Efficient Synthesis of Amylbenzenes over Zeolite Catalysts

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The liquid-phase heterogeneous alkylation of benzene with 2-methyl-2-butene takes place actively and selectively over large-pore zeolite catalysts, which implies an environmentally friendly route for the synthesis of *tert*-amylbenzene.

tert-Amylbenzene (*t*-AB) is an important intermediate chemical in the production of 2-amylanthraquinone (AMQ) which serves as an efficient working solution in the manufacture of H_2O_2.[1,2] Having a better solubility, AMQ gives the higher catalytic activity, stability, and H_2O_2 yield than conventional 2-ethylanthraquinone. With an increasing development of H_2O_2-based clean chemical processes, the needs of AMQ are anticipated to increase annually. The conventional manufacturing methods for *t*-AB, the raw material for AMQ synthesis, are thus becoming a bottleneck restraining its wide application. Moreover, *t*-AB with good solvent properties and a low vapor pressure proves to be a suitable solvent in pharmaceutical, fine chemical and electronical manufactures.[3]

The conventional processes for *t*-AB production are based on two kinds of catalytic reactions. One is the Friedel–Crafts alkylation of benzene with 2-methyl-2-butene (MeB) catalyzed by homogeneous catalysts such as H_2SO_4, BF_3, $AlCl_3$, $FeCl_2$, etc.[1] The other is the side-chain alkylation of cumene or ethylene performed on the solid base catalysts such as alkali metals, alkaline earth metal compounds, and alkali metal hydrides.[4] Both methods suffer the problems such as hard handling, danger, corrosion, and waste disposal. It is urgent to develop alternative heterogeneous catalyst systems which are environmentally benign, benefit, and sustainable.

Zeolites have been applied successfully to the commercial processes for the clean production of alkylbenzenes such as cumene and ethylbenzene.[5] These have substituted the conventional alkylation processes operated with phosphoric acid and $AlCl_3$ catalysts. Analogously, it is desirable to develop zeolite-based innovative, green and heterogeneous chemical process for *t*-AB synthesis via benzene alkylation. Nevertheless, unlike ethylene and propylene, MeB as an alkylation agent is characteristic of bulkier molecular dimension and higher polymerization reactivity. This may lead to complicated product distribution and alkylation behaviors. We communicate here for the first time the catalytic properties and product distribution of benzene alkylation with MeB over various zeolites. Large-pore zeolites of 12-membered ring (MR) have been found to be promising catalysts for the selective formation of *t*-AB. The reaction pathways have been clarified on the basis of the results achieved with various reaction conditions.

Proton-type zeolites (ZSM-5, Beta, MCM-22, and USY) were physically mixed with γ-Al_2O_3 binder at a weight ratio of 70 to 30 and shaped into particles of 0.83–1-mm diameter. The alkylation of benzene with MeB was conducted in liquid-phase at 3.5 MPa using a down-flow fixed-bed microreactor. The reaction was started by injecting the mixture of benzene and MeB (95%, Acros) into the reactor, and conducted continuously.

The benzene isopentylation showed a relatively complicated product distribution. The careful analyses with GC-MS have identified various products. According to the alkylation mechanism shown latter, they could be classified into five categories, that is, the main product of *t*-AB; its isomers of *sec*-amylbenzene (*s*-AB); *t*-butylbenzene (*t*-BB), and hexylbenzene (HB) isomers; oligomers (mostly C_{10}-olefins); and heavy products like dialkylbenzenes.

Table 1 compares the catalytic activity and product selectivity among ZSM-5, USY, MCM-22, and Beta zeolites. The activity of ZSM-5 was very poor even when the alkylation was carried out at a higher temperature of 350 °C in gas-phase (No. 1). The constrained 10-MR pores of MFI structure restricted the formation of bulky alkylbenzene like *t*-AB. MCM-22, Beta and USY zeolites, on the other hand, turned to be significantly active. Particularly, Beta and USY were capable of converting MeB completely (Nos. 3–6). It is reasonable that the *t*-AB formation requires a relative open reaction space. These results are very similar to the benzene alkylation with propene to cumene.[6]

MCM-22, a talent catalyst used successfully in the selective production of ethylene and cumene,[7] was less active (No. 2). Owing to the space hindrance effects on bulky molecules, the benzene isopentylation were presumably restricted to the 12-MR side pockets on the external surface of crystals rather than two interlayer and interlayer 10-MR channels.[8] The interlayer supercages accessible through only 10-MR windows are seemingly not useful to the present alkylation. Furthermore, MCM-22 produced more undesirable butylbenzene, hexylbenzene, and heavy products.

Compared with Beta, USY gave an enhanced selectivity for BB and HB, and a lower selectivity to *s*-AB (Nos. 3 and 4). A declined *s*-AB selectivity would be favorable of increasing the *t*-AB selectivity in ultimate amylbenzene products. Thus, the

Table 1. The results of benzene isopentylation on zeolites[a]

No.	Cat	Si/Al	Conv. /%	Product distribution/%					Coke[c] /%
				$C_{10}^{=}$	*t*-AB	*s*-AB	BB+HB	Heavy	
1[b]	ZSM-5	25	<10	—	—	—	—	—	4.6
2	MCM-22	15	91	2.3	64.6	8.3	18.5	6.1	6.8
3	USY	3.4	100	0	72.8	6.2	18.5	2.5	8.0
4	Beta1	12	100	0	76.4	14.6	7.1	1.9	6.6
5	Beta2	23	100	0	73.9	14.0	8.8	3.2	5.4
6	Beta3	34	98	0	71.6	12.1	10.2	6.0	5.6

[a]Reaction condition: cat., 0.5 g; pressure, 3.5 MPa; $B/C_5^{=}$, 60; WHSV, 36 h^{-1}; Temp, 175 °C. [b]This reaction was carried out at 350 °C in gas phase. No reliable selectivity was obtained because of too low yield of products. [c]Accumulated amount of coke at 7 h of TOS (analyzed with TG-DTA).

