

Unsymmetrical alkylation of benzene over large pore zeolites

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Abstract

One pot unsymmetrical alkylation of benzene with different alkylating agents is an interesting reaction, as the alkylated products have important commercial applications. Keeping this in view, one pot ethylation and isopropylation of benzene with diethyl carbonate and isopropyl alcohol were carried out over H β (Si/Al = 15), HY (Si/Al = 3) and HM (Si/Al = 10) zeolites in the vapour phase. In addition to homo-alkylated products, unsymmetrical dialkylated products were also obtained with significant selectivity. Nearly similar trend in selectivity was obtained over all the catalysts with increase in temperature. The zeolites with high density of acid sites are suggested to be beneficial for unsymmetrical alkylation, as they could provide more probability for the formation of both the alkyl cations together. The proper control of concentration of alkylating agents based on their formation and reactivity also appears to be important in enhancing unsymmetrical alkylation. The effect of temperature, feed ratio, WHSV and time-on-stream on the selectivity to unsymmetrical alkylation was studied and the results are presented in the manuscript.

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1. Introduction

Alkylated aromatics such as ethylbenzene, isopropylbenzene, diisopropylbenzene, ethyltoluene, *tert*-butylbenzene, iso-butyltoluene, *tert*-butyltoluene and C₁₀–C₁₄ linear alkyl benzenes are important chemical intermediates and they are obtained by acid catalysed alkylation of appropriate aromatics [1]. These alkylation reactions are still performed in many petrochemical plants with hazardous catalysts such as HF and AlCl₃–HCl, which have drawbacks like safety, handling, corrosion and waste disposal [2]. In this context solid acid catalysts like zeolites are convenient and eco-friendly alternatives [3]. Though many zeolites have been tested for alkylation, only a few have been employed successfully for industrial alkylation of aromatics [4]. In most of these reactions the substrates are subjected to alkylation with a single alkylating agent like an alcohol, olefin or alkyl halide with the view to reduce prod-

ucts complexity [5]. In order to achieve unsymmetrical dialkylated products, generally appropriate alkyl aromatics are subjected to subsequent alkylation with a suitable alkylating agent. But there are problems in such reactions, as the process requires pure monoalkylated products which may be expensive. Hence, one pot unsymmetrical alkylation of benzene with two different alkylating agents appears to be an interesting and technologically important reaction since benzene is available in plenty and the conventional two stage conversions are reduced to one stage. As the reaction involves consecutive electrophilic reaction of two different alkyl cations with benzene, both the alkyl cations are required to be present simultaneously on the catalyst surface. To effect this, it is required to run the reaction (i) beyond the activation energy of their formation and (ii) the alkyl cations must be thoroughly mixed without forming colony of any of the cation type on the catalyst surface. It is rather difficult to reach this state as the alkyl cations may differently interact with catalyst surface due to different hydrophilic and hydrophobic regions of catalyst surface [6]. Keeping such limitations in mind, it has been

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planned in the present investigation to study one pot synthesis of ethyl isopropylbenzene using diethyl carbonate and isopropyl alcohol as the alkylating agents. Ethylation and isopropylation of benzene and other alkyl aromatics have already been reported in the literature [7]. Hence, unsymmetrical alkylation appears to be a feasible process, although symmetrical alkylation is a competing one. Although the carbocations react with benzene in a sequential manner within the pores of zeolites, the order of substitution can not be maintained as both are reactive under the given set of conditions. With these limitations the unsymmetrical alkylation of benzene with diethyl carbonate and isopropyl alcohol has been carried out over H β , HY and HM zeolites and the results are discussed below.

2. Experimental

2.1. Materials and methods

The sodium form of zeolite beta (Si/Al = 15), zeolite Y (Si/Al = 3) and H-form of mordenite (Si/Al = 10) were obtained from Sud-chemie India Ltd. The sodium form of zeolites was converted into H-form by ion-exchange with 1 M NH₄NO₃ solution at 80 °C for 24 h and this procedure was repeated thrice. The resulting mixture was then filtered and washed with distilled water. The product was dried overnight at 80 °C and calcined in the presence of air at 550 °C for 6 h to obtain H-form of zeolites.

