Organic Process Research & Development **2002**, *6,* 132–137

# Alkylation of Phenol with Tertiary Butyl Alcohol over Zeolites

A. V. Krishnan, Keka Ojha, and Narayan C. Pradhan*

*Department of Chemical Engineering, Indian Institute of Technology, Kharagpur - 721 302, India*

## Abstract:

**Alkylation of phenol was carried out with *tert*-butyl alcohol (TBA) producing *p*-*tert*-butyl phenol over a variety of zeolite catalysts, namely, zeolite Beta, 13X zeolite, Ce-exchanged 13X zeolite, and zeolite prepared from fly ash. Zeolite Beta showed the highest activity for the reaction under otherwise identical conditions. The activity of 13X zeolite was found to increase with an increase in cerium content in the catalyst, which was accomplished through ion exchange. The activity of zeolite (obtained from fly ash by hydrothermal treatment) in catalyzing the reaction was tested with highly encouraging results. The effects of various parameters such as reaction temperature, reactant ratio (mole ratio of phenol to that of *tert*-butyl alcohol), and catalyst loading on the rate of reaction were also studied. The alkylation reaction was found to be surface-reaction controlled with negligible interparticle mass-transfer resistance.**

## Introduction

The alkylation reaction of phenol with *tert*-butyl alcohol is of industrial relevance and also of academic interest. The product, *p*-*tert*-butyl phenol (*p*-TBP) is used as a raw material for the production of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, and so forth. Other applications of *p*-TBP include surface-active agents, rubber chemicals, antioxidants, fungicides, and petroleum additives. Although both homogeneous and heterogeneous catalysts are used in alkylation reaction systems, the trend is definitely towards solid heterogeneous catalysts, especially zeolites due to the inherent advantages of their higher activity, better selectivity, ease of separation from reaction products, chemical stability, reusability, environmental friendliness, and absence of corrosion problems. The present work is concerned with the alkylation of phenol with *tert*-butyl alcohol (TBA) for producing *p*-*tert*-butyl phenol, primarily using a variety of heterogeneous catalysts.

Published literature on the alkylation of phenol with alcohols is very scanty. Moreover, very few studies have been done using the zeolite catalysts for the phenol *tert*-butylation, except for a few reports on the study of the reaction over $SiO_2-Al_2O_3$ catalyst in gas or liquid phases.

Alkylation of phenolic compounds by isobutanol has been studied using zinc chloride, phosphoric acid, 70% sulphuric acid, aluminium chloride, and cation-exchange resin.[1,2] Most of the studies have been carried out using large quantities of the catalysts, and the effects of parameters such as catalyst concentration on the progress of the reaction have not been investigated systematically. Alkylation of phenol and catechol with isobutyl alcohol has been studied using a variety of superacid catalysts.[3]

Tsvetkov et al.[4] have reported that the reaction between phenol and higher olefins at 130 °C in the presence of KU-2 cation exchanger provides a 90.5% yield of monoalkyl phenol. Shkaraputra et al.[5] have developed a mathematical model for the alkylation of phenol and $\alpha$-olefins using KU-2 cation exchanger as the catalyst.

Zieborak and co-workers[6] have reported the synthesis of *p*-cumyl phenol (PCP) in the presence of cation-exchange resin Amberlyst 15. Macho et al.[7] studied the reaction of phenol with a mixture of $\alpha$-methyl styrene (AMS) and AMS dimers in the presence of active earth, polyphosphates, and zeolites in the temperature range 60−240 °C. The alkylation of phenol with $\alpha$-methyl styrene and several alkenes has been studied using both heterogeneous as well as homogeneous catalysts.[8] The ortho/para product ratio was reported to vary considerably for different olefins, between solid catalysts and homogeneous catalysts, and also between macroporous cation-exchange resins Amberlyst 15 and partly $Ag^+$-exchanged Amberlyst 15.

The ortho/para product distribution in the alkylation of phenol with alkenes has been shown to vary with the nature of the olefin. Widdecke and Klein[9] reported a ratio of 67:33 for ortho- and para-alkylated products in the alkylation of phenol with propylene in the presence of dry Amberlyst 15 at 98 °C. Lysenko et al.[10] studied the alkylation of phenol with isobutylene and butenes and observed that the yields of *p*-$(CH_3)_3CC_6H_4OH$ (from isobutylene) and *p*-$MeCHEtC_6H_4$-OH (from butenes) were 95.4 and 49.3%, respectively.

