

Gas phase toluene isopropylation over high silica mordenite

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Abstract. Mordenite (HM) catalysts with three different Si/Al ratios were compared for their activity and selectivities in gas phase toluene isopropylation with isopropanol. Catalyst with Si/Al ratio 44.9 offered better cumene selectivity, hence, it was chosen for detailed kinetic investigations. The influence of various process parameters like temperature, time-on-stream, weight hourly space velocity (WHSV), reactant mole ratio on this catalyst activity are discussed. The cymene selectivity was found to increase with reaction temperature and passed through a maximum at 473 K. The deactivation with time-on-stream is almost negligible. Lower isopropyl alcohol concentration in the feed improved cymene selectivity. The conversion and selectivity to cymenes were compared with those of the large pore beta catalyst. The rate constant and activation energy were found to be 7.34 m³/kg h and 41.84 kJ/mol, respectively using homogeneous kinetic model.

Keywords. Mordenite; cymene; *p*-cymene; kinetics; isopropylation; toluene; silica.

1. Introduction

In recent times, considerable attention is given on the selective synthesis of para-dialkylbenzenes, like xylene, ethyl toluene, diethyl benzene via alkylation reactions catalysed by shape selective zeolites. Isopropyl toluene (cymene), in particular, the para-isomer of it, is one such commercially important dialkylbenzene. It is used as an important starting material for the production of a range of intermediates and end products, such as cresols, isopropyl phenols, fragrances, pharmaceuticals, herbicides, heat transfer media, etc.

The alkylation of toluene over zeolites is normally considered to follow the well-known Friedel–Crafts mechanism which evidently proceeds by direct ortho-para attack of the ring followed by positional isomerisation producing the meta isomer.^{1,2} Modification of zeolites can alter the chemical properties of the catalytic center so that it ceases to partially or completely facilitate isomerisation, thus increasing the selective yield of the important para-isomer. Fraenkel and Levy³ studied toluene isopropylation reaction on medium pore HZSM-5 zeolites differing in crystal size and morphology and proposed a reaction mechanism. They also compared the product distribution of the reaction on these medium pore zeolites with large pore HY and HM. While HM and

HY produced only cymenes, HZSM-5 catalysts gave a very high proportion of *n*-propyl toluene. Parikh *et al.*⁴ studied the same reaction over zeolites varying in pore system, crystal size after silylation and proposed a more realistic mechanism on ZSM-5. Guo *et al.*⁵ investigated the alkylation of toluene by propylene over HZM-12 zeolite and obtained cymene isomers with a near thermodynamic equilibrium composition. Cejka *et al.*⁶ investigated the factors controlling *iso*-/*n*- and para-selectivity in the alkylation of toluene with isopropyl alcohol on molecular sieves possessing different acidity (Al- and Fe-silicates) and structure type (Y, mordenite and MFI structure). The *n*-propyl toluene is a result of product selectivity on the MFI type catalysts. It comes out easily, whereas the formation of stable secondary carbocation is favoured, which should give isopropyl toluene. However, due to the size constraints, *n*-propyl selectivity is increased. Toluene isopropylation on beta zeolites has been reported by Reddy *et al.*⁷ These zeolites were observed to be highly stable with no shape selectivity. Witcherlova *et al.*⁸ also studied the selective formation of *p*-cymene on Al and Fe silicates.

From the above discussion, it is evident that although the reaction has been studied over mordenite catalysts for the purpose of comparing with other catalysts, a detailed study of this reaction over

high silica mordenite has not been reported. Mordenite, a large pore zeolite has shown promise in acid catalysis of many hydrocarbon reactions involving large aromatic molecules. The pore size of mordenite is near to the kinetic diameters of toluene and cymene molecules. However, it has not been investigated thoroughly in this reaction by earlier workers, especially with varying Si content/acidity. Hence, this work was taken up to study the kinetics of this reaction in detail over this zeolite and the effect of various parameters on the yield and cymene selectivity.

2. Experimental

2.1 Materials

The various mordenite samples used in this investigation were obtained from M/s Süd Chemie AG, Germany. The beta zeolite used for comparative study was supplied by PQ Corporation, USA. The catalyst powder was pelletised, crushed and sieved to 30–50 mesh particles before loading in the reactor.