2.2. Characterization

The powder X-ray diffraction patterns were recorded using a Siemens D5005 Stereoscan diffractometer with the nickel filtered Cu K α radiation source (operating at 40 KV and 30 mA) and a liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range 1–40° in steps of 0.02° with a count time of 15 s. Nitrogen adsorption and desorption experiments were carried out using a Quantachrome Autosorb 1 sorption analyzer. Prior to adsorption of nitrogen at –196 °C, the samples were outgassed for 3 h under 10^{–5} mbar at 250 °C.

2.3. Reaction set-up

Unsymmetrical alkylation of benzene was carried out in a fixed bed, continuous, downward flow glass reactor of 40 cm length and 1 cm internal diameter. About 1.0 g of the catalyst was taken in the middle of reactor and the reaction mixture was fed into it by a motor driven syringe pump at pre-determined flow rates. The analysis of products collected for 1 h, after discarding the products collected in the first 10 min was carried out in a gas chromatograph (Hewlett Packard 5890 A) equipped with a flame ionisation detector (FID) using an OV 17 column and nitrogen as the carrier gas. The identification of products was performed on a Perkin–Elmer Auto System XL

gas chromatograph connected to turbo mass spectrometer (Turbo) with helium as the carrier gas (1 ml/h). After completion of each catalytic run, the reactor system was flushed with nitrogen to remove the adsorbed impurities and the catalyst was regenerated at 500 °C in a current of moisture-free air for 6 h.

3. Results and discussion

3.1. Physico-chemical characterization

Physico-chemical properties of H β , HY and HM zeolites are presented in Table 1. The high intensity of peaks in the XRD patterns indicated that the zeolite samples are highly crystalline. The X-ray diffraction patterns and N₂ sorption studies of zeolites matched with those already reported in the literature (not shown) [8–10]. The typical characteristics of zeolites are summarized in Table 1.

3.2. Unsymmetrical alkylation of benzene with diethyl carbonate and isopropyl alcohol over large pore H β , HY and HM zeolites

The vapour phase unsymmetrical alkylation of benzene with diethyl carbonate and isopropyl alcohol was studied over H β , HY and HM zeolites. The effect of temperature, feed ratio, WHSV and time-on-stream was studied to improve the conversion of benzene and selectivity of the alkylated products. The influence of these reaction parameters over conversion and selectivity of products is discussed below.

3.2.1. Effect of temperature

The unsymmetrical alkylation of benzene with diethyl carbonate and isopropyl alcohol was carried out at 200, 250, 300, 350 and 400 °C over H β , HY and HM zeolites. The feed ratio (benzene:isopropyl alcohol:diethyl carbonate) was set at 1:1.5:1.5 and the flow rate at 2 ml/h. The products as identified by GC–MS were found to be diethyl benzene (DEB) isomers, *ortho*-isopropyl ethylbenzene (*o*-IPEB), *para*-isopropyl ethylbenzene (*p*-IPEB), diisopropylbenzene (DIPB) isomers, triethylbenzene (tri-EB) isomers, tetraethylbenzene (tetra-EB) isomers, 3,5-diethyl isopropylbenzene (3,5-DEIPB), 3,4-diethyl isopropylbenzene (3,4-DEIPB) isomers, 3,5-diisopropyl ethylbenzene (3,5-DIPEB) and 2,5-diisopropyl ethylbenzene (2,5-DIPEB). The conversion of benzene and products selectivity at different temperatures are presented in Table 2. The conversion

Table 1
Physico-chemical properties of the catalysts

Catalyst	Si/Al ratio	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
H β	15	575	0.225	5.7 × 7.5
HY	3	750	0.285	7.4
HM	10	515	0.234	5.7 × 7.1

