Phenol *tert*-butylation over zirconia-supported 12-molybdophosphoric acid catalyst

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Abstract

The alkylation of phenol with *tert*-butanol was investigated using zirconia-supported 12-molybdophosphoric acid (MPA) as catalyst. The catalysts with different MPA loading (5–25 wt.% calcined at 700 °C) and calcination temperature (15 wt.% calcined from 500 to 750 °C) were prepared by suspending zirconium oxyhydroxide in methanol solution of MPA followed by drying and calcination. These catalysts were characterized by X-ray diffraction and ^{31}P MAS NMR spectroscopy measurements. The XRD results indicated that MPA stabilizes the tetragonal phase of zirconia. ^{31}P MAS NMR spectra showed the presence of three types of phosphorous species, phosphomolybdate in interaction with zirconia, decomposition product of MPA and an unidentified species. FTIR pyridine adsorption on 15% MPA catalyst calcined at different temperatures showed the presence of both Brönsted and Lewis acidity and the catalyst calcined at 700 °C showed the highest relative Brönsted acidity. Under the reaction conditions of 140 °C, *tert*-butanol/phenol molar ratio of 2 and LHSV of 4 h^{-1}, the phenol conversion was 80.6% at 2 h (selectivity to 2-TBP 11.5%, 2,4-DTBP 55.2%, and 4-TBP 25.7%), which decreased slowly with time and at 31 h, it was 58.5% (selectivity to 2-TBP 15.2%, 2,4-DTBP 41.6%, and 4-TBP 38.4%). The major reason for the catalyst deactivation was the reduction and leaching of MPA from the catalyst surface.
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1. Introduction

Heteropoly acids (HPAs) are a unique class of materials active both in redox and acid catalysis [1,2]. These are polyoxometallates made up of heteropoly anions having metal–oxygen octahedra as the basic structural unit. They are strong Brönsted acid catalysts and their strength of acidity is higher than that of conventional solid acids like zeolites and mixed oxides. HPAs can be used either directly as a bulk material or in supported form. The use in supported form is preferable because of its high surface area compared to the bulk material (5–8 m^2 g^{-1}) and better accessibility of reactants to the active sites. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports [3].

In recent years zirconia has attracted much attention both as catalyst and catalyst support because of its high thermal stability and the amphoteric character of its surface hydroxyl groups

[4,5]. Recently, we have shown that zirconia can be used as a suitable support for heteropolyacids [6].

Alkylation of phenol with *tert*-butanol is industrially important as it is used for the production of *tert*-butylated phenols. For instance, 2-*tert*-butyl phenol (2-TBP) is a starting material for the synthesis of antioxidants and agrochemicals, whereas 4-*tert*-butyl phenol (4-TBP) is used to make fragrances and phosphate esters, 2,4-di-*tert*-butyl phenol (2,4-DTBP) is used in the synthesis of substituted triaryl phosphites. Commercially *tert*-butyl phenols are produced by the reaction of phenol with isobutene in presence of homogeneous catalysts. The use of these catalysts gives rise to many problems concerning handling, safety, corrosion, and waste disposal. Therefore, considerable efforts have been made for the development of suitable heterogeneous catalysts. The various catalysts reported for this reaction include metal oxides [7], zeolites [8], various microporous and mesoporous materials [9], clays and clay-based materials [10]. Both the formation of C- and O-alkylated products are possible depending on reaction conditions such as reaction temperature and type of catalyst. The catalyst with strong acidic sites or at high reaction temperature, the reaction results in the formation of C-alkylated products, while catalysts with weak acidic sites or

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at low reaction temperature leads to the formation of O-alkylated product [11,12].

The present work deals with alkylation of phenol with *tert*-butanol using zirconia-supported 12-molybdophosphoric acid as the catalysts. The reaction was carried out with an aim to maximize phenol conversion together with the selectivity to 4-*tert*-butyl phenol and 2,4-di-*tert*-butyl phenol. The influence of MPA loading and catalyst calcination temperature on phenol conversion and product selectivity is studied. The catalyst with highest activity was used to study the effect of various reaction parameters such as temperature, molar ratio, space velocity and time-on-stream on phenol conversion and product selectivity.

2. Experimental

2.1. Materials

Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and ammonia (25%) were procured from S.D. Fine Chemicals Ltd., Mumbai. Phenol, *tert*-butanol and methanol were obtained from Merck (India) Ltd., Mumbai. 12-Molybdophosphoric acid ($H_3PMo_{12}O_{40} \cdot xH_2O$) was purchased from Aldrich. All the chemicals were research grade and were used as received without further purification.