All the samples used in this study have been found to be highly crystalline as revealed by XRD studies. The Si/Al ratios of the three mordenite catalysts are 9.9, 22.5 and 44.9 and these are designated as HM-1, HM-2 and HM-3 respectively. The Si/Al ratio of the beta catalyst was 13.

Toluene and isopropyl alcohol (IPA) used in the present study were obtained from E Merck (India) Ltd. and Qualigens Fine Chemicals, India respectively and were of 'Analytical Reagent' grade.

2.2 Procedure

The experiments were conducted in a down flow fixed bed reactor (15 mm i.d.) with 2×10^{-3} kg of catalyst. Nitrogen was used as the carrier gas. Toluene to isopropyl alcohol mole ratio in the feed was maintained at 6:1 during the runs. A feed flow rate of 6.8×10^{-3} kg/h and more was used for the kinetic study. The products of the reaction were analysed using flame ionization detector (FID) on a SHIMADZU 15A Gas chromatograph fitted with a 'CP-Xylenes' capillary (50 m, 0.32 mm i.d.) column.

3 Results and discussion

In the present study, toluene was taken in excess and isopropyl alcohol (IPA) was the limiting reactant.

Hence, pseudo first order kinetics were investigated based on isopropyl alcohol. The term 'conversion of IPA' is defined as IPA conversion (mol%) = (moles of IPA consumed/moles of IPA fed per unit time) \times 100.

The terms toluene conversion, cymene selectivity, *p*-cymene selectivity are defined as follows:

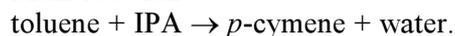
Toluene conversion (wt%) = [(toluene in product)/toluene in feed] \times 100.

Cymene selectivity (wt%) = [(cymenes in product)/total aromatics (excluding toluene) in product] \times 100

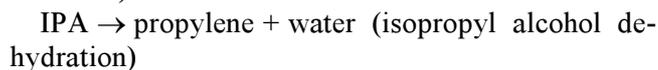
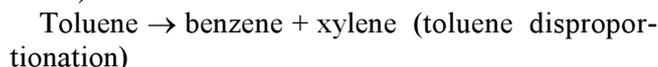
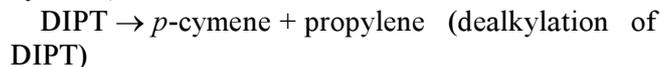
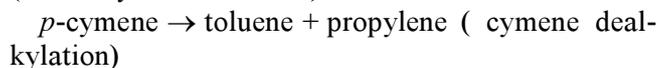
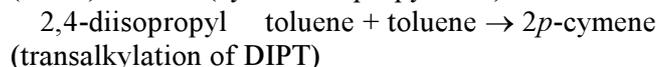
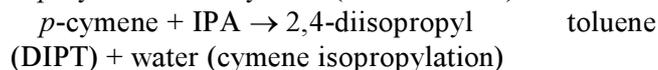
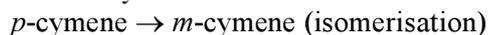
p-cymene selectivity (wt%) = [(yield of *p*-cymene)/total yield of cymenes] \times 100.

Based on the product distribution pattern shown in table 1, the reaction scheme of toluene isopropylation with IPA over the HM catalysts may be represented as

Main reaction:



Secondary reactions:



3.1 Effect of Si/Al ratio on activity of HM

Variation of Si/Al ratio is expected to influence the acidity characteristics of mordenite catalysts, which in turn relates to their activity in toluene alkylation with isopropyl alcohol. Table 1 shows the effect of variation of Si/Al ratio on the product distribution. The cymene selectivity, in general, increased with the increase in Si/Al ratio until an optimum ratio of 22.5, while a simultaneous reduction in aliphatics content was observed. This shows that side reactions yielding aliphatics were suppressed, improving the alkylation selectivity. Product distribution shows that there are considerable amounts of benzene and

Table 1. Comparison of activities of mordenite samples with varying Si/Al ratio.^a

Catalyst Si/Al ratio	HM-1 9.9	HM-2 22.5	HM-3 44.9
Product yields (wt%)			
Aliphatics	Trace	Trace	Trace
Benzene	Trace	Trace	Trace
Toluene	77	77	77
C ₈ aromatics	Trace	Trace	bd*
Cumene	Trace	Trace	Trace
<i>p</i> -Cymene	6	6	10
<i>m</i> -Cymene	15	15	11
<i>o</i> -Cymene	bd*	bd*	bd*
DIPTs [#]	1	Trace	2
Total cymenes (%)	21	21	21
Cymene sel ^a (%)	91	93	92
<i>p</i> -Cymene sel ^b (%)	30	30	48

^aConditions: temperature = 453 K; IPA/toluene mole ratio = 1 : 6; WHSV = 3 h⁻¹.

