

Fresh and calcined supported 12-tungstosilicicacid: Synthesis, characterization and application to some acid catalyzed reactions

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Abstract

A series of catalyst containing 20–70% of 12-tungstosilicicacid (TSA) supported onto neutral alumina (A) has been synthesized, characterized and evaluated for esterification of 1° and 2° alcohols. The best catalyst, TSA₃/A (30% loading of 12-tungstosilicicacid onto neutral alumina) has been compared with TSA₃/Z (30% loading of 12-tungstosilicicacid onto hydrous zirconia) in order to see the effect of nature of support. The catalytic activity of TSA₃/A and TSA₃/Z has also been explored for *tert*-butylation of phenol by varying different parameters. Both the catalysts were calcined in the temperature range of 300–500 °C and characterized by FT-IR, DRS and XRD to see the structural change in the calcined materials. Their catalytic activity was also evaluated for the esterification as well as *tert*-butylation of phenol under optimized conditions. An attempt has also been made to regenerate and to reuse the present catalysts, especially for *tert*-butylation of phenol.

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1. Introduction

The acid catalyzed reactions comprise a wide range from dehydration, esterification up to alkylation, acylation and generally are carried out by traditional Bronsted acids such as H₂SO₄, HCl, H₃PO₄, HNO₃, HF and Lewis acids such as AlCl₃, BF₃, ZnCl₂. Among these, due to the known important industrial applications of esters as well as of obtained alkyl phenols, esterification of alcohols and alkylation of phenol has attracted worldwide attention. The replacement of the traditional environmental hazardous and corrosive homogeneous catalysts by heterogeneous catalysts in order to achieve clean technology is one of the demands of the society.

Among the solid acid catalysts, heteropolyacids (HPAs) are more efficient catalyst and have many advantages over conventional acid catalysts. The known disadvantages of HPAs can be overcome by supporting them onto suitable supports. In recent times, supported HPAs have been gaining importance as acid catalyzed reactions such as esterification [1–6] alkylation [7–12] and acylation [8,13–16].

Among HPAs, Keggin type 12-tungstophosphoricacid is the most widely studied from the viewpoint of acidic strength [17–19] as well as thermal stability [18–20]. Literature survey shows that not much work has been carried out on 12-tungstosilicicacid [21–26], next acidic and stable HPA in the Keggin series. So we have thought of carrying out study on 12-tungstosilicicacid.

The synthesis, characterization and catalytic activity of 12-tungstosilicicacid (TSA) supported onto hydrous zirconia (Z) was studied by us [27] and 30% loading of 12-tungstosilicicacid (TSA₃/Z) onto hydrous zirconia was found to be best. It is known that support does not play always merely a mechanical role but it can also modify the catalytic properties of the HPAs. In order to see the effect of support, it was thought to use different support and hence neutral alumina has been used as the support.

In the present work, a series of catalysts containing 20–70% loading of 12-tungstosilicicacid (TSA) on to neutral alumina (A) were synthesised. The support and new amorphous catalysts have been characterised by various physico-chemical techniques. Their catalytic properties were evaluated for the esterification of 1° alcohols and 2° alcohols by varying different parameters. The catalytic activity of best catalyst TSA₃/A (30% loading of 12-tungstosilicicacid on to neutral alumina) was com-

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pared with the TSA₃/Z (30% loading of 12-tungstosilicic acid on to hydrous zirconia) to see the effect of the nature of the support.

Since, the obtained results for esterification reactions are very promising; in order to perform a new contribution to the field of acid catalyzed reactions, the use of same catalysts for the alkylation of phenol has been explored. *tert*-Butylation of phenol with best catalyst (TSA₃/A, TSA₃/Z) was carried out by varying different parameters such as temperature, time, and mole ratio of alcohol to phenol to optimize the conditions.