Table 2
Effect of temperature on benzene conversion and products selectivity

Catalyst	Temperature (°C)	Benzene conversion (%)	Selectivity of the products (%)																				
			DEB isomers	<i>o</i> -IPEB	<i>p</i> -IPEB	DIPB isomers	tri-EB isomers	3,5-DEIPB	3,4-DEIPB tetra-EB isomers	3,5-DIPEB	2,5-DIPEB	Others											
H β	200	88.8	34.3	5.8	6.5	19.8	23.8	–	–	–	–	–	–	–	–	–	–	–	–	–	–		
	250	93.1	35.1	7.1	7.2	21.0	16.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
	300	95.0	46.0	5.0	5.1	10.2	9.1	1.4	1.2	1.6	1.4	1.6	1.6	1.4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
	350	98.2	43.4	4.1	4.2	8.0	6.2	3.4	3.1	3.5	3.1	20.0	3.5	3.1	20.0	3.1	20.0	3.1	20.0	3.1	20.0	3.1	20.0
	400	100	41.1	2.2	2.3	2.6	3.0	5.0	5.5	7.1	7.1	22.1	7.1	7.3	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
HY	200	87.5	32.3	8.8	9.4	22.7	21.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	250	96.8	33.3	11.2	11.0	23.3	11.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	300	97.8	45.3	6.7	6.3	10.6	7.5	1.3	1.4	1.8	1.4	16.0	1.8	2.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	350	98.9	42.2	4.7	6.4	7.8	4.0	2.7	3.2	3.3	21.0	3.3	3.3	3.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	400	100	39.0	3.8	4.4	4.6	2.9	3.1	3.6	7.2	24.0	7.2	6.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
HM	200	75.0	42.1	1.2	2.8	12.1	28.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	250	85.8	43.1	3.1	4.2	13.2	17.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	300	97.0	51.4	2.6	3.7	7.1	8.1	1.3	1.5	1.1	1.5	21.0	1.1	1.2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	350	98.5	46.0	1.8	2.7	5.3	4.8	3.4	3.1	3.4	24.5	3.4	3.1	4.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	400	100	43.8	1.0	1.2	2.5	2.0	5.5	4.6	4.4	28.2	4.4	5.3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Note: Feed ratio = 1:1.5:1.5 (benzene:isopropyl alcohol:diethyl carbonate); WHSV = 1.30 h⁻¹.

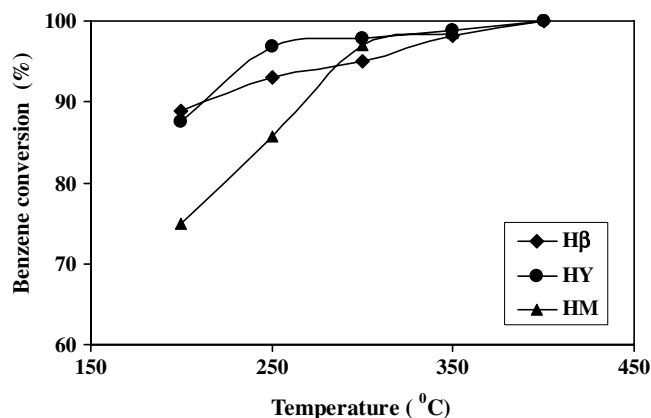
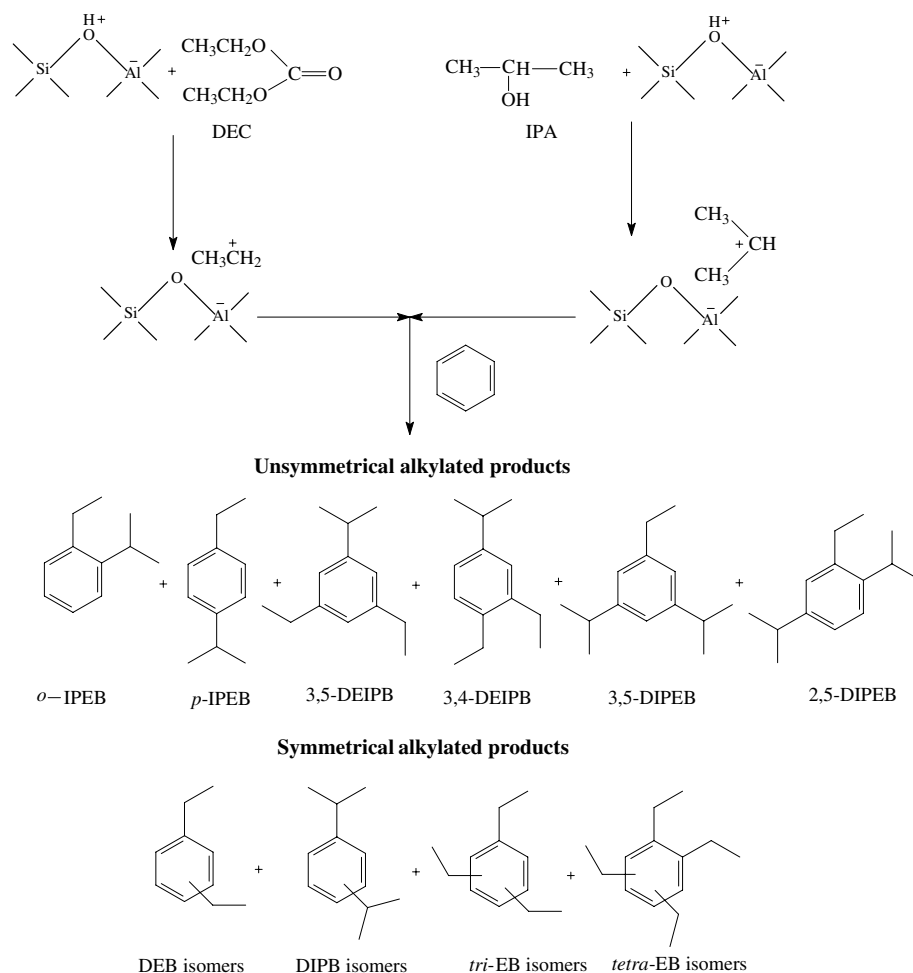


