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Transalkylation of diisopropylbenzene with benzene over SAPO-5 catalyst: a kinetic study

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Abstract

BACKGROUND: The objective of this work was to improve the selective yield of cumene by transalkylating the (diisopropylbenzene) DIPB formed in benzene alkylation with propene and select the optimum process conditions for this transalkylation over SAPO-5 catalyst.

RESULTS: Higher benzene/DIPB mole ratios and higher space velocities were found to give better cumene selectivity. An apparent activation energy value of 130.2 kJ mol^{-1} was obtained for the reaction with SAPO-5 as the catalyst.

CONCLUSION: SAPO-5 shows promise when loaded with a small quantity of platinum (0.005% w/w) in the transalkylation of commercial DIPB (cumene column bottoms) with benzene. The kinetic investigations help in selecting optimum process operating conditions for maximizing the cumene yields in transalkylation of commercial DIPB over SAPO-5.

Keywords: transalkylation; cumene; diisopropylbenzene; SAPO-5; Pt-SAPO-5

NOTATION

A_O	Apparent Arrhenius frequency factor
C_{DIPB}	Concentration of DIPB (kgmol m^{-3})
C_{DIPBO}	Initial concentration of DIPB (kgmol m^{-3})
E_a	Apparent activation energy (kJ mol^{-1})
F_{DIPBO}	Feed flow rate (kg mol h^{-1})
ΔH°	Standard enthalpy of adsorption (kJ mol^{-1})
k	Pseudo-first-order rate constant (m^3 kg^{-1} h^{-1})
n-PB	*n*-propylbenzene
P_i	Partial pressure of species i (Pa)
r_i	Rate of disappearance of species i (kgmol kgcat^{-1} h^{-1}
R	Ideal gas law constant (8.314 J mol^{-1} K^{-1})
ΔS°_{ad}	Difference in standard entropy between adsorbed component to the same component in gas phase (at 101.325 kPa) (kJ mol^{-1} K^{-1})
S°_g	Standard total entropy in gas phase (kJ mol^{-1} K^{-1})
τ	Space time (kg h kgmol^{-1})
W	Weight of catalyst (kg)
WHSV	Weight Hourly Space Velocity (kgmol kg^{-1} h^{-1})
X_{DIPB}	Fractional conversion of DIPB

Subscripts

B	Benzene
C	Cumene
DIPB	Diisopropylbenzene

INTRODUCTION

In alkylation reactions of aromatics, formation of the monoalkylated products is always accompanied by 5–15% w/w of dialkylated products. The final yield of the monoalkylated product can be improved by either transalkylating the dialkylated products in a separate reactor or recycling into the same reactor. Transfer of the alkyl group between two similar or dissimilar molecules is descriptively known as disproportionation or transalkylation. These reactions are of industrial significance and are normally carried out in a vapour phase, over solid acid catalysts such as silica–alumina or zeolites, at elevated temperatures and pressures.[1,2]

In the case of the alkylation of benzene with propylene to cumene, the major byproducts formed are diisopropylbenzene (DIPB) isomers up to 5–10% w/w. The DIPB fraction in many commercial plants is diverted to a fuel pool, resulting in additional raw material consumption. This affects the economy of the process. Some of the plants do have a separate facility to transalkylate DIPB with benzene, to yield additional cumene, but these processes suffer substantially from environmental problems.

Early research work in this field was carried out to convert toluene to benzene and xylenes.[3] Later,

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this work was extended to the transalkylation of trimethylbenzenes, with toluene, to xylenes. Best and Wojciechowski[4] studied the kinetics of transalkylation of cumene on a LaY catalyst. Slaugh[5] obtained a US patent for transalkylation over a silica gel impregnated AlH_3 catalyst. Bakas and Barger[6] of UOP Inc. patented a high-yield cumene process by transalkylation of the diisopropyl benzene to cumene over an acid-modified crystalline aluminosilicate zeolite. Lee *et al.*[7] of Dow Chemicals, USA, patented a process for the transalkylation of alkylbenzenes over an acidic mordenite-type catalyst in 1991. Robaato *et al.*[8] of Chevron Research Co., Japan, patented a liquid-phase transalkylation process using beta zeolites (Si/Al ratios of 5:1 to 100:1) in 1991.

