

Alkylation of toluene with isopropyl alcohol over SAPO-5 catalyst

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Abstract. Isopropylation of toluene with isopropyl alcohol was studied over the large pore silicon aluminophosphate molecular sieves (SAPO-5) with varying Si content. Toluene conversion was found to increase with increase in the Si of the catalysts. The effect of temperature on yields of cymene was studied in the range of 453 to 553 K. The highest yield and selectivity for cymene was observed at 513 K. Good cymene selectivity was confirmed with the absence of *n*-propyl toluene in the product. The catalyst activity, in terms of *p*-cymene selectivity, remained almost stable during a nine hour time on stream run. Enhanced cymene selectivity and decreased *p*-cymene selectivity was observed with increase in the toluene to isopropyl alcohol feed mole ratio from 2 to 8. Power law model and L–H–H–W model fitted the experimental data well and are used to explain the kinetics of this reaction.

Keywords. Cymene; *p*-cymene; isopropylation; toluene; SAPO-5.

1. Introduction

In most of the industrial alkylation processes, catalysts such as mineral acids and anhydrous AlCl_3 are used. The relatively high volumes of catalyst in these processes make them highly polluting. Also, a lot of energy is consumed, annually, to separate the acid catalyst from product. In recent times, considerable attention is focused on the selective production of para-dialkylbenzenes, like xylene, ethyl toluene, diethyl benzene via alkylation reactions catalysed by shape selective zeolites or other solid acid catalysts.^{1–5} 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, pesticides, fungicides, fragrances, pharmaceuticals, herbicides, heat transfer media, etc.

The alkylation of toluene over zeolites follows the well known Friedel–Crafts mechanism. It proceeds by direct *ortho*–*para* attack of the ring followed by positional isomerisation producing the meta isomer.^{6,7} Modification of a zeolite can alter the chemical properties of the catalytic centers so that it ceases to partially or completely facilitate isomerisation, thus, increasing the selective yield of the important para-isomer. Fraenkel and Levy⁸ 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 over these medium pore zeolites with that over the large pore HY and HM. While HM and HY yielded cymenes selectively, a very high proportion of *n*-propyl toluene was observed over HZSM-5. Parikh *et al.*⁹ studied the same reaction over zeolites varying in pore size distribution, crystal size and proposed a more realistic mechanism on ZSM-5. Guo *et al.*¹⁰ investigated the alkylation of toluene by propylene over HZSM-12 zeolite and obtained cymene isomers with a near thermodynamic equilibrium composition. Čejka *et al.*¹¹ investigated the factors controlling para-selectivity in the alkylation of toluene with isopropyl alcohol over molecular sieves possessing different acidity (Al- and Fe-silicates) and structure type (Y, mordenite and MFI structure). They concluded that the MFI structure and high acidity of the molecular sieves tend to increase the *n*-propyl toluene yield. According to them, the alkylation activity does not follow the acidity, but the reaction is controlled by the desorption/transport rate of bulky cymenes and cumene. Toluene isopropylation on beta zeolites has been reported by Reddy *et al.*¹² These zeolites were observed to be highly stable but possess negligible shape selectivity in toluene isopropylation. Witcher-

Table 1. Synthesis gel ratios and crystallization conditions for SAPO-5 catalysts.

| Sample | Gel composition | | | | Reaction conditions | | |
|---------|--------------------------------|-------------------------------|------------------|-----|---------------------|-----------|----------|
| | Al ₂ O ₃ | P ₂ O ₅ | SiO ₂ | R | H ₂ O | Temp (°C) | Time (h) |
| SAPO-5b | 1.0 | 0.975 | 0.05 | 1.1 | 55 | 200 | 24 |
| SAPO-5c | 1.0 | 0.95 | 0.10 | 1.1 | 55 | 200 | 24 |
| SAPO-5d | 1.0 | 0.925 | 0.20 | 1.1 | 55 | 200 | 24 |

R, Template; di-*n*-propylamine for SAPO-11 and tri-ethylamine for SAPO-5s

lova *et al*¹³ studied the selective formation of *p*-cymene over Al and Fe silicates.

From the above discussion, it is evident that although toluene isopropylation has been studied over a variety of catalysts, mostly zeolites, yet, no attempt has been made till date to use silicon substituted alumino phosphates (SAPOs) as catalysts for this reaction. Hence, the present study was undertaken with an objective to investigate the effect of various process parameters and the kinetics of toluene alkylation with isopropyl alcohol over SAPO-5 catalyst.