2.2. Catalyst preparation

The catalysts were prepared by suspending a known amount of dried zirconium oxyhydroxide powder in a methanol solution of MPA. Zirconium oxyhydroxide was prepared by hydrolysis of 0.5 M zirconium oxychloride solution by the drop wise addition of aqueous NH_3 (10 M) to a final pH of 10. The precipitate was filtered and washed with ammonical water (pH 8) until free from chloride ions by the silver nitrate test. The zirconium oxyhydroxide thus obtained was dried at 120 °C for 12 h, powdered well and continued drying for another 12 h. Each time, 4 ml of methanol per gram of solid support was used and the mixture was stirred in a rotary evaporator for 8–10 h. After stirring, the excess of methanol was removed at ca. 50 °C under vacuum. The resulting solid materials were dried at 120 °C for 24 h and ground well. A series of catalysts with different MPA loading (5–25 wt.%) were prepared by changing the MPA concentration in methanol. The dried samples were then calcined in air at 700 °C. Samples with 15% MPA were calcined between 500 and 750 °C to understand the role of the calcination temperature on the activity of the catalysts. The samples were heated at a rate of 5 °C min⁻¹ to the final temperature and held for 4 h under static conditions, and cooled at a rate of 5 °C min⁻¹ to room temperature and stored in desiccator. The catalysts are represented by *x*MZ-*T* where *x* represents wt.%, M represents MPA, Z represents zirconia and *T* denotes calcination temperature in °C.

2.3. Characterization

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex

diffractometer equipped with Ni filtered CuKα radiation (λ = 1.5418 Å).

³¹P MAS NMR spectra (Bruker DSX-300 spectrometer) were recorded at 121.5 MHz with high power decoupling with a Bruker 4 mm probe head. The spinning rate was 10 KHz and the delay between two pulses was varied between 1 and 30 s to ensure that complete relaxation of the ³¹P nuclei occurred. The chemical shifts are given relative to external 85% H_3PO_4.

The Brönsted and Lewis acidity of the catalyst 15 MZ calcined at different temperatures are characterized by in situ FTIR spectroscopy with chemisorbed pyridine. The pyridine adsorption studies were carried out in the DRIFT (diffuse reflectance infrared Fourier transform) mode using a Shimadzu SSU 8000 instrument. A calcined powder sample in a sample holder was placed in a specially designed cell. The samples were then heated in situ from room temperature to 400 °C at a heating rate of 5 °C min⁻¹ in a flowing stream (40 ml min⁻¹) of pure N_2. The samples were kept at 400 °C for 3 h and then cooled to 100 °C and then pyridine vapor (20 μl) was introduced under N_2 flow and the IR spectra were recorded at different temperatures up to 400 °C. A resolution of 4 cm⁻¹ was attained after averaging over 500 scans for the IR spectra reported here.

2.4. Catalytic measurements

The alkylation of phenol 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 (1.5 ml), 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 phenol and *tert*-butanol of desired molar ratio was introduced into the reactor with a fixed space velocity using a syringe pump (Sage Instruments, Model 352, USA). Nitrogen was used as a carrier gas with a flow rate of 35 ml/min. The products were collected in a cold trap and analyzed by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using SE-52 packed column. The products were identified by GC-MS and by comparing with authentic samples. Conversion is defined as the percentage of phenol converted into products.

3. Results and discussion

3.1. Characterization

3.1.1. X-ray diffraction

The XRD pattern of the catalysts with different MPA loading calcined at 700 °C (Fig. 1A) shows that, the presence of MPA strongly influences the crystallization of zirconium oxyhydroxide into zirconia. Pure zirconia calcined at 700 °C is mainly monoclinic with small amount of the tetragonal phase. For catalysts with low MPA loading calcined at 700 °C, the XRD pattern can be described as the sum of the monoclinic and tetragonal
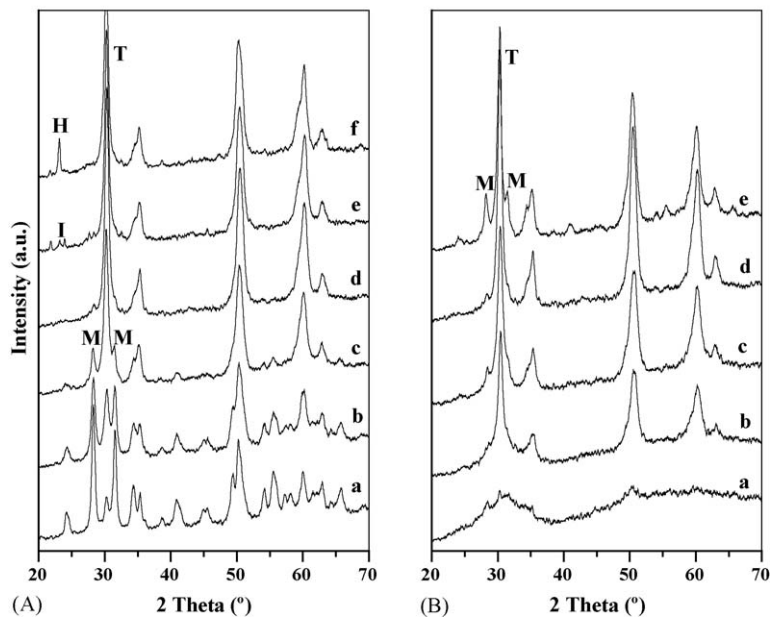
Fig. 1. X-ray diffraction patterns of: (A) catalysts with different MPA loading calcined at 700 °C (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25% and (B) 15 MZ catalyst calcined at different temperature (a) 400, (b) 500, (c) 600, (d) 700, (e) 750 °C; T = tetragonal ZrO$_2$, M = monoclinic ZrO$_2$, I = MoO$_3$, H = ZrMo$_2$O$_8$.

phases of zirconia, this latter phase becoming dominant for catalyst with 15% MPA. This can be explained as the strong interaction of MPA with the support reduces the surface diffusion of zirconia, inhibits sintering and stabilizes the tetragonal phase of zirconia. It can also be seen that up to a 15% MPA loading, no diffraction lines, which could be attributed to the polyacid or to its decomposition products, are observed. The catalyst 20 MZ-700 shows the presence of new diffraction lines characteristic of MoO$_3$ and for 25% catalyst formation of ZrMo$_2$O$_8$ is observed. This indicated that, MPA decomposed to molybdenum oxide, forming relatively large particles and also reacting with the support forms ZrMo$_2$O$_8$ [13].

