

Pseudocomponent Test of the Relative Utilization of Feed Components in Fluid Catalytic Cracking

ROBERT H. HARDING, ROBERT R. GATTE, AND CARMO J. PEREIRA

W. R. Grace & Co.—Conn., Washington Research Center, Columbia, Maryland 21044

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A pseudocomponent mixture is used to test the relative reactivity of hydrocarbon classes over a range of zeolite catalysts (USY, CREY, Beta, Omega, and ZSM-5) under industrial fluid catalytic cracking (FCC) conditions. The hydrocarbon mixture (32.7% *n*-hexadecane, 45.3% phenyloctane, 17.3% cyclohexyloctane, and 2.3% 2-methylhexadecane) was chosen to reflect the molecular distribution of *n*-paraffins, *i*-paraffins, naphthenes, and aromatics in a standard FCC gas oil feed. Analysis of the cracking results of the hydrocarbon mixture determines relative kinetic reaction rates which are decoupled from deactivation, volume expansion, and some adsorption terms. Each zeolite type cracks the hydrocarbons in the mixture at different relative rates, which reflects differences in competitive adsorption, relative diffusion rates, and acid site strength. The relative reaction rates of the hydrocarbon classes over a given zeolite are a strong determinant of the molecular distribution of the gasoline produced by that zeolite catalyst for both the pseudocomponent mixture and the full gas oil. © 1993 Academic Press, Inc.

1. INTRODUCTION

Fluid catalytic cracking (FCC) is an important industrial process that upgrades natural heavy gas oil feedstocks to gasoline and other light products (1). Cracking catalysts, which contain a mixture of zeolites, clay, and an aluminosilicate binder, have a wide range of pore-size length scales which control the diffusion and sorption rates of the gas oil hydrocarbons (2, 3). Catalyst deactivation in FCC is also a complex function of the architecture and connectivity of the zeolite channel system (4–6). The primary problem in studying the kinetics of FCC, then, is the decoupling of the interactions between the kinetic rates, the diffusion limitations, the adsorption effects, and the deactivation of the catalyst.

The Clean Air Act Amendments of 1990 place restrictions on the composition of gasoline (such as low aromatic content and the incorporation of oxygenates) that may produce large changes in the optimum qualities of FCC catalysts (7). These changes may cause the commercial catalysts based on ze-

olite Y and ZSM-5 to be replaced or enhanced with other zeolites. Since there are over 150 known natural or synthetic zeolite structures, an understanding of the effect of zeolite type on kinetic and transport properties is crucial to the development of suitable catalysts for reformulated gasoline.

Kinetic models of FCC often treat the complex gas-oil mixture as a group of kinetically invariant lumps with first- and second-order unimolecular rate laws (8–10). These models describe the global characteristics of the reaction (such as gasoline selectivity and catalyst deactivation) quite well, but do not include the necessary molecular specificity to predict detailed product quality (such as gasoline octane number) (11). Other have proposed an approach in which the cracking products of a group of 100–10,000 representative molecules are used to estimate product quality (12, 13). The representative molecules (or *pseudocomponents*) are chosen to reflect the average properties of a specific gas oil. Both the kinetic lumping approach and the pseudocomponent approach are catalyst specific: a

key objective of the development of modeling methodologies is to include the interaction of the catalyst properties with the reaction chemistry.

In this paper we describe the first experimental study of the cracking of a well-defined multicomponent hydrocarbon mixture over a series of FCC catalysts. This study is the experimental analogue of the pseudocomponent approach described above. A group of four feed components was selected to mimic the molecular distribution of a standard gas oil. We characterized each catalyst by examining the relative cracking rates of these pseudocomponent molecules and the product distribution of this pseudocomponent mixture.

We find that the experimental use of a pseudocomponent mixture is a powerful tool to determine the ratio of effective rate constants of the feed components, which is independent of decay and volume expansion but dependent on the catalyst diffusion and adsorption properties. We provide a theoretical estimation of the error associated with the rate constant ratios estimated in this way for both averaged and instantaneous data collection procedures.

Each zeolite has a different set of ratios of effective rate constants for each pair of feed molecules. This variation in effective reaction rate changes the proportions of the feed molecules that are cracked at a given overall conversion. Since the feed molecules have significantly different product selectivities, the relative utilization of each type of feed molecule has a dramatic impact on the total product selectivity of the feed mixture. The relative feed utilization of the pseudocomponent molecules in our tests correlate very well with the product selectivity observed in standard microactivity tests of a complete gas oil. This result indicates that the product selectivity of a gas oil is due, in part, to the proportions of feed molecules that are cracked into the gasoline range. Secondary reactions such as hydrogen transfer (14) and olefin disproportionation also affect product selectivity.

