SCHEME 1. Reaction scheme for catalytic cracking of tetralin. See Table 3 for symbols.

TABLE 4

Molar Selectivities to Gaseous Products and P/O Ratio Obtained from the Reaction of Naphthenes

	Gases		P/O	
Catalyst	Tetralin	Decalin	Tetralin	Decalin
ZSM-5	0.4450	1.0872	0.07	0.27
MCM-22	0.2630	1.1540	0.60	0.49
ITQ-2	0.2763	0.9869	1.14	0.62
Beta	0.2797	0.6606	0.51	0.70
USY	0.2426	0.2677	1.85	2.32
USY-24.26	0.2647	—	1.30	—
UTD-1	0.1656	0.2734	2.23	1.09
Al-MCM-41	0.0669	0.8632	0.27	0.24

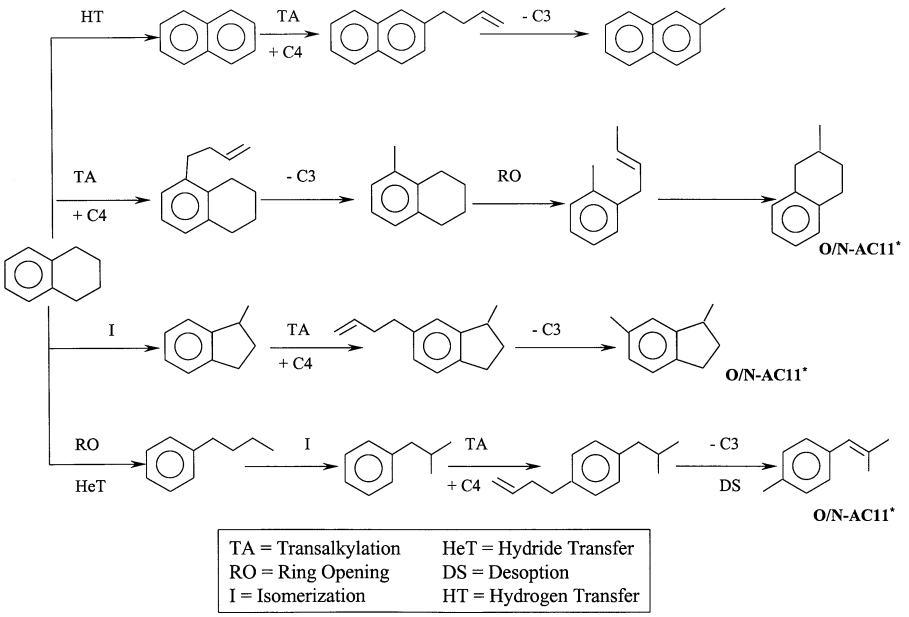
former due to the well-defined 12 MR “cups” of ~7 × 12 Å (16). This is supported by the fact that, when the number of those “cups” at the external surface increases after the delamination process (2) that produces the ITQ-2 structure, hydrogen transfer increases, even when the density of the acid sites in ITQ-2 is half that in MCM-22 (Table 1).

In the case of ZSM-5 when the naphthenic ring is opened, the long-chain alkyl or alkenyl group in the resultant alkylbenzene rapidly cracks, giving propene and benzene as the major products.

For a more quantitative comparison of the selectivity of dealkylation of the different zeolites, we calculated the dealkylation selectivity of tetralin based on the reactions represented by Schemes 1 and 2. According to these schemes, each aromatic molecule with 10 or more carbon atoms is probably obtained from one tetralin molecule which has not undergone dealkylation. Moreover, due to the instability of methylcarbenium ions, alkyl C9 aromatics cannot form by cracking of tetralin and the low selectivity of methane over all the catalysts shows that a minimum number of olefinic or naphthenic C9 aromatics is produced through this route. Thus, C9 aromatics must be produced through disproportionation reactions. On the other hand, coke selectivity (Table 3) is expressed as a hypothetical molecular formula of $C_{10}H_8$ and was based on the experimental H/C ratio of coke (0.8). Coke clearly has a more complex structure, and a higher molecular weight, in which polyaromatic condensed rings exist, but we assume that coke aggregates and their selectivity increase as tetralin molecules become attached to the coke aggregates and dehydrogenate. If this is so, then the sum of the selectivities of coke and aromatics with more than 10 carbon atoms is a good indication of the molecules that not to dealkylate, being equal to the difference between unity and the selectivity to dealkylation. Thus, we can calculate the dealkylation selectivity during tetralin cracking from Eq. [1]. The dealkylation selectivity values obtained from Eq. [1] and the selectivities given in Table 3 are reported in Table 5.

