Selective *C*-methylation of phenol with methanol over borate zirconia solid catalyst

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Abstract

Selective *C*-methylation of phenol to *o*-cresol and 2,6-xylenol in high yields has been carried out with methanol over borate zirconia solid acid catalyst. The maximum conversion of 70 and 65% selectivity for corresponding *ortho*-alkylated products (*o*-cresol and 2,6-xylenol) was obtained with 1–2% anisole as *O*-alkylated product. A series of borate zirconia catalysts with 5–30 mol% B_2O_3 loading were prepared and calcined at different temperatures. The XRD results reveal the formation of single phase cubic zirconia after addition of B_2O_3. The cubic structure was stable up to 650 °C, above which it transformed to monoclinic structure. Borate zirconia containing 5 mol% B_2O_3 calcined at 650 °C was found to be the most active catalyst among the series indicating the influence of composition and structure on the conversion and selectivity. The FTIR results provided the evidence for the vertical orientation of phenol aromatic ring on the catalyst surface, which explains the selective *C*-alkylation of phenol. The influence of various experimental parameters on phenol conversion and product selectivity has been investigated. The catalyst was active for 150 h time on stream without any deactivation showing its longer life. The catalytic activity and selectivity is correlated with its acidity and structure.
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1. Introduction

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites and metal oxides constitutes a class of reactions important both academically and industrially. Among alkylation reactions, methylation of phenol has attracted considerable attention due to industrial importance of methyl phenols as chemical intermediates in the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [1]. In particular, *ortho*-alkylated phenols such as *o*-cresol, 2,6-xylenol and trialkyl substituted phenols are more important alkyl phenols. For example, epoxy cresol novolac (ECN) and polyphenylene oxide (PPO) used in the electronic industries and automobile industries are derived from *o*-cresol and 2,6-xylenol, respectively [1]. After suitable processing *o*-cresol is used in the synthesis of herbicides as well as in sealing material for integrated circuits, whereas

2,6-xylenol is used in manufacture of disinfectant and in high impact resistant resins [2]. A variety of catalysts such as hydrotalcites, ferrospinels, zeolites like H-beta, ZSM-5, H-Y, acidic and basic oxides have been previously used for alkylation of phenol [3–6]. Coking due to reaction products of phenol methylation gives rise to fast deactivation in case of most of the catalysts [7]. The alkylation of phenol with methanol being an acid–base catalyzed reaction; the product selectivity depends upon the acidity as well as basicity of the catalyst. Phenol alkylation using various acid and base catalysts has been reported. Phenol conversion as well as product selectivity is found to depend on the acid–base properties of the catalyst, temperature [8] and residence time [9]. Most of the acid catalyzed reactions are reported to give predominantly *C*-alkylation i.e. *o*-cresol and 2,6-xylenol in wide temperature range. Phenol alkylation using Cu–Al–HT to give selectively *C*-alkylation is due to its high acidity. In this case, selectivity for anisole increases slightly (∼10%) at lower temperature (300–350 °C) [3]. Solid base catalysts are reported to give *O*-alkylated product i.e. anisole at lower temperature (200–250 °C), however at higher temperature same catalyst gives *C*-alkylated products. The *C*-alkylated product

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formation is reported to proceed through anisole formation. Effect of basicity using cation exchanged zeolite X showed that increase in basicity increases selectivity for *O*-alkylation of phenol upto 100% in case of superbase catalyst (Cs exchanged zeolite X) [10]. Basic zeolite X gives anisole at lower temperature (220–290 °C) whereas basic Mn_2O_3 is reported to give *o*-cresol and 2,6-xylenol at 475 °C [11]. This shows the effect of temperature on product selectivity. Low acidity is also reported to favor *O*-alkylation at lower temperature. *O*-Alkylation is also affected by residence time. Basic Mg–Al–HT shows higher selectivity for anisole at low residence time where as at higher residence time selectivity for *C*-alkylation increases at the expense of anisole [12]. Hence it is proposed that at lower temperature and lower residence time anisole is formed which undergoes rearrangement and further alkylation at higher temperature and high residence time to give *o*-cresol and 2,6-xylenol at the expense of anisole. Methylating agents such as methyl carbonates favors *O*-alkylation and almost quantitative yields of anisole has been reported with dimethyl carbonate [13,14]. Hence it can be concluded that basicity or very low acidity favors *O*-alkylation at lower temperature whereas moderate or high acidity favors *C*-alkylation. The selective *C*-alkylation of phenol with methanol over basic MgO has been also explained on the basis of vertical orientation of phenoxide aromatic ring on the catalyst surface and *O*-alkylation due to its parallel orientation on acid catalyst surface [15]. These previous results indicate lot of discrepancies in correlation of acidic and basic nature of catalyst and its influence on *C*- or *O*-alkylation of phenol.