Earlier studies of the cracking of binary model compound mixtures have found several nonlinear kinetic effects including the inhibition or enhancement of paraffin cracking with olefins (15–17) and the competitive adsorption of aromatics and paraffins (18). Paraffin inhibition of paraffin cracking has also been observed in hydrocracking (19). Binary feed mixtures have also been used to provide a measure of the effective pore size of zeolites (20).

2. EXPERIMENTAL

The properties of the gas oil used in this study (SIHGO feed, an FCC feed obtained from the Davison Chemical Division of W. R. Grace & Co.—Conn.) are described in Table 1. This feedstock is representative of an imported heavy gas oil with high sulfur content. The gas-oil microactivity test data presented were collected with a variation of the ASTM method D3907.

The pseudocomponent mixture employed in this study was composed of 17.3% cyclohexyloctane (TCI America), 45.3% phenyloctane (Aldrich), 32.7% hexadecane (Aldrich), and 2.3% 2-methylhexadecane (Pfaltz and Bauer) by weight determined by gas chromatography (Hewlett–Packard 5890 equipped with a 19091S-001 50 m Fused Silica Capillary column). The molecular distribution of these components was chosen to correspond to the gas-oil distribution. Complete separation of the peaks was achieved with the temperature program: 0 to 35°C at 3°C/min, 1.5°C/min to 70°C, 3.0°C/min to 250°C, hold at 250°C for 5 min. The remaining 2.4 wt% is the sum of the hydrocarbon impurities introduced with each of the individual components. Repeated GC runs demonstrated a variation of less than 0.1 wt% in these concentrations.

For the model compound tests each catalyst was pressed to 40/80 mesh size, placed in a quartz reaction tube, and preheated for 30 min at 500°C under 10 cc/min nitrogen flow. The reaction tube was maintained at temperature with a three zone furnace, and actual catalyst temperature was measured

TABLE 1
Comparison of Gas Oil and Pseudocomponent Properties

	Gas oil	Pseudocomponent mixture
Molecular distribution (GC/MS)		
Aromatic molecules	42.9%	46.3%
<i>n</i> -Paraffinic molecules	40.0%	32.4%
Isoparaffins and naphthenic molecules	12.9%	19.7%
n-d-m Method		
C _A % Aromatic carbons	21.7%	20.2%
C _N % Naphthenic carbons	19.6%	7.5%
C _P % Paraffinic carbons	58.7%	72.3%
API	22.5	0.00
Sulfur (wt%)	2.6	0.00
Total nitrogen wt%	0.086	0.00
Conradson carbon	0.25	
Refractive index (20°C)	1.5107	
Distillation (°F)		
IBP	423	
10	615	
30	684	
50	755	
70	834	
90	932	
FBP	1027	
UOP <i>K</i> Factor	11.52	

with a type-K thermocouple in the center of the catalyst bed. The pseudocomponent mixture was pumped into the reaction chamber with a syringe infusion pump (Harvard Apparatus #22) at the rate of 0.6 g/min. Nitrogen was cofed with the hydrocarbons at the rate of 10 cc/min (at STP) set by mass flow controller. The cracking reactions were run for 3 min time on stream at 500°C, 0–2 psig. Space velocity was varied by changing the amount of catalyst in the reactor tube. To maintain constant reactor heat capacity the catalyst was diluted with alundum (EM Science, calcined for 2 h at 1300°F) to a constant bed volume of 4 ml. Alundum alone shows less than 1% conversion for this pseudocomponent mixture.

Liquid products were collected in an ice bath and then analyzed on the gas chromatograph. The volume of the gas products was determined by water displacement. The gas

products were analyzed by FID and TCD on a Varian Vista 6000 Gas Chromatograph equipped with a 50-m Chrompack Fused Silica column 7515. Coke levels were determined by mass difference between the catalyst after 100°C calcination and 540°C calcination for 1 h. Only mass balances above 97% are reported in this study. Typical mass balances were 100 ± 1 wt%. Prior to cracking experiments, each catalyst was steam-deactivated for 4 h at 750°C (95% steam).

