

tert-Butylation of *p*-cresol over WO_x/ZrO_2 solid acid catalysts

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Abstract

The *tert*-butylation of *p*-cresol with *tert*-butanol was carried out over WO_x/ZrO_2 catalysts under flow conditions. The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide and ammonium metatungstate. Catalysts with different WO_3 loading (5–30 wt.%) were prepared and calcined at 800 °C and catalyst with 15% WO_3 was calcined from 600 to 900 °C. The catalysts were characterized by surface area, XRD, FTIR and TEM. The catalyst 15% WO_3/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⁻¹, *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 β zeolites and montmorillonite K-10 under the optimized reaction conditions. The activity of sulfated zirconia is lower than that of 15% WO_3/ZrO_2 catalyst calcined at 800 °C and other catalysts showed very low activity. © 2005 Elsevier B.V. All rights reserved.

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, WO_x/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 WO_x/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 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% WO₃/ZrO₂ catalyst calcined at 800 °C with sulfated zirconia (SZ), zeolites like USY, H β and montmorillonite K-10 (clay).

2. Experimental

2.1. Materials

Zirconium oxychloride (ZrOCl₂·8H₂O) 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 ((NH₄)₆H₂W₁₂O₄₀·xH₂O) and montmorillonite K-10 were purchased from Aldrich. Sulfated zirconia was obtained from MEL Chemicals, zeolites USY (Si/Al=9) and H β (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 NH₃. 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 WO₃ 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% WO₃/ZrO₂ was calcined from 600 to 900 °C. The catalysts are represented by *x* WZ-*t* where, *x* represents wt.%, WZ represents WO_{*x*}/ZrO₂ and *t* denotes calcination temperature in °C.

2.3. Characterization

The specific surface area of the catalysts were measured by N₂ 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 N₂ flow for 2 h before N₂ physisorption measurements.

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered Cu K α 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⁻¹. 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 μ 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 m² g⁻¹. After calcination at 800 °C, the surface area decreased to 10 m² g⁻¹. Addition of WO₃ to the support results in an increase of the surface area, which becomes maximum at ca. 61 m² g⁻¹ for 15% WO₃ loading (Fig. 1). This can be explained as the added WO₃ 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% WO₃ loading, XRD indicates the formation of crystalline WO₃, which probably narrows or plugs pores of the samples, thus leading to the decrease in the specific surface area [14].

The nominal WO₃ 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⁻²) and were calculated using the equation: surface density of W = {[WO₃ loading (wt.)/100] \times 6.023 \times 10²³}/[231.8

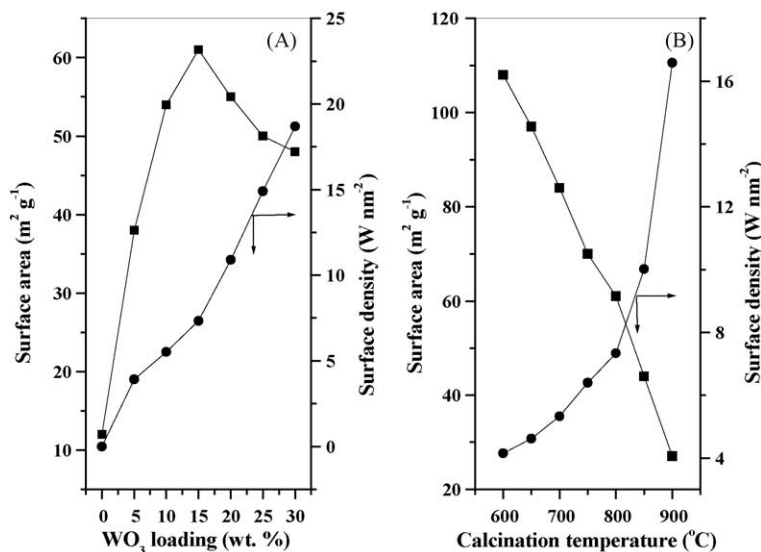


Fig. 1. Surface area and surface density of (A) catalysts with different WO₃ loading calcined at 800 °C and (B) 15 WZ catalyst calcined at different temperatures.