To our knowledge there are no reports on methylation of phenol using superacid catalyst. B_2O_3 supported on zirconium oxide containing 30 mol% of boron has been reported as a superacid catalyst (acidic strength $H_o = -13$) by Arata and coworkers [16,17] and Xu et al. [18,19] have used B_2O_3/ZrO_2 catalyst for gas phase Beckman Rearrangement of cyclohexanone oxime. Recently we have also utilized the acidic property of this catalyst for benzoylation of anisole [20]. It is well established that the catalytic properties of zirconia-based catalysts are very sensitive to the methods of preparation and subsequent heat treatments [21]. Considering the chemical inertness and amphoteric nature of zirconia support as well as superacidic nature of borate zirconia, methylation of phenol using this catalyst seemed to be an interesting study from selectivity and catalyst life point of view. In the present article we report the performance of B_2O_3/ZrO_2 catalyst for alkylation of phenol with methanol.

2. Experimental

2.1. Chemicals

Boric acid and phenol (AR grade) were obtained from S.D. Fine Chemicals. Zirconyl oxichloride (AR grade, Loba), and 25% aqueous ammonia (Merck) were used as such without further purification. Methanol (AR grade, Thomas Becker) was purified by standard literature method and freshly distilled prior to use.

2.2. Catalyst preparation

Zirconyl oxychloride [$ZrOCl_2 \cdot 8H_2O$] (39.7 g, 123.2 mmol) was dissolved in 110 ml distilled water to which aqueous ammonia (25%) was added dropwise with constant stirring till the solution became alkaline (pH 10) and zirconyl hydroxide precipitates as white solid. The resultant solution was filtered and the residue was washed with hot distilled water till free from chloride ions. The residue was dried in an oven at 85 °C for 12 h. Boric acid [H_3BO_3] (0.79 g, 12.9 mmol) was dissolved in 150 ml distilled water. Zirconyl hydroxide obtained above was added to the boric acid solution with constant stirring to obtain a slurry. It was heated to dryness and further heated in an oven at 110 °C for 5 h and calcined at various temperatures (in the range 500–750 °C). The molar composition of this catalyst was 0.05 B_2O_3:0.95 ZrO_2. Similarly a series of the catalysts containing 1, 3, 10, 15, 20 and 30 mol% B_2O_3 were prepared by the above method by using corresponding amount of boric acid and zirconium oxichloride.

2.3. Catalyst characterization

X-ray diffraction (XRD) analysis was done using Rigaku miniflex (Cu Kα radiation) and BET surface area was determined using NOVA 1200 Quanta chrome. Scanning electron microscope JEOL JSM 500 was used for SEM images. Thermal analysis (TG-DTA) was done on Mettler-Toledo whereas TGA/DTA was done on TGA/SDTA 851 instrument. Micromeritics Autochem 2910 was used for temperature programmed desorption (TPD) of ammonia. Shimadzu FTIR 8000 series with DRIFT assembly was used for phenol adsorption studies on the catalyst surface.

2.4. Vapor phase methylation of phenol

The catalyst prepared by the above method was molded in the form of a pellet, which was granulated to −10 to +20 mesh size. Vapor phase methylation experiments were performed in a fixed-bed continuous down flow glass reactor at the atmospheric pressure. A tubular glass reactor of 10 mm diameter and 25 cm length was loaded with 3 g of the borate zirconia catalyst in granulated form. The upper part of the reactor was packed with inert ceramic beads as the preheating zone. The catalyst was preheated at 450 °C for 12 h in a 10 ml/min airflow. The reactions were carried out by passing a mixture of phenol and methanol using syringe pump (sage feed pump), in the temperature range of 350–450 °C with nitrogen as carrier gas at the rate of 10 ml/min. The weight hourly space velocity (WHSV) was varied from 1 to 4 h^{-1}. The reaction mixture was collected in a receiver maintained at 9 °C.

Product analysis was done using gas chromatography on Perkin Elmer autosystem XL equipped with capillary column PE-1 (30 m length, 0.25 mm internal diameter and 1 μm film thickness) and flame ionization detector. Products were characterized by GC-MS (Shimadzu, DB-I column) and GC-IR (Perkin Elmer Spectrum 2001, column DB-1, 25 m length, 0.32 mm internal diameter).

