Alkylation of benzene with isopropyl alcohol over SAPO-5 catalyst in an integral pressure reactor

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The alkylation of benzene with isopropyl alcohol was studied in an integral pressure reactor over silicon substituted aluminophosphate molecular sieves, SAPO-5. The influence of various process parameters such as temperature, pressure, time on stream, weight hourly space velocity, and mole ratio of reactants on cumene yield and selectivity were investigated. The activity of SAPO-5 was compared with that of Hbeta for this reaction under similar conditions and in the same reactor. At pressures higher than atmospheric, almost the theoretical maximum yields of cumene were achieved on this SAPO-5. Among the diisopropyl benzenes formed by the alkylation of cumene, the meta-isomer was found to form in a significant amount followed by the para-isomer. The ortho-isomer with relatively high strain energy of 4.26 kcal/mol was almost negligible. The cumene yield goes through a maximum in the temperature range 498–543 K studied. Cumene selectivity was found to decrease at higher temperatures, higher pressures and lower benzene to isopropanol mole ratios.

KEY WORDS: benzene; isopropyl alcohol; cumene; SAPO-5; alkylation; selectivity.

1. Introduction

Cumene is still used as the chief starting material for the co-production of phenol and acetone. The demand for cumene is expected to grow at a rate of 3.5% a year over the next five years mainly because of the increased demand for bisphenol-A [1]. Until recently, solid phosphoric acid and Friedel–Crafts catalysts like $AlCl_3$ and BF_3 were used for its commercial production. The solid phosphoric acid process has many disadvantages, such as lower activity, catalyst non-regenerability, unloading of spent catalyst from the reactor, relatively high selectivity to hexylbenzenes and significant yields of DIPB and other "heavies". The $AlCl_3$ route requires special materials and coatings to prevent corrosion of equipment, and an additional washing step for catalyst removal. Disposal of spent catalyst also creates great environmental hazard. Hence, alternative routes employing environmentally benign molecular sieve catalysts are favoured over the conventional ones.

Several catalytic processes using ZSM-5 [2], Y-type [3], mordenite [4] and beta [5,6] have been disclosed very recently for the production of cumene by alkylation of benzene with propylene. Among the various zeolitic systems investigated, zeolite beta and modified mordenite have been proving to be potential catalysts due to their high activity, selectivity and stability, both in liquid and vapour phase conditions [6–12]. Many cumene plants throughout the world have started retrofitting their processes using Hbeta as catalyst. Besides the above zeolites, silicon substituted aluminophosphate (SAPO) molecular sieves are considered as interesting catalysts for various petrochemical applications [13–15]. The alkylation activity of molecular sieve catalysts is determined by their Brønsted acidity. In addition to the concentration of these Brønsted acid sites, their strength also plays a key role in the selectivity of the products. In contrast to zeolites, SAPOs show mild acidity [16,17], though their acid strengths are substantially higher than that of the corresponding $AlPO_4$ materials [17]. SAPO-5 showed good cumene selectivity when tested for its activity in an atmospheric micro reactor [18]. Hence, it was considered important to evaluate and report its performance in this reaction in an integral pressure reactor.

2. Experimental

2.1. Materials

In a typical synthesis of AlPO-5, about 20.43 g of pseudo-boehmite was added slowly to 30 g of distilled water and stirred for 2 h. Then about 13.84 g of phosphoric acid diluted with 18 g of distilled water was added drop-wise to the mixture and stirred for 0.5 h. Finally, the template triethylamine (TEA, 14.42 g) was added slowly to the mixture and stirred for 1 h. The pH of the

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gel was noted at the end of the stirring. The pH was in the range 3.5–4.5. The gel was then transferred into an autoclave and was heated in an oven at 200 °C for 24 h. After heating was complete, the mother liquor was removed, the gel dried at 120 °C for 12 h and calcined at 550 °C for 20 h. For synthesis of SAPO-5, silicon source (fumed silica) was added prior to the addition of template. The synthesis gel ratios and crystallization condition for the SAPO-5 are

$$Al_2O_3 : 0.2SiO_2 : 0.925P_2O_5 : 1.1R : 55H_2O$$

where R = triethylamine. Beta zeolite of 1.5 mm (extrudates with 20% binder) in its active proton form with an Si/Al ratio of 15 was obtained from M/s UCIL, India. The benzene and isopropyl alcohol used in this study were of analytical reagent grade and obtained from E. Merck (India) Ltd. and Qualigens Fine Chemicals, both of Mumbai, India.