(formula weight of WO₃) × BET surface area (m² g⁻¹) × 10¹⁸]} and are shown in Fig. 1. They show that an increase of the WO₃ loading results in an increase of the W surface density. The specific surface area of WZ catalyst also depends on the calcination temperature. The W surface density increased with the calcination temperature because of the concomitant decrease in the ZrO₂ surface area (Fig. 1).

3.1.2. X-ray diffraction

The XRD pattern of the catalysts with different WO₃ loading calcined at 800 °C (Fig. 2) show that, the presence of WO₃ strongly influences the crystallization of zirconium oxyhydroxide into zirconia. Pure zirconia calcined at 800 °C is mainly monoclinic with only a small amount of the tetragonal phase. For catalysts with low WO₃ loading calcined at 800 °C, the XRD pattern can be described as the sum of the monoclinic and tetragonal phases of zirconia, this latter phase becoming dominant for catalyst with 15% WO₃. The tetragonal content of zirconia at a fixed loading depends on the calcination temperature and for 15% catalyst, zirconia exists mainly in the tetragonal form up to 800 °C and the tetragonal content decreases with further increase in calcination temperature. At high calcination temperature, WO_x species agglomerate into monoclinic WO₃ crystallites and become less effective sintering inhibitors.

Thus, the added WO₃ stabilizes the tetragonal phase of zirconia and such stabilization of tetragonal ZrO₂ in presence of WO₃ and other oxides has been reported in the literature [12,14]. It can also be seen that up to a 10% WO₃ loading for catalysts calcined at 800 °C and for 15% catalyst, up to 750 °C calcination, no XRD peaks which could be attributed to the crystalline WO₃ are observed, indicating that WO₃ is highly dispersed on the support. When the WO₃ loading is

higher than 10%, or when the calcination temperature exceeds 750 °C for 15% loading, new peaks appear in the 2θ region of 23–25°, characteristic of monoclinic WO₃ [15]. Thus, when the W surface density exceeds the theoretical monolayer capacity of ZrO₂ (7 W nm⁻²) i.e., WO₃ loading exceeds monolayer coverage, XRD spectra shows the presence of bulk crystalline WO₃.

3.1.3. FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy is considered as an important tool for analyzing the nature of the surface tungsten oxide species on zirconia. The catalyst 20 WZ-800 shows three distinct bands centered at about 791, 992, 1110 cm⁻¹ (not shown). The band at 791 cm⁻¹ was assigned to a W–O vibration and this band possibly come from both crystalline and non-crystalline species [16]. XRD spectrum of this sample showed the presence of monoclinic WO₃ crystallites, hence this unambiguously indicates the connection between the 1110 cm⁻¹ band and the WO₃ phase. The band at 1110 cm⁻¹ is due to the presence of a fraction of monoclinic WO₃ phase, and the band at 992 cm⁻¹ is due to a polytungstate structure with tungsten in octahedral coordination [17]. This band appears at lower wave number than those reported in the literature [18,19].

3.1.4. Transmission electron microscopy (TEM)

From the TEM images of 5 WZ-800 and 15 WZ-800 catalysts (Fig. 3), it is clear that the ZrO₂ particle size is smaller in 15 WZ-800 catalyst compared to 5 WZ-800 catalyst. The particle size of 5 WZ is in the range of 23–27 nm, while that of 15 WZ was >20 nm. This clearly indicates that WO_x interacts strongly with ZrO₂ and prevents the growth of crystallite size and stabilize ZrO₂ in tetragonal form.

