Shape-Selective Reactions with Zeolite Catalysts

VI. Alkylation of Benzene with Propylene to Produce Cumene

INTRODUCTION

Alkylation of benzene with propylene to produce cumene is a well-known reaction. Commercial production began in May 1942 to supply high-performance fuel for military aircraft. A vapor-phase process with a phosphoric acid on kieselguhr catalyst and a liquid-phase alkylation in the presence of sulfuric acid was used (*1*). Postwar production of phenol and acetone by oxidation of cumene, by a new process, provided a growing need for large-scale production (*2*). Phosphoric acid on silica, "Solid Phosphoric Acid—SPA," became a dominant commercial catalyst for this reaction (*3, 4*). Other Friedel–Crafts catalysts, especially aluminum chloride, have also been used for this alkylation reaction (*5, 6*).

Zeolite catalysts have also been tested for alkylation of benzene with propylene to produce cumene (*7*) and cymene from toluene by alkylation with propylene (*8*). Conditions of reaction were optimized with certain rare-earth-modified zeolites to give 75–80% cumene yields (*9*).

Previous papers in this series have been concerned primarily with alkylation of benzene or toluene with methanol or ethylene (*10*). The latter reagents are very active under alkylating conditions and will oligomerize and react to give a variety of undesired by-products. Five to ten molar excesses of the aromatic component are needed to promote the desired alkylation reaction. Propylene is also very active and requires a similar excess of the aromatic component. In addition, there is potential for production of *n*- and isopropylbenzene. Our re-

sults from alkylation of benzene with propylene using HZSM-5 are discussed here.

EXPERIMENTAL

Materials. High-purity benzene, propylene, and propane were used without further treatment. Corrections were made for traces of propane in propylene.

Catalysts. Procedures for synthesis of HZSM-5 catalysts have been described (*11*). All zeolites were free of amorphous impurities after synthesis and were formulated with an alumina binder. The HZSM-5 used for the experiments summarized in Table 1 had a 70/1 silica/alumina molar ratio. The HZSM-5 used for those summarized in Table 2 had a 250/1 ratio. The weight hourly space velocities are calculated on the basis of the pure zeolite component. All zeolites were prepared in the Mobil Research and Development Corporation laboratories, Paulsboro, N.J.

Five to twenty grams of catalyst was positioned in a $\frac{5}{8}''$ or 1.0″ stainless steel, fixed-bed, continuous, down-flow, electrically heated reactor containing a centered thermowell. The temperature was measured at three positions in the catalyst bed and the highest reading was recorded. Benzene was delivered by a metering pump to a vaporizer and mixed with propylene or propane/propylene mixtures at rates determined by mass flow meters. The reactor products were passed through cold water condensers to remove the liquid fraction and the remaining gas volume was measured by a wet test meter or a dry gas tower with a mercury-sealed float. A $\frac{1}{8}'' \times 10'$ silica-gel gas chromatography column was used to ana-

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lyze gases, and a $\frac{1}{8}''$ × 14', 5% SP-1200/5% Bentone on Supelcoport column was used for the organic liquid.

All equipment was automated to permit continuous, unattended operation. Generally, reaction products were collected for analysis and material balances were calculated for 1–2 hr periods after equilibrium had been established. Material balances were calculated for all runs and were generally within 100 ± 2%.

Definitions. Weight hourly space velocity (WHSV): weight of reactor feed per unit weight of zeolite component in the catalyst per hour. Selectivity to products: weight of each product obtained divided by the weight of starting materials consumed, normalized to 100%. Conversion: weight of starting material consumed divided by weight of starting material.
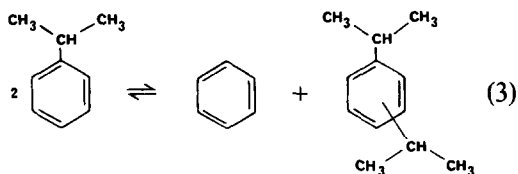
RESULTS AND DISCUSSION

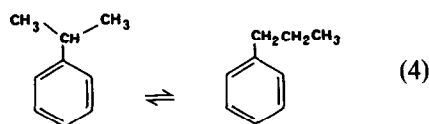Benzene was alkylated with propylene to produce cumene (Eq. 1) and diisopro-

$$(1)$$
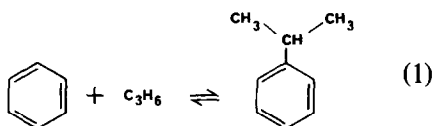
pylbenzene (Eq. 2). Disproportionation and

$$(2)$$
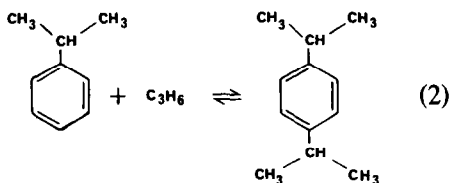
transalkylation reactions (Eq. 3) also occur

$$(3)$$

readily. Under certain conditions, especially at high temperatures, *n*-propylbenzene is also produced by secondary isomerization of cumene (Eq. 4).

$$(4)$$

Experiments were carried out with HZSM-5 catalysts to evaluate feasibility for production of cumene. Major reaction products were identified. Various conditions of reaction and results of initial scoping studies are summarized in Table 1.

