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Liquid-Phase Alkylation of Benzene with Light Olefins Catalyzed by β Zeolites

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The catalytic performance of zeolite β in the liquid-phase alkylation of benzene is compared with that of other solid catalysts. Zeolite β is more active and more selective than zeolite Y in the alkylation with propylene and ethylene to cumene and ethylbenzene (EB). In the alkylation with propylene the overall selectivity of β is higher than that of the traditional "solid phosphoric acid." The catalytic activity is affected by the composition and the particle size of zeolite β samples. Decreasing the framework Al content, by direct synthesis or by partial substitution of Al for B, produces a decrease in both conversion and selectivity in cumene and EB synthesis. A hypothesis to explain this behavior is given. The catalytic activity of zeolite β is limited by intraparticle diffusion, as evidenced by the decreased activity corresponding to the particle size increase. © 1995 Academic Press, Inc.

INTRODUCTION

The alkylation of benzene with ethylene and propylene to produce ethylbenzene (EB) and cumene, respectively, is widely used in the petrochemical industry. Cumene is an important chemical intermediate mainly used for the production of phenol and acetone (1), while EB is the intermediate for styrene production. In the petrochemical industry these benzene alkylations are usually catalyzed by $AlCl_3$ (EB) and by "solid phosphoric acid" (cumene). The use of both catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal. Much effort has been put into developing alternative catalyst systems.

In the production of EB, the $AlCl_3$-based processes are progressively substituted with zeolite-based processes. Since 1976 the medium-pore zeolite ZSM-5 has been in use in the Mobil–Badger process for the vapor-phase alkylation of benzene with ethylene (2). Recently a new process was developed by UOP/Lummus/Monsanto/Unocal/Chemical Research Licensing (3). The catalyst is based on a Y-type zeolite and it operates at much lower temperatures and higher pressure, at which the feedstock is in liquid phase. This process has the advantage of better thermal control and longer catalyst life, which allow off-site catalyst regeneration and therefore an easier control of pollution.

Zeolite-based catalyst systems have been extensively evaluated for the cumene process also. Two commercial cumene processes, catalyzed by zeolites, have been developed by Mobil and CDTECH. The former, called the Mobil–Badger Cumene Process (4) operates in a fixed-bed reactor system. The latter is based on a Y-type zeolite and operates in a catalytic distillation column reactor (5).

Very recently Dow has claimed the development of a new cumene process based on a highly dealuminated mordenite catalyst (6).

Good performances of zeolite β were also reported for the benzene alkylation in liquid phase, with both ethylene and propylene (7). Furthermore, among the large-pore zeolites, better stability and selectivity in the liquid-phase alkylation of benzene with propylene were observed over ZSM-12 and β zeolites in comparison with Y zeolites (8). Among the 12-membered ring zeolites H-β was also found to be the best catalyst for the vapor-phase alkylation of benzene with isopropanol, followed by H-ZSM-12 and H-mordenite (9). β zeolites can be prepared with different Al contents by direct synthesis of the silico-aluminate (10) or by isomorphous substitution of Al for B (11). In any case this results in a modification of the overall acidity (12) and of the catalytic behavior (9). This paper reports the results of an investigation on the catalytic behavior of β zeolites with different Si/Al in the liquid-phase alkylation of benzene with propylene and ethylene, performed in our laboratories as a part of our research activity in this field.

EXPERIMENTAL SECTION

Zeolite Preparation

Zeolite β samples with Si/Al = 14, 17.5, and 35 were synthesized as described elsewhere (13). In order to obtain a further reduction of Al content (Si/Al = 41 and 112), Al was then substituted with B following Ref. (11).

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TABLE 1

Relevant Characteristics of the Catalysts Employed

Catalyst	Nature	Origin	Product	S_{BET} (m^2/g)	Si/Al mol ratio	Si/B mol ratio	Particle size[a] (μm)
PA	Supported H_3PO_4	Enichem synthesis	CA 113	4.5	—	—	—
H-ZSM-5	Zeolite ZSM-5	Conteka BV	CBV 5020	410	20	—	—
USY	Zeolite Y	Tosoh	TSZ HUA 330	500–600	3	—	—
B1	zeolite β	This lab		693	14	—	≅0.2
B2	zeolite β	This lab		700	17.5	—	≅0.7
B3	zeolite β	This lab		680	35	—	≅0.7
B4	zeolite β	This lab		690	14	—	≅0.4
B5	zeolite β	This lab		680	14	—	≅0.7
B6	zeolite β	This lab		670	13	—	>1
B7	zeolite β	This lab		705	41	53	≅0.8
B8	zeolite β	This lab		670	112	40	≅0.8

[a] Determined by transmission electron microscopy.

