

Vapour phase tertiary butylation of phenol over sulfated zirconia catalyst

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Vapour phase butylation of phenol was carried out over a sulfated zirconia solid superacid catalyst in the temperature range 448–473 K using *t*-butyl alcohol as the alkylating agent. A good substrate (phenol) conversion and excellent product (*para*-tertiary BP) selectivity was obtained. The catalytic activity remains nearly the same on repeated use of the catalyst. Further, the catalyst was not deactivated when the reaction was carried out for a longer duration, i.e., even after several hours of reaction.

KEY WORDS: *p*-*t*-butylphenol; sulfated zirconia; alkylation of phenol; solid acid catalyst

1. Introduction

Para-tertiary-butylphenol (*p*-*t*-BP) is widely used in the manufacture of phenolic resins as well as antioxidants and polymerization inhibitors [1,2]. In general, tertiary butylation of phenol is carried out in homogeneous medium using sulfuric acid, fluoro sulphonic acid, arene sulfonic acid, phosphoric acid, and aluminium chloride–boric acid or boron trifluoride etherate as catalysts [1]. However, owing to environmental problems, such as disposal of liquid waste, separation of product from the catalyst, considerable attention has been focussed towards the development of solid acid catalysts such as cation-exchange resins, pillared clays, molecular sieves, etc. [3–14]. It is reported that the molecular sieve based catalysts like SAPO-11 [4], zeolite [12], AIMCM-41 [13], and FeMCM-41 [14] were proved to be potential catalysts for the tertiary butylation of phenol among the various solid acid catalysts. However, the reaction of tertiary butylation of phenol gives numerous products depending on the nature of the catalysts as well as on the reaction temperature [1,3–6,11–17]. For example, weak acid catalysts such as zeolite-Y [1,11] favour oxygen alkylated product viz., *t*-butyl phenyl ether (*t*-BPE). Strong acid catalysts, for example zeolite [17], lead to *m*-*t*-butylphenol (*m*-*t*-BP). On the other hand, moderate acid catalysts [4–16], like SAPO-11, MCM-41, etc. produce *o*-*t*- and *p*-*t*-butylphenol (*o*-*t*-BP and *p*-*t*-BP). To our knowledge, no report is available in literature on the tertiary butylation of phenol over sulfated zirconia catalysts. Further, it is interesting to note that this solid superacid based (sulfated zirconia) catalyst yields very good selectivity for the alkylation of phenol using isobutyl alcohol [10] and methyl tertiary-butyl ether [18]. Therefore, in the present investigation we have used the sulfated zirconia catalyst for the phe-

nol tertiary butylation reaction. In this letter, we report the results of vapour phase butylation of phenol using *t*-butyl alcohol (*t*-BA) over sulfated zirconia catalyst.

2. Experimental

Sulfated zirconia catalyst was prepared as per the procedure described in [19,20]. First, zirconium hydroxide was freshly prepared by hydrolysis of zirconium oxychloride (25 g in 200 ml of distilled water) at 371 K with vigorous stirring. Liquor ammonia was added dropwise until the pH becomes 9.3. The precipitated zirconium hydroxide was washed with deionised water until all the chloride ions were removed. The resulting sample was then dried at 383 K for 24 h. The dried sample was powdered and subsequently sieved through 100 mesh. The homogeneous zirconium hydroxide powder (1 g) thus obtained was then sulfated using 1 N sulfuric acid (15 ml). The slurry was stirred for 15–20 min and then it was filtered, dried and calcined in air at 873 K for 3 h. The calcined sample is designated as sulfated zirconia catalyst. All the samples were characterized by various analytical and spectroscopic techniques, viz., powder X-ray diffraction (XRD; Philips PW-1710), surface area (Sorptometer 201A), Fourier transform-infrared (FT-IR; Nicolet Impact 400) and thermogravimetry–differential thermal analysis (TG-DTA; Shimadzu DT-30). The sulfur content in the sample was analyzed using a micro-analyzer (Carlo-Erba Strumentazione, elemental analyzer 1106).

The *t*-butylation of phenol was carried out using 1 g of the calcined catalyst in a fixed-bed flow reactor. The catalyst was activated at 573 K in a flow of air for 8 h followed by cooling to reaction temperature in nitrogen atmosphere. After an hour, the reactant mixture, viz., phenol and *t*-BA, with a desired ratio and weight hour space velocity (WHSV) was

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fed into the reactor using a liquid injection pump (Sigmamotor) and nitrogen as the carrier gas. The gaseous products were cooled, and the condensed liquid products were collected at every 30 min interval. The products, viz., *p*-*t*-BP, *o*-*t*-BP, and 2,4-di-*t*-BP, were identified by gas chromatography (NUCON 5700) with a SE-30 column. The *m*-*t*-BP was identified using an AT-1000 column. Further, the products were confirmed using a combined gas chromatograph–mass spectrometer (GC-MS; Hewlett G1800A) with a HP-5 capillary column.