2. Experimental

2.1 Materials

The SAPO-5 molecular sieves SAPO-5b, SAPO-5c and SAPO-5d respectively were prepared following procedure described by Lok *et al*¹⁴ and characterized as detailed below.

Three SAPO-5 samples with 0.05, 0.1 and 0.2 M silica in the starting gel were synthesized and these were designated as SAPO-5b, SAPO-5c and SAPO-5d respectively. The gel ratios and synthesis conditions are given in table 1. In a typical synthesis (for SAPO-5c), 34.68 g of Pseudoboehmite was added to dilute phosphoric acid (54.765 g of H₃PO₄ in 160 g of water) slowly, in a constantly stirred autoclave. After the addition of the aluminium source, stirring was continued at least for one hour. Subsequently, SiO₂ in 47.6 g of water was added to the above and stirring continued for another hour. To this mixture, 26.562 g of tri-ethylamine was added under vigorous stirring. The gel thus obtained was stirred further, filled in a teflon lined autoclave and kept for heating at 200°C under autogeneous pressure. After heating for 24 h, the crystalline product was separated from mother liquor and repeatedly washed with distilled water. The crystals were dried for 12 h at 110°C and subsequently, calcined at 550°C for 12 h to remove the template.

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). They were found to be highly crystalline pure phases.

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

3. Results and discussions

In the present study, toluene was used 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' used in the kinetic studies is defined as

$$\text{IPA conversion (mol\%)} = \frac{\text{moles of IPA consumed/}}{\text{moles of IPA fed per unit time}} \times 100.$$

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

Table 2. Comparison of activities of various SAPO-5 catalysts in toluene isopropylation reaction^a.

| Catalyst | SAPO-5b | SAPO-5c | SAPO-5d | SAPO-11 | SAPO-11 [#] |
|----------------------------|------------|------------|------------|------------|----------------------|
| Product yield (wt%) | | | | | |
| Aliphatics | <i>bd*</i> | <i>bd*</i> | <i>bd*</i> | 2.01 | 1.67 |
| Benzene | <i>bd*</i> | <i>bd*</i> | 0.056 | 0.12 | 0.10 |
| Toluene | 81.24 | 80.13 | 78.57 | 97.30 | 94.17 |
| C ₈ aromatics | <i>bd*</i> | <i>bd*</i> | <i>bd*</i> | <i>bd*</i> | <i>bd*</i> |
| Cumene | <i>bd*</i> | <i>bd*</i> | 0.074 | <i>bd*</i> | <i>bd*</i> |
| <i>p</i> -Cymene | 6.99 | 7.34 | 7.91 | 0.565 | 3.52 |
| <i>m</i> -Cymene | 8.85 | 10.52 | 11.40 | <i>bd*</i> | 0.43 |
| <i>o</i> -Cymene | 1.99 | 1.51 | 1.44 | <i>bd*</i> | 0.08 |
| DIPT | 0.83 | 0.70 | 0.56 | <i>bd*</i> | 0.03 |
| Cymenes (wt%) | 17.92 | 19.37 | 20.75 | 0.57 | 4.03 |
| Cymenes sel (wt%) | 95.57 | 96.51 | 96.80 | 82.12 | 96.88 |
| <i>p</i> -Cymene sel (wt%) | 37.25 | 37.89 | 38.14 | 99.99 | 87.35 |

^aConditions: temperature, 473 K; WHSV, 3 h⁻¹; toluene/IPA mole ratio, 6:1 DIPT: diisopropyl toluene; *below detectable limits; #: at 573 K

$$\text{Toluene conversion (wt\%)} = \frac{[(\text{toluene in product})/\text{toluene in feed}] \times 100}{}$$

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

$$p\text{-cymene selectivity (wt\%)} = \frac{[(\text{yield of } p\text{-cymene})/\text{total yield of cymenes}] \times 100}{}$$

3.1 Effect of acidity

It is known that acidity of SAPO-5 catalysts depends upon the amount and mode of silicon substituted into the framework and increases with increase in Si content of the catalyst.¹⁵ Studies based on ²⁹Si NMR and acidity measurements show that the acidity of the catalysts is in order of SAPO-5d>SAPO-5c>SAPO-5b. The cymene yield also decreased in the same order for the SAPO-5 series. Table 2 shows the effect of variation of Si content on cymene yield, selectivity. The yields of meta- and para-cymenes increased with the increase in Si content while that of the ortho-isomer decreased. Also, the cymene selectivity increased from 95.57% over SAPO-5b to 96.8% over SAPO-5d. In particular, *p*-cymene selectivity, increased from 37.89% to 40.73% with the increase in Si content which can be attributed to the increased conversion of toluene over SAPO-5b compared to SAPO-5d.