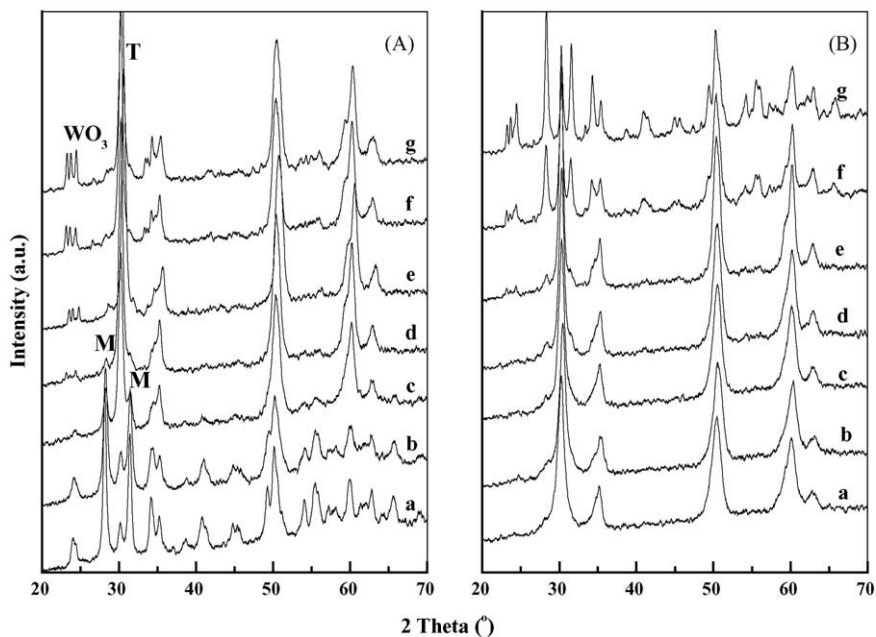
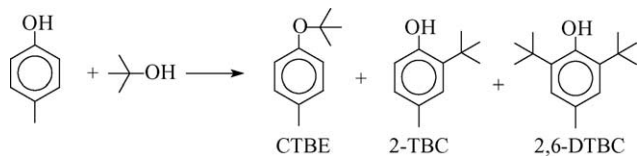


Fig. 2. XRD patterns of (A) (a) ZrO₂, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25, and (g) 30 WZ-800 catalysts and (B) 15 WZ catalyst calcined at (a) 600, (b) 650, (c) 700, (d) 750, (e) 800, (f) 850, and (g) 900 °C.

3.2. Catalytic activity

The main products of the *tert*-butylation of *p*-cresol are 2-*tert*-butyl-*p*-cresol (2-TBC), 2,6-di-*tert*-butyl-*p*-cresol (2,6-DTBC) and *p*-cresol-*tert*-butyl ether (CTBE) (Scheme 1). C₈ and C₁₂ olefins, formed by the oligomerization of isobutene are also observed in the reaction mixture, where, isobutene is formed by the acid catalyzed dehydration of *tert*-butanol.



Scheme 1.

3.3. Effect of WO₃ loading

In order to investigate the effect of WO₃ loading, 5–30 WZ-800 catalysts are used in alkylation of *p*-cresol with *tert*-butanol at 120 °C with a flow rate of 10 ml h⁻¹ (Fig. 4). Pure ZrO₂ calcined at 800 °C shows negligible activity. Among the catalysts with different WO₃ content, the catalyst 5 WZ showed the lowest *p*-cresol conversion (7.7%), while the catalyst 15 WZ gave the highest conversion (26.7%). Further increase in WO₃ loading decreases the *p*-cresol conversion, as for 30 WZ it is 24.1%.

The selectivity to different alkylated products also depends on WO₃ loading. The catalyst 5 WZ shows the highest selectivity to CTBE. As the *p*-cresol conversion increases from 7.7% for 5 WZ catalyst to 26.7% for 15 WZ catalyst, the selectivity to CTBE decreases from 94.5 to 12.1%. The catalyst 5 WZ shows 5.5% selectivity to 2-TBC and it increases

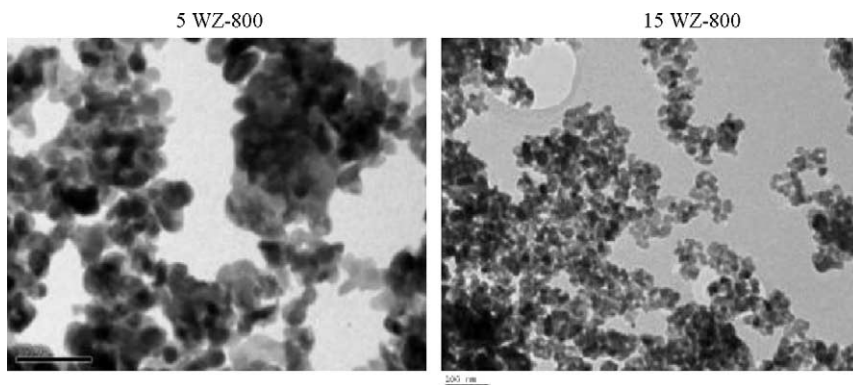


Fig. 3. TEM images of 5 and 15 WZ-800 catalysts.