Commercial samples of kieselguhr-supported phosphoric acid (PA), ultrastable Y zeolite (USY), and H-ZSM-5 were used as supplied by Enichem Synthesis, Tosoh, and Conteka BV, respectively.

Table 1 reports the main characteristics of the samples tested.

Apparatus, Procedure, and Analysis

The catalytic tests were carried out either in a stirred batch reactor or in a continuous flow, fixed-bed catalytic reactor.

Benzene was a C. Erba reagent, ≥99% pure. Ethylene and propylene were supplied by SIAD, ≥99.9% pure. All these reagents were used as supplied.

For the cumene synthesis, 0.4 g zeolite powder and 400 ml benzene were loaded in a nitrogen-purged half-liter autoclave, then the temperature was raised to 150°C and propylene was rapidly fed to reach a benzene/propylene molar ratio = 7.4. The reactor was then pressurized at 3 MPa by feeding nitrogen. Several liquid samples were withdrawn during the reaction time. The liquid samples were analyzed by high-performance gas chromatography (Perkin-Elmer 8200, fitted with a FID detector), using a DB-1 (J&W) wide-bore capillary column.

Three cumene selectivities were evaluated for each sample:

—cumene selectivity referred to benzene ([C9]/[C6]);

—cumene selectivity referred to propylene ([C9]/[C3]);

—selectivity of isopropylbenzenes (IPBs) (cumene, diisopropylbenzenes, triisopropylbenzenes) referred to propylene ([IPBs]/[C3]).

For the EB synthesis, 0.8 g zeolite powder and 400 ml benzene were loaded in a nitrogen-purged half-liter autoclave, then the temperature was raised up to 180°C and ethylene was rapidly fed to reach a benzene/ethylene molar ratio = 4.5. The reactor was then pressurized at 4.5 MPa by feeding nitrogen. Several liquid samples were withdrawn during the reaction time.

To perform the tests under continuous flow, the reactor was charged with a sample of zeolite, crushed from 1.5 tons/cm^2 pelletized wafers and sieved to 20–40 mesh particles. The liquid samples were analyzed by the same procedure (high-performance gas chromatography) used for cumene. Three EB selectivities were evaluated for each sample:

—EB selectivity referred to benzene ([C8]/[C6]);

—EB selectivity referred to ethylene ([C8]/[C2]);

—selectivity of ethylbenzenes (EBs) (ethylbenzene, diethyl-, and triethylbenzenes) referred to ethylene ([EBs]/[C2]).

For sake of comparison the compositions and the selectivities of the samples withdrawn during the catalytic test performed batchwise are referred to a normalized reaction time τ, defined as follows: $\tau = W/F^*t$, where W is the catalyst weight (g), F is the amount of benzene–olefin mixture (g), and t is the reaction time (min).

RESULTS

Benzene Alkylation with Propylene

Zeolite comparison. In Table 2 the catalytic activities of H-ZSM-5, USY, and zeolite β (sample B1) are compared after 1 h under the reaction conditions given above. The ZSM-5 is almost not active in these conditions, whereas β- and Y-type zeolites show a significant activity. The initial activity and selectivity of zeolite β are higher than those of the commercial USY zeolite. It must be remarked that

TABLE 2

Catalytic Activity of β (sample B1), USY, and ZSM-5 in benzene alkylation with propylene (T = 150°C, P = 3 MPa, benzene/propylene = 7.4, τ = 0.06 min)

	B1	USY	H-ZSM-5
Benzene conversion (%)	11.8	4.4	0.31

assuming a 100% selectivity and according to the stoichiometry, 100% propylene conversion corresponds to 13.51% benzene conversion. Therefore with zeolite β the conversion of propylene is almost complete after 1 h. The USY sample used in this experiment was chosen from among several commercial Y zeolites with different aluminum contents because it was the most active, according to its lowest Si/Al.

