

# Supported 12-tungstophosphoricacid: An efficient and selective solid acid catalyst for *tert*-butylation of phenol and cresols

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## Abstract

12-Tungstophosphoricacid (30%) supported onto zirconia was synthesized by impregnation. The synthesized catalyst was characterized by solid state NMR and XPS in order to study the nature of active species on support surface. The acidity of the catalyst was measured by temperature programmed desorption (TPD) of NH<sub>3</sub>. Liquid phase alkylation of phenol and cresols with *tert*-butyl alcohol was carried out using fresh as well as calcined catalyst under mild conditions. The catalysts show high activity in terms of conversion and selectivity for the desired product under mild conditions. The process could be economically viable as the un-reacted phenol could be separated by simple distillation and reused for further reaction. Studies also reveal that the regenerated catalyst could be used for achieving high yield transformation.

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## 1. Introduction

The alkylation of phenol and substituted phenol with *tert*-butyl alcohol is an industrially important reaction since products obtained thereby are used directly or as chemical intermediates for bulk industries like petrochemicals, fine chemicals and agrochemical industries, etc. Generally alkylation reaction is carried out by using Friedel–Crafts catalysts such as AlCl<sub>3</sub>, BF<sub>3</sub>, FeCl<sub>3</sub> and ZnCl<sub>2</sub>. The known disadvantages of these traditional liquid acid catalysts result in major search for cleaner technology. Cleaner technology could be possible by making use of environment friendly catalyst. A number of solid acids [1–8] have great capability to take account instead of Friedel–Crafts catalysts.

Among the solid acid catalysts, heteropoly acids (HPAs) are promising one for Friedel–Crafts reactions. Among Keggin type HPAs, 12-tungstophosphoricacid (TPA) is thermally more stable and acidic than any other HPAs [9,10]. Literature reports reveal that most alkylation reactions were carried out either in vapor phase, or at high temperature or in ionic solvents. Additionally, to the best of our knowledge, no report is there with more than 80% selectivity for *p-tert*-butyl phenol formation with 54.2% conversion in liquid phase under mild conditions [7]. Though there are report available in the literature on alkylation of phenol with *tert*-butyl alcohol, obtaining 100% conversion and >80% selectivity for the desired product is a challenging task.

12-Tungstophosphoricacid supported onto different supports [8,11,12] are known to be used for the alkylation of various aromatic substrate. Although the heteropolyacids are active for alkylation reaction, deactivation during the reactions is significant due to the coke formation. Traditionally, removal of coke from the catalyst was carried

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out by heating the catalyst at 500 °C. The traditional method cannot be applied to the heteropolyacids as they decompose at that temperature [13]. It is also known that the recycling of heteropolyacid catalyst is the key issue to their applications as subsequent regeneration of the same is quite difficult.

In this paper, we report the liquid phase alkylation of phenol/cresol under mild conditions using hybrid catalyst derived from 12-tungstophosphoricacid supported onto zirconia. Detailed characterization of the solid catalyst by solid state NMR, XPS and TPD of NH<sub>3</sub> is also reported. It also describes a simple process for the regeneration of the catalyst. We have surprisingly found that heteropolyacid catalyst can be regenerated and also reused for the same alkylation reaction. Here, for the first time we are reporting a method for regenerating the heteropolyacid by heating at 300 °C.

## 2. Experimental

### 2.1. Synthesis of catalyst

#### 2.1.1. Synthesis of the support, hydrous zirconia (ZrO<sub>2</sub>)

Hydrous zirconia was synthesized by adding an aqueous ammonia solution to an aqueous solution of ZrOCl<sub>2</sub> · 8H<sub>2</sub>O up to pH 8.5. The resulted precipitates were aged at 100 °C over a water bath for 1 h, filtered, washed with conductivity water until chloride free water was obtained and dried at 100 °C for 10 h. The obtained material is designated as ZrO<sub>2</sub>.

#### 2.1.2. Supporting of 12-tungstophosphoricacid (TPA) onto hydrous zirconia (TPA/ZrO<sub>2</sub>)

12-Tungstophosphoricacid was supported on hydrous zirconia by wet impregnation method. One gram of ZrO<sub>2</sub> was impregnated with an aqueous solution of TPA (0.3 g/30 ml of conductivity water). The water from the suspension was allowed to evaporate at 100 °C in an oven. Then the resulting mixture was dried at 100 °C with stirring for 10 h. Material thus obtained was designated as TPA/ZrO<sub>2</sub>. The synthesized catalyst was calcined at 300 °C in air for 5 h and designated as C-TPA/ZrO<sub>2</sub>.