As shown in Fig. 1B, 15% catalyst was amorphous, when it was calcined below 400 °C and the crystalline nature of zirconia increases with calcination temperature. As the calcination temperature increases from 500 to 700 °C, zirconia crystallizes to tetragonal phase and at 750 °C, the formation of monoclinic phase is indicated. Thus, the added MPA stabilizes the tetragonal phase of zirconia and such stabilization of tetragonal ZrO$_2$ in presence of other heteropoly acid is reported earlier [6].

3.1.2. ^{31}P MAS NMR

This is one of the most important characterization techniques to study the state of phosphorous in heteropoly acids. The chemical shift depends upon the phosphorous environment, which in turn depends upon factors like hydration number, addenda metal ion, support, etc [14–18]. The bulk MPA shows a sharp intense peak at −3.5 ppm in the ^{31}P MAS NMR spectrum, due to the uniform phosphorous environment in highly hydrated structure of the MPA, while the small peak observed near to the main peak at 6.3 ppm may be due to part of the sample containing different degrees of hydration [19]. The ^{31}P MAS NMR spectra of catalysts with 5–25% MPA calcined at 700 °C and 15%

MPA calcined from 600 to 750 °C shows that the state of phosphorous in catalysts depend on MPA loading and calcination temperature. The spectra of catalysts with different MPA loading (5–25 MZ-700) are shown in Fig. 2A. For 5% MPA catalyst, NMR shows a peak at −8.6 ppm assigned to the presence of phosphomolybdate in interaction with zirconia [20,21]. The up field shift compared to pure MPA may be due to the strong interaction of MPA with zirconia [21]. However, when the MPA loading increased to 10%, NMR show peaks at −3.5, −8.2 and 18 ppm respectively. The peak at −3.5 ppm is assigned to microcrystalline MPA, similar to unsupported MPA [21,22] and the chemical shift at −8.2 ppm is due to MPA interacting strongly with the surface of zirconia. The origin of the peak at 18 ppm is not clear at present. For catalysts with 15% MPA loading and above, an additional peak at −30 ppm is observed, which is attributed to phosphorous oxide (P–O–P) resulting from the decomposition of the polyoxometallate [23]. However, the catalyst 15 MZ-700 gave the highest phenol conversion and the ^{31}P CP/MAS NMR spectrum of this catalyst showed the peak at −8.5 ppm due the presence of MPA strongly interacting with surface of zirconia (Fig. 2C).

The ^{31}P MAS NMR spectra of 15 MZ catalyst calcined form 500–750 °C are shown in Fig. 2B. At a calcination temperature of 500 °C, NMR spectrum shows two peaks, one at −8 ppm and the other at 17.2 ppm. As the calcination temperature is increased to 600 °C, NMR spectrum shows peaks at −3.5, −8.2 and 18 ppm, similar to the NMR spectrum of the catalyst 10 MZ-700. The catalyst 15 MZ-750 shows a sharp peak at −30 ppm.

