Silicotungstate-modified zirconia as an efficient catalyst for phenol *tert*-butylation

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Abstract

The alkylation of phenol with *tert*-butanol was investigated using zirconia modified with silicotungstic acid (STA) as catalysts. The catalysts with different STA loading (5–25 wt.% calcined at 750 °C) and calcination temperature (15 wt.% calcined from 350 to 850 °C) were prepared and characterized by X-ray diffraction and NH$_3$-TPD measurements. The XRD results indicate that STA stabilizes the tetragonal phase of zirconia. The catalyst with 15% STA on ZrO$_2$ calcined at 750 °C shows the highest acidity and hence highest activity. Under the reaction conditions of 140 °C, *tert*-butanol/phenol molar ratio of 2 and LHSV of 4 h^{-1}, phenol conversion was 95.4% with selectivity to 2-*tert*-butyl phenol 4.3%, 4-*tert*-butyl phenol 59.2% and 2,4-di-*tert*-butyl phenol 35.8%. The reaction was studied as a function of time for 50 h without appreciable change in phenol conversion and product selectivity. The deactivated catalyst could be regenerated by calcination with out appreciable lose in catalytic activity and product selectivity.

1. Introduction

The alkylation of phenol with different alcohols is industrially important as it is used for the production of a variety of products [1]. Among them, alkylation of phenol with *tert*-butanol 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 phophites. 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. There fore, considerable efforts have been made for the de-

velopment of suitable heterogeneous catalysts. The various catalysts reported for this reaction include metal oxides [2], zeolites [3], various microporous and mesoporous materials [4], clays and clay-based materials [5]. 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 at low reaction temperature leads to the formation of O-alkylated product [6,7]. Even though many of the catalyst systems reported for this reactions show good activity, they do not provide sustainable catalytic activities and hence limits their successful application in large-scale production.

Zirconia based solid acids are attracting much attention in recent years. Sulfated zirconia is proved to be a highly active solid acid catalyst [8]. Their poor stability, and tendency to form volatile sulfur compounds during catalysis and regeneration limit its applicability [9]. Zirconia modified

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by isopolytungstate, tungsten oxide–zirconia (WO_x–ZrO_2) is shown to be an alternative and extensive studies were carried out on this catalyst system [10]. But, relatively few works are available on zirconia modified by heteropolytungstates [11]. Recently we had shown that zirconia-supported phosphotungstic acid acts as an efficient catalyst for alkylation and acylation of aromatics [12].

The present work deals with alkylation of phenol with *tert*-butanol using zirconia modified with silicotungstic 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 STA loading and catalyst calcination temperature on phenol conversion and product selectivity was studied. The catalyst with highest activity was used to study various reaction parameters such as temperature, molar ratio and space velocity. The catalyst regeneration and life studies were also examined in the above reaction.

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. Silicotungstic acid ($H_4SiW_{12}O_{40} \cdot xH_2O$) 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 impregnation method using zirconium oxyhydroxide as the support according to our previous procedure [12]. The support was prepared by the hydrolysis of an aqueous solution of zirconium oxychloride with aqueous NH_3. The precipitate obtained was washed till free from chloride and dried at 120 °C. To a methanolic solution of silicotungstic acid, zirconium oxyhydroxide powder was added and the mixture was stirred for 8–10 h. The excess of methanol was evaporated to dryness and the obtained product was dried at 120 °C and calcined in air at different temperatures.

A series of catalyst with different STA loading (5–25%) on zirconia was prepared and calcined at 750 °C. In order to study influence of calcination temperature on activity, catalyst with 15% STA on zirconia was calcined from 350 to 850 °C.

2.3. Characterization

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å).