Corma *et al.*[9] studied the transalkylation of aromatics and the influence of structural parameters of dealuminated Y zeolites. They discussed the influence of extra framework Al on the activity, selectivity and adsorption properties of zeolites. Pradhan and Rao[10] carried out the transalkylation of DIPB over large-pore zeolites and found zeolite beta to be very active. Rao *et al.*[11] obtained a European patent in 1993 for a cumene process which recycles DIPBs for transalkylation into the reactor containing a single catalyst bed of beta catalyst. Forni *et al.*[12] studied transalkylation of *m*-ethylbenzene with benzene to ethylbenzene over β- and Y-zeolites at 483–543 K and 48 bar total pressure. They tried to identify the mechanism and proposed a simple kinetic scheme for the overall process. Collins *et al.*[13] of Mobil Oil Corp., USA, obtained a US patent for a process producing alkyl aromatics, especially cumene, which involves introduction of feed to a transalkylating zone over zeolite beta/alumina and then feeding to an alkylating zone where MCM-22/alumina catalyst was used.

Cejka *et al.*[14] studied the transalkylation of trimethylbenzene with toluene over large-pore zeolites. Perego and Ingallina[15] discussed the combined alkylation and transalkylation for alkyl aromatic production. They evaluated the performance of different catalysts based on their selectivity, Si/Al ratio, and pore structure. They concluded that MCM-22 and beta are the most promising zeolites for liquid-phase production of both EB and cumene. Serra *et al.*[16] studied the transalkylation of alkyl-aromatics with acid zeolites with improved methyl-transalkylation activity under hydrogen pressure. They concluded that Nu-87 and mordenite are the preferred zeolites for an acceptable level of dealkylation and transalkylation activities. In another paper Serra *et al.*[17] studied the influence of zeolite structure on the performance of heavy reformate transalkylation catalysts. Recently Sotelo *et al.*[18] made a comparative study on transalkylation of DIPB with benzene over beta, Y and mordenite with different aluminium content (or Si/Al ratio) in supercritical CO_2 and liquid phase. The influence of Si/Al ratio on the catalytic activity was explained in terms of cumene yield and selectivity, taking into account the competitive isomerization and by-product formation. They concluded that use of supercritical CO_2 did not result in superior catalytic transalkylation activity for the Y zeolite. On the contrary, an important improvement in product yield was obtained with the beta and mordenite zeolites, and these results were related to mass transport properties and catalyst structure.

The SAPO molecular sieves are considered as potentially interesting catalysts for various petrochemical applications.[18,19] Since SAPO-5 has proved to be a good catalyst for the cumene reaction,[20] it was felt necessary to investigate further this potential catalyst for the transalkylation of DIPB with benzene to obtain higher cumene yields. Since commercial cumene column bottoms were chosen as feed, in this case too, platinum-loaded SAPO-5 was used for better catalyst stability. The effects of temperature, reactant mole ratio and weight hourly space velocity were studied and the kinetic parameters were estimated by employing power law kinetics. During the kinetic study, pure feed components with a *m*-diisopropyl and *p*-diisopropyl benzene ratio similar to that of commercial mixtures and a benzene to DIPB isomer mole ratio of 10:1 were chosen. Kinetics of the reaction were also studied over unmodified SAPO-5.

EXPERIMENTAL

Catalysts

The SAPO-5 molecular sieve was prepared following the procedure described by Lok *et al.*,[21] with 0.2 mol L^{-1} silica as the starting gel and characterized for its phase purity, crystallinity and morphology using X-ray diffraction (XRD) and scanning electron microscopy (SEM).[22] It was found to contain pure phases and to be highly crystalline, with a final composition of: Al, 0.505; P, 0.452; and Si, 0.032.

In a typical Pt loading procedure, say for a loading of 0.005% w/w Pt on SAPO-5, 1.885 mg of the platinum complex $[Pt(NH_3)_4Cl_2]$ was taken in 40 mL of water. 22 g of SAPO-5 was then added to this and heated with a little agitation until nearly all the water evaporated. The catalyst was then evacuated to expel moisture and dried at about 353 K. Thus prepared, Pt loaded catalyst was calcined in the reactor at 723 K in the presence of air for 6 h to expel ammonia. It was then reduced at 623 K in a stream of hydrogen for 3 h before the transalkylation reaction was conducted.