3.1.3. FTIR pyridine adsorption

The nature of acidic sites present in the catalyst 15 MZ-700 measured by FTIR pyridine adsorption spectroscopy in the temperature range 100–400 °C is shown in Fig. 3. The
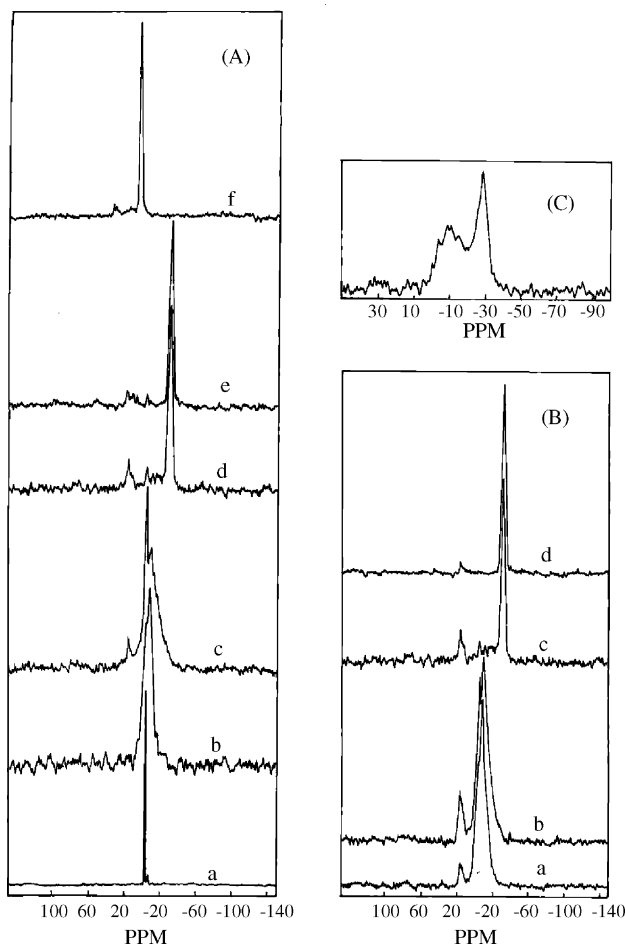
Fig. 2. ^{31}P MAS NMR spectra of: (A) catalysts with different MPA loading (a) pure MPA, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25% (where b–f calcined at 700 °C); (B) 15 MZ catalyst calcined at different temperature (a) 500, (b) 600, (c) 700, (d) 750 °C and (C) ^{31}P CP/MAS NMR spectrum of 15 MZ catalyst calcined at 700 °C.
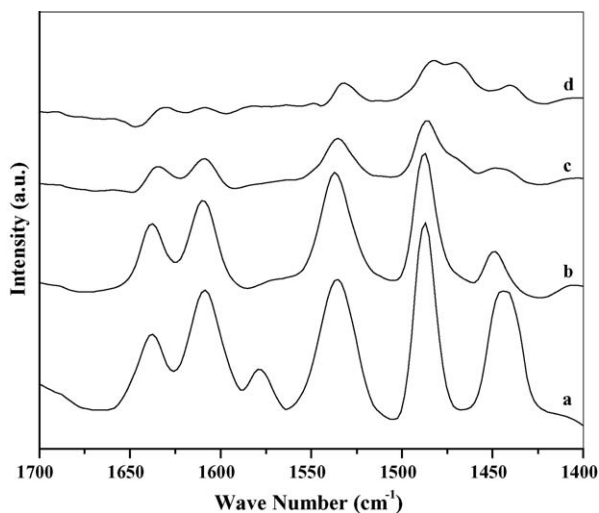

Fig. 3. The IR spectra of pyridine adsorbed on 15 MZ-700 catalyst after in situ activation at: (a) 100; (b) 200; (c) 300; (d) 400 °C.

spectrum recorded at 100 °C show peaks at 1609, 1579, 1487 and 1443 cm^{-1} termed 8a, 8b, 19a and 19b, respectively [24,25]. Additionally, the spectrum shows two other peaks, one at 1637 and the other at 1535 cm^{-1}. The peak at 1579 cm^{-1} is found to be very labile and its stability on the surface is temperature dependant. When the temperature is increased to 200 °C, this peak almost disappears, confirming its labile nature and hence, it is concluded that this species bound to the surface OH groups via H-bonding. Pyridine molecules bonded to Lewis acid sites absorbed at 1609 and 1443 cm^{-1} (ascribed to the 8a and 19b-ring mode of pyridine), while those responsible for Brönsted acid sites (pyridinium ion) show absorbance at 1535 and at 1637 cm^{-1} [26]. The band at 1487 cm^{-1} (19a-ring mode of pyridine) is a combined band originating from pyridine bonded to both Brönsted and Lewis acid sites.

The Brönsted/Lewis (B/L) site ratio of 15 MZ catalyst calcined at different temperatures (600, 700 and 750 °C) calculated from the IR absorbance intensities of bands at 1536 and 1442 cm^{-1} [27] are shown in Fig. 4. The results indicate that an increase of activation temperature decreases both Brönsted and Lewis acidity but an overall increase in Brönsted character of the catalyst up to an activation temperature of 200 °C for 15 MZ-650 and 15 MZ-750 catalysts and up to 300 °C for 15 MZ-700 catalyst. This indicates the presence of stronger Brönsted acid sites in 15 MZ-700 catalyst and this catalyst also possesses relatively higher Brönsted acidity.

3.2. Catalytic activity

The main products of the *tert*-butylation of phenol were 2-*tert*-butyl phenol (2-TBP), 4-*tert*-butyl phenol (4-TBP), 2,4-di-*tert*-butyl phenol (2,4-DTBP) and *tert*-butyl phenyl ether (TBPE). The products like 2,6-di-*tert*-butyl phenol and 2,4,6-tri-*tert*-butyl phenol (TTBP) were formed in small amounts. C$_8$ and C$_{12}$ olefins, formed by the oligomerization of isobutene, were also observed in the reaction, where isobutene is formed by the acid catalyzed dehydration of *tert*-butanol. Scheme 1 represents the formation of different products during *tert*-butylation of phenol.

3.2.1. Effect of MPA loading

In order to investigate the effect of MPA loading, catalysts with 5–25% MPA on zirconia calcined at 700 °C were used in alkylation of phenol with *tert*-butanol at 120 °C with a space velocity of 4 h^{-1} (Fig. 5). Out of the catalysts with different MPA content, the 5% MPA catalyst showed the lowest phenol conversion (41.9%), while the catalyst with 15% MPA gave the highest conversion (64.6%). Further increase in MPA loading decreases phenol conversion as for 25% catalyst it was 60.8%.

