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# Reactions of *n*-Alkanes over H-ZSM-5: Detection of Reactive Intermediates

## INTRODUCTION

Alkanes have, until recently, been regarded (*1*) as inert end products of the conversion of methanol and other small molecules over H-ZSM-5 zeolites. Recently, however, a number of reports (*2*) on conversion of alkanes have appeared. We present here a systematic survey of this reactivity and report on an investigation of the nature of reaction intermediates formed in alkane conversion.

## EXPERIMENTAL

The equipment, catalyst, and methods used in this study have been previously described (*3*). The benzene sequestration test for reactive intermediates is described elsewhere (*4*).

## RESULTS AND DISCUSSION

*Conversion.* Yields from conversion of alkanes $C_1$–$C_7$ are listed in Table 1 with yields from the conversion of methanol for comparison.

Gasoline produced from *n*-heptane is similar to that produced from methanol. At 370°C the products contain more alkanes, presumably from the cracking of *n*-heptane, but at 410°C this effect largely disappears and the similarity to gasoline produced from methanol increases.

For $C_5$–$C_7$ *n*-alkanes conversion is 70 to 80% complete under the conditions used. In comparison, ethylene conversion is 87% complete under the same conditions (*4*).

Alkanes of more than four carbon atoms are clearly converted over H-ZSM-5.

An interesting effect was observed when using freshly regenerated catalyst. This produced low yields of aromatics (an experiment close to zero time gave zero yields) but yields increased with time up to a steady state after 30 min. Results are shown in Fig. 1. This induction period is not seen, however, if the catalyst has been used to convert methanol since regeneration. It appears that the conversion of methanol deposits some reactive species on the catalyst surface that facilitate heptane conversion.

*Reactive short-lived intermediates.* The apparent similarity in the pattern of products obtained from *n*-alkanes and from methanol prompts the question, "Do conversions of these two types of molecules proceed by similar pathways?"

A partial answer to this query may be made by studying the pattern of short-lived intermediates produced in the two systems.

Fort and Davis (*5*) have suggested the use of benzene to detect a reactive $C_2$ "precursor to chain growth" in the conversion of ethanol. Our own studies (*4*) in which benzene has been added to a variety of feedstocks have confirmed the usefulness of this test for $C_2$ reactive intermediates, and we have extended the test to cover $C_1$ and $C_3$ intermediates.

The test is conducted by adding 1 mol of benzene to 10 mol of the feed and examining the products of conversion for increased yields of alkyl aromatics, especially methyl, ethyl, and propyl benzenes. The results of using this test on *n*-heptane conversion are shown in Table 2 as increments (wt%) in yields of alkyl benzenes on addition of benzene. Data from Ref. (*4*) for conversion of methanol and of ethylene are included for comparison.

Although yield increments for methyl-

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TABLE I

Conversion of $n$-Alkane Hydrocarbons over H-ZSM-5

| | Feedstock | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | MeOH | $n$-$C_7$ | $n$-$C_7$ | $n$-$C_6$ | $n$-$C_5$ | $n$-$C_4$ | $n$-$C_3$ | $n$-$C_2$ | $n$-$C_1$ |
| | Reaction conditions | | | | | | | | |
| Temperature (°C) | 370 | 410 | 370 | 410 | 410 | 400 | 400 | 400 | 400 |
| Conversion (%) | 100 | 87.3 | 81.2 | 78.6 | 68.4 | 6.1 | 4.3 | 0 | 0 |
| Feed rate MHSV ($h^{-1}$) | 0.44 | 0.44 | 0.44 | 0.44 | 0.44 | 1.5 | 1.2 | 0.8 | 0.8 |
| | Hydrocarbon distribution (wt%) | | | | | | | | |
| Methane | 2.8 | 0.7 | 0.3 | 1.9 | 1.1 | 0.1 | 0.1 | — | 100 |
| Ethane ethylene | 4.1 | 2.2 | 1.8 | 2.5 | 2.7 | 0.2 | 0.1 | 100 | — |
| Propane propylene | 5.8 | 5.8 | 5.3 | 5.4 | 6.1 | 1.0 | 95.7 | — | — |
| Isobutane | 7.3 | 5.7 | 5.6 | 4.8 | 5.8 | — | 0.1 | — | — |
| $n$-butane | 1.2 | 7.2 | 8.5 | 5.3 | 9.8 | 93.9 | 0.1 | — | — |
| $n$-Pentane | 1.9 | 5.3 | 8.2 | 6.9 | 31.6 | — | — | — | — |
| $n$-Hexane | 0.6 | 0.8 | 1.6 | 21.4 | — | — | — | — | — |
| $n$-Heptane | 0.2 | 12.8 | 18.8 | — | — | — | — | — | — |
| Other $C_5$–$C_7$ aliphatics | 35.0 | 26.4 | 26.3 | 21.8 | 23.5 | 0.4 | — | — | — |
| Toluene | 8.7 | 10.8 | 7.7 | 7.4 | 7.5 | 1.8 | 1.9 | — | — |
| Ethylbenzene | 0.8 | 1.9 | 1.4 | 1.4 | 0.9 | 0.1 | 0.1 | — | — |
| Xylenes | 18.3 | 12.4 | 8.9 | 18.0 | 8.1 | 2.0 | 1.9 | — | — |
| Other aromatics | 13.3 | 8.0 | 5.6 | 4.2 | 3.5 | 0.5 | — | — | — |

*Note.* MHSV is mass hourly space velocity (g $g^{-1}$ $h^{-1}$).

