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Liquidphase *tert*-butylation of cresols catalysed by 12-tungstophosphoricacid and 12-tungstosilicicacid supported onto neutral alumina

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A comparative study on *tert*-butylation of cresols such as o-cresol, m-cresol and p-cresol with tert-butyl alcohol was carried out over 30% 12-tungstophosphoricacid and 12-tungstosilicicacid supported onto neutral alumina in liquid phase under mild conditions. The catalysts show high activity in terms of % conversion and % selectivity for the products, *p-tert* butyl *o*-cresol, *o-tert* butyl *m*-cresol, *o-tert* butyl *p*-cresol, under mild conditions.

KEY WORDS: *tert*-butylation; cresols; 12-tungstophosphoricacid; 12-tungstosilicicacid; neutral alumina.

1. Introduction

The *tertiary* butylation of cresols with *tertiary* butyl alcohol is an industrially important since the reaction gives a variety of corresponding value added products. Among these, *tert*-butylation of *p*-cresol is most important as the obtained products, *o-tert*-butyl-*p*-cresol, *o*-di-*tert*-butyl-*p*-cresol, are widely used in the production of varnish, resins, as antioxidants [1] and polymerization inhibitors [2]. In general, this reaction is carried out using Friedel-Crafts catalysts such as $AlCl_3$, BF_3, $FeCl_3$ and $ZnCl_2$. Due to the known disadvantages of the homogeneous catalysts, the use of solids as catalytic materials in liquid-phase reactions has recently been a major goal in catalytic research. Liquid acids are being replaced with solid acids.

A literature survey shows that, even though *tert*-butylation of cresols is equally important as that of *tert*-butylation of phenol, not much work has been carried out for the same. Solid acids such as cation exchange resins [3, 4], sulfated zirconia [5], zirconia supported heteropolyacids and tungsten oxide [6, 7], modified K-10 [8] are being evaluated for the *tert*-butylation of cresols. Most of the reported heterogeneous catalysts are active in vapour phase *tert*-butylation reactions.

Heteropolyacids (HPAs) are promising solid acid catalysts due to their stronger Bronsted acidity and supported heteropolyacids have been gaining importance as alkylating and acylating catalysts. Among them, the keggin type, 12-tungstophosphoricacid (TPA) has been widely studied [9, 10] as it is most stable and strongest acid in the series. TPA supported onto different supports has been used for the alkylation of various substrates [6, 11, 12]. It was also observed that all used supports are acidic in nature. It is well known that basic support cannot be used for supporting HPAs, since it gets decomposed on the same. So, in the present paper we have made use of neutral alumina as the support. It is available in 3 different pH ranges: basic, acidic and neutral. Neutral alumina at pH of 6–8 is best as a support. To the best of our knowledge, no study has been carried out on *tert*-butylation of cresols using TPA supported on to neutral alumina. It was also found that no study was carried out using supported 12-tungsotsilicicacid (TSA), next stronger acid in the HPA series for the same. From our earlier studies [13, 14] it was found that 30% TPA and TSA supported onto neutral alumina is best as acid catalyst for esterification reactions. So, in the present paper, we have made effort to explore the use of same catalyst for alkylation reaction, one of the most important industrial reaction. We report the detailed study of the *tert*-butylation of cresols using TPA and TSA supported onto neutral alumina under mild conditions. *Tert-butylation* of *p*- cresol was carried out by varying different parameters such as temperature, mole ratio of cresol to *tert*-butyl alcohol (*t*-BA), amount of the catalyst and reaction time to optimize the conditions for *maximum* % conversion as well as % selectivity for *o*-isomer. The *tert*-butylation of *o*-cresol and *m*-cresol was carried out under optimized conditions.

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2. Experimental

2.1. Materials

All chemicals used were of A. R. grade. $H_3PW_{12}O_{40}$ nH_2O and $H_4SiW_{12}O_{40}$ nH_2O, *o*-cresol and *p*-cresol (Lobachemie, Mumbai) were used as received. Neutral alumina, *tert*-butyl alcohol and *m*-cresol were obtained from Merck and used as received.

