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Kinetics of batch alkylation of phenol with *tert*-butyl alcohol over a catalyst synthesized from coal fly ash

Keka Ojha, Narayan C. Pradhan*, Amar Nath Samanta

Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721302, India

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Abstract

Alkylation of phenol with *tert*-butyl alcohol (TBA) was carried out in batch mode over a zeolite catalyst, synthesized from fly ash by hydrothermal treatment. The effects of various parameters, such as reaction temperature, reactant ratio (molar ratio of phenol to *tert*-butyl alcohol) and catalyst loading on the rate of reaction of phenol were studied with the synthesized catalyst. The alkylation reaction was found to be surface reaction controlled with negligible mass transfer resistance. An Langmuir–Hinshelwood–Hougen–Watson (L–H–H–W) surface reaction controlled kinetic model was developed and the model parameters were estimated. From the estimated kinetic constant at different temperatures, the activation energy of the phenol alkylation reaction was determined to be 37.3 kJ/mol.

Keywords: Phenol; *tert*-Butyl alcohol; Alkylation; Fly ash; Zeolite X; Kinetics

1. Introduction

The alkylation reaction of phenol with *tert*-butyl alcohol gives *p*-*tert*-butyl phenol (*p*-TBP) as the major product. This *p*-TBP is used as a raw material for the production of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, anti-oxidants, fungicides and as petroleum additives. Studying this reaction is, therefore, of great commercial as well academic interests. Though both homogeneous and heterogeneous catalysts are used in alkylation reaction systems, the trend is definitely towards solid heterogeneous catalysts, especially zeolites due to their inherent advantages. The present work is concerned with the alkylation of phenol with *tert*-butyl alcohol (TBA) for producing *p*-*tert*-butyl phenol primarily, using a non-conventional heterogeneous catalyst, synthesized from fly ash.

In spite of industrial importance, literatures on butylation of phenol with alcohol over zeolite catalysts are very limited. Most of the alkylation of phenolic compounds with alcohol has been studied using zinc chloride, phosphoric acid, sulphuric acid, aluminium chloride and cation exchange resin [1] and a variety of super acid catalysts [2].

The reactions of phenol with olefins have been studied by many investigators [3–6] in the presence of cation exchange resins as the catalysts in the temperature range of 371–373 K. The synthesis of *p*-cumyl phenol (PCP) in the presence of cation exchange resin Amberlyst 15 has been reported by Zieborak et al. [7]. The reaction of phenol with a mixture of α-methyl styrene (AMS) and AMS dimer has been studied in the presence of active earth, polyphosphates and zeolites in the temperature range 333–513 K [8]. Chaudhuri and Sharma [9] have studied the alkylation of phenol with α-methyl styrene and several alkenes using both heterogeneous as well as homogeneous catalysts. The *ortho*/*para* product ratio was reported to vary considerably for different olefins, and also with variation of catalysts.

Methyl tertiary butyl ether (MTBE) has been used as the alkylating agent to produce *tert*-butyl phenol in the presence of Amberlyst 15 as catalyst [10,11]. Schulz et al. [12] have obtained a 95% yield of *p*-*tert*-butyl phenol on reacting 1 mol each of phenol and MTBE in the presence of 1 mol H_2SO_4 as catalyst. A higher selective method to obtain *p*-TBP has been reported by Sartori et al. [13] using $ZrCl_4$ as catalyst.

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* Corresponding author. Tel.: +91 3222 283940; fax: +91 3222 255303.
E-mail address: ncp@che.iitkgp.ernet.in (N.C. Pradhan).

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Nomenclature

A	*tert*-butyl alcohol
B	phenol
C	*p*-*tert*-butyl phenol
C_A	concentration of *tert*-butyl alcohol, kgmol/m^3
C_B	concentration of phenol, kgmol/m^3
C_C	concentration of *p*-*tert*-butyl phenol, kgmol/m^3
C_D	concentration of 2,4-di-*tert*-butyl phenol, kgmol/m^3
D	2,4-di-*tert*-butyl phenol
E_a	activation energy, kJ/mol
k_1	rate constant for reaction $R1$, kg/(kg mol h)
k_2	rate constant for reaction $R2$, kg/(kg mol h)
k_3	rate constant for reaction $R3$, h^{-1}
K_A, K_B, K_C, K_D	adsorption constants for A, B, C, and D, respectively, m^3/kg
r_B	rate of reaction of phenol, kgmol/(kg h)
t	time, h
TBA	*tert*-butyl alcohol
o-TBP	*o*-*tert*-butyl phenol
p-TBP	*p*-*tert*-butyl phenol
2,4-DTBP	2,4-di-*tert*-butyl phenol

