



ALKYLATION OF BENZENE TO CUMENE OVER MOR ZEOLITE CATALYSTS

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The vapor phase alkylation of benzene to cumene (isopropyl benzene) is studied over MOR (mordenite) type zeolite at different process parameters. The reaction was also studied by adopting different methodologies (pyridine poisoning, passing of moist propylene, alkali dominant mordenite, use of coked catalyst and metal impregnated zeolite) to check the nature of product distribution and the extent of activity and selectivity to alkylated product IPB, DIPB (isopropyl benzene and diisopropyl benzene) and n-PB (n-propyl benzene). It is revealed that the adoption of different methodologies affects the activity and selectivity significantly by suppressing of alkylation / isomerisation reactions.

INTRODUCTION

Alkylation of benzene with propylene to produce cumene is a well-known reaction. Cumene is an important chemical intermediate mainly used for the production of phenol and acetone.¹ Cumene production is one of the potential routes for manufacture m-DIPB and p-DIPB isomers, two important intermediates for polymer industries. In the petrochemical industry, phosphoric acid is the catalyst used for benzene alkylation.² AlCl₃ has also been used as a catalyst for benzene alkylation.³ The major drawback of these catalysts is their corrosive and environmentally hazardous nature. In view of these limitations, there are worldwide efforts to find out an alternative catalyst system. In this work we are presenting our results on alkylation of benzene to cumene over MOR (mordenite zeolite) with the results of the experiments carried out by adopting different methodologies (either by modifying zeolite or passing pyridine in the feed). The effect of different methodologies adopted is monitored in terms of activity (conversion) and selectivity to different products (mainly IPB, DIPB, n-PB).

RESULTS AND DISCUSSION

Effect of calcination temperature is described in Table 1. It is seen that the isopropanol conversion to alkyl benzene (IPB, n-PB and DIPB) is maximum at 480 °C and it drops at higher calcination temperature. The yield of n-propyl benzene is maximum at 400 °C. Further, a decrease in the concentration of aliphatics and other impurities (toluene, C8 aromatics) is observed. The reduction in activity may be attributed to the effect of calcination temperature on acidity. The thermo analytical studies indicated decrease in number of acidic OH groups per unit cell with increase in temperature of calcination (Table 2).⁴ In zeolites like faujasites and mordenites dehydroxylation causes conversion of Brönsted acid sites to Lewis acid sites. Karge reported the existence of Brönsted and Lewis acid sites even below 450 °C but above this temperature Brönsted sites are converted to Lewis sites.⁵ Since alkylation reaction need Brönsted acidity the reduction in activity can be correlated with the reduction in Brönsted acid sites upon dehydroxylation.

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Table 1

Influence of calcination temperature on alkylation activity

Calcination temp. (°C)	400	480	560	640	720	800
Product weight %						
Aliphatics	0.13	0.11	0.11	1.28	1.42	2.3
Benzene	83.59	82.01	83.67	85.76	86.06	88.17
Toluene	0.08	0.09	0.06	0.04	0.03	-
C ₈ Aromatics	0.06	0.05	0.03	0.01	-	-
Cumene	14.92	16.42	14.56	11.85	8.43	6.51
n-propylbenzene	0.55	0.49	0.28	-	-	-
C ₉ -C ₁₁ Aromatics	0.03	0.03	0.01	0.02	-	-
DIPB (m)	0.42	0.50	0.44	0.65	2.62	1.44
(o)	-	-	-	-	-	-
(p)	0.22	0.24	0.21	0.29	1.33	1.44
∑DIPB	0.64	0.75	0.65	0.94	3.95	2.88
HBF	0.06	0.05	0.01	0.09	0.11	0.13
∑Alkylates (α)%	91.12	99.9	87.7	73.48	79.25	59.8
Selectivity to IPB%	90.8	91.2	92.14	89.5	59.03	60.4

Catalyst: HM. Reaction temp. = 210 °C

(Benzene: Isopropanol) mole = 8, WHSV = 2.2 h⁻¹

Table 2

Thermogravimetric data of H-mordenite zeolite*

Calcination Temperature °C	Percent weight loss ^a		Loss of OH group per u.c.
	Total	Dehydroxylation	
560	14.8	0.4	1.29
680	15.0	0.6	1.93
850	15.35	0.95	3.06
930	15.42	1.02	3.29
1000	15.60	1.2	3.87