$$S_{\text{dealkylation}} = 1 - S_{\text{coke}} - S_{\text{C12 aromatic}} - S_{\text{C11 aromatic}} - S_{\text{C10 aromatic}} - S_{\text{C9 aromatic}}. \quad [1]$$

Thus, we suggest that cracking LCO in the FCC unit, with a ZSM-5 additive in the catalyst, will crack the alkyl chains of the cyclic products present in LCO to give mainly propene, leaving highly refractory aromatic rings. However, with aromatic–naphthenic rings, ZSM-5 will be less active



SCHEME 2. Possible disproportionation reactions (transalkylation + cracking) in tetralin cracking. See Table 3 for symbols.

TABLE 5

Molar Selectivities to Dealkylation[a] Obtained in Tetralin and Decalin Cracking

Catalyst	Tetralin	Decalin
ZSM-5	0.525	0.548
MCM-22	0.311	0.737
ITQ-2	0.280	0.671
Beta	0.256	0.521
USY	0.223	0.224
UTD-1	0.157	0.232
Al-MCM-41	0.082	0.540

[a] Calculated from Eq. [1].

for ring opening, which will occur mainly on the external surface of the crystallites.

Thus, in a first approximation, a suitable catalyst for cracking LCO, while producing propene, should involve a catalytic function able to open the naphthenic rings together with ZSM-5 zeolite that can crack the branched naphthenic or alkylaromatic molecules while producing propene.

On the other hand, if the goal is to improve the quality of the LCO to be introduced into the diesel pool by hydrotreating the LCO with a bifunctional catalyst based on a zeolite, ZSM-5 or other medium-pore zeolites do not