2.2. Synthesis of the catalyst

2.2.1. Supporting of 12-tungstophosphoricacid and 12-tungstosilicicacid onto neutral alumina (TPA/Al_2O_3, TSA/Al_2O_3).

A catalyst containing 30% of HPA was synthesized by impregnating 1 g of Al_2O_3 with an aqueous solution of HPA (0.3-g/30 ml of conductivity water) with stirring for 35 h and dried at 100 °C for 10 h. The obtained material was designated as TPA/Al_2O_3 and TSA/Al_2O_3.

2.3. Characterization

The support and supported catalysts were well characterized by us earlier [13, 14]. The main characterizations are shown in table 1.

2.4. Catalytic reaction

2.4.1. Tert- butylation of cresols

The alkylation reaction was carried out in a 50 ml glass batch reactor provided with a double walled air condenser, magnetic starrier and a guard tube. Cresol to *t*-butyl alcohol was taken in 10:1 (10.5 ml: 0.95 ml) ratio and catalyst was added in the required amount. The resultant mixture was heated at 80 °C on magnetic stirrer for 1 h. Same reaction was carried out by varying *t*-BA to cresol mole ratio, temperature, amount of the catalyst and reaction time. Products formed after completion of reactions were analyzed on Gas Chromatograph using SE-30 column and product identification was done by a combined Gas Chromatography-Mass Spectrometry.

3. Results and discussion

Test performed for the chemical stability of the synthesized material shows that it is stable and not any visible change appears in the material up to 4 molar concentration of the various conventional acids and bases. It also shows stability in cresols, *tert* butyl alcohol and reaction mixture.

Table 1
Main characterization of TPA/Al_2O_3 and TSA/Al_2O_3

Catalyst	Total acidity (mmol NH_3/g)	BET surface area (m^2/g)	Particle size (μm)	IEC (meq/g)
Al_2O_3	0.47	81	114	0.00
TPA/Al_2O_3	0.76	109	42	1.06
TSA/Al_2O_3	0.60	122	42	0.39

Any leaching of the catalyst from the support would make the catalyst unattractive for reusing. So it is necessary to study the stability of heteropolyacid onto neutral alumina as well as leaching of HPA from the support in order to reuse the catalyst. HPA can be quantitatively characterized by the heteropoly blue (Tungsten blue) colour that is observed when it is reacted with a mild reducing agent such as ascorbic acid [15].

Standard samples amounting to 1–5% of 12-tungstosilicicacid in water were prepared. To 10 ml of above samples 1 ml of 10% ascorbic acid was added. The mixture was diluted to 25 ml. The resultant solution was scanned at a λ_{max} of 785 cm^{-1} for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance with percentage solution. 1 gm of catalyst with 10 ml of reactants was refluxed for 4 h than 1 ml of the supernent solution was treated with 10% ascorbic acid. No development of blue colour indicating no leaching. Leaching test has been carried out in cresols, tert-butyl alcohol and in reaction mixture after completion of the reaction. No leaching was found indicating the stability of the synthesized material.

As reported by us earlier [13, 16], X-Ray Differaction, Particle Size Distribution and Scanning Electron Microscopy studies shows the uniform distribution of heteropolyanion, as a layer not as crystals, on the surface of the support.

The values for Ion Exchange Capacity, Surface Area measurement, Particle Size Distribution and Total Acidity obtained from Temperature Program Desorption for TSA/Al_2O_3 are also presented in table 1.

