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Conversion of Methanol to Hydrocarbons

III. Methylation, Ethylation, and Propylation of Benzene with Methanol

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Methanol is converted to hydrocarbons (and water) over HZSM-5 zeolite catalyst in the presence of 1–8 M excesses of benzene. Methanol products are primarily aliphatic hydrocarbon gases and C_1 to C_4 aliphatic substituents on the aromatic ring. Methylation of benzene to produce toluene increases as the feed ratio of methanol/benzene decreases. Mild conditions minimize aromatic ring production from methanol. Molar distribution of the methylene group ($-CH_2-$), in the product, is tabulated according to carbon number. Methane plus methyl substituents on the aromatic ring measure C_1; ethane, ethylene, and ethyl ring substituents measure C_2, etc. At temperatures up to 325°C, methylene distribution in the product is methyl = ethyl > propyl ≫ butyl. Above 350°C, methyl ≫ ethyl > propyl. This distribution of the methylene group, under mild conditions, may be a measure of the early production of light olefins, from methanol, within the zeolite pores.

INTRODUCTION

In the 1970s, many zeolite catalysts were evaluated in this laboratory for the alkylation of toluene with methanol to produce xylenes, especially the *para* isomer (*1*). Small amounts of other aromatic products were always produced such as benzene, ethylbenzene, ethyltoluene, pseudocumene, durene, etc. Conditions of reactions were optimized to reduce the yields of these by-products. Occasionally, high amounts of *ethyl*toluene unexpectedly appeared in the product under certain reaction conditions (*2*). An objective of this work was to learn more about the source of this ethyl group and evaluate the potential for producing ethyl- and propylaromatic derivatives by direct reaction of the aromatic compound with methanol. In this regard, reaction conditions and catalysts were sought to maximize, rather than minimize, the production of these higher aromatic derivatives. Benzene was used as the aromatic model substrate to minimize product isomers.

As work progressed to give increased yields of the higher aromatic derivatives, information emerged regarding the mechanism of methanol conversion to hydrocarbons. This topic has been reviewed recently by Chang (*3*).

EXPERIMENTAL

Tubular, quartz screening reactors with catalyst beds having length/diameter ratios of 5–10 were used at atmospheric pressure. Liquid products were condensed in water-cooled traps. The organic and water phases were separated, weighed, and analyzed by gas chromatography (GC). For the water phase, a $\frac{1}{8}$-in. × 3-ft Porapak T column was used to measure the methanol and methyl ether present. A 50-m WSCOT, 0.32-i.d. capillary column coated with CP Sil 5CB was used for the organic liquid, including methanol and methyl ether. The gaseous reaction products were collected and measured in a mercury-sealed, dry-gas tower and analyzed with a $\frac{1}{8}$-in. × 9-ft Supelco silica gel, Grade 12 column with an argon carrier gas to permit analysis for hydrogen.

High-quality benzene and methanol were

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used without further purification. The ammonium form of ZSM-5 catalyst with a molar silica/alumina ratio of 70/1, was steamed for 1 hr at 500°C and converted to the acid form by calcination with air at 500°C. The catalyst was diluted with 5–10 parts of 14–20 mesh quartz chips to dissipate the heat of reaction and prevent autocatalysis.

Material balances (wt%) were calculated for every run. Compounds were lumped and identified by the scheme described in the following section for Table 1. In a series of 12 runs, temperatures ranging from 250 to 375°C, the average balances (wt out/wt in) were as follows: Overall balance, 99.5 ± 3%; C, 99.0 ± 3%; H, 101.5 ± 4%; O, 98.8 + 10%; arom. ring, 99.2 ± 4%; and $-CH_2-$ from methanol, 103.2 ± 10%. The results for the run in Table 1 are 99.6%, 99.2%, 101.6%, 97.3%, 99.3%, 107.8%, respectively.