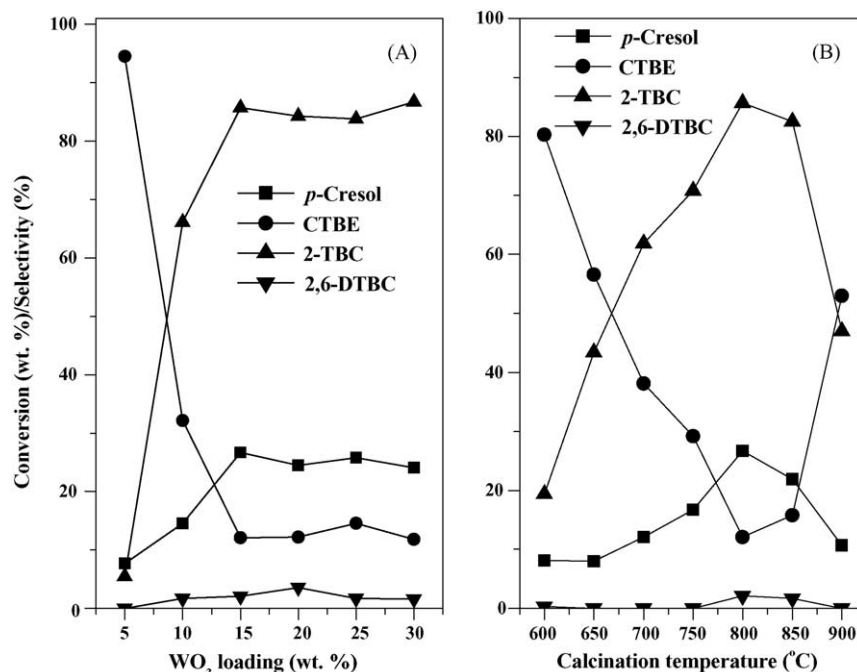


Fig. 4. Effect of (A) WO₃ loading and (B) calcination temperature on *p*-cresol conversion and product selectivity. Conditions: temperature = 120 °C; *tert*-butanol/*p*-cresol molar ratio = 1, flow rate = 10 ml h⁻¹, time = 2 h.

to 85.7% for 15 WZ catalyst. The catalyst 15 WZ shows 2,6-DTBC selectivity of 2.1%.

3.4. Effect of calcination temperature

The catalyst 15 WZ calcined from 600 to 900 is used to study the change in catalytic activity with calcination temperature. From Fig. 4, it is clear that calcination temperature has a profound effect on catalytic activity. The catalyst calcined at 600 °C shows 8.1% *p*-cresol conversion, which increases to 26.7% at 800 °C. Further increase in calcination temperature decreases *p*-cresol conversion.

The selectivity to different alkylated products also varies with calcination temperature. As the conversion increased from 8.1% for the catalyst calcined at 600 °C to 26.7% for the one calcined at 800 °C, while the selectivity to CTBE decreased from 80.3 to 12.1%. A decrease in CTBE selectivity results in an increase in 2-TBC selectivity from 19.4 to 85.7%. As the calcination temperature increased from 800 to 900 °C, the selectivity to CTBE increased from 12.1 to 53%, while the selectivity to 2-TBC decreased from 85.7 to 47%.

Iglesia co workers from in situ acidity measurements showed that Brönsted acidity of WZ catalysts increases up to monolayer coverage of WO₃ on zirconia [20]. The change in catalytic activity with loading and calcination temperature shows that the catalyst 15 WZ-800 shows the highest catalytic activity. The W surface density of this catalyst is found to be 7.34 W nm⁻², which is slightly higher than the monolayer coverage of WO₃ on zirconia [20]. At high W surface densities, XRD shows the presence of bulk crystalline WO₃ and hence the active sites are inaccessible to the reactants

and this decreases the catalytic activity. The highest catalytic activity at a surface density of 7.34 W nm⁻² clearly indicates that irrespective of WO₃ loading and calcination temperature, catalytic activity depends on WO₃ coverage and the highest activity corresponds to monolayer of WO₃ on zirconia.