Fig. 1. Conversion of benzene over H β , HY and HM zeolites. Feed ratio = 1:1.5:1.5 (B:IPA:DEC); WHSV = 1.30 h⁻¹.

increases with increase in temperature over all the catalysts and attains 100% at 400 °C as shown in Fig. 1. The conversion observed in this study is higher than that of mono-alkylation of benzene with the respective alkylating agent separately over the zeolites [11–13]. Although benzene is not much active for electrophilic reaction, the high conversion reflects compensation obtained at the cost of high reactivity of ethyl and isopropyl cations resting on the catalyst surface (Scheme 1) [14,15]. HY and H β zeolites exhibit nearly similar activity. The activity of HM zeolite is not much different from other catalysts.

Among the products, the selectivity to DEB isomers is higher than other products over all the catalysts. The selectivity increases from 200 to 300 °C but decreases above 300 °C. The decrease is due to its subsequent alkylation to higher alkylated products, as the zeolites have large pore size [16–18]. The selectivity to *o*-IPEB and *p*-IPEB increases from 200 to 250 °C and above 250 °C it decreases. Although unsymmetrical alkylation particularly unsymmetrical dialkylation was principally aimed in this reaction, the products distribution illustrates partial fulfillment of the main interest. But several other products along with unsymmetrical alkylation were also obtained.

Based on the high selectivity of DEB isomers it is concluded that ethyl cation is more reactive than isopropyl cation. Hence benzene is readily attacked by ethyl cation and subsequent alkylation is also favored by the same. Although isopropyl cation can also react readily with ethyl benzene compared to benzene, isopropylation is not as much predominant as ethylation. This is due to high concentration of ethyl cations, as each mole of diethyl carbonate can produce 2 mol of ethyl cations compared to isopropyl alcohol, which can produce only one mole of isopropyl cation [19]. Hence, the higher amount of ethylation than isopropylation is only due to high content of ethyl cations and not due to its reactivity. Although there is a difference in reactivity for the alkyl cations at any of the reaction temperature, the difference may not be high. It is also supported by the



Scheme 1. Unsymmetrical alkylation of benzene with diethyl carbonate and isopropyl alcohol.

formation of exclusive DIPB isomers. Hence, it can be ascertained that free benzene or alkylated benzene cannot just exercise any selectivity property for further alkylation. Hence, irrespective of the nature of alkyl group in benzene, the alkyl aromatics can react with every other cations available without any selectivity. In this context it can be concluded that the formation of tri-EB and tetra-EB isomers is due to exclusive availability of ethyl cations for electrophilic reaction [20]. The distribution of products selectivity is not the same over H β and HY, although their activities are similar. But HM zeolite shows some difference in products selectivity compared to H β and HY zeolites. Since unsymmetrical alkylation is successful with these catalysts, the effect of feed ratio was examined to enhance the selectivity of unsymmetrical alkylated products and the results are discussed in the next session.