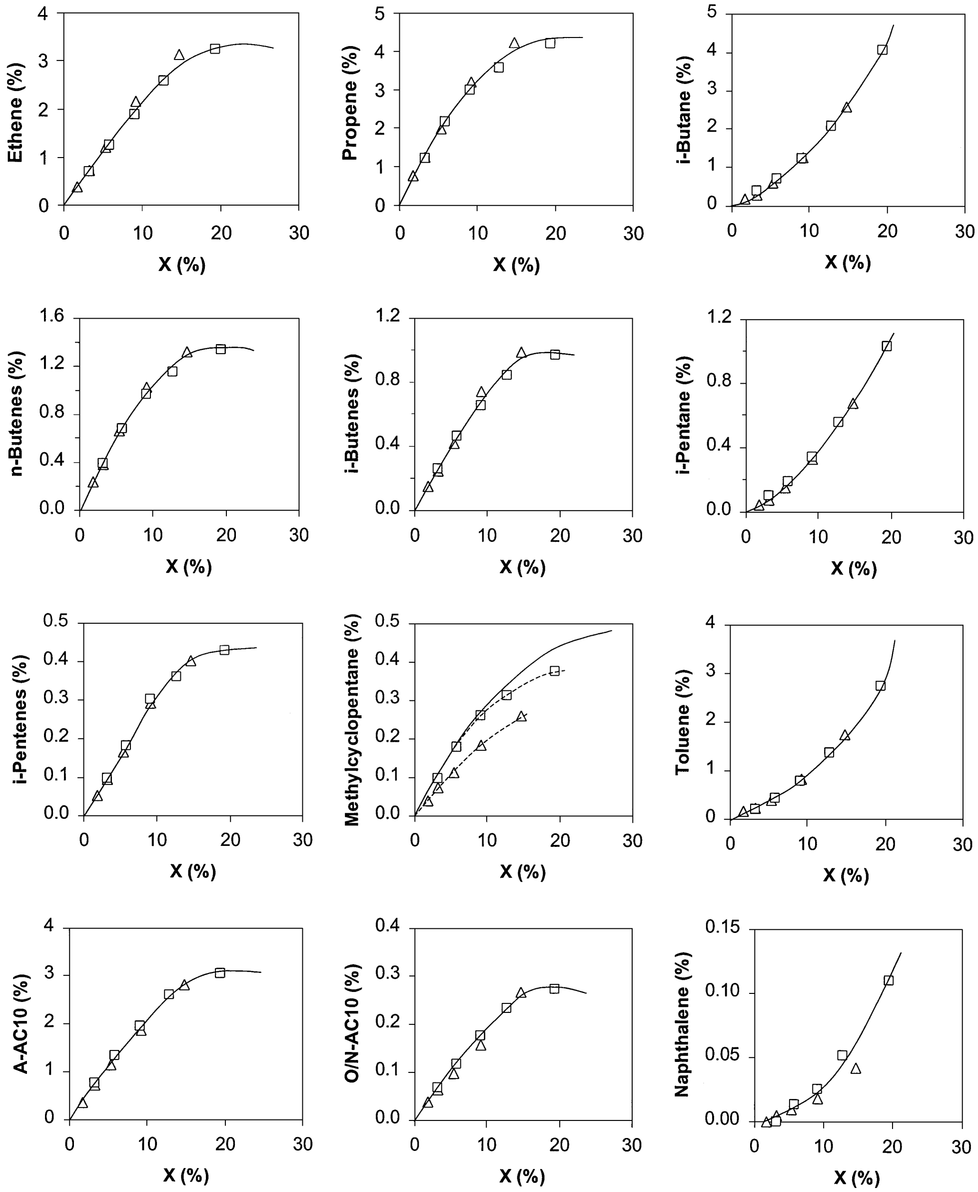


FIG. 4. Yield (mol%) versus conversion for primary products in decalin cracking over ZSM-5 zeolite. Experimental points: (△) 0.0125 and (☐) 0.0250 catalyst/oil ratios. Solid lines represent catalyst behavior without deactivation.

seem to be suitable as an acid function, since they can hardly deal with the polyaromatic and aromatic–naphthenic rings present in the LCO fraction. Moreover, after opening of the rings, the cracking of the alkyl or alkenyl chains takes place too rapidly, leading to too many gaseous molecules.

In the case of 12 and 14 MR zeolites, it is seen (Table 3) that USY and UTD-1 produce a large amount of naphthalene and coke. It is remarkable that UTD-1, even with a very high Si/Al ratio (80), is still highly selective for bimolecular reactions. This is probably due to the unidirectional character and the size of the pores that enable the close fit of two molecules at distances great enough for bimolecular reactions to occur (see Fig. 1).

In order to differentiate between the influence of the framework Si/Al ratio and the influence of the pore topology, a second USY zeolite with a framework Si/Al ratio of 60 (unit cell size = 24.26 Å) was also studied. The results show (Tables 3 and 4) that hydrogen transfer and coke formation decrease with the increasing ratio of the framework Si/Al of the zeolite. Based on this and the selectivity obtained with UTD-1, we suggest that the pore topology of UTD-1, or even the presence of traces of cobalt, plays an important role in the high hydrogen transfer and coke yields.

Of the 12 MR zeolites, Beta is a good all-round zeolite as far as activity, yield of gases, alkylaromatic formation, and hydrogen transfer are concerned. Indeed, from the LCO cracking point of view, Beta may be a good component of an acid catalyst, since it produces the smallest amount of naphthalene and coke of the large-pore zeolites studied. It shows good selectivity to alkylaromatics or naphthenoaromatics and the highest selectivity to propene. Thus, Beta zeolite, in combination with ZSM-5, may be a very suitable catalyst in the FCC unit for the cracking of LCO to propene.

Because of the characteristics of Beta zeolite outlined above and its high selectivity to ring opening and low selectivity to gaseous molecules, it may also be a suitable catalyst component for LCO partial hydrogenation and ring opening.

In conclusion, when reacting aromatic–naphthenic condensed rings as present in LCO, and if one only wants to open the ring in order to improve the cetane number, then a large-pore zeolite is preferred over medium-pore zeolites. In that case USY or Beta would be preferred. On the other hand, if LCO has to be cracked, to increase the yield of propene, then a catalyst with a large-pore zeolite, in particular Beta and ZSM-5, would be more suitable.

