

Kinetics of propylation of benzene over H-beta and SAPO-5 catalysts: a comparison

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Abstract

A comparative study of the reaction kinetics involving the vapour phase isopropylation of benzene with *iso*-propanol over H-beta and SAPO-5 catalysts is taken up to evaluate the performance of these two potential catalysts for the industrially important cumene synthesis. Their activity is compared in the temperature range 378–513 K. A lab scale fixed bed flow reactor was used at atmospheric pressure for the experiments. Power law equation assuming pseudo first-order kinetics for *iso*-propanol conversion fit the data reasonably well. Kinetic parameters such as activation energy (E_a) and Arrhenius frequency factor ($\ln A_0$) for the disappearance of *iso*-propanol over a series of SAPO-5 molecular sieves with varying acidity and over zeolite beta have been evaluated at 383 K. The reaction rate on beta is higher than that of the most active SAPO-5 catalyst at the same temperature. The existence of the compensation effect between E_a and $\ln A_0$ has been tested over the SAPO-5 catalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Propylation of benzene to yield cumene is an industrially important reaction as cumene is the only starting material for the co-production of phenol and acetone. Recent statistics show a significant increase in cumene production capacity all over the world owing to the continued demand of phenol. The earlier Friedel–Crafts catalysts and solid phosphoric acid catalysts are rapidly being replaced by molecular sieve catalysts to avoid environmental and corrosion problems. High-silica zeolite molecular sieves

are expected to be potential catalysts on account of their thermal, hydrothermal, acid stabilities and good resistance to ageing and hydrophobicity. Several catalytic processes using ZSM-5, Y-type, mordenite [1] and H-beta have been reported recently for the production of cumene by alkylation of benzene with propylene. Among the various zeolitic systems investigated, zeolite beta and modified mordenite have been proved to be potential catalysts due to their high activity, selectivity and stability, both in liquid and vapour phase conditions [2–8]. Besides the above zeolites, silicon substituted alumino-phosphate (SAPO) molecular sieves are considered as interesting catalysts for various petro-chemical applications [9,10]. Alkylation activity of molecular sieve catalysts is determined by their Brønsted acidity. In addition to

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the concentration of these Brønsted acid sites, their strength also plays a key role in the selectivity of the products. In contrast to zeolites, SAPOs show mild acidity [11,12], though their acid strengths are substantially higher than that of the corresponding AlPO_4 materials. It was observed that formation of *n*-propylbenzene was minimal over large pore zeolites while it constitutes a higher fraction over medium pore zeolites. Here, we report a detailed study involving kinetics of *iso*-propanol conversion on beta as well as SAPO-5, both of which showed good stability [13]. The term ‘conversion’ used in the kinetic studies is defined as *iso*-propanol conversion (mol%) = (moles of *iso*-propanol consumed/moles fed per unit time) \times 100.

2. Experimental

The SAPO-5 molecular sieves were synthesised with 0.025, 0.05, 0.1 and 0.2 M silica in the starting gel and these were designated as SAPO-5/1, SAPO-5/2, SAPO-5/3 and SAPO-5/4, respectively. The as-synthesised SAPO-5 molecular sieves were characterised for their phase purity, crystallinity and morphology using XRD and SEM and found to be highly crystalline pure phases. Surface areas of calcined SAPO-5 samples were determined through nitrogen adsorption at 77 K using Omnisorb 100 CX (Coulter, USA). Total acidity of SAPO-5 catalysts was estimated through temperature programmed desorption of ammonia (TPDA), using an indigenously assembled apparatus. Extrudates of beta (80%, 1.5 mm) in its active ‘H’ form with Si/Al ratio of 15 were obtained from United Catalysts India Ltd.

All the experiments were conducted in a vertical flow fixed bed reactor (15 mm ID) with 2 g of catalyst using nitrogen as carrier gas. For the kinetic study, the

optimum feed mole ratio of *iso*-propanol to benzene was maintained at 1:8 and a feed flow rate of 6.8 g h^{-1} and above was maintained to eliminate external mass transfer effects.