The selectivity to different alkylated products also depends on the loading of MPA. The catalyst with 5% MPA shows the highest selectivity to TBPE. As the phenol conversion increased from 51.9% for 5% catalyst to 64.6% for 15% catalyst, the selectivity to TBPE decreased from 10.3 to 1.6%. The 5% catalyst shows 2-TBP selectivity of 25% and 4-TBP selectivity of 21.1%. When MPA content was increased to 10%, the selectivity to 2-TBP was decreased to 20.2%, while selectivity to 4-TBP was similar to
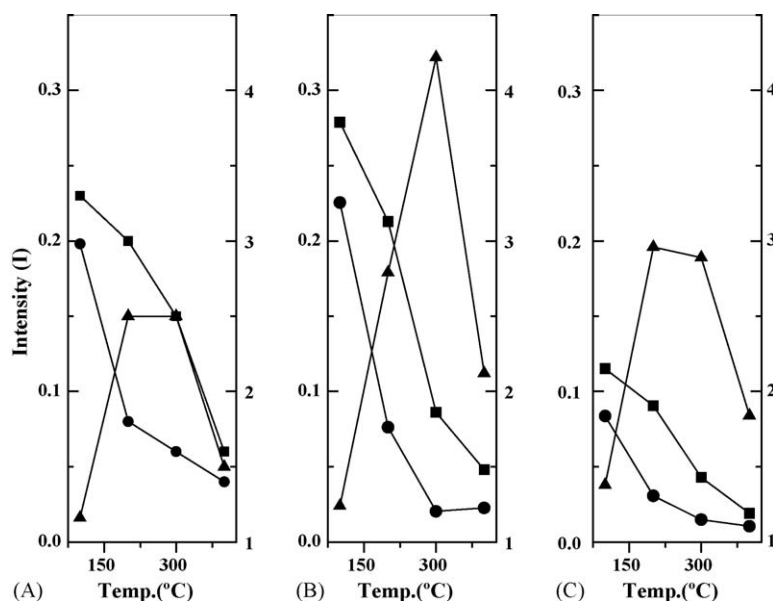
Fig. 4. The change in Brönsted acidity (■) (B), Lewis acidity (●) (L) and B/L ratio (▲) (I(B)/I(L)) with activation temperature for the catalysts: (A) 15 MZ-600, (B) 15 MZ-700 and (C) 15 MZ-750.

that of 5% catalyst. The catalysts with higher MPA content gave products with similar selectivity to 2-TBP and 4-TBP as that of 10% catalyst. The selectivity to 2,4-DTBP increased up to 15% MPA loading (52.2%) and further increases in MPA loading decreases its selectivity.

3.2.2. Effect of calcination temperature

The catalyst with 15% MPA calcined from 500 to 750 °C were used to study the change in catalytic activity with calcination temperature (Fig. 6). From the figure it is clear that calcination temperature has a profound effect on catalytic activity. The cat-

Scheme 1. (A) *tert*-Butyl phenyl ether, (B) 2-*tert*-butyl phenol, (C) 4-*tert*-butyl phenol and, (D) 2,4-di-*tert*-butyl phenol.

alyst calcined at 500 °C, shows 40% phenol conversion and it increased to 64.6% at a calcination temperature of 700 °C. Further increase in calcination temperature decreases the conversion of phenol.

The selectivity to different alkylated products also varies with calcination temperature as that observed in the case of catalysts with different MPA loading. As the conversion increased from 40% for the catalyst calcined at 500 °C to 64.6% for the one calcined at 700 °C, the selectivity to TBPE decreased from 12.5 to 1.6%, 2-TBP from 26.5 to 19% and 4-TBP from 25.8 to 20.5%. However, the selectivity to 2,4-DTBP was increased with calcination temperature up to 700 °C (52.2%) and further increase in calcination temperature decreases its selectivity.

The acidity measurements of the catalysts by FTIR pyridine adsorption shows that the catalyst 15 MZ-700 possess the highest relative Brönsted acidity, which indicates that alkylation of phenol by *tert*-butanol is catalyzed by Brönsted acid sites present in the supported-catalyst.

3.2.3. Effect of reaction temperature

The reaction was studied in the temperature range of 80–180 °C using 15 MZ-700 catalyst. The changes in the conversion of phenol and selectivity to different products as a function of temperature are shown in Fig. 7. At 80 °C, phenol conversion was 21.3% and increased to 76.5% at 140 °C. An increase of reaction temperature above 140 °C decreases the conversion of phenol. The decrease in conversion of phenol could be due to the dealkylation of *tert*-butyl phenol to phenol at high temperature and also the diminishing availability of *tert*-butanol as it undergoes oligomerization rather than alkylation [9].

