

## The Influence of Olefins on Cracking Reactions of Saturated Hydrocarbons

There have been a number of reports in the literature concerning the influence of olefins on cracking reactions of saturated hydrocarbons on solid acid catalysts (1-17). Most of these studies have been made using linear paraffins as the feed (1-12), ranging from *n*-propane (8) to *n*-hexadecane (1, 9, 12). Various types of acid catalyst have also been used, including amorphous silica-alumina (1, 9), zeolites (2-4, 6, 7), and solid super acids (13). Some investigators have reported that olefin addition produces a significant increase in cracking rate for reactions of linear paraffins (1-4), others report little or no effect (6, 7, 13), while a marked increase in reaction rate has also been reported when olefins are removed from the system (8). Recent investigations by the present author (6, 10-12) have concluded that there is a significant inhibiting effect on reaction of linear paraffins when olefinic products are formed.

Explanations for these phenomena have been proposed in terms of molecular structure of the feed hydrocarbon (14-17). Reaction conditions may also be important, as it has been suggested that different mechanisms may become dominant as the reaction temperature is varied (18). However, there still appear to be contradictory observations concerning the influence of olefins during these catalytic processes, and the subject requires further discussion.

All experiments were carried out by using an integral, fixed bed, gas-phase flow reactor. The experimental apparatus and procedures used were similar to those described previously (19). The source, exchange, and pretreatment of the HY zeolite used have also been reported previously (11, 19).

HZSM-5 was prepared according to methods in the literature (20), and steamed at 200°C for 24 h before use. Catalysts were calcined at 500°C after exchange with ammonium nitrate solution.

Figure 1a shows that addition of ~1% *n*-hexene to *n*-hexane has little influence on conversion of this paraffin on HY at 500°C. Increasing the initial proportion of olefin present (above the 1% level) caused a decrease in the conversion of *n*-hexane. Figure 1b shows that there is also a significant reduction in conversion produced by olefin addition for reaction of *n*-octane on HY at 400°C. These results are consistent with a kinetic analysis of cracking reactions of linear paraffins on HY (10). For reactions in the range 400-500°C, product olefins have been found to inhibit, rather than accelerate the reaction, (10-12) and this is reflected in the negative value for parameter B in the kinetic model (10), which approaches a value of -1 when there is strong inhibition (Table 1). Figure 1c shows that addition of small amounts of olefin to the feed also inhibits reaction of cycloparaffins on HY at 400°C. Kinetic analysis for reaction of cyclohexane and cyclooctane on HY gave a positive value for parameter B (15), showing that these reactions are not strongly inhibited by product formation (Table 1). However, this is to be expected, as olefins are not formed as significant products under these conditions (15, 21), where isomerization is the dominant process.

Figure 1d shows that there is an accelerating effect when small amount of olefin is initially introduced to the feed for reaction of 2,3-dimethylbutane on HY at 500°C (14). It will also be noted that the general shape