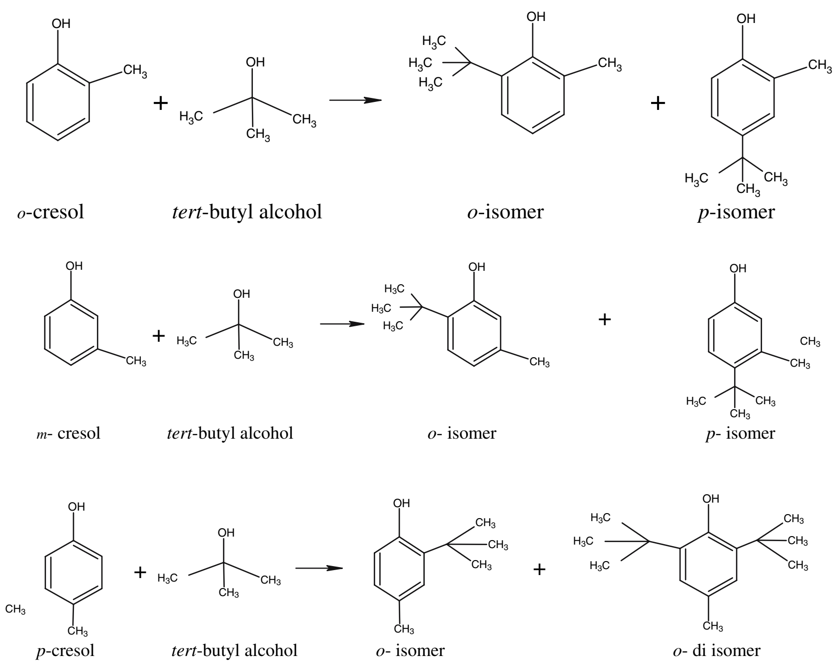
3.1. Tert- butylation of cresols

Alkylation of cresol with *t*-BA is a typical Friedel-crafts reaction and generally catalyzed by acid catalysts. *Tert*- butylation of cresols results in a mixture of different products as shown in Scheme 1.

Alkylation reaction carried out using support shows that the support is inactive for the *tert*-butylation of cresols.

3.2. Effect of mole ratio of t-BA to p-cresol and temperature

The reaction was carried out by varying mole ratio of *t*-BA to cresol with different amount of the catalyst for 6 h at two temperature; ambient temperature and 80 °C. At ambient temperature, the % conversion is found to be zero. The results obtained at 80 °C for both the catalysts are shown in table 2. It is seen from the table that with increase the concentration of *t*-BA, there is drastic change in the % conversion and % selectivity of the products. The decrease in % conversion may be due to the steric hindrance of *t*-BA group. As number of



Scheme 1.

tert-butyl molecules increases on the surface of the support, less site remain available on the surface of the support for the other reactant, which is *p*-cresol, and it is fact that if both the reactant was not in contact, reaction will not takes place.

Formation of the second product may be because of more resident time of the first substituted product on surface of the support. As resident time is more on the surface of the support, second substitution may also take place with the carbocation generated on the surface of the catalyst.

The % conversion is 97 and 94% with 100% selectivity for *o*-isomer is found at 1:10 mole ratio with 0.25 g of the catalyst for TPA/Al_2O_3 and TSA/Al_2O_3 respectively.

3.3. *Effect of amount of the catalyst*

The reaction was carried out with different amount of the catalysts keeping the mole ratio of cresol to *t*-BA 10:1 for 6 h. The % conversion and % selectivity of different products is reported in figure 1. The activity increases with an increase in the amount of the supported heteropolyaicds. The obtained results are in good agreement with the earlier reported [17–20]. 97% and 94% conversion was found with 0.25 g of the catalysts for TPA/Al_2O_3 and TSA/Al_2O_3 respectively with 100% selectivity for *o*-isomer.

Table 2

% conversion and % selectivity of *tert*-butylation of *p*-cresol with different mole ratio of *t*-BA to p-cresol as well as different amount of the catalyst

Amount of the catalyst TPA/$Al_2\mathbf{O}_3$/ TSA/Al_2O_3 (g)	Mole ratio	% Conversion	% Selectivity	
			o-*t*-b *p*-cresol	*o*-di *t*-b *p*-cresol
0.25	1:10	97.0/94.0	100/100	–/–
	3:10	19.3/28.7	76.4/100	23.6/–
	6:10	10.0/9.4	44.8/57.0	55.2/–
0.5	1:10	97.0/96.5	100/100	–/–
	3:10	35.9/27.8	67.3/89.3	32.7/10.7
	6:10	19.0/9.0	92.4/80.0	7.6/20.0
0.75	1:10	100/100	100/100	–/–
	3:10	30.5/44.0	100/100	–/–
	6:10	20.0/21.9	93.0/100	7.0/–

Conversion based on *t*-BA, Reaction temperature:80 °C, reaction time:6 h.