The performances of both β and USY zeolites during the same experiments are compared with those of PA. In Table 3 the composition (benzene free) of the samples withdrawn from the autoclave, at the same propylene conversion (≅90%) is reported. A higher temperature (200°C) is required by PA in order to reach a comparable activity. PA produces the largest amount of propylene oligomers but the smallest amount of diisopropylbenzenes (DIPBs). So both cumene selectivities ([C9]/[C6]; [C9]/[C3]) are the highest. USY produces more *n*-propylbenzene, butyl- and pentylbenzenes, and DIPBs. This accounts for the lowest cumene selectivities. However, the selectivity of IPBs with respect to propylene is lower for PA than for β and USY zeolites.

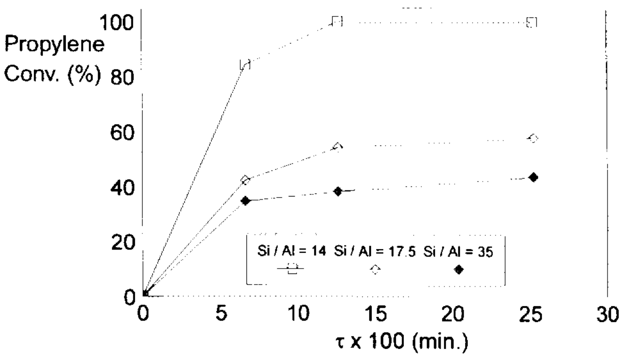

FIG. 1. Benzene alkylation with propylene (T = 150°C, P = 3 MPa, benzene/propylene = 7.4), influence of Si/Al (samples B5, B2, B3).

Influence of framework composition in zeolite β. Figure 1 reports the kinetic experiments performed with β zeolites with different Si/Al (samples B5, B2, and B3) but almost the same particle size. Decreasing the amount of framework aluminum in zeolite β (increasing the Si/Al), a decrease in catalytic activity is observed. Besides, after an initial increase, the conversion grows very slowly for B2 and B3 samples. This seems to indicate that β zeolites with low Al content deactivate more rapidly. The selectivities determined for selected samples during the same experiments are compared in Table 4. Even at low propylene

TABLE 3

Comparison of Zeolite β, USY, and PA in Benzene Alkylation with Propylene[a]

	B1 (Si/Al = 14)	USY (Si/Al = 3)	PA[b]
Product wt.% (benzene free)	0.3	0.3	1.1
Oligomers	0.3	0.3	0.3
Toluene, ethylbenzene	193.0	477.0	200.0
n-Propylbenz. (ppm)	94.3	89.9	95.1
Cumene	175.0	848.0	400.0
Phenyl-(C4) (ppm)	82.0	530.0	400.0
Phenyl-(C5) (ppm)	4.5	8.8	3.2
Diisopropylbenzenes	0.0	159.0	200.0
Triisopropylb. (ppm)	0.3	0.4	0.2
>Phenyl-(C6)			
Selectivity (%)[c]			
[C9]/[C6]	95.7	92.5	97.0
[C9]/[C3]	91.8	85.7	91.8
[IPBs]/[C3]	98.3	98.2	96.4

[a] T = 150°C; P = 3 MPa; Benzene/propylene = 7.4.
[b] T = 200°C.
[c] Propylene conversion ~90%.

TABLE 4

Benzene Alkylation with Propylene: Influence of Si/Al[a]

	B5 (Si/Al = 14)	B2 (Si/Al = 17.5)	B3 (Si/Al = 35)
Product wt.% (benzene free)			
Oligomers	0.8	1.5	2.5
Toluene, ethylbenzene	0.4	0.6	0.8
n-Propylbenz. (ppm)	140.0	123.0	194.0
Cumene	93.4	93.3	92.9
Phenyl-(C4) (ppm)	220.0	308.0	207.0
Phenyl-(C5) (ppm)	135.0	135.0	87.0
Diisopropylbenzenes	4.8	4.3	3.4
Triisopropylb. (ppm)	50.0	173.0	132.0
>Phenyl-(C6)	0.5	0.2	0.3
Propylene conversion (%)	84.3	57.8[b]	43.6[b]
Selectivity (%)			
[C9]/[C6]	95.5	95.8	96.2
[C9]/[C3]	89.9	89.0	87.5
[IPBs]/[C3]	96.7	95.2	92.8

[a] T = 150°C; P = 3 MPa; Benzene/propylene = 7.4.
[b] Maximum propylene conversion achieved.