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of 30% B_2O_3/ZrO_2 catalyst calcined at various temperatures are shown in Fig. 1. At 500 °C (1a) the catalyst shows absence of any crystalline phase whereas at 550 °C (1b) small peaks start developing suggesting the beginning of formation of a crystalline phase. At 600 °C (1c) a crystalline cubic phase of zirconia is clearly visible which is stable up to 650 °C (1d). However it is interesting to note that at 700 °C the cubic phase is almost completely transformed in to monoclinic phase. This shows higher thermal stability of cubic zirconia catalyst (up to 650 °C), which is at least 150 °C higher than pure zirconia. Pure zirconia transforms from metastable cubic phase to monoclinic phase at about 500 °C. Fig. 2 shows the X-ray diffraction
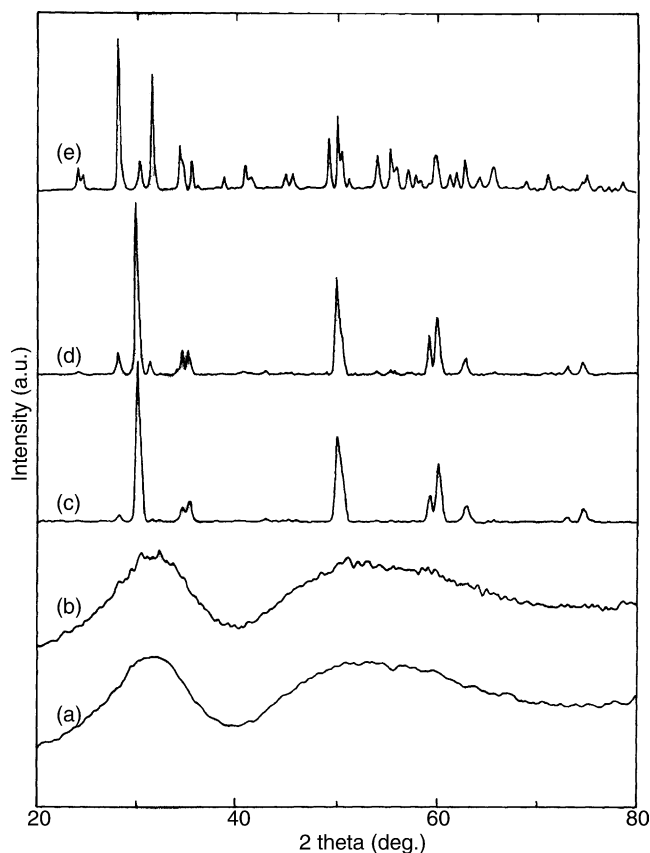

Fig. 2. X-ray diffraction pattern of: (a) pure ZrO_2; (b) 1% B_2O_3/ZrO_2; (c) 5% B_2O_3/ZrO_2; (d) 10% B_2O_3/ZrO_2; (e) 20% B_2O_3/ZrO_2; (f) 30% B_2O_3/ZrO_2 calcined at 650 °C.

pattern of a series of catalysts with different boron oxide content, calcined at 650 °C. Pure zirconia shows monoclinic phase (2a). It is seen that addition of 1% boron oxide stabilizes zirconia into cubic fluorite phase (2b) with a small impurity of monoclinic phase. This monoclinic phase impurity decreases with further addition of boron oxide up to 30%. The surface area of the borate zirconia catalysts was found to be in the range of 100–125 m^2/g as compared to 62 m^2/g for pure zirconia. The increased surface area of zirconia after impregnation with boron oxide shows the better dispersion of boron oxide on the surface of zirconia. XPS study showed the binding energy to be 191.9 eV for B 1 s, which is in good agreement with standard value of 192 eV for B^{3+}. SEM of 5% B_2O_3/ZrO_2 calcined at 650 °C (Fig. 3) shows the particle size to be in the range of 1–2 μ with agglomerates and non-uniform distribution

Fig. 1. X-ray diffraction pattern of 30% B_2O_3/ZrO_2 calcined at temperatures: (a) 500 °C; (b) 550 °C; (c) 600 °C; (d) 650 °C; (e) 700 °C.
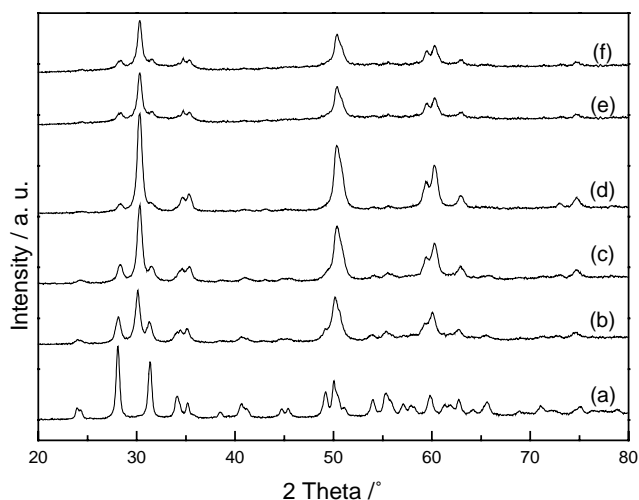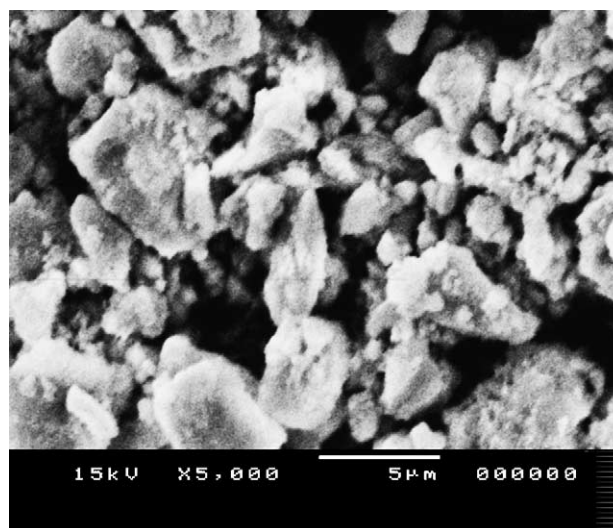