The acidity of the catalysts were measured by temperature programmed desorption of NH_3 (NH_3-TPD) using micromeritics AutoChem-2910 instrument. It was carried out after ~0.5 g of the catalyst sample was dehydrated at 600 °C in He (30 cm^3 min^{-1}) for 1 h. The temperature was decreased to 100 °C and NH_3 was adsorbed by exposing samples treated in this manner to a stream containing 10% NH_3 in He for 1 h at 100 °C. It was then flushed with He for another 1 h to remove physorbed NH_3. The desorption of NH_3 was carried out in He flow (30 cm^3 min^{-1}) by increasing the temperature to 600 °C at 10 °C min^{-1} measuring NH_3 desorption using TCD detector.

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 o.d.). 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 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. Although fresh catalysts were used every time for different measurements, the reusability of the catalyst was also studied, by regenerating the catalyst by thermal treatment in presence of air at 500 °C and reusing it. 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 was 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 STA loading calcined at 750 °C (Fig. 1A) shows that, the presence of STA strongly influences the crystallization of zirconium oxyhydroxide into zirconia. Pure zirconia calcined at 750 °C is mainly monoclinic with only a small amount of the tetragonal phase. For catalysts with low STA loading calcined at 750 °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% STA.
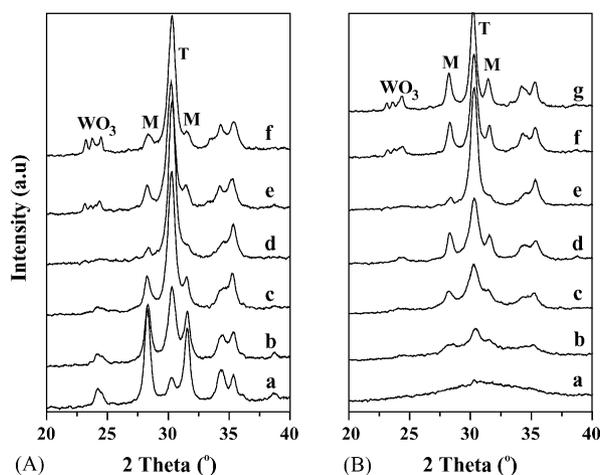
Fig. 1. XRD patterns of (A) (a) ZrO_2, (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 25% catalysts calcined at 750 °C and (B) 15% catalyst calcined at (a) 350 °C, (b) 450 °C, (c) 550 °C, (d) 650 °C, (e) 750 °C, (f) 800 °C, and (g) 850 °C.

As shown in Fig. 1B, 15% catalyst was amorphous when it was calcined below 450 °C and as the calcination temperature increases, zirconia crystallizes progressively to tetragonal phase. Thus, the added STA stabilizes the tetragonal phase of zirconia and such stabilization of tetragonal ZrO_2 in presence of other heteropoly acid is reported earlier [12]. When the STA loading is higher than 15%, or when the calcination temperature exceeds 750 °C for 15% loading, new peaks appear in the region of 23–25°, characteristic of crystalline WO_3.

3.1.2. Acidity measurement (NH₃-TPD)

This adsorption–desorption technique enables the determination of the total acidity of the catalysts. The acidity of the catalysts with different STA loading is given in Fig. 2 and it is evident from the figure that, the acidity of the catalysts increased up to 15% STA loading and then decreased at higher loadings. For a catalyst with 15% loading, calcined at different temperatures (650, 750 and 800 °C) the amount of
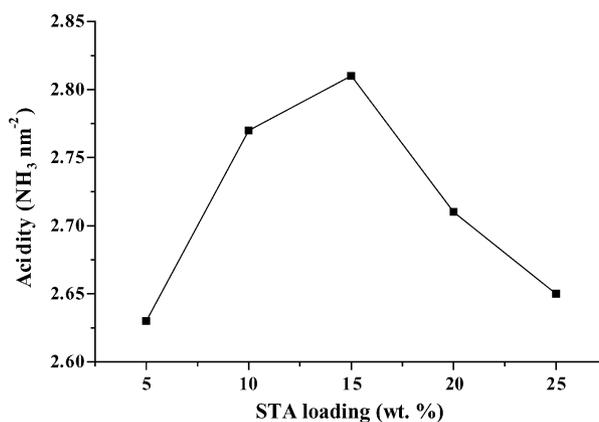
Table 1
Effect of calcination temperature on acidity

| Calcination temperature (°C)	Acidity (NH₃ nm⁻²)
650	1.93
750	2.81
800	2.61

desorbed ammonia shows its maximum at 750 °C (Table 1). The pre-activation temperature used for TPD analysis limits acidity measurement of the catalysts, which were calcined at lower temperatures.