Further, both the catalysts were calcined and characterized for FT-IR, DRS and XRD to see any structural change of supported TSA species as well as the effect of calcinations on catalytic activity. The difference in the performance of the catalysts was correlated with the nature of the support. On the basis of the stability as well as results obtained from esterification and alkylation reactions, best support among two has been proposed.

It is known that the traditional method for regeneration cannot be applied to the heteropolyacids as they decompose at low temperature [28]. In the present paper, a simple method for the regeneration of the HPA catalysts has also been described.

2. Experimental

2.1. Materials

All chemicals used were of A.R. grade. 12-Tungstosilicic acid, H₄SiW₁₂O₄₀·*n*H₂O (Lobachemie, Mumbai), Zirconium oxychloride, ZrOCl₂·8H₂O (SD Fine chemicals, Mumbai) were used as received. Neutral active Al₂O₃, *n*-butanol, *iso*-butanol, 2-butanol, cyclohexanol, formic acid, glacial acetic acid, propionic acid, phenol and *tert*-butyl alcohol were obtained from Merck and used as received.

2.2. Synthesis of the catalysts

2.2.1. Supporting of TSA onto neutral alumina (A)

A series of catalysts containing 20–70% of TSA were synthesized by impregnating 1 g of A with an aqueous solution of TSA (0.2–0.7 g/20–70 ml of conductivity water) with stirring for 35 h and dried at 100 °C for 10 h. The obtained materials were designated as TSA₂/A, TSA₃/A, TSA₄/A, TSA₅/A and TSA₇/A. The selected best catalyst (TSA₃/A) was calcinated at 300, 400 and 500 °C in air for 5 h and designated as C₃-TSA₃/A, C₄-TSA₃/A and C₅-TSA₃/A, respectively.

2.2.2. Supporting of TSA onto hydrous zirconia (Z)

The support Z and the catalyst TSA₃/Z was synthesized by reported method [27]. The catalyst was calcinated at 300 and 400 °C in air for 5 h and designated as C₃-TSA₃/Z and C₄-TSA₃/Z, respectively.

2.3. Characterization

Different mineral acids and alcohols were used for checking the chemical stability of the materials. The ion-exchange capacity was determined by the process as reported earlier [27]. Differential scanning calorimetric of the sample was

carried out on TA INSTRUMENTS DSC-2010 instrument. Adsorption–desorption isotherms of samples were recorded on a Micromeritics ASAP 2010 Surface area analyser at –196 °C. From the adsorption desorption isotherms, specific surface area was calculated using BET method. The FT-IR spectrum of the sample was obtained by using KBr wafer on Parkin-Elmer. The DRS spectrum of TSA and TSA₃/A was recorded on a Shimadzu PR1 instrument using barium sulphate as a reference. The XRD pattern was obtained by using PHILIPS X'PERT, MPD SYSTEM. The conditions used were: Cu K α radiation (1.5417 Å), scanning angle from 5° to 60°. The study on particle size distribution for A and TSA₃/A was carried out on Malvern particle size analyser, Mastersizer 2000. The surface morphology of the support (A) and supported HPAs (TSA₃/A) was studied by scanning electron microscopy using a Jeol SEM instrument (model-JSM-5610 LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range and images taken at a magnification of 200 \times for A, 250 \times and single particle image at 500 \times for TSA₃/A.

2.4. Acidity measurement

The chemisorption of pure ammonia gas on the surface of the sample was carried out using Micromeritics Pulse Chemisorb-2705. The sample, prepared by heating at predetermined temperature (300 °C) was kept in a U-shaped quartz tube and the tube was placed in a split furnace. The sample was first heated in situ at 300 °C in flowing of argon (99.95%) for 2 h to remove the moisture which might have adsorbed during the transfer of sample at various stages. The chemisorption of pure ammonia on the preheated sample was carried out at 120 °C by repeatedly injecting the pulse of pure ammonia gas onto the sample till the saturation was observed. The amount of ammonia chemisorbed on the sample in every pulse was shown by thermal conductivity detector (TCD) in the form of integrated area of the ammonia peak. From the peak areas, the acidity in terms of mmol of ammonia chemisorbed per gram of sample was calculated.