Our experiments compare a variety of zeolites and catalysts with properties listed in Table 2. We examine four zeolites (Y, Beta, ZSM-5, and Omega). Each zeolite has been ammonium-exchanged and calcined to its acidic form. Zeolite Y is prepared in two catalyst preparations (CREY and USY) with zeolite spray-dried with kaolin clay and a silica binder. The CREY catalyst has 22%

TABLE 2
 Properties of Catalysts Examined

	CREY	USY	Beta	Omega	ZSM-5
Mean particle size (μm)	40.0	63.8	62.2	7.7	5.6
BET surface area (sq. m/g)	103	190	470	126	360
Nominal pore size (Angstroms)	7.4	7.4	7.5×5.7	7.4	5.6
Pore volume (cc/g)	0.11	0.16	0.40	0.20	0.20
Bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$	5.4	6.2	30.3	5.6	40.2

zeolite exchanged with approximately 15 wt% rare earth elements, while the USY catalyst has 40% low-sodium ultrastable faujasite. The other zeolites were tested without clay or binder. The clay and binder materials were tested separately and showed less than 4% conversion for this pseudocomponent mixture. Neither clay nor binder showed significant cracking activity for the pseudocomponent mixture. Nonzeolitic activity is expected to play a larger role in the cracking of high-boiling-point hydrocarbons not included in this pseudocomponent mixture.

Particle size was determined with a Malvern MasterSizer after 15 min sonication. Surface area and pore volume were determined by nitrogen porosimetry at 77 K.

3. THEORETICAL BACKGROUND

To describe the kinetics of the cracking of a mixture of four hydrocarbons we follow the work of Abbot and Wojciechowski (16). We have four coupled nonlinear equations

$$-\frac{dC_i}{dt} = \frac{K_i \sum_j k_{ij} C_i [1 + G\tau]^{-N} / [VE]}{1 + [\sum_i K_i C_i + \sum_j \sum_j [C_{i0} - C_i] K_{ij} n_{ij}] / [VE]}, \quad (1)$$

where C_i is the concentration of hydrocarbon i , K_i is the Langmuir-Hinshelwood-Hougen-Watson (LHHW) adsorption constant of hydrocarbon i , k_{ij} is the first-order reaction of hydrocarbon i through the j th reaction pathway, G and N are the decay

parameters for time on stream τ , C_{i0} is the initial concentration of hydrocarbon i in the reaction mixture, K_{ij} is the adsorption constant of the products of hydrocarbon i through reaction pathway j , n_{ij} is the stoichiometry of reaction pathway j , and $[VE]$ is the volume expansion term given by

$$[VE] = \frac{\sum_i [C_{i0} + \varepsilon_i (C_{i0} - C_i)]}{\sum_i C_{i0}}, \quad (2)$$

where ε_i represents the net molar expansion of hydrocarbon i after reaction.

Equation (1) assumes that each hydrocarbon cracks through an independent series of first-order reactions, that the decay sites and deactivation rate are the same for all hydrocarbons, and that the reactants and products competitively adsorb with the LHHW mechanism. Similar assumptions for hydrocarbons have been made in the literature (8, 10, 16). The equation also assumes that no product-activated conversion occurs, as has been observed with the olefins and paraffins (15). Diffusion is not treated explicitly in Eq. (1) and we assume that it can be included within the k_{ij} with an effectiveness factor.

Equation (1) does not imply that each hydrocarbon in the mixture has the same deactivation rate when cracked individually. Distinct values of G and N are necessary to describe each hydrocarbon for uncoupled cracking reactions. Our primary assumption is that a catalyst with a given amount and a given distribution of coke reduces the crack-

ing activity of the catalyst for each hydrocarbon in the same proportion. This approximation should break down at high coke levels where spatial constraints within the zeolite pore restrict some of the feed molecules and not others. However, our pseudo-component experiments were performed at coke levels below 0.4 wt%.

To simplify the mathematical characterization of the cracking of the pseudocomponent mixture we note that for each pair of reactants A and B

$$\frac{dC_A}{dC_B} = \frac{K_A \sum_j k_{A_j} C_A}{K_B \sum_j k_{B_j} C_B} = \frac{K'_A C_A}{K'_B C_B} \quad (3)$$

Equation (3) reduces to

$$\left(\frac{C_A}{C_{A0}} \right) = \left(\frac{C_B}{C_{B0}} \right)^{K'_A/K'_B} \quad (4)$$

By examining the relative conversions of each pair of hydrocarbons in the mixture we can use Eq. (4) to determine a ratio of effective rate constants K' that is independent of the decay rate, most competitive sorption terms, and the volume expansion of the mixture. Further, these ratios can be used to describe the relative utilization rates of different hydrocarbon classes for each catalyst.

At this point in the derivation we have assumed instantaneous measurements for clarity. Our experimental results are averaged over a range of times-on-stream. In Appendix A we calculate the error associated with using Eq. (4) with averaged experiments in lieu of instantaneous ones and find that the associated error is minimal in the cases we examine.