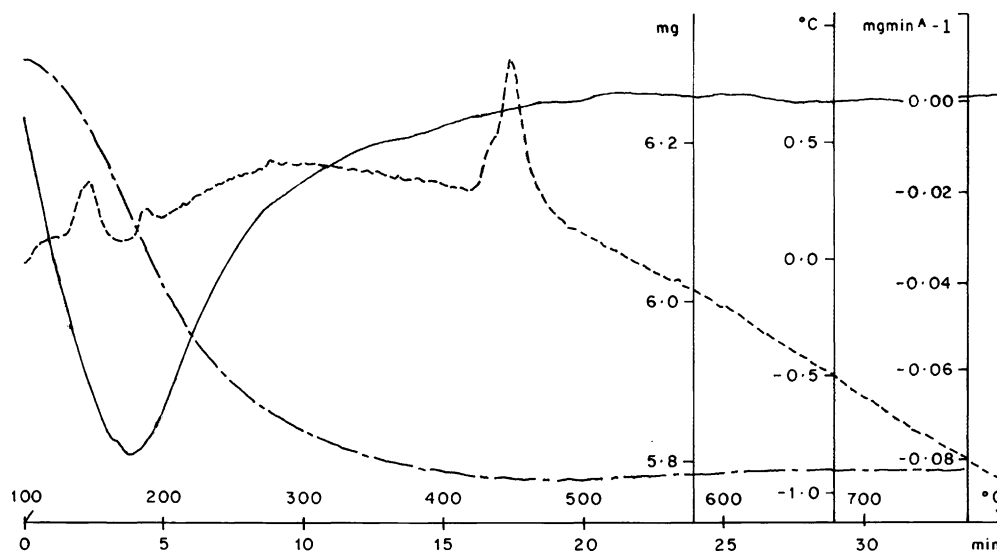Fig. 3. SEM image of 5% borate zirconia calcined at 650 °C.

Fig. 4. TG/DTA/DTG of 5% B_2O_3/ZrO_2 calcined at 650 °C.

of the particles. TG/DTA/DTG analysis of 5% borate zirconia (calcination temperature 650 °C) is shown in Fig. 4. Initial weight loss of 5.3% (up to 250 °C) as evident from the TG curve is attributed to the loss of adsorbed moisture on the surface of the catalyst while marginal weight loss of 3.9% over a wide temperature range (250–750 °C) shows the thermal stability of the catalyst. DTA plot of $Zr(OH)_4$ and $B(OH)_3$ with $Zr(OH)_4$ (Fig. 5) shows a sharp peak at 450 °C for pure $Zr(OH)_4$ which corresponds to the phase change from crystalline cubic to monoclinic while the corresponding peak for boria supported zirconia is shifted to 725 °C suggesting enhanced thermal stability of cubic zirconia due to the addition of boron oxide. Fig. 6 shows comparison of TPD of B_2O_3/ZrO_2 with 5 and 30% borate on zirconia. Ammonia was desorbed below 400 °C in case
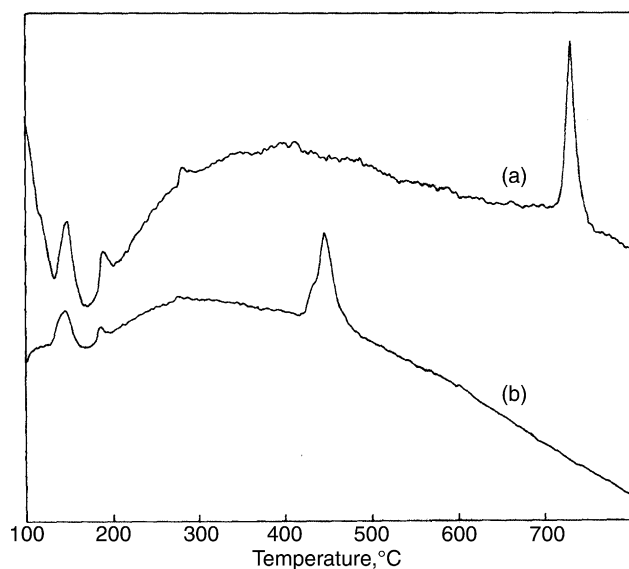
of both the samples. The acid site density was found to be 0.263 mmol/g for 5% B_2O_3/ZrO_2 and 0.386 mmol/g in case of 30% B_2O_3/ZrO_2. The 30% B_2O_3/ZrO_2 shows strong (270–320 °C) as well medium acid sites (150–230 °C), while 5% B_2O_3/ZrO_2 shows only medium acid sites (150–250 °C) which indicates the moderate acidity of 5% B_2O_3/ZrO_2. The acid site density in case of 30% B_2O_3/ZrO_2 is quite high for its use as a solid acid catalyst.