* Calculated from TG curve (Ref.4)

a Weight loss due to dehydration (At 400 °C) = 14.4%

Table 3 explains the influence of reaction temperature on conversion and selectivity. It is evident that the optimum temperature to produce highest yield of IPB at lower content of n-PB (undesirable product) lies in the range of 210-215 °C. At lower temperature than 210 °C, the liquid hydrocarbon product consisted of significant amounts of DIPB and polyalkylated products resulting in the lower yield and selectivity to IPB. Above 230 °C, the concentration of xylenes and to

lesser degree that of toluene increases. Also increase of n-PB concentration was significant at higher temperature. At temperature below 185 °C, the catalyst showed the tendency of rapid deactivation due to blocking of the active sites by strongly chemisorbed organic molecules having low mobility. In all these experiments, the conversion of isopropanol is complete. This implies that the 210 °C is the optimum temperature under the set experimental parameters.

Table 3

Alkylation of benzene with isopropanol over H-mordenite

Temperature °C	150	185	215	230	250	275	300
Product weight %							
Aliphatics	0.4	0.48	0.31	0.32	0.11	0.32	0.80
Benzene	90.86	86.5	82.8	83.0	84.4	87.0	91.1
Toluene	-	-	-	0.03	0.06	0.18	0.45
C ₈ Aromatics	-	-	0.02	0.08	0.22	0.54	0.87
Cumene (IPB)	5.66	7.4	15.1	15.6	13.75	9.84	4.40

Table 3 (continued)

n-propyl benzene	0.01	0.02	0.02	0.14	0.65	1.4	2.06
C ₉ -C ₁₁ Aromatics	-	-	0.01	0.04	0.11	0.32	-
DIPB	2.96	5.6	1.72	0.80	0.63	0.32	0.34
HBF	-	-	0.06	0.01	0.04	0.13	-
Σ Alkylates (α)%	51.36	80.28	90.23	86.43	78.34	59.82	35.56
iproH→	28.95	37.89	77.21	80.38	73.54	57.40	32.99
Propylbenzenes							
Composition (%)							
Isopropylbenzene	99.82	99.73	99.87	99.11	95.48	87.54	68.11
n-propylbenzene	0.18	0.27	0.13	0.89	4.52	12.46	31.89

Influence of reaction temperature (Benzene: Isopropanol) mole = 7.32, WHSV (h⁻¹) = 2.2

Influence of pyridine injection (along with feed mixture of benzene and isopropanol) on activity and selectivity, is depicted in Table 4. It is known that bases like pyridine and amines reduce activity due to poisoning of active acid sites by reacting with the acidic sites which are active in the zeolite catalyzed alkylation reaction.⁸ Experiments were carried out to determine optimum level of pyridine. With increase in pyridine in the feed from 0 to 80 ppm, the catalytic activity gradually dropped from almost 100 % to 75 %. It seems that the drop is more pronounced between 40 to 80 ppm of pyridine in the feed. Proportionately, conversion to IPB is also decreased whereas selectivity to IPB is nearly unaffected. The fall in activity is ascribed to reaction of pyridine with the acidic sites of zeolite. The lower conversion of pyridine with less acidic zeolite is as expected where as constant selectivity of IPB is due to the differences in site occupation by pyridine. Up to 60 ppm level the sites needed for alkylation are not much affected even though total conversion is reduced. However, further increase in pyridine concentration reduced the active sites with

drastic fall in activity. The selectivity being a property of the zeolite structure is not much affected due the reduction in acidic sites. Table 5 depicts influence of steam injection (moist propylene is passed through H₂O trap) along with benzene (in this case no isopropanol was introduced over the catalyst). It is seen that there is decrease in the formation of IPB and increase in the formation of DIPB when moist propylene is passed through catalyst bed. The impurities (toluene, C8 aromatics and n-PB) are reduced indicating the neutralization of some acidic sites with water molecules. The increase in DIPB concentration is due to lower acidity. Both high temperature and acidity are needed for reversible trans alkylation reaction. Temperature, being constant in reaction with and without water vapor, the high concentration of DIPB may be related to lower number of acid sites due to which trans alkylation and dialkylation of DIPB is reduced. The presence of water (steam) may also facilitate easier removal of DIPB in the presence of water.