At a 9/1 molar benzene/propylene feed ratio, virtually all of the propylene was converted to products at 182–282°C (Table 1). Cumene is the major product and diisopropylbenzenes (DIPB) are the major by-products. In addition, *n*-propylbenzene was detected, especially at the higher temperatures. Propylene oligomers were also observed.

Another series of reactions with HZSM-5 were studied at 175–300°C, 500 psig pressure (Table 2). Two 1-hr runs were made at each temperature after an initial half-hour period to stabilize reaction conditions. This catalyst, 250/1 molar silica/alumina ratio, has low activity, as indicated by low propylene conversion at 175–225°C, by comparison with the catalyst in Table 1, 70/1 ratio. This was expected because of the

TABLE 1

Alkylation of Benzene With Propylene[a]

	1	2	3	4	5
Conditions					
T (°C)	182	232	282	238	271
Pressure (psig)	450	400	400	600	600
WHSV	18	177	177	28	28
Bz/C₃H₆/C₃H₈ (mol)	9/1/0	9/1/0	9/1/0	9/1/0.6	9/1/0.6
Conversion to C₃H₆ (%)	98	95+	98	100	100
Time on stream (hr)	0–4[b]	0–2[b]	8–58	52[b]	126–150
Selectivity to products (wt% av. for time on stream range)					
Cumene	78.7	95	84.2	89.3	86.2
n-PrBz	0.8	0.4	6.9	0.6	1.2
C₁₀₊ Aromatic	14.5	4.6	8.9	5.5	12.5
Oligomer	0.6	0	0	4.6	0.1
Total	100	100	100	100	100

[a] Catalyst, HZSM-5; SiO_2/Al_2O_3, molar ratio, 70/1.
[b] Catalyst calcined before run.

TABLE 2

Alkylation of Benzene with Propylene to Produce Cumene[a]

Conditions										
T (°C)	175	175	200	200	225	225	250	250	300	300
Time on stream (hr)	1	2	3	4	5	6	7	8	9	10
Conversion%, Bz	1.8	3.3	4.6	7.4	8.1	7.6	12.6	14.5	18.9	18.9
Conversion%, C_3H_6	41.4	27.3	43.6	38.6	67	65.2	99.9	99.2	99.9	99.9
Selectivity to products (wt%)										
Cumene	92.7	94.4	91.9	92.5	88.4	89.1	66.5	69.1	38.2	38.7
n-PrBz	0.5	0.0	0.3	0.4	0.2	0.1	1.0	1.2	36.1	36.6
p-DIPB	2.4	2.3	4.0	3.5	4.8	4.6	1.9	2.3	0.7	0.7
m-DIPB	1.1	1.4	2.0	2.0	2.5	2.4	1.0	1.1	0.9	1.1
o-DIPB	0.4	0.5	0.7	0.6	0.8	0.8	0.3	0.1	0.6	0.5
C_{10+}	0.0	0.0	0.4	0.0	1.9	1.6	28.0	25.0	21.7	20.7
C_3H_8	1.3	1.1	0.6	0.8	0.4	1.0	1.1	0.9	0.8	0.8
C_4H_{10}	0.7	0.2	0.1	0.1	0.8	0.3	0.2	0.2	0.3	0.3
C_4H_8	0.9	0.1	0.0	0.1	0.1	0.0	0.0	0.1	0.1	0.1
C_5–C_9	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.6	0.5
Total	100	100	100	100	100	100	100	100	100	100
DIPB isomers										
para	61	54	60	58	60	59	61	66	32	32
meta	29	34	30	32	30	31	30	32	42	45
ortho	10	12	10	10	10	10	9	2	26	23

[a] Catalyst, HZSM-5; SiO_2/Al_2O_3, molar ratio, 250/1; pressure, 500 psig; WHSV, Bz 21.7, C_3H_6 2.5.

lower number of acid sites in the catalyst. The catalyst (Table 2) was not calcined between any of the runs. At the lower temperatures, 175 and 200°C, conversion of starting materials was low and catalyst performance during the second hour differed from that during the first. In contrast, results were similar for both pairs of runs at temperatures of 225–300°C, indicating stable performance.

