JOURNAL OF CATALYSIS 12, 341–346 (1968)

The Chemistry of Catalytic Cracking with Molecular Sieve Catalysts

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Received July 22, 1968; revised August 30, 1968

In the commercial catalytic cracking of high-boiling petroleum fractions, the crystalline molecular sieve type catalysts exhibit three outstanding differences in comparison to the noncrystalline silica-alumina catalysts. (1) They are more active. (2) The gasoline contains more paraffins and aromatics and fewer olefins. (3) A greater proportion of the petroleum can be cracked before cracking ("over-cracking") of the gasoline begins. It is proposed that the primary cracking step is the same for both catalysts and the differences are ascribed to differences in secondary reactions of a hydrogen transfer nature. With the molecular sieve catalysts, the gas-oil molecules are too large to enter the catalyst cavities, so cracking occurs on the external surface, but the gasoline molecules can enter the cavities and the secondary reactions occur there. With the large pores of the noncrystalline silica-alumina, there is no separation of sites for the primary and secondary reactions. The observed differences are rationalized using these concepts.

It is now well established that molecular sieve type cracking catalysts have three readily identifiable differences from conventional, noncrystalline silica-alumina when cracking high-boiling petroleum distillates: (1) They are more active. (2) They permit higher conversions per pass without excessive gas and coke formation. (3) The gasoline contains more paraffins plus aromatics and fewer olefins.

The objective of the present work is to describe catalyst features and reaction paths which rationalize these differences. This is done fully realizing that the proposed mechanism is not unique, but with the hope it will encourage others to contribute to understanding cracking catalysis.

NATURE OF MOLECULAR SIEVE CRACKING CATALYSTS

Commercial cracking catalysts are made up of a minor part, usually 5–15%, of faujasite-type molecular sieve on or in a support. The support nature can vary widely, but is usually an aluminosilicate material of some type. Often it is conventional silica-alumina of the same type and composition as the noncrystalline cracking catalyst. It usually has some activity as a cracking catalyst.

CRACKING WITH COMMERCIAL MOLECULAR SIEVE CRACKING CATALYSTS

To examine cracking with molecular sieves, it is desirable to separate its cracking from cracking by the matrix since both will be contributing to the overall cracking rate. Commercial plant data are available (*1*) which permit an approximate separation. The data were obtained using Durabead 1, a conventional, noncrystalline, silica-alumina catalyst and Durabead 5, a molecular sieve catalyst, operating under comparable conditions with three different feed stocks.

NATURE OF THE MOLECULAR SIEVE CATALYST

Our examination of a sample of Durabead 5 is consistent with published descriptions (*2*, *3*, *4*). It can be summarized as about 10% rare earth-exchanged faujasite particles supported in a 90% amorphous silica-alumina matrix. The 1000 Å "fissures" described in ref. (*2*) were present in the matrix.

Independent tests on synthetic faujasite using standard X-ray diffraction techniques (*5*) indicated a crystallite size of about 1500 Å (*6*). The ~1-μ particles usually seen are probably polycrystalline.

From this description, it is useful to identify three different site locations, each which its own intrinsic activity:

(1) The amorphous silica-alumina matrix which has activity typical of such catalysts.

(2) The external surface of the molecular sieve crystallite.

(3) Inside the supercavity of the molecular sieve.

The following table summarizes the conversions obtained with three different feed stocks and the two catalysts at 480°.

Feed stock	Volume % conversion obtained	
	Durabead 5	Durabead 1
California gas-oil	73.4	49.5
Coker gas-oil	58.8	48.6
Gachsaran gas-oil	78.2	61.2

From the data in ref. (*1*) the molecular weights of the combined feeds (including recycle) were estimated: California Gas Oil, 245; Coker Gas Oil, 175 and Gachsaran, 252. Taking 0.8 and 0.75 as the bulk densities for Durabead 5 and 1, respectively, and converting volume % conversion to weight % conversion on the combined feed (initial + recycle), it was possible to estimate cracking rates as molecules cracking sec^{-1} g^{-1} catalyst.