TABLE 1

Reaction of Methanol with Benzene—HZSM-5 Catalyst

Product	Selectivity (wt%)	-CH2- from methanol distrib. (mole%)
Toluene	40.9	19.9
Xylene	7.1	6.0
1/3 Ethyltoluene[a]	0.9	1.0
Pseudocumene	0.5	0.5
Durene	0.2	0.2
Methane	0.1	0.2
Total, Methyl	49.7	27.8
Ethylbenzene	18.2	15.4
2/3 Ethyltoluene[a]	1.9	2.1
Diethylbenzene	2.1	2.8
Ethane	0.0	0.1
Ethylene	2.0	6.2
Total, Ethyl	24.2	26.6
Cumene	10.2	11.4
n-Propylbenzene	7.0	7.8
Propane	0.9	2.8
Propylene	0.1	0.4
Total, Propyl	18.2	22.4
Butane	1.0	3.0
Butene	0.3	0.8
Total, Butyl	1.3	3.8
C_5	0.4	0.6
C_6	0.2	0.4
C_7	0.1	0.6
C_8	0.0	0.0
C_9	0.0	0.0
C_{10+}	5.9	17.8
Total, C_{5+}	6.6	19.4
Totals	100.0	100.0

[a] Allocated to methyl and ethyl. Reaction conditions: Benzene/methanol mole ratio 4/1, total WHSV 3.9; temp. 325°C; atm. pressure. conversion (wt%): benzene 10.8%; methanol 100% to hydrocarbons.

RESULTS

When benzene is treated with methanol over ZSM-5 catalyst, the primary product is toluene. Some di-, tri-, and tetramethylated derivatives are also produced. Methylation of the aromatic ring is the major and expected reaction. At relatively low temperatures, however, a number of ethyl- and propylaromatic derivatives are also observed. Results at 325°C are summarized in Table 1. We arranged and compared compounds in groups containing methyl-, ethyl-, and propylsubstituted aromatic compounds and their corresponding C_1, C_2, and C_3 aliphatic gases. The C_4 aliphatic gases and all other C_{5+} compounds are placed in the fourth and fifth groups, respectively. Amounts are listed as weight percent selectivity to products in the first column. Their corresponding molar amounts of $-CH_2-$ hydrocarbon component originating from methanol, appearing in the product for each group, is tabulated in the second column of Table 1.

Identification of the various C_6–C_9 aromatic compounds, in the presence of similar molecular weight aliphatic products, is clear and accurate with the capillary column used. The remaining peaks in this range are lumped in the corresponding C_4–C_9 carbon number aliphatic compounds. Therefore, a C_4 aliphatic compound would require 4 mol of methanol, C_5, 5 mol, etc. The C_{10+} compounds are assumed to consist of an aromatic ring from the benzene starting material plus an average of 5 mol of methanol for the side chains. In the run detailed in Table 1, 17 individual, small GC peaks were present in the C_{10+} fraction. By this technique, the distribution of the methylene group coming from methanol is tabu-

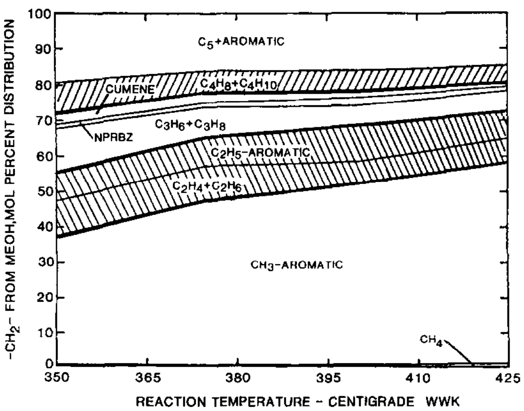


FIG. 1. Alkylation of benzene with methanol-HZSM-5. Conditions: WHSV, 3.8; MeOH/Bz molar feed ratio, 1/1.

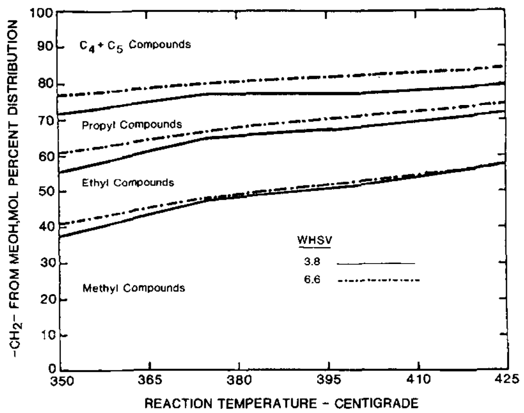


FIG. 2. Alkylation of benzene with methanol-HZSM-5. Conditions: WHSV, 3.8–6.6; MeOH/Bz molar feed ratio, 1/1.

lated. Although some aromatic rings could be formed from methanol, calculations do not include this possibility. The amounts would be very small as indicated by the observed low yields of gaseous paraffins, coproducts with aromatic formation.