Crozat et al.[11] have claimed to have obtained *tert*-butyl phenol from reaction of phenol and methyl tertiary butyl ether (MTBE) (1:1 ratio) in the presence of Amberlyst 15 as catalyst. They have reported a ratio of 2- to 4-*tert*-butyl phenol of 0.5 at 63% conversion of phenol. Chandra and

---

* To whom correspondence should be addressed. E-mail: ncp@che.iitkgp.ernet.in.

(1) Isagulyants, V. I. *Gaz. Prom. Im. Gubkina* **1957**, *24*, 286; *Chem. Abstr*. **1960**, *54*, 13497i.

(2) Scheriesheism, A. *Friedel−Crafts Relat. React.* **1964**, *II*, Part 1, 477−595.

(3) Rajadhyaksha, R. A.; Chaudhari, D. D. *Ind. Eng. Chem. Res.* **1987**, *26*, 1276.

(4) Tsvetkov, O. N.; Monastvrskii, V. N.; Shirokov, A. N.; Kovenev, K. D. *Chem. Abstr*. **1972**, *76*, 585385.

(5) Shkaraputa, L. N.; Lediev, R. Y.; Lebedev, E. V.; Sklyar, V. T.; Manoilo, A. M.; Danilenko, V. V. *Khim. Tekhnol. (Kiev)* **1973**, *6*, 41; *Chem. Abstr*. **1974**, *80*, 70466g.

(6) Zieborak, Z.; Rutajezak, W.; Kowalska, H. *Chem. Stosowana* **1981**, *3−4*, 341.

(7) Macho, V.; Matuskova, M.; Kavala, M.; Holuik, J. *Chem. Abstr*. **1981**, *95*, 16891.

(8) Chaudhuri, B.; Sharma, M. M. *Ind. Eng. Chem. Res.* **1991**, *30*, 227.

(9) Widdecke, H.; Klein, J. *Chem. Ing. Tech.* **1981**, *53*, 94.

(10) Lysenko, A. P.; Yakumna, G. I.; Zelentsova, M. I. *Chem. Abstr*. **1975**, *83*, 27778.

(11) Crozat, M. C.; Barriac, J. M.; Aikawa, L. T.; Bornholdt, L.; Braz, P. *Chem. Abstr*. **1982**, *96*, 142455.

10.1021/op010077n CCC: $22.00

***Table 1.*** **Chemical compositions and characteristics of different catalysts**

| compounds | fly ash | zeolite from fly ash | 13X zeolite | zeolite Beta |
|---|---|---|---|---|
| $Na_2O$ | 2.12 | 14.52 | 15.67 | 0.30 |
| $Al_2O_3$ | 31.95 | 24.97 | 31.87 | 6.42 |
| $SiO_2$ | 55.18 | 49.35 | 48.26 | 92.02 |
| $K_2O$ | 1.40 | 0.98 | 0.07 | 0.07 |
| CaO | 0.77 | 2.20 | 0.37 | 0.22 |
| $TiO_2$ | 2.74 | 2.68 | 0.08 | 0.11 |
| $Fe_2O_3$ | 4.58 | 5.08 | 3.17 | 0.28 |
| BaO | 1.28 | 0.00 | 0.00 | 0.00 |
| $SO_3$ | 0.00 | 0.23 | 0.51 | 0.39 |
| MgO | 0.00 | 0.00 | 0.00 | 0.09 |
| surface area (BET), $m^2/g$ | 2.9 | 376 | 478 | 745 |

Sharma[12] have studied the alkylation of phenol with MTBE and other ethers over cation-exchange resins. They have reported the selectivity of the reaction with respect to 2- and 4-*tert*-butyl phenol.

Schulz et al.[13] have claimed a yield of 95% 4-*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 4-TBP has been reported by Sartori et al.[14] using $ZrCl_4$ as catalyst. They have used 0.1 mol of catalyst for 0.1 mol each of phenol and MTBE.