Zhang et al. [14] have studied the reaction of phenol with *tert*-butyl alcohol over zeolite HY in a continuous flow reactor and reported a phenol conversion of 49% at 448 K under atmospheric pressure with gas hourly space velocity (GHSV) of 2000 h^{-1} and a molar ratio of *tert*-butyl alcohol to phenol of 1:2. Kijiya and Okazaki [15] have studied the effect of acidity of various catalysts (SiO_2-Al_2O_3, Al_2O_3 and zeolite X) on the *tert*-butylation of phenol in a continuous flow reactor under normal pressure at 455–523 K.

From the above discussion, it is evident that there is limited information on the reaction of phenol with TBA in the published literature. Moreover, there is no information in the published literature on the use of non-conventional catalysts, such as fly ash or zeolite from fly ash for this industrially important reaction.

Fly ash, a solid waste of thermal power plants, has posed great threat to the environment. As a result, attempts have been and are being made to reduce the environmental pollution caused by fly ash by converting it to environment friendly ones. Because of the presence of SiO_2 and Al_2O_3 in high proportions in fly ash, it is a very good starting material for preparing crystalline aluminosilicates or zeolites. Several methods have been reported in the literatures for the preparation of zeolites from fly ash [16–21]. The zeolite prepared from fly ash has also been successfully used in catalyzing cracking reactions of heavy oil residues [22]. The same zeolite with active acid sites could be efficient in catalyzing alkylation reactions as well. It was, therefore, thought desirable to study *tert*-butylation of phenol over zeolite prepared from fly ash and to compare its activity with commercially available NaX zeolite.

2. Experimental

2.1. Materials

The NaX zeolite used in the present study was obtained from SISCO Research Laboratories, Mumbai, India. Phenol was obtained from Qualigens (India) Ltd., Mumbai, India and *tert*-butyl alcohol from S.D. Fine Chemicals Pvt. Ltd., Boisar, India. The purity of all chemicals was >99%. The fly ash used in the present work was obtained from an electrostatic precipitator of Kolaghat Thermal Power Plant, West Bengal, India. The fly ash used in the present study was treated with 20% hydrochloric acid, calcined and then used in the reactor.

2.2. Synthesis of zeolite from fly ash

The fly ash was converted to zeolite by fusion with sodium hydroxide followed by hydrothermal treatment [23]. The zeolite was prepared by fusing NaOH and fly ash mixture in the ratio of 1:1.3. The resultant fused mixture was cooled to room temperature, mixed with water and then stirred for 18 h. The slurry was then kept at around 363 K for 6 h without any disturbance. The resultant precipitates were filtered, washed repeatedly with water and dried overnight at 383 K.

2.3. Characterization of prepared zeolite

Powder X-ray diffraction (XRD) pattern for the various samples were obtained using Co Kα radiation at 4 kV and 30 mA in a Philips BW1710 automated powder diffractometer. The diffraction patterns of the original fly ash and zeolite synthesized from fly ash (by hydrothermal treatment) were taken and compared with the XRD pattern of typical NaX zeolite. The formation of zeolite was thus confirmed from this comparison. Compositions of the samples under experiment were determined with the help of scanning electron microscope (Model: JEOL, JSM 5800), which were further verified by X-ray fluorescence (XRF) spectroscopy (Phillips PW 2400). The chemical compositions of fly ash, synthesized zeolite (ZOP-31) and commercial NaX zeolite are shown in Table 1. The BET surface areas of these catalysts are also reported in the same table.