2.2. *Characterization*

The as-synthesized SAPO-5 molecular sieves were characterized for their phase purity, crystallinity and morphology using X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray powder diffraction patterns were recorded on a Rigaku Miniflex X-ray diffractometer using Ni-filtered Cu K_α radiation ($\alpha = 1.540$ Å) indicating the presence of crystalline phases of high purity.

2.3. *Catalytic reactions*

The experiments were conducted in a vertical flow fixed-bed reactor (SS) with 10 g of catalyst in the form of extrudates (prepared using 20% binder) loaded in it. Hydrogen was used as a carrier gas during the experimental runs to minimize catalyst deactivation by coking. The product was condensed in a chilled water condenser connected to the down stream of the reactor. The liquid samples were then collected from a separator vessel and analysed in a 'Xylene Master' capillary column in a Shimadzu 15 Å gas chromatograph unit.

3. Results and discussions

3.1. *Effect of total pressure on product distribution*

The catalyst activity was tested at different total pressures in the range 1–19 atm. The results obtained are summarized in table 1. From the table, it is observed that there is a noticeable increase in cumene yield from 13.7% to 16.54% and DIPB yield from 0.73% to 1.78% when the pressure is increased from 1 atm to 4 atm. With further increase in pressure, however, no significant change in the yields of cumene and DIPB was observed. Moreover, after a decrease in cumene selectivity from 92.13% at atmospheric pressure to about 88.97% at 4 atm, the selectivity to cumene also remains almost constant with the increase in pressure from 4 atm to 19 atm. A possible explanation for these observations is that total pressure may influence the rate of reaction in two ways. First, an increase in total pressure increases sorbed phase concentration, which would increase the reaction rate reflected in the higher yields at 4 atm. Second, an increase in sorbed phase concentration results in a decrease in diffusivity, which may adversely affect the reaction rate. In the Henry's law region where the sorbed phase concentration increases linearly with total pressure, an increase in reaction rate and hence an increase in yield may be expected as observed from 1 atm to 4 atm total pressure. Above 4 atm, the molecular sieves will be saturated and in equilibrium with the liquid phase, and hence an increase in pressure will not result in any appreciable increase in the yield of the desired cumene product.

Table 1
Effect of total pressure on product distribution (wt%)

	Pressure (atm)			
	1	4	10	19
Aliphatics	0.78	0.68	0.69	0.66
Benzene	84.48	80.75	80.59	81.01
Toluene	0.12	0.11	0.10	0.10
C_8 aromatics	0.07	bd[a]	0.01	bd
Cumene	13.70	16.54	16.60	16.16
n-PB	0.12	0.11	0.10	0.06
C_{10} aromatics	bd	bd	bd	bd
1,3-DIPB	0.48	1.23	1.30	1.40
1,2-DIPB	0.07	bd	bd	bd
1,4-DIPB	0.18	0.55	0.62	0.60
Higher aromatics	0.13	0.05	bd	bd
Total benzene conversion (wt%)	0.73	1.78	1.92	2.0
Cumene selectivity (wt%)	92.13	88.97	88.63	88.21

Reaction conditions: temperature, 513 K; WHSV, 3 h^{-1}; benzene/IPA mole ratio, 8 : 1.

[a] bd, below detectable limits.

3.2. *Effect of temperature on cumene yield and selectivity at above atmospheric pressures*

Table 2 summarizes the effect of temperature at 4 atm pressure on the product distribution. From the table it is observed that the yield of cumene is maximum at 513 K. At higher temperatures there is a considerable decrease in the formation of diisopropyl benzene (DIPB) while the *n*-propyl benzene (*n*-PB) content increases in the product. The formation of *n*-propyl benzene decreases the selectivity to cumene at higher temperatures. The highest yield of cumene was observed at 513 K and hence further studies were carried out at this temperature only.