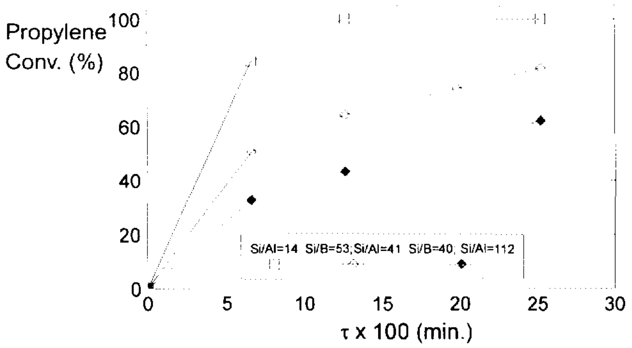

FIG. 2. Benzene alkylation with propylene (T = 150°C, P = 3 MPa, benzene/propylene = 7.4), influence of Si/Al and Si/B (samples B5, B7, B8).

conversion, less active catalysts (B2 and B3) produce more propylene oligomers. As a consequence the selectivity of IPBs is reduced. Similar results were observed when Al was partially replaced by B. The kinetic experiments performed with increasing Si/Al ratio and decreasing Si/B ratio (samples B5, B7, and B8) are reported in Fig. 2. Again decreasing Al content and increasing B content produces a decrease in the catalytic activity and an increase in the oligomer production (Table 5).

Influence of particle size. The influence of particle size on catalytic activity is reported in Fig. 3. The propylene conversion is very much reduced when the mean particle size is above 1 μm. Also, the selectivity is affected by the particle size. Table 6 reports the composition of selected samples obtained during the same experiments. An increase in oligomer and triisopropylbenzene formation corresponds to the increase in particle size.

Benzene Alkylation with Ethylene

Zeolite comparison. The catalytic behavior of β and Y zeolites were compared in a continuous flow test. Table 7 reports the selectivities of EB and the main by-products obtained with zeolite β (sample B1) and USY zeolite, corresponding to the complete conversion of ethylene. Zeolite β produces more diethylbenzenes and triethylbenzenes than Y-type zeolite, but the latter produces much more heavier by-products (higher alkylbenzenes such as biphenyl and diphenylethane). The selectivity of EBs is higher for zeolite β.

Influence of framework composition of zeolite β. The kinetic experiments with β zeolites with different aluminum content (samples B5, B2, and B3) are reported in Fig.

TABLE 5

Benzene Alkylation with Propylene: Influence of Si/Al and Si/B[a]

	B5 (Si/Al = 14)	B7 (Si/Al = 41; Si/B = 53)	B8 (Si/Al = 112; Si/B = 40)
Product wt.% (benzene free)			
Oligomers	0.8	2.0	2.9
Toluene, ethylbenzene	0.4	0.2	0.3
n-Propylbenz. (ppm)	140.0	213.0	247.0
Cumene	93.4	92.8	92.9
Phenyl-(C4) (ppm)	220.0	211.0	405.0
Phenyl-(C5) (ppm)	135.0	743.0	1,000.0
Diisopropylbenzene	4.8	4.2	3.2
Triisopropylb. (ppm)	50.0	127.0	26.0
>Phenyl-(C6)	0.5	0.5	0.5
Propylene conversion (%)	84.3	81.7[b]	62.1[b]
Selectivity (%)			
[C9]/[C6]	95.5	96.0	96.7
[C9]/[C3]	89.9	87.7	86.7
[IPBs]/[C3]	96.7	93.6	91.9

[a] T = 150°C; P = 3 MPa; Benzene/propylene = 7.4.
[b] Maximum propylene conversion achieved.

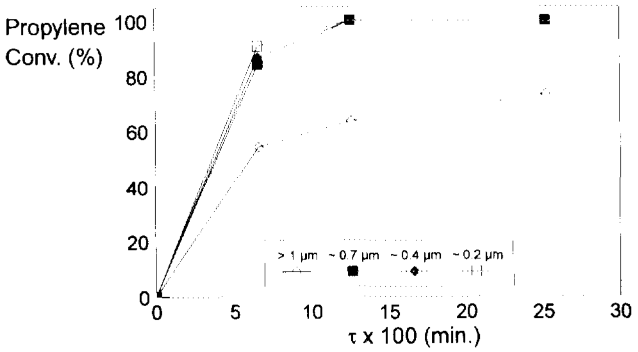

FIG. 3. Benzene alkylation with propylene (T = 150°C, P = 3 MPa, benzene/propylene = 7.4), influence of particle size (samples B1, B4, B5, B6).