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 were detected in trace amounts in some runs. C_8 and C_{12} olefins, formed by the olegomerization 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 STA loading

In order to investigate the effect of STA loading, catalysts with 5–25% STA on zirconia calcined at 750 °C were used in alkylation of phenol with *tert*-butanol at 120 °C with a space velocity of $6.7 \, h^{-1}$ (Fig. 3). Pure ZrO_2 calcined at 750 °C shows only negligible activity. Out of the catalysts with different STA content, the 5% STA catalyst showed the lowest phenol conversion (29.1%), while the catalyst with 15% STA gave the highest conversion (59.2%). Further increase in STA

Fig. 2. Effect of STA loading on acidity.
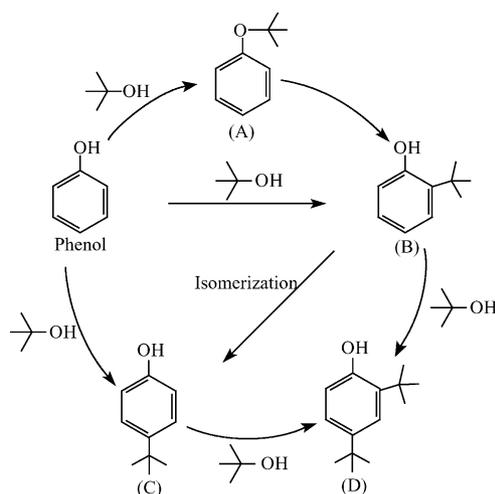
Scheme 1. (A) *tert*-butyl phenyl ether, (B) 2-*tert*-butyl phenol, (C) 4-*tert*-butyl phenol and (D) 2,4-di-*tert*-butyl phenol.
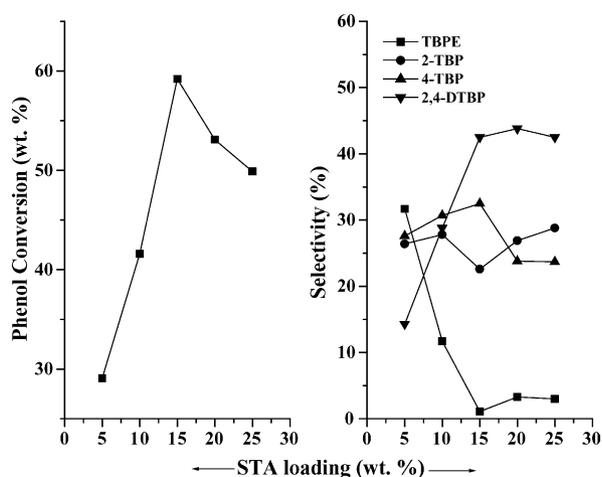
Fig. 3. Effect of STA loading on phenol conversion and product selectivity. Conditions: temperature = 120 °C; *tert*-butanol/phenol molar ratio = 1; LHSV = 6.7 h^{-1}; time = 2 h.

Fig. 4. Effect of calcination temperature on phenol conversion and product selectivity. Conditions: same as that in Fig. 2.

loading results in a decrease of phenol conversion as for 25% catalyst it was 49.9%.