3.5. Effect of reaction temperature

The reaction is studied at various temperatures from 110 to 160 °C using the catalyst 15 WZ-800. The variation of *p*-cresol conversion and selectivity to different products with temperature are shown in Fig. 5. At 110 °C, *p*-cresol conversion was 15.2% and it increased to 47.7% at 130 °C. An increase of reaction temperature above 130 °C results in decrease of *p*-cresol conversion. The decrease in conversion may be due to the dealkylation of 2-TBC to *p*-cresol at high temperature and also the diminishing availability of *tert*-butanol as it undergoes oligomerization rather than alkylation [21].

The selectivity to CTBE was 37.5% at 110 °C and as the temperature increases, the selectivity to CTBE decreased to 1.5% at 130 °C. The decrease in CTBE selectivity with temperature may be due to its rearrangement to C-alkylated product. This is clear from the fact that as the temperature increases from 110 to 130 °C, 2-TBC selectivity increased from 62.6 to 93.7%. Indeed, it has been shown that such rearrangements occurred on heating in presence of an acid catalyst [22]. The highest selectivity to 2,6-DTBC is found to be at 130 °C (4.8%) due to the higher stability and the availability of *tert*-butyl cation at lower reaction temperature.

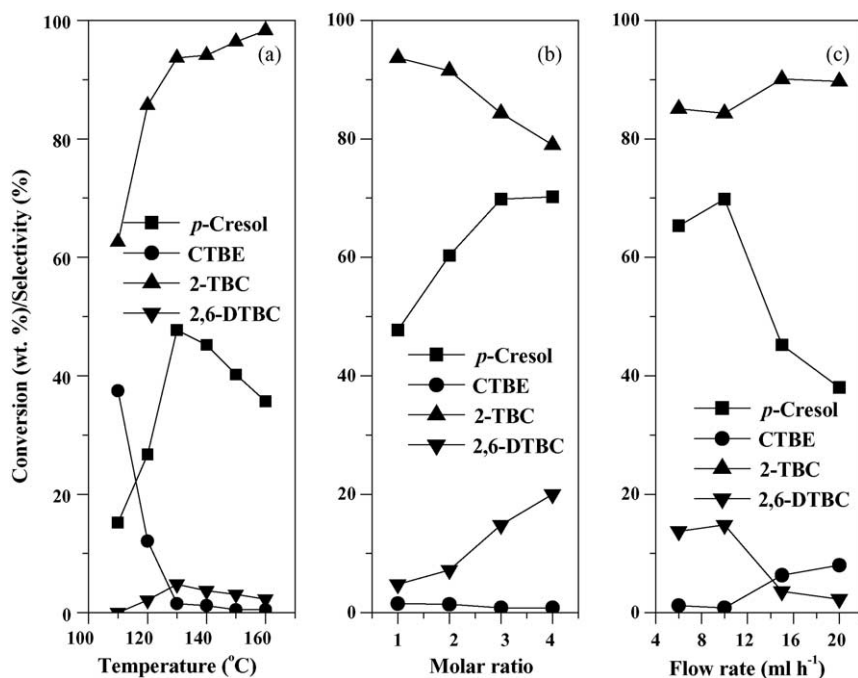


Fig. 5. (a) Effect of reaction temperature on *p*-cresol conversion and product selectivity. Conditions: *tert*-butanol/*p*-cresol molar ratio = 1, flow rate = 10 ml h⁻¹, time = 2 h. (b) Effect of molar ratio on *p*-cresol conversion and product selectivity. Conditions: temperature = 130 °C; flow rate = 10 ml h⁻¹, time = 2 h. (c) Effect of flow rate on *p*-cresol conversion and product selectivity. Conditions: temperature = 130 °C; *tert*-butanol/*p*-cresol molar ratio = 3, time = 2 h.

3.6. Effect of molar ratio

The effect of molar ratio on *p*-cresol conversion and product selectivity is studied at 130 °C with *tert*-butanol/*p*-cresol molar ratio of 1 to 4 (Fig. 5). Generally, the *p*-cresol conversion increased with an increase in the amount of *tert*-butanol. At a molar ratio of 1, *p*-cresol conversion is found to be 47.7%, which increased to 60.3% at a molar ratio of 2. An increase of mole ratio from 2 to 3 added an additional 9.5% conversion. A further increase in mole ratio had no effect on *p*-cresol conversion. It was shown that the polar molecule such as methanol and higher alcohols compete with phenolic compounds for adsorption sites and an increase in the molar excess of alkylating agent results in an increase in conversion [23].