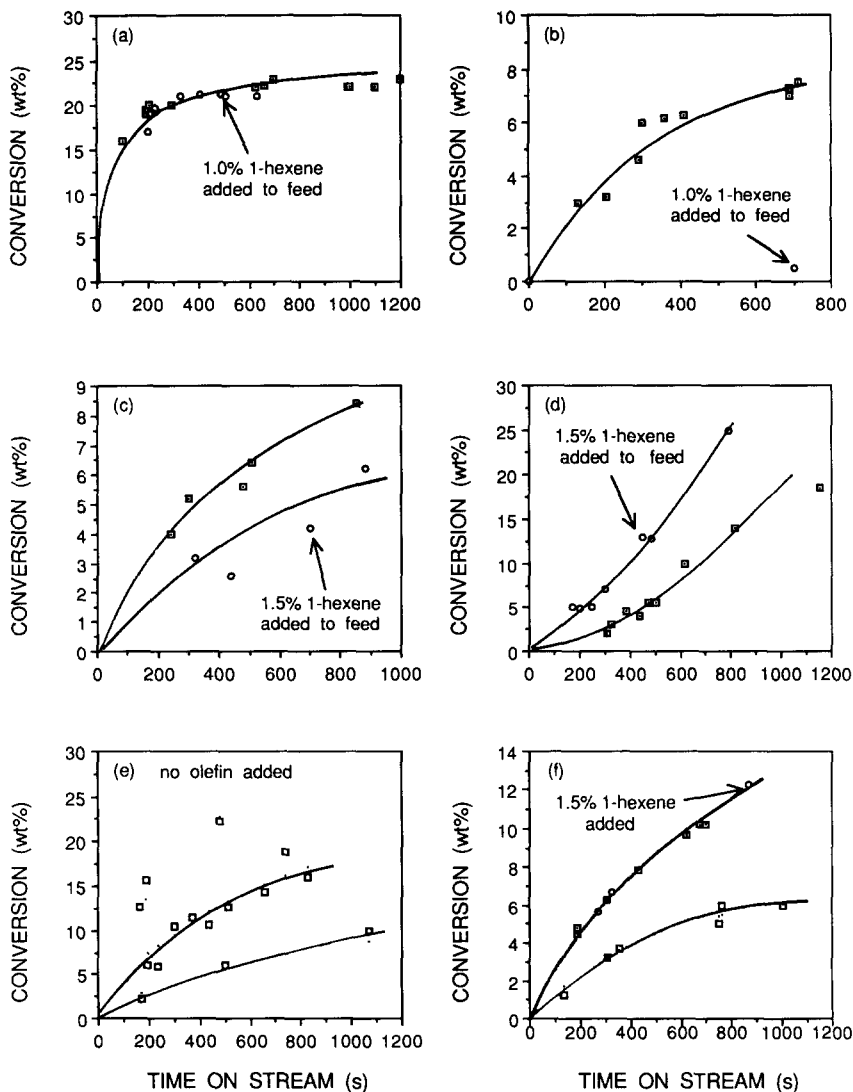


FIG. 1. The influence of olefin addition on reactions of saturated hydrocarbons: (a) *n*-hexane on HY at 500°C, (b) *n*-octane on HY at 400°C, (c) cyclohexane on HY at 400°C, (d) 2,3-dimethylbutane on HY at 500°C, (e) 3-methylpentane on HZSM-5 at 500°C, (f) 3-methylpentane on HZSM-5 at 350°C. No olefin addition: □; with olefin addition: ○.

of the curve relating conversion to time on stream differs from cases (a-c) where there is no accelerating effect due to olefin addition (17). Figure 1d shows that in the absence of initial olefin addition, there is a kinetic induction effect, with the reaction being accelerated as product olefins are formed. This effect has also been observed for reaction of the methylpentanes under

these conditions (17). It should be noted that this induction effect has not been observed for reactions of linear paraffins on zeolites (10-12) as shown in Fig. 1a and 1b.

The phenomena described above can be explained by assuming that cracking and isomerization reactions of saturated hydrocarbons on HY zeolite occur on Brønsted sites (11, 22-25). Initiation of the reaction

TABLE 1

Values of Parameter B for Reactions of Paraffins and Cycloparaffins on Aluminosilicate Catalysts

Reactant	Catalyst	Temp. C°	B	Reference
<i>n</i> -Hexane	HY	500	-0.89	(31)
<i>n</i> -Octane	HY	400	-0.99	(10)
<i>n</i> -Dodecane	HY	400	-0.99	(10)
<i>n</i> -Hexadecane	HY	400	-0.99	(10)
<i>n</i> -Hexane	HZSM-5	500	-0.61	(30)
<i>n</i> -Dodecane	HZSM-5	400	-0.79	(11)
<i>n</i> -Dodecane	LaY	400	-0.98	(11)
<i>n</i> -Dodecane	Silica-alumina	400	-0.80	(11)
<i>n</i> -Dodecane	H-Mordenite	400	-0.69	(11)
<i>n</i> -Heptane	HY	430	-0.92 <sup>a</sup>	(25)
<i>n</i> -Heptane	HY	450	-0.91 <sup>a</sup>	(25)
Cyclohexane	HY	400	211	(15)
Cyclooctane	HY	400	65	(15)

<sup>a</sup> These values were calculated by applying the four-parameter kinetic model (10) to results of Corma *et al.* (25).

occurs through protonation of the feed molecule (11, 18, 25) and subsequent cleavage of C-H or C-C bonds. Adsorption of product olefins or olefins initially introduced will effectively replace the original free Brønsted sites with Lewis centers (i.e., adsorbed carbenium ions). Subsequent observation of inhibition or acceleration will depend on the relative rates of reaction through the initiation process (via protonation) and through hydride ion abstraction to produce a carbenium ion from a feed molecule (11) which can subsequently crack through the  $\beta$ -scission process. Acceleration of the initial reaction rate is observed when the feed structure has a tertiary C-H bond so that cracking via hydride ion abstraction followed by  $\beta$ -scission is faster than protolysis. For feed hydrocarbon molecules with only primary or secondary C-H bonds the reverse is true, and inhibition is observed. It must be assumed here that the carbenium ion initially derived from 2,3-dimethylbutane isomerizes to give the secondary 2-methylpentenyl ion prior to  $\beta$ -scission, as the initial tertiary carbenium ion cannot undergo simple cleavage to produce two C<sub>3</sub> fragments. Indeed, similar kinetic behavior has also been observed for reaction of 2-methylpentane on HY at 500°C (17), which can form the same intermediate species by

direct removal of the hydride ion at the tertiary carbon atom.

This picture is self consistent in describing the influence of olefins on the reactions of saturated hydrocarbons on this particular HY catalyst. However, the results of other studies must now be considered within this context. It should be possible to explain apparent differences in reported observations in terms of reaction conditions or the nature of the catalyst itself.