2.5. Acid catalyzed reactions

2.5.1. Esterification

The esterification reaction of *n*-butanol with acetic acid (mole ratio 1:4.4) was carried out in a round bottom flask containing catalyst at 80 °C with continuous stirring for 4 h. Dean–Stark apparatus was attached with round bottom flask to separate the water formed during the reaction. Same reaction was carried out by changing the corresponding acid concentration with different amount of the catalyst. For esterification of *iso*-butanol, 2-butanol and cyclohexanol the used mole ratio of alcohol to acid was 1:4.4, 1:4.4, and 1:3, respectively. The obtained esters were analysed on a Gas Chromatograph (Nucon-5700) using Carbowax 20 column.

2.5.2. Alkylation of phenol with *tert*-butyl alcohol (*t*-BA)

Alkylation reaction was carried out in a 50 ml round bottom flask provided with a double walled air condenser, magnetic stirrer and a guard tube. Alkylating agent, *tert*-butyl alcohol

to phenol was taken in 1:10 mole ratio and the 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 *tert*-butyl alcohol to phenol mole ratio, amount of the catalyst, reaction time and temperature. Among different products formed, the products 2-*tert*-butyl phenol (*o*-TBP), 4-*tert*-butyl phenol (*p*-TBP) and 2,4-*tert*-butyl phenol (*o,p*-DTBP) were identified on gas chromatograph (Nucon 5700) using SE-30 column while 3-*tert*-butyl phenol (*m*-TBP) was identified by AT-1000 column. The 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 C₁₈ column and identified by ¹H NMR.

3. Results and discussion

Leaching is a negative property for any catalyst. Any leaching of the catalyst from the support would make the catalyst unattractive. So it is necessary to study the stability of supported TSA in order to reuse the catalyst. When heteropolyacid react with a mild reducing agent such as ascorbic acid [29], it develops blue coloration, which can be used for the quantitative characterisation for the leaching of heteropolyacid from the support. In the present study the same method was used, for determining the leaching of TSA from the support.

Standard samples amounting to 1–5% of TSA in water were prepared. To 10 ml of above sample 1 ml of 10% ascorbic acid was added and the mixture was diluted to 25 ml with water. 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. One gram of TSA₃/A with 10 ml *n*-butanol was refluxed for 4 h, then 1 ml of the supernat solution was treated with 10% ascorbic acid. No development of blue colour indicates no leaching. The same procedure was repeated with water, *iso*-butanol, cyclohexanol, 2-butanol, formic acid, acetic acid, propionic acid, phenol, *tert*-butyl alcohol and with the filtrate of the reaction mixture after the reaction. The above procedure was followed for all catalysts and no leaching was found. The study shows the presence of chemical interaction between the TSA and the support. Thus present catalysts are stable under reaction conditions.

TGA of TSA shows 4–6% weight loss within a temperature range of 100–180 °C and 1–3% weight loss at 250–280 °C which is due to the loss of adsorbed water molecules and loss of crystallization water molecules, respectively. Further it shows 1–3% weight loss at 330–350 °C which may be due to the decomposition of TSA and this is in good agreement with reported one [19]. TGA of TSA₃/A shows 6–9% weight loss within 100–180 °C temperature range due to the loss of adsorbed water and no appreciable change in weight till 500 °C indicating an increase in the stability of the TSA. The decrease in percentage weight loss indicates the presence of chemical interaction between the support and TSA. DSC of TSA₃/A shows an endothermic peak at 126 °C, indicating the loss of adsorbed water molecules. Absences of any endothermic peak up to 500 °C indicates no decomposition of the supported species.