3. Results and discussion

The powder XRD pattern of the calcined sulfated zirconia sample showed the typical characteristics of tetragonal structure with $a = 5.118 \text{ \AA}$ and $c = 5.248 \text{ \AA}$ [21–23]. The surface area of the catalyst was found to be $122 \text{ m}^2 \text{ g}^{-1}$ and microanalyses result shows 1.88% sulfur contents in the samples, which are in good agreement with literature [19,24]. The TG pattern of the catalyst indicates two major weight losses, one ($\sim 20 \text{ wt\%}$) corresponding to water loss (323–493 K) and the other (12 wt%) to the decomposition of sulfate ions ($> 773 \text{ K}$). The latter observation is in excellent agreement with the microanalysis results. The two-stage decomposition is well supported by the respective DTA (endothermic) transitions in the same region. Further, the presence of sulfate ions in the catalyst is confirmed from the FT-IR spectrum, which shows an asymmetric band around 1400 cm^{-1} corresponding to the free S=O group of the sulfate molecule [25,26]. In addition, the bands appearing between 1100 and 800 cm^{-1} are characteristic of S–O asymmetric and symmetric vibrations [20,22].

The results of *t*-butylation of phenol over the sulfated zirconia catalyst with various phenol : *t*-BA ratios are summarized in table 1. It can be seen from the table that the catalyst shows a very good conversion and excellent *para* selectivity of the products. Further, the phenol conversion increases with increase in *t*-BA content due to a competitive adsorption of *t*-BA over phenol. A similar observation was also made earlier for this reaction [4,13,16]. Hence, for the further study, we have chosen the optimum phenol : *t*-BA ratio as 1 : 2. However, the *p*-*t*-BP selectivity decreases considerably at lower phenol : *t*-BA ratios due to the formation of dialkylated product, 2,4-di-*t*-BP. Surprisingly, there was no

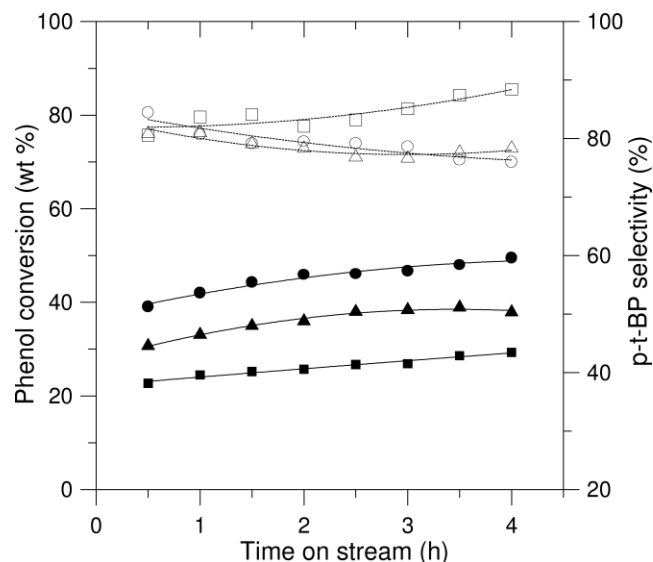


Figure 1. Effect of time on stream for the *t*-butylation of phenol with different phenol : *t*-BA ratios at 448 K, with WHSV = 4.8 h^{-1} ; filled symbols – phenol conversion; open symbols – *p*-*t*-BP selectivity; phenol : *t*-BA ratio: (□, ■) 2 : 1, (Δ, ▲) 1 : 1, and (○, ●) 1 : 2.

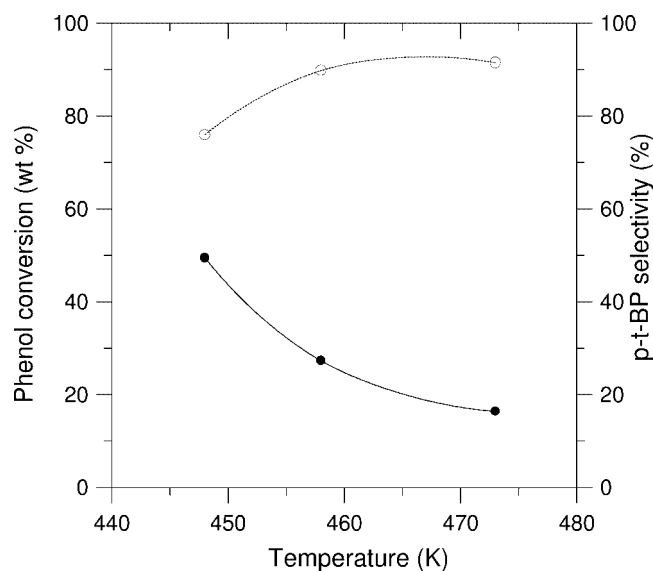


Figure 2. Effect of reaction temperature on phenol conversion and *p*-*t*-BP selectivity with phenol : *t*-BA ratio 2 : 1, TOS = 4 h and WHSV = 4.8 h^{-1} ; filled symbols – phenol conversion; open symbols – *p*-*t*-BP selectivity.