Feed	Molecules cracked sec^{-1} g^{-1} catalyst	
	Durabead 5	Durabead 1
California gas-oil	3.25×10^{17}	2.06×10^{17}
Coker gas-oil	3.95×10^{17}	2.81×10^{17}
Gachsaran gas-oil	3.27×10^{17}	2.37×10^{17}

Assuming that the silica-alumina matrix cracks at the same rate as the Durabead 1 silica-alumina, the rates of cracking on the two parts of Durabead 5 can be estimated.

Feed	Rate of cracking on Durabead 5	
	Molecular sieve	Matrix
California gas-oil	1.4×10^{17}	1.9×10^{17}
Coker gas-oil	1.4×10^{17}	2.5×10^{17}
Gachsaran gas-oil	1.2×10^{17}	2.1×10^{17}

From these data, it is possible to calculate a rate for 100% molecular sieve and it is about 13×10^{17} molecules sec^{-1} g^{-1}. This compares with about 2.4×10^{17} for silica-alumina (Durabead 1) so that, under these conditions and with these feed stocks, the molecular sieve catalyst is about five times as active as the conventional silica-alumina. This compares with a factor of 256 found for Mid-continent Gas Oil, but using a different method of calculation (*7*).

Where Does the Molecular Sieve Cracking Occur?

We propose to present evidence suggesting that the primary cracking of the gas-oil molecules occurs on the external surface of the molecular sieve crystallite, rather than inside the supercavity.

Taking 13 300 as the "molecular weight" of the unit cell of the rare earth molecular sieve with 192 tetrahedra, there are 4.5×10^{19} unit cells per gram of molecular sieve. Avoiding defining an "active site," we calculate the number of gas-oil molecules cracking per second per unit cell as 2.9×10^{-2} at 480°. Considering the difference in temperature, this is small compared to some of the turnover rates (molecules reacted per site per second) published for cracking. Using quinoline to count active sites, a value of 0.2 molecules per site per sec was found for cracking cumene on silica-alumina at 425° (*8*). Data in the same reference can be used to estimate a value of 0.02–0.03 molecules per site per sec for light East Texas gas-oil on the same catalyst at the same temperature.

These values differ from those obtained by kinetic counting of active sites using absolute reaction rate theory. For example, 3×10^5 was calculated for cumene on silica-alumina at 420° (*9*). Using similar principles, a value of about 10 was obtained cracking cumene on H faujasite at 225° (*10*).

The small turnover rate per unit cell for gas-oil cracking suggests that not many unit cells have active sites or that only part of the unit cells are available to the gas-oils. Taking 25 Å as the size of the unit cell and 1500 Å as the crystallite size, about 10% of the unit cells are exposed on the external surface of the crystallite. This gives a rate of about 0.3 molecules per unit cell per second. We judge this value to be an indication that the molecular sieve cracking of gas-oil takes place primarily on the external surface.

For the gas-oil to crack inside the crystallite, it must get there through the windows and pores. Using accepted methods for calculating gaseous diffusion rates (*11, 12, 13*), we find that the rate of diffusion of gas-oil molecules through the molecular sieve windows is qualitatively far too slow to account for the rate of cracking observed. We believe this evidence is consistent with the view that the gas-oil cracking step takes place on the surface of the crystallite and principally outside the supercavity. It is not conclusive since the possibility of surface diffusion has not been eliminated.

TABLE 1
COMPARISON OF GASOLINE COMPOSITIONS FROM SIEVE VS. CONVENTIONAL CRACKING CATALYSTS[a]

Feed:	Calif. virgin gas-oil		Calif. coker gas-oil		Gachsaran gas-oil	
Catalyst, Durabead:	5	1	5	1	5	1
Gasoline						
% Paraffins	21.0	8.7	21.8	12.0	31.9	21.2
% Cycloparaffins	19.3	10.4	13.4	9.5	14.3	15.7
% Olefins	14.6	43.7	19.0	42.8	16.3	30.2
% Aromatics	45.0	37.3	45.9	35.8	37.4	33.1

[a] From reference (*1*).