The reaction products were analysed with a ‘Xylene Master’ capillary column on a SHIMADZU 15A Gas chromatograph unit. Quantification of various products was accomplished using response factors of typical standard mixtures.

3. Results and discussion

The chemical composition and surface areas of various SAPO-5 catalysts are given in Table 1. The amount of silicon incorporated into these frameworks follows the order SAPO-5/4 > SAPO-5/3 > SAPO-5/2 > SAPO-5/1. Total acidity, deduced from millimoles of ammonia desorbed in the 373–823 K temperature range, has increased with increasing amounts of silicon, showing that most of the silicon incorporation took place at the phosphorus site. Surface areas of these catalysts are on the expected lines and these values are higher for samples with high silicon content.

It is known that alkylation of benzene with various alcohols requires moderate to strong acidity. Due to the variation of silicon content, the catalysts are expected to have varying acidity which has a strong influence on their activity for benzene alkylation with *iso*-propanol. The acidity of the SAPO-5 catalysts is in the order, SAPO-5/4 > SAPO-5/3 > SAPO-5/2 > SAPO-5/1, while beta is expected to have stronger acidity than SAPO-5. The cumene yield has decreased in the same order of their acidities for the SAPO-5 series. The cumene yield and selectivities obtained with SAPO-5/4 is comparable to that on beta as shown in Table 2.

Table 1
Chemical composition and acidity of SAPO-5 samples

Sample	Chemical composition (mole fractions)			Surface area (m^2/g)	Acidity ^a (mmol g^{-1})
	AlO_2	PO_2	SiO_2		
SAPO-5/1	0.49	0.49	0.02	299	–
SAPO-5/2	0.48	0.49	0.03	313	0.399
SAPO-5/3	0.49	0.47	0.05	329	0.615
SAPO-5/4	0.49	0.45	0.06	340	0.626

^a Estimated from ammonia desorbed in the temperature range 373–823 K.

Table 2

Comparison of activities of H-beta and SAPO-5 (WHSV: 3.4 h⁻¹; benzene:IPA: 8:1 (mol))

	H-beta	H-beta	SAPO-5/4
Temperature (K)	513	483	513
Product yield (wt.%)			
Aliphatics	0.15	0.09	0.03
Benzene	81.20	80.68	80.56
Toluene	0.29	0.08	0.05
C ₈ aromatics	0.39	0.16	0.08
Cumene	16.54	17.37	17.97
NPB	0.42	0.09	0.12
C ₉ /C ₁₀ aromatics	0.09	1.11	bd ^a
1,3-DIPB	0.69	0.37	0.84
1,4-DIPB	0.23	0.04	0.36
Total DIPB	0.92	0.41	1.20
Cumene selectivity (wt.%)	88.71	90.37	92.53

^a Below detection limit.

The cumene yield as well as its selectivity over SAPO-5 are considerably high as compared to beta when their activities are compared at 513 K. In this reaction, other than alkylation (of benzene and cumene), undesired side reactions such as isomerisation, cracking and transalkylation of alkyl aromatics occurred to a considerable extent. It appears that strong acidity of beta promotes these undesirable reactions and as a result, the product contains high concentrations of C₉ and C₁₀ aromatics. This affected the selectivity of cumene on beta catalyst. Also, the yield of *n*-propylbenzene (NPB), an undesirable component in the products, was very high on beta while the di-isopropylbenzene (DIPB) yield was low. Thus, SAPO-5 appears to have certain advantages over beta.

When the activities of both the catalyst systems were compared at similar conversion levels, beta attained maximum theoretical conversion at 483 K while SAPO-5 needed a higher reaction temperature of 513 K. The NPB yield over beta was comparatively low at this (483 K) temperature but the cumene selectivity was higher on SAPO-5. The low cumene selectivity over beta even at this temperature may be attributed to the formation of C₉ and C₁₀ aromatics.