Procedure

The experiments were carried out in a fixed-bed glass reactor (15 mm i.d., 40 cm long) and the liquid products were collected from a condenser, downstream of the reactor. Hydrogen was used as a carrier gas during all the experiments with Pt-loaded catalysts. The condensed reactor effluent stream was analysed for its components in a Shimadzu 15A gas chromatograph unit (Kyoto, Japan) using a 'CP xylene' capillary column. The terms 'DIPB conversion' and 'cumene selectivity' used here are defined as follows:

$$\text{DIPB conversion (wt\%)} = \frac{\text{DIPB in feed} - \text{DIPB in products}}{\text{DIPB in feed}} \times 100$$

$$\text{Cumene selectivity (wt\%)} = \frac{\text{Cumene in the product mixture}}{\text{Aromatics in products}} \times 100$$

(*excluding benzene and DIPBs*)

RESULTS AND DISCUSSION

Effect of feed quality and platinum loading on product yields

Table 1 shows the product yields of the DIPB transalkylation reaction using pure components in the feed and also using commercial cumene column bottoms over SAPO-5 catalyst. The DIPB conversion and cumene yield are lower over SAPO-5 using this commercial feed mixture, as seen from the table, as compared to the conversion over Pt-loaded SAPO-5. To increase the DIPB conversion and cumene selectivity, the SAPO-5 was loaded with 0.005% platinum and subsequently the DIPB conversion and cumene yield increased. Taking pure feed mixture with no impurities, it is seen that the conversion of DIPB has increased from 79.2% with commercial feed to 83.8% over the same unmodified SAPO-5. The DIPB conversion further increased to 93.1% over 0.005% w/w Pt-loaded SAPO-5. However, considerable amounts of *n*-propylbenzene (*n*-PB) and C_8, C_{10} aromatics are also formed, as seen in the product Table 1. This may be due to the increase in the rate of side reactions such as cumene isomerization, xylene and C_8 aromatics formation over the highly active metal-loaded SAPO-5. But this low cumene selectivity was only observed in the initial 2–3 h, after which the cumene selectivity also increased and the yield of cumene remained high. This is probably because the highly active metal-loaded sites deactivate slightly with time, rendering the catalyst active enough to give high cumene selectivity. The platinum-loaded SAPO-5 was chosen for further activity tests with commercial feed mixture.

Catalyst stability

Both SAPO-5 and platinum loaded SAPO-5 were tested for stable activity during a 6 h time-on-stream run and the variation of cumene yield and selectivity with time are shown in Fig. 1. It is evident from the figure that the cumene yield remained high over the platinum-loaded SAPO-5. The unmodified SAPO-5 deactivated rapidly when commercial feed mixture was used. The impurities present in the commercial feed accelerated the formation of coke precursors, thus leading to deactivation by coking. The cumene selectivity remained high and increased with time on stream when the feed was pure and free from impurities, although the yield of cumene decreased considerably. This stability test further confirmed the advantage of using the Pt-modified SAPO-5 (Pt-SAPO-5) for transalkylating commercial feed stocks such as the bottom fraction of cumene column.

Effect of temperature on transalkylation activity of Pt-SAPO-5

Table 2 shows the product yields at three temperatures chosen for testing the effect of temperature on the transalkylation of DIPB with benzene. The cumene yield increases from 18.6% at 498 K to 20.3% at 548 K. However, the cumene selectivity decreased from 96.8% to 94.9% in the same temperature range. In this temperature range, *n*-PB, C_8 and C_{10} aromatics increase with increase in temperature, leading to decreased cumene selectivity. It is seen that the aliphatics in the products also increased

Table 1. Effect of feed quality and platinum loading on product yields over SAPO-5 catalyst

Catalyst	Commercial feed composition	0.0005% Pt SAPO-5	SAPO-5	SAPO-5
Feed type[b]		Commercial	Commercial	Pure
Product yields (wt%)				
Aliphatics	0.67	1.2	1.0	0.8
Benzene	82.90	75.5	76.1	74.9
Toluene	0.14	0.5	0.2	0.3
C_8	bd[a]	0.8	0.1	0.5
Cumene	bd[a]	19.6	19.0	20.3
n-PB	bd[a]	0.9	0.1	0.4
C_{10}	0.09	0.3	0.1	0.3
1,3-DIPB	12.72	0.8	2.3	1.9
1,2-DIPB	bd[a]	bd[a]	bd[a]	bd[a]
1,4-DIPB	2.95	0.3	0.9	0.7
Higher	0.53	0.1	0.1	<0.1
DIPB conversion (%)		93.1	79.2	83.8

[a] Below detectable limits.

[b] Commercial feed composition .

Conditions: temperature = 523 K; WHSV = 3 h^{-1}; benzene/DIPB mole ratio = 10:1.

with temperature, which become responsible for faster deactivation of the catalyst by coking.