DIFFERENCES IN GASOLINE COMPOSITION

The gasoline from Durabead 5 cracking contained more paraffins and aromatics with fewer olefins than the gasoline from Durabead 1, Table 1. We propose that the main source of the difference between the composition of the gasolines is a difference in the amount of secondary reactions sponsored by the two catalyst types. Of the several types of hydrocarbons encountered in catalytic cracking, i.e., aromatics, paraffins, cycloparaffins, and olefins, it is well known that the olefins are the most reactive (*14*). It has been shown with conventional cracking catalysts, that besides cracking, hydrogen transfer to form paraffins and aromatics from the olefins takes place (*15*) and that a part of the aromatics remains on the catalyst and deactivates it (*16–20*). It has also been shown that similar hydrogen transfer takes place with molecular sieve catalysts (*21, 22*). Generically, these reactions can be written:

$$4C_nH_{2n} \rightarrow 3C_nH_{2n+2} + C_nH_{2n-6} \qquad (1)$$

in which C_nH_{2n+2} is a paraffin and C_nH_{2n-6} is an aromatic and

$$3C_mH_{2m-2} \rightarrow 2C_mH_{2m} + C_mH_{2m-6} \qquad (2)$$

where C_mH_{2m-2} is a cycloolefin and C_mH_{2m} is a cycloparaffin.

Alternatively, a cycloparaffin (hydroaromatic) can furnish the hydrogen:

$$C_mH_{2m} + 3C_nH_{2n} \rightarrow 3C_nH_{2n+2} + C_mH_{2m-6} \quad (3)$$

We propose that gasoline of substantially identical composition is produced in the *primary* cracking step with amorphous silica-alumina and molecular sieve-containing catalysts and that the differences observed are due to differences in the extent of hydrogen transfer such as represented by Eqs. (1)–(3).

As long as there is no loss of hydrogen, the change in olefins and cycloparaffins in going from Durabead 1 to Durabead 5 gasoline, along with Eqs. (1)–(3), were used to calculate the paraffin and aromatic contents of the Durabead 5 gasolines. These are as follows:

	Calif. gas-oil		Coker gas-oil		Gachsaran gas-oil	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Paraffins	21.0	20.5	21.8	25.5	31.9	31.7
Aromatics	45.0	45.7	45.9	42.3	37.4	36.9

The agreement is satisfactory considering the data came from commercial plant-scale runs. Using other published plant data comparisons (*23*) gives the same agreement. This agreement is consistent with our postulate that the difference in gasoline composition is due to the molecular sieve type catalyst carrying hydrogen transfer reactions more nearly to completion than does the conventional silica-alumina catalyst.

NATURE OF THE HYDROGEN TRANSFER PROCESS

The hydrogen transfer process has the characteristics expected of a higher temperature version of "conjunct polymerization" (*24*) in which an olefin is converted by a strong acid into paraffins and hydrogen-deficient products. In strong sulfuric acid, the hydrogen-deficient products are acid-soluble and have been shown to be cyclic allylic carbonium ions (*25*). At the higher temperatures used in catalytic cracking, it is presumed that a similar process occurs initially but proceeds further with a part of the initially formed cyclic allylic carbonium ions continuing in similar reactions to yield paraffins or cycloparaffins, plus aromatic hydrocarbons which are desorbed and appear as products. A part of the aromatics or cyclic allylic carbonium ions surrenders more hydrogen to olefins, forming paraffins or cycloparaffins; the hydrogen-deficient products stay on the catalyst as catalyst "coke." Using ethylene as the initial olefin, a molecular sieve catalyst below cracking temperatures causes hydrogen transfer to take place so that paraffins, especially isobutane, are formed along with high-boiling aromatics which are trapped in the cages of the molecular sieve (*22*). Declining catalyst activity for this reaction was attributed to blocking or obliterating active sites by such high-boiling materials. At the higher temperatures used in catalytic cracking, such aromatics are presumably formed, but are trapped and go to coke.

