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NOTES

Catalytic Cracking of Long-Chain Paraffins and Olefins on HY Zeolite

INTRODUCTION

Cracking reactions of olefins on solid acid catalysts (*1–5*) have been much less extensively studied than those of paraffins. There is general agreement that olefins react at Brønsted sites on aluminosilicate catalysts (*6, 7*) via formation of a carbenium ion, which can undergo rearrangement, as well as cracking via a β-scission process. The mechanism of paraffin cracking on solid acid catalysts is more controversial, regarding both the nature of active sites and the types of intermediates produced. Roles for both Brønsted and Lewis sites as the active centers have been discussed (*8–11*), and intermediates proposed include carbenium ions, carbonium ions, and also free radicals (*11–16*). Recent studies on cracking of paraffins have focused on molecules with seven or less carbon atoms (*8, 9, 12*) where results are generally easier to analyze than those from higher molecular weight reactants. However, the latter compose the major component of industrial gas–oil feedstocks, and this study examines the behavior of a long-chain paraffin and an olefin under cracking conditions.

RESULTS AND DISCUSSION

Product Distribution

Initial selectives for products from reaction of hexadecene on HY at 400°C were obtained by plotting yield–conversion curves, as previously reported for reaction of *n*-hexadecane under the same reaction conditions and experimental procedures (*17, 18*). For reaction of both feeds, the major initial products are acyclic olefins and paraffins, with mononuclear aromatics and coke also produced as primary products. Figure 1 shows a comparison between initial distributions obtained, according to carbon number. It is clear that these distributions differ and that there is a higher probability of forming a larger cracking fragment initially from the C_{16} olefin. The product distribution observed for reaction of *n*-hexadecane is very similar to that previously observed by Emmett and co-workers (*19, 20*), who also observed a maximum at C_4.

It is generally believed that initiation of reactions of olefins on aluminosilicates occurs through adsorption of the hydrocarbon at Brønsted sites, producing a carbenium ion. Subsequent rearrangement and cracking via β-scission can lead to olefin products of shorter chain length. For cracking of linear paraffins, some authors believe Lewis sites are the dominant active centers (*9*) with reaction via hydride ion abstraction and carbenium ion intermediates. On HY zeolite, however, studies of the influence of reversible dehydration of the catalyst show that Brønsted sites are required for cracking of linear paraffins (*21*).

In the absence of molecular hydrogen as a product, the initiation of reaction for saturated molecules at Brønsted sites can be explained through formation of a carbonium ion. The shift in the initial product distribution (Fig. 1) may be partly explained on this basis, if the C_{16} carbonium ion preferentially cracks to give smaller fragments than the corresponding carbenium ion. Small cracking fragments such as methane and ethane

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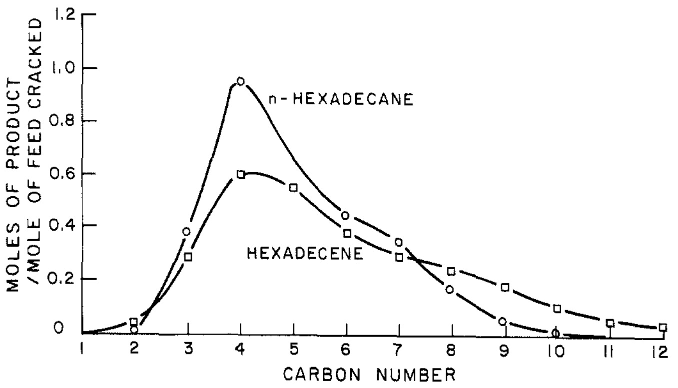

FIG. 1. Initial molar product distributions from reactions of hexadecene and *n*-hexadecane on HY at 400°C.

have been observed as produced from processes attributed to protonation of paraffins (*22*), while formation of these products is known to be unfavorable by a β-scission process. Methane was not observed as an initial product during the present study, and C_2 fragments were only found in trace amounts. This should not be taken as evidence against initiation of cracking through a carbonium ion pathway. These products are also observed only in trace amounts during cracking reactions in liquid superacid media, when the chain length exceeds seven to eight carbon atoms (*23*).