Table 2
Effect of temperature on product distribution (wt%)

	Temperature (K)			
	498	513	528	543
Aliphatics	0.47	0.68	0.67	0.65
Benzene	82.98	80.75	81.24	82.96
Toluene	0.10	0.11	0.14	0.16
C_8 aromatics	bd[a]	bd	0.08	0.17
Cumene	15.41	16.54	16.12	14.75
n-PB	bd	0.11	0.19	0.38
1,3-DIPB	0.77	1.23	1.04	0.58
1,2-DIPB	bd	bd	0.09	0.12
1,4-DIPB	0.28	0.55	0.28	0.22
Other aromatics	bd	0.05	bd	0.06
Total DIPB	1.05	1.78	1.41	0.92
Cumene selectivity (wt%)	93.06	88.97	89.86	89.72

Reaction conditions: WHSV, 3 h^{-1}; benzene/IPA mole ratio, 8 : 1; pressure, 4 atm.

[a] bd, below detectable limits.

3.3. *Effect of time on stream on yield and selectivity of cumene at high pressure*

The catalyst activity was tested at 4 atm pressure for about 45 h and the results are shown in figure 1. There was no significant decrease in the yield of cumene during this time period. However, cumene selectivity was found to decrease quickly initially, and then slowly. The decrease in cumene selectivity is mainly due to the increased formation of diisopropyl benzenes initially, as is evident from the DIPB yield curve. The continuing increase in DIPB yield may also be attributed to the gradual loss of transalkylation activity of the catalyst. Since DIPB forms inside the molecular sieve by reaction of cumene and IPA, the increase in DIPB in the product indicates a loss of conversion by the route of benzene + DIPB $\leftrightarrow$ 2 cumene and simple outward diffusion of DIPB is occurring from the interior of the sieve. The yield of *n*-propyl benzene was also found to decrease with time on stream.

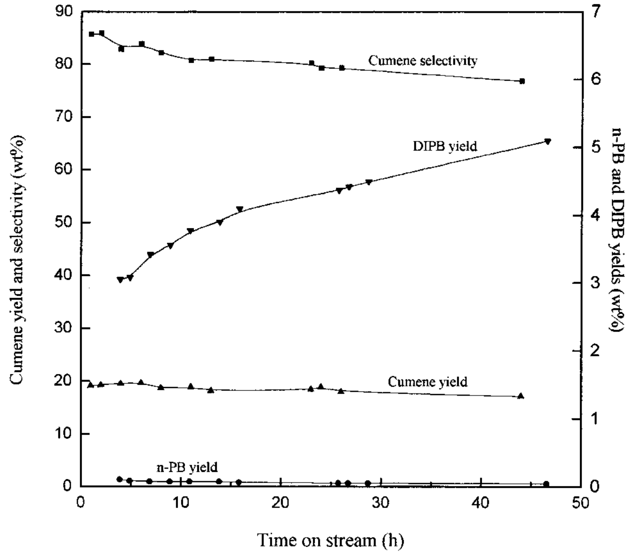

Figure 1. Effect of time on stream on activity of SAPO-5. Conditions: temperature, 513 K; WHSV, 3 h^{-1}; pressure, 4 atm; benzene/IPA mole ratio, 6 : 1.

Table 3
Effect of benzene/isopropyl alcohol (IPA) feed mole ratio on product distribution (wt%)

	Benzene/IPA mole ratio			
	10	8	6	4
Aliphatics	0.33	0.68	0.88	0.38
Benzene	81.58	80.75	70.20	65.19
Toluene	0.21	0.11	0.20	0.16
C_8 aromatics	0.03	bd[a]	0.03	bd
Cumene	16.44	16.54	23.41	26.52
n-PB	0.11	0.11	0.08	0.06
C_{10} aromatics	bd	bd	bd	bd
1,3-DIPB	0.59	1.23	2.98	5.53
1,2-DIPB	0.09	bd	0.17	0.28
1,4-DIPB	0.18	0.55	0.97	1.47
Higher aromatics	0.13	0.05	0.11	0.38
Total benzene conversion (wt%)	12.14	11.50	20.797	22.27
Cumene selectivity (wt%)	92.46	88.97	83.760	77.09
Selectivity to cumene and DIPB	5.52	10.23	15.140	21.44
DIPB/IPB	0.052	0.108	0.176	0.2745
n-PB/PB	0.0067	0.0067	0.0034	0.0023

Reaction conditions: temperature, 513 K; WHSV, 3 h^{-1}; pressure, 4 atm.

[a] bd, below detectable limits.