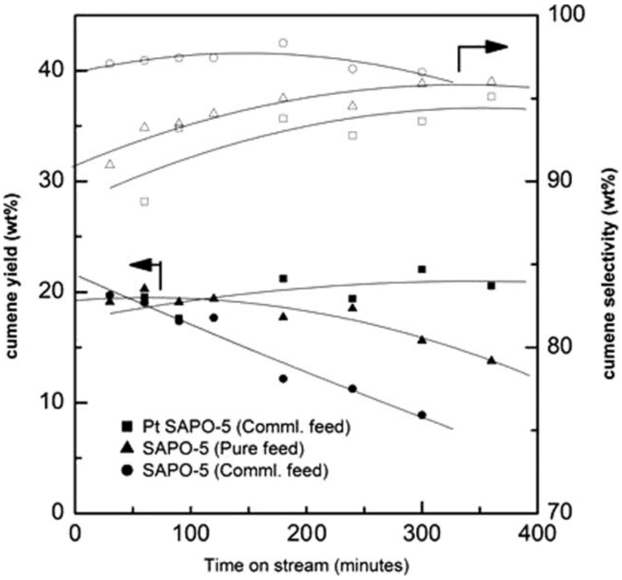

Figure 1. Effect of Pt and feed quality on transalkylation over SAPO-5.

Table 2. Effect of temperature in transalkylation of DIPB over Pt-SAPO-5

	Temperature (K)		
Product yields (wt%)	498	523	548
Aliphatics	0.9	1.0	1.0
Benzene	74.4	76.2	75.8
Toluene	0.3	0.2	0.2
C_8	<0.1	0.2	0.3
Cumene	18.6	19.7	20.3
n-PB	<0.1	0.1	0.3
C_{10}	0.1	<0.1	0.2
1,3-DIPB	4.0	1.7	1.2
1,2-DIPB	bd[a]	bd[a]	bd[a]
1,4-DIPB	1.4	0.8	0.6
Higher	0.1	0.1	0.1
Cumene selectivity (wt%)	96.8	96.9	94.9
DIPB conversion (%)	65.0	84.1	88.3

[a] Below detectable limits.

Conditions: WHSV = 3 h^{-1}; benzene/DIPB feed mole ratio = 10:1.

Effect of benzene to DIPB mole ratio on product yield

The feed mole ratio of benzene to DIPB was varied from 10:1 to 6:1 and the product yield for these reactant ratios is summarized in Table 3. Cumene yield was found to be high at a ratio of 8:1 and, in general, increased with increase in DIPB concentration in the feed. However, the cumene selectivity decreased with this increase in DIPB in the feed since the increased DIPB also contributes to the formation of undesirable C_8, C_{10} and polysubstituted aromatics along with cumene. Some of the feed impurities are due to DIPB, which are exhibited in the Table. Hence, higher benzene to DIPB mole ratio is desirable for better cumene selectivity.

Table 3. Effect of benzene/DIPB mole ratio on product yield over Pt-SAPO-5

	Benzene/DIPB mole ratio		
Product yields (wt%)	10	8	6
Aliphatics	1.0	1.0	1.0
Benzene	76.2	70.8	66.9
Toluene	0.2	0.1	0.1
C_8	0.2	0.2	0.1
Cumene	19.7	22.3	21.6
n-PB	0.1	0.2	0.1
C_{10}	0.1	0.2	0.2
1,3-DIPB	1.7	3.7	7.0
1,2-DIPB	bd[a]	bd[a]	bd[a]
1,4-DIPB	0.8	1.5	2.3
Higher	0.1	0.2	0.5
Cumene selectivity (wt%)	96.9	96.4	95.7

[a] Below detectable limits.

Conditions: temperature = 523 K; WHSV = 3 h^{-1}.

Effect of WHSV on product yield and cumene selectivities

The cumene yield and selectivity as well as the yields of other products at three different space velocities are shown in Table 4. The yield of cumene evidently decreased from 19.7% at a feed space velocity of 3 h^{-1} to a mere 9.7% for a space velocity of 9.6 h^{-1}. This is due to the decreased residence time in the reactor at higher feed velocities. The cumene selectivity, however, shows a marginal increase with increased space velocity due to suppression of the side reactions.

Mass transfer considerations

The external and internal mass transfer resistance-free region is to be determined first for any kinetic study. In order to determine the external diffusional effects, experiments were carried out with constant space time (W/F_{DIPBO}) and catalyst size, but with varying feed rates. The results are shown in Table 5, which

Table 4. Effect of WHSV on cumene yield and selectivity over Pt -SAPO-5

	WHSV (h^{-1})		
Product yields (wt%)	3	6	9.6
Aliphatics	1.0	1.0	0.9
Benzene	76.2	77.5	79.5
Toluene	0.2	0.1	0.1
C_8	0.2	<0.1	<0.1
Cumene	19.7	15.1	9.7
n-PB	0.1	0.1	<0.1
C_{10}	0.1	0.1	0.1
1,3-DIPB	1.7	4.5	7.6
1,2-DIPB	bd[a]	bd[a]	bd[a]
1,4-DIPB	0.8	1.3	2.0
Higher	0.1	0.2	bd[a]
Cumene selectivity (wt%)	96.9	96.2	97.5

[a] Below detectable limits.