3.2.2. Effect of feed ratio

The effect of feed ratio on benzene conversion and products selectivity over HY zeolite was examined with different feed ratios of benzene: isopropyl alcohol: diethyl carbonate (1.0:1.5:1.5, 1.0:1.0:1.0, 1.0:1.0:0.5) with a flow

rate of 1.5 ml/h at 250 °C. The results are presented in Table 3. The benzene conversion shows a slow decrease with decrease in diethyl carbonate content in the feed, which clearly establishes ethyl cation as the more active electrophilic agent for benzene conversion (Fig. 2). It is well supported by the feed ratio 1.0:1.0:0.5 in which the number of moles of alkyl cation that could be formed from each alkylating agent is the same. Hence benzene conversion mostly depends on the concentration of ethyl cation. This might be due to easy decomposition of diethyl carbonate in comparison to isopropyl alcohol as discussed above. In addition to high reactivity of ethyl cation, high content of isopropyl cation might also be a significant contributing factor for high conversion of benzene. The selectivity of diethylbenzene isomers is higher than all others and the value decreases with decrease in diethyl carbonate content in the feed. The DEB dependent products, namely, tri-EB and tetra-EB isomers also show decrease in selectivity with decrease in diethyl carbonate content in the feed as expected. Contrary to diethylbenzene, the selectivity to *o*-IPEB and *p*-IPEB increases downwards. The increase clearly illustrates reduced probability for diethylation with less content of diethyl

Table 3
Effect of feed ratio on unsymmetrical alkylation of benzene over HY zeolite

Feed ratio (B:IPA:DEC)*	Benzene conversion (%)	Selectivity of the products (%)												
		DEB isomers	<i>o</i> -IPEB	<i>p</i> -IPEB	DIPB isomers	tri-EB isomers	3,5- DEIPB	3,4- DEIPB	tetra-EB isomers	2,5- DIPEB	Others			
1.0: 1.5: 1.5	96.8	33.3	11.2	11.0	23.3	11.0	—	—	10.2	—	—	—	—	—
1.0: 1.0: 1.0	93.8	32.5	13.2	14.5	12.5	15.6	—	—	11.7	—	—	—	—	—
1.0: 1.0: 0.5	89.0	30.3	20.6	22.7	13.0	9.0	—	—	4.4	—	—	—	—	—

Note: Temperature = 250 °C; catalyst = HY.

* (B, benzene, IPA, isopropyl alcohol, DEC, diethyl carbonate).

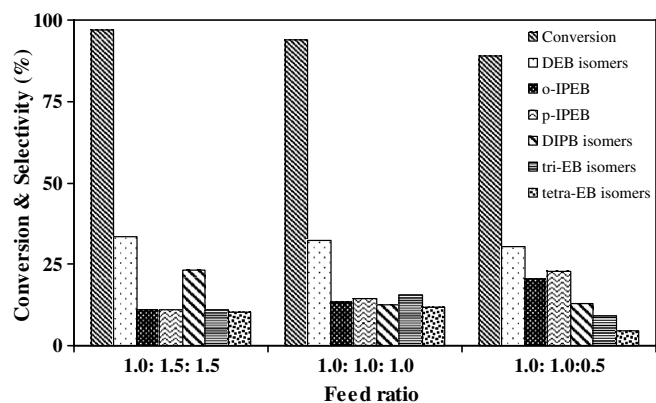


Fig. 2. Effect of feed ratio on benzene conversion and products selectivity over HY zeolite. Temperature = 250 °C; catalyst = HY.