Zhang et al.[15] have carried out the reaction of phenol with *tert*-butyl alcohol over zeolite HY in a continuous flow reactor and found that the phenol conversion is 49% at 448 K under atmospheric pressure with gas hourly space velocity (GHSV) of 2000 $h^{-1}$ and a mole ratio of *tert*-butyl alcohol to phenol of 1:2.

From the above discussion, it is evident that there is very little information on the reaction of phenol with tertiary butyl alcohol in the published literature. It was, therefore, thought desirable to study this commercially important reaction system over a variety of catalysts, mostly zeolites. A further objective of this study was to explore the catalytic effect of fly ash and zeolite prepared from fly ash on the reaction under investigation.

## Experimental Section

**Materials.** The 13X 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. Its composition is given in Table 1. The fly ash used in the present study was treated with 20% hydrochloric acid, calcined, and then used in the reactor.

Zeolite Beta used in the present study was obtained from National Chemical Laboratoty (NCL), Pune, India. It was in its active proton form.

**Preparation of Ce-Exchanged 13X Zeolite.** The commercially available 13X zeolite was first calcined to remove moisture and kept ready for cation exchange. The catalyst particles were first heated with 2% $NH_4NO_3$ solution at 90 ± 10 °C for 6 h, for three times, each time with a fresh 2% $NH_4NO_3$ solution with subsequent calcining of the particles at 350 °C in between. The catalyst particles thus obtained after a total of 18 h heating and containing about 5−6% of Na (determined by flame photometer) were boiled with a required percentage of cerium ammonium nitrate solution for about 16 h, thereby modifying the 13X zeolite. This was then dried and calcined at 350 °C and ready for use in the reactor.

**Determination of Cerium Exchanged on the Catalyst.** Accurately, 2 g of freshly calcined catalyst containing cerium was taken in a conical flask and digested with concentrated HCl for about an hour. The digested material was then diluted with distilled water and filtered through a filter paper. The filtrate containing the cerium in solution was transferred to a 500 mL beaker, and its volume was raised to about 250 mL by adding distilled water. To this solution 50 mL of saturated oxalic acid solution was added, which gave rise to a white precipitate of cerium oxalate. The precipitate was filtered through a Whatman No. 40 ashless filter paper and was thoroughly washed with distilled water. The white precipitate along with the filter paper was then ignited over a previously weighed silica crucible at 900 ± 10 °C to a constant weight. On heating, the cerium oxalate was converted to $Ce_2O_3$, which was a yellow solid. The percentage of cerium was then calculated from the weight of the $Ce_2O_3$.

$$\text{cerium in catalyst} = \frac{0.7448 \times \text{wt of } Ce_2O_3 \times 100\ \%}{\text{wt of the catalyst}}$$

**Preparation of Zeolite from Fly Ash.** The fly ash was converted to zeolite by fusion with sodium hydroxide followed by hydrothermal treatment.[16] The zeolite was prepared by fusing NaOH and the fly ash mixture in the ratio of 1:1.2. The resultant fused mixture was cooled to room temperature, mixed with water, and then stirred for 12 h. The slurry was then kept at around 90 °C for 6 h without stirring. The precipitates were filtered, washed repeatedly with water, and dried overnight at 100 °C.

**Characterization of Prepared Zeolite.** Powder X-ray diffraction (XRD) patterns for the various samples were obtained using Co Kα radiation at 4 kV and 30 mA in a Philips BW1710 automated power diffractometer. The diffraction patterns of the treated (hydrothermally) and untreated fly ash were taken and compared with the XRD pattern of typical 13X (NaX) zeolite. The formation of zeolite was thus confirmed from this comparison as evident in Figure 1. Compositions of the samples under experiment were determined with the help of a scanning electron microscope (model JEOL, JSM 5800). The compositions of treated fly ash, commercial 13X zeolite, and zeolite Beta are also shown in Table 1. The characteristics of these catalysts are also reported in the same table. The X-ray diffractogram of Ce-

---

[12] Chandra, K. G.; Sharma, M. M. *Catal. Lett.* **1993**, *19*, 309.

[13] Schulz, M.; Seiffarth, M. N.; Bayer, C. *Chem. Abstr.* **1989**, *111*, 232291.