3.2. Phenol adsorption on B_2O_3/ZrO_2

Selectivity in phenol alkylation (*O*- or *C*-alkylation) is reported to depend on the acid–base properties of the catalyst [22]. While basic MgO catalyst favors *C*-alkylation, acidic SiO_2–Al_2O_3 catalyst does not favor this reaction (it gives *O*-alkylation) due to the orientation of phenol aromatic ring with respect to the catalyst surface as shown in Fig. 7a [23]. IR studies have shown that after adsorption on the catalyst
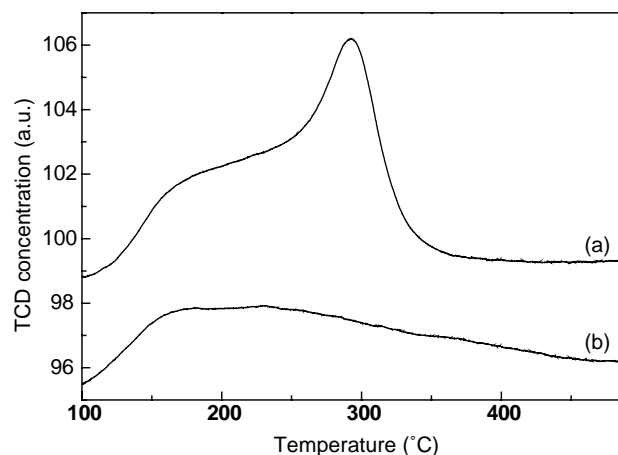

Fig. 5. DTA analysis of as synthesized: (a) ZrO_2; (b) 5% B_2O_3/ZrO_2 calcined at 650 °C.

Fig. 6. Temperature programmed desorption of ammonia on: (a) 30% B_2O_3/ZrO_2 and (b) 5% B_2O_3/ZrO_2.
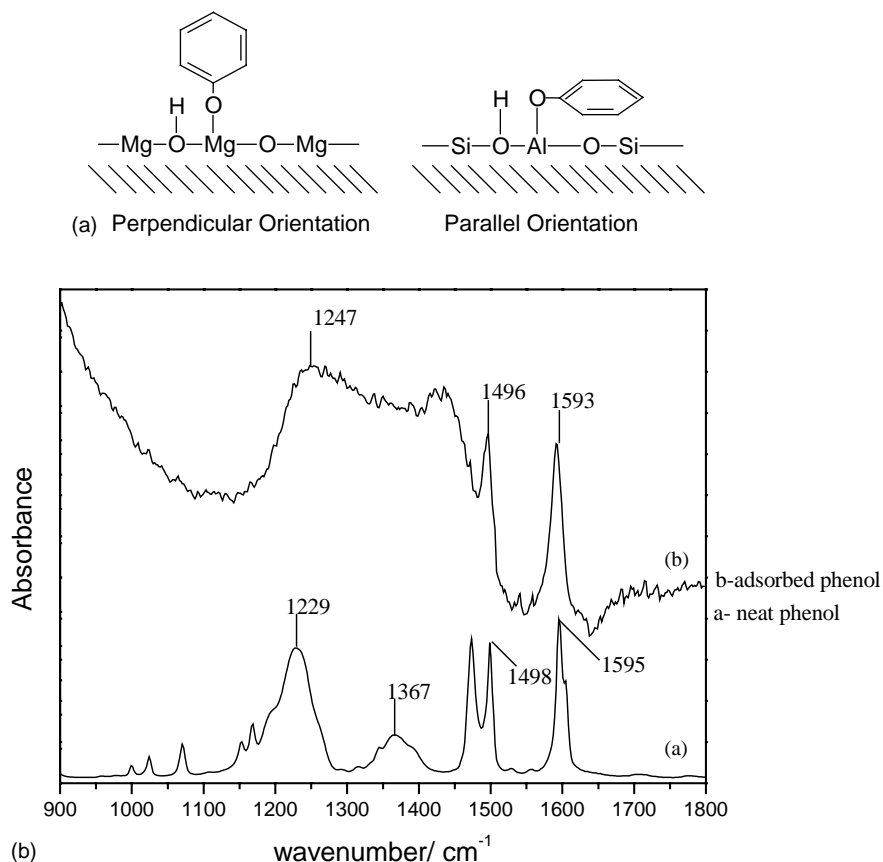
Fig. 7. (a) Orientation of phenol on the surface of basic and acidic catalyst. (b) FTIR spectra of neat phenol and phenol adsorbed on the 5% B_2O_3/ZrO_2 catalyst.