*Below detectable limits. [#]Diisopropyl toluenes.

cumene, indicating that the dealkylation/realkylation reactions cannot be neglected. On the catalyst with Si/Al ratio of 44.9, the yield of cumene was negligible. From table 1, it is also observed that when the Si/Al ratio is increased from 22.5 to 44.9, there is a slight drop in the yield and selectivity of cymenes due to increase in the yield of diisopropyl toluene. On catalysts with lower Si content, dealkylation/transalkylation of DIPT with toluene may not be taking place to the required levels. As a result, DIPTs are retained in the product. Whereas, DIPTs are converted to cymenes over the catalysts with optimum Si content. The selectivity to *p*-cymene showed a remarkable increase from 30% for Si/Al ratio of 9.9 to 48% for the Si/Al ratio of 44.9. This increase in *p*-selectivity may be attributed to suppression of isomerisation of *p*-cymene as a result of low density of acid sites due to low Si/Al ratio. It is reported that during isopropylation of toluene on MCM-41 catalysts, more *p*-cymene was observed in the product mixture as a result of lower acid site density on the catalysts and also easier diffusion of primary product, i.e. *p*-cymene.⁹ Based on these observations, the catalyst (HM-3) with Si/Al ratio of 44.9 was chosen for further study.

3.2 Effect of temperature on cymenes yield and selectivity over HM

Table 2 summarizes the effect of temperature on the yield and selectivity of cymenes, and product distribution in the temperature range of 433–493 K for

the catalyst HM-3. The yield and total cymene selectivity was observed to increase with increase in temperature up to an optimum value of 473 K. Thereafter, a slight decrease in the cymene yield and selectivity was noticed when the reaction temperature was raised further.

At higher temperatures, dealkylation reactions become pronounced and hence yield and selectivity of total cymenes are reduced. Also, as the temperature is increased from 433 to 493 K, the selective yield of *p*-cymene reaches 30% which is nearer to the equilibrium cymene distribution value of around 28.5%. At higher temperatures, as a result of isomerisation, the *p*-cymene is formed in almost equilibrium yield. An interesting observation is that there is no *o*-cymene in the product. The reason for this absence could be that the *o*-cymene formed inside the pores of HM may not be able to diffuse out of the unidimensional channels of this large pore zeolite. Similar observations were made by Wichterlova and Cejka,¹⁰ and they concluded that zeolite channel geometry plays a decisive role in the formation of products.

3.3 Effect of time-on-stream on toluene conversion and cymene selectivity over HM

From figure 1, it is evident that the activity of HM-3 catalyst is almost steady during the 4 h of time-on-stream. The toluene conversion and total cymene selectivity showed negligible variation. Only a slight fall in *m*-cymene yield was noticed with a simulta-

Table 2. Effect of temperature on product distribution.^a

Temperature (K)	433	453	473	493
Product distribution (wt%)				
Aliphatics	Trace	Trace	bd*	bd*
Benzene	Trace	Trace	Trace	Trace
Toluene	77	77	78	78
C ₈ aromatics	bd*	bd*	Trace	Trace
Cumene	bd*	Trace	Trace	Trace
<i>p</i> -Cymene	9	10	8	6
<i>m</i> -Cymene	8	11	13	14
<i>o</i> -Cymene	bd*	bd*	bd*	bd*
Diisopropyl toluenes	Trace	6	2	Trace
Total cymenes (%)	17	21	21	21
Cymene sel (%)	74	92	96	92
<i>p</i> -Cymene sel (%) (28.22)**	54	48	38	30
<i>m</i> -Cymene sel (%) (56.44)**	46	52	62	70

^aConditions: IPA/toluene mole ratio = 1 : 6; WHSV = 3 h⁻¹.