2.4. Modification of the synthesized zeolite

The synthesized zeolite was modified by exchanging its Na^+ ions by H^+ (HZOP-31) as the H-form of the zeolite was found to be more active than the Na-form. For this freshly prepared zeolite was refluxed with 5% NH_4NO_3 solutions for 18 h in three steps, each with 6 h duration. In between two refluxes, the catalyst was filtered and calcined at 623 K for

Table 1
Chemical compositions and surface areas of various catalysts

Components	Fly ash	Compositions (wt%) of zeolite from fly ash	NaX zeolite
Na_2O	2.12	15.57	15.67
Al_2O_3	30.01	27.20	31.87
SiO_2	55.19	48.03	48.26
K_2O	1.40	0.77	0.07
CaO	0.77	1.47	0.37
TiO_2	2.74	2.12	0.08
Fe_2O_3	4.58	3.57	3.17
BaO	1.28	0.78	0.00
MgO	1.91	0.49	0.00
SO_3	0.0	0.00	0.51
Surface area (BET, m^2/g)	2.9	376	478

deammoniation to give H-form of the zeolite. X-ray diffraction pattern of the H-form of zeolite exactly matched with that of the parent zeolite, indicating no structural change during ion exchange.

2.5. Alkylation reaction and product analysis

All experiments were carried out in a 500 mL batch reactor (Parr Instrument Co., USA). For the experimental runs, the reactor was filled with reactants at a pre-determined molar ratio and fixed amount of catalyst and the temperature was set using the control panel while the cooling water was circulated through the coil. The reactants–catalyst mixture was continuously agitated with the help of a stirrer. The stirrer speed was varied within the range of 600–1000 rpm. The product samples were withdrawn at a regular interval of time.

Liquid samples withdrawn at different time intervals were then analyzed for product compositions. Analysis of the samples was done using a Gas Chromatograph (Chemito 8610), manufactured by Toshniwal Instruments (India) Ltd., with flame ionization detector and SE-30 column with nitrogen as the carrier gas.

3. Results and discussion

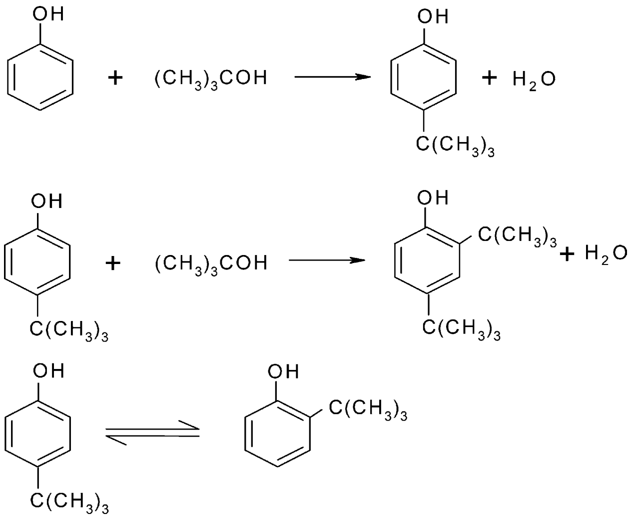
The reactions of phenol with *tert*-butyl alcohol were carried out in batch mode in a 500 mL reactor (PARR Instruments Co., USA). The effects of different parameters on conversion of phenol were studied. There was no change in the overall conversion of phenol when the speed of agitation was varied from 600 to 1000 rpm as shown in Table 2. Therefore, the reaction system was assumed to be free from external mass transfer resistance in the above range of speed of agitation.

Table 2
Effect of speed of agitation on phenol conversion

Speed of agitation (rev/min)	Phenol conversion (%) at a temperature (K) of		
	323	333	343
600	17.85	23.05	24.75
800	18.32	23.17	24.98
1000	18.50	23.43	25.12

Conditions: phenol/TBA mole ratio, 2:1; catalyst, zeolite from fly ash (HZOP-31); catalyst loading, 10% (w/w); batch time, 6 h.

In the alkylation of phenol with *tert*-butyl alcohol, *p*-*tert*-butyl phenol, *o*-*tert*-butyl phenol (*o*-TBP) and 2,4-di-*tert*-butyl phenol (2,4-DTBP) and *tert*-butyl ether (TBE) are generally isolated as reaction products. In the present study, the *p*-isomer (*p*-TBP) was isolated as major product with selectivity greater than 90%, followed by *o*-TBP and then 2,4-DTBP. The formation of TBE was not detected in the present study. Accordingly, the reaction scheme may be depicted as follows:



3.1. Comparison of catalytic activities of various catalysts

The phenol *tert*-butylation reactions were carried out with three catalysts, namely fly ash, zeolite from fly ash and commercial NaX zeolite and the phenol conversions obtained with these catalysts are presented in Fig. 1. The conversion of phenol using fly ash was found to be very low. Better conversion of phenol was obtained when it was converted to zeolite and used as catalyst. NaX zeolite was found to give low conversions of phenol when compared with zeolite obtained from fly ash. The activity of the synthesized catalyst from fly ash was also found to remain unaltered even after five-repeated batch of experiments. Further experiments were, therefore, carried out with this catalyst only.