Effect of Reaction Conditions

Temperature plays an important role in the distribution of reaction products (Fig. 1). Designated areas show the relative amounts of various products in the 350–425°C range. Distributions of the methylene group originating from methanol among the methyl, ethyl, etc., analogs are shown. Methyl compound selectivity (the primary methylated aromatic products) increased from 38 to 58% as temperature increased. Roughly equal amounts of the ethyl groups were divided between ethylated aromatics and ethane and ethylene, primarily the latter. Methane is a minor product.

Weight hourly space velocity (*WHSV*). Methyl compound yields at any given temperature are virtually unchanged in the 3.8- to 6.6-hr^{-1} WHSV range (Fig. 2). Modest increases in the corresponding ethyl and propyl derivatives are shown at the higher rate. In contrast with methyl, only small changes in the amounts of ethyl and propyl compounds occurred by changes in temperature and space velocity.

Methanol/benzene molar feed ratios of 1/1, 1/4, and 1/8 were tested at 350–425°C over ZSM-5 catalyst. The distribution of methylene groups from methanol, in the products, to produce methyl, ethyl, propyl, and C_{4+} compounds have been calculated as defined in Table 1. In a manner similar to Fig. 1, results are shown in Fig. 3 for the

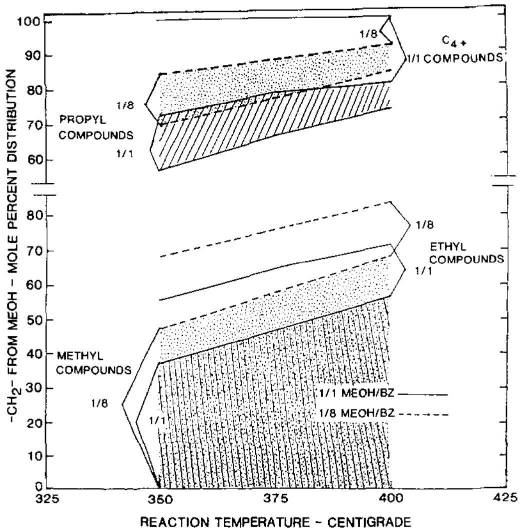


FIG. 3. Alkylation of benzene with methanol-HZSM-5. Conditions: WHSV, 3.9; MeOH/Bz molar feed ratio, 1/1–1/8.

1/1 and 1/8 methanol/benzene molar feed ratios for comparison. In Fig. 3, for example, the lower slanted-line area shows the production of methyl compounds for the 1/1 ratio. The dotted area shows the 1/8 ratio area. The dotted area above the slant-line area shows a 10–15% increase in methyl derivative production when the 1/8 ratio feed is used. Lines defining the ranges for each are shown on the lower-left starting at 350°C. Methyl products increase with increased temperature and with higher amounts of benzene in the feed, 1/8 > 1/1.

Ethyl compounds for 1/1 and 1/8 ratios are shown directly above the methyl compounds. Boundary lines are labeled on the middle-right side of Fig. 3. Since these lines do not start with the same base, as with methyl, they are displaced and overlap. This also occurs for the propyl and other groups above. The upper unshaded area (for ethyl) bounded by the dashed lines shows the ethyl compounds produced by the 1/8 M methanol/benzene feed ratio. The 1/1 ethyl compound area, bounded by solid lines and partially shaded with dots, is directly below and overlaps the 1/8 methyl area. In contrast to methyl, changes in ethyl compound yields with temperature or molar feed ratios have little effect on the selectivity of this group of compounds.

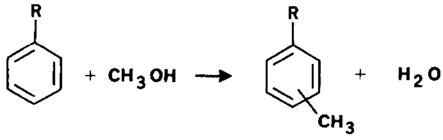
In a similar manner, the propyl compound selectivities for 1/1 and 1/8 M methanol/benzene feed ratios are shown in the upper-left part of Fig. 3. A separation on the vertical axis has been made from the methyl and ethyl compounds below to prevent overlap with ethyl compounds. The lower slanted-line area, between solid lines, shows the propyl products for a 1/1 molar methanol/benzene feed ratio and the upper dotted area, between dashed lines, shows the 1/8 ratio feed over the 350–400°C temperature range. Only a modest decrease in production of propyl analogs is observed with increased temperature, similar to the ethyl compounds.