The selectivity to different alkylated products also depends on the loading of STA. The catalyst with 5% STA shows the highest selectivity to TBPE. As the phenol conversion increased from 29.1% for 5% catalyst to 59.2% for 15% catalyst, the selectivity to TBPE decreased from 31.7 to 1.1%. The 5% catalyst shows 2-TBP selectivity of 26.4% and 4-TBP selectivity of 27.6%. When STA content was increased to 10%, the selectivity to 2-TBP was similar to that of 5% STA catalyst (27.8%), while selectivity to 4-TBP was increased to 30.7%. The 15% STA catalyst shows the lowest 2-TBP selectivity (22.6%), and the highest 4-TBP selectivity (32.5%). The catalysts with still higher STA content again gave products with similar selectivity to 2-TBP and 4-TBP. The selectivity to 2,4-DTBP increased up to 15% STA loading (42.5%). Further increase in STA content does not result in an appreciable change in its selectivity.

Subramanian et al. have shown that 2-TBP can undergo isomerization to 4-TBP and alkylation to 2,4-DTBP [4]. Thus, the lower 2-TBP selectivity shown by 15% STA-750 catalyst might be due to the isomerization of 2-TBP to 4-TBP and/or the successive alkylation of 2-TBP to 2,4-DTBP.

3.2.2. Effect of calcination temperature

The catalyst with 15% STA calcined from 350 to 850 °C were used to study the change in catalytic activity with calcination temperature (Fig. 4). From the figure it is clear that calcination temperature has a profound effect on catalytic activity. The catalyst calcined at 350 °C, shows 12.9% phenol conversion and it increased to 59.2% at a calcination temperature of 750 °C. Further increase in calcination temperature results in the decrease of phenol conversion.

The selectivity to different alkylated products varies with calcination temperature as that observed in the case of cat-
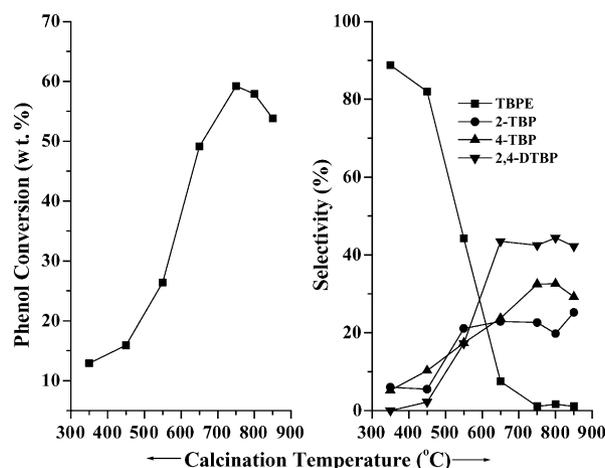
alysts with different STA loading. As the conversion increased from 12.9% for the catalyst calcined at 350 °C to 49.1% for the one calcined at 650 °C, the selectivity to TBPE decreased from 88.8 to 7.5%. A decrease in TBPE selectivity results in an increase in 2-TBP selectivity from 6 to 22.9%. Further increase in calcination temperature to 750 °C resulted in the decrease of TBPE selectivity to 1.1%. On the other hand, the selectivity to 4-TBP increased continuously up to 750 °C. Further increase in calcination temperature not changes its selectivity appreciably. The selectivity to 2,4-DTBP was increased up to 650 °C (43.5%) and further increase in calcination temperature does not change its selectivity.

The variation of phenol conversion and product selectivity with STA loading and calcination temperature follows the acidity of the catalysts. The acidity measurement by NH$_3$-TPD shows that the catalyst 15% STA/ZrO$_2$ calcined at 750 °C has the high acidity and hence this catalyst shows highest activity.

3.2.3. Effect of reaction temperature

The reaction was studied at various temperatures from 80 to 180 °C using 15% STA on ZrO$_2$ calcined at 750 °C as the catalyst. The variation of phenol conversion and selectivity to different products with temperature are shown in Fig. 5. At 80 °C, phenol conversion was only 15.6% and it increased to 69.3% at 140 °C. An increase of reaction temperature above this results in decrease in phenol conversion. The decrease in conversion may 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 olegomerization rather than alkylation [4].