### 2.2. Characterization

Detail characterization of the catalyst can be found in our earlier reports [14,15]. In addition, the catalyst was further characterized for solid state NMR, XPS and TPD of NH<sub>3</sub>.

The magic-angle spinning (MAS) solid state NMR study was carried out on a Bruker Avance DSX -300 NMR spectrometer under ambient conditions. The <sup>31</sup>P NMR spectra were recorded at 121.48 MHz using a 7 mm rotor probe with 85% phosphoric acid as an external standard. The spinning rate was 4–5 kHz. Catalyst samples after treatment were kept in a desiccator over P<sub>2</sub>O<sub>5</sub> until the NMR measurement.

XPS studies were performed on ESCA LAB Mark II spectrometer (vacuum generator, UK). The spectra were obtained using a Mg K $\alpha$  radiation (1253.6 eV) with 50 eV pass energy. The working pressure in the analyzer chamber was maintained below 10<sup>-9</sup> torr. The peak positions were assigned by setting C 1s contamination signal to a binding energy (B.E.) of 284.0 eV.

The chemisorption of ammonia gas (pure) on the surface of the sample was carried out using Micromerities Pulse Chemisorb-2705.

### 2.3. Catalytic reaction

The alkylation of phenol/cresol was carried out in a 50 ml glass reactor provided with a double walled air condenser, magnetic stirrer and a guard tube. Mole ratio of phenol/cresol and alkylating agent used for the catalytic studies was in 10:1 and the catalyst was added in the required amount. The resultant mixture was heated at 80 °C on magnetic stirrer for 6 h. The same reactions were carried out by varying different parameters such as amount of the catalyst, temperature, time and mole ratio of phenol/cresol to alkylating agent to optimized the conditions. For alkylation of phenol with *tert*-butyl alcohol, products obtained were identified as *o*-*t*-BP, *p*-*t*-BP and *o*,*p*-di-*t*-BP by gas chromatograph (Nucon 5700) using SE-30 column while *m*-*t*-BP was identified by AT-1000 column. Product identification was done by comparison with authentic samples as well as by a combined gas chromatography–mass spectrometry. Further, the isomers were separated by HPLC (Shimadzu) using Nucleosil C<sub>18</sub> column and identified by <sup>1</sup>H NMR.

For alkylation of cresols with *tert*-butyl alcohol the reaction products were analyzed using SE-30 column, and product identification was done by a combined gas chromatography–mass spectrometry.

## 3. Results and discussion

### 3.1. Characterization

The <sup>31</sup>P NMR spectra of TPA and TPA/ZrO<sub>2</sub> are shown in Fig. 1. The value of chemical shift for TPA is –15.626 ppm and is in good agreement with the reported value [16]. The value of chemical shift for the catalyst is –15.523 ppm. No appreciable change in chemical shift value reveals that the surrounding environment for the supported TPA does not change after supporting onto ZrO<sub>2</sub> surface. In other words the structure of the keggin ion remains intact after supporting onto ZrO<sub>2</sub>. Line broadening may be due to the supporting of TPA onto support.

The observed and theoretical values of binding energy (B.E.) for Zr 3d<sub>5/2</sub>, O 3d<sub>3/2</sub>, 1s and W 4d<sub>5/2</sub>, 4d<sub>3/2</sub> are presented in Table 1. It is well known that as the Zr contains strong Lewis acidity, it will withdraw some of the charge density from TPA when supported onto ZrO<sub>2</sub>. As a result, there is an increase in B.E. of Zr. Further, the B.E. of O 1s