4. RESULTS

4.1. Cracking of the Pseudocomponent Mixture

The molecular constituents of the pseudo-component mixture were chosen to represent the relative concentrations of molecular classes in SIHGO. Phenyltoluene (PO), cyclohexyltoluene (CHO), hexadecane (H),

and 2-methylhexadecane (IC17) were chosen to represent aromatics, naphthenes, *n*-paraffins, and isoparaffins, respectively. A comparison of the atomic and molecular distributions of the gas oil and the pseudo-component mixture is given in Table 1. The small number of pseudocomponents chosen (for simplicity) prevented us from matching both atomic and molecular distributions. We chose to emphasize the molecular distribution of the gas oil in these experiments. A larger set of pseudocomponents which includes hydroaromatic molecules would improve the correlation with the atomic distributions.

Of course this representation of a gas oil is incomplete: multiringed structures and multiply branched molecules have not been included. Also, this mixture does not approximate other gas-oil features such as boiling point range, carbon distribution, sulfur content, metal content, or Conradson carbon. A combination of individual components that could represent a gas oil completely would be almost as complex as the gas oil itself. Our aim is to provide useful information on the relative utilization of different hydrocarbon classes in the gas oil. Representative molecules were chosen based on availability, similar cracking rates, and intermediate boiling point range.

Figure 1 shows the relative conversion of hexadecane and phenyltoluene in the cracking of the pseudocomponent mixture for the five catalysts. Each set of data is connected with the line determined by a least-squares fit of Eq. (4). The resulting ratios of effective rate constants are listed in Table 3 for each pair of reactants on each catalyst. We see that the simple equation fits each data point very well. The relative effective rate constants for each pair of feed components is dramatically affected by the zeolite present. Errors in Table 3 were estimated by assuming 1 wt% variance in the reactant yields in Fig. 1. In Fig. 1 we observe that ZSM-5 and Omega crack more phenyltoluene than hexadecane at the same overall conversion compared with CREY and USY. In con-

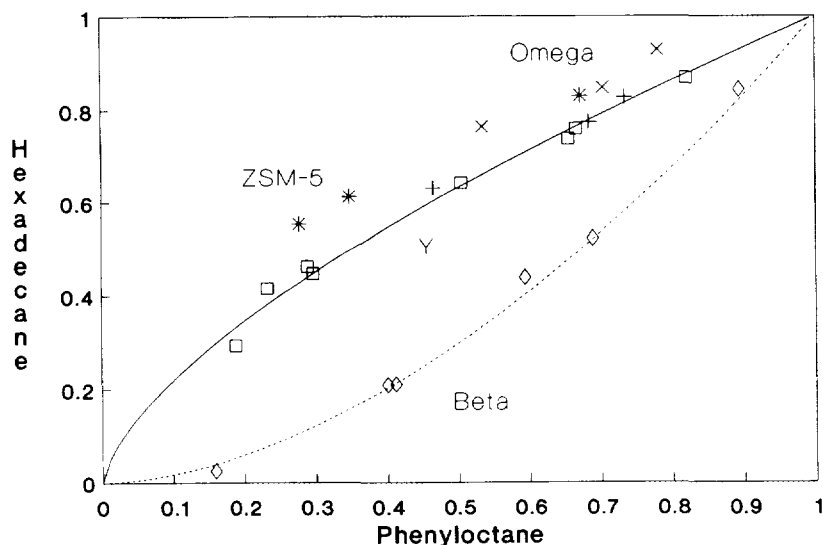


FIG. 1. Fraction of unconverted hexadecane vs the fraction of unconverted phenyloctane remaining after the pseudocomponent mixture is cracked over ZSM-5 (*), Omega (x), CREY (□), USY (+), and Beta (◇) zeolite catalysts. Lines represent the predictions of Eq. (4) for $K_{PO}/K_H = 0.57$ (dashed), 1.50 (solid), and 2.36 (dotted).

trast, zeolite Beta cracks phenyloctane at a lower effective rate than it cracks hexadecane.

Each zeolite has a characteristic pattern of relative rate constants. In this test, the rare earth exchange had no effect on the relative utilization of feed components: CREY and USY had identical rate ratios. The small difference observed in the K_{IC17}/K_H ratio in Table 3 is within the experimental uncertainty in this measurement. The larger error bars are due to the small proportion (2.5 wt%) of 2-methylhexadecane in the feed. The rate ratios are also independent of overall activity. In this study the CREY was

roughly three times as active as the USY for hexadecane cracking.