Corma and co-workers (7) have shown that on Y zeolites small amounts of olefin added to *n*-heptane has little effect on conversion in the temperature range 400–500°C. These investigators did not include the effects of adsorption in their kinetic model. However, their results were obtained by similar experimental techniques to the present studies, and recalculation of parameters from their reported results (26) yields negative values for parameter B as shown in Table 1. The plots of conversion against time on stream reported by Corma *et al.* (7, 26) are also seen to be of the same general type as described here for reactions of linear paraffins, with no obvious induction effect. Their results are therefore similar to those from the present studies using Y zeolite.

Other investigators have reported (2–4) that there is a significant acceleration observed when an olefin is added to *n*-octane during cracking reactions over HY at ~400°C. These observations appear to conflict with those already described. The only explanation that can be offered at present relates to catalyst pretreatment prior to actual measurements on cracking phenomena. This may include effects of heat pretreatment (22, 23) and steaming (27). It has also been shown that factors such as unit cell size and Si/Al ratio in a zeolite can have a significant influence on the relative ease of hydrogen transfer processes (28). Another important factor concerns whether the measurements are made on a fresh catalyst or on an aged catalyst. With regard to the latter, there are generally two types of experi-

mental results reported in the literature from cracking studies. In the first type, used in the present studies and also by Corma *et al.*, the feed is introduced onto a fresh catalyst, usually in a plug flow reactor system (19). In the second type a circulation system is often used (2-4, 29) and the catalyst may have reached some steady-state activity after coke deposition.

In the proposed mechanism for cracking of *n*-alkanes (17), initiation of reaction occurs on strong Brønsted sites (24, 25), which has an effect on the hydrocarbon comparable to liquid super acid systems (30). If these sites are eliminated by heat pretreatment, steaming effects or poisoning by coke, the behavior of the catalyst may be quite different. It is possible that under suitable conditions, all or most of the strong Brønsted sites required for direct protonation of a hydrocarbon molecule have been eliminated, and the observed kinetic behavior during cracking experiments will be changed, with other mechanisms such as hydride abstraction leading to  $\beta$ -scission becoming dominant, even under initial conditions.

Similar apparently contradictory reports on the influence of olefins on reactions of saturated hydrocarbons on other catalysts may be explained in the same way. For example, on amorphous silica-alumina the present studies show that this catalyst behaves in a very similar way to HY, although the activity is much lower. Cracking of *n*-dodecane is inhibited by product olefin formation (11), while the rate of reaction is accelerated for reaction of 3-methylpentane at 500°C (16). Other investigations have also reported product inhibition by olefins on amorphous silica-alumina (9) for reaction of *n*-hexadecane. Reaction of *n*-butane was also found to be accelerated by removal of the product olefins on this catalyst (8). In contrast, for other studies of *n*-hexadecane cracking on amorphous silica-alumina at ~400°C (1) an accelerating influence due to addition of 1-octene was reported. Addition of the olefin to the feed was also found to eliminate an observed induction effect in

these experiments (1). Again, the only explanation appears to relate to the state of the catalyst and the sites available prior to the cracking experiments.

It has been reported that the temperature of reaction can have an important influence on the dominant mechanism during cracking processes. At high temperatures (450-500°C) cracking of paraffins through protonation reactions (18, 31, 32) has been suggested as the major route, while at lower temperatures (~350°C) cracking by  $\beta$ -scission may become dominant (18). This effect has been discussed with regard to cracking of  $C_6$  paraffins on both HY and on HZSM-5 (18). In the present series of studies no effects due to such a transition in mechanism with temperature change have yet been identified. Effects due to increased production of highly unsaturated coke deposits and an associated increase in paraffin fragments have been reported (12). However, a transition from the type of kinetic behavior typical of linear paraffins to that found for feedstocks with tertiary C-H bonds (i.e., a clear induction effect) has not yet been found by changing reaction temperature.

It is difficult, therefore, to give a clear indication of the importance of reaction temperature during observation of the influence of olefins on cracking processes. Previous reports (18) suggest that cracking via a hydride abstraction process leading to  $\beta$ -scission for reaction of 3-methylpentane on HZSM-5 should become more important as the temperature is lowered to ~350°C. Figure 1e shows kinetic curves for reaction of 3-methylpentane on HZSM-5 at 500°C. No induction effect is observed here, and the dominant cracking process occurs through a monomolecular process through protonation (31). The absence of the induction effect, seen for reaction of 3-methylpentane on HY or amorphous silica-alumina, arises because the alternative mechanism involving abstraction of the tertiary C-H at Lewis centers created by adsorption of product olefins at Brønsted sites is a bimolecular process, not favored in the narrow pore pen-

tasil. As the reaction temperature is lowered to 350°C, there is no obvious change in general kinetic behavior (Fig. 1f), as there is still no induction effect. Addition of a small amount of olefin to the feed (33) also has no accelerating influence on the cracking process under these conditions (Fig. 1f), as would indeed be expected from the present analysis of cracking behavior.

The present studies show that the influences of olefin addition during reaction of paraffins and cycloparaffins are consistent for a set of observations obtained by the same experimental procedures. Reported observations on these effects obtained by other investigators which reveal apparently conflicting behavior are probably attributable to differences in experimental techniques, particularly with regard to whether measurements are obtained using fresh or aged catalysts.

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