*Below detectable limits.

**Equilibrium distribution of isomers in the temperature range of 400–500 K.

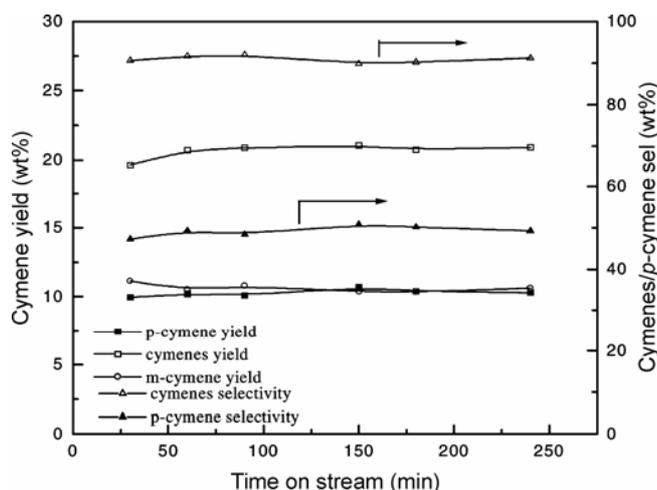


Figure 1. Effect of time on stream on yield and selectivity of cymenes over HM-3.

neous rise in the yield of *p*-cymene, which may be attributed to pore blockage due to coke.

Figure 2 shows the activity of the three HM catalysts with respect to time-on-stream. It is observed that toluene conversion and cymene yield on HM-1, with the lowest Si/Al ratio, is comparatively low and decreases rapidly with time-on-stream. HM-2 catalyst showed high initial toluene conversion and cymene yield, however, this catalyst was also found to deactivate fast after the first hour. HM-3 showed stable activity as evident from the toluene conversion and cymene yield curves in the figure. This shows that an optimum acidity is important to maintain the stability of the mordenite catalysts.

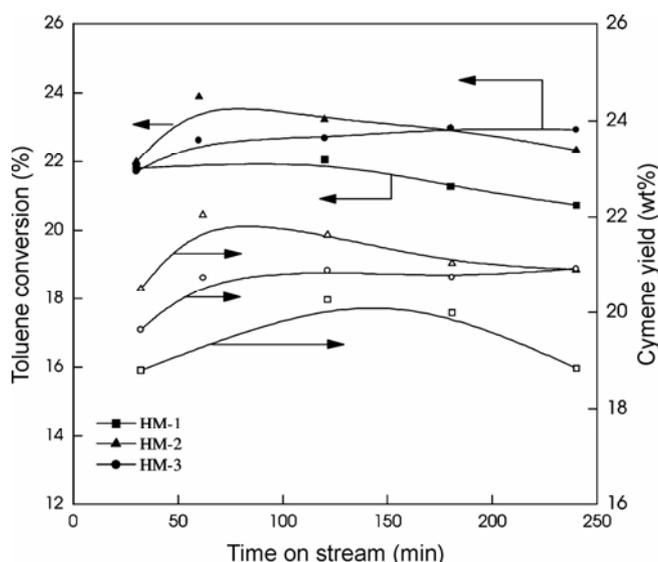


Figure 2. Variation of activities of three mordenite catalysts with time on stream.

3.4 Effect of feed mole ratio on toluene conversion and cymene selectivity over HM

Figure 3 shows the effect of feed mole ratio on toluene conversion, cymene yield and *p*-cymene selectivity. At lower toluene to isopropyl alcohol feed ratios, although toluene conversion is high, the cymene yield is low due to the formation of undesirable side products. At higher toluene to isopropyl alcohol mole ratios, these undesirable side products are reduced showing an increase in the total cymene

Table 3. Effect of weight hourly space velocity (WHSV) on product distribution.^a

WHSV (h ⁻¹)	3	6	7.2	9.6	12
Product distribution(wt%)					
Aliphatics	bd*	bd*	bd*	bd*	Trace
Benzene	Trace	Trace	Trace	Trace	Trace
Toluene	78	78	79	80	83
C ₈ aromatics	Trace	bd*	bd*	bd*	bd*
Cumene	Trace	Trace	Trace	Trace	bd*
<i>p</i> -Cymene	8	9	10	9	8
<i>m</i> -Cymene	13	12	10	8	6
<i>o</i> -Cymene	bd*	bd*	bd*	bd*	bd*
DIPTs	Trace	Trace	1	2	4
Total cymenes	21	21	20	18	13
Cymene sel (%)	96	95	93	88	79
<i>p</i> -Cymene sel (%)	38	45	49	53	58

^aConditions: temperature = 473 K; IPA/toluene mole ratio = 1 : 6.