In Table 4 we examine the product selectivities of the pseudocomponent mixtures interpolated to a 40% overall conversion. We find that the zeolite type has a large influence on the product selectivities of the pseudocomponent mixture. USY and CREY have the same proportion of aromatics in the gasoline range. As expected, the rare-earth-exchanged CREY shows more hydrogen transfer than USY, with a greater yield of isoparaffins and a lower yield of olefins. Beta zeolite produces fewer aromatics than Y, while Omega produces more aro-

TABLE 3

Ratios of Effective Rate Constants by Catalyst

	CREY	USY	Beta	Omega	ZSM-5	Error
K'_{CHO}/K'_H	1.58	1.60	0.90	0.52	0.53	± 0.09
K'_{PO}/K'_H	1.51	1.50	0.57	2.36	2.16	± 0.05
K'_{IC17}/K'_H	2.6	3.4	2.2	4.1	1.0	± 0.8

TABLE 4
Interpolated Pseudocomponent Mixture Results

Catalyst:	Beta	Omega	USY	CREY	ZSM-5
Conversion	40.0	40.0	40.0	40.0	40.0
Product yields (wt%)					
Light gas (C1-C4)	13.3	10.3	7.3	7.8	17.3
Gasoline (C5-C12)	26.6	28.7	27.4	28.9	21.1
LCO (Nonfeed C13+)	0.1	1.0	5.2	3.3	1.6
Coke	0.05	0.03	0.11	0.06	0.11
Gasoline composition (wt%)					
Paraffins	8.0	4.2	4.7	5.4	6.2
Isoparaffins	14.4	20.4	26.4	32.3	4.4
Olefins	47.2	30.8	21.2	15.7	30.2
Naphthenes	7.1	8.6	18.0	17.3	2.3
Aromatics	23.3	36.0	29.7	29.3	56.7
Calculated octane number					
RON	91.4	94.9	89.1	90.9	97.2
MON	78.3	81.5	79.3	79.7	83.4

matics. ZSM-5 shows the highest level of aromatics in the gasoline. Calculated motor octane numbers (11) increase with increasing aromatic levels.

4.2. Cracking Selectivities of the Individual Pseudocomponents

For comparison we examine the product selectivities of each pseudocomponent cracked individually over a single catalyst (CREY). The results are shown in Table 5. We find the expected result that phenyloctane, which has an aromatic ring present in every feed molecule, has a large increase in the proportion of aromatics in the gasoline range with respect to hexadecane. Similarly, the cyclohexyloctane has an increased number of naphthenes in the gasoline range compared to hexadecane, and an increased gasoline yield. The phenyloctane, cyclohexyloctane, and 2-methylhexadecane feeds also produced increased light cycle oil (C13+) yields compared to hexadecane. In each case the relative reaction rate of the feed molecule was significantly increased with respect to the rate of the secondary cracking reactions which produce light gas.

We note that the rate constants for hexadecane and phenyloctane cracked individually on CREY are almost identical (equiva-

lent conversion under the same conditions). However, the ratio of rate constants for these two molecules in the mixture over CREY is listed as 1.5 in Table 3. Aromatics are known to competitively adsorb on the catalyst surface and slow the effective reaction rate of paraffins (8). Thus a feed mixture may have different effective rate constants than the individual feed components. In another paper we report that mixtures of hexadecane and phenyloctane change not only the overall reaction rates but also the detailed selectivities of each component (21). The interaction between hexadecane and phenyloctane is catalyst specific: we find that the observed cracking rates of hexadecane in the pseudocomponent mixture were *larger* than that of phenyloctane with zeolite Beta (Table 3). These observations may help to explain the difficulties associated with using the cracking of individual molecules to explain gas-oil MAT selectivity.

4.3. Cracking Selectivities of the Catalysts with a Gas-Oil Feed

When the gas-oil feed was cracked over the catalysts we found the product selectivities interpolated to 60% given in Table 6. ZSM-5 is not included because the medium-pore-size sieve does not crack gas-oil-size

TABLE 5
Selectivities of Individual Pseudocomponents over CREY

	Hexadecane	Phenyltoluene	Cyclohexyltoluene	IC17
Conversion	60.0	60.0	60.0	60.0
Grams catalyst	0.5	0.5	0.2	0.05
Product yields (wt%)				
Light gas (C1-C4)	17.7	9.9	10.9	10.9
Gasoline (C5-C12)	40.5	40.6	45.1	38.4
LCO (nonfeed C13+)	1.5	9.9	4.0	10.7
Coke	0.42	0.26	0.10	0.06
Gasoline composition (wt%)				
Paraffins	11.0	3.0	6.3	7.7
Isoparaffins	41.1	26.3	35.1	33.3
Olefins	35.1	5.0	20.5	48.3
Naphthenes	5.5	3.2	25.3	6.6
Aromatics	7.3	62.5	12.8	4.1
Calculated octane number				
RON	84.6	95.6	84.7	88.4
MON	74.7	86.6	76.1	77.6

molecules at the 60% conversion level. Omega is tested as a 50/50 mixture with USY to bring the conversion to the desired level.