The yields of diisopropyl toluenes (DIPTs) were also observed to decrease with the increase in the Si

content. This could be because of the absence of sufficient number of active acid sites for realkylation of cymenes. It is also observed from the product distribution pattern in table 2 that small quantities of cumene and benzene are formed due to toluene disproportionation and benzene isopropylation side reactions. These side reactions do not seem to take place over the catalysts with lower Si content or acidity. Despite these side reactions, the cymene selectivity is the highest over SAPO-5d among the SAPO-5 catalysts tested. Hence, this catalyst was chosen for detailed kinetic investigations.

The same table also compares the activity of the medium pore SAPO-11 catalyst with SAPO-5. It has been observed that the SAPO-11 which has milder acidity than SAPO-5 is not active in the isopropylation of toluene even at a higher reaction temperature (573 K) yielding only 4.03 wt% cymenes.

3.2 Effect of temperature on cymene yield and selectivity

Figure 1 summarizes the effect of temperature on the yield and selectivity of cymenes. The yield and total cymene selectivity has been observed to rise with increasing temperature up to an optimum temperature of 513 K. Thereafter, a decrease in the cymene yield and selectivity was observed. At lower temperatures, the *p*-cymene selectivity is 40%, above that of the equilibrium value, but with the increase in temperature, the *p*-cymene yield reduces and moves towards the equilibrium value of 28% (within

the temperature range considered). The decrease in *p*-cymene selectivity with temperature is attributed to the isomerization reaction to form *m*-cymene which is favoured at higher temperature.

However, the *o*-cymene was found to be always much lower than the equilibrium value. This can be attributed to the isomerization to *m*-cymene, favoured at higher temperatures, and also, the diffusional resistance in the pores of the catalyst. The selectivity to *m*-cymene reaches a maximum of 12.5% at 513 K and falls with further increase in temperature. At temperatures higher than 513 K, the active sites for the isomerisation of *p*-cymene to *m*-cymene could be blocked by coke formed by side reactions like alkyl aromatic cracking.

3.3 Effect of time on stream on toluene conversion and cymene selectivity

Figure 2 shows the variation of activity of the catalyst during a 9 h time on stream run. The toluene conversion was observed to decrease by about 5% at the end of 8 h 30 min time on stream. The cymene selectivity almost remains constant until the end of 6 h and then drops by 3–5%. Selectivity to *p*-cymene is observed to remain almost constant at 40% throughout the run. The decrease in the conversion of toluene is attributed to the deactivation of the catalysts due to coke formation reaction and subsequent pore blocking. The deactivation kinetics follow a parallel mechanism in the aromatics alkylation

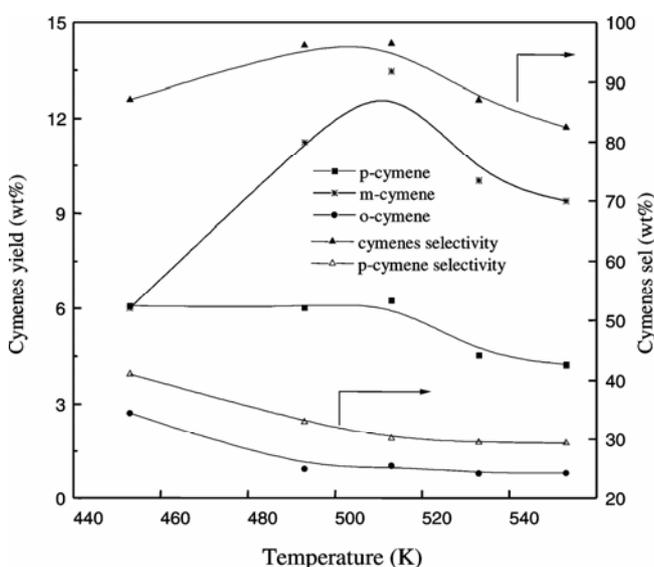


Figure 1. Effect of temperature on cymenes yield and selectivity.

with isopropyl alcohol over SAPO-5 and reported in an earlier paper.⁵ The experimental data for the kinetic study was collected within the time of stable activity of the catalyst.

