

Alkylation of *p*-cresol with *tert*-butanol catalyzed by heteropoly acid supported on zirconia catalyst

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Abstract

Butylation of *p*-cresol by *tert*-butanol was catalyzed by 12-tungstophosphoric acid supported on zirconia (TPA/ZrO₂) under flow conditions. Catalysts prepared with different TPA loading (5–30 wt.%) were calcined at 1023 K and acidity was estimated by temperature programmed desorption (TPD) of NH₃. Fifteen percent TPA/ZrO₂ showed the highest acidity and found to be the most active catalyst in butylation of *p*-cresol. The effects of temperature, space velocity (LHSV) and molar ratio of the reactants on the conversion of *p*-cresol and products selectivities were optimized and the optimum reaction conditions evaluated were 403 K, *tert*-butanol/*p*-cresol (Bu/Cr) molar ratio 3 and LHSV 4 h⁻¹. Under the optimized conditions, conversion of *p*-cresol was found to be 61 mol% with product selectivity for 2-*tert*-butyl-*p*-cresol (TBC) 81.4%, 2,6-di-*tert*-butyl-*p*-cresol (DTBC) 18.1% and *tert*-butyl-*p*-tolyl ether (ether) 0.5%. Study of time on stream (TOS) performed as a function of time for 100 h showed that the loss in activity in terms of conversion of *p*-cresol was 6%.

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1. Introduction

Eco-friendly and commercially viable catalyst systems are in demand for selective alkylation and acylation of aromatic substrates to corresponding value added products. Alkylation of aromatics is still carried out commercially using Friedel–Crafts catalysts such as AlCl₃, FeCl₃ and ZnCl₂. But these catalyst systems are least preferred as alkylating agents since they generate many problems such as pollution, handling, safety, corrosion and tedious work up. Strong solid acids based on supported transition metal oxides are potential replacements for liquid acids and halide containing solids [1,2]. Alkylation of *p*-cresol with *tert*-butanol gives 2-*tert*-butyl-*p*-cresol and 2,6-di-*tert*-butyl-*p*-cresol, commercially known as butylated hydroxy toluene (BHT), which are widely used in the manufacture of phenolic resins, as antioxidants [3] and polymerization inhibitors [4].

Alkylation of *p*-cresol with benzyl alcohol using stoichiometric amount of AlCl₃ [5] and butylation of *o*-cresol with *tert*-butanol using stoichiometric amount of H₃PO₄ [6] have been reported. In spite of the industrial importance of the butylation of *p*-cresol to get BHT, not much work has been reported in the literature. Solid acid catalysts such as cation exchange resins have been used as catalysts for the above reaction [7,8]. 12-Tungstophosphoric acid immobilized on macroporous phenol-furfural sulfonic acid resin using γ -aminopropyltriethoxy silane catalyst has been used for butylation of *p*-cresol [9]. Butylation of *p*-cresol has been carried out with isobutylene as an alkylating agent using sulfated zirconia [10]. Heteropoly acids supported on solid metal oxides have been gaining importance as alkylating and acylating catalysts [11–15]. In our earlier study, we have shown that TPA/ZrO₂ catalyst is highly active and stable catalyst and could be used efficiently in the alkylation reactions [16]. However, the detail study involving solid acid catalyst, such as TPA/ZrO₂ has not been studied for the above reaction. In this paper, we report the detailed study on the performance of TPA/ZrO₂ catalyst in the butylation of *p*-cresol with *tert*-butanol.

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2. Experimental

2.1. Materials

12-Tungstophosphoric acid and *p*-cresol were supplied by Aldrich. *tert*-Butanol was purchased from S.D. Fine Chemicals Ltd., Mumbai. Zirconium oxychloride was procured from Loba Chemie Ltd., Mumbai. Methanol was purchased from E. Merck India Ltd., Mumbai. All the above materials were used as received without further purification.

2.2. Preparation and characterization of TPA/ZrO₂ catalyst

The catalyst was prepared by wet impregnation method, following the procedure described in our earlier publication [16]. Zirconium hydroxide obtained by the hydrolysis of zirconium oxychloride was added to a methanolic solution of TPA. It was stirred well and evaporated to dryness and calcined in air at 1023 K. Similarly, catalysts with different TPA loading (5–30 wt.%) were prepared and calcined at 1023 K.

Acidity of the catalyst was measured by temperature programmed desorption (TPD) of NH₃. It is seen from the graph of acidity (NH₃ nm⁻²) vs. TPA loading (Fig. 1) that the acidity increased up to 15% and then decreased with further increase in TPA loading, which was due to monolayer coverage of TPA on the support [16].

