

## *tert*-Butylation of *p*-cresol over $\text{WO}_x/\text{ZrO}_2$ solid acid catalysts

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### Abstract

The *tert*-butylation of *p*-cresol with *tert*-butanol was carried out over  $\text{WO}_x/\text{ZrO}_2$  catalysts under flow conditions. The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide and ammonium metatungstate. Catalysts with different  $\text{WO}_3$  loading (5–30 wt.%) were prepared and calcined at 800 °C and catalyst with 15%  $\text{WO}_3$  was calcined from 600 to 900 °C. The catalysts were characterized by surface area, XRD, FTIR and TEM. The catalyst 15%  $\text{WO}_3/\text{ZrO}_2$  calcined at 800 °C found to be the most active in the reaction. The effect of temperature, space velocity and molar ratio of the reactants on the conversion of *p*-cresol and products selectivities were studied. Under the optimized reaction conditions of 130 °C, *tert*-butanol/*p*-cresol molar ratio of 3 and flow rate of 10 ml h<sup>-1</sup>, *p*-cresol conversion was 69.8% with selectivity to 2-*tert*-butyl-*p*-cresol 92.4%, 2,6-di-*tert*-butyl-*p*-cresol 6.3% and *p*-cresol *tert*-butyl ether 1.3%. The catalytic activity is compared with sulfated zirconia, USY, H $\beta$  zeolites and montmorillonite K-10 under the optimized reaction conditions. The activity of sulfated zirconia is lower than that of 15%  $\text{WO}_3/\text{ZrO}_2$  catalyst calcined at 800 °C and other catalysts showed very low activity.  
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**Keywords:** Zirconia; Tungsten oxide; *p*-Cresol; *tert*-Butylation

### 1. Introduction

The alkylation of phenol and its derivatives with different alcohols is industrially important as it is used for the production of a variety of products [1]. Among these, alkylation of *p*-cresol with *tert*-butanol used for the production of 2-*tert*-butyl-*p*-cresol, precursor for agidol-2, and 2,6-di-*tert*-butyl-*p*-cresol or butylated hydroxy toluene (BHT), which are important commercial antioxidants. Conventionally this reaction is carried out by the reaction of *p*-cresol with isobutene in presence of sulfuric acid or cation-exchange resin. The use of homogeneous catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal. Though, cation-exchange resin catalysts are environmentally friendly, they have the disadvantages like low activity and less stability at high temperatures [2,3]. Therefore, considerable efforts have been made for the development of suitable heterogeneous catalysts. The catalysts reported for this re-

action includes sulfated zirconia, immobilized and zirconia-supported heteropoly acids [4–6]. Both the formation of C- and O-alkylated products are possible depending on reaction conditions such as reaction temperature and type of the catalyst. The catalyst with strong acidic sites or high reaction temperature, the reaction results in the formation of C-alkylated products, while catalysts with weak acidic sites or low reaction temperature leads to the formation of O-alkylated products [7,8].

Zirconia based solid acids are attracting much attention in recent years. Sulfated zirconia is proved to be a highly active solid acid catalyst [9]. But, its poor stability and tendency to form volatile sulfur compounds during catalysis and regeneration limit its applicability [10]. Zirconia-supported tungsten oxide,  $\text{WO}_x/\text{ZrO}_2$  is shown to be an alternative to sulfated zirconia [11–14].

The present work deals with alkylation of *p*-cresol with *tert*-butanol using  $\text{WO}_x/\text{ZrO}_2$  as the catalyst. The reaction was carried out with an aim to maximize *p*-cresol conversion together with the selectivity to 2-*tert*-butyl-*p*-cresol and 2,6-di-*tert*-butyl-*p*-cresol. The influence of  $\text{WO}_3$  loading and

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catalyst calcination temperature on *p*-cresol conversion and product selectivity were studied. The catalyst with highest activity was used to study various reaction parameters such as temperature, molar ratio and flow rate. The present work includes the comparative study of 15% WO<sub>3</sub>/ZrO<sub>2</sub> catalyst calcined at 800 °C with sulfated zirconia (SZ), zeolites like USY, H $\beta$  and montmorillonite K-10 (clay).