At 80 °C TBPE obtained as the major product (86.1%) 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 to C-alkylated product. Indeed, it has been shown that such re-
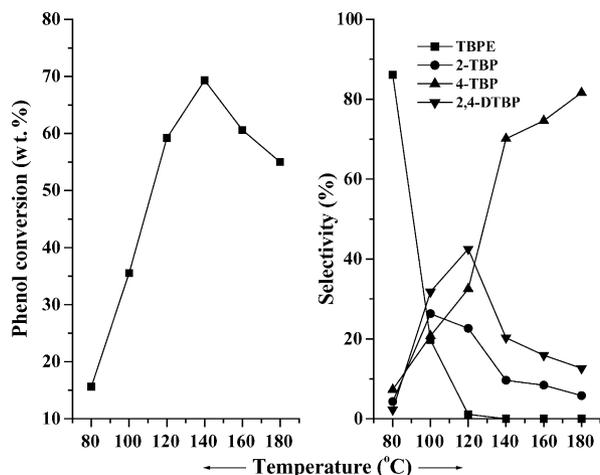
Fig. 5. Effect of reaction temperature on phenol conversion and product selectivity. Conditions: *tert*-butanol/phenol molar ratio = 1; LHSV = 6.7 h^{-1}; time = 2 h.

arrangements occurred on heating or by contact with an acid catalyst [12]. The highest selectivity to 2-TBP was found to be at 100 °C (26.3%), while, selectivity to 2,4-DTBP (42.5%) was highest at 120 °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 lower 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 140 °C with *tert*-butanol/phenol molar ratio of 0.5–4 (Fig. 6). Generally, the phenol conversion was increased with an increase in the amount of *tert*-butanol. At a molar ratio of 0.5, phenol conversion was found to be 52.3% and it is increased to 89.3% at a molar ratio of 2. An
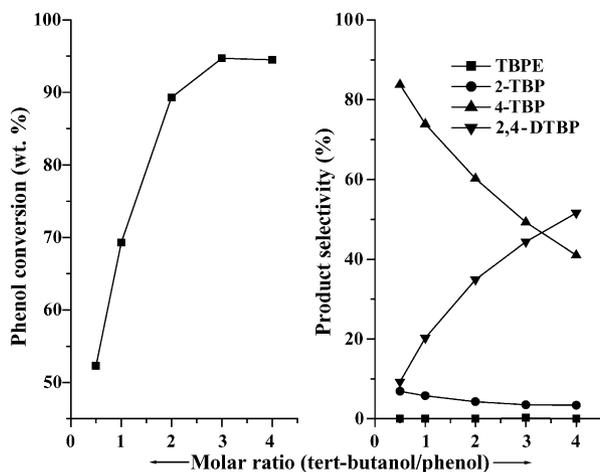

Fig. 6. Effect of molar ratio on phenol conversion and product selectivity. Conditions: temperature = 140 °C; LHSV = 6.7 h^{-1}; time = 2 h.
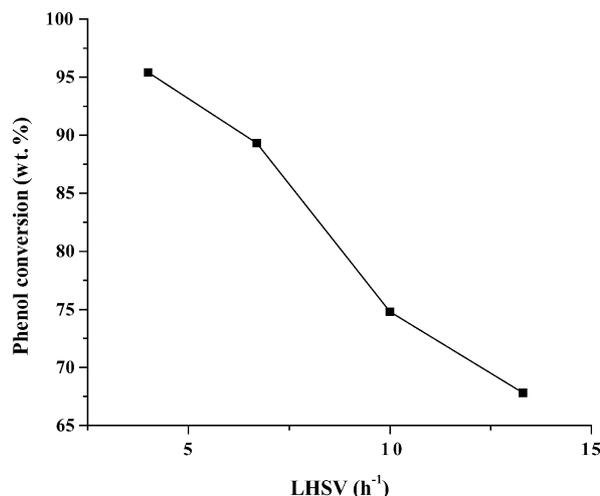

Fig. 7. Effect of space velocity on phenol conversion. Conditions: temperature = 140 °C; *tert*-butanol/phenol molar ratio = 2; time = 2 h.

increase of mole ratio from 2 to 3 added an additional 5.4% conversion. A further increase in mole ratio had no effect on phenol conversion. It was shown that the polar molecule, such as methanol and higher alcohols compete with phenol for adsorption sites and an increase in the molar excess of alkylating agent results in an increase in phenol conversion as observed in the present study [3].