We find that the gasoline range selectivities for the gas-oil feed can be explained by the relative utilization of the different feed components listed in Table 3. Zeolite Beta, which produces fewer aromatics in the gasoline range than the Y zeolites, cracks fewer

aromatics from the gas oil. Zeolite Omega, which produces more aromatics in the gasoline range than Y, cracks a larger percentage of aromatics from the gas oil. The relative utilization of different feed components has a dramatic effect on overall product selectivity.

A comparison of the cracking products of CREY and USY reveals that feedstock utilization is not the only determinant of gasoline product selectivity. Both of these catalysts have identical ratios of feed rate constants. The more traditional explanations of hydrogen transfer and bimolecular reactions contribute to the differences in product selectivity observed.

5. DISCUSSION

We find that reacting a group of model compounds together over a zeolite catalyst has significant advantages over reacting each model compound individually. Other authors have stressed the importance of comparing relative reaction rates at equivalent coke on catalyst levels (22). Relative rate constants are easily determined with a pseudocomponent mixture that reflect constant coke conditions. The reaction of a mixture

TABLE 6
Interpolated MAT Results

Catalyst:	Beta	Omega	USY	CREY
WHSV (h ⁻¹)	23.3	19.0	27.7	34.2
Catalyst/oil	5.1	6.3	4.3	3.5
Conversion	60.0	60.0	60.0	60.0
Product yields (wt%)				
Light gas (C1-C4)	22.7	16.1	17.7	16.8
Gasoline (C5-C12)	34.5	42.0	39.6	40.1
Light cycle oil	19.6	23.7	21.6	20.5
Heavy cycle oil	20.4	16.5	18.4	19.5
Coke	2.5	1.7	2.5	2.9
Gasoline composition (wt%)				
Paraffins	4.6	5.2	3.8	4.8
Isoparaffins	22.3	27.0	33.2	43.2
Olefins	38.9	28.9	24.7	13.1
Naphthenes	7.4	8.3	9.1	8.4
Aromatics	26.9	30.6	29.2	30.6
Calculated octane number				
RON	93.8	92.0	92.4	90.9
MON	80.3	80.6	80.3	79.7

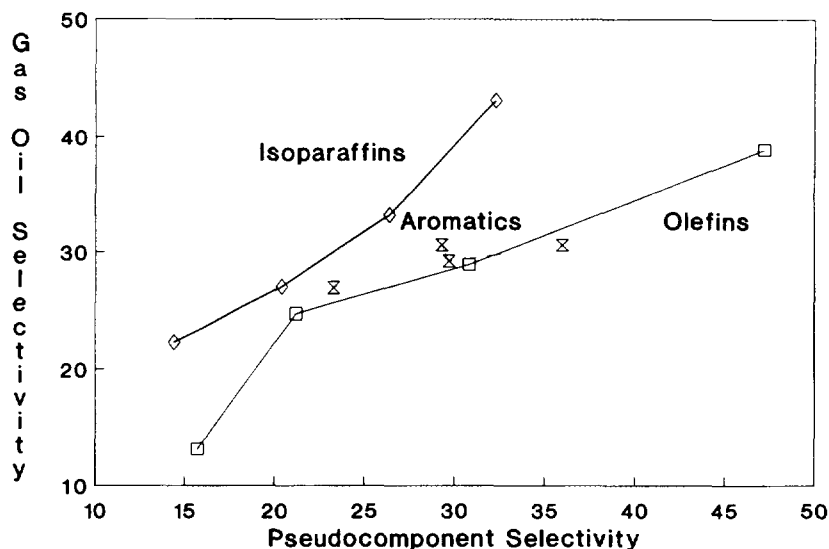


FIG. 2. Relationships between gasoline isoparaffin, olefin, and aromatic wt% selectivities of the pseudocomponent mixture at 40% conversion and the corresponding selectivities of SIHGO gas oil at 60% conversion over Omega, REY, USY, and Beta zeolite catalysts.

also allows the cracking of model compounds to be studied in more realistic chemical environments that reflect the competitive adsorption processes found in gas oils.

Our results have shown that the relative utilization of different feed components in a complex mixture cracked by a zeolite catalyst can be elucidated by a simple pseudocomponent test. The effective reaction rates of the four molecular species are greatly affected by the zeolite type. We expect zeolite crystal structure to affect relative utilization by altering the relative diffusion and adsorption rates of the gas-oil constituent molecules and examine this phenomenon with the four pseudocomponent molecules.