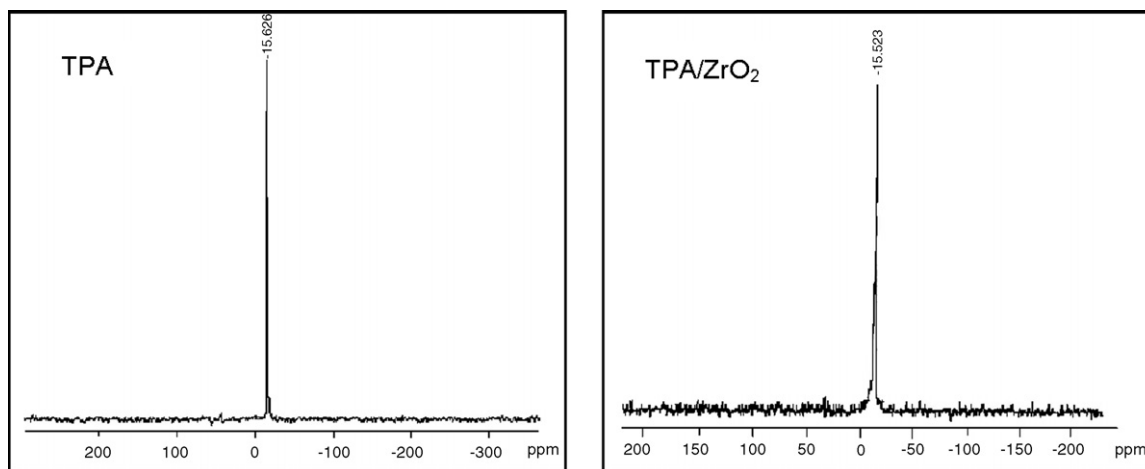
Fig. 1. Solid state NMR of TPA and TPA/ZrO<sub>2</sub>.

Table 1

Core electron binding energies for different elements in catalyst TPA<sub>3</sub>/ZrO<sub>2</sub>

XPS core level	Energy level	B.E. (eV)	
		Standard	Observed
Zr (Zr(OH) <sub>4</sub> )	3d <sub>5/2</sub>	178.7	179.1
	3d <sub>3/2</sub>	181.4	181.8
O (WO <sub>3</sub> )	1s	531	531.7
	4d <sub>5/2</sub>	227.7	227.8
W (WO <sub>3</sub> )	4d <sub>3/2</sub>	230.9	231.0

is shifted to the higher value and the band becomes broader indicating the presence of different types of oxygen atoms in the heteropolyanion. The observed B.E. for W 4d is almost same as theoretical value confirming the +6 oxidation state of W. The study confirms that the surface of ZrO<sub>2</sub> is composed of unchanged heteropolyanion species.

It is well known that HPAs are stronger Bronsted acid than conventional solid acid catalysts [17,18]. Especially, the acidity of TPA falls in the super acid region [19]. The value of total acidity obtained from TPD of NH<sub>3</sub> for TPA is 1.05 mmol NH<sub>3</sub>/g [20] while that for TPA/ZrO<sub>2</sub> is 0.84 mmol NH<sub>3</sub>/g. Small difference in the values indicate that TPA remains unaltered after supporting onto zirconia. Hence, supported catalyst is also expected to behave as a super acid catalyst.

### 3.2. Catalytic reaction

Alkylation of phenol/cresols with *tert*-butyl alcohol in presence of acid catalysts generally results in a mixture of different products as shown in Scheme 1.

The % conversion and % selectivity for different products obtained from the *tert*-butylation of phenol/cresols using TPA/ZrO<sub>2</sub> as catalyst under optimized conditions are reported in Table 2. The present catalyst gives 100% conversion at 6 h, with 97.2% selectivity for the *p*-*tert* butyl phenol (*p*-isomer). In case of *o*-cresol the major product is *p*-isomer. In case of *o*-cresol, there is a possibility for both

isomers; *ortho* as well as *para* isomer 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, *o*-*tert* butyl *m*-methyl phenol (*o*-isomer) is found. In *m*-cresol, the 2nd and 4th positions are not favorably susceptible to electrophilic attack by *tert*-butyl cation as they are sterically hindered by the adjacent methyl group, only 6th position is left for alkylation. This could nicely explain the result. In case of *p*-cresol the present catalyst gives 97% conversion with 100% selectivity for *o*-*tert* butyl *p*-cresol (*o*-isomer).

Almost complete conversion with high selectivity for the desired product has given by this heteropolyacid catalyst which is a clear edge over the other solid Lewis acid catalyst used for related reactions. In order to check stability of the catalyst as well as the possibility of any significant deactivation that may occur during the course of reaction, the effect of reaction time on *tert*-butylation of phenol was studied (ES).