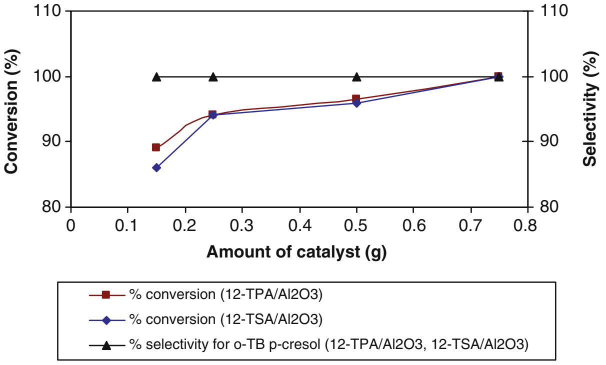


Figure 1. % conversion and % selectivity of *tert*-butylation of *p*-cresol with different amount of the catalyst. Conversion based on *t*-BA, Mole ratio of *t-BA* to *p*-cresol: 1:10, reaction temperature: 80 °C, reaction time is 6 h.

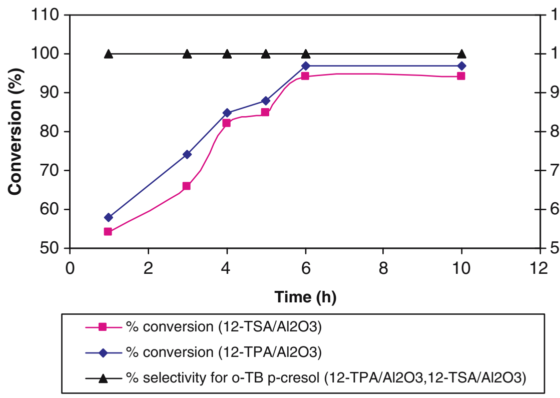


Figure 2. % conversion and % selectivity of *tert-b*utylation of *p*-cresol with different reaction time. Conversion based on *t*-BA, Mole ratio of *t-BA* to *p*-cresol: 1:10, reaction temperature: 80 °C, amount of the catalyst: 0.25 g.

3.4. Effect of reaction time

The effect of reaction time on *tert*-butylation of *p*-cresol was studied at a mole ratio of 10:1 using 0.25 g catalyst. The results are presented in figure 2. It is seen from the figure that with increase in reaction time, the % conversion also increases. It is also seen from the figure that initially, the increase in % conversion is fast and after 3 h slow increase is observed. This may be due to the fact that as *t*-BA consume in the reaction, less molecules are left in the reaction mixture and more time required to generate the carbocation from the *t*-BA. Further, initially rate of desorption of the product from the catalyst surface is high and as concentration of the product increases in the reaction mixture the rate become slow.

The optimum conditions for the present reaction are as follows.

Mole ratio of cresol to *t*-BA-Ã	10.1
Amount of the catalyst	0.25 g
Temperature	80 *degr*C
Reaction time	6 h

3.5. Recycling of the catalyst

Both the catalysts were recycled for two times in order to test its activity as well as stability. The 1st recycling (R1) was carried out after separating it from reaction mixture only by filtration, washing with conductivity water (double distilled water [21]), drying at 100 °C and treating at 300 °C. The 2nd recycling (R2) was carried out by separating R1 from reaction mixture only by filtration, washing with conductivity water and drying at 100 °C. Table 3 shows the results for the regenerated catalysts. There was not any change in selectivity, however little decrease in % conversion is observed.

Table 3

Recyclability of the catalyst for *tert*-butylation of *p*-cresol at 80 °C

Cycle No. TPA/Al_2O_3/ TSA/Al_2O_3	% Conversion	% Selectivity		TON
		o-*t*-b *p*-cresol	*o*-di *t*-b *p*-cresol	
R_1/R_1	88/85	100/100	–	415/400
R_2/R_2	87/83	100/100	–	411/391

Conversion based on *t*-BA, Mole ratio of *t-BA* to *p*-cresol: 1:10, Reaction temperature: 80 °C, reaction time: 6 h.