Conditions: temperature = 523 K; benzene/DIPB feed mole ratio = 10:1.

Table 5. Effect of external mass transfer resistance on conversion of DIPB over SAPO-5

	$X_{(\mathrm{DIPB})}$, fractional conversion of DIPB	
W/F_{Ao} (kg h kgmol^{-1})	b	c
87	0.04	0.04
98	0.04	0.04
112	0.10	0.10
131	0.10	0.10
157	0.11	0.11

Conditions: temperature = 478 K; benzene to DIPB mole ratio = 10:1; catalyst size = 0.42 mm; b, with 0.002 kg catalyst; c, with 0.004 kg catalyst.

Table 6. Effect of intraparticle diffusion on conversion of DIPB

Particle size (mm)	Fractional conversion of DIPB with W/F_{Ao} (kg h kgmol^{-1})		
	87	112	157
0.42	0.04	0.10	0.11
1.50	0.04	0.10	0.11

Conditions: temperature = 478 K; benzene to DIPB mole ratio = 10:1.

indicates the absence of external diffusional resistance in the liquid feed range studied. Also, experiments were conducted to test the intraparticle diffusional limitations by varying the catalyst particle size, keeping the space time constant. The experimental data obtained are presented in Table 6. The results showed that there was no change in DIPB conversion with catalyst size, indicating negligible intraparticle mass transfer resistance in the particle size range studied. The particle sizes employed in the kinetic study fall within the intraparticle diffusion free range.

Kinetic modelling

Kinetic data were collected at three different temperatures, 478 K, 498 K, 523 K, respectively, at atmospheric pressure. At each temperature, the space time, W/F_{DIPBO}, was varied by changing the liquid feed rate. In all these runs, the mole ratio of benzene to diisopropyl alcohol was kept at 10, whereas the ratio of liquid hydrocarbon feed to carrier gas nitrogen was maintained at 0.5. Within experimental error, the balance of the aromatic ring was always 100%. The variation of DIPB conversion with W/F_{DIPBO} shows that the diisopropyl alcohol conversion increases with space time at all the three temperatures.

In accordance with product yields, the system can be described by the following reactions:

Main reaction:

$$\text{DIPB} + \text{benzene} \longrightarrow 2\ \text{cumene}$$

Secondary reactions:

$$p\text{-DIPB} \longrightarrow m\text{-DIPB (isomerization)}$$

$$\text{DIPB} \longrightarrow \text{benzene} + 2\ \text{propylene (dealkylation)}$$

$$\text{propylene} \longrightarrow \text{aliphatics (oligomerization)}$$

$$\text{benzene} + \text{aliphatics} \longrightarrow \text{alkylbenzenes (benzene alkylation)}$$

$$\text{DIPB} + \text{aliphatics} \longrightarrow \text{Higher aromatics}$$

The main reaction and the isomerization reaction together were chosen for development of a kinetic model. Since yields of the other products were significantly low, the other secondary reactions were not considered.

In the kinetic model developed here, DIPB alkylation to cumene has been considered to be an irreversible first-order reaction due to the higher benzene/DIPB ratio and lower concentration of *p*-DIPB, as can be seen in Table 4 at various space times.

Both homogeneous and heterogeneous models were developed and tested. In the homogeneous model the DIPB isomers were lumped. However, lumping was avoided in the heterogeneous model since there were pore diffusional constraints for the *m*-DIPB (8.4 ´Å kinetic diameter) molecule in the 7.3 ´Å pores of SAPO-5 compared to the *p*-DIPB molecules (7.3 ´Å kinetic diameter).

Homogeneous model

To determine the reaction rate parameters for the conversion of DIPB, a differential plug flow reactor was assumed. The first-order rate equation for a differential plug flow reactor for DIPB is written as follows:

$$-r_{\mathrm{DIPB}} = \frac{\mathrm{d}X_{\mathrm{DIPB}}}{\mathrm{d}\tau} = \frac{\mathrm{d}X_{\mathrm{DIPB}}}{\mathrm{d}(W/F_{\mathrm{DIPBO}})} = kC_{\mathrm{DIPB}} \quad (1)$$

where W is the weight of the catalyst (kg), F_{DIPBO} is the feed flow rate (kgmol h^{-1}), X_{DIPB} is the fractional conversion of DIPB, τ is the space time (kg h kgmol^{-1}), k is the rate constant and C_{DIPB} is the concentration of DIPB (kgmol m^{-3}).