[14] Sartori, G.; Bigi, F.; Casiraghi, G.; Carnati, G.; Chiesi, L.; Arduini, A. *Chem. Ind.* **1985**, *22*, 762.

[15] Zhang, K.; He, F.; Wang, Y.; Xu, G. *Proceedings of the Asia-Pacific Chemical Reaction Engineering Symposium-99 (APCRE99)*; Hong Kong University of Science and Technology: Hong Kong, 1999; pp 87−94.

[16] Ojha, K.; Pradhan, N. C. *Indian J. Eng. Mater. Sci.* **2001**, *8*, 100.

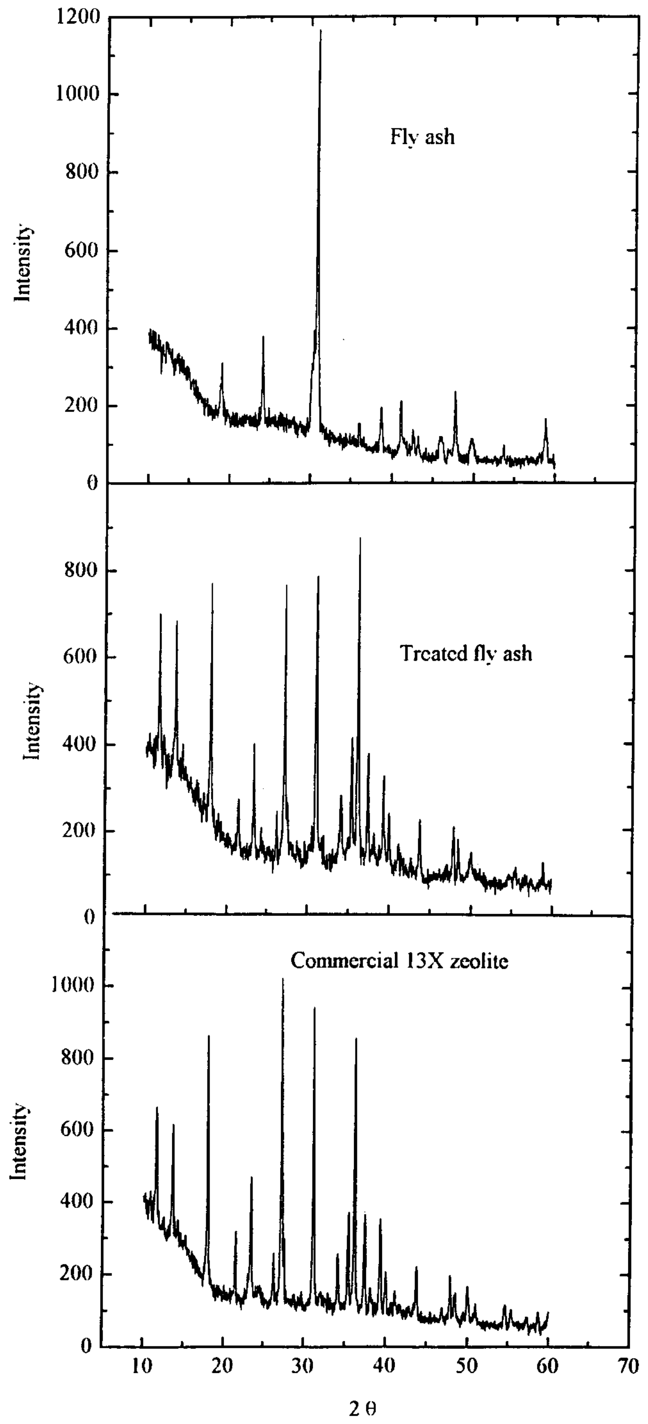


***Figure 1.*** **X-ray diffraction patterns of fly ash, treated fly ash, and 13X zeolite.**

exchanged 13X zeolite exactly matched with the parent unmodified zeolite, indicating no structural change with Ce exchange.