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

Figure 3 shows the effect of feed mole ratio on toluene conversion, total cymene selectivity and *p*-cymene

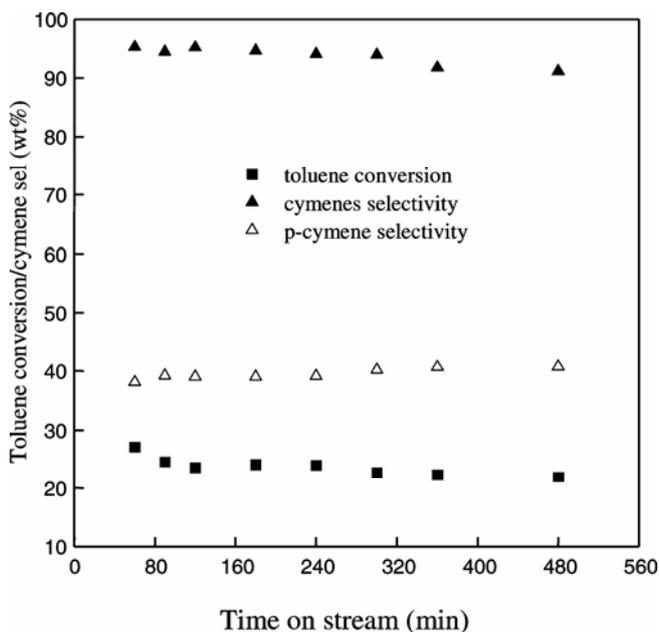


Figure 2. Effect of time on stream on toluene conversion and cymene selectivity.

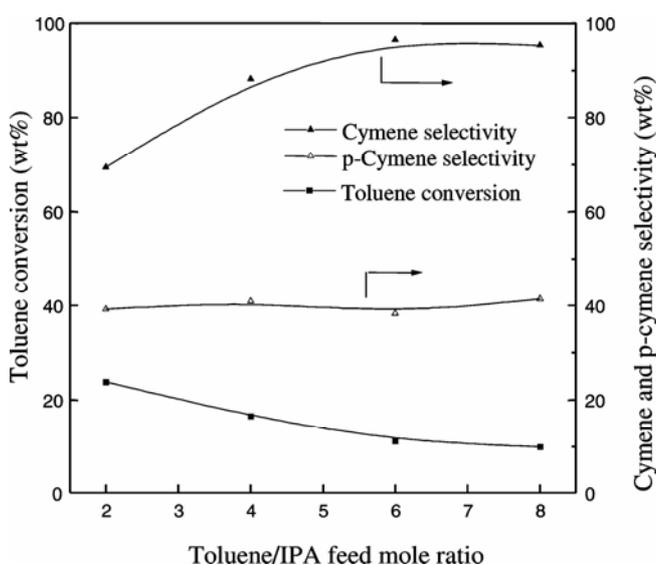


Figure 3. Effect of feed composition on toluene conversion and cymene selectivity.

Table 3. Effect of WHSV on cymenes yield and selectivity over SAPO-5^a.

| WHSV (h ⁻¹) | 3.0 | 6.3 | 9.6 | 12.0 |
|----------------------------|-------------|-------------|-------------|-------|
| Product distribution (wt%) | | | | |
| Aliphatics | <i>bd</i> * | <i>bd</i> * | <i>bd</i> * | 0.11 |
| Toluene | 80.13 | 82.02 | 81.59 | 82.64 |
| <i>p</i> -cymene | 7.34 | 6.62 | 7.15 | 6.45 |
| <i>m</i> -cymene | 10.52 | 8.55 | 8.27 | 6.37 |
| <i>o</i> -cymene | 1.51 | 2.08 | 2.13 | 3.03 |
| DIPTs | 0.70 | 0.73 | 0.86 | 1.40 |
| Cymenes (wt%) | 19.37 | 17.26 | 17.55 | 15.85 |
| Cymenes sel (wt%) | 96.51 | 95.95 | 95.32 | 91.88 |
| <i>p</i> -Cymene sel (wt%) | 37.89 | 38.84 | 40.73 | 40.73 |