3.2. Effect of phenol to tert-butyl alcohol mole ratio on phenol conversion

The alkylation of phenol was carried out by varying the mole ratio of phenol to *tert*-butyl alcohol from 0.5 to 4. It was observed that with increase in phenol/*tert*-butyl alcohol mole ratio, the conversion of phenol passed through a maximum. As can be seen from Fig. 2, the maximum conversion was

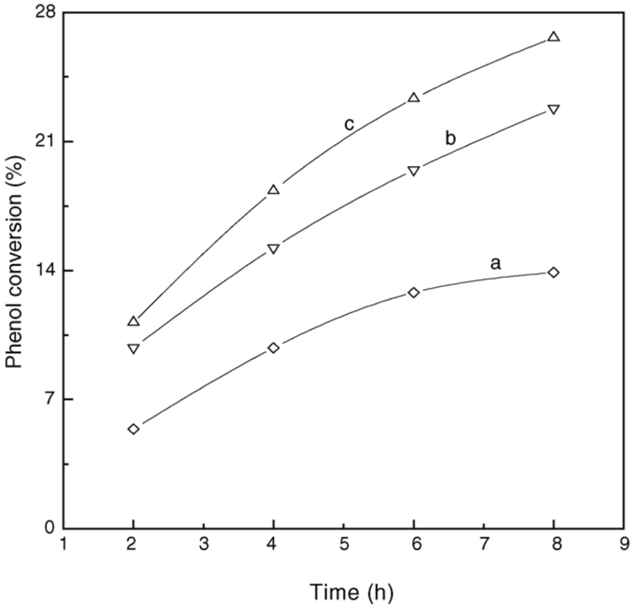


Fig. 1. Activity of various catalysts in the alkylation of phenol with *tert*-butyl alcohol. Conditions: temperature, 333 K; phenol to *tert*-butyl alcohol molar ratio, 2:1; speed of agitation, 800 rpm; catalyst loading, 10% (w/w). (a) Fly ash; (b) commercial NaX zeolite and (c) zeolite from fly ash (HZOP-31).

obtained at a phenol to TBA mole ratio of 2:1. The reason for this could be the more affinity of phenol to get adsorbed on the active sites compared to TBA at higher phenol/TBA ratios. During the course of reaction, carbenium ions are generated first on the active sites, which then react with phenol molecules adsorbed on the nearby sites. Initially with lower concentrations of phenol, sufficient active sites are left for the adsorption of TBA and the conversion of phenol increases with increase in concentration of phenol. After an optimum, the conversion decreases due to preferred adsorption of phenol on the active sites, which prevents adsorption of TBA and subsequent generation of active carbenium ions.

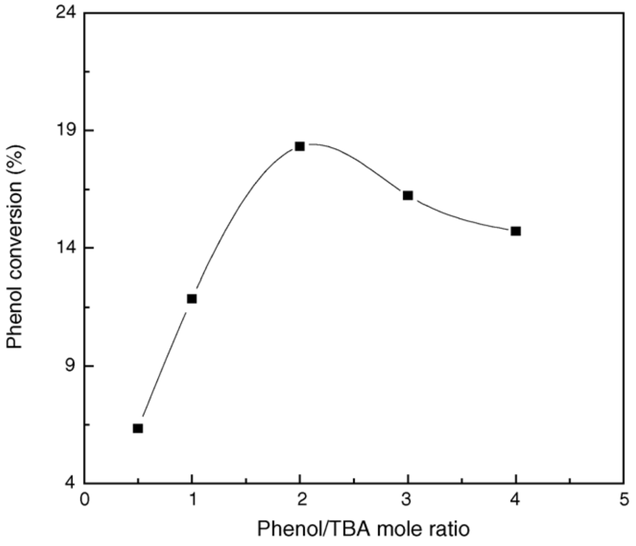


Fig. 2. Effect of phenol to TBA mole ratio on phenol conversion. Conditions: catalyst, HZOP-31; catalyst loading, 10% (w/w); temperature, 333 K; speed of agitation, 800 rpm; time, 4 h.