3.4. *Effect of mole ratio of reactants on product distribution*

Table 3 shows the effect of the mole ratio of benzene to isopropyl alcohol on product distribution. With the decrease in aromatic to alcohol mole ratio, the cumene selectivity was found to decrease from 92.46%, at a mole ratio of 10, to 77.09%, at a mole ratio of 4. This is due to the formation of more diisopropyl benzenes in the product at lower aromatic to alcohol ratios as is evident from the increasing ratio of DIPB to cumene (IPB) in the table. The yield of *n*-propyl benzene, however, was found to be low at lower aromatic to alcohol ratios.

3.5. *Effect of weight hourly space velocity*

The effect of weight hourly space velocity (WHSV) was studied in the range 3–16 h^{-1}. The result is shown in table 4. An increase in space velocity resulted in a decrease in cumene selectivity in the product from 91.46% at 6.5 h^{-1} to 86.78% at 16 h^{-1} due to the formation of diisopropyl benzene. These DIPBs are formed from cumene alkylation due to the higher concentration of reactants around the active sites of the catalyst at higher feed flow rates. Moreover, the higher DIPB with higher WHSV results from less residence time for transalkylation reaction of benzene and DIPB to produce

Table 4
Effect of weight hourly space velocity (WHSV) on product distribution (wt%)

	WHSV (h^{-1})				
	3	6.5	9	12	16
Aliphatics	0.68	0.63	0.64	0.66	0.37
Benzene	80.75	81.62	82.54	82.76	82.80
Toluene	0.11	0.11	0.11	0.11	0.11
C_8 aromatics	bd[a]	bd	bd	bd	bd
Cumene	16.54	16.23	15.17	14.39	14.37
n-PB	0.11	0.07	0.05	0.04	0.01
C_{10} aromatics	bd	bd	bd	bd	bd
1,3-DIPB	1.23	0.94	1.03	1.49	1.54
1,2-DIPB	bd	0.06	0.06	0.05	bd
1,4-DIPB	0.55	0.33	0.36	0.50	0.53
Higher aromatics	0.05	bd	bd	bd	bd
Total DIPB	1.78	1.33	1.45	2.04	2.07
Cumene selectivity (wt%)	88.97	91.49	90.41	86.79	86.78
DIPB/IPB	0.11	0.08	0.10	0.14	0.14
n-PB/PB	0.0067	0.0043	0.0033	0.0028	0.0007

Reaction conditions: temperature, 513 K; pressure, 4 atm; benzene/IPA mole ratio, 8 : 1.

[a] bd, below detectable limits.

Table 5
Comparison of product distribution in a differential reactor and integral reactor at similar reaction conditions

	Production distribution (wt%)	
	Differential reactor	Integral reactor
Aliphatics	0.03	0.56
Benzene	80.55	84.27
Toluene	0.05	0.11
C_8 aromatics	0.08	0.10
Cumene	17.97	13.99
n-PB	0.12	0.19
C_{10} aromatics	bd[a]	bd
1,3-DIPB	0.84	0.51
1,2-DIPB	bd	bd
1,4-DIPB	0.36	0.27
Higher aromatics	bd	bd
Cumene selectivity (wt%)	92.53	92.21
Selectivity to cumene and DIPB	98.71	97.36
DIPB/IPB	0.067	0.056
n-PB/PB	0.0066	0.013

Reaction conditions: temperature, 513 K; WHSV, 3 h^{-1}; pressure, 1 atm.

[a] bd, below detectable limits.

cumene. However, the total selectivity to cumene and di-isopropyl benzene remains almost constant.

3.6. *Comparison of activity of SAPO-5 in differential and integral reactors*

The product distribution for benzene alkylation with isopropyl alcohol over SAPO-5 in a differential as well as integral reactor is compared at similar reaction conditions in table 5. The table shows that the cumene yield is considerably lower in the integral reactor at atmospheric pressure than in a differential flow reactor. This is due to the mass transfer resistances offered by interparticle and intraparticle diffusion, prevalent in an integral reactor loaded with large amounts of catalyst (30 g compared with 2 g in a differential reactor). The fraction of *n*-propyl benzene isomer is also found to be high in the integral reactor. This may be attributed to more isomerization of cumene at higher residence times in this reactor. However, the cumene selectivity of an integral reactor is comparable with that of a differential reactor due to the low yield of DIPB of the former.