^aConditions: temperature, 473 K; IPA/toluene mole ratio, 1:6; catalyst, SAPO-5d; below detectable limits

selectivity. Toluene conversion decreases with lower percentage of isopropyl alcohol in the feed which is as expected. At lower toluene to isopropyl alcohol ratios in the feed, the cymenes selectivity decreased from 95% (at 6–8 mole ratio of toluene to IPA) to 70% (at 2 mole ratio of toluene and IPA) due to the formation of undesirable side products by oligomerisation reactions of propylene formed by dehydration of isopropyl alcohol whose concentration is increased in the feed. At higher toluene to isopropyl alcohol mole ratios, these undesirable side products are reduced, showing an increase in the total cymene selectivity. The *p*-cymene selectivity, however, remains almost constant with the increase in toluene to isopropyl alcohol mole ratio.

3.5 Effect of weight hourly space velocity (WHSV)

Table 3 summarizes the effect of space velocity on product distribution. The cymenes yield and selectivity were observed to decrease with increased space velocity due to decrease in residence time in the reactor. However, the *p*-cymene selectivity was observed to increase at higher space velocities probably, due to the suppression of the *p*-cymene isomerisation to the meta isomer. From the product distribution, we see that at the highest space velocity, even aliphatics are present in the product due to incomplete conversion of isopropyl alcohol.

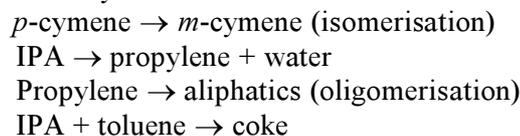
3.6 Kinetic study

To determine the reaction rate parameters for the conversion of isopropyl alcohol, a differential plug flow reactor was assumed, since, the conversion of

isopropyl alcohol in the temperature range (401–415 K) studied, were below 30%. At this lower temperature range, diisopropyl toluenes or other side products were not detected in the product stream. The reaction scheme in this low temperature range can be written as

Main reaction: toluene + IPA → *p*-cymene + water

Secondary reactions:



3.6a *Homogeneous kinetic model:* Using the first order rate equation for a differential plug flow reactor, the rate of disappearance of isopropyl alcohol may be written as

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

where W is the weight of the catalyst in kilograms, F_{AO} is the feed isopropyl alcohol flow rate in kgmol/h, X_A is the fractional conversion of IPA, τ is the space time in kg h/kg mol, k is the rate constant and C_A is the concentration of isopropanol in kgmol/m³. Figure 4 shows the isopropyl alcohol conversion at different space times at 401 K, 405 K, and 408 K. The straight lines confirm a differential conversion at all these three temperatures.

Integration of equation (1) yields,

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

The plot of $-\ln(1-X_A)$ against W/F_{AO} over SAPO-5d gave a straight line passing through the origin as illustrated in figure 5 at various temperatures.

The rate of isopropyl alcohol conversion is, therefore, first order with respect to isopropyl alcohol, which is the limiting reactant, and is of zero order with respect to toluene which is in large excess. From the slopes of the lines and with C_{A0} as 1.39×10^{-3} kg mol/m³, the rate constant (k) was calculated to be 3.50 m³/kg h at 415 K, with C_{A0} as 1.42×10^{-3} kg mol/m³ rate constant (k) was 2.74 m³/kg h at 408 K and with C_{A0} as 1.45×10^{-3} kg mol/m³ rate constant (k) was 2.07 m³/kg h at 401 K on SAPO-5d.