The selectivity to CTBE is very low under these conditions. With an increase in molar ratio from 1 to 4, the selectivity to 2-TBC is decreased from 93.7 to 79%, while 2,6-DTBC selectivity increased from 4.8 to 20%. This could be due to the higher availability of *tert*-butanol, which leads to the formation of the dialkylated product.

3.7. Effect of flow rate

The effect of flow rate was studied at 130 °C using *tert*-butanol/*p*-cresol molar ratio of 3 (Fig. 5). With an increase in flow rate from 6 to 10 ml h⁻¹, *p*-cresol conversion increased from 65.3 to 69.8% and further increases in flow rate, decreases the conversion as for the flow rate of 20 ml h⁻¹ the conversion was 38%. The decrease in conversion with an in-

crease in flow rate is due to the lower time available for the reactants to be in contact with the active sites.

The selectivity to different products also varies with flow rate. The selectivity to 2-TBC increased slightly from 85.1 to 89.7% as the flow rate increased from 6 to 15 ml h⁻¹. As the flow rate increased from 6 to 20 ml h⁻¹, CTBE selectivity increased from 1.2 to 8%, while 2,6-DTBC selectivity decreased from 13.7 to 2.3%.

3.8. Effect of time on stream

In order to study the deactivation behavior of the catalyst, the reaction is studied at 130 °C with a flow rate of 10 ml h⁻¹ (WHSV = 4.3 h⁻¹) using *tert*-butanol/*p*-cresol molar ratio of 3, for 25 h (Fig. 6). The *p*-cresol conversion is found to be 69.8% at second hour with selectivity to 2-TBC 92.4%, 2,6-DTBC 6.3% and CTBE 1.3%. Conversion of *p*-cresol decreased from 69.8 to 52.2% in the course of 25 h, while the selectivity to different products is similar during the time of the reaction.

For comparison *tert*-butylation of *p*-cresol is also carried out over sulfated zirconia, SZ (Fig. 6). The catalyst shows lower activity compared to 15 WZ-800 catalyst as it shows 55% *p*-cresol conversion at second hour with selectivity to 2-TBC 90.3%, 2,6-DTBC 7.3 and CTBE 2.5%. The conversion is decreased to 39.5% after 25 h keeping product selectivity similar. Both the catalysts 15 WZ-800 and SZ shows about 15% loss in conversion in 25 h, suggesting the catalyst deactivation is mainly due to the presence of heavy products on the catalyst surface.