3.7 *Comparison of activity of SAPO-5 with Hbeta for cumene synthesis*

Figure 2 compares the yields and selectivity of cumene over SAPO-5 with those obtained over Hbeta (protonic form of beta zeolite) at the same reaction conditions. The cumene yield is more over Hbeta while the yield of DIPB and cumene selectivity is almost the same on both catalysts. The lower cumene yield over SAPO-5 is due to its lower acidity than Hbeta. Hence, to obtain similar conversion levels over SAPO-5, slightly higher temperatures than that used for Hbeta are required. However, at lower benzene to isopropyl alcohol ratios in the feed, beta was found to show better performance only at higher temperatures [19].

Figure 3 shows the *n*-propyl benzene (*n*-PB) yield with respect to the total propyl benzenes at various temperatures at 6 : 1 benzene to alcohol ratio. An interesting observation is that the *n*-PB fraction is low over SAPO-5 at all the reaction temperatures. Moreover, its increase with temperature is not rapid, unlike on Hbeta, as is evident from the slopes of the curves in the figure.

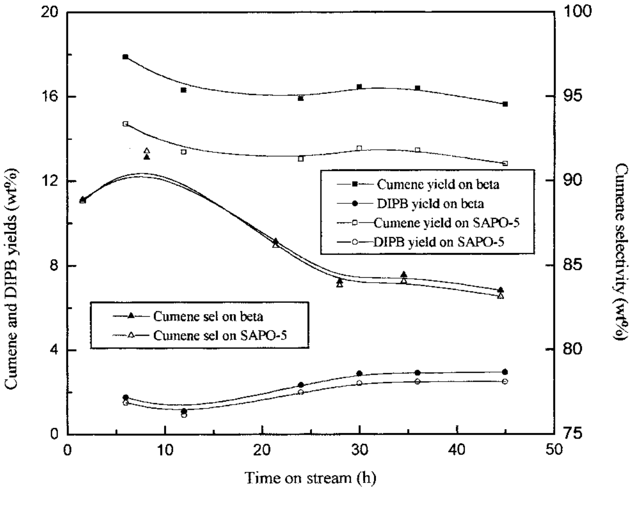

Figure 2. Comparison of activities of beta and SAPO-5 for cumene synthesis. Conditions: temperature, 513 K; WHSV, 3 h^{-1}; pressure, 1 atm; benzene/IPA mole ratio, 8 : 1.

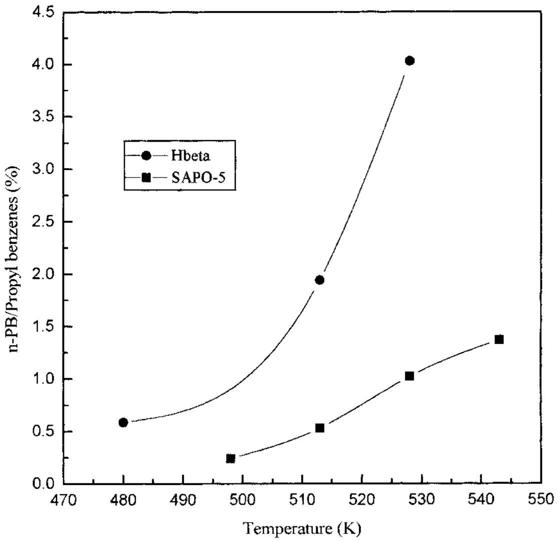

Figure 3. Comparison of Hbeta and SAPO-5 for fraction of *n*-PB in propyl benzenes.

4. Conclusions

The alkylation of benzene with isopropyl alcohol was studied over a large pore molecular sieve, SAPO-5, at above atmospheric pressures. For maximum yield of cumene on this catalyst, the reaction conditions are at 513 K temperature and 4 atm pressure, with a benzene to isopropanol mole ratio of about 6 and a WHSV of 3–6.5 h^{-1}. The performance of the catalyst in terms of cumene yield was found to be better in a differential reactor than in an integral reactor at atmospheric pressure. The selectivity to cumene on SAPO-5 catalyst was similar to that obtained on Hbeta. The yield of the undesirable isomer of cumene, *n*-PB, was observed to be lower over SAPO-5 when compared with beta, showing SAPO-5 to be a promising catalyst for cumene synthesis.

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