3.6. Tert-butylation of o-cresol and m-cresol

The same catalysts are also evaluated for the *t*-butylation of *o*-cresol and *m*-cresol under optimised conditions and the results are shown in table 4. In case of *o*-cresol, there is possibility of both isomers; *ortho* as well as *para* due to the steric effect of alkylating agent. The obtained results are in good agreement with the same, however, the major product is *p*-isomer. In case of *m*-cresol the formation of only one product, 2-*ter*- butyl 5 methyl phenol (*o*-isomer) is formed. In *m*-cresol, since the 2nd and 4th positions are not favourably susceptible to electrophilic attack by *tert*-butyl cation as they are sterically hindered by the adjacent methyl group, only sixth position is left for alkylation. Thus the obtained results are as expected.

It seen from the results that in all cases, the activity of TPA/Al_2O_3 is more than that of TSA/Al_2O_3. It is known that [10, 21] that the catalytic activity of heteropolyacids, both in homogeneous and heterogeneous systems, usually parallels to their acid strength i.e. $H_3[PW_{12}O_{40}]$ > $H_4[SiW_{12}O_{40}]$ > $H_3[PMo_{12}O_{40}]$ > $H_4[SiMo_{12}O_{40}]$. It is also known that the difference in the activity is not much appreciable as the acidity is also depends on the addenda atom. Since in the present case, the addenda atom is the same, not appreciable difference in the activity should observed. The obtained results are in good agreement with the above trend. The results are also supported by the value of the total acidity, 0.76 meq/g and 0.60 meq/g for TPA/Al_2O_3 and TSA/Al_2O_3 respectively. However, there is no appropriate change in % conversion, it is important to note that the

Table 4

% conversion and % selectivity for *tert*-butylation of cresols

Catalyst	Substrate	% Conversion	% Selectivity		TON
			o-isomer	*p*-isomer	
TPA/Al_2O_3	*o*-cresol	94.0	24	76	443
TSA/Al_2O_3		89.0	26.6	73.4	419
TPA/Al_2O_3	*m*-cresol	97.0	100	–	457
TSA/Al_2O_3		94.0	100	–	442
TPA/Al_2O_3	*p*-cresol	97.0	100	–	457
TSA/Al_2O_3		94.0	100	–	442

% conversion is based on t-BA, amt. of catalyst: 0.25 g, mole ration of phenol to t-BA is 10:1, reaction temperature: 80 °C, reaction time: 6 h.

Table 5

Comparison of % conversion of phenol and % selectivity for p-tert butyl phenol of TPA/ Al_2O_3 and TSA/Al_2O_3 with other catalysts

Catalyst	Ref.	Mole ratio[a]	Reaction condition[b]	Conversion (%)	Selectivity (%)		
					o-t-b *p*-cresol	*m-t*-b *p*-cresol	*o*-di *t*-b *p*-cresol
TPA/ Al_2O_3	This work	10:1	353; 1; 0.25	97[c]	100	–	–
TSA/Al_2O_3	This work	10:1	353; 1; 0.25	94[c]	100	–	–
$FeCl_3$/K-10 clay	[8]	10:1	353; 0.5; 0.5	100[c]	86.5	11.6	1.7
WOx/ZrO_2[e]	[7]	1:3	403; 2; 2	69.8[d]	92,4	–	6,3
TPA/ZrO_2[f]	[6]	1:3	403; 5; 2	61.0[d]	81.4	–	18.1

[a] Phenol: *t*-BA. [b] Reaction temperature (K); reaction time (h); catalyst amount (g). [c] Conversion based on *t*-BA. [d] Conversion based on *p*-cresol. [e] catalyst calcinated at 1,073 K, [f] catalyst calcinated at 1,023 K.

present catalyst is not surface type-ordinary heterogeneous catalyst in which catalytic activity is directly proportional to the surface area of the catalyst, but it is pseudo liquid-bulk I type catalyst in which catalytic activity is directly proportional to the total acidity of the catalyst.