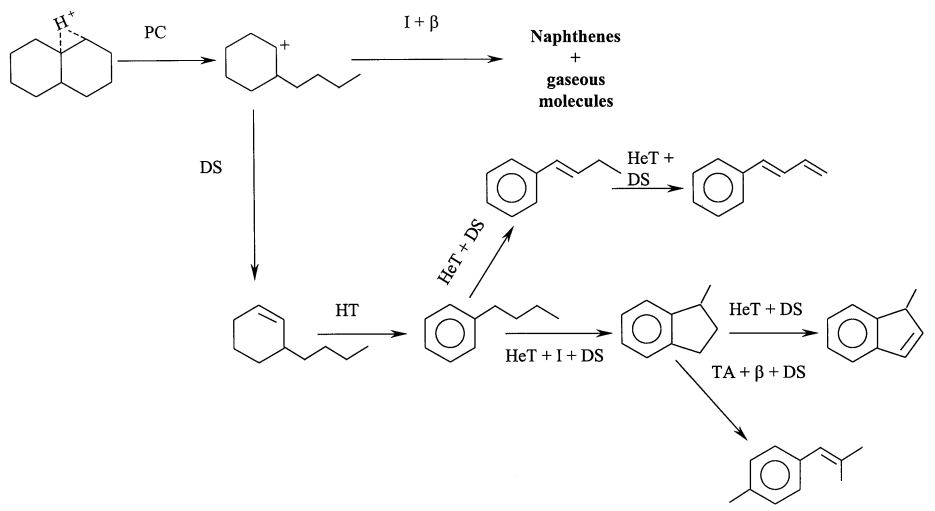
Decalin cracking. During the cracking of decalin, gaseous molecules, C6 naphthenics (mainly methylcyclopentane), and C10 aromatics (butylbenzenes) are produced in especially large amounts (Fig. 4 and Table 6). Moreover, the amount of tetralin and naphthalene formed

TABLE 6

Initial Molar Selectivities of the Products in Decalin Cracking at 723 K

	Catalyst						
Product	ZSM-5	MCM-22	ITQ-2	Beta	USY	UTD-1	Al-MCM-41
Methane	0.0003	0.0000	0.0080	0.0037	0.0000	0.0006	0.0028
Ethene	0.2199	0.1248	0.0733	0.0197	0.0046	0.0101	0.0327
Propane	0.0810	0.1136	0.0419	0.0220	0.0253	0.0072	0.0183
Propene	0.4336	0.3206	0.3088	0.1710	0.0431	0.0638	0.2962
C4 Fraction	0.3523	0.5950	0.5520	0.4434	0.1946	0.1915	0.5133
C5 Fraction	0.0817	0.1001	0.1252	0.1624	0.0573	0.0532	0.1072
C6 Aliphatics	0.0234	0.0575	0.0607	0.0651	0.0303	0.0318	0.0868
C6 Naphthenics	0.0559	0.1164	0.1208	0.1433	0.1017	0.1071	0.1756
AC6[a]	0.0168	0.0176	0.0127	0.0090	0.0031	0.0020	0.0035
C7 Aliphatics	0.0183	0.0458	0.0403	0.0392	0.0317	0.0313	0.0259
C7 Naphthenics	0.0101	0.0556	0.0369	0.0325	0.0066	0.0190	0.0057
AC7[a] + AC8[a]	0.1407	0.1514	0.0900	0.0501	0.0275	0.0193	0.0258
A-AC9[a]	0.1298	0.1045	0.1155	0.1527	0.2828	0.2403	0.1676
O/N-AC9[a]	0.0320	0.0044	0.0185	0.0405	0.0585	0.0550	0.0465
A-AC10[a]	0.2371	0.0642	0.1321	0.2076	0.3313	0.3765	0.1826
O/N-AC10[a]	0.0215	0.0392	0.0257	0.0325	0.0347	0.0383	0.0198
DO/NO-AC10[a]	0.0000	0.0252	0.0135	0.0148	0.0408	0.0156	0.0042
Tetralin	0.0099	0.0000	0.0000	0.0000	0.0000	0.0086	0.0000
Naphthalene	0.0000	0.0032	0.0048	0.0007	0.0036	0.0046	0.0000
O/N-AC11[a]	0.0019	0.0091	0.0045	0.0073	0.0071	0.0041	0.0000
Methylnaphthalenes	0.0000	0.0009	0.0000	0.0023	0.0016	0.0033	0.0000
O/N-AC12[a]	0.0000	0.0000	0.0000	0.0006	0.0000	0.0005	0.0000
Coke	0.0199	0.0125	0.0140	0.0200	0.0165	0.0209	0.0395

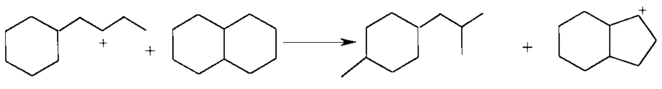
[a] Abbreviations as in Table 3.