Table 4

Influence of pyridine injection of alkylation activity

Pyridine in feed (ppm)	0	40	80
Product weight %			
Aliphatics	0.06	1.02	2.8
Benzene	82.14	81.77	83.77
Toluene	0.03	0.01	0.01
C ₈ Aromatics	0.08	0.04	0.01
Cumene	16.33	16.02	12.66
npB	0.49	0.39	0.21
C ₉ -C ₁₁ Aromatics	0.04	0.03	0.01
DIPB (m)	0.51	0.46	0.32
(o)	-	-	-
(p)	0.24	0.21	0.17
Σ DIPB	0.75	0.67	0.50
HBF	0.07	0.05	0.03
Prop. Conv. to IPB %	90.63	88.91	70.26
Σ Alkylates (α) %	99.51	96.57	75.53
Sel to IPb %	91.07	92.06	93.02

Catalyst: HM (SiO₂/Al₂O₃ ratio = 13), Temperature °C = 210, (Benzene: Isopropanol) mole = 7.32, WHSV (h⁻¹) = 2.2

Table 5
Alkylation of benzene with propylene

Product weight %	-	*
Aliphatics	0.09	0.04
Benzene	80.8	82.65
Toluene	0.08	0.01
C ₈ Aromatics	0.13	-
Cumene	16.88	14.20
nPB	0.56	0.02
C ₉ -C ₁₁ Aromatics	0.10	-
DIPB (m)	0.79	2.20
(o)	-	-
(p)	0.33	0.83
Σ DIPB	1.12	3.03
HBF	0.20	-
Prop. Conv. to IPB %	87.10	73.27
Σ Alkylates (α) %	98.54	96.53
Sel to IPB %	88.39	75.90

Influence of steam injection

Catalyst: HM (SiO₂/Al₂O₃ ratio = 13), Temperature °C = 175, (Benzene: Propylene) mole = 7.4, WHSV (h⁻¹) = 2

* Propylene passed through H₂O trap

Comparison of fresh and coked catalyst is presented in Table 6. As can be seen from Table 6, the conversion of isopropanol (in turn of propylene on insitu dehydration of isopropanol) is decreased where as selectivity to IPB is increased. Among the DIPB, p-isomer predominates over the m-isomer with absence of n-PB formation over coked catalyst. The deposition of coke within the catalyst pores or on the external surface eliminates strong acid sites responsible for cracking and other secondary reactions. Also coke deposition within catalyst gradually reduces the pore geometry and facilitates the formation of p-isomer among dialkylbenzenes. Absence of higher boiling fractions also supports this conclusion. Deposition of coke on the catalyst leading to increased selectivity to IPB suggests coke induced shape selectivity.⁶ The most accessible surface sites could be covered to reduce the formation of undesirable products.

The catalytic performance of rare earth exchanged sodium mordenite is shown in Table 7. These experiments were performed at activation and reaction temperature of 250 °C after optimization of the parameters.⁶ It is seen that with decrease in sodium content, the propylene conversion is increased. The reduction in propylene conversion is as expected due to reduction in Brönsted acid centers that are needed for alkylation.⁷ As the mordenite channels are

comparatively larger than medium pore zeolites, the shape selectivity arising out of structural factors is not significant hence the observed near constancy of p/m DIPB.

The nature of product distribution on phosphorous impregnated zeolite (phosphorous impregnated = 0.6 and 1 wt %) is shown in Table 8 with that of H-mordenite. It can be seen that there is major change in the catalytic activity. It is suggested by Kaeding and Butter that elemental phosphorous binds the zeolite framework through oxygen and reduces acidic sites.^{7,8} In the process some of the pore mouths are blocked by phosphorous complex. Also inside channels these complexes change the channel tortuosity resulting in the formation of para selective products in the dialkylbenzenes. With increase in phosphorous content the drop in catalytic activity, increasing DIPB formation and increase in p-diisopropyl benzene is observed. On further increase in phosphorous content (at 1 wt % P), a drop in activity leading to the decrease in formation of all the products is noticed. It is observed that there is reduction in toluene, ethylbenzene and xylenes, which are formed due to cracking on the external surface.⁹