2.3. Experimental procedure

Butylation of *p*-cresol using *tert*-butanol was carried out under flow conditions in a down flow fixed bed glass reactor (30 cm length and 1.3 cm OD) using 2 g of the catalyst. The catalyst was activated at 773 K in a flow of dry air for 5 h followed by cooling to the desired reaction temperature in

nitrogen atmosphere (40 ml min⁻¹). Feed containing a mixture of *p*-cresol and *tert*-butanol of desired molar ratio was passed into the reactor with a fixed space velocity (LHSV) using a syringe pump (Sage instruments model 352) and nitrogen as a carrier gas at the desired reaction temperature. The reaction mixture was cooled (ice trap) to room temperature after passing through the catalyst bed and samples were collected at every 1 h interval. Analysis of the sample was carried out by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using SE-52 packed column. The identity of the products was confirmed by GC–MS (Shimadzu QP-5000).

3. Results and discussion

Butylation of *p*-cresol by *tert*-butanol catalyzed by TPA/ZrO₂ gave mainly TBC, DTBC and ether as products. The reaction is as shown in Scheme 1. This reaction is an example of electrophilic substitution, where *tert*-butyl cation formed by *tert*-butanol substituted on the aromatic ring to give C-alkylated products and also small amounts of O-alkylated products.

3.1. Effect of TPA loading

The catalysts with different TPA loading (5–30 wt.%) on ZrO₂ were prepared and calcined at 1023 K. The reactions were carried out at temperature 403 K, LHSV 4 h⁻¹ and Bu/Cr molar ratio of 3. Fig. 2 shows the effect of TPA loading on the conversion of *p*-cresol and the product selectivities. Catalyst with 15% TPA loading was found to be the most active and gave TBC (81.4 mol%) and DTBC (18.1 mol%) at conversion of *p*-cresol (61 mol%). These observations are in concurrence with the catalyst

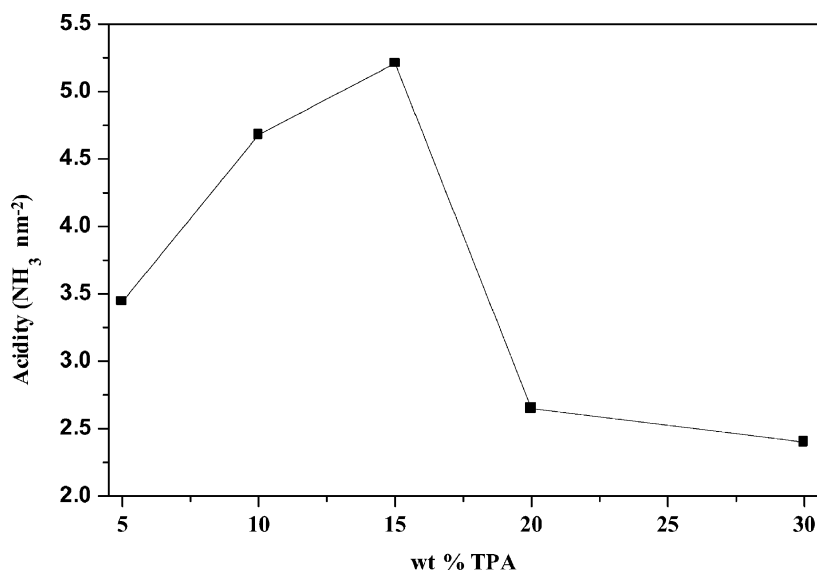
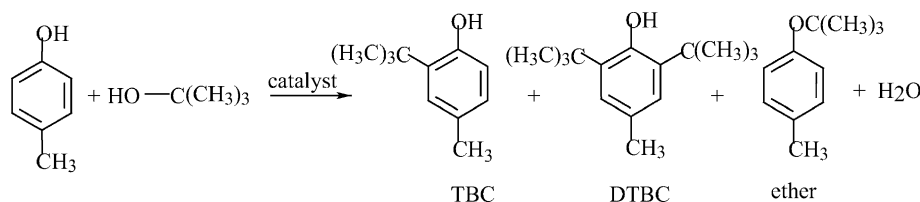


Fig. 1. Acidity data.



Scheme 1.

characterization, which indicated that 15% TPA loaded catalyst has the highest acidity (Fig. 1) and hence most active in the butylation of *p*-cresol by *tert*-butanol. Interestingly, 5 and 30% loaded catalysts under the above reaction conditions gave less conversion of *p*-cresol and produced more of ether. This indicated that the catalysts having less acidity favored O-alkylation to form ether.