carbonate in the feed. So, this observation offers a route to enhance selectivity to unsymmetrical alkylation. The concentration of highly reactive alkylating agent might be made less than that of less reactive alkylating agent. But at the same time the concentration of less reactive alkyl cation may not be increased linearly with gradual decrease in the concentration of high reactive alkylating agent as it could lead to symmetrical diisopropylation. Again the catalyst surface should be made to keep both the alkylating agents together, with slightly higher preference to less active agent than the other. The problem in maintaining unsymmetrical alkylation with high concentration of weakly alkylating agent is once again reflected in the selectivity of DIPB isomers. When its selectivity is compared for the feed ratios 1.0:1.0:1.0 and 1.0:1.0:0.5, there is only 0.5% enhancement in selectivity. It appears to be important that the concentration of weak alkylating agent should not be linearly increased with gradual decrease in the concentration of strong alkylating agent. The selectivity to tri-EB isomers decreases with decrease in diethyl carbonate content in the feed as expected. Similar reason is also applied to tetra ethylbenzene isomers. Hence it is concluded that proper control of the alkylating agents, based on their activity is very much important in the enhancement of unsymmetrical alkylation. Since 1 mol of isopropyl alcohol and 0.5 mol of diethyl carbonate can give two moles of alkyl cations, even the feed ratio of 1.0:1.0:0.5 can give high conversion of benzene. The selectivity to DEB isomers slightly decreases with decrease in diethyl carbonate content in the feed but the selectivity to *o*-IPEB and *p*-IPEB increases significantly. The increase in the selectivity of *o*-IPEB and *p*-IPEB is due to decrease in the selectivity of tri-EB and tetra-EB isomers with decrease in the diethyl carbonate content in the feed. The selectivity to DIPB isomers becomes less at 1:1:0.5 due to more conversion of isopropyl benzene to *o*-IPEB and *p*-IPEB isomers. This study revealed that low level of diethyl carbonate in the feed enhance the selectivity to unsymmetrical alkylation. Ethylation is more predominant than isopropylation as diethyl carbonate can be

Table 4
Effect of WHSV on benzene conversion and products selectivity

WHSV (h ⁻¹)	Benzene conversion (%)	Selectivity of the products (%)										
		DEB isomers	<i>o</i> -IPEB	<i>p</i> -IPEB	DIPB isomers	tri-EB isomers	3,5- DEIPB	3,4- DEIPB	tetra-EB isomers	3,5- DIPEB	2,5- DIPEB	Others
0.83	97.8	45.4	13.8	14.1	10.5	6.3	1.7	2.0	3.3	1.6	1.3	–
1.25	93.8	30.3	20.6	22.7	13.0	9.0	–	–	4.4	–	–	–
1.67	80.8	51.2	6.5	7.2	23.8	7.7	–	–	1.2	–	–	2.4

Note: Feed ratio = 1:1:0.5 (benzene:isopropyl alcohol:diethyl carbonate); Temperature = 250 °C; catalyst = HY.

cleaved better than isopropyl alcohol, which is capable of clustering around the protonic sites without much dissociation [21].

3.2.3. Effect of WHSV

The effect of WHSV on benzene conversion and products selectivity was studied over HY with a feed ratio (benzene:diethyl carbonate:isopropyl alcohol) 1:1:0.5 at 250 °C. The results are presented in Table 4. The usual trend of decrease in benzene conversion with increase in WHSV was observed. The selectivity to DEB isomers decreases with the increase in WHSV from 0.83 to 1.25 h⁻¹ due to their conversion to tri-EB and tetra-EB isomers. But a WHSV of 1.67 h⁻¹, the selectivity to DEB isomers increases due to decrease of conversion to tri-EB and tetra-EB isomers. The time dependent formation of tri-EB and tetra-EB isomers well establishes alkylation in a sequential manner to form polyalkylated isomers [22]. The selectivity to unsymmetrical alkylated products, *o*-IPEB and *p*-IPEB, follows similar trend. The selectivity to *p*-IPEB is higher than that of *o*-IPEB.