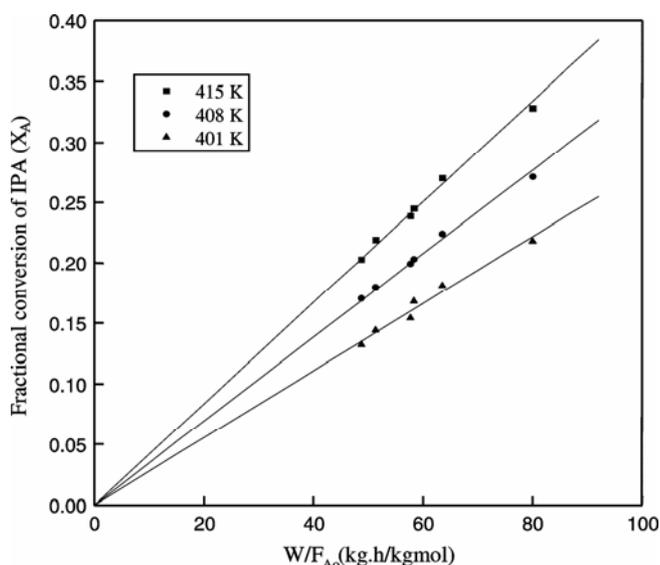


Figure 4. Effect of space time on IPA conversion.

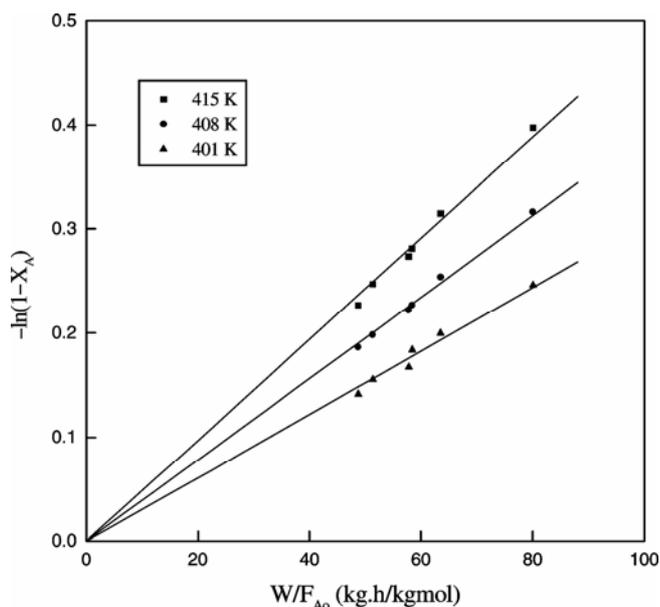


Figure 5. First order kinetic plot for toluene isopropylation over SAPO-5d.

Employing the power law equation from Power law kinetics,¹⁶ the rate of the reaction for the present system would be,

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

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, $-r_A = (F_{A0}/W)X_A$, (3) can be modified as

$$(F_{A0}/W)X_A = A \exp(-E_a/RT) C_A, \quad (4)$$

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

$$\ln(X_A/1 - X_A) = \ln A_0 - E_a/RT, \quad (5)$$

where A_0 is the apparent Arrhenius frequency factor which includes a constant such as W/F_{A0} as well as C_{A0} (initial concentration of isopropyl alcohol) 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_0 can be obtained.

The Arrhenius plot for the isopropyl alcohol conversion employing (5) is shown in figure 6. The value of E_a from the plot is 55.36 kJ/mol and A_0 is 4.538×10^6 . The apparent activation energy evaluated is comparable to the activation energies reported by earlier workers for alkylation of toluene over zeolites. Parikh *et al*¹⁷ reported an apparent activation energy of 50 kJ/mol for toluene isopropylation