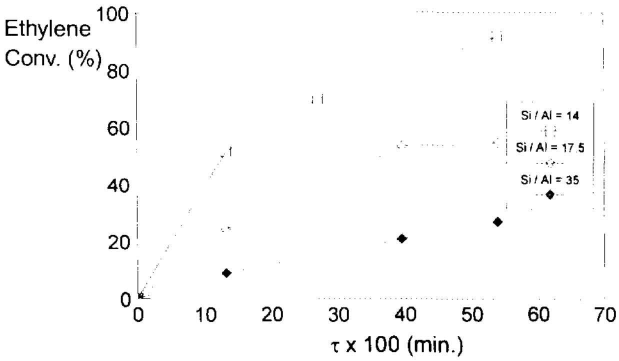

FIG. 4. Benzene alkylation with ethylene (T = 180°C, P = 4.5 MPa, benzene/ethylene = 4.5), influence of Si/Al (samples B5, B2, B3).

TABLE 6

Benzene Alkylation with Propylene: Influence of Particle Size[a]

	B6 (>1 μm)	B5 (~0.7 μm)	B4 (~0.4 μm)	B1 (~0.2 μm)
Product wt.% (benzene free)				
Oligomers	1.9	0.8	1.1	0.3
Toluene, ethylbenzene	0.6	0.4	0.5	0.6
n-Propylbenz. (ppm)	160.0	140.0	180.0	193.0
Cumene	92.4	93.4	93.8	94.3
Phenyl-(C4) (ppm)	159.0	220.0	330.0	175.0
Phenyl-(C5) (ppm)	93.0	135.0	198.0	82.0
Diisopropylbenzenes	4.6	4.8	4.2	4.5
Triisopropylb. (ppm)	330.0	50.0	40.0	0.0
>Phenyl-(C6)	0.4	0.5	0.3	0.3
Propylene conversion (%)	73.4[b]	84.3	86.8	90.9
Selectivity (%)				
[C9]/[C6]	95.4	95.5	95.9	95.7
[C9]/[C3]	87.4	89.8	90.1	91.8
[IPBs/[C3]	93.9	96.7	96.6	98.3

[a] T = 150°C; P = 3 MPa; Benzene/propylene = 7.4.

[b] Maximum propylene conversion achieved.

4. The conversion decreases through a decrease in the framework aluminum content. The selectivities obtained during the same experiments, corresponding to selected samples, are reported in Table 8. Though the ethylene conversion is low (26.5%), sample B3, with the highest Si/Al, produces more ethylene oligomers and hence shows the lowest selectivity of EBs.

Similar results were observed when Al was partially replaced by B. The kinetic experiments performed with increasing Si/Al and decreasing Si/B (samples B5, B7 and B8) are reported in Fig. 5. The decrease in Al content determines a decrease in the catalytic activity. Again less active zeolites produce more ethylene oligomers (Table 9) and show low selectivities.

TABLE 7

Comparison between Zeolite β (sample B1) and USY in Benzene Alkylation with Ethylene[a]

	B1 (Si/Al = 14)	USY (Si/Al = 3)
Ethylene conversion (%)	100	100
Selectivity		
[C8]/[C6]	88.8	89.1
[Diethylbenzenes]/[C6]	9.7	7.3
[Triethylbenzenes]/[C6]	0.8	1.2
[Higher alkylbenzenes]/[C6]	0.05	1.8
[C8]/[C2]	79.6	76.6
[EBs]/[C2]	99.1	92.3

[a] T = 170°C; P = 3.5 MPa; benzene/ethylene = 5; contact time (catalyst weight/feed rate) = 10.2 min.

Influence of particle size. Figure 6 reports the kinetic experiments performed by changing the particle size. The ethylene conversion is reduced when the mean particle diameter increases. Table 10 reports the composition obtained with the different zeolite samples at almost the same ethylene conversion. An increased amount of toluene and propylbenzenes is obtained when the size increases. However such small differences do not affect the selectivities.