Figure 2 shows the strong correlations between the isoparaffin, aromatic, and olefinic gasoline selectivities of the pseudocomponent test and those of the gas oil MAT test. We find that in each product category the selectivities of the pseudocomponent mixture correlate well with the MAT selectivities.

If the zeolite dependence of the relative rate of reaction were primarily due to

changes in diffusion then the relative rates of molecules with larger kinetic diameters should decrease as pore size decreases. In this rough approximation we would expect the relative cracking rates of cyclohexylcane and phenyloctane to decrease with respect to the rate of hexadecane in the order $Y \approx \text{Omega} > \text{Beta} > \text{ZSM-5}$ (based on the pore sizes listed in Table 2). We find in Table 3 that the relative reaction rates do not follow this simple ordering. Pore size alone is not an adequate predictor of diffusion rate in zeolites due to the complex channel architecture (23), the possibility of cage effects, and the different crystal sizes of the tested materials. Simple size exclusion based on the zeolite pore size is not important for this choice of zeolites and pseudocomponents (24).

The one-dimensional channel system of zeolite Omega may produce highly different mass transfer characteristics than the other zeolites with three-dimensional channels. If we exclude Omega on these grounds, then the relative rates of both cyclohexylcane and 2-methylhexadecane decrease with re-

spect to the rate of hexadecane in the simple pore-size ordering.

Phenylotane does not follow this simple trend, however. Zeolite Beta has a much lower ratio of phenylotane to hexadecane cracking than would be expected by these simple arguments. We speculate that differences in relative hydrocarbon adsorption between the zeolites account for the relative rates of phenylotane cracking. Aromatic molecules should be most sensitive to changes in adsorption. In Ref. (21) we find that the rate of hexadecane cracking on CREY is decreased in the presence of aromatics, indicating a competitive adsorption process. No analogous decrease is observed for these materials over zeolite Beta.

A strong determinant of the product selectivity of a gas oil is the relative conversion of each class of molecular species. Table 5 shows that each pseudocomponent has a distinct product distribution. The relative amounts of each reactant molecule that is cracked determine the initial selectivity of the mixture. The relative reaction rates of the feed materials over each zeolite listed in Table 3 coupled with the distinct product distribution listed in Table 5 correlate very well with the final distributions of both the pseudocomponent mixture (Table 4) and the full gas oil (Table 6). For example, Table 3 shows that Beta cracks fewer aromatics from the gas oil than Y zeolite, Table 4 shows that aromatics crack into smaller aromatics, and therefore we expect that Beta to have a lower aromatic gasoline selectivity than Y zeolite. In contrast, Table 3 shows that Omega cracks more aromatics from the gas oil than Y and therefore we expect Omega to have a higher gasoline aromatic selectivity than Y. We focus this discussion on the aromatic selectivities because the low aromatic requirement is one of the most challenging aspects of gasoline reformulation.

6. CONCLUSIONS

The relative utilization of the components in a complex gas-oil mixture is a major determinant of overall product selectivity. Our

results show that the molecular species which are cracked into the gasoline range are highly dependent on the choice of zeolite. This effect determines the initial selectivity of the gas oil. Traditional secondary reactions such as hydrogen transfer and bimolecular reaction subsequently affect the product selectivity. A simple pseudocomponent model compound test provides a good experimental measure of these complex mechanisms.

APPENDIX A

In this Appendix we examine the error introduced in the relative rate constants listed in Table 3 by determining the ratio of rate constants from data averaged over a range of times on stream instead of instantaneous data. We find that the error depends on the rate of catalyst deactivation and the relative sizes of the rate constants themselves. The error is small but increases with both deactivation rate and rate ratio.

For each pair of hydrocarbons A and B, Eq. (4) is true instantaneously at every time on stream. One assumption used in deriving this result was that the decay sites and deactivation rate are the same for all hydrocarbons. The ratio of rate constants that we estimate is given by

$$\left(\frac{K'_A}{K'_B}\right) = \text{Ln}\left(\frac{C_A}{C_{A0}}\right) / \text{Ln}\left(\frac{C_B}{C_{B0}}\right). \quad (\text{A1})$$

Our measurements obtain \bar{C}_A and \bar{C}_B , which are averages over the range of times on stream of the experiment. We seek to obtain the error associated with replacing C_A and C_B in Eq. (A1) with \bar{C}_A and \bar{C}_B respectively. If we let p represent a time on stream in the middle of the experimental run, then

$$\begin{aligned} & \text{Ln}\left(\frac{\bar{C}_A}{C_{A0}}\right) / \text{Ln}\left(\frac{\bar{C}_B}{C_{B0}}\right) \\ &= \text{Ln}\left(\frac{C_{Ap}}{C_{A0}} + \left[\frac{\bar{C}_A}{C_{A0}} - \frac{C_{Ap}}{C_{A0}}\right]\right) / \quad (\text{A2}) \\ & \quad \text{Ln}\left(\frac{C_{Bp}}{C_{B0}} + \left[\frac{\bar{C}_B}{C_{B0}} - \frac{C_{Bp}}{C_{B0}}\right]\right). \end{aligned}$$