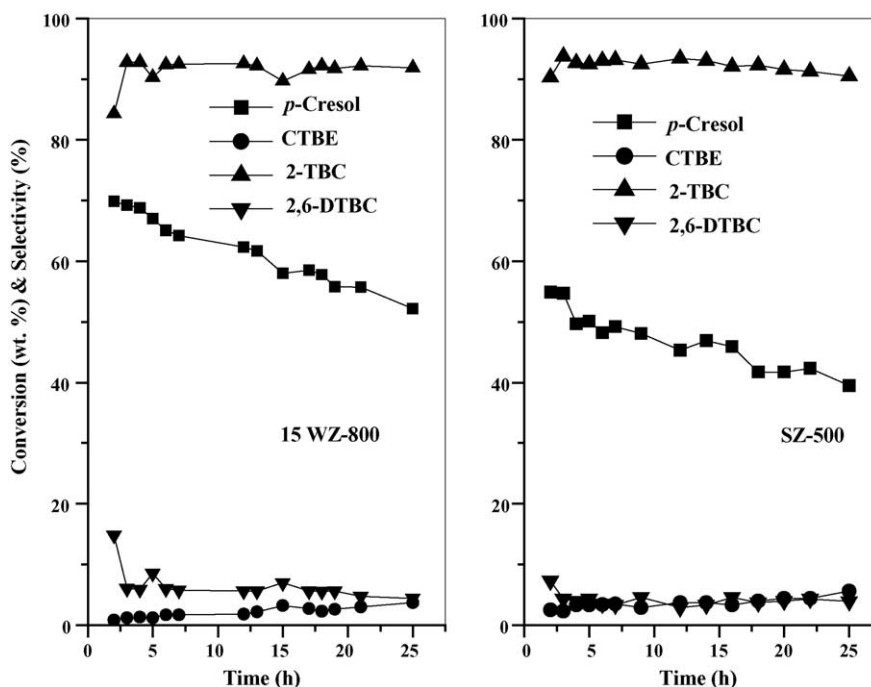


Fig. 6. Effect of time on stream on phenol conversion and product selectivity over 15 WZ-800 and SZ-500 catalysts. Conditions: temperature = 130 °C; flow rate = 10 ml h⁻¹; *tert*-butanol/*p*-cresol molar ratio = 3.

3.9. Comparison with zeolites and montmorillonite K-10

The alkylation of *p*-cresol with *tert*-butanol was studied using zeolites like USY, H β and montmorillonite K-10 (Fig. 7). The activity of USY is higher than

H β and K-10. For USY, K-10, and H β , *p*-cresol conversion is less than 25% under the reaction conditions. The difference in activity among these catalysts may be due to the difference in pore structure and acidity.

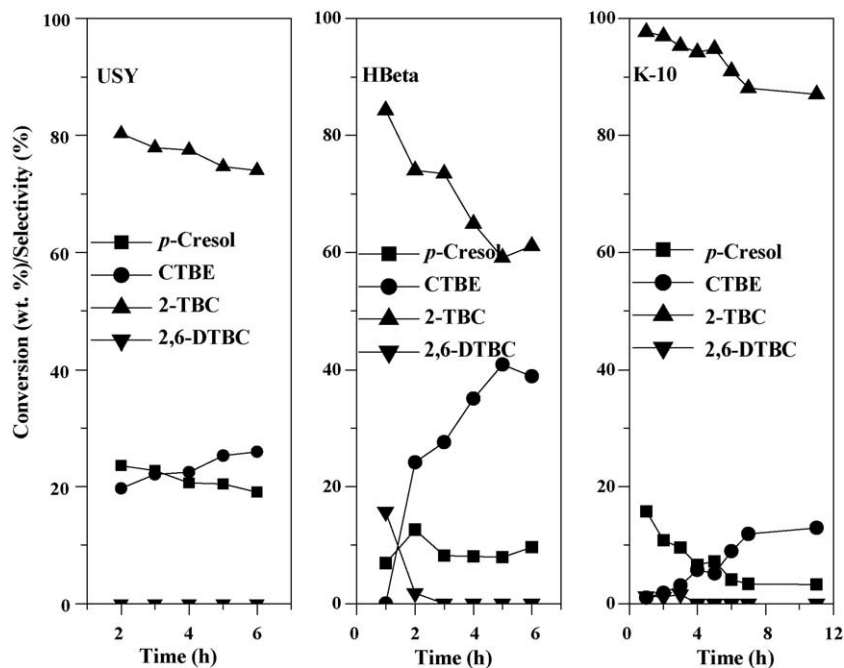


Fig. 7. Effect of time on stream on *p*-cresol conversion and product selectivity over USY, H β , and montmorillonite K-10 catalysts. Conditions: temperature = 130 °C; flow rate = 10 ml h⁻¹; *tert*-butanol/*p*-cresol molar ratio = 3.

4. Conclusions

The alkylation of *p*-cresol with *tert*-butanol has been studied in detail using WO_x/ZrO_2 catalysts in a continuous fixed-bed down flow reactor and the catalytic activity is compared with sulfated zirconia, zeolites like USY, H β and montmorillonite K-10 under the optimized reaction conditions. The catalyst 15% WO_3/ZrO_2 calcined at 800 °C was found to be the most active catalyst. Under the optimized reaction conditions of 130 °C, *tert*-butanol/*p*-cresol molar ratio of 3 and WHSV of 4.3 h⁻¹, *p*-cresol conversion was 69.8% with selectivity to 2-TBC 92.4%, 2,6-DTBC 6.3% and CTBE 1.3%. The activity of sulfated zirconia is found to be lower than that of 15% WO_3/ZrO_2 catalyst calcined at 800 °C and other catalysts show very low catalytic activity.

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