DISCUSSION

Benzene Alkylation with Propylene

The alkylation of benzene with propylene is an electrophilic substitution on the aromatic ring. Alkylation reac-

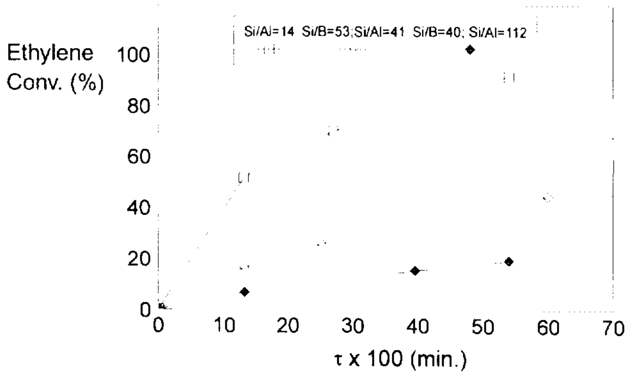

FIG. 5. Benzene alkylation with ethylene (T = 180°C, P = 4.5 MPa, benzene/ethylene = 4.5), influence of Si/Al and Si/B (samples B5, B7, B8).

TABLE 8

Benzene Alkylation with Ethylene: Influence of Si/Al[a]

	B5 (Si/Al = 14)	B2 (Si/Al = 17.5)	B3 (Si/Al = 35)
Product wt.% (benzene free)			
Oligomers	0.1	0.2	0.5
Toluene (ppm)	750.0	361.0	400.0
Ethylbenzene	94.6	93.2	94.5
Phenyl-(C3)	0.4	0.5	0.7
Diethylbenzenes	4.8	5.3	3.4
Triethylbenz. (ppm)	1.000.0	389.0	415.0
>Phenyl-(C6)	0.0	0.4	0.4
Ethylene conversion (%)	51.6	54.3[b]	26.5[b]
Selectivity (%)			
[C8]/[C6]	95.7	95.0	96.3
[C8]/[C2]	91.6	89.7	91.2
[EBs]/[C2]	99.1	0.8	1.2
[Higher alkylbenzenes]/[C6]	0.05	1.8	
[C8]/[C2]	79.6	76.6	
[EBs]/[C2]	99.1	92.3	

[a] $T = 170°C$; $P = 3.5$ MPa; benzene/ethylene = 5; contact time (catalyst weight/feed rate) = 10.2 min.

TABLE 9

Benzene Alkylation with Ethylene: Influence of Si/Al and Si/B[a]

	B5 (Si/Al = 14)	B7 (Si/Al = 41; Si/B = 53)	B8 (Si/Al = 112; Si/B = 40)
Product wt.% (benzene free)			
Oligomers	0.1	0.2	0.8
Toluene (ppm)	750.0	703.0	1,000.0
Ethylbenzene	94.6	93.4	93.8
Phenyl-(C3)	0.4	0.5	0.7
Diethylbenzenes	4.8	5.7	3.9
Triethylbenzenes	0.1	0.1	0.1
>Phenyl-(C6) (ppm)	0.0	0.0	553.0
Ethylene conversion (%)	51.6	44.5[b]	19.3[b]
Selectivity (%)			
[C8]/[C6]	95.7	94.8	95.9
[C8]/[C2]	91.6	89.7	89.9
[EBs]/[C2]	99.1	98.6	96.0

[a] $T = 180°C$; $P = 4.5$ MPa; Benzene/ethylene = 4.5.

[b] Maximum ethylene conversion achieved.

tions catalyzed by acidic zeolites are commonly considered as proceeding via carbonium-ion-type mechanisms (14). On Brønsted acid catalysts the mechanism of the propylation may be described as reported in Fig. 7. Propylene is protonated by the acid sites to form the active species. The latter can follow two major routes; it can react with benzene, producing cumene, which can later on undergo other reactions producing mainly di- and triisopropylbenzenes, or it can react with another propylene molecule, producing a C_6 species which can be further transformed through oligomerization, cracking, isomerization, and alkylation, giving olefins and other alkylbenzenes. It must be remarked that the presence of by-products different from IPBs affects both the yield and the quality of cumene. The latter can heavily influence the efficiency of the subsequent process for conversion of cumene to phenol and acetone (15).