At 80 °C TBPE obtained as the major product (53.5%) and as phenol conversion increases, TBPE selectivity decreases and it was completely absent at 140 °C. The decrease in TBPE selectivity with temperature may be due to its rearrangement
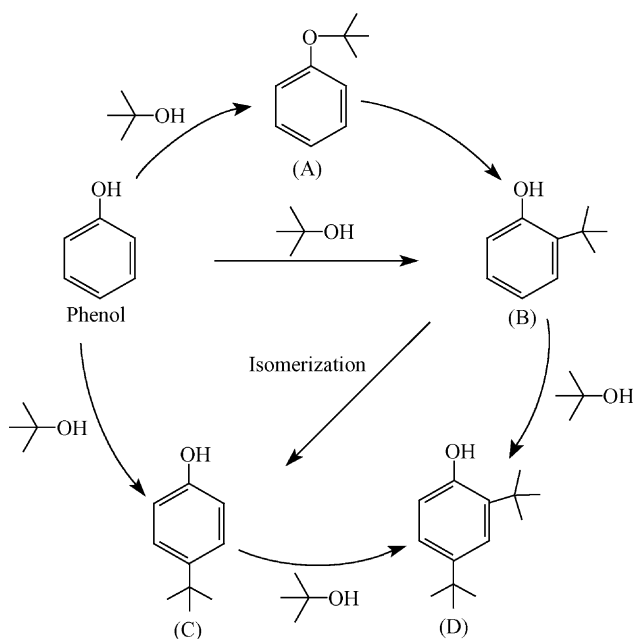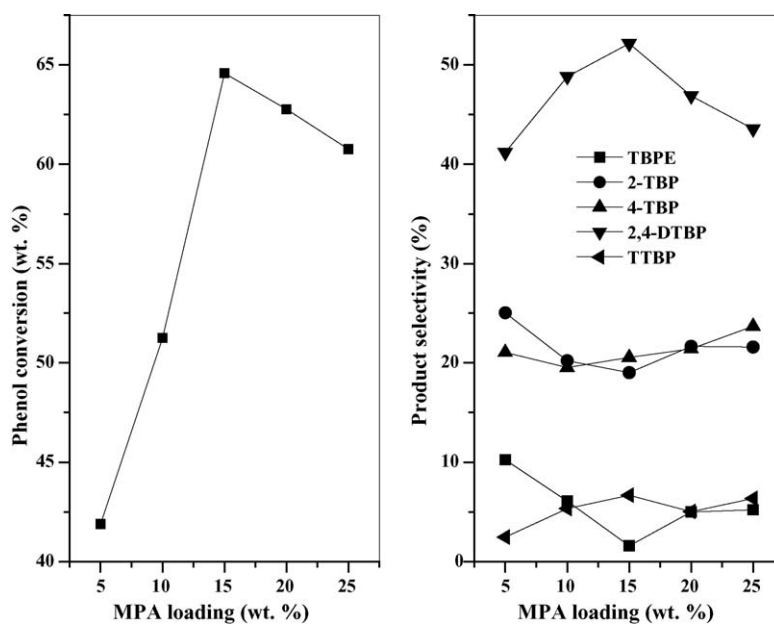
Fig. 5. Effect of MPA loading on phenol conversion and product selectivity. Reaction conditions: temperature, 120 °C; *tert*-butanol/phenol molar ratio = 2; LHSV = 4 h^{-1}; time, 2 h.

to C-alkylated product. Indeed, it has been shown that such rearrangement occurred on heating by contact with an acid catalyst [6(c)]. The highest selectivity to 2-TBP was found to be at 100–120 °C (21%), while, selectivity to 2,4-DTBP (45%) was highest at 140 °C. The higher selectivity of 2,4-DTBP at this temperature may be due to the higher stability and the availability of *tert*-butyl cation at this reaction temperature. The formation of 4-TBP is favored at high temperature as it is the thermodynamically stable product and hence an increase of temperature always results in an increase of its selectivity.

3.2.4. Effect of molar ratio

The effect of molar ratio on phenol conversion and product selectivity was studied at 120 °C with *tert*-butanol/phenol molar ratio of 1–4 (Fig. 8). Generally, the phenol conversion was increased with an increase in the amount of *tert*-butanol. At a molar ratio of 1, phenol conversion was 58.1%, which increased to 80.6% at a molar ratio of 3. A further increase in molar ratio had no appreciable effect on phenol conversion. It was shown that the polar molecule, such as methanol and higher alcohols compete with phenol for adsorption sites and
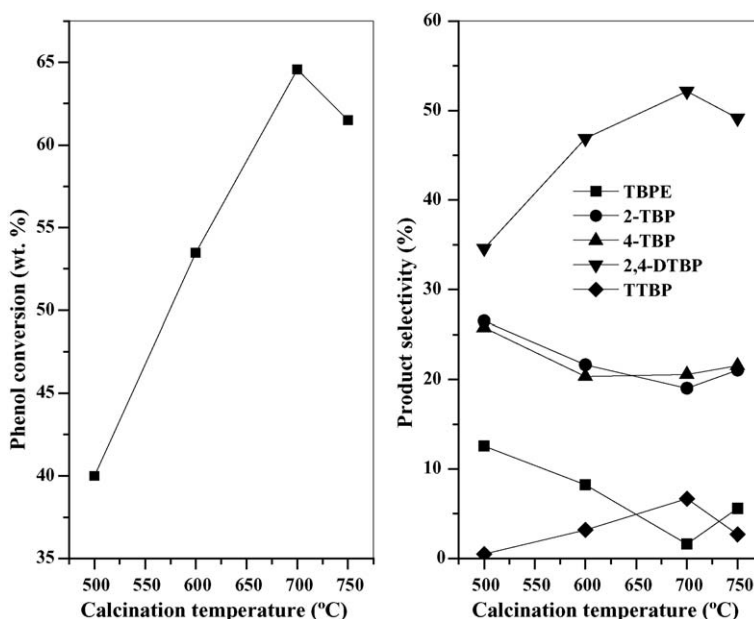