surface, phenol dissociates in to phenoxide ion and proton. In case of basic catalyst (MgO) the aromatic ring is shown to be perpendicular to the catalyst surface facilitating *ortho*-alkylation. However in case of acidic SiO_2–Al_2O_3 the aromatic ring is parallel to the catalyst surface and the π electrons of the ring interact with the catalyst surface. When phenol was adsorbed on B_2O_3/ZrO_2, the comparison of IR spectra of neat phenol with phenol adsorbed on the surface of 5% borate zirconia (Fig. 7b) clearly indicated vertical orientation of the aromatic ring. Disappearance of C–O–H in plane bending vibration peak of free phenol (at $1385\,cm^{-1}$), in case of adsorbed phenol clearly shows the dissociation of O–H bond and formation of phenoxide ion. The C–O stretching vibration at $1229\,cm^{-1}$ (free phenol melt) is shifted to a higher frequency to $1250\,cm^{-1}$, which indicates that C–O bond of adsorbed phenol is stronger than in free phenol. It is due to dissociation of stronger O–H bond and the formation of weaker O–Zr bond. The minor shift in the aromatic ring vibrations (1595, 1498 shifted to 1593 and $1496\,cm^{-1}$, respectively) shows absence of any direct interaction of aromatic π electrons with the catalyst surface, which rules out the possibility of horizontal orientation of aromatic ring with respect to the catalyst surface. Li et al. [24] have reported the adsorption of phenol on zeolite HY and have shown the interaction of phenol oxygen with acidic hydroxyl groups of HY.

In this it is shown that after adsorption, the OH stretching vibration of free phenol at $3657\,cm^{-1}$ has disappeared and the C–O–H in plane bending vibrational band at $1385\,cm^{-1}$ has shifted to $1360\,cm^{-1}$, whereas no change in the aromatic ring vibration at 1600 and $1500\,cm^{-1}$ (vapor phase) was observed after adsorption. From the shift in the IR frequencies after phenol adsorption on B_2O_3/ZrO_2 it can be said that aromatic ring is perpendicular to the catalyst surface minimizing the interaction of π electrons with the surface. This orientation facilitates the attack of adsorbed alkyl moiety at *ortho* position giving high yields of *o*-cresol and 2,6-xylenol.

3.3. Catalytic activity for methylation of phenol

The methylation of phenol using 30% B_2O_3/ZrO_2 catalyst calcined at 550 °C showed 12% conversion with the selectivity for *o*-alkylated product in the range of 60–65%, the conversion was increased up to 54% when the calcination temperature was gradually increased to 650 °C (Fig. 8). However at still higher calcination temperatures, 700 and 750 °C, there is a decrease in conversion to 35 and 6%, respectively. Initial increase and later decrease in the phenol conversion is attributed to the structural change in the catalyst at the respective calcination temperatures. In the temperature range of 500–650 °C the crystallinity of the cat-
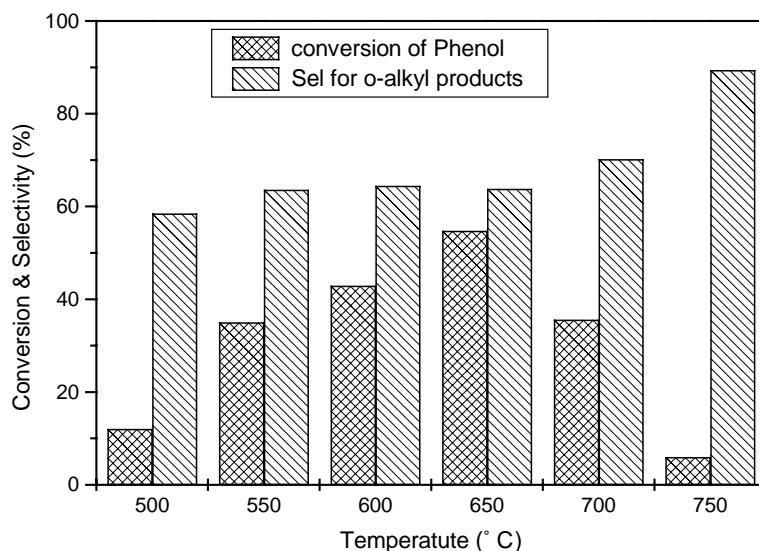
Fig. 8. Effect of calcination temperature on conversion and selectivity.

alyst gradually increases and a cubic structure of zirconia is observed till 650 °C, whereas above 650 °C, the structure is transformed in to monoclinic phase (Fig. 1). This indicates the non-active nature of the monoclinic phase of the catalyst. The product analysis showed 97.65% selectivity for C-alkylated products viz. o- and p-cresol, 2,6-, 2,5- and 3,5-xylenols, mesitols and durenols. Only 2.35% of anisole is formed as O-alkylated product indicating favored C-alkylation of phenol over strong and medium acid sites of the 30% B₂O₃/ZrO₂ catalyst.