Table 6

Alkylation of benzene with isopropanol. Comparison of fresh and coked catalyst

Catalyst	Fresh	Coked
Product weight %		
Aliphatics	0.10	5.75
Benzene	82.01	92.47
Toluene	0.01	0.12
C ₈ Aromatics	0.05	-
Cumene	16.49	1.49
npB	0.49	-
C ₉ -C ₁₁ Aromatics	0.03	-
DIPB (m)	0.51	0.02
(o)	-	-
(p)	0.24	0.05
Σ DIPB	0.75	0.07
HBF	0.05	-
Prop. Conv. to IPB %	91.52	8.27
Sel to IPB %	91.20	93.45
DIPB (p)		
————— × 10 ²	47.06	250
DIPB (m)		

Catalyst: HM (SiO₂/Al₂O₃ ratio = 13), Temperature °C = 210, (Benzene: Propylene) mole = 8, WHSV (h⁻¹) = 2.2

Table 7

Isopropylation of benzene over sodium mordenite*

Na ppm × 10 ⁻³	39.0	28.5	24.5	19.0
Product weight %				
Aliphatics	0.35	0.33	0.33	0.21
Benzene	93.98	93.58	93.12	92.76
Toluene	0.03	0.01	-	-
C ₈ Aromatics	-	-	-	-
Cumene	4.48	4.85	5.18	5.46
npB	-	-	-	-
C ₉ -C ₁₁ aromatics	-	-	-	-
DIPB (m)	0.51	0.56	0.65	0.78
DIPB (o)	-	-	-	-
DIPB (p)	0.47	0.49	0.53	0.58
DIPB	0.98	1.05	1.18	0.19
Σ HBF	0.18	0.17	0.18	0.19
Prop. Conv. to IPB %	24.86	26.91	28.75	30.3
Σ Alkylates (α) %	32.92	35.54	38.45	41.48
DIPB $\left(\frac{p}{m}\right) \times 10^2$	92.15	87.5	81.53	74.35

* Other cation is RE³⁺

Table 8

Influence of phosphorus impregnation on catalytic performance

Catalyst*	HM	PHM (0.64)	PHM (1.0)
Product weight %			
Aliphatics	0.03	0.11	0.44
Benzene	82.77	83.97	96.48
Toluene	0.04	0.03	0.02
C ₈ Aromatics	0.11	0.08	0.01
Cumene	15.37	14.42	2.45
npB	0.95	0.63	0.08
C ₉ -C ₁₁ Aromatics	0.03	0.03	-
DIPB (m)	0.41	0.38	0.22
(o)	-	-	-
(p)	0.22	0.19	0.26
Σ DIPB	0.63	0.57	0.48
HBF	0.07	0.16	0.04
Prop. Conv. to IPB %	85.30	80.03	13.59
Total Prop. Conv. (α) %	95.74	88.20	17.97

* Values in parenthesis indicate weight % phosphorus impregnation
Temperature = 210 °C, (Benzene:Isopropanol) mole = 8, WHSV (h⁻¹) = 2.2

EXPERIMENTAL

Materials

Benzene and isopropanol were high purity chemicals (Loba Chemie) and were used without further purification. o-phosphoric acid from Loba Chemie was used as a precursor for phosphorous impregnation. A solution containing 3.03 % RE₂O₃ by weight was used for ion exchange. Propylene containing 2.7 % propane was used.

Catalysts preparation

Mordenite Zeolites: The zeolite mordenite was synthesized hydro thermally at autogenous pressure in an autoclave. The as synthesized zeolite was converted to Na-zeolite by calcination, which was converted to catalytically active form H-zeolite by repeated treatments with ammonium nitrate at water bath temperature (95 °C). The detail procedure is given elsewhere.¹⁰ Some of the Na-zeolite was preserved for treatment with the rare-earth ions.

PHM Zeolites: The phosphorous modified H-mordenite was prepared by impregnating H-mordenite with appropriate quantity of o-phosphoric acid (Loba Chemie) in aqueous solution. The well-homogenized slurry was slowly evaporated at 95 °C for 12 h and calcined in the muffle furnace at 450 °C for 10 h to give the corresponding catalyst in oxide form. These samples were designated as PHM (0.6 wt % and 1.0 wt % phosphorous impregnated samples were prepared). Benzene and isopropanol were high purity reagents (Loba Chemie) and were used without further purification.