Studies have shown that the Brønsted sites on HY are distributed over a range of acidity (*24, 25*). Variation in initial product distributions for cracking of *n*-dodecane on different catalysts have been explained in terms of differences in acidity distribution (*26*). Other recent work (*27*) has shown that for cracking of *n*-decane the product distribution is shifted toward lower molecular weight fragments with increasing Si/Al ratio of a protonic faujasite, which would also correlate with increasing acid strength. The shift in the distribution for cracking of hexadecene, favoring higher molecular weight fragments, may also correspond to utilization of a higher proportion of Brønsted sites of lower acidity. It is known that for liquid acid media, reaction of alkenes occurs easily in normal acids, whereas little or no reaction is observed for saturated hydrocarbons unless superacids are used (*23*).

Both linear and branched paraffins in the range C_4–C_9 were produced initially from reaction of *n*-hexdecane on HY at 400°C. However, apart from propane, only branched paraffins were produced initially from hexadecene. We can conclude that skeletal rearrangement of the C_{16} carbenium ion must occur more rapidly than the β-scission and hydrogen transfer processes leading to a saturated cracking product.

Aromatics and Coke

Aromatics and coke were initial products from reaction of both feedstocks on HY at 400°C. The initial selectivity for coke was significantly higher for reaction of the olefin by a factor of ~8.5. The coke produced during reaction of *n*-hexadecane is observed mainly as a secondary product. This is in agreement with the work of Emmett and coworkers (*19, 20*), who found that coke was formed by secondary reactions of small olefins (C_4 and C_5) using tracer studies. Figure 2a shows that the degree of unsaturation of the coke formed from hexadecene on HY at 400°C (as measured by the C/H atomic ratio) is greater than that produced from *n*-hexadecane, at all levels of conversion studied. The initial C/H ratio for coke from the paraf-

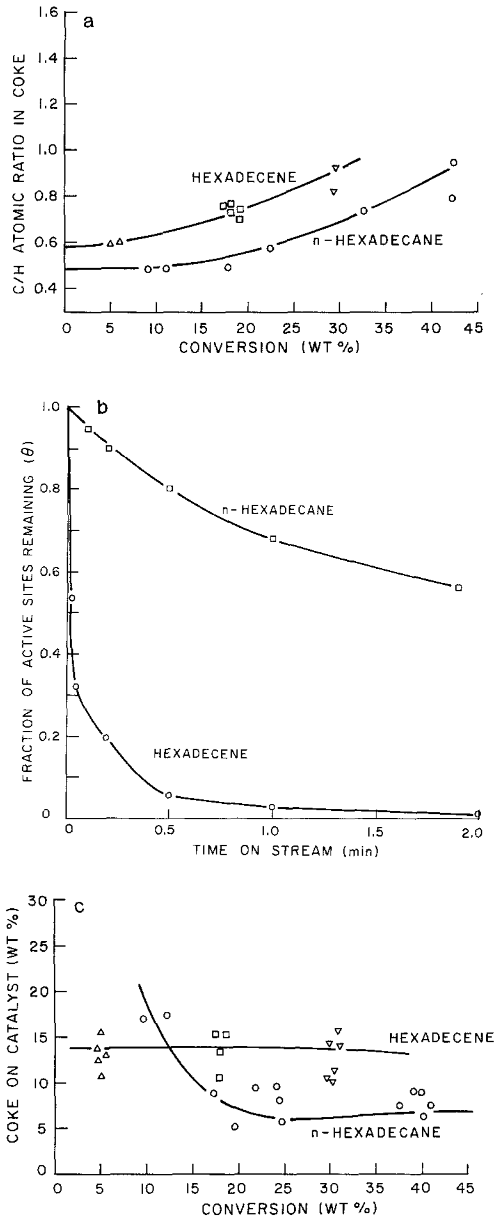

FIG. 2. (a) Variation in C/H atomic ratios for coke formation from hexadecene and *n*-hexadecane on HY at 400°C. (b) Fraction of active sites (θ) remaining as a function of time on stream for reaction of *n*-hexadecane and hexadecene on HY at 400°C. (c) Ratios of coke-on-catalyst plotted as a function of conversion for reactions of *n*-hexadecane and hexadecene on HY at 400°C.