1-Hexene has been adsorbed on hydrogen faujasite and the reaction followed by infrared spectra at successively increasing temperatures (*21*). At 140° spectra indicative of olefinic groups in a conjugated polyene type of structure appeared. As the temperature was increased, the band shifted to the characteristic of an aromatic ring. This band was not decreased in intensity by evacuation or heating to 427°. The authors concluded that hydrogen-deficient, aromatic ring structures of low volatility were formed which were probably the precursors to coke formation. A similar band has been reported for cokes isolated from amorphous silica-alumina cracking catalysts (*18*). Thus, there is adequate evidence that the molecular sieve catalysts do, indeed, catalyze the hydrogen transfer type reactions already well established for conventional cracking catalysts and that the mechanism of this part of the coke formation is the same.

DIFFERENCES IN THE TWO TYPES OF CATALYST

If both types of catalyst induce hydrogen transfer reactions and these partly determine gasoline composition, then why are the gasolines different? Even though the primary cracking of these big gas-oil molecules occurs outside the supercavities, i.e., in the matrix or on the external surface of the crystallite, the cracked fragments are presumed small enough to get into the cavities by surface diffusion or by desorption and gas diffusion. This postulate seems reasonable in view of the known diffusion of *n*-hexane into the cavities (*26*). Once inside, hydrogen transfer is assumed to occur. Note that the fragments undergoing hydrogen transfer in the cavities do not have to compete with large gas-oil molecules for active sites. With noncrystalline silica-alumina catalysts, the pores are 30–80 Å in diameter or larger and permit the ready entrance of the large gas-oil molecules for the *primary* cracking reaction. The cracked products can undergo hydrogen transfer, but to do so, they must compete for active sites with the much larger, more readily adsorbed gas-oil molecules. As a result, there is less hydrogen transfer than with the molecular sieve catalysts where there is no such competition.

CATALYTIC CRACKING ACTIVITIES DIFFER

In considering differences in cracking activities, it must be kept in mind that the cracking catalysts stay in contact with oil vapor only 2 to 10 min before being removed and regenerated. At no time is a "steady state" attained. Instead, carbonaceous material continuously accumulates on the catalyst and the activity continuously declines. Also it must be recalled that not all the "coke" is removed from the catalyst during regeneration so that "regenerated" catalyst already contains some coke when it again contacts the hot oil.

Even with the wide variation in the commercial sieve type catalyst, the concepts outlined above can in some instances be reconciled with commercial experience. For example, the concept is consistent with the plant observation that coke on the regenerated catalyst must be kept at a low level (i.e., coke left in the cages interferes with the catalytic action) if the benefits of molecular sieve catalysts are to be realized (*27*, *28*). The fact that the benefits are especially noticeable at high catalyst-to-oil ratios (lots of catalyst cages and hydrogen transfer sites available) is also pertinent (*29*).

However, not all commercial data fall into this simple pattern. For example, at constant coke yield, the molecular sieve catalysts give a larger volume yield of gasoline than the conventional silica-alumina catalysts (*27, 30*).

This is a simple and important, practical observation. This observation is not entirely consistent with the hypothesis as presented. If hydrogen transfer is the principle source of coke and the sieve catalysts promote more hydrogen transfer than amorphous silica-alumina, then the sieve catalysts should form more coke for comparable conversions and not less, as commonly observed commercially. We propose that the ratio of the rate of the hydrogen transfer reactions forming volatile aromatic hydrocarbons to the rate of the reactions forming coke is larger with sieve catalysts than with amorphous silica-alumina catalysts. One can ascribe this difference to the catalytic selectivity inside the cages being different from the selectivity of the amorphous silica-alumina.

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