Na-RE Zeolites: Na-mordenite was treated with calculated amount of RE³⁺ ion from the solution containing 3.03 % by weight at 90 °C. Samples with higher degree of exchange were obtained by repeated treatments and dried in an air oven at 110 °C for 12 h. The degree of exchange was calculated on the

basis of estimation of sodium by atomic absorption spectrometry (AAS) in the filtrate of exchanged samples.

Characterization

The H-mordenite was gravimetrically analyzed. It has the unit cell formula H_{5.84}Na_{0.46}[(AlO₂)_{6.3}(SiO₂)_{41.76}] (SiO₂/Al₂O₃ molar ratio = 13.3). It showed the typical characteristic XRD spectra of mordenite structure with prominent peaks between 2θ ranging between 19-31°. The total acidity of H-M was found to be 15.1 (acid sites per unit cell). The water and benzene equilibrium sorption capacity at P/P₀ = 0.5 was 9.33 and 1.24 m moles g⁻¹ respectively.¹¹

Reaction procedure and analysis of the products

The catalytic alkylation reactions were carried out at atmospheric pressure using fixed bed, down flow integral silica reactor. The zeolite H-mordenite (HM) (2g, 10-20 mesh particles) was loaded in a silica reactor and was first activated in dry air at 475 °C for 8 h and cooled to reaction temperature in the flow of dry nitrogen. Reaction feed mixture (benzene to isopropanol molar ratio = 8) was fed from the top using a syringe feed pump (Model 352, Sage instrument Co., USA) at desired rate to maintain the weight hourly space velocity (WHSV) at 2.2 h⁻¹ as these were found to be optimum reaction parameters.⁶ The feed was vaporized in a preheater assembly packed with inert material and then passed through catalyst bed. All temperatures were recorded with a centrally placed calibrated chromel-alumel thermocouple. The vapor from the reactor was cooled by passing through chilled water condensers and the reaction products were analyzed by gas chromatography (Shimadzu gas chromatograph, model GC R1A) fitted with Apiezone L column (2M, 1/8" i.d.) and FID detector isothermally at 125 °C. The percent isopropanol conversion and selectivity to isopropyl benzene (IPB), n-propyl benzene (n-PB) and diisopropyl benzene (DIPB) are defined as follows:

$$\% \text{ Conversion of isopropanol to IPB/n-PB/DIPB} = \frac{\text{Moles of IPB/n-PB/DIPB produced}}{\text{Moles of isopropanol fed}} \times 100$$

$$\% \text{ Total isopropanol conversion} = \text{Summation of isopropanol converted to IPB, nPB and DIPB}$$

$$\text{DIPB/IPB} \times 100 = \text{Ratio of moles of DIPB to Moles of IPB obtained multiplied by 100}$$

$$\% \text{ Selectivity to IPB (Cumene)} = \frac{\text{Isopropanol conversion to IPB}}{\text{Total isopropanol conversion}} \times 100$$

In the isopropylation of benzene to cumene the major products were isopropyl benzene (cumene) and diisopropyl benzene. Small amounts of toluene, xylenes, ethyl toluene, ethylbenzene, n-propyl benzene and butyl benzene were also formed. Propyl benzene (tri and above) was formed only in very small quantities. For convenient representation, the products other than isopropyl benzene, n-propyl benzene and diisopropyl benzene have been grouped into C8, C9-C11 and HBF (higher boiling fractions) aromatics. C8 represents xylenes, ethyl benzene, C9 aromatics constituting ethyl toluenes and C10-C11 aromatics constituting of those boiling above diethyl benzenes.

CONCLUSIONS

The alkylation of benzene with isopropanol to form isopropyl benzene is a Brönsted acid catalyzed reaction. The optimum calcination temperature and reaction temperatures are found to be in the ranges of 460-500 °C and 210-215 °C respectively for H-mordenite zeolite. Though isomerisation of isopropyl benzene to n-propyl benzene is a temperature dependent reaction, the

IPB to n-PB ratio can be increased by high temperature calcination. The use of moist propylene facilitated secondary alkylation leading to DIPB due to lower acid sites density inhibiting the reversible trans alkylation reaction. Injection of pyridine in the feed reduces Brønsted acid sites needed for alkylation; however this minimizes n-PB formation. The extent of p-DIPB predominates over m-DIPB using coked catalyst due to reduction in pore geometry. Incorporation of phosphorus reduces surface hydroxyl groups. Also a reduction in activity and elimination of cracked products was observed.

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