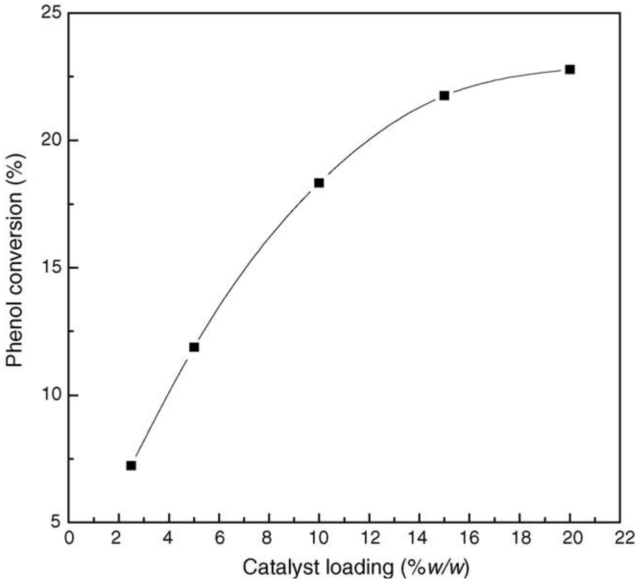


Fig. 3. Effect of catalyst loading on phenol conversion. Conditions: catalyst, HZOP-31; phenol to TBA molar ratio, 2:1; temperature, 333 K; speed of agitation, 800 rpm; reaction time, 4 h.

The para-selectivity was also found to increase with mole ratio. Increasing the phenol concentration of the reaction mixture decreases the formation of side products, other than *p*-TBP. Large excess of phenol (ratio more than 1) may, therefore, be used to minimize the formation of dialkylated products. As maximum phenol conversion was obtained at phenol:*tert*-butyl alcohol ratio of 2:1, all further experiments were carried out with this molar ratio only.

3.3. *Effect of catalyst loading on phenol conversion*

The effect of catalyst loading on the reaction was studied by varying it from 2.5 to 20% (w/w) of the reactants. It is evident from Fig. 3 that the conversion of phenol increases sharply with increase in the catalyst loading up to 10%. Beyond 10% catalyst loading, the rate of reaction was found to increase slowly.

3.4. *Effect of temperature on phenol conversion*

The effect of temperature on the conversion of phenol was studied in the temperature range of 313–343 K. To prevent excessive vaporization of TBA at the reaction condition, and thereby lowering in concentration in the reactive phase (liquid), the temperature of the reaction was not raised above 343 K (normal boiling point of TBA is 356 K). As can be seen from Fig. 4, the conversion of phenol increases with increase in temperature. It was also observed that the *p*-TBP selectivity increased as the temperature was raised from 313 to 343 K, decreasing the selectivity of other side products as shown in Table 3.

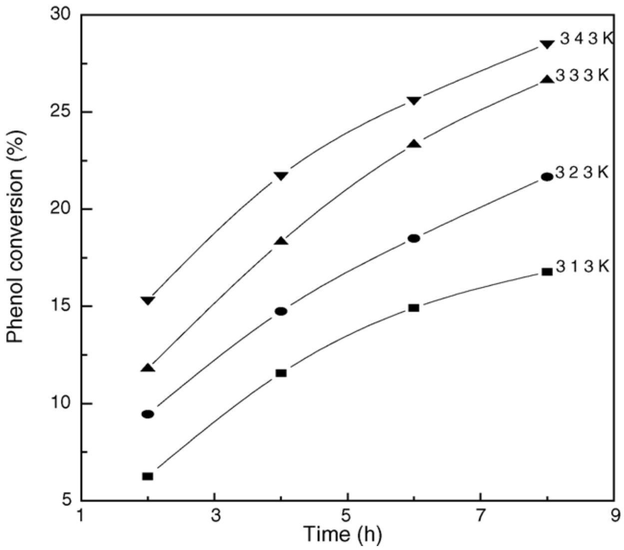


Fig. 4. Effect of temperature on phenol conversion. Conditions: catalyst, HZOP-31; phenol to TBA molar ratio, 2:1; catalyst loading, 10% (w/w); speed of agitation, 800 rpm.