3.2. Effect of reaction temperature

The reaction was carried out using 15% TPA/ZrO₂ at different temperatures ranging from 383 to 463 K with LHSV 6.7 h⁻¹ and Bu/Cr mole ratio 2. The conversion of *p*-cresol was maximum in the range 403–423 K (Fig. 3) with not much change in product selectivities. Ether was formed considerably (20.6%) at 383 K indicated that lower temperature favored ether formation. When the temperature was increased above the conversion of *p*-cresol was decreased. This could be due to dealkylation of the alkylated products [17]. Considering the above observations 403 K was chosen as the suitable reaction temperature for further optimization of reaction conditions.

3.3. Effect of molar ratio

The reaction was carried out with Bu/Cr molar ratios ranging from 1 to 4, at 403 K and LHSV 6.7 h⁻¹. Conversion of *p*-cresol was increased up to Bu/Cr molar ratio 3 and then decreased with further increase. However, selectivities for C- and O-alkylated products remained almost the same (Fig. 4) having higher selectivities for TBC. The conversion of *p*-cresol was low at lower molar ratios, which could be due to the preferential adsorption of *p*-cresol on the catalyst surface reducing the adsorption of *tert*-butanol over the catalyst surface. Hence higher *tert*-butanol concentration (Bu/Cr molar ratio 3) gave higher conversion of *p*-cresol. However, the conversion of *p*-cresol decreased at Bu/Cr molar ratio 4.

3.4. Effect of space velocity (LHSV)

The result of butylation of *p*-cresol carried out at different space velocity (LHSV) ranging from 4 to 10 h⁻¹ at 403 K and Bu/Cr molar ratio of 3 is shown in Fig. 5. Conversion of *p*-cresol decreased with increase in LHSV due to shorter contact time at higher space velocities. The

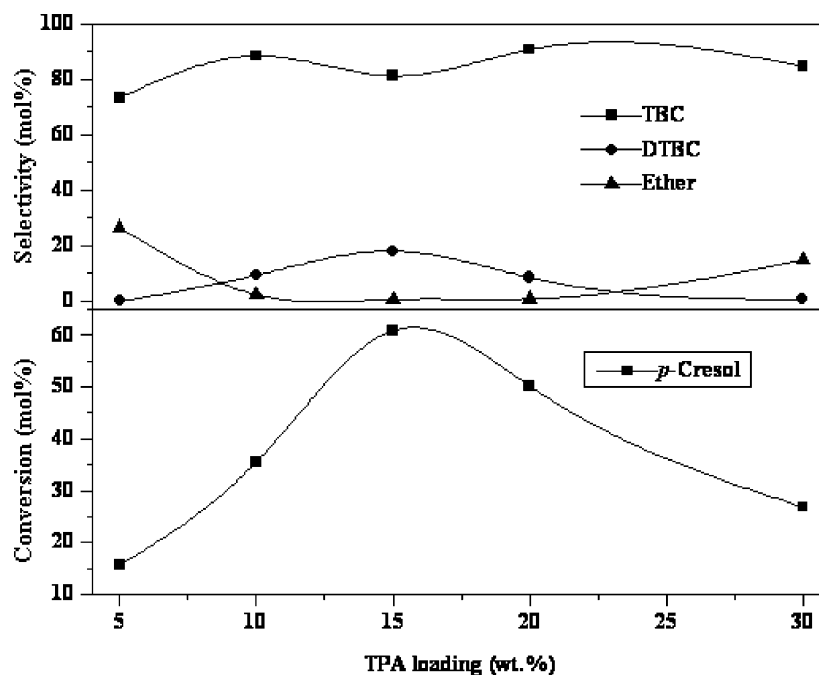


Fig. 2. Effect of different TPA loading (wt.%) on ZrO₂. Conditions: catalyst calcination = 1023 K; temperature = 403 K; LHSV = 4 h⁻¹; Bu/Cr mole ratio = 3; time = 5 h.