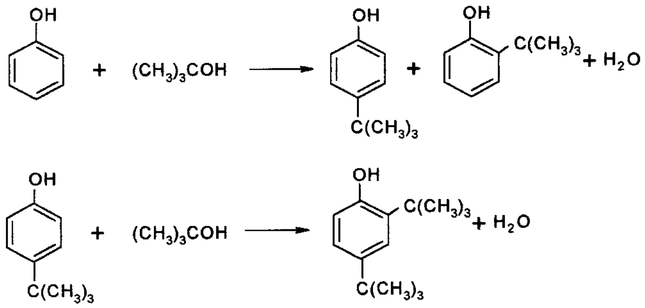
**Experimental Procedure.** All experiments were carried out in a 500 mL PARR reactor. For the experimental runs, the reactor was filled with the required ratios of reactants and calculated quantity of the catalyst, and the temperature was set using the control panel while the cooling water was circulated through the coil. At regular intervals of time, the product samples were collected, and the reactor was sealed again for further reaction until the time period was over. The various catalysts used in the reactions were acid-treated fly ash, zeolite obtained from fly ash, 13X zeolite, Ce-modified 13X zeolite, and zeolite Beta. The zeolite catalysts were washed with acetone and dried at 300 °C for 4−5 h before use.

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

## Results and Discussion

The reactions of phenol with *tert*-butyl alcohol (TBA) were carried out in batch mode in a PARR reactor. The effects of different parameters on the 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. Therefore, the reaction system was free from external mass transfer resistance in the above range of speed of agitation.

In the alkylation of phenol with *tert*-butyl alcohol, *o*-*tert*-butyl phenol (*o*-TBP), *p*-*tert*-butyl phenol (*p*-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:



**Activity of Various Catalysts.** 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. 13X zeolite was found to give low conversions of phenol when compared with those of zeolite Beta and zeolite obtained from fly ash. Moreover, Ce-modified 13X zeolite gave better phenol conversion compared with those of both fly ash and unmodified 13X zeolite. All these data are shown in Figure 2. Although the acidic strength of zeolite Beta is less than that of other conventional zeolites, the rate of reaction over zeolite Beta was observed to be much higher mainly because of its large pore size. The low activity of 13X zeolites can be due to its small channel structure. 13X zeolites possess good concentration of strong acid sites. However, the acid sites are located within their narrow pores and are inaccessible to the reactants. Some weak and medium acid sites located on the external surface effectively catalyze the reaction, giving low conversions. As

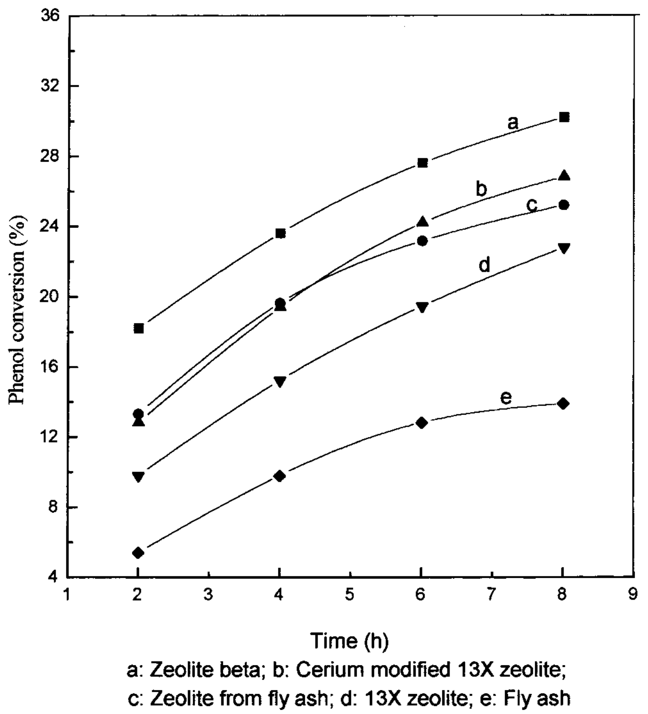


***Figure 2.*** **Activity of various catalysts in the alkylation of phenol with *tert*-butyl alcohol. Conditions: temperature, 60 °C; phenol-to-*tert*-butyl alcohol mole ratio, 2:1; speed of agitation, 800 rpm; catalyst loading, 10% (W/W).**