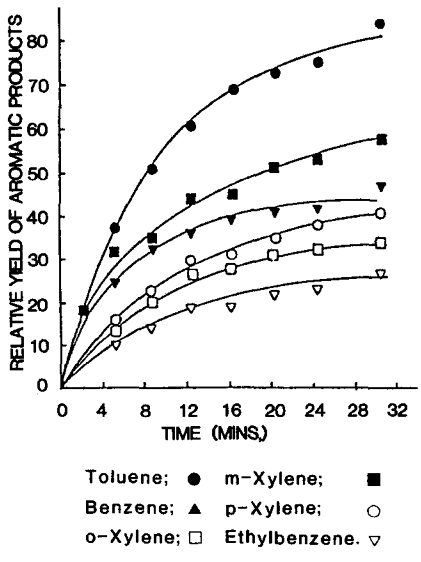

FIG. 1. Effect of time on stream for conversion of $n$-heptane.

benzenes are large for methanol feed, they are small or negative for $n$-heptane and ethylene conversions. We infer that a short-lived $C_1$ intermediate is present in methanol conversion but absent in $n$-heptane and ethylene conversions.

Yield increments for ethyl aromatics are large for $n$-heptane and ethylene feeds but small for methanol feeds. We infer that a reactive $C_2$ intermediate is abundant in $n$-heptane and in ethylene conversions but of low abundance in methanol conversion.

*Effect of temperature.* A more complete picture of the presence and the abundance of reactive intermediates is obtained by measuring yield increments of alkyl aromatics on addition of benzene over a range of temperatures. Results for $n$-heptane conversion are shown in Fig. 2.

TABLE 2

Effect of Adding Benzene to Feedstock in the Conversion of *n*-Heptane, Methanol, and Ethylene over H-ZSM-5 at 400°C

| Feedstock | *n*-Heptane/ benzene | Methanol/ benzene | Ethylene/ benzene |
|---|---|---|---|
| | Reaction conditions | | |
| Temperature (°C) | 400 | 400 | 400 |
| Feed rate MHSV ($h^{-1}$) | 0.44/0.1 | 0.44/0.1 | 0.44/0.1 |
| | Aromatic yield increment (wt%) | | |
| Toluene | −0.02 | +10.35 | +1.17 |
| Ethylbenzene | +2.76 | +0.76 | +14.62 |
| Xylenes | −0.63 | +22.47 | 0.0 |
| Isopropylbenzene | +0.63 | +0.30 | +0.42 |
| *n*-Propylbenzene | +0.97 | +0.05 | +0.57 |
| Ethyltoluene | −0.12 | +1.44 | +0.71 |
| Pseudocumene | 0.0 | +6.95 | 0.0 |
| Diethylbenzene | 0.0 | 0.0 | +5.48 |
| Durene | 0.0 | +0.66 | 0.0 |

Yield increments for methylbenzenes are zero from 200 to 400°C. We conclude that reactive $C_1$ intermediates are absent. Although toluene is a significant product of the conversion of *n*-heptane, its yield is not increased by adding benzene. It appears that toluene is not produced by methylation by an active $C_1$ species in this system. Toluene is probably produced by ring closure of the heptane ring. The largest yield increment at low temperatures is that for isopropylbenzene, reaching a maximum at ca. 250°C. Separate studies have shown (*4*) that isopropylbenzene is labile over H-ZSM-5 above 250°C and hence part of the yield will be lost.

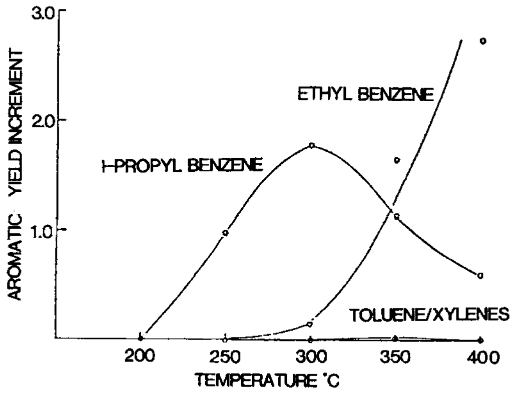

FIG. 2. *n*-Heptane conversion with added benzene. Effect of temperature on increment in aromatic yield.

We infer (i) that a $C_3$ reactive intermediate is dominant at 250°C and (ii) that the $C_3$ reactive intermediate is probably also important at higher temperatures but cannot be detected quantitatively by benzene sequestration at these temperatures.

Ethylbenzene shows a significant increment in yield at temperatures above ca. 350°C, indicating the presence of a $C_2$ reactive intermediate at these temperatures. A difficulty with this interpretation arises from the thermal instability of isopropylbenzene (see above) so that ethylbenzene might be formed from the cracking of isopropylbenzene, rather than from a $C_2$ reactive intermediate. Separate studies (*4*) have shown, however, that yields of ethylbenze from such cracking are small. The evidence for the production of $C_2^{\ddagger}$ at higher temperatures therefore stands.

## CONCLUSIONS

Alkanes of more than four carbon atoms convert well over H-ZSM-5, nearly as completely as ethylene. These should not be regarded as inert end products but as long-lived intermediates capable of further reaction in converting systems.

Reactive, short-lived intermediates can be sequestered by adding benzene to alkane feed stocks in conversion reactions over H-ZSM-5.

Conversion of *n*-heptane shows a complete absence of $C_1$ reactive intermediates just as conversion of ethylene does.

A $C_3$ reactive intermediate is dominant in the conversion of *n*-heptane at temperatures below 300°C, presumably produced by cracking of the heptane chain. At higher temperatures the lability of isopropylbenzene prevents detection of such $C_3$ intermediates.

A $C_2$ reactive intermediate appears in significant amounts of above ca. 350°C, suggesting that cracking of the heptane yields a $C_2$ fragment. The abundance of this intermediate appears to be too high to be attributed to secondary decomposition of isopropylbenzene.

Toluene is not produced by methylation but is probably produced by direct ring closure.

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