TABLE I

Optimum Values of Kinetic Parameters for Cracking of Hexadecene and *n*-Hexadecane on HY at 400°C

Reactant	*A* (mol/g cat/min)	*B*	*N*	*G* (min^{-1})
Hexadecene	11500	188	0.91	49.4
n-Hexadecane	1.72	−0.998	0.42	1.52

fin (0.48) shows that this consists mainly of adsorbed paraffins. In contrast, the coke initially formed from reaction of hexadecene has a higher degree of unsaturation than the feed, as reflected by the C/H ratio (0.60).

Aromatics initially produced from the reaction of both feedstocks were found to be mononuclear species in the range C_7–C_{10}. Benzene was not detected at any level of conversion. The total initial molar selectivity for aromatics formed from the C_{16} olefin was greater than that produced from the paraffin by a factor of ~2. Taking into account both coke and aromatics, the total initial selectivity for hydrogen transfer processes leading to these unsaturated products was ~3 times greater for reaction of the C_{16} olefin.

Product Distribution and Kinetics

A kinetic equation has been previously developed which describes the behavior of paraffins and olefins during reaction on aluminosilicate catalysts (*26, 28*). Parameters obtained (*A, B, N,* and *G*) can be related to the initial rate of reaction, the degree of product inhibition, and the rate of decay of catalytic activity. The kinetic model has now been applied to reaction of hexadecene on HY at 400°C, and the optimum values of kinetic parameters are presented in Table 1, together with corresponding parameters for reaction of *n*-hexadecane (*18*) under the same conditions.

Table 1 shows that, while the value of parameter *B* is −1 for reaction of *n*-hexadecane, this parameter has a positive value for reaction of hexadecene. The value of B approaches a value of -1 when product molecules are more strongly adsorbed at the active sites than the feedstock molecules, i.e., when there is strong competitive inhibition by products. This inhibition can be attributed to the olefins (and aromatic) products, which are known to be more strongly adsorbed than paraffins on zeolites (*29*).

In contrast, the positive value of B for reaction of hexadecene on HY at 400°C indicates that the feed molecule is more strongly adsorbed at the active sites than the product molecules, mainly acyclic paraffins and olefins in the range C_3–C_{10}. It would be expected that *n*-hexadecene would adsorb more strongly than the paraffinic products and studies of olefin adsorption also show that adsorption affinity on zeolites increases with chain length (*29*).

Figure 2b shows there is also a marked change in the rate of catalyst decay when reactions of hexadecene and *n*-hexadecane on HY at 400°C are compared. The rate of loss of active sites can be described by θ, the fraction of active sites remaining at time t (*18*) which can be calculated from the parameters N and G.

Levels of coke on catalyst produced during the reactions are shown in Fig. 2c. Although somewhat more coke is formed during reaction of the olefin, the higher rate of catalyst decay is probably influenced more by the nature of the coke deposited. Figure 2a shows that the coke formed during reaction of the long-chain olefin is more highly dehydrogenated than that produced from the paraffin at corresponding levels of conversion.

CONCLUSION

Catalytic reactions of a long-chain (C_{16}) paraffin and olefin have been studied at 400°C on HY. Differences in initial product selectivity can be explained in terms of formation of a different carbocation intermediate, and variation in the ranges of acidity of Brønsted sites utilized in each process. Kinetic analysis shows that product inhibition is much more pronounced during reaction of the C_{16} paraffin, while catalyst decay occurs more rapidly during reaction of the olefin.

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