Equation (A2) can be expanded to

$$\begin{aligned} & \text{Ln} \left(\frac{\bar{C}_A}{C_{A0}} \right) / \text{Ln} \left(\frac{\bar{C}_B}{C_{B0}} \right) \\ &= \left[\text{Ln} \left(\frac{C_{Ap}}{C_{A0}} \right) + \text{Ln} \left(1 + \left[\frac{\bar{C}_A - C_{Ap}}{C_{Ap}} \right] \right) \right] / \\ & \left[\text{Ln} \left(\frac{C_{Bp}}{C_{B0}} \right) + \text{Ln} \left(1 + \left[\frac{\bar{C}_B - C_{Bp}}{C_{Bp}} \right] \right) \right]. \quad (\text{A3}) \end{aligned}$$

To simplify Eq. (A3) we can choose the time p such that the instantaneous value of C_{Bp} is equal to the average value \bar{C}_B ($C_{Bp} = \bar{C}_B$). Then

$$\begin{aligned} & \text{Ln} \left(\frac{\bar{C}_A}{C_{A0}} \right) / \text{Ln} \left(\frac{\bar{C}_B}{C_{B0}} \right) \\ &= \left[\text{Ln} \left(\frac{C_{Ap}}{C_{A0}} \right) + \text{Ln} \left(1 + \left[\frac{\bar{C}_A - C_{Ap}}{C_{Ap}} \right] \right) \right] / \\ & \text{Ln} \left(\frac{C_{Bp}}{C_{B0}} \right), \quad (\text{A4}) \end{aligned}$$

which is equal to

$$\begin{aligned} & \text{Ln} \left(\frac{\bar{C}_A}{C_{A0}} \right) / \text{Ln} \left(\frac{\bar{C}_B}{C_{B0}} \right) \\ &= \left(\frac{K'_A}{K'_B} \right) + \text{Ln} \left(1 + \left[\frac{\bar{C}_A - C_{Ap}}{C_{Ap}} \right] \right) / \\ & \text{Ln} \left(\frac{C_{Bp}}{C_{B0}} \right), \quad (\text{A5}) \end{aligned}$$

where the second term on the right-hand side of Eq. (A5) is the error associated with averaged measurements (at a given time p).

To determine the magnitude of this error term, we performed a series of calculations with two uncoupled equations of the form

$$\begin{aligned} -\frac{dC_A}{dt} &= K'_A C_A [1 + G\tau]^{-N} \\ -\frac{dC_B}{dt} &= K'_B C_B [1 + G\tau]^{-N}. \end{aligned} \quad (\text{A6})$$

Parameter values $G = 0.2$, $N = 1.2$, and $K = 34$ were chosen to reflect the typical decay patterns in our experiments. Overall activity of the catalyst was assumed to decrease by $\frac{1}{3}$ during the experiment. The per-

cent error obtained with Eq. (A5) over a range of K'_B/K'_A ratios shows that the error introduced by averaging over a range of times on stream does not exceed 7% of the estimated value for ratios below 10. The error goes to zero as expected when the rates are equal ($K'_B = K'_A$). We have also varied the decay parameter G (with N altered commensurately to keep the total decay constant) for $K'_B/K'_A = 2$. We found that the shape of the decay curve has a small effect on the total error.

APPENDIX B: NOMENCLATURE

C_i	Concentration of hydrocarbon i
\bar{C}_i	Average concentration on hydrocarbon i
C_{i0}	Initial concentration of hydrocarbon i
C_{it}	Concentration of hydrocarbon i at time t
ε_i	Net molar expansion of hydrocarbon i after reaction
G	Decay parameter
i	Hydrocarbon subscript
j	Reaction pathway subscript
k_{ij}	First-order reaction rate of hydrocarbon i through the j th reaction pathway
K_i	LHHW adsorption constant of hydrocarbon i
K'_i	Effective reaction rate of hydrocarbon i
K_{ij}	Adsorption constant of the products of hydrocarbon i through reaction pathway j
n	Decay parameter
n_{ij}	Stoichiometry of reaction pathway j for hydrocarbon i
p	Instantaneous time on stream
τ	Time on stream
$[VE]$	Volume expansion term

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