The formation of TBPE was not observed under these conditions. The selectivity to 2-TBP was low and it decreased from 6.9 to 3.4% when the molar ratio increased from 0.5 to 4. With an increase in molar ratio from 0.5 to 4 the selectivity to 4-TBP decreased from 83.8 to 41%, while 2,4-DTBP selectivity increased from 9.3 to 51.6%. 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 2 from LHSV of 4 to 13.3 h^{-1} and the results are shown in Fig. 7. With an increase of space velocity from 4 to 13.3 h^{-1}, phenol conversion was changed from 95.4 to 67.8%. 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.

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 2, for 50 h (Fig. 8a). The phenol conversion was found to be 95.4% at 2nd h with selectivity to 4-TBP 59.2%, 2,4-DTBP 35.8% and 2-TBP 4.3%. Thus, the activity of this catalyst is found to be similar to that of large pore zeolites [3] and much higher than that of mesoporous materials [4]. There was no change in phenol conversion and selectivity to different products was observed after 50 h of reaction.
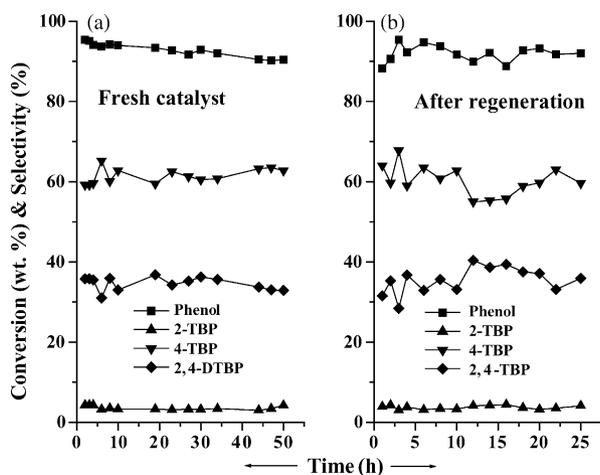
Fig. 8. Effect of time on phenol conversion and product selectivity. Conditions: temperature $= 140\,^\circ$C; LHSV $= 4\,$h^{-1}; *tert*-butanol/phenol molar ratio $= 2$.

The regenerability of the catalyst was also tested. Since there was no appreciable change in conversion after 50 h of reaction, the catalyst was subjected to accelerated deactivation by performing the reaction at higher temperature. After 6 h of reaction at 250 $^\circ$C, the phenol conversion was dropped to 20%. At this point, the reaction was stopped and reactor was flushed with N$_2$ and the catalyst was regenerated with air at 500 $^\circ$C for 6 h. The reaction was again studied with the regenerated catalyst for another 25 h (Fig. 8b) and the catalyst shows similar performance as that of the fresh catalyst and no appreciable change in phenol conversion and product selectivity was observed during the reaction time.

4. Conclusions

The alkylation of phenol with *tert*-butanol was studied using silicotungstate-modified zirconia as catalysts in a continuous fixed-bed down flow reactor. The activity of the catalyst depends on both STA loading and calcination temperature and catalyst with 15% STA on ZrO$_2$ calcined at 750 $^\circ$C was found to be the most active catalyst. Under the reaction conditions of 140 $^\circ$C, *tert*-butanol/phenol molar ratio of 2 and LHSV of 4 h^{-1}, phenol conversion with this catalyst was 95.2% with selectivity to 2-*tert*-butyl phenol 4.3%, 4-*tert*-butyl phenol 59.2% and 2,4-di-*tert*-butyl phenol 35.8%. The catalyst shows stable long-term activity and it can be regenerated by calcination with out appreciable lose in catalytic activity and product selectivity.

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