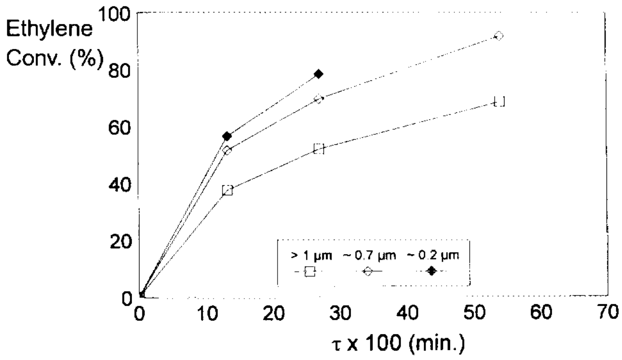

FIG. 6. Benzene alkylation with ethylene ($T = 180°C$, $P = 4.5$ MPa, benzene/ethylene = 4.5), influence of particle size (samples B1, B5, B6).

In liquid-phase alkylation and at low temperature the activity of ZSM-5 is very poor (Table 2). This is probably because of diffusion limitations, due to the constrained pores (10-membered ring openings). On the contrary, 12-membered ring opening zeolites, such as β and Y, are very active. The selectivities of IPBs of both zeolites are comparable (Table 3). The major difference is the enan-

TABLE 10

Benzene Alkylation with Ethylene: Influence of Particle Size[a]

	B6 (>1 μm)	B5 (~0.7 μm)	B1 (~0.2 μm)
Product wt.% (benzene free)			
Oligomers	0.1	0.1	0.1
Toluene (ppm)	671.0	750.0	327.0
Ethylbenzene	94.6	94.6	93.7
Phenyl-(C3)	0.6	0.4	0.3
Diethylbenzenes	4.5	4.8	5.7
Triethylbenzenes	0.1	0.1	0.1
>Phenyl-(C6) (ppm)	0.0	0.0	0.0
Ethylene conversion (%)	52.0	51.6	56.5
Selectivity (%)			
[C8]/[C6]	95.7	95.7	95.1
[C8]/[C2]	91.8	91.6	90.4
[EBs]/[C2]	98.8	99.1	99.2

[a] $T = 180°C$; $P = 4.5$ MPa; Benzene/ethylene = 4.5.

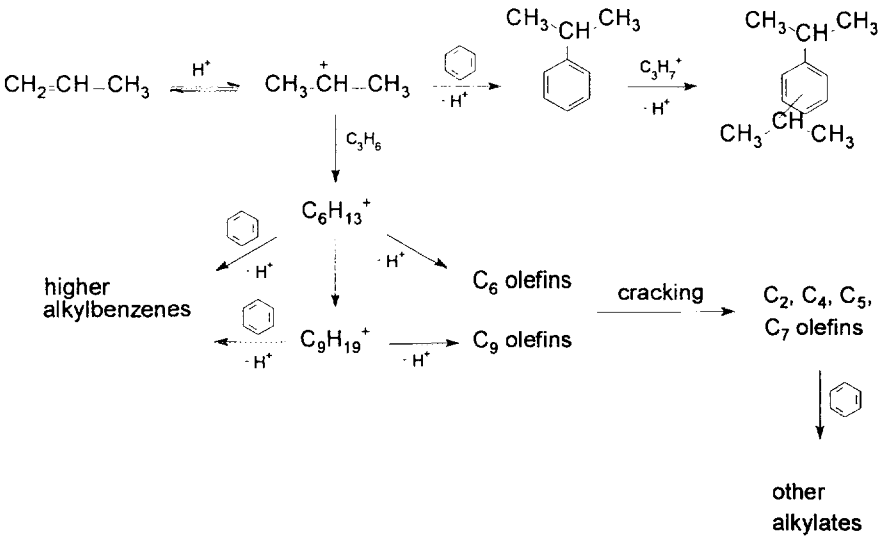

FIG. 7. Benzene alkylation with propylene, reaction pathways.

ched formation of phenyl-C_4, -C_5, and heavier, via oligomerization, cracking, isomerization, and alkylation, observed with USY. This seems to be reasonable because of the presence of supercages (diameter 12 Å). In contrast, zeolite β contains channels with access openings (5.7 × 7.5 Å and 6.5 × 5.6 Å (16)) that are only slightly larger than the size of benzene molecule. Therefore this catalyst should not permit the formation of those molecules with critical diameters that exceed significantly those of benzene. Zeolite β is also more active and more selective than PA, if di- and triisopropylbenzenes are considered as useful by-products. In fact they can be recovered by transalkylation with benzene to cumene (17).