3.5. *Kinetic modeling*

Kinetic runs were conducted at four different temperatures, from 313 to 343 K at 10° interval. At each temperature, the products samples were collected at a regular time interval. In all these runs, the phenol to TBA mole ratio was kept at 2.0 and the catalyst loading at 10% (w/w). The variation on phenol conversion with time is shown in Fig. 1 and the effect of temperature in Fig. 4. The *ortho*-isomer of *tert*-butyl phenol (*o*-TBP) was detected in very small amount compared to the *para*-isomer. This is probably due to relatively high strain between the two bulky groups in the ring at the *ortho* position. Also DTBP cracking has been excluded, since it is negligible at this lower temperature. At the lower conversion levels, the reactions were assumed to be irreversible, i.e. the equilibrium of these reactions has not been reached yet. Similar approach has been followed by other investigators also [24,25]. In accordance with the product distribution, the system can be described by the following reaction scheme:

Primary reaction:

Alkylation of phenol

$$\text{Phenol} + \text{TBA} \xrightarrow{k_1} p\text{-TBP} + \text{H}_2\text{O} \qquad \text{(R1)}$$

Table 3
Effect of temperature on product distribution

Component	Composition (mol %) at			
	313 K	323 K	333 K	343 K
o-TBP	4.85	4.15	3.02	2.64
p-TBP	90.52	92.41	94.35	95.75
2,4-DTBP	4.63	3.44	2.63	1.61

Conditions: phenol/TBA mole ratio, 2:1; catalyst, zeolite from fly ash (HZOP-31); catalyst loading, 10% (w/w); speed of agitation, 800 rpm; batch time, 6 h.

Undesired reactions:

Alkylation of TBP

$$\text{TBA} + p\text{-TBP} \xrightarrow{k_2} 2,4\text{-DTBP} + \text{H}_2\text{O} \qquad \text{(R2)}$$

Isomerization $$p\text{-TBP} \xrightarrow{k_3} o\text{-TBP} \qquad \text{(R3)}$$

For the rate of disappearance of phenol, different models from simple stoichiometric model to the Langmuir–Hinshelwood–Hougen–Watson (L–H–H–W) models with surface reaction controlling (single site and dual site mechanisms), adsorption controlling and desorption controlling were attempted to fit the experimental data. All the models except the surface reaction controlling one presented below gave negative constants, and hence were not reported here.

The following rate equation for dual site mechanism with all the components adsorbed on the catalyst surface was found to fit the experimental data reasonably well

$$r_{\text{B}} = -\frac{\text{d}C_{\text{B}}}{\text{d}t} = \frac{k_1 K_{\text{A}} K_{\text{B}} C_{\text{A}} C_{\text{B}}}{Z^2} \qquad (1)$$

where,

$$Z = 1 + K_{\text{A}}C_{\text{A}} + K_{\text{B}}C_{\text{B}} + K_{\text{C}}C_{\text{C}} + K_{\text{D}}C_{\text{D}}. \qquad (2)$$

Adsorption of water is neglected in the above model. Adsorption of the largest molecule, DTBP is also assumed to be much less, compared to the others, i.e.,

$$1 + K_{\text{A}}C_{\text{A}} + K_{\text{B}}C_{\text{B}} + K_{\text{C}}C_{\text{C}} \gg K_{\text{D}}C_{\text{D}}.$$

Hence,

$$Z = 1 + K_{\text{A}}C_{\text{A}} + K_{\text{B}}C_{\text{B}} + K_{\text{C}}C_{\text{C}} \qquad (3)$$

A non-linear regression algorithm [26] was used to estimate the adsorption parameters and kinetic constants at four temperatures. The parameters estimated from model Eq. (1) are summarized in Table 4. The optimum values of the parameters were estimated by minimizing the average absolute percentage error (AAR) as

$$\text{AAR} = \frac{\sum_{i=1}^{n}[(r_{\text{B,pred}})_i - (r_{\text{B,exp}})_i]}{n} \times 100\% \qquad (4)$$

The experimental reaction rate and the rate of phenol consumption computed from the model Eq. (1) were plotted in Fig. 5. This figure shows the suitability and accuracy of the

Table 4
Variation of kinetic and adsorption parameters with temperature

Parameters	Temperature (K)			
	313	323	333	343
k_1 (kg/kg mol h)	0.158	0.246	0.374	0.55
K_{A} (m^3/kg)	4.58	4.15	3.79	3.47
K_{B} (m^3/kg)	10.30	10.20	10.10	10.01
K_{C} (m^3/kg)	0.56	0.55	0.55	0.54