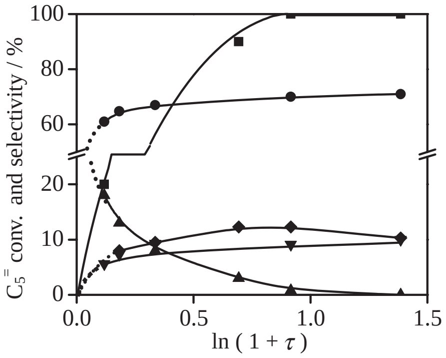

Figure 1. Dependence of $C_5^=$ olefin conversion (■), selectivity of *t*-AB (●), *s*-AB (▼), oligomers (▲), and the sum of BB and HB (◆) on ln (1 + τ). Condition: Beta1, 0.5–1 g; pressure, 3.5 MPa; B/$C_5^=$, 60; Temp, 150 °C. τ, contact time, the reciprocal of WHSV in min.

t-AB selectivity was very comparable between USY and Beta. However, USY with high acid concentration suffered a fatal drawback of shorter catalytic life. It deactivated severely after 2 h of time on stream (TOS) owing to rapid coke deposition inside the pores, whereas the life time of Beta prolonged to a TOS of 24 h.

Beta zeolites with various Si/Al ratios have been synthesized and then applied to the alkylation. With increasing Si/Al ratio, the catalytic activity decreased slightly, while the production of oligomers, BB and HB tended to be enhanced (Nos. 4–6). These trends suggest that a lower framework Al content, that is smaller amount of acid sites, favors the oligomerization versus the alkylation reaction.[9]

Figure 1 shows the dependence of MeB conversion and product selectivities on the reaction contact time. The selectivity of oligomers ascended sharply when the contact time approached to zero. Oligomerization, taking place parallel to the benzene isopentylation, was undoubtedly one of primary reactions. With increasing contact time, the oligomer selectivity decreased gradually, whereas that of BB and HB increased correlatively and reached a maximum flexion. These results implied that BB and HB were the secondary products of oligomers. Additionally, the selectivities of *t*-AB and *s*-AB increased monotonously with prolonging contact time.

The reaction mixture cumulatively collected was injected into the reactor containing Beta zeolite. The composition essentially remained the same, which confirmed us that neither monomolecule isomerization of *t*-AB nor bimolecular trans-alkylation between *t*-AB and benzene was feasible because of the thermodynamic respect and the great space hindrance in the channel of zeolites. *s*-AB, BB, and HB were thus not the secondary products from *t*-AB.

A tentative reaction pathway for the benzene alkylation with MeB over zeolite catalysts was obtained on the basis of the reaction results (Figure 2). MeB is initially protonated on the acid sites to form the active intermediate, *t*-amyl cations. The carbenium ions induce uphill isomerization forming the secondary cations[10] as well as oligomerization producing the oligomers of C_{10} olefins. The successive alkylations of *t*- and *s*-amyl cations yield the alkylbenzenes of *t*-AB and *s*-AB, respectively. The C_{10} oligomers formed, in succession, crack into *t*-butyl cation and hexene isomers which further alkylate benzene to produce BB and HB. All above monoalkylbenzenes undergo further alkylation reactions to yield dialkylbenzenes.

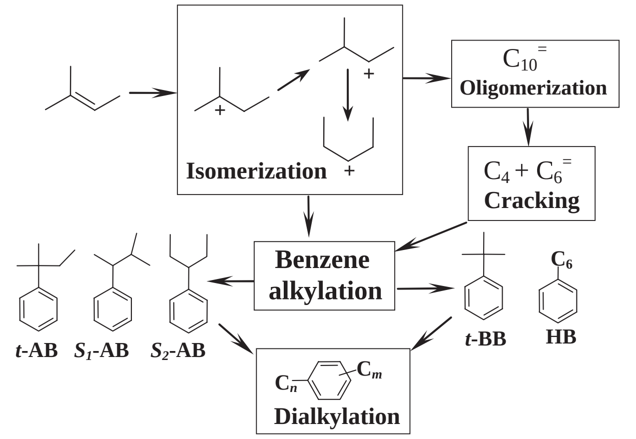

Figure 2. Reaction pathways.

The AB selectivity reached ca. 90% when increasing the benzene/$C_5^=$ molar ratio to 60. Like the longer contact time, the lower olefin concentration favored the formation of amylbenzenes but disfavored the production of oligomers, BB and HB, which further supported the reaction pathway proposed.

In conclusion, Beta zeolite appears to be one of the most efficient catalysts for liquid-phase alkylation of benzene with MeB. By controlling the framework Al content and reaction conditions such as contact time, reaction temperature and benzene/$C_5^=$ ratio, the selective and green production of amylbenzenes proves to be possible with Beta zeolite catalysts.

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