3.2.4. Effect of time-on-stream

The effect of time-on-stream on unsymmetrical alkylation was studied over HY zeolite at 250 °C. The reaction conditions and the results are presented in Table 5. The conversion decreases with increase in time-on-stream (Fig. 3) due to coke formation. The selectivity to DEB isomers increases for 3 h of time-on-stream but decreases thereafter. Similar trend is also observed in the selectivity to tri-EB isomers but the decrease in the selectivity starts at the end of second hour of time-on-stream. The selectivity to *o*-IPEB and *p*-IPEB decreases with increase in time-on-stream. Hence blocking of active sites by coke formation is not beneficial for unsymmetrical dialkyl substitution whereas this may be beneficial for unsymmetrical trialkyl substitution. The selectivity to 3,4- and 3,5-DEIPB and 2,5- and 3,5-DIPEB increases with increase in time-on-stream. The selectivity to DIPB isomers shows similar trend as that of tetra-EB isomers. Generally coke formation mainly blocks strong acid sites leaving weak acid sites. But the former sites are important for the formation of isopropyl cations. Hence, isopropyl cation formation might be largely suppressed because of coke formation. The increase in selectivity to 3,5- and 2,5-DIPEB isomers might be due to conversion of DIPB isomers by ethylation. This observation therefore illustrates that blocking of strong acid sites may favour ethylation of dialkyl isomers. The increase in selectivity of 3,5- and 3,4-DEIPB isomers with increase in time-on-stream also suggest that their main precursors are *o*-IPEB and *p*-IPEB, respectively. Thus the time-on-stream study proves that the catalyst deactivation is not beneficial for enhanced selectivity to unsymmetrical dialkylation.

Table 5
Effect of time-on-stream on benzene conversion and products selectivity

Time (h)	Benzene conversion (%)	Selectivity of the products (%)										
		DEB isomers	<i>o</i> -IPEB	<i>p</i> -IPEB	DIPB isomers	tri-EB isomers	3,5-DEIPB	3,4-DEIPB	tetra-EB isomers	3,5-DIPEB	2,5-DIPEB	Others
1	93.8	30.3	20.6	22.7	13.0	9.0	–	–	4.4	–	–	–
2	91.0	32.5	16.0	15.6	15.1	14.6	–	–	6.2	–	–	–
3	88.8	33.5	11.4	10.6	17.7	10.4	1.2	1.2	10.0	1.3	1.1	1.1
4	81.7	25.1	10.8	10.3	23.1	9.3	1.8	1.6	12.1	2.3	1.4	1.4
5	73.2	23.2	9.2	8.4	20.3	8.0	4.1	4.0	7.5	6.1	2.0	2.0
6	63.0	21.0	7.8	6.0	15.2	6.5	7.2	6.3	5.4	9.3	3.5	3.5

Note: Feed ratio = 1:1:0.5 (benzene:isopropyl alcohol:diethyl carbonate); Temperature = 250 °C; catalyst = HY; WHSV = 1.25 h⁻¹.

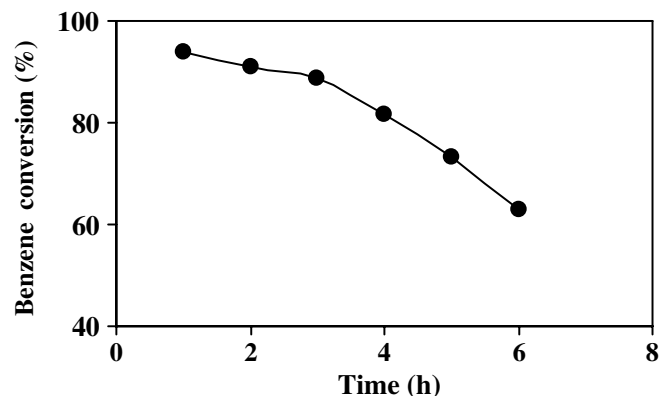


Fig. 3. Effect of time-on-stream on benzene conversion over HY zeolite. Feed ratio = 1:1:0.5 (B:IPA:DEC); temperature = 250 °C; catalyst = HY; WHSV = 1.25 h⁻¹.

4. Conclusion

It is concluded that unsymmetrical alkylation over large pore zeolites is a feasible process. The meticulous control of temperature, WHSV and feed ratio in conjunction with Si/Al ratio of the zeolites, it is possible to enhance unsymmetrical alkylation of benzene with suitable alkylating agents. Zeolites with high acid sites may be beneficial for unsymmetrical alkylation as it may help random distribution of alkyl cations on the catalyst surface. It is also an important parameter for the enhancement of unsymmetrical alkylation.

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