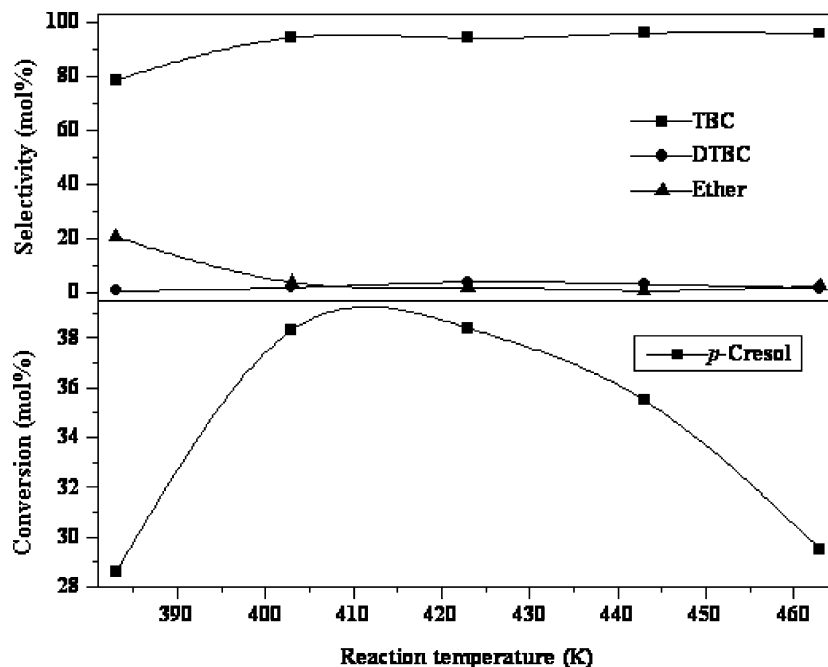


Fig. 3. Effect of reaction temperature. Conditions: catalyst = 15% TPA/ZrO₂; LHSV = 6.7 h⁻¹; Bu/Cr mole ratio = 2; time = 5 h.

selectivity for TBC remained almost unchanged. However, selectivity for DTBC was found to be more at LHSV 4 h⁻¹ and decreased with further increase. However, selectivity for ether increased with increase in LHSV.

3.5. Study of time on stream

The activity of the 15% TPA/ZrO₂ catalyst was studied as a function of time in the butylation of *p*-cresol at

403 K, LHSV 4 h⁻¹ and Bu/Cr molar ratio of 3 and the results are shown in Fig. 6. The reaction was carried out for 100 h and products were collected and analyzed at every 5 h interval. Conversion of *p*-cresol decreased from 61.0 to 54.5 mol% in the course of 100 h. The selectivity for TBC increased, while that of DTBC decreased till 20 h and then attained steady state. Only trace amount of ether was formed throughout the reaction. This demonstrates the catalyst's fairly stable in presence of polar reactants

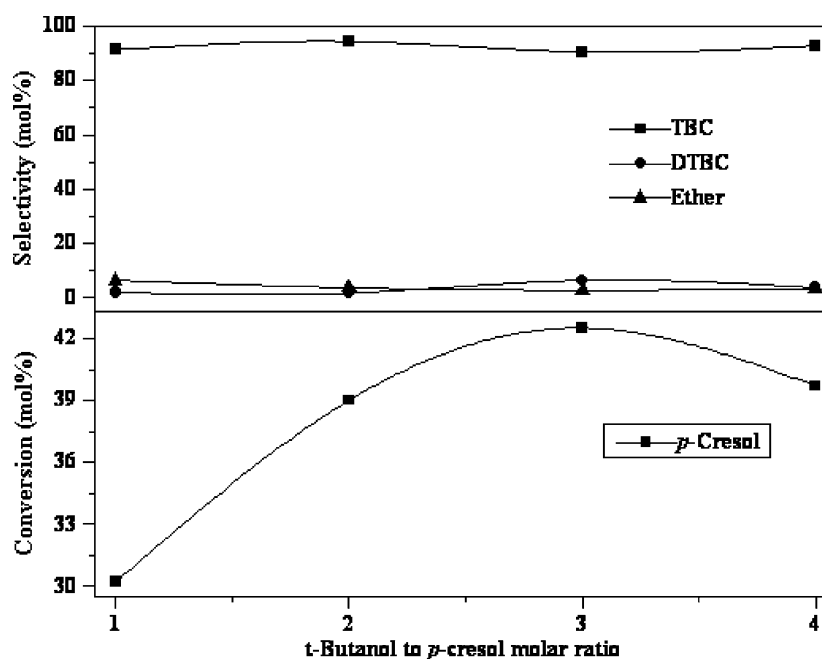


Fig. 4. Effect of *tert*-butanol to *p*-cresol molar ratio. Conditions: catalyst = 15% TPA/ZrO₂; temperature = 403 K; LHSV = 6.7 h⁻¹; time = 5 h.