*Below detectable limits.

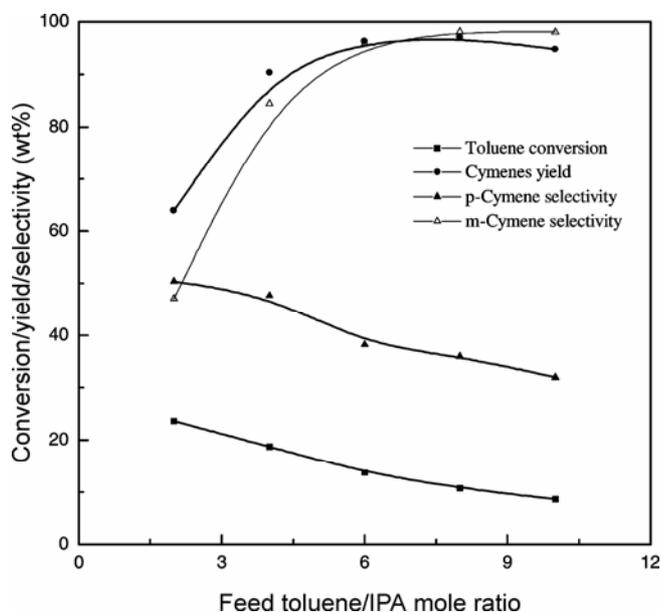


Figure 3. Effect of reactants mole ratio on toluene conversion and cymene selectivity over HM-3.

yield. At the same time, the isomerisation of para- to meta- isomer seems to increase and hence a decrease in para selectivity was observed with increasing toluene to isopropanol feed mole ratio. Toluene conversion fell, as expected, with lesser availability of the alkylating agent in the feed.

3.5 Effect of weight hourly space velocity (WHSV)

Table 3 summarizes the effect of space velocity on product distribution. The yield of cymenes was

observed to decrease with increased space velocity (decrease in residence time).

It is clear from the table that there is a clear cut link between yield of DIPTs and total cymene selectivity. When the yield of the former increased with decreasing space velocity, the yield of cymene decreased. However, the cymene selectivity, in general, and *p*-cymene selectivity, in particular, is observed to increase at higher space velocities. Improvement in *p*-cymene selectivity is probably due to the suppression of isomerisation of para- to meta-isomer.

3.6 Comparison of activity of HM with Hbeta in toluene isopropylation reaction

Table 4 shows a comparison of product distribution and cymene selectivities over HM and Hbeta catalyst at 473 K, 3.5 h⁻¹ WHSV, using a toluene to isopropyl alcohol feed mole ratio of 8 : 1. The cymene yield was almost the same (about 17%) on both the catalysts, however, HM shows a better selectivity to cymenes and *p*-cymene, in particular. Reddy *et al*⁷ found that HM (Si/Al ~ 10) did not give a better cymene selectivity compared to Hbeta but a higher Si/Al ratio of HM enhanced the selective formation of cymenes as a result of narrow distribution of acidity, which is suited for alkylation selectivity. Higher reaction temperatures and high Si/Al ratios help in accelerating the transalkylation of diisopropyl toluenes. This is clearly reflected in the table as catalyst HM-3 yields less amount of DIPTs. It is also to be noted that on HM-3 catalyst, small