Integration of Eqn (1) yields

$$-\ln(1 - X_{\mathrm{DIPB}}) = kC_{\mathrm{DIPBO}}\left(\frac{W}{F_{\mathrm{DIPBO}}}\right) \quad (2)$$

A plot of $-\ln(1 - X_{\mathrm{DIPB}})$ *versus* W/F_{DIPBO} over SAPO-5 gave a straight line passing through the origin, as illustrated in Fig. 2 at various temperatures.

The rate of DIPB conversion is therefore first order with respect to DIPB, which is the limiting reactant, and is of zero order with respect to benzene, which is in large excess.

From Fig. 2, the rate constant (k) was calculated to be 0.91 m^3 (kg h)$^{-1}$ at 478 K with C_{DIPBO} of 7.7×10^{-4} kgmol m^{-3}; with C_{DIPBO} of 7.4×10^{-4} kgmol m^{-3} the rate constant (k) was 2.3 m^3 (kg h)$^{-1}$ at 498 K and with C_{DIPBO} of

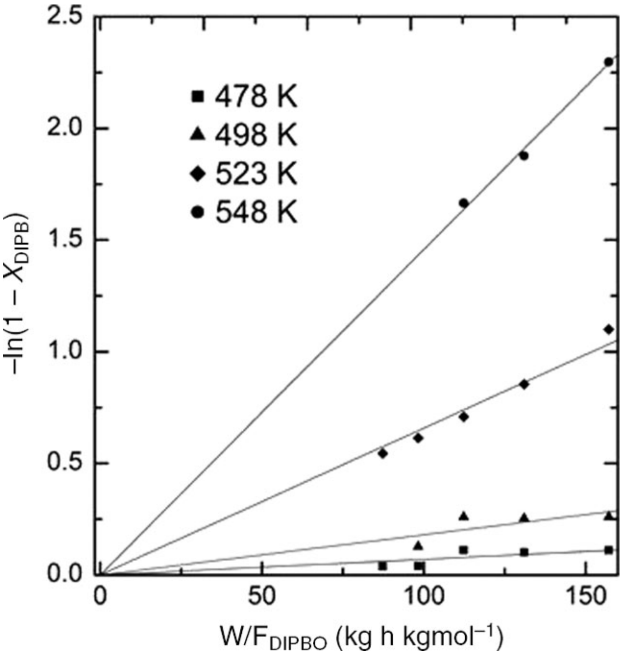

Figure 2. First-order plot for DIPB conversion over SAPO-5.

7.1×10^{-4} kgmol m^{-3}, the rate constant (k) was $9.3\,\mathrm{m^3\,(kg\,h)^{-1}}$ at 523 K. Employing power law kinetics and differential plug flow analysis, the rate of the reaction in the Arrhenius form can be expressed in terms of initial concentration and fractional conversion of DIPB as follows:

$$\ln\left(\frac{X_{\mathrm{DIPB}}}{1 - X_{\mathrm{DIPB}}}\right) = \ln A_{\mathrm{O}} - \frac{E_{\mathrm{a}}}{RT} \tag{3}$$

where A_{o} is the apparent Arrhenius frequency factor, which includes a constant such as W/F_{DIPBO} as well as C_{DIPBO} (initial concentration of DIPB), and E_{a} is the apparent activation energy. From Eqn (3) it is clear that a plot of $\ln(X_{\mathrm{DIPB}}/1 - X_{\mathrm{DIPB}})$ against $1/T$ (Fig. 3) would give a straight line from which E_{a} and A_{o} can be obtained.

The value of E_{a} from Fig. 3 is 130.2 kJ mol^{-1} and A_{o} is 1.1×10^{13}. The apparent activation energy obtained is comparable to the activation energies reported by earlier workers for transalkylation reactions over large-pore zeolites. Corma *et al.*[9] reported apparent activation energies varying from 95.5 to 119.4 kJ mol^{-1} for transalkylation of *m*-xylene over a series of dealuminated HY in the temperature range 513–593 K. Forni *et al.*[23] reported activation energy values varying from 46 to 104.6 kJ mol^{-1} in the temperature range 483–543 K for the transalkylation of *m*-diethylbenzene over beta zeolite. The higher activation energy value in this present work further checks that the kinetic data falls in the range where diffusional effects are not rate limiting.