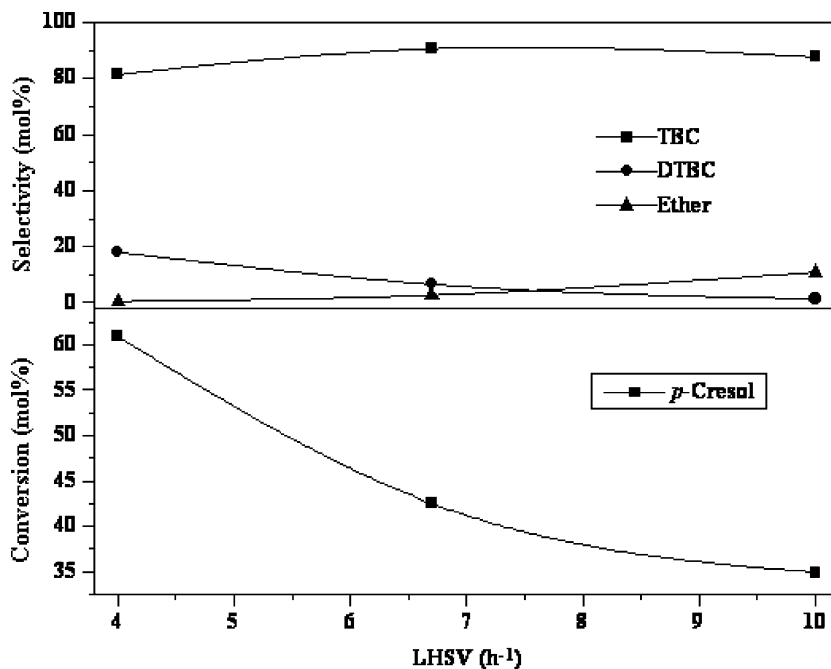


Fig. 5. Effect of space velocity (LHSV). Conditions: catalyst = 15% TPA/ZrO₂; temperature = 403 K; Bu/Cr mole ratio = 3; time = 5 h.

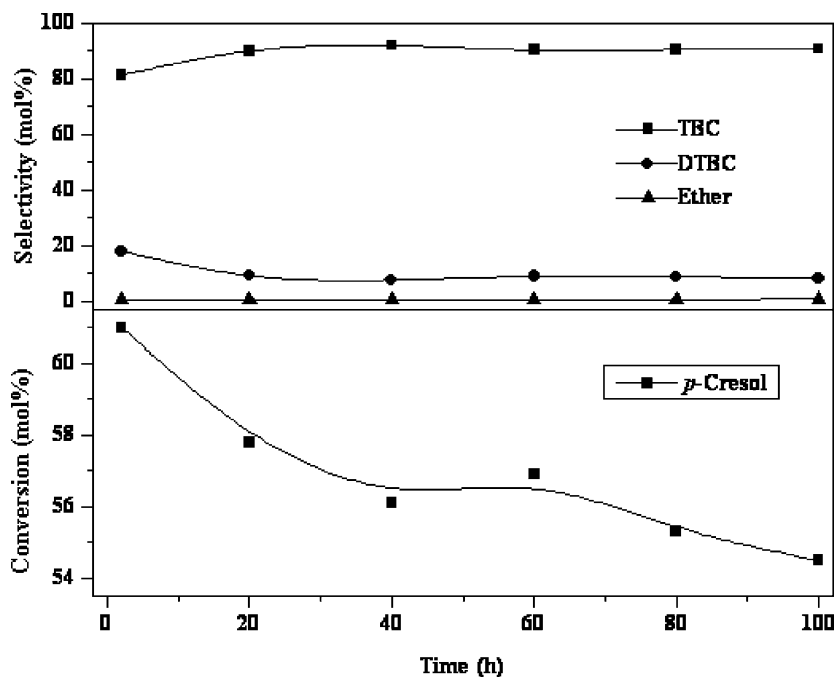


Fig. 6. Study of time on stream. Conditions: catalyst = 15% TPA/ZrO₂; temperature = 403 K; Bu/Cr mole ratio = 3; LHSV = 4 h⁻¹.

and could find industrial applications in acid catalyzed reactions.

4. Conclusions

Fifteen percent TPA/ZrO₂ calcined at 1023 K was found to be the most active catalyst in the butylation of *p*-cresol by

tert-butanol. The lower temperature (~383 K) favored the formation of ether, while at higher temperatures (>423 K) dealkylation of DTBC to TBC was observed. Higher Bu/Cr molar ratio (~3), 403 K and lower LHSV 4 h⁻¹ were found to be most suitable for higher conversions of *p*-cresol and product selectivities. The lower LHSV favored the formation of DTBC, while higher LHSV and lower reaction temperature facilitated the ether formation. The TPA/ZrO₂ is

fairly stable in presence of polar reactants and could find industrial applications in acid catalyzed reactions.

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