Table 4. Comparison of activities of HM with Hbeta in toluene isopropylation.^a

Catalyst	Hbeta	HM-3
Si/Al	13	44.9
Product distribution (wt%)		
Aliphatics	Trace	bd*
Benzene	Trace	Trace
Toluene	81	83
C ₈ aromatics	Trace	Trace
Cumene	Trace	Trace
<i>p</i> -Cymene	5	6
<i>m</i> -Cymene	11	11
<i>o</i> -Cymene	Trace	bd*
Diisopropyl toluenes(DIPTs)	Trace	Trace
Total cymenes (%)	17	17
Cymene sel (%)	90	97
<i>p</i> -Cymene sel (%) (28.22)**	29	36
<i>m</i> -Cymene sel (%) (56.44)**	66	64
<i>o</i> -Cymene sel (%) (15.34)**	5	0

^aConditions: temperature = 473 K; IPA/toluene mole ratio = 1 : 8; WHSV = 3.5 h⁻¹.

*Below detectable limits. **Equilibrium distribution of isomers.

amounts of benzene are produced indicating suppression of dealkylation reactions. Cymene selectivity on HM-3 is also enhanced.

3.7 Kinetic study

To determine the reaction rate parameters for the conversion of isopropyl alcohol, a differential plug flow reactor was assumed since the conversions of isopropyl alcohol in the temperature range studied were below 30%. The first order rate equation for a differential plug flow reactor can be written as:

$$-r_A = dX_A/d\tau = dX_A/d(W/F_{A0}) = kC_A, \quad (1)$$

where W is the weight of the catalyst in kilograms, F_{A0} is the feed isopropyl alcohol flow rate in kgmol/h, τ is the space time in kg h/kg mol, k is the pseudo-first order rate constant in m³/kg h and C_A is the concentration of isopropyl alcohol in kg mol/m³.

Integrating (1) yields,

$$-\ln(1 - X_A) = kC_{A0}(W/F_{A0}), \quad (2)$$

where X_A is the fractional conversion of isopropyl alcohol.

A plot of $-\ln(1 - X_A)$ against W/F_{A0} over HM gave a straight line passing through the origin as illustrated in figure 4 at 403 K.

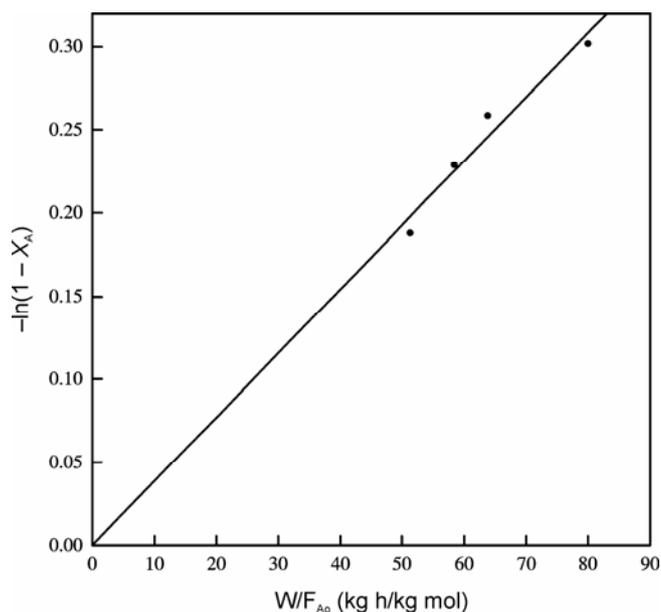


Figure 4. First order kinetic plot for toluene isopropylation at 403 K over HM-3.

The rate of reaction of isopropyl alcohol is, therefore, first order with respect to IPA which is the limiting reactant and is of zero order with respect to toluene which is in excess. From the slope of the line and with C_{A0} as 5.32×10^{-4} kg mol/m³, the rate constant (k) was calculated to be 7.34 m³/kg h at 403 K. Employing the power law equation from Power law kinetics,¹¹ the rate of reaction for the present system would be,