Further, TPA/ZrO<sub>2</sub>, was recycled for two times and the results are reported in Table 3. The 1st recycling (R<sub>1</sub>) was carried out after separating it from reaction mixture by filtration followed by washing with conductivity water, drying at 100 °C and treating at 300 °C. The 2nd recycling (R<sub>2</sub>) was carried out by separating R<sub>1</sub> from reaction mixture by filtration followed by washing with conductivity water and drying at 100 °C. For C-TPA/ZrO<sub>2</sub>, recycling was carried out by separating the catalysts from reaction mixture by filtration and washed with conductivity water and drying at 100 °C (R<sub>1</sub>C-TPA/ZrO<sub>2</sub>).

The % conversion and % selectivity for the *tert*-butylation of phenol for all the catalysts are reported in Table 3. It is seen from the table that 90% conversion is achieved with TPA/ZrO<sub>2</sub> at 1 h only whereas for the R<sub>1</sub>-TPA/ZrO<sub>2</sub>, R<sub>2</sub>-TPA/ZrO<sub>2</sub>, C-TPA/ZrO<sub>2</sub>, and R<sub>1</sub>C-TPA/ZrO<sub>2</sub>, 88.5, 82.5, 89.0 and 81.0% conversion is obtained at 6 h, respectively. It is seen from the table that all catalysts, fresh, regenerated, calcined and calcined regenerated, give almost



Table 2  
% Conversion and % selectivity for *tert*-butylation of phenol and cresols over TPA/ZrO<sub>2</sub>

Substrate	Conversion (%)	Selectivity (%)		TON <sup>b</sup>
		<i>o</i> - <i>t</i> -BP	<i>p</i> - <i>t</i> -BP	
Phenol	100 (90) <sup>a</sup>	2.8 (–) <sup>a</sup>	97.2 (100) <sup>a</sup>	471 (421) <sup>a</sup>
<i>o</i> -Cresol	95.0 (82) <sup>a</sup>	19.2 (–) <sup>a</sup>	81.8 (100) <sup>a</sup>	445 (384) <sup>a</sup>
<i>m</i> -Cresol	95.0 (77.4) <sup>a</sup>	100 (100) <sup>a</sup>	– (–) <sup>a</sup>	445 (362) <sup>a</sup>
<i>p</i> -Cresol	97.0 (83) <sup>a</sup>	100 (100) <sup>a</sup>	– (–) <sup>a</sup>	454 (389) <sup>a</sup>

% Conversion is based on *tert*-butyl alcohol, amount of catalyst is 0.25 g, mole ration of phenol to *tert*-butyl alcohol is 10:1, temperature: 80 °C, time: 6 h.

<sup>a</sup> The number in parentheses indicate the result under homogeneous condition.

<sup>b</sup> TON is defined as mole substrate reacted per mole catalyst.

Table 3  
% Conversion and % selectivity for *tert*-butylation of phenol

Catalyst	Conversion (%)	Selectivity (%)		TON
		<i>o</i> - <i>t</i> -BP	<i>p</i> - <i>t</i> -BP	
TPA/ZrO <sub>2</sub>	100 (90) <sup>a</sup>	2.8	97.2	471 (421)
R <sub>1</sub> -TPA/ZrO <sub>2</sub>	88.5	3.0	97.0	414
R <sub>2</sub> -TPA/ZrO <sub>2</sub>	82.5	3.0	97.0	386
C-TPA/ZrO <sub>2</sub>	89.0	4.4	95.6	417
R <sub>1</sub> C-TPA/ZrO <sub>2</sub>	81.0	3.4	96.6	379
ZrO <sub>2</sub>	–	–	–	–
TPA	90.0	–	100	421

% Conversion is based on *tert*-butyl alcohol, amount of catalyst is 0.25 g, mole ratio of phenol to *tert*-butyl alcohol is 10:1, temperature: 80 °C.

<sup>a</sup> Time: 1 h, 6 h.

Table 4  
% Conversion and % selectivity for *tert*-butylation of phenol (with and without catalyst)

Catalyst	Conversion (%)	Selectivity (%)	
		<i>o</i> - <i>t</i> -BP	<i>p</i> - <i>t</i> -BP
TPA/ZrO <sub>2</sub> (1 h)	90	2.8	97.2
Filtrate (6 h)	90	2.9	97.1

% Conversion is based on *tert*-butyl alcohol, amount of catalyst is 0.25 g, mole ration of phenol to *tert*-butyl alcohol is 10:1, temperature: 80 °C.