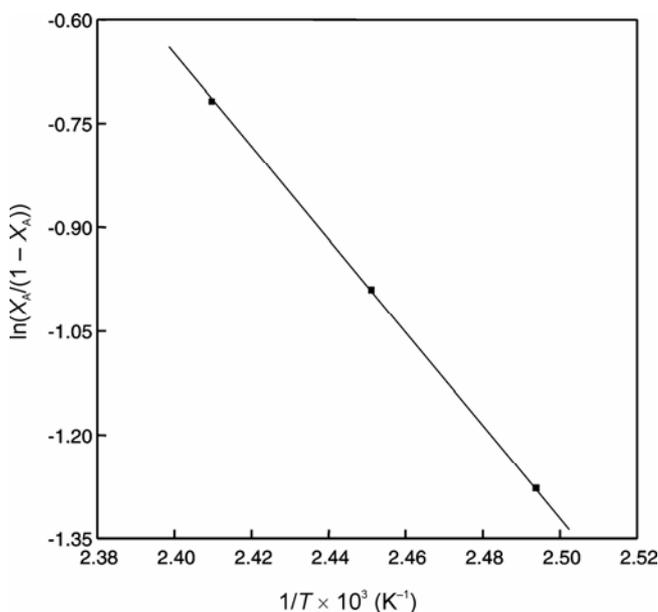
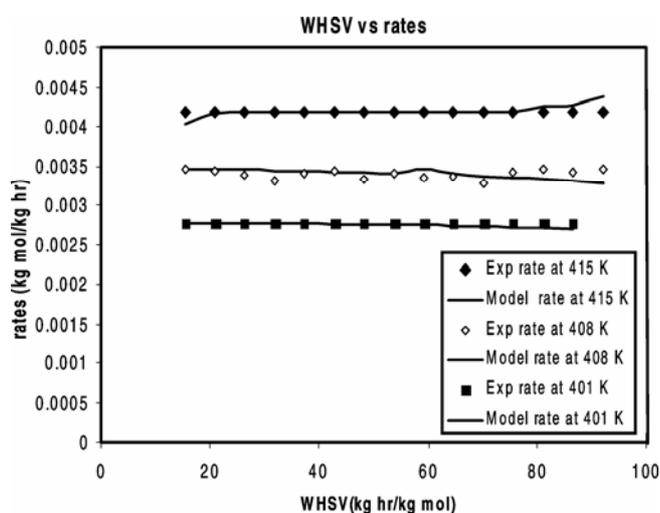


Figure 6. Arrhenius plot with SAPO-5d as the catalyst.

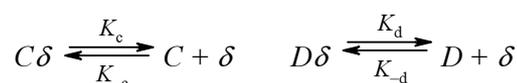
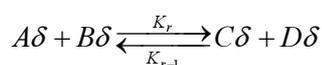
Table 4. Parameter estimation for heterogeneous kinetic model.

| Temp. (K) | k (rate constant, kg mol/kg h) | K_A (atm ⁻¹) | K_B (atm ⁻¹) | K_C (atm ⁻¹) | K_D (atm ⁻¹) | K_r (kg mol/kg h atm ²) |
|-----------|----------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|---------------------------------------|
| 401 | 0.734 | 35.8486 | 0.0378 | 30.6653 | 0.0776 | 1.00515 |
| 408 | 0.805 | 33.7507 | 0.0356 | 19.7297 | 0.021 | 1.00149 |
| 415 | 0.8567 | 26.2048 | 0.0345 | 0.0142 | 0.019 | 1.00152 |

**Figure 7.** Comparison of experimental and heterogeneous model predicted rates.

over ZSM-5 and a rate constant of 1.714 g mol/h/gcat/atm² at 498 K which is only very slightly higher than our rates due to the higher temperature range considered by them. Bhat *et al*¹⁸ reported an apparent activation energy of 63 kJ/mol for toluene ethylation over HZSM-8 with only a slightly higher rate constant of 1.862 mol/g atm h at much higher temperature of 673 K.

3.6b Heterogeneous kinetic model: The heterogeneous model is based on the Langmuir–Hinshelwood–Hougen–Watson kinetics wherein the main reaction forming *p*-cymenes and water is catalysed by the active sites on the catalyst. According to this, toluene and isopropyl alcohol are chemisorbed on dual adjacent active sites of the catalyst to form different carbonium ions. Both chemisorbed IPA and toluene react with each other to form cymenes and water followed by desorption of cymenes and water from the active sites. Here, the dual-site surface reaction is the rate controlling step. These steps are summarized as given below.



$A = \text{IPA}$; $B = \text{toluene}$; $C = p\text{-cymene}$; $D = \text{water}$ and $\delta = \text{vacant active site}$.

The overall rate expression following the surface reaction controlling dual site mechanism is expressed in concentration terms (C_A , C_B , C_C , C_D) as

$$-r_s = \frac{k(K_A \cdot K_B \cdot C_B \cdot C_A - K_D \cdot K_C \cdot C_C \cdot C_D / K_r)}{(1 + K_A \cdot C_A + K_B \cdot C_B + K_D \cdot C_D + K_C \cdot C_C)^2}$$

where K_A = equilibrium adsorption constant of IPA; K_B = equilibrium adsorption constant of toluene; K_C = equilibrium desorption constant of *p*-cymene and K_D = equilibrium desorption constant of water, K_r = equilibrium constant for overall dual-site surface reaction.