Table 1

Effect of phenol : *t*-BA molar ratio on phenol *t*-butylation reaction over sulfated zirconia at 448 K, WHSV = 4.8 h^{-1} and TOS = 4 h.

	Phenol : <i>t</i> -BA (molar ratio)		
	2 : 1	1 : 1	1 : 2
Conversion (wt%)	29.4	36.8	49.5
Selectivity (%)			
<i>o</i> - <i>t</i> -BP	12.6	14.4	11.0
<i>m</i> - <i>t</i> -BP	–	–	–
<i>p</i> - <i>t</i> -BP	83.0	78.5	76.0
2,4-di- <i>t</i> -BP	4.4	7.1	13.0

Table 2

Effect of space velocity on phenol *t*-butylation reaction over sulfated zirconia with phenol : *t*-BA ratio of 1 : 2; at 448 K and TOS = 4 h.

	Space velocity (h^{-1})				
	3.0	4.0	4.8	5.2	6.0
Conversion (wt%)	22.4	31.3	49.5	57.8	35.5
Selectivity (%)					
<i>o</i> - <i>t</i> -BP	4.5	7.6	11.0	6.8	1.0
<i>m</i> - <i>t</i> -BP	–	–	–	–	–
<i>p</i> - <i>t</i> -BP	94.6	90.4	76.0	86.5	97.0
2,4-di- <i>t</i> -BP	0.9	2.0	13.0	6.7	2.0

Table 3
Comparison of phenol conversion and *p-t*-BP selectivity over sulfated zirconia with other catalysts under optimum conditions.

Catalyst	Sulfated zirconia [This work]	AlMCM-41 [13]	FeMCM-41 [14]	SAPO-11 [4]	Zeolite [17]
Phenol : <i>t</i> -BA (molar ratio)	1 : 2	1 : 2	1 : 2	1 : 2	4 : 1
WHSV (h ⁻¹)	5.2	4.8	4.8	2.0	2.0
Phenol conversion (wt%)	57.8	35.9	21.1	59.0	25.4
Selectivity (%)					
<i>o-t</i> -BP	6.8	8.1	9.5	8.7	3.3
<i>m-t</i> -BP	—	4.7	—	—	58.1
<i>p-t</i> -BP	86.5	83.4	87.0	76.3	38.2
2,4-di- <i>t</i> -BP	6.7	3.9	3.5	15.0	0.4

meta-product formation which, however, can be explained as follows: It is known that the alkylation (methyl *t*-butyl ether) of phenol over sulfated zirconia is a Brønsted acid catalyzed reaction [18]. Further, it was also demonstrated that the Brønsted acid sites in sulfated zirconia catalyst are weaker than in H-ZSM-5 [25,27] and therefore no *meta*-product is expected. Figure 1 shows the effect of time-on-stream on phenol conversion and *p-t*-BP selectivity. It is clear from the figure that, unlike the molecular sieves based solid acid catalysts such as SAPO-11 [4] and AlMCM-41 [13], the catalytic activity of the sulfated zirconia remains constant even after several hours. This could, however, be due to the formation of water molecules during the reaction, which may convert some of Lewis acid sites into Brønsted sites [18,28].

Figure 2 shows the effect of reaction temperature (448–473 K) on the phenol conversion. It can be seen from the figure that the phenol conversion decreases with increase in reaction temperature, which could be due to a simultaneous dealkylation of the product BP into phenol and other lower hydrocarbons [4,12,13]. However, at higher temperatures, the observed higher *p-t*-BP selectivity could be due to the absence of a secondary alkylation reaction [12]. Table 2 presents the effect of space velocity at 448 K. It was observed that increasing space velocity increases the phenol conversion but after 5.2 h⁻¹ again the phenol conversion decreased. The lower conversion at lower space velocity could be due to dealkylation of the alkylated products as well as coke formation because of more contact time [4,13] while at higher space velocity, it could be due to the high diffusion rate of the reaction mixture through the catalyst. However, at the optimum conditions (phenol : *t*-BA ratio = 1 : 2, temperature = 448 K and WHSV = 5.2 h⁻¹), the sulfated zirconia catalyst gave good conversion and *p-t*-BP selectivity compared to the other catalysts reported for this reaction, see table 3 [4,13,14,17]. Recently, Zhang et al. [12] reported very high *p-t*-BP selectivity using zeolite- β catalyst, which is in contrast to the results of Mitra [17], where the *m*-isomer was obtained as the major product. This discrepancy can be explained based on the fact that the latter has used both a SE-30 and an AT-1000 column for the product

analysis while the former have employed a SE-30 column, which, however, cannot separate *p*- and *m*-isomers. Further, the reaction did not show any conversion without catalyst and the turnover frequency at optimum reaction conditions was found to be $5.88 \times 10^{-3} \text{ s}^{-1}$, thus indicating that reaction was catalytic.

4. Conclusion

The present study demonstrates that the sulfated zirconia catalyst is promising for the vapour phase butylation of phenol. A good substrate (phenol) and excellent (*p-t*-BP) selectivity of the products were obtained. Further, it is interesting to note that the catalytic activity remained the same even after several hours or even on repeated use of the catalyst.

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