Finally, the boundaries of the C_{4+} products are shown on the top-right of Fig. 3. The unshaded area, from the dashed line to the top of the figure, indicates yields from the 1/8 M feed ratio. The much larger 1/1 ratio area is bounded by the solid line and the top of the figure. It overlaps the 1/8 propyl area. A very significant reduction in the C_{4+} fraction occurred when going from 1/1 to 1/8 M feed ratio over the entire temperature range.

DISCUSSION

Results show that significant amounts of ethyl- and propylaromatic compounds, along with the expected methylbenzenes, are produced by the reaction of methanol with benzene over HZSM-5. Increases in temperature give higher yields of methylaromatic compounds at the expense of C_{4+} products (Fig. 3). Yields of ethyl- and propylaromatic derivatives diminish only slightly and remain relatively constant over the temperature range studied (Figs. 1 and 3). Although single-product synthetic methods are usually preferred, a mixture of products may have merit in special situations. Toluene or other aromatic substrates, instead of benzene, may also lead to valuable compounds.

The products observed here are the result of several competing reactions which occur within the zeolite pores. The major reaction is direct methylation of benzene to produce toluene and higher methylated derivatives:



(1)

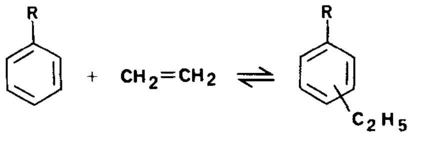
A simplistic interpretation for production of ethyl and higher alkylated benzenes is an initial production of ethylene and water from methanol:

$$2\,CH_3OH \longrightarrow CH_2{=}CH_2 + 2\,H_2O \qquad (2)$$

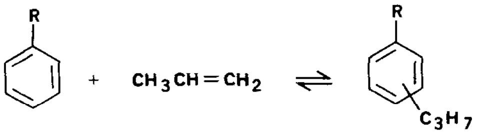
Alkylation of ethylene with methanol produces propylene:

$$CH_2{=}CH_2 + CH_3OH \longrightarrow CH_3CH{=}CH_2 + H_2O \qquad (3)$$

Higher olefins result from successive methylations of the corresponding intermediate olefins. Benzene is then alkylated with olefins present to produce the corresponding ethyl-, propyl-,



(4)



(5)

and higher molecule weight alkylbenzenes.

In our laboratories, ethylene has been proposed as the initial hydrocarbon produced from methanol (*4, 5*). In addition, the alkylation of ethylene with methanol to produce propylene and propylene to butylene, etc., has been shown to follow the chain-growth kinetics defined by the Flory equation (*6*). This reaction has been studied with certain six-carbon olefins by Behrsing and co-workers with ^{13}C-labeled methanol (*7*). Major amounts of labeled C_7 aliphatic products were isolated. This is especially significant because it documents potential precursors for aromatic ring formation from methanol over HZSM-5. At higher temperatures, however, Dessau has shown that methanol is consumed by other reactions and little ethylene is formed directly (*8*). Frost and Davis studied the ethylation of benzene with 1-^{14}C-ethanol (which rapidly produced ethylene by dehydration) and concluded that little exchange of carbon between the ring and side chain of product ethylbenzene occurred (*9*). This reduces the probability of ring expansion/contraction reactions.

These observations and our earlier work (*5*) indicate that intermediate olefins grow in size by alkylations with methanol. Simultaneously the olefins oligomerize or crack to produce other olefins. This results in a complex scrambling of methylene units, originating from methanol, before the final olefin, paraffin, or alkylated benzene emerges from the pores.

However, experience with ethylation of benzene (*10*), toluene (*11*), and ethylbenzene (*12*), with ethylene, over zeolite catalysts, show high yields and conversions to the corresponding ethylated analogs. This suggests that ethylene oligomerization and cracking reactions are not very important. Propylation of benzene with propylene also gives good yields of cumene in the presence of a 5-M excess of benzene under mild conditions (*13*). However, depropylation occurs easily when pure cumene is passed over HZSM-5. This suggests the occurrence of an alkylation/dealkylation equilibration reaction. The propyl group on the cumene isolated in this study, where excess benzene is used, probably has been passed back and forth between many benzene rings (transalkylation) before emerging from the catalyst. The net result, therefore, is preservation of the initial propylene reaction unit on an aromatic ring. In this situation the integrity of the initial olefin is retained and would be a measure of the primary olefins produced from methanol.

We believe there is a good probability that significant amounts of low molecular weight olefins produced from methanol, under mild conditions, are trapped by alkylation and preserved with the large amounts of benzene present. This would give a measure of the ratio of olefins produced initially from methanol.

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