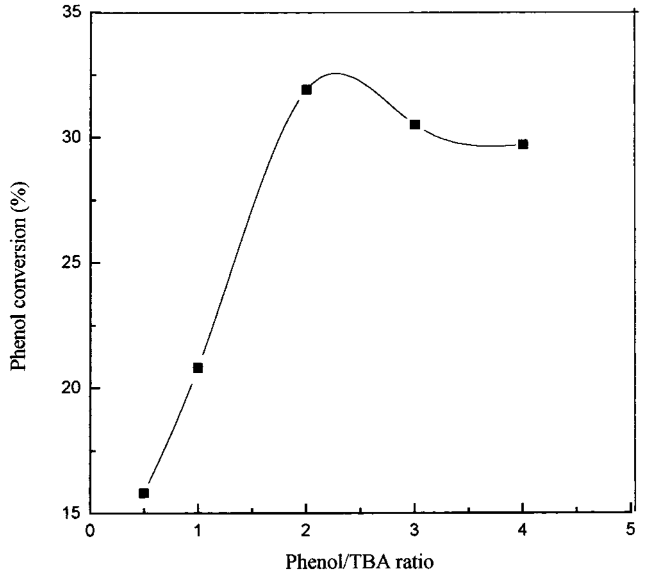


***Figure 3.*** **Effect of phenol-to-TBA ratio on phenol conversion. Conditions: catalyst, zeolite Beta; catalyst loading, 10% (w/w); temperature 50 °C; speed of agitation, 800 rpm; time, 4 h.**

zeolite Beta gave maximum conversion, most of the other experiments were carried out with this catalyst.

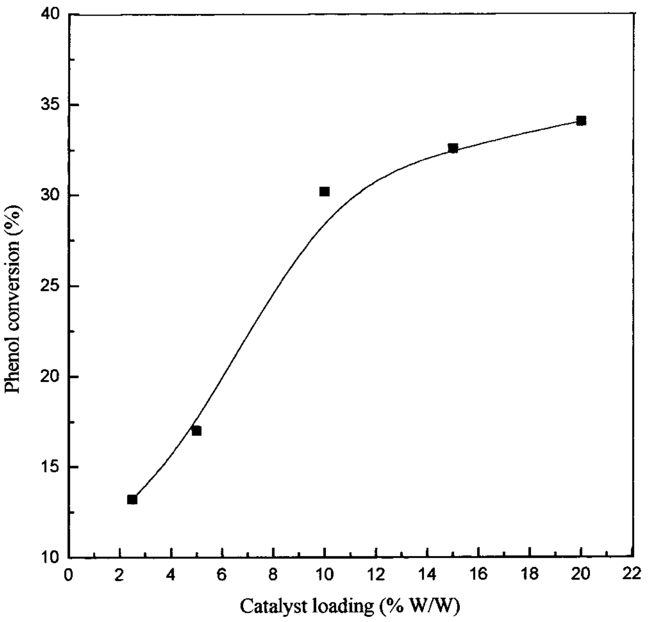


***Figure 4.*** **Effect of catalyst loading on phenol conversion. Conditions: catalyst, zeolite Beta; phenol-to-TBA mole ratio, 2:1; temperature, 60 °C; speed of agitation, 800 rpm; reaction time, 8 h.**

**Effect of Phenol to *tert*-Butyl Alcohol Mole Ratio.** The reactions were carried out by varying the mole ratio of phenol to *tert*-butyl alcohol (TBA) from 0.5 to 4. It was observed that with an increase in the phenol/*tert*-butyl alcohol mole ratio, the conversion of phenol passed through a maximum. This is shown in Figure 3. As can be seen from this figure, the maximum conversion was obtained at a phenol-to-TBA mole ratio of 2:1. The para selectivity was also found to increase with the mole ratio. Increasing the phenol concentration of the reaction mixture decreases the formation of side products, other than *p*-TBP. Therefore, a large excess of phenol (ratio > 1) may 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 mole ratio only.

**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. Up to 10% loading, the conversion of phenol increased sharply with the increase in the catalyst loading. Beyond 10%, the rate of reaction increased slowly. This is shown in Figure 4.