LHHW Model

Three different models – Langmuir–Hinshelwood–Hougen–Watson (LHHW), Eley–Rideal and bimolecular models – were tried on similar and different sites; two of them were discarded because they led to negative values of kinetic parameters. The rate expression derived from the dual-site mechanism for surface reaction as a rate-controlling step is

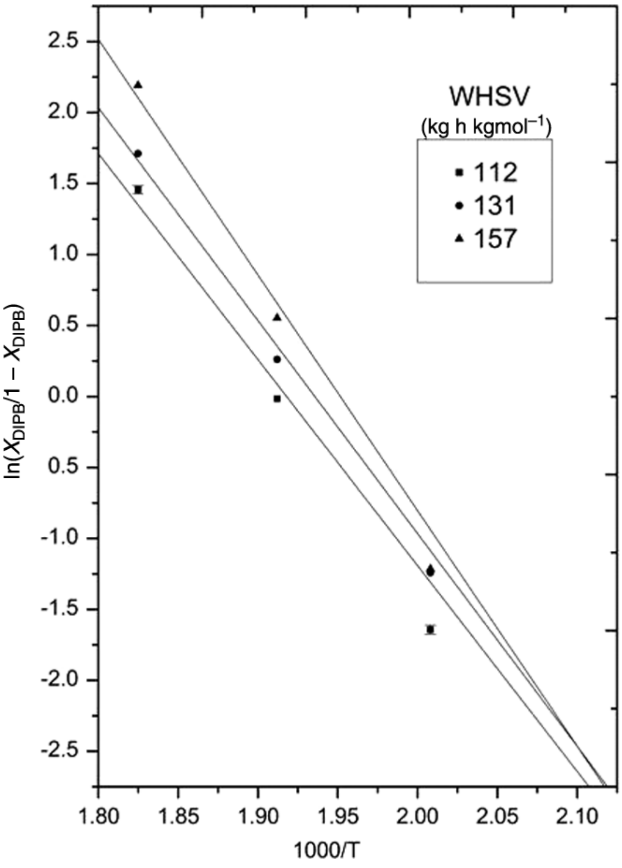

Figure 3. Arrhenius plots at various space velocities over SAPO-5.

$$\mathrm{Rate} = \frac{C_{\mathrm{T}} k_3 K_{\mathrm{p-DIPB}} K_{\mathrm{B}} \left(p_{\mathrm{p-DIPB}} p_{\mathrm{B}} - \dfrac{p_{\mathrm{C}}^2}{K_{\mathrm{eq}}}\right)}{(1 + K_{\mathrm{p-DIPB}} p_{\mathrm{p-DIPB}} + K_{\mathrm{B}} p_{\mathrm{B}} + K_{\mathrm{C}} p_{\mathrm{C}})^2} \tag{4}$$

where K_{A}, K_{B}, K_{C} are the adsorption equilibrium constants, and K_{eq} is the overall reaction equilibrium constant. C_{T} represents the total active sites.

Since the adsorption of cumene on active sites is very weak compared to benzene and DIPB, the final surface reaction model can be written as follows:

$$\mathrm{Rate} = \frac{C_{\mathrm{T}} k_3 K_{\mathrm{p-DIPB}} K_{\mathrm{B}} \left(p_{\mathrm{p-DIPB}} p_{\mathrm{B}}\right)}{\left(1 + K_{\mathrm{p-DIPB}} p_{\mathrm{p-DIPB}} + K_{\mathrm{B}} p_{\mathrm{B}}\right)^2} \tag{5}$$

The partial pressures in the above equations are related to fractional conversions and total pressure P as given by the following expressions. The fractional conversions are related to the amounts of different products present at a DIPB conversion of X_{DIPB}. Initially, 1 mol of DIPB was taken as the basis. The total moles computed by stoichiometry from the chemical equations given above sum to 33. Hence:

$$p_{\mathrm{DIPB}} = (1 - X_{\mathrm{DIPB}})P/33 \tag{6.1}$$

$$p_{\mathrm{B}} = (10 - X_{\mathrm{B}})P/33 \tag{6.2}$$

$$p_{\mathrm{C}} = (X_{\mathrm{C}})P/33 \tag{6.3}$$

The kinetic constants were estimated at three temperatures by a nonlinear regression toolbox in Matlab 7.0 and presented in Table 7. The optimum values of various constants were estimated by minimizing the objective function that reads:

$$\phi = \sum_{i=1}^{n} [(r_{\text{pred}})_i - 9r_{\text{exp}})_i]^2 \qquad (7)$$

where r_{pred} is the predicted rate from the LHHW model, r_{exp} is the experimentally observed reaction rate, and n is the number of observations.