At 225°C, similar conversions of starting materials for runs at 5 and 6 hr on stream are observed. Selectivity to cumene plus diisopropylbenzenes ranged from 97.1 to 99.1%. Only small amounts of n-propylbenzene were found. This suggests that the isopropyl cation, produced by protonation of propylene by the catalyst, is the active alkylation species. Traces of propane and butane in the gaseous product appear to be the only other by-products produced.

At higher temperatures, 250–300°C, significant reductions in cumene selectivities (69 to 38%) are observed (Table 2). Disproportionation and dealkylation reactions become significant at these higher temperatures, as shown by independent experiments starting with cumene. Propylene oligomerization accounts, in part, for the large increase in the C10+ high-boiling fraction. In addition, n-propylbenzene becomes a major product, 36% selectivity, at 300°C, presumably by subsequent isomerization of cumene (Eq. 4). However, at temperatures below 250°C, cumene isomerization is not a favorable reaction since there is a wide departure from the thermodynamic equilibrium ratios calculated for propylbenzenes, Table 3 (12).

Vapor pressure/temperature data suggest the presence of liquid-organic/solid-catalyst reaction phases at 225°C and lower,

TABLE 3

Calculated Thermodynamic Equilibria

T (°C)	Isopropylbenzene	n-Propylbenzene	
150	41.4	58.6	
200	38.6	61.4	
250	36.5	63.5	
300	34.7	65.3	
	Diisopropylbenzene		
	Para	Meta	Ortho
50	33.1	59.0	7.9
100	32.5	58.5	9.0

changing to gaseous/solid phases at 300°C. A mixed organic phase (gas and liquid) reaction probably occurs in the 250°C region. A thousandfold decrease in diffusivity for hydrocarbons in the liquid phase, compared with the vapor phase, may be a major factor in the variations observed in conversion of starting materials and product selectivity.

Previous papers in this series (10) have been concerned with various factors leading to para selectivity with disubstituted benzene products from alkylation or disproportionation reactions over various ZSM-5 catalysts. Toluene disproportionation to give xylenes and toluene alkylation with ethylene to produce ethyltoluene over a modified ZSM-5 have been studied (13). As alkyl groups on the benzene ring increase in size from methyl–methyl to methyl–ethyl, para selectivity increases. For example, about 95% p-ethyltoluene is produced from alkylation of toluene with ethylene, but only 75% p-xylene is obtained by toluene disproportionation under identical catalyst conditions using the same para-selective ZSM-5 catalyst. With a similar catalyst, 99% p-diethylbenzene is produced by alkylation of ethylbenzene with ethylene (10). Since the para isomer has the smallest minimum dimension and fastest rate of diffusion, as substituent groups increase in size, para selectivity increases. This is consistent with predictions for reactions which

take place within the sterically constrained zeolite pores.

In this work, the ratio of by-product diisopropylbenzene isomers during cumene production was also measured (Table 2). The HZSM-5 catalyst used here (not modified with reagents to give para selectivity) gives thermodynamic equilibrium mixtures of xylene isomers from toluene disproportionation (24% para) (14) and ethyltoluene from alkylation of toluene with ethylene (32% para) (13). The observed diisopropylbenzene isomers were similar in the 175–250°C temperature range (Table 2), averaging 60% para, 31% meta, and 8% ortho isomers. Calculated thermodynamic equilibra for diisopropylbenzene at 100°C (Table 3) indicates a para/meta/ortho ratio of roughly 33/58/9 (15). The observed values of 60/31/8 at 225–230°C (Table 2) show a strong preference for the para isomer. Para selectivity is achieved for this unmodified catalyst because of the relatively large isopropyl groups present. To summarize, para selectivity over ZSM-5 catalysts for alkyl groups on the benzene ring increase in the order methyl–methyl < methyl–ethyl < ethyl–ethyl ≪ isopropyl–isopropyl.

This work indicates that HZSM-5 is a catalyst for production of cumene by alkylation of benzene with propylene. The primary by-product is diisopropylbenzene. Preliminary experiments indicate that the latter can be recycled with fresh benzene over the same ZSM-5 catalyst to produce additional cumene in good yields by a transalkylation reaction. Potential process advantages for this zeolite over the established SPA catalyst are catalyst regenerability, elimination of downstream phosphoric acid contamination, elimination of need for metered water in the feed stream, high catalyst activity, and reduction in pollution and disposal problems.

SUMMARY

Benzene was alkylated with propylene over HZSM-5 zeolite catalysts to produce cumene with 88–94% selectivity. The major

by-product was 4–6% diisopropylbenzene, which may be recycled to produce more cumene by transalkylation with benzene. At reaction temperatures above 300°C, unwanted *n*-propylbenzene is also produced, 36% selectivity, along with high-boiling by-products.

ACKNOWLEDGMENTS

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