According to the previous mechanism the activity of a zeolite should depend on Brønsted acid site concentration. It is well known that the reduction of aluminum content determines the reduction of the acid site density (12). As reported above, decreasing the framework aluminum content of zeolite β, by changing the zeolite synthesis conditions, we observed that the catalytic activity decreased (Fig. 1 and 2) and the production of propylene oligomers increased (Tables 4 and 5). As the Brønsted site density and the propylene concentration in the zeolite pores are of the same order of magnitude,[1] the probability for an active species to react with a propylene molecule is higher when the active site density is lower. Therefore, according to the above considerations the observed behavior, that is, fewer acid sites leading to more oligomers and more acid sites leading to fewer oligomers, could be explained.

The more rapid deactivation of the samples with lower Al content (B2 and B3 in Fig. 1) can be related to the higher oligomer formation. As is well known, oligomers can undergo cyclization and aromatization reactions on acidic catalysts. This results in the formation of polyaromatics (coke precursors) and leads to the catalyst deactivation (18). However, when the Al is partially replaced by B, the tendency to deactivate is reduced (compare B7 and B8 to B2 and B3 in Figs. 2 and 1), though the oligomer formation is comparable on all samples (Tables 4 and 5). This seems to indicate that the subsequent transformation of the oligomers into coke is more difficult on the zeolite-containing B.

The decrease of catalytic activity by increasing the particle size (Fig. 3) can be attributed to the influence of intraparticle diffusion. This is in agreement with the results obtained by other authors for the alkylation of benzene with olefins, catalyzed by zeolites (19).

Benzene Alkylation with Ethylene

The mechanism of benzene ethylation may be described as similar to that already reported for propylene. The first step is again a protonation by a Brønsted acid site to form the active species (20). However, as the proton affinity of ethylene is lower than that of propylene (160.6 vs 180.4 kcal/mol) (21), a reduced activity is expected for ethylene. Indeed, in order to reach comparable olefin conversions, higher temperature (180 vs 150°C) and longer reaction time are required.

The reaction of benzene and ethylene produces significant amounts of higher alkylates (e.g., biphenyl and diphenylethane) when Y-type zeolite is used (Table 7). On the contrary, zeolite β is more selective with respect to ethylene ([C8]/[C2] selectivity in Table 7), since it produces a

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[1] The pore volume and Brønsted site density (determined by pyridine adsorption experiments (13)) of a zeolite β sample (e.g., B1) are, respectively, 0.23 cm^3/g and 0.26 mmole/g. At the reaction conditions described above, the amount of propylene filling the pores of 1 g of zeolite is ≅0.3 mmole, which is comparable to the acid site density.

lower amount of higher alkybenzenes. The different behavior is much more evident when one considers the selectivity of EBs, which means taking into account the possibility of recovering di- and triethylbenzenes by transalkylation (22). Again the inferior performance of Y can be attributed to the presence of supercages.

Decreasing the framework aluminum content of zeolite β by direct synthesis or by isomorphous substitution with B, a decrease in catalytic activity and selectivity (see Figs. 4 and 5, Tables 8 and 9) is observed. Such behavior can also be explained by the above discussion of propylene.

Concerning the catalytic performance, when the particle size changes, ethylene behaves similarly to propylene; when the particle size (Fig. 6) was increased a decrease in catalytic activity was observed. This is further evidence of the influence of intraparticle diffusion in the liquid-phase alkylation of benzene with light olefins catalyzed by zeolites.

CONCLUSIONS

Among the catalysts studied here, zeolite β appears to be one of the most efficient catalysts for liquid-phase alkylation of benzene with light olefins. The catalytic activity of β is affected by the composition; the increase of framework Al content produces an increase in both conversion and selectivity in cumene and EB synthesis.

Zeolite β is more active and more selective than Y-type zeolites for the alkylation of benzene with propylene. Zeolite β is also more active and selective than PA, the traditional catalyst for cumene production, provided that a polyalkylate transalkylation step is applied. In EB synthesis the production of di- and triethylbenzenes is higher for β than Y zeolite; once more, considering the transalkylation, the overall selectivity is higher with β.

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