**Effect of Temperature on Phenol Conversion.** The effect of temperature on the conversion of phenol was studied in the temperature range of 40−70 °C. 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 70 °C (normal boiling point of TBA is 83 °C). As can be seen from Figure 5, 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 40 to 70 °C, decreasing the selectivity of other side products as shown in Table 2.

**Effect of Ce-Content of 13X Zeolite on Phenol Conversion.** Commercially available 13X zeolite was treated to exchange its sodium ions with cerium ions. This exchange was carried out with cerium nitrate solutions of different concentrations. The cerium content of the exchanged catalyst was found to vary linearly with the cerium concentration of the solution from which it was exchanged, and this is quite expected. Figure 6 shows the plot of cerium nitrate solution concentration versus phenol conversion obtained after 4 h

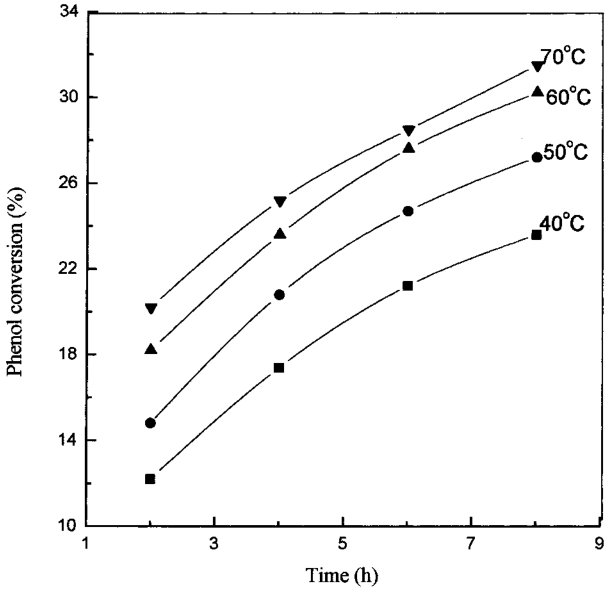


*Figure 5.* **Effect of temperature on phenol conversion. Conditions: catalyst, zeolite Beta; phenol-to-TBA mole ratio, 2:1; catalyst loading, 10% (W/W); speed of agitation, 800 rpm.**

*Table 2.* **Effect of temperature on product distribution**[a]

| component | composition (atom %) 40 °C | 50 °C | 60 °C | 70 °C |
|---|---|---|---|---|
| *o*-TBP | 5.08 | 4.17 | 3.24 | 2.75 |
| *p*-TBP | 91.74 | 93.65 | 95.43 | 96.21 |
| 2,4-DTBP | 3.18 | 2.18 | 1.33 | 1.04 |

[a] Conditions: phenol/TBA mole ratio, 2:1; catalyst, zeolite Beta; catalyst loading, 10% (w/w); speed of agitation, 800 rpm; batch time, 6h.

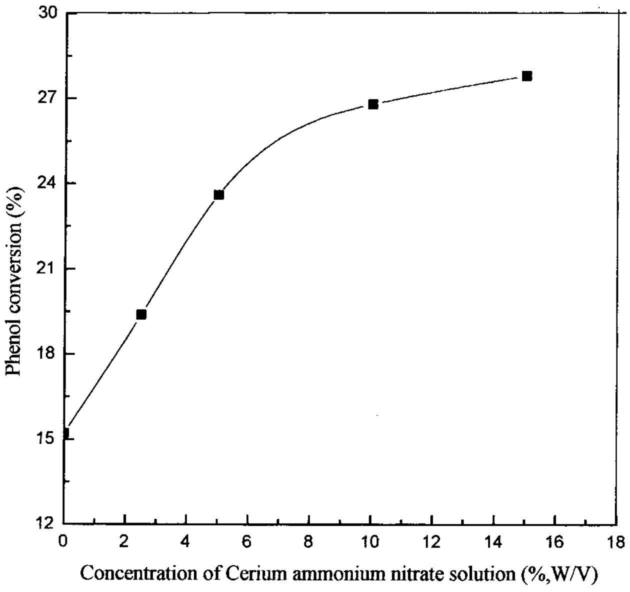


*Figure 6.* **Effect of cerium content of 13X zeolite on phenol conversion. Conditions: temperature, 60 °C; phenol-to-TBA mole ratio, 2:1; speed of agitation, 800 rpm; reaction time, 4 h.**

at a phenol-to-TBA mole ratio of 2:1 and at a temperature of 60 °C. As can be found from this figure, the phenol conversion increases with increase in cerium content in the 13X, zeolite and this may be due to strong acid sites generated by the exchange.