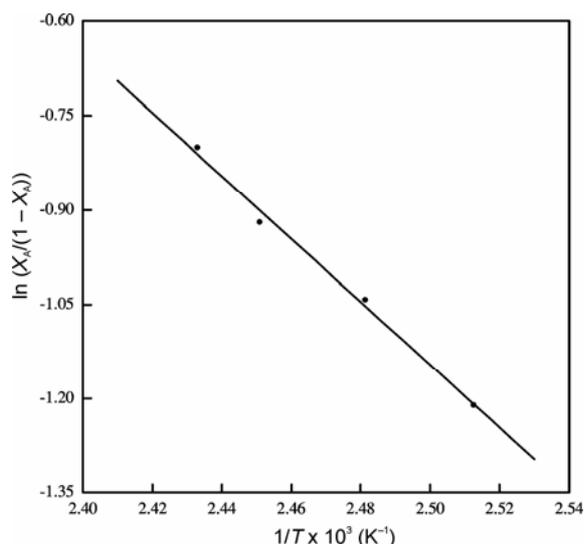


Figure 5. Arrhenius plot with HM-3 as the catalyst.

$$-r_A = A \exp(-E_a/RT) C_A, \quad (3)$$

where E_a is the apparent activation energy and A is the Arrhenius frequency factor. Since, for a reaction in a differential plug flow reactor, $-r_A = (F_{AO}/W)X_A$, (3) can be modified as

$$(F_{AO}/W)X_A = A \exp(-E_a/RT) C_A. \quad (4)$$

writing C_A in terms of initial concentration and fractional conversion of IPA and rearranging the equation, we obtain,

$$\ln(X_A/1 - X_A) = \ln A_o - E_a/RT, \quad (5)$$

where A_o is the apparent Arrhenius frequency factor which includes a constant such as W/F_{AO} as well as C_{AO} (initial concentration of IPA) and E_a is the apparent activation energy. From (5), it is clear that a plot of $\ln(X_A/1 - X_A)$ against $1/T$ would give a straight line from which E_a and the A_o can be obtained.

The Arrhenius plot for the IPA conversion employing (5) is shown in figure 5. The value of E_a from the plot is 41.84 kJ/mol and A_o is 8.93×10^4 . The apparent activation energies evaluated is comparable to the activation energies reported by earlier workers for isopropyl alcohol conversion on large pore molecular sieves for benzene alkylation.^{12,13}

4. Conclusions

The isopropylation of toluene conducted on HM catalysts with varying Si/Al ratio showed an increase in toluene conversion with increasing Si/Al ratio

until an optimum of 22.5. However, the catalyst with Si/Al ratio of 44.9 showed good stability with time-on-stream. Also, *p*-cymene selectivity over this catalyst was significantly higher than the other two HM catalysts studied. The yield of cymenes went through a maximum as the reaction temperature was increased from 433 to 493 K. The highest yield and cymene selectivity was observed at 473 K. Stable catalyst activity was observed throughout the experiments. A change in toluene to isopropyl alcohol feed ratio from 2 to 10 resulted in enhanced cymene yield and decreased *p*-cymene selectivity. High silica mordenite (HM) showed similar conversion as Hbeta, but HM proved to be comparatively a better cymene selective catalyst under similar reaction conditions.

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References

- Allen R H and Yats L D 1961 *J. Amer. Chem. Soc.* **83** 2799
- Olah G A, Kuhn S J and Flood S H 1962 *J. Amer. Chem. Soc.* **84** 1688
- Fraenkel D and Levy M 1989 *J. Catal.* **118** 10
- Parikh P A, Subrahmanyam N, Bhat Y S and Halgeri A B 1992 *Appl. Catal. A* **90** 1
- Guo H, Han C and Wang X 1993 *Shiyou Xuebao Shiyou Jiagong* **9** 41
- Čejka J, Kapustin G A and Witchterlová B 1994 *Appl. Catal.* **A108** 187
- Reddy K S N, Rao B S and Shiralkar V P 1995 *Appl. Catal.* **A121** 191
- Witchterlová B, Čejka J and Zilkova N 1996 *Micro-porous Mater.* **6** 405
- Medina-Valtierra J, Sanchez M A, Montoya J A, Navarrete J and De Los Reyes J A 1997 *Appl. Catal.* **A158** 11
- Witchterlová B and Čejka J 1994 *J. Catal.* **146** 523
- Yue P L and Olaofe O 1984 *Chem. Eng. Res. Des.* **62** 167
- Palekar M G and Rajadhyaksha R A 1986 *Catal. Rev. Sci. Eng.* **28** 371
- Parikh P A, Subrahmanyam N, Bhat Y S and Halgeri A B 1991 *Chem. Eng. J.* **54** 79