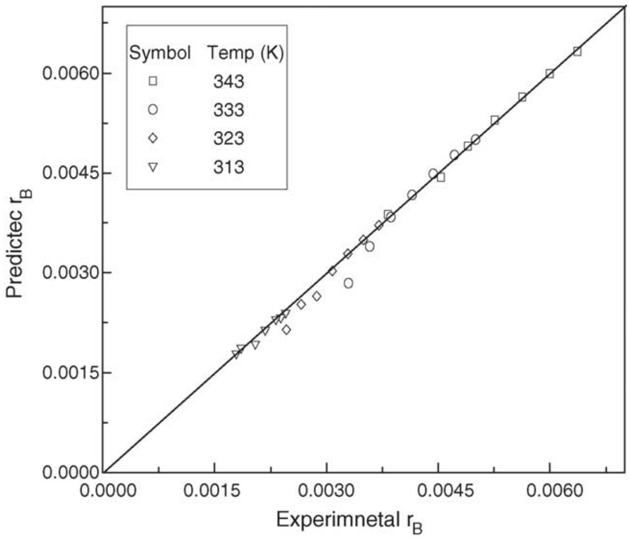


Fig. 5. Experimental vs. predicted rate of reaction of phenol.

model. The adsorption constant for the phenol is high compared to those for TBA and TBP. This may be interpreted as evidence of strong adsorption of phenol on the active sites of catalyst and comparatively weak adsorption of TBA and TBP. This observation supports the explanation for the effect of phenol/TBA mole ratio on phenol conversion as discussed earlier.

The apparent activation energy for the surface reaction was estimated from the Arrhenius plot (Fig. 6). Similar method was used to estimate the apparent activation energies for adsorption of phenol, TBA and TBP, which are listed in Table 5. The negative value of activation energy of adsorption is for decrease in adsorption with increase in temperature. The value of activation energy of phenol butylation is in the same range of the values reported on similar catalysts [27].

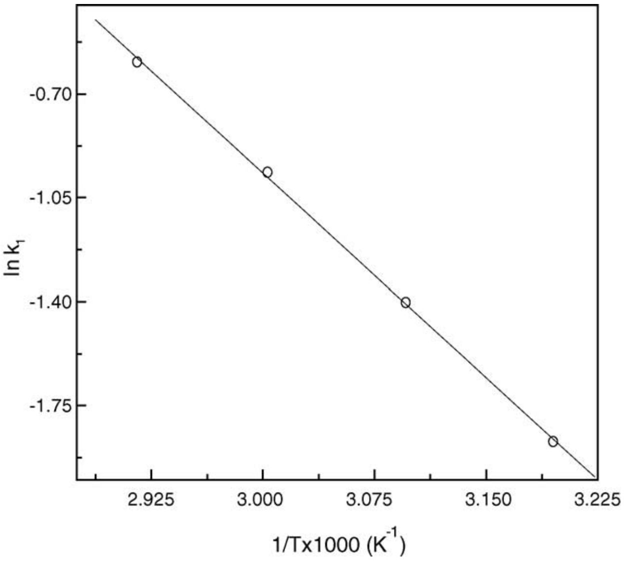


Fig. 6. Arrhenius plot for phenol alkylation over HZOP-31.

Table 5
Apparent activation energies and pre-exponential factors

	E_a (kJ/mol)	Pre-exponential factor (in consistent unit)
Phenol alkylation	37.29	2.64×10^5
TBA adsorption	−8.202	0.196
Phenol adsorption	−0.831	7.48
TBP adsorption	−6.258	0.44

4. Conclusions

The alkylation of phenol with *tert*-butyl alcohol was carried out in batch mode over a zeolite prepared from fly ash. Complete conversion of the limiting reactant could be obtained with this catalyst. The effects of various parameters, such as temperature, reactant composition, catalyst loading, etc. on phenol conversion as well as product selectivity were studied. Based on the product distribution, a reaction scheme was proposed and a kinetic model was developed. The model was found to fit the experimental data reasonably well. From the estimated kinetic and adsorption parameters, the activation energies for various steps were determined.

An interesting feature of this study is the use of fly ash for the preparation of catalyst for alkylation reaction. Fly ash, which is a liability to the thermal power plants due to environmental pollution, could be converted to assets by suitable treatment.

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