Fig. 6. Effect of catalyst calcination temperature on phenol conversion and product selectivity. Reaction conditions: same as that in Fig. 5.
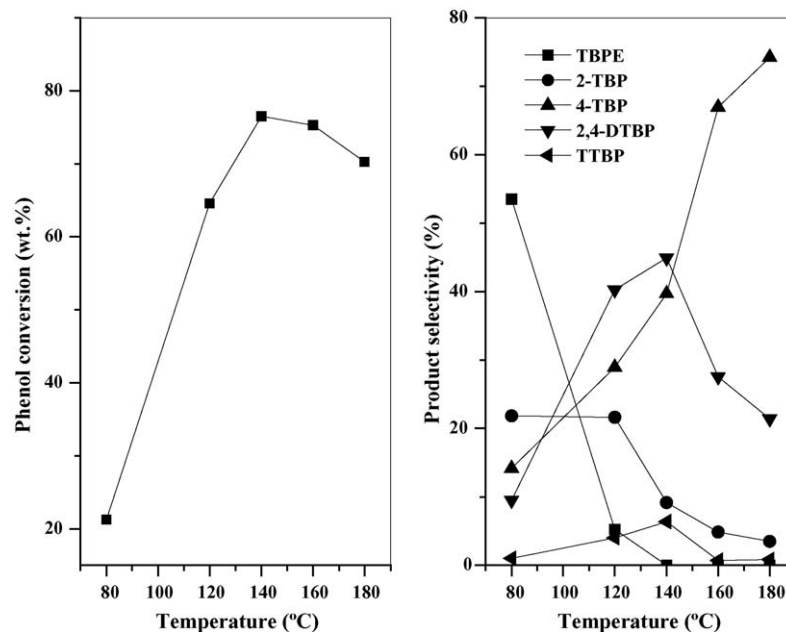
Fig. 7. Effect of reaction temperature on phenol conversion and product selectivity. Reaction conditions: *tert*-butanol/phenol molar ratio = 2; LHSV = 4 h^{-1}; time, 2 h.

an increase in the molar excess of alkylating agent results in an increase in phenol conversion as observed in the present study [8(c)].

The formation of TBPE was observed in small amount under these conditions. The selectivity to 2-TBP was low and it decreased from 17.3 to 9.8% when the molar ratio increased from 1 to 4. With an increase in molar ratio from 1 to 4 the selectivity to 4-TBP decreased from 41.3 to 21.3%, while 2,4-DTBP selectivity increased from 38 to 64.6%. This could be due to the higher availability of *tert*-butanol, which leads to the formation of the dialkylated product.

3.2.5. Effect of space velocity

The effect of space velocity was studied at 140 °C using *tert*-butanol/phenol molar ratio of 3 from LHSV of 2 to 10 h^{-1} and the results are shown in Fig. 9. With an increase of space velocity from 2 to 10 h^{-1}, phenol conversion was changed from 82 to 62.4%. The decrease in conversion with an increase in space velocity is due to the lower time available for the reactants to be in contact with the active sites of the catalyst. With decrease in the conversion of phenol, the selectivity to 2,4-DTBP decreased from 60.5 to 44.6%. However, change in space velocity had no appreciable effect on the selectivity of other products.
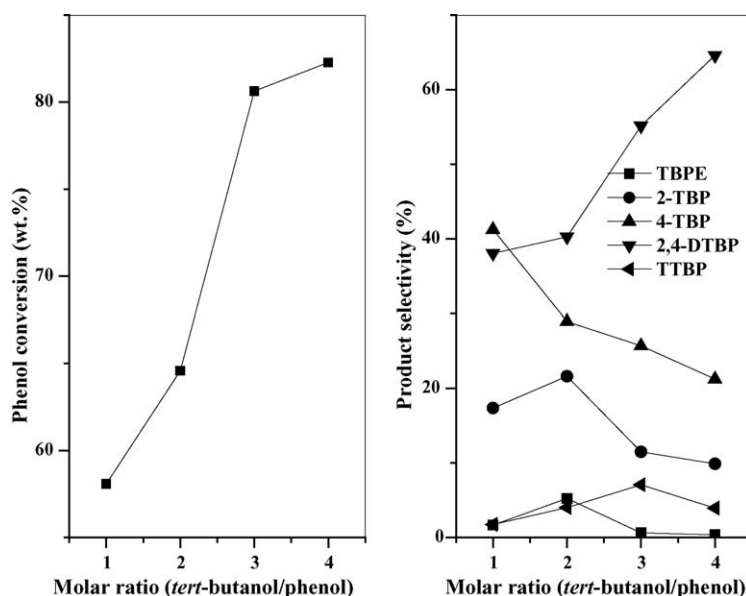

