Treated fly ash: A potential catalyst for alkylation of phenol
with tert-butyl alcohol

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Alkylation of phenol was carried out with tert-butyl alcohol (TBA) over a variety of non-conventional catalysts, namely fly ash, zeolite prepared from fly ash, and commercial 13X zeolite. Zeolite prepared from fly ash by hydrothermal treatment showed the highest activity for the reaction under otherwise identical conditions. 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 catalyst prepared from fly ash. The alkylation reaction was found to be surface reaction controlled with negligible inter-particle mass transfer resistance.

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, anti-oxidants, fungicides and as petroleum additives. 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 variety of non-conventional heterogeneous catalysts.

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 1-2 and a variety of superacid catalysts 3.

The reactions between phenol and olefins have been studied by many investigators 4-7 in the presence of cation exchange resins, as the catalysts, at lower temperatures (98-100°C). Zieborak and co-workers 8 have reported the synthesis of p-cumyl phenol (PCP) in the presence of cation exchange resin Amberlyst 15. Macho et al. 9 studied the reaction of phenol with a mixture of α-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 α-methyl styrene and several alkenes has been studied using both heterogeneous as well as homogeneous catalysts 10.

The ortho/para product ratio was reported to vary considerably for different olefins, and also with variation of catalysts.

Crozat et al. 11 and Chandra and Sharma 12 have claimed to have obtained tert-butyl phenol from reaction of phenol and methyl tertiary butyl ether (MTBE) in the presence of Amberlyst 15 as catalyst. Schulz et al. 13 have obtained a yield of 95% 4-tert-butyl phenol on reacting 1 mol each of phenol and MTBE in the presence of 1 mol H₂SO₄ as catalyst. A higher selective method to obtain 4-TBP has been reported by Sartori et al. 14 using ZrCl₄ as catalyst.

The reaction of phenol with tert-butyl alcohol over zeolite HY has been studied in a continuous flow reactor and a phenol conversion of 49% has been reported at 175°C 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 by Zhang et al. 15. Effect of acidity of various catalysts (SiO₂-Al₂O₃, Al₂O₃ and Zeolite X) on the tert-butylation of phenol was studied by Kijiya & Okazaki 16 in a continuous flow reactor under normal pressure at 182-250°C.

From the above discussion, it is evident that there is very little 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 catalyst such as fly ash in catalyzing this commercially important reaction.

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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 one. Because of the presence of SiO₂ and Al₂O₃ 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 literature for the preparation of zeolites from fly ash. The zeolite prepared from fly ash has also been successfully used in catalyzing cracking reactions of heavy oil residues. 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 13X zeolite.

Experimental Procedure

Materials

The 13X zeolite used in the present study was obtained from SISCO Research Laboratories, Mumbai, India. Phenol was obtained from Qualigen (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.

Synthesis of zeolite from fly ash

The fly ash was converted to zeolite by fusion with sodium hydroxide followed by hydrothermal treatment. The zeolite was prepared by fusing NaOH and 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 any disturbance. The resultant precipitates were filtered, washed repeatedly with water and dried overnight at 100°C.

Characterization of prepared zeolite

Powder X-Ray Diffraction (XRD) pattern for the various samples were obtained using CoKα radiation at 4 kV and 30 mA in a Philips PW1710 automated powder 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. 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, treated fly ash and commercial 13X zeolite are also shown in Table 1. The BET surface areas of these catalysts are also reported in the same table.

Alkylation reaction and product analysis

All experiments were carried out in a 500 mL PARR reactor. For the experimental runs, the reactor was filled with required ratios of reactants and calculated quantity 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 regular intervals of time. The various catalysts used in the reactions were acid treated fly ash, zeolite synthesized from fly ash and 13X zeolite. 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 flame ionization detector and SE-30 column. The column temperature was 80°C to 290°C. The initial temperature was set at 80°C and maintained for 2
min, then increased at the rate of 10°C/min and held at 290°C for 4 min. Detector temperature was maintained at 300°C. The nitrogen gas was used as the carrier gas and flow rate was maintained at 5.0 x 10⁻⁷ m³/s. The peak area normalization method was used for quantification of the components present in the reaction mixture.

Results and Discussion

The reactions of phenol with tert-butyl alcohol (TBA) were carried out in batch mode in a 500 mL PARR reactor (autoclave). 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. Therefore, the reaction system was assumed to be 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 activity of three catalysts, namely fly ash, zeolite from fly ash and commercial 13X zeolite was studied and 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. 13X 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.

Effect of phenol to tert-butyl alcohol mole ratio

The alkylation of phenol was carried out by varying the mole ratio of phenol to tert-butyl alcohol (TBA) 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. This is shown in Fig. 2. As can be seen from this figure, the maximum conversion was 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 phenol to TBA mole ratio. After an optimum ratio, the conversion decreases because preferred adsorption of phenol on the active sites prevents adsorption of TBA and subsequent generation of active carbenium ions.

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 excluding 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 attained at phenol: tert-butyl alcohol ratio of 2:1, all further experiments were carried out with this molar 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. It is evident from Fig. 3 that the conversion of phenol increased sharply with increase in the catalyst loading up to 10%. Beyond 10% catalyst loading, the rate of reaction was found to increase slowly.

**Effect of temperature on phenol conversion**

The effect of temperature on the conversion of phenol was studied in the temperature range of 40 to 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 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 40 to 70°C, decreasing the selectivity of other side products as shown in Table 2.

**Determination of activation energy**

The effect of temperature on conversion of phenol with different catalysts was studied. Fig. 4 shows the

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\begin{array}{c|c|c|c|c|c|c}
\text{Component} & \text{Composition (mole %) at} \\
& 40°C & 50°C & 60°C & 70°C \\
\hline
\alpha\text{-TBP} & 4.83 & 4.12 & 3.05 & 2.62 \\
p\text{-TBP} & 95.56 & 92.45 & 94.36 & 95.72 \\
2,4\text{-DTBP} & 4.61 & 3.43 & 2.59 & 1.66 \\
\hline
\end{array}
\]

Conditions: phenol/TBA mole ratio, 2:1; catalyst, zeolite from fly ash; catalyst loading, 10% (w/w); speed of agitation, 800 rpm; batch time, 6 h.
phenol conversion obtained at different temperatures and at different batch times with zeolite prepared from fly ash 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 inverse of temperature (T) gave straight lines. This is shown in Fig. 5 for three catalysts, fly ash, zeolite from fly ash and commercial 13X zeolite, respectively. 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 7.0 kcal/mole, indicating the process 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 Fig. 1), which is quite expected.

**Conclusions**

The alkylation of phenol with tert-butyl alcohol was carried out in batch mode with various catalysts of the non-conventional type. The zeolite prepared from fly ash was observed to be the most efficient. Complete conversion of the limiting reactant could be obtained with this catalyst. The effects of various parameters like temperature, reactant composition, catalyst loading, etc. on phenol conversion as well as product selectivity were studied.

An interesting feature of this study is the use of fly ash as 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. Thus the present result is useful in opening up a new way for disposal of industrial solid waste products to control the pollution for environmental protection.

**References**

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