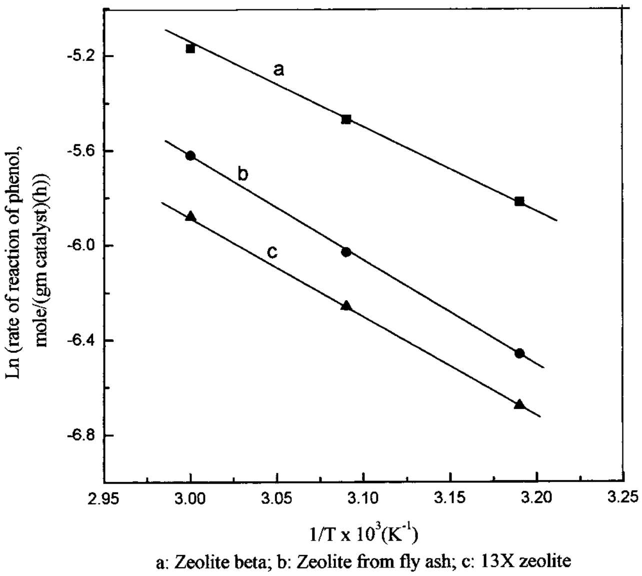


*Figure 7.* **Arrhenius plot for different catalysts.**

*Table 3.* **Apparent activation energies for phenol alkylation with different catalysts**

| catalyst | apparent activation energy (kcal/mol) |
|---|---|
| fly ash | 12.02 |
| 13X zeolite | 8.75 |
| Ce-exchanged 13X zeolite[a] | 8.04 |
| zeolite from fly ash | 7.85 |
| zeolite Beta | 6.52 |

[a] Cerium content, 10%.

**Determination of Activation Energy.** The effect of temperature on the conversion of phenol with different catalysts was studied. Figure 5 shows the phenol conversion obtained at different temperatures and at different batch times with zeolite Beta as the catalyst. Similar experiments were also carried out with other catalysts. From the initial concentration of phenol and time required for 10% conversion, the rate of reaction of phenol was calculated. A plot of ln(rate) against 1/$T$ gave straight lines. This is shown in Figure 7 for three catalysts, zeolite Beta, zeolite from fly ash, and 13X zeolite. From the slope of the straight lines, the apparent activation energies for the reaction were computed for various catalysts. Table 3 gives the apparent activation energy values obtained with different catalysts used in the phenol alkylation reaction. It is evident from this table that the apparent activation energy values are greater than 6.5 kcal/mol, indicating the reaction to be controlled by surface reaction. Moreover, the activation energy values were found to decrease in the same order as the activity of the catalysts increased (as presented in Figure 2), which is quite expected.

## Conclusions

The alkylation of phenol with *tert*-butyl alcohol was carried out in batch mode with various catalysts. The zeolite Beta catalyst was observed to be the most efficient. Complete conversion of the limiting reactant could be observed with zeolite Beta catalyst. The zeolite obtained from fly ash and

Ce-modified 13X zeolite also showed better results. The 13X zeolite and virgin fly ash appeared to be less active when compared on the basis of equal loading. However, the activity of Ce-exchanged 13X zeolite was found to be comparable to other catalysts. The effects of various parameters, such as temperature, reactant composition, catalyst loading, and so forth, on phenol conversion as well as product selectivity were studied.

An interesting feature of this study is the use of fly ash as the catalyst for the phenol alkylation reaction. Fly ash, which is a disadvantage to thermal power plants due to environmental pollution, could be converted to harmless byproducts by suitable treatment. This will definitely open up new areas of research.

## Acknowledgment

A part of this work was supported by Council of Scientific and Industrial Research (CSIR), New Delhi, India (Grant 22(0306)/99/EMR-II).

Received for review September 12, 2001.

OP010077N