

Fates of Reactive Intermediates Sequestered by Benzene in the Conversion of Ethylene to Gasoline over H-ZSM-5 Catalyst

We have recently reported (1) on the development of the "Benzene Sequestration Test" for reactive intermediates present in the conversion of methanol and other small molecules to gasoline over the "Mobil" catalyst, H-ZSM-5. We showed that C_1^* , C_2^* , and C_3^* type intermediates can be sequestered from the surface of the catalyst as alkyl benzenes in considerable amounts when 10 mol% of benzene is added to the feed. Some 12 wt% of chain forming intermediates were sequestered in methanol conversion and 7 wt% in ethylene conversion at 400°C.

If, as we believe, these large amounts of sequestered materials are active chain-forming intermediates in the conversion of benzene-free feeds, then addition of benzene should cause a lowering of selectivities of the products formed by the further reaction of these intermediates in the next and subsequent steps of the chain forming process. If such reduced selectivities should be found for a group of related compounds this could indicate that these are products of reactions of these intermediates, and so give an indication of the course of the reactions suffered by such reactive intermediates.

This paper reports on a search carried out for such reduced selectivities among the light gas products from ethylene feed stock when 10 mol% of benzene is added. Ethylene, rather than methanol, was chosen as feed as the Δ_B values ($\Delta_B(X) = \text{mass \% change in selectivity of product } X \text{ on adding benzene}$) are seen (1) to give a less complex pattern than that obtained for methanol feed, showing both clear positive and negative values for different products at 400°C. A lower temperature, 250°C, was chosen for this study in an attempt to reduce the proportion of secondary reactions.

The fates of alkylbenzenes were also studied.

EXPERIMENTAL

The apparatus used has been described (2) as has also the procedure in which benzene is added to the feed as it enters the catalyst chamber in the case of "benzene + substrate" feeds, but is added in the same amount to the effluent as it leaves the catalyst chamber in the case of "benzene-free" feeds (1). The procedure was adopted so that the total carbon base of all analytical samples taken from conversion of ethylene/benzene mixed feeds and from ethylene feeds should be the same.

RESULTS

Selectivities of the lighter gases and of alkyl benzenes formed when ethylene is converted over H-ZSM-5 with, and without, added benzene at 25°C are reported in Table 1 together with $\Delta_B(X)$ values for these products.

The following points are noteworthy.

1. The degree of conversion of ethylene is only slightly affected by adding benzene, the benzene-free feed giving a slightly higher degree of conversion than the mixed feed.
2. Selectivities of the alkenes, propylene, 1-butene, and *trans*-2-butene showed small but definite decreases on adding benzene.
3. Selectivities of ethylbenzene, *i*-propylbenzene and other higher alkyl benzenes are increased markedly on adding benzene, the $\Delta_B(X)$ values being +3.1, +3.6, and +3.8 wt%, respectively.
4. We have previously reported (7) that there are no increments in selectivities of toluene or xylenes at 250°C and increments

TABLE 1

Effect of Added Benzene on the Selectivities of Hydrocarbon Products in the Conversion of Ethylene over H-ZSM-5 at 250°C and MHSV 0.4 hr⁻¹ (Selectivities of Hydrocarbon Products Shown as wt%)

Feedstock	Ethylene (benzene added after catalyst ^a)	Ethylene/ benzene mixture ^b	Δ_B wt%
Ethane/ethylene	32.1	33.1	+1.0
Propylene	0.7	0.5	-0.2
Propane	1.4	2.4	+1.0
<i>i</i> -Butane	2.0	3.1	+1.1
<i>n</i> -Butane	1.8	2.2	+0.4
1-Butene	1.3	0.9	-0.4
<i>trans</i> -2-Butene	0.6	0.4	-0.2
Other C ₄ -C ₆ aliphatics	14.4	10.7	-3.7
Benzene (added)	34.2	24.7	-9.5
Ethylbenzene	3.1	6.2	+3.1
<i>i</i> -Propylbenzene	2.1	5.7	+3.6
Other alkyl aromatics	6.3	10.1	+3.8

^a Benzene is added at MHSV 0.1 hr⁻¹ after the catalyst and allowed to mix with products prior to analysis.

^b Benzene is added at MHSV 0.1 hr⁻¹ to the feedstock as it enters the catalyst chamber. Feedstock rate 0.4 hr⁻¹.

are small at higher temperatures when ethylene is converted. (See Fig. 1 in Ref (7).)