Table 5  
Comparison of % conversion of phenol and % selectivity for *p*-*tert*butyl phenol of TPA/ZrO<sub>2</sub> with other catalysts

Catalyst	Mole ratio <sup>a</sup>	Reaction condition <sup>b</sup>	Conversion <sup>c</sup> (%)	Selectivity (%)		
				<i>o</i> - <i>t</i> -BP	<i>p</i> - <i>t</i> -BP	<i>o</i> , <i>p</i> - <i>di</i> - <i>t</i> -BP
TPA/ZrO <sub>2</sub>	10:1	353; 1; 250	100	2.8	97.2	–
TPA/ZrO <sub>2</sub>	10:6	353; 1; 250	20	3.6	96.4	–
K-10 clay [16]	10:1	353; 6; 500	100	35.4	62.0	2.6
FeCl <sub>3</sub> /K-10 clay [28]	10:1	353; 0.5; 500	100	30.5	66.8	2.7
USY [7]	10:6	343; 3; 200	52.7 <sup>d</sup>	63.0	23.0	13.1
Zeolite-β [7]	10:6	343; 3; 200	54.2 <sup>d</sup>	18.3	80.3	1.4
Mordenite [7]	10:6	343; 8; 200	28.8 <sup>d</sup>	48.1	49.1	2.8
TPA/MCM-41 <sup>e</sup> [8]	1:2	333; 4; 282	44.8 <sup>d</sup>	29.0	49.0	21.2

<sup>a</sup> Phenol: *t*-BA.

<sup>b</sup> Reaction temperature (K); reaction time (h); catalyst amount (mg).

<sup>c</sup> Conversion based on *tert*-butyl alcohol.

<sup>d</sup> Conversion based on phenol, i.e., % conversion is calculated on the basis of unreacted phenol.

<sup>e</sup> TPA – 12-tungstophosphoric acid.

alyst does not give good % conversion as compared to the reported catalysts [7] in 10:6 mole ratio. It is known that initially phenol gets adsorbed on the available Bronsted acid sites and *tertiary* carbocation interact with adsorbed phenol forming a  $\pi$  complex, which rearrange to  $\sigma$  complex by the electrophile attack to a ring carbon atom. The  $\sigma$  complex on proton elimination gives *tert*-butyl phenol [22]. The drastic decrease in the conversion might be due to the increase in number of *tert*-butyl carbocation, which prevent the chemisorptions of phenol. With decrease in the availability of chemisorbed phenol, the decrease in conversion is expected.

The reported catalysts required pre-activation at 433 K and pressure below 1 torr. In addition reaction has been carried out in presence of CCl<sub>4</sub>, which is not an environment friendly solvent. The present catalyst does not require any pre-activation, pressure or solvent. Further more expensive phenol can be separated by simple distillation from the reaction mixture and can be reused.

For *tert*-butylation of phenol the study on recyclability has also been carried out in detail. Our regenerated catalyst gives high % selectivity for *p*-isomer than the other reported catalysts (Table 4). High *p*-selectivity for present catalyst may be due to presence of TPA, which is proved to be a pure Bronsted acid [23].

As discussed earlier, presumably formation of  $\pi$  complex took place which was then converted to a  $\sigma$  complex giving *tert*-butyl phenol. It has been suggested [24–27] that the Bronsted acid site interacts with the  $\pi$ -cloud of aromatic ring bringing the molecule parallel to the surface. This will allow alkylation at the *para* position easier as compared to the *ortho* positions. As present catalyst contains pure Bronsted acidity, high selectivity for *p*-isomer is expected.

The present work provides an improved process for the *tert*-butylation of phenol in liquid phase under mild (80 °C, atmospheric pressure) conditions with 100% conversion and 97.2% selectivity for *p*-*tert*-butyl phenol (Filed Patent No: 2113/DEL/2006). The advantage of the process lies



in the simple regeneration of the catalyst near complete conversion and high selectivity. The regenerated catalyst also gives comparable selectivity for *p*-*tert*-butyl phenol. The present catalysts are not only efficient and selective but also promising from the view point of the environmental issue.

#### 4. Conclusion

<sup>31</sup>P NMR study indicates that the structure of TPA remains intact after supporting. XPS studies confirm that W retains its +6 oxidation state after supporting.

The present paper reports, liquid phase alkylation of phenol/cresol at low temperature. It provides remarkable economical advantage. Moreover in all reactions, removal of the catalyst as well as the products consists of the single filtration. The catalysts can be reused after a simple workup.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.catcom.2007.12.027](https://doi.org/10.1016/j.catcom.2007.12.027).

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