3.3.1. Effect of borate loading

Effect of borate loading on the conversion of phenol is shown in Fig. 9. The maximum conversion of 62.3% was observed for the catalyst with 5% borate loading, this might

be due to the higher uniform dispersion of borate on zirconia support as well as moderate acidity. At higher boria loading the decrease in the conversion could be due to the non-uniform distribution of borate on zirconia support as well as higher acidity. These results suggest that the moderate acidity is more favorable for this reaction than strong acidity.

3.3.2. Effect of temperature

The results of the phenol methylation carried out at various temeperatures showed maximum conversion (62.3%) at 400 °C and 62% selectivity for ortho-alkylated products (Fig. 10). At lower temperature (350 °C) the maximum selectivity of 85% was observed however with low conversion (12%). As expected the rate of reaction and conversion increases with temperature. The formation of poly-methylated
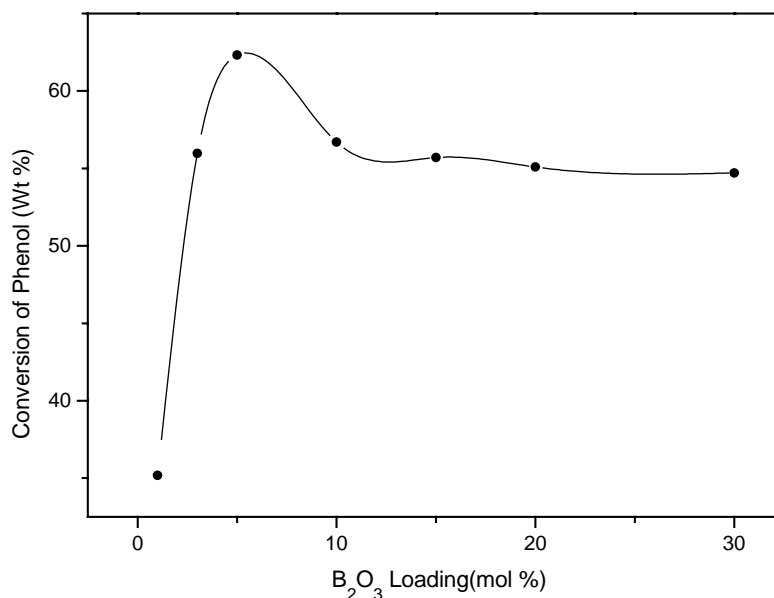

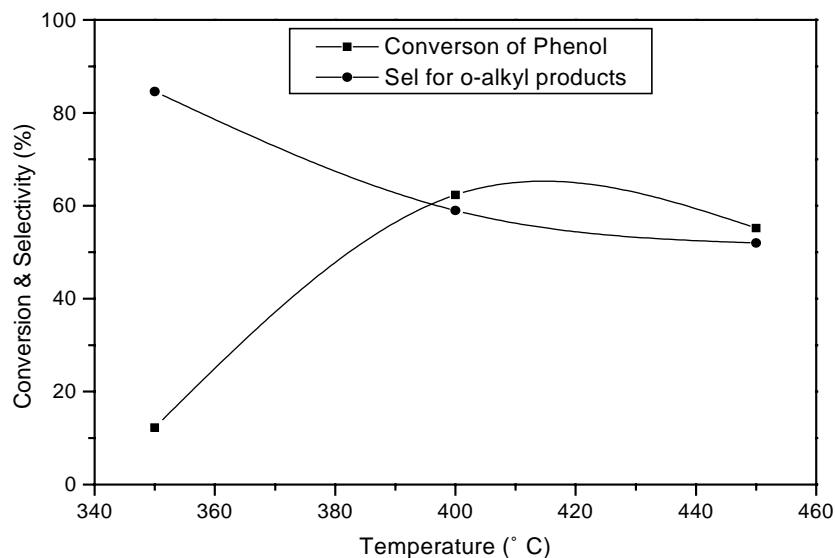Fig. 9. Effect of boria loading on phenol conversion.

Fig. 10. Effect of temperature on the conversion and selectivity for *ortho*-alkylated products.

products is the reason for decrease in selectivity at higher temperature.

3.3.3. Effect of mole ratio

Effect of change in methanol:phenol mol ratio on conversion and selectivity is shown in Fig. 11. Conversion of phenol goes up as the mol ratio is increased from 1 to 10 due to the availability of additional methyl groups for the reaction; however selectivity for *ortho*-alkylated products decreases due to the favored poly-methylation.