5. Selectivities of the alkanes, propane, *i*-butane, and *n*-butane increased markedly on adding benzene to the ethylene feed. Ethane and ethylene were not separated by the GLC column, but the peak labeled "ethylene/ethane" is predominantly ethylene, so that changes in selectivity of ethane could not be monitored.

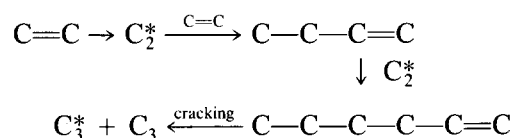
DISCUSSION

The zero values found for Δ_B (toluene) and Δ_B (xylenes) imply that reactive intermediates of type C₁^{*} are absent, and hence that chain growth in this system does not proceed by methylation.

On the other hand, Δ_B values for ethylbenzene and *i*-propylbenzene show substantial positive values, Δ_B values being as large as the benzene-free selectivities. Thus C₂^{*} and C₃^{*} are abundant species and presumably active in chain growth. A high value for Δ_B (ethylbenzene) would be expected for ethylene feed, but the even higher value for Δ_B (*i*-propylbenzene) calls for more consideration. Since, as stated above, C₁^{*} is absent

the presence of C₃^{*} species cannot be attributed to methylation of C₂^{*}, and we are forced to attribute this to cracking of longer chains (4).

If we assume that homologation proceeds according to scheme 1, then we may account



SCHEME 1

for the abundance of C₃^{*} by supposing the C₆⁼ species to suffer cracking as shown. This model accounts naturally for the fact that selectivities of the higher alkenes, 1-butene, and *trans*-2-butene, are decreased by adding benzene which sequesters the chain lengthening intermediates.

While these observations do not help us to decide whether C₂^{*} is ethylene or some other C₂ species, they do require that C₂^{*}, the active chain builder which is sequestered by benzene, be rapidly formed from ethylene. Support is also given to the view (8) that chain building, at least in the smaller molecules, occurs through alkene intermediates.

Selectivities of alkanes increase markedly on adding benzene to the ethylene feed. The origin of this effect is not immediately clear. Mole (5) has suggested that ethyl aromatics crack on the catalyst yielding ethylene, so this reaction did not appear, at first sight, to be a promising source of alkanes.

We had studied earlier (6) ethylbenzene and *p*-ethyltoluene as possible sources of ethylene and found yields to be low, being some 3.3 and 4.4 wt%, respectively, from conversion of the pure alkylbenzenes at 380°C. To test the matter further, we have now carried out conversion studies on *n*-butylbenzene and *i*-propylbenzene and examined the light gases produced. Results are in Table 2. It is clear that selectivities of alkanes from the cracking of alkylbenzenes on this catalyst are some 10 times greater than those for alkenes at 250°C and some 5

TABLE 2

Light Gases Formed from the Conversion of *n*-Butylbenzene and *i*-Propylbenzene on H-ZSM-5

Feed	<i>n</i> -Butylbenzene	<i>i</i> -Propylbenzene	<i>i</i> -Propylbenzene
Temp. °C	250	250	350
Feed rate MHSV (hr ⁻¹)	0.4	0.4	0.4
Conversion %	43	76	92
Selectivities (wt%)			
Methane	0	0	0
Ethane/ethylene	0	0	0.1
Propane	2.0	2.7	4.1
Propylene	0.3	0.2	0.9
<i>n</i> -Butane	1.6)	1.8)	1.6)
) 4.1) 6.0) 5.9
<i>i</i> -Butane	2.5)	4.2)	4.3)
1-Butene	0.2)	0.4)	0.8)
) 0.3) 0.4) 1.2
<i>trans</i> -2-Butene	0.1)	0)	0.4)

times greater at 350°C. This result suggests that cracking of alkylbenzenes produced during the sequestration of C₂* and C₃* by benzene is the source of the increased selectivities of alkanes. These increases in alkane selectivities are thus seen as the ultimate fate of the reactive intermediates removed by benzene sequestration.

If these substantial amounts of alkanes are, indeed, produced by the cracking of alkyl benzenes then alkene by-products of this reaction would be expected to occur in about 10% of the abundance of alkanes (see Table 2). These products would make a small positive contribution to the selectivities of the alkenes, but not large enough

to seriously upset the pattern of observed negative Δ_B values for alkenes.

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