The parameters are estimated by non-linear regression technique and summarized for the three temperatures in table 4. The model predicted rates agree well with the experimental rates as shown in figure 7.

3.7 Thermodynamics and equilibrium constant evaluation

The equilibrium constant for a chemical reaction is defined as

$$\Delta F^\circ = -RT \ln K_p, \quad (6)$$

where ΔF° is the free energy change in the reaction, R is the universal gas constant, K_p is the thermodynamic equilibrium constant based on pressure.

Now, by Van Krevlen method, the free energy of formation of a compound at any temperature T is given by

$$\Delta F_f^\circ = A + BT, \quad (7)$$

where A and B are constants as given in the standard tables by Reid and Sherwood.¹⁹

The equilibrium constants for the reversible isomerisation reaction of *p*-cymene to *m*-cymene at 401 K, 408 K and 415 K were determined as follows:

At 401 K

$$\Delta F_f^\circ \text{ (for } p\text{-cymene)} = A + BT = 0.93 \text{ kcal/gmol}$$

$$\Delta F_f^\circ \text{ (for } m\text{-cymene)} = -0.31 \text{ kcal/gmol.}$$

Therefore, (6) can be written as

$$\Delta F^\circ = \Delta F_f^\circ(\text{products}) - \Delta F_f^\circ(\text{reactants}) = -RT \ln K_p.$$

Substituting the above values of ΔF_f° of *p*-cymene, *m*-cymene and $R = 1.987 \text{ cal/mol K}$.

$$K_p = 1.00516 \text{ atm}^{-1} \text{ at } 401 \text{ K.}$$

Similarly, the values of K_p are 1.00153 atm^{-1} at 408 K and 1.0015 atm^{-1} at 415 K.

4. Conclusions

Alkylation of toluene with isopropyl alcohol was studied over a variety of SAPO-5 molecular sieves. Toluene conversion was found to increase with increase in Si content of the SAPO-5 catalysts. The yield of cymenes went through a maximum as the reaction temperature was increased from 453 K to 553 K. The highest yield and selectivity for cymene was observed at 513 K. Undesirable side product like *n*-propyl toluene was absent over this catalyst. The *p*-cymene selectivity remained almost constant during a nine hour time on stream run. A change in toluene to isopropyl alcohol feed ratio from 2 to 8 resulted in enhanced cymene selectivity and decreased *p*-cymene selectivity. Both Power law model, assuming pseudo-first order reaction, and L-H-H-W model fit the experimental data fairly well in the temperature range of 401–415 K. The activation energy compares well with earlier reports on similar reactions over molecular sieves.

Nomenclature

| | |
|----------|--|
| Al | Alumina |
| A | Arrhenius frequency factor |
| A_o | Apparent Arrhenius frequency factor |
| C_{A0} | Concentration of isopropanol in feed, kgmol/m ³ |
| C_A | Concentration of isopropanol, kgmol/m ³ |
| DIPT | 2,4-diisopropyl toluene |
| E_a | Apparent activation energy, kJ/mol |
| F_{A0} | Feed flow rate of isopropanol, kg mol/h |
| F_f | Free energy of formation in Kcal/g mol |
| HM | Hydrogen Mordenite |
| IPA | Isopropanol |

| | |
|------------|--|
| k | Pseudo-first order rate constant in m ³ /kg. |
| $^\circ$ | Thermodynamic equilibrium constant based on pressure atm ⁻¹ |
| m | Meta |
| o | Ortho |
| p | Para |
| R | Ideal gas law constant, 82.06 cm ³ atm/gm-mol. (°K) |
| r_A | Rates of reaction of isopropanol, kgmol/kg of cat. h. |
| Si | Silica |
| T | Reaction temperature, K |
| W | Catalyst weight, kg |
| WHSV | Weight hourly space velocity, h ⁻¹ |
| W/F_{A0} | Space time, kg.h/kgmol referred to isopropanol feed rate |
| X_A | Fractional conversion of isopropanol |

Greek letters

| | |
|----------|-------------------------------|
| Δ | change space time, kg h/kgmol |
|----------|-------------------------------|

Subscripts

| | |
|-------|------------------|
| A | isopropanol |
| A_o | feed isopropanol |
| a | apparent |
| f | formation |
| p | pressure |

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