Table 5 highlights the better performance of the present catalysts for *tert*-butylation of *p*-cresol in comparison with other reported catalysts. The superiority of the present catalysts lies in obtaining high % conversion and % selectivity. The obtained results are very unique and outstanding. The recycling of HPA catalysts is the key issue to their applications. Conventional recycling i.e. burning of coke at 500–550 °C, is not applicable to HPAs as their thermal stability is not high enough [22]. Therefore, the development of a technique which leads to a reduction in the burning temperature of coke is of very important. Here first time we have reported the recycling of the supported catalysts by heating at temperature 300 °C. It is seen from the table that the catalysts give 100% selectivity and 88/85 and 87/83 % conversion even after two cycles.

4. Conclusion

In the present study, we have demonstrated the use of supported TPA as well as TSA for the selective *t*-butylation of cresols. The obtained results are very unique and outstanding in terms of %conversion as well as % selectivity for the desired product. The results are indeed promising as compared to those achieved by using other catalysts earlier. Moreover in all reactions, removal of the catalyst as well as the products consists of the single filtration. In addition more expensive cresols can be separated by simple distillation from the reaction mixture and can be reused. The catalysts can also be reused after a simple workup. Thus the present catalysts are not only selective but also promising cleaner alternative to the environmentally hazardous traditional catalysts for liquid phase alkylation process.

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References

[1] J. Pospisil, Polym. Degrad. Stabil. 20 (1988) 181.
[2] J. Murphy, *The additives for Plastics Handbook* (Elsevier Advanced Technology, Oxford, 1996).
[3] E. Santacesaria, R. Silvani, P. Wilkinson and S. Carra, Ind. Eng. Chem. Res. 27 (1988) 541.
[4] W. Hartmut, Chem-Ing-Tech. 52 (1980) 825.
[5] G.D. Yadav and T.S. Thorat, Ind. Eng. Chem. Res. 35 (1996) 721.
[6] B.M. Devassy, G.V. Shanbhag, F. Lefebvre and S.B. Halligudi, J. Mol. Catal. A: Chem 210 (2004) 125.
[7] S. Sarish, B.M. Devassy and S.B. Halligudi, J. Mol. Catal. A: Chem 235 (2005) 44.
[8] A.B. Shinde, N.B. Shrigadi and S.D. Samant, Appl. Catal. A: Gen. 276 (2004) 5.
[9] N. Mizuno and M Misono, Chem. Rev. 98 (1998) 199.
[10] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[11] J. Mao, Y. Kamiya and T. Okuhara, Appl. Catal. A: Gen. 255 (2003) 337.
[12] I.V. Kozhevnikov, A. Sinnema, R.J. Janse, K. Pamin and H.V. Bekkum, Catal. Lett. 30 (1995) 241.
[13] P. Sharma, S. Vyas and A. Patel, J. Mol. Catal. A: Chem. 214 (2004) 281.
[14] N. Bhatt, A.J. Patel, Mol. Catal. A. (in press).
[15] G.D. Yadav and V.V. Bokade, Appl. Catal. A 147 (1996) 299.
[16] N. Bhatt, A. Patel, (Comunicated, Chinese journal of Catalysis).
[17] I.V. Kozhevnikov and M.N. Timofeeva, J. Mol. Catal. 75 (1992) 179.
[18] V.M. Mastikhin, V.V. Tersskih, M.N. Timofeeva and O.P. Krivoruchko, J. Mol. Catal. A: Chem. 95 (1995) 135.
[19] Y. Izumi, R. Hasebe and K. Urabe, J. Catal. 84 (1983) 403.
[20] Y. Izumi, N. Natsume, H. Takamine, I. Tamaoki and K. Urabe, Bull. Chem. Soc. Jpn. 62 (1989) 2159.
[21] G.H. Jeffery, J. Basett, J. Mendhem and R.C. Donney, *Text book of Quntitative Chemical Analysis* 5 ed.(Longman, Singapore, 1989).
[22] I.V. Kozhevnikov, in: *Catalysis by Polyoxometalates*, Vol. 2, (Wilay, Chichester, 2002).