By using the numerical values obtained from the model Eqn (5) shown in Table 7, a plot (Fig. 4) of experimental *versus* predicted conversion was drawn. Similarly, for the predicted data the standard error estimate for rate of disappearance of DIPB was $\pm 3.3 \times 10^{-6}$. From Fig. 4 and the error estimates, it seems that the model fits the data mathematically well. The model is checked for thermodynamic and kinetic constants (Fig. 5, Table 8) using the Mears–Vannice criteria.[24]

To check the Mears-Vannice criteria, enthalpy and entropy of adsorption were calculated using relation

$$K = e^{\left(\Delta S/R\right)} e^{\left(-H^\circ/RT\right)}$$

Table 7. Kinetic and adsorption coefficients

Temperature	K_{DIPB} (Pa^{-1})	K_{B} (Pa^{-1})	$K_3.C_{\text{T}}$ (kgmol (kg h)$^{-1}$)
476	0.04	18.8	21.1
498	0.04	16.5	40.7
523	0.03	12.7	94.4

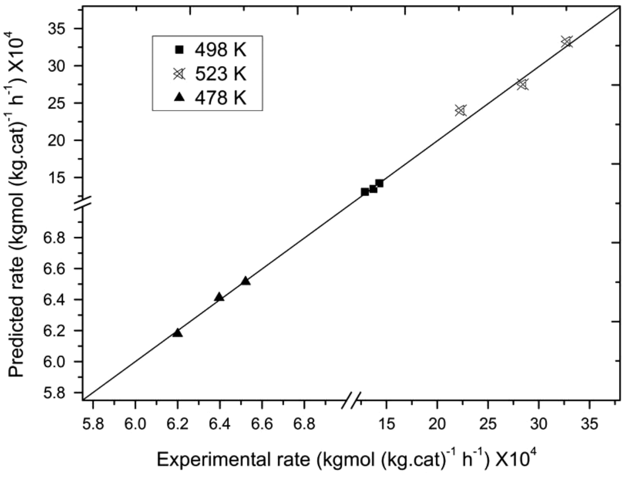

Figure 4. Predicted rate *versus* experimental rate of DIPB to cumene.

Table 8. Thermodynamic adsorption parameters for benzene and DIPB

	$\Delta H^\circ_{\text{ad}}$ (kJ mol^{-1})	$\Delta S^\circ_{\text{ad}}$ (J mol^{-1} K^{-1})	$\Delta S^\circ_{\text{g}}$ (J mol^{-1} K^{-1})
DIPB	−11.7	−11.8	269.3
Benzene	−1.3	−32.8	510.4

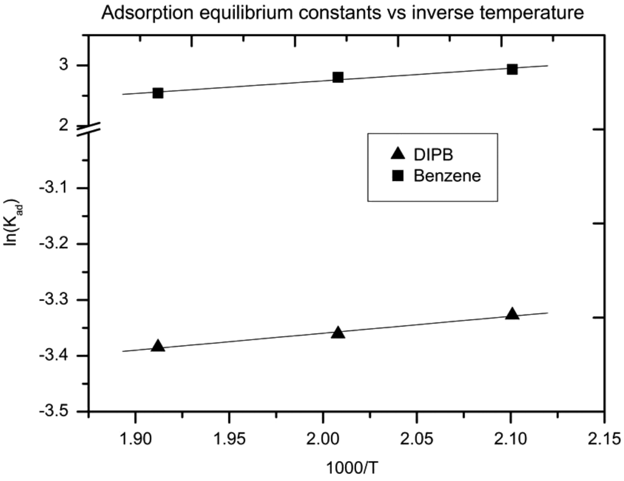

Figure 5. Arrhenius plots for adsorption equilibrium constants.

$$\ln(K) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S}{R}$$

Calculated heat of enthalpy and entropy change are reported in Table 8 and check the criteria satisfactorily. The adsorption equilibrium constants are plotted in Fig. 5, which also show a satisfactory trend.

CONCLUSIONS

Transalkylation of DIPB with benzene was carried out over SAPO-5 and Pt-SAPO-5 catalysts. SAPO-5 was found to show good activity and stability when loaded with a very small quantity of platinum (0.005% w/w) in the transalkylation of commercial DIPB (cumene column bottoms) with benzene. Higher reactant ratios and higher space velocities were found to give better cumene selectivity. The apparent activation energy obtained agrees well with those reported by other workers for similar reactions on large pore zeolites. LHHW dual site mechanism predicts the reaction mechanism satisfactorily with a standard error estimate of $\pm 3.3 \times 10^{-6}$ for the rate of disappearance of DIPB.

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