In order to have a better understanding, lower temperatures were chosen to study the kinetics of this reaction based on differential conversion of *iso*-propanol.

3.1. Kinetic study

To determine the reaction rate parameters for the disappearance of *iso*-propanol a differential plug flow reactor is assumed since the conversions of *iso*-propanol in the temperature range studied are below 30%. Hence, using the first-order rate equation for a differential plug flow reactor

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

where W is the weight of the catalyst in g, F_{AO} the feed *iso*-propanol flow rate in mol/h, τ the space time in g h g mol⁻¹, k the rate constant and C_A the concentration of *iso*-propanol in mol l⁻¹ and X_A the fractional conversion of *iso*-propanol. Integrating Eq. (1) yields

$$-\ln(1 - X_A) = k \left(\frac{W}{F_{AO}} \right) \quad (2)$$

The plots of $-\ln(1 - X_A)$ against W/F_{AO} over SAPO-5/4 and beta gave straight lines passing through the origin as illustrated in Figs. 1 and 2 at different temperatures. The plots show that the rate of *iso*-propanol conversion has a first-order dependence on both the catalysts with respect to *iso*-propanol which is the limiting reactant, while it is of zero-order with respect to benzene which is in large excess. From these plots, the reaction rate constant k evaluated

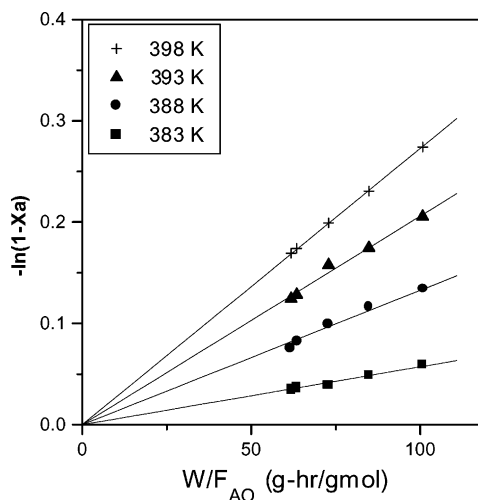


Fig. 1. Pseudo first-order kinetic plot for isopropylation of benzene over SAPO-5/4.

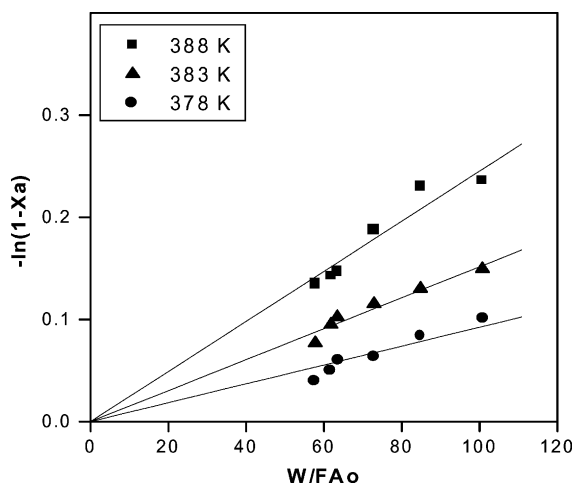


Fig. 2. Pseudo first-order kinetic plot over H-beta.

are $1.67 \times 10^{-4} \text{ mol s}^{-1} \text{ kg}^{-1}$ over SAPO-5/4 and $4.2 \times 10^{-4} \text{ mol s}^{-1} \text{ kg}^{-1}$ over beta at 383 K. A lower value of rate constant over SAPO-5/4 as compared to that over beta is on expected lines. Higher activation energy is required over SAPO-5/4 when compared to beta as the later has higher acidity. This is reflected in the apparent activation energy values over these two catalysts as shown in Table 3. Employing the power law equation from power law kinetics [14], the rate of the reaction for the present system would be

$$-r_A = kC_A = A \exp\left(-\frac{E_a}{RT}\right) C_A \quad (3)$$

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

$$\left(\frac{F_{AO}}{W}\right) X_A = A \exp\left(-\frac{E_a}{RT}\right) C_A \quad (4)$$