SCHEME 3. Mechanisms of reactions of decalin over acid catalysts (capital letters as in Schemes 1 and 2).

is very small, indicating that the direct dehydrogenation of decalin by hydrogen transfer is negligible. Consequently, when reacting decalin, the ring is opened first, followed by dealkylation and hydrogen transfer. Based on this and the nature of the rest of the products formed (Table 6), we can draw the reaction scheme for decalin (Scheme 3). The reaction is initiated by the attack of a Brønsted site on a carbon–carbon bond of the decalin (11) forming a carbonium ion, which cracks protolytically to an alkylnaphthene carbenium ion. The formation of gaseous molecules and naphthenes lighter than the feed can be explained by unimolecular reactions, involving the isomerization and β-scission of the alkylnaphthene carbenium ion. Meanwhile, bimolecular hydrogen transfer and hydride transfer produce C10 alkyl, alkenyl, or naphthene aromatics. Other bimolecular disproportionation reactions, involving transalkylation and cracking, are also responsible for the formation of aromatics with more carbon atoms than the feed. Furthermore, C9 aromatics can be formed by a bimolecular process such as that represented by Scheme 4. The naphthenic species included in Scheme 4 can react further by hydride and hydrogen transfer to give the corresponding aromatics.

At this point by analyzing the rates of the reaction for decalin (Table 2), the selectivities for dealkylation and gaseous molecules (Tables 5 and 4), and the hydrogen transfer (P/O ratio) (Table 4), we conclude the following: Decalin reacts faster than tetralin, and 10 MR zeolites are much less active than 12 MR zeolites in reaction with decalin (Table 2). This is also a clear indication that decalin hardly penetrates the channels of the medium-pore zeolite. In the case of MCM-22, the reaction occurs on the external surface and, consequently, the activity per site increases strongly (Tables 1 and 2) when the external surface is increased by delamination (ITQ-2 sample). In the case of the 12 MR zeolites, the order of activity is the same as that previously observed when reacting tetralin; again the high activity per site of the 14 MR UTD-1 zeolite is surprising.



SCHEME 4. Possible reaction for formation of C9 species.

As far as selectivity is concerned, it is remarkable that no alkylnaphthenes with longer chains are found. They readily crack and transfer hydrogen, giving alkylaromatics. Thus, even ZSM-5 gives a reasonable number of alkylaromatics but a smaller number than that produced with 12 MR zeolites. In the case of decalin, UTD-1 is again the most active catalyst in the bimolecular reactions and, more specifically, hydrogen transfer. On the other hand, the dealkylation and gas selectivities are higher for the 10 MR than for 12 MR zeolites. Of the large-pore zeolites, Beta gives the greatest number of gaseous molecules. This correlates well with the pore dimensions of the zeolites, because the smaller the pores, the greater the probability of secondary unimolecular reactions such as dealkylation and cracking reactions. The relatively large amounts of ethene produced by ZSM-5 and MCM-22 and the fact that Beta zeolite produces the highest yield of propene of the 12 MR zeolites is noteworthy.

These results suggest that a good LCO cracking catalyst for the production of naphthenes should involve a large-pore zeolite for primary cracking. Beta is a very suitable zeolite for this, together with ZSM-5 that can crack the smaller products formed after the primary cracking on Beta zeolite to give high yields of propene and ethene.

CONCLUSIONS

Decalin and tetralin are excellent probe molecules for studying the cracking behavior of cycloalkanes and aromatic naphthene condensed ring molecules in the LCO fraction on either monofunctional or bifunctional zeolite-based catalysts. Thus, studying the reactivity of these two molecules on a series of 10, 12, and 14 MR zeolites showed the following:

If the aim is to crack LCO in the FCC unit and to maximize the amount of propene formed, a "cocktail" of large- and medium-pore zeolites is preferred. The large-pore zeolite (preferably Beta) will open the naphthenic ring, while the 10 MR zeolite (ZSM-5 or MCM-22) will crack the branched naphthenics or alkylaromatics formed to propene.

If, on the other hand, the goal is to improve the quality of the LCO, i.e., to decrease the number of aromatics and increase the CI, the LCO should be hydrotreated with a bifunctional catalyst based on a 12 MR zeolite (USY or even better Beta zeolite). The partially hydrogenated polycyclic aromatic rings will then open and the cracking of the resultant alkyl chains will be minimized.

In the case of the FCC operation, the aromatic naphthene condensed rings will crack on large-pore USY or Beta zeolite, opening the naphthene ring and minimizing the dealkylation of the alkylaromatic formed.

It is remarkable that, owing to its pore size and shape, UTD-1 has higher activity per active site than any of the other zeolites studied and is highly selective for bimolecular reactions (hydrogen transfer) owing to the possibility of fitting two molecules that are in close proximity in the channels.

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