3.3.4. Effect of WHSV

When weight hourly space velocity is 3, optimum results in terms of conversion and selectivity are observed (Fig. 12). At lower WHSV although conversion is high, selectivity for *ortho*-alkyl products is very low due to longer residence time at the catalyst surface leading to the formation of polyalkylated products.

According to literature basic catalysts favor *O*-alkylation at lower temperature and lower residence time, whereas *C*-alkylation is favored by strong or medium acid sites. High temperature also favors *C*-alkylation. Our results are in good agreement with the literature. Borate zirconia catalyst, which is moderately acidic, gives selective *C*-alkylation at high temperature (350–450 °C).

Phenol methylation using 5 mol% B_2O_3/ZrO_2, $2\,h^{-1}$ WHSV and methanol:phenol mol ratio of 4 showed no deactivation of the catalyst till 150 h time on stream. At 150 h time on stream, the conversion of phenol was 63% with 58% selectivity for the *ortho*-alkylated products.
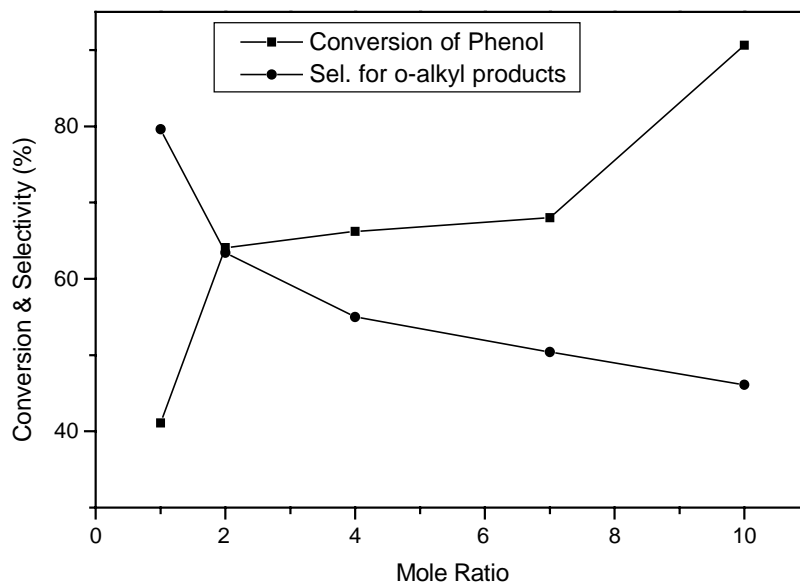

Fig. 11. Effect of methanol:phenol mole ratio on conversion and selectivity for *ortho*-alkylated products.
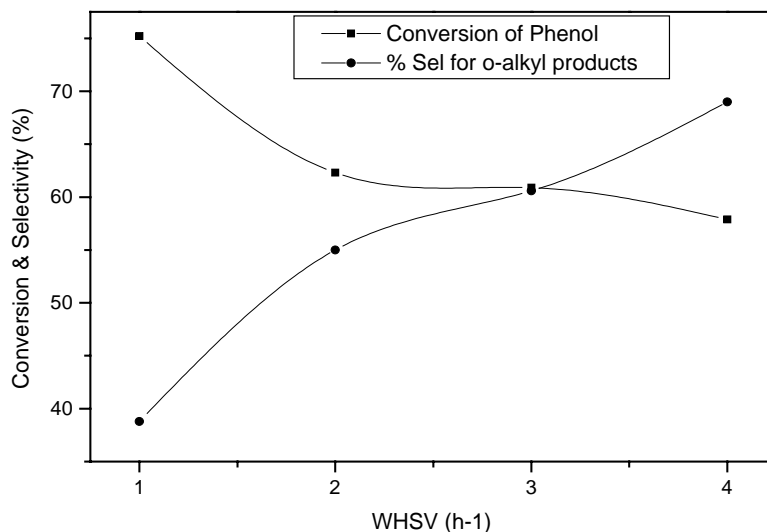
Fig. 12. Effect of WHSV on conversion and selectivity for *ortho*-alkylated products.

4. Conclusions

The effect of boria loading, WHSV as well as temperature on conversion and product selectivity has been studied for phenol methylation using borate zirconia solid acid catalyst prepared by wet impregnation technique. The results show maximum efficiency of the catalyst with respect to conversion as well as selectivity for *ortho*-alkylated products when boria loading is 5 mol% and calcination temperature is 650 °C. Other *C*-alkylated products are mesitols and durenols whereas around 2% anisole is obtained as *O*-alkylated product. Preferential *C*-alkylation can be attributed to large number of weak and medium acid sites whereas preferential *ortho*-alkylation is due to perpendicular orientation of phenol aromatic ring on catalyst surface. The catalyst is highly stable and does not deactivate even after 150 h.

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