Table 3
Kinetic parameters for various catalysts

Catalyst	Kinetic parameter		Exp. rate at 393 K, r_a ($\text{mol s}^{-1} \text{ kg}^{-1}$)
	E_a (kJ mol^{-1})	$\ln A_0$	
H-beta	119.1 ± 0.7	35.6	7.1×10^{-4}
SAPO-5/4	135.6 ± 2.6	40.1	5.10×10^{-4}
SAPO-5/3	73.1 ± 0.9	19.9	2.00×10^{-4}
SAPO-5/2	42.0 ± 2.7	9.9	1.27×10^{-4}
SAPO-5/1	41.2 ± 2.5	9.6	1.21×10^{-4}

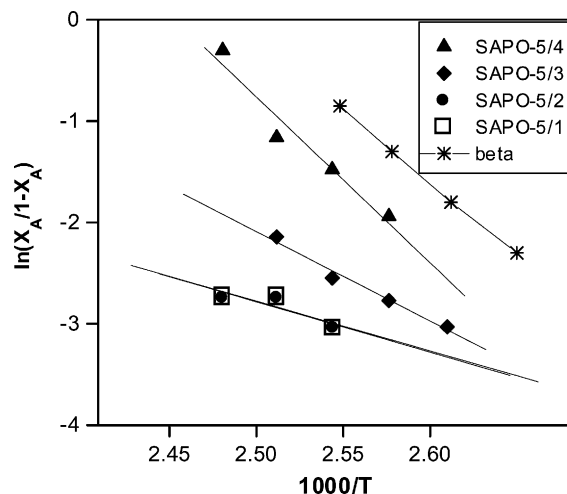


Fig. 3. Arrhenius plots.

writing the C_A in terms of initial concentration and fractional conversion of *iso*-propanol and rearranging the equation, we obtain

$$\ln\left(\frac{X_A}{1-X_A}\right) = \ln A_0 - \frac{E_a}{RT} \quad (5)$$

where $\ln A_0$ is the apparent Arrhenius frequency factor which includes a constant such as W/F_{AO} as well as C_{AO} (initial concentration of *iso*-propanol) and E_a the apparent activation energy. From Eq. (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 $\ln A_0$ can be obtained.

The representative Arrhenius plots for the *iso*-propanol conversion employing Eq. (5) are shown in Fig. 3. The values of E_a and $\ln A_0$ derived from these plots are presented in Table 3. The apparent activation energies vary in the same range as reported by earlier workers for *iso*-propanol conversion on large pore molecular sieves [14–18]. SAPO-5/4 which was found to be the most active catalyst of the SAPO-5 series showed the highest activation energy $135.9 \text{ kJ mol}^{-1}$ which is higher than that obtained over beta ($119.1 \text{ kJ mol}^{-1}$). This is expected since beta having higher acidity than SAPO-5 needs lower activation energy and catalyses the reaction faster at the same temperature.

However, the temperature behaviour of the kinetic constants for the SAPO-5 series has revealed a few

surprises. A quick look at Table 3 indicates that even though the apparent activation energies are increasing from SAPO-5/1 to SAPO-5/4, the rates of reaction also show an increasing trend. Although this is unusual, it is not unheard of, in literature. It means, entropy factors are important and it is best to interpret these results in terms of the theory of absolute reaction rates and a quasi-thermodynamic interpretation [19].

The expression for rate constant is within the format of the theory of absolute reaction rates.

$$k = e^2 \left(\frac{kT}{h} \right) e^{\Delta S^*/R} e^{-E_a/RT} \quad (6)$$

$$E_a = \Delta H^* + 2RT \quad (\text{for bimolecular reaction}) \quad (7)$$

where ΔS^* and ΔH^* represent the net entropy and enthalpy of activation.