Fig. 8. Effect of molar ratio on phenol conversion and product selectivity. Reaction conditions: temperature, 120 °C; LHSV = 4 h^{-1}; time, 2 h.
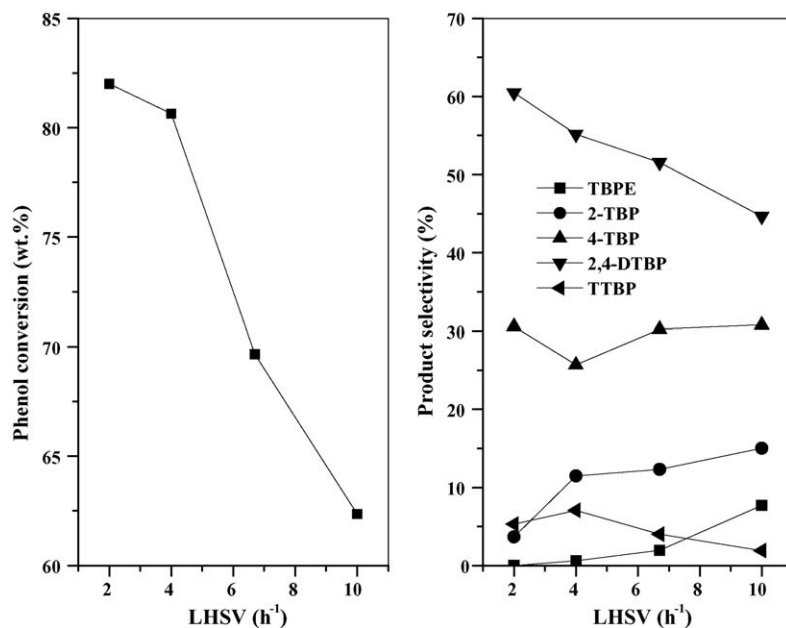
Fig. 9. Effect of space velocity on phenol conversion and product selectivity. Reaction conditions: temperature, 140 °C; *tert*-butanol/phenol molar ratio = 3; time, 2 h.

3.2.6. Effect of time on stream

In order to study the deactivation behavior of the catalyst, the reaction was studied at 140 °C with LHSV of $4\,h^{-1}$ using *tert*-butanol/phenol molar ratio of 3, for 31 h (Fig. 10). The conversion of phenol was found to be 80.6% after 2 h with selectivity to 2-TBP 11.5%, 2,4-DTBP 55.2%, and 4-TBP 25.7%, and after 31 h, the conversion of phenol was decreased to be 58.5% with selectivity to 2-TBP 15.2%, 2,4-DTBP 41.6%, and

4-TBP 38.4%. However, the major drawback of MPA/ZrO$_2$ catalyst is its deactivation, which is in sharp contrast with the catalytic behavior of zirconia-supported silicotungstic acid catalyst, where the catalyst is found to be stable and regenerable [6(c)]. The color of the product mixture obtained from 15 MZ-700 catalyst was found to be dark blue and it indicated the major reason for the catalyst deactivation is due to the reduction [28] and leaching of MPA from the catalyst surface.
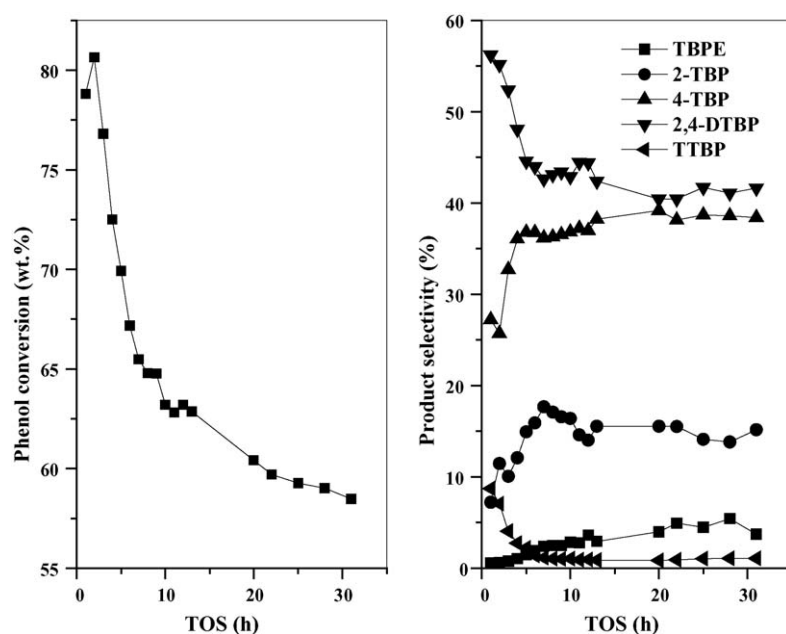

Fig. 10. Effect of time-on-stream (TOS) on phenol conversion and product selectivity. Reaction conditions: temperature, 140 °C; LHSV = $4\,h^{-1}$; *tert*-butanol/phenol molar ratio = 3.

4. Conclusions

The alkylation of phenol with *tert*-butanol was studied using zirconia-supported 12-molybdophosphoric acid (MPA) as the catalysts in a continuous fixed-bed down flow reactor. The activity of the catalyst depends on both MPA loading and calcination temperature and catalyst with 15% MPA on ZrO_2 calcined at 700 °C was found to be the most active catalyst. The catalyst shows good conversion and selectivity to alkylation under mild conditions but deactivate with time due to reduction and leaching of MPA from the catalyst surface. The deactivation of MPA/ZrO_2 catalyst by leaching of MPA from the catalyst surface restricts the use of this catalyst in presence of highly polar reactants.

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