## 2. Experimental

### 2.1. Materials

Zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) and ammonia (25%) were procured from S.D. Fine Chemicals Ltd. Mumbai. *p*-Cresol and *tert*-butanol was obtained from Merck (India) Ltd. Mumbai. Ammonium metatungstate hydrate ((NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O) and montmorillonite K-10 were purchased from Aldrich. Sulfated zirconia was obtained from MEL Chemicals, zeolites USY (Si/Al=9) and H $\beta$  (Si/Al=40) were, provided by the PQ corporation. All the chemicals were research grade and were used as received without further purification.

### 2.2. Catalyst preparation

The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide as the support and ammonium metatungstate as tungsten precursor. The support was prepared by the hydrolysis of an aqueous solution of zirconium oxychloride with aqueous NH<sub>3</sub>. The precipitate obtained was washed till free from chloride and dried at 120 °C. To an aqueous solution of ammonium metatungstate, zirconium oxyhydroxide powder was added and the mixture was stirred for 8–10 h. The excess of water was evaporated to dryness and the obtained product was dried at 120 °C and calcined in air at different temperatures. A series of catalysts with different WO<sub>3</sub> loading (5–30 wt.% of zirconium oxyhydroxide) were prepared and calcined at 800 °C. In order to study the influence of calcination temperature on catalytic activity, the catalyst 15% WO<sub>3</sub>/ZrO<sub>2</sub> was calcined from 600 to 900 °C. The catalysts are represented by *x* WZ-*t* where, *x* represents wt.%, WZ represents WO<sub>*x*</sub>/ZrO<sub>2</sub> and *t* denotes calcination temperature in °C.

### 2.3. Characterization

The specific surface area of the catalysts were measured by N<sub>2</sub> physisorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer and standard multi point BET analysis methods. Samples were dried at 300 °C in N<sub>2</sub> flow for 2 h before N<sub>2</sub> physisorption measurements.

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

The FTIR spectra of the samples were recorded on a Shimadzu (Model-820 PC) spectrophotometer and TEM images were obtained on a JEOL JEM-1200 EX instrument with 100 kV acceleration voltage to probe the material.

### 2.4. Catalytic activity measurements

The alkylation of *p*-cresol with *tert*-butanol was carried out under atmospheric pressure using a fixed-bed down flow glass reactor (30 cm length and 1.3 cm OD). The catalyst (2 g, 30–40-mesh size) was loaded at the center of the reactor in such a way that the catalyst bed was sandwiched between inert porcelain beads. The reactor was placed in a double-zone furnace equipped with a thermocouple for sensing the reaction temperature. The catalyst was activated at 500 °C for 5 h in a flow of dry air and cooled to the reaction temperature in presence of dry nitrogen before the reactions were conducted. The feed containing a mixture of *p*-cresol and *tert*-butanol of desired molar ratio was introduced into the reactor with a fixed flow rate using a syringe pump (Sage Instruments, Model 352, USA). Nitrogen was used as a carrier gas with a flow rate of 35 ml min<sup>-1</sup>. The products were collected in a cold trap and analyzed by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using HP-5 capillary column (cross linked 5% ME silicone, 30 m  $\times$  0.53  $\times$  1.5  $\mu$ m film thickness). The products were identified by GC-MS and by comparing with authentic samples. Conversion was defined as the percentage of *p*-cresol converted into products.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

#### 3.1.1. Surface area

The pure zirconium oxyhydroxide dried at 120 °C showed a surface area of 331.6 m<sup>2</sup> g<sup>-1</sup>. After calcination at 800 °C, the surface area decreased to 10 m<sup>2</sup> g<sup>-1</sup>. Addition of WO<sub>3</sub> to the support results in an increase of the surface area, which becomes maximum at ca. 61 m<sup>2</sup> g<sup>-1</sup> for 15% WO<sub>3</sub> loading (Fig. 1). This can be explained as the added WO<sub>3</sub> forms a surface over layer that reduces the surface diffusion of zirconia and inhibits sintering [12] and stabilizes the tetragonal phase of zirconia, which leads to an increase in surface area. Above 15% WO<sub>3</sub> loading, XRD indicates the formation of crystalline WO<sub>3</sub>, which probably narrows or plugs pores of the samples, thus leading to the decrease in the specific surface area [14].

The nominal WO<sub>3</sub> loading corresponding to each loading and calcination temperature is determined to calculate the tungsten (W) surface density using the measured surface area. The tungsten surface densities, expressed as the number of W atoms per nanometer square area (W atoms nm<sup>-2</sup>) and were calculated using the equation: surface density of W = {[WO<sub>3</sub> loading (wt.)/100]  $\times$  6.023  $\times$  10<sup>23</sup>}/[231.8

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