Now, with an increase in enthalpy of activation if the entropy also increases, then the entropy factors outweigh the enthalpy increase and drive the reaction in the forward direction. Hence, the rates of the reaction show an increasing trend from SAPO-5/1 to SAPO-5/4 despite the increase in the apparent activation energies.

It has been shown by several authors that a good correlation exists between E_a and $\ln A$ for a single reaction taking place over a series of identical catalysts or different reactions taking place over the same

catalyst [20–23]. Such a correlation is represented as ‘compensation effect’ in the literature [23,24] and can be written as

$$E_a = a + b \ln A_0 \quad (8)$$

where a and b are constants called compensation parameters. One of the consequences of the compensation effect is that isokinetic temperature is displayed for a group of catalysts. Irrespective of the enthalpy and entropy factors, their activities are the same at the isokinetic temperature. In other words, all the Arrhenius plots cross at the isokinetic temperature at which the rate constant will be the same for all the catalysts. In the present case, on extrapolation of the plots for the SAPO-5 catalysts, the isokinetic temperature is estimated to be 373 K. It is known that above the isokinetic temperature, the faster reaction has the higher activation energy [25], which is observed in this case since the kinetics are studied in the temperature range 378–398 K, i.e., above the isokinetic temperature. A plot of E_a vs. $\ln A_0$ for the SAPO-5 series gave a straight line as seen in Fig. 4 with a linear regression coefficient (R) equal to 0.993 indicating the existence of a good compensation effect. The values of a and b evaluated from this plot are 11.826 and 3.0594 kJ mol⁻¹, respectively.

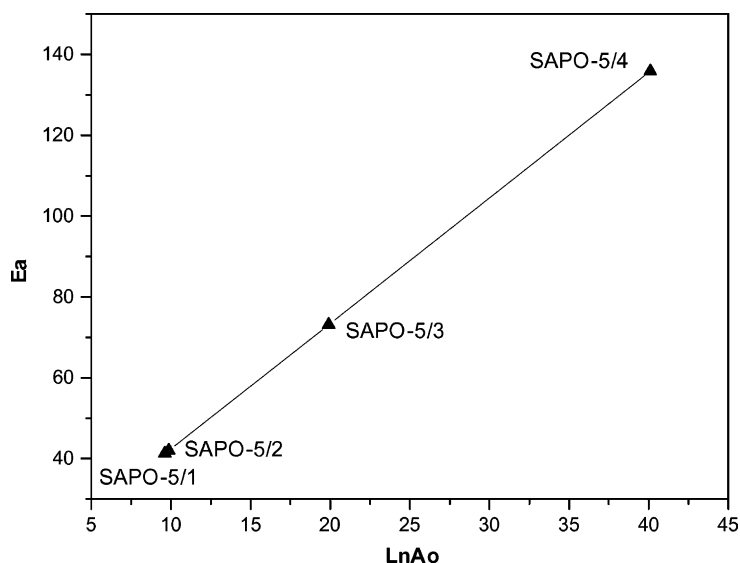


Fig. 4. Compensation effect for *iso*-propanol conversion over SAPO-5 catalysts.

4. Conclusions

H-beta seems to attain maximum theoretical conversion at about 30 K lower temperature than SAPO-5. However, cumene selectivity was found to be lower over beta as compared to SAPO-5 due to the formation of C₉ and C₁₀ aromatics. The activation energy over beta was lower than over SAPO-5 confirming these trends in conversion levels. The values of apparent activation energy E_a vary in the same range (40–135 kJ mol⁻¹) as reported by earlier workers for conversion of *iso*-propanol over large pore molecular sieves indicating the validity of the power law equation employed in the present study. Entropy factors are important in interpreting the rates of reaction on the series of SAPO-5 catalysts. The existence of a good compensation effect between E_a and $\ln A_0$ for the set of SAPO-5 molecular sieves was evident.

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