Table 1
Ion-exchange capacity and surface area of materials

Material	Ion-exchange capacity (mequiv./g)	Surface area (m ² /g)
A	0.00	81
TSA ₂ /A	0.35	199
TSA ₃ /A	0.39	122
TSA ₄ /A	0.41	101
TSA ₅ /A	0.44	100
TSA ₇ /A	0.51	100

The above study indicates that TSA is thermally stable up to 500 °C when supported onto neutral alumina.

The measurement of ion exchange capacity is an indirect way to determine the Bronsted acidity of the materials. Table 1 shows the value of ion-exchange capacity. It is seen from Table 1 that the value of ion exchange capacity increases as the amount of heteropolyacid supported onto support increases.

The values of surface area for all materials are listed in Table 1. It is known [30] that there may be decrease in surface area in case of the supported catalyst in which oxides are used as supports. This is because of strong interaction of HPA with the oxide support. The value for surface area decreases with an increase in the %loading of TSA. This may be due to strong interaction with the support. Almost the same value of surface area for TSA₄/A, TSA₅/A and TSA₇/A indicates the stabilization/blocking of the sites.

The FT-IR spectra of TSA₃/A shows bands at 970, a shoulder at 916 and 799 cm⁻¹ corresponding to the symmetric stretching of W=O, Si=O and W–O–W banding, respectively. The positions are in good agreement with those reported earlier [19].

The graph for average particle distribution for A and TSA₃/A shows the uniform distribution of particles. The significant decrease in the average particle size diameter of TSA₃/A (42.3 μm) as compare to that of the A (114 μm) may be due to the supporting of TSA as well as uniform dispersion of the TSA onto the surface of the support.

The SEM of A and TSA₃/A taken at magnification of 250× and 250× shows that surface of the support is distinctly altered. TSA₃/A exhibits considerable surface shining as compared to that of A. Picture taken at higher magnification shows clearly the alteration and shining of the surface.

The catalyst having 30% TSA onto hydrous zirconia has been well characterized by us earlier [27]. The main characteristics, i.e. total acidity, total surface area, average particle diameter, ion exchange capacity and thermo gravimetric analysis of Al₂O₃ (A) and ZrO₂ (Z), TSA₃/A and TSA₃/Z are shown in Table 2.

The calcined materials have also been characterized for FT-IR, DRS and XRD in order to see the stability of the catalyst as well as any structural change. FT-IR spectra of the calcined samples of TSA₃/A and TSA₃/Z shows band at 965, a shoulder at 912 and a band at 805 cm⁻¹ indicating that the TSA keeps its Keggin type structure up to 500 and 400 °C, respectively.

The electronic spectra gives information about the non-reduced heteropolyanion due to ligand (oxygen) to metal charge transfer [30]. It gives an evidence for the presences of HPA. The electronic spectra of TSA, TSA₃/A, TSA₃/Z and calcined

Table 2
Main characterizations of supports, TSA₃/A and TSA₃/Z

Catalyst	Total acidity (mmol NH ₃ /g)	Total surface area (m ² /g)	Avg. particle diameter (μm)	IEC (mequiv./g)	Thermo gravimetric analysis (°C)	
					Endothermic	Exothermic
A	0.47	81	114.0	0.0	NA	NA
Z	0.64	170	112.15	0.16	100–180	NA
TSA ₃ /A	0.6	122	42.3	0.39	100–180	–
TSA ₃ /Z	0.72	208	69.6	0.45	100–180	430–460

samples of TSA₃/A, TSA₃/Z shows λ_{\max} at 260 nm, which is in good agreement with reported earlier [19] and suggesting the presence of the undegraded TSA species onto the surface of support.

The XRD of TSA shows crystalline phase. The XRD pattern of TSA₃/A, C₃-TSA₃/A, C₄-TSA₃/A, C₅-TSA₃/A and TSA₃/Z, C₃-TSA₃/A and C₄-TSA₃/A are shown in Figs. 1 and 2, respectively. Fig. 1 shows a broad diffraction peak appeared at $2\theta = 8^\circ$, characteristic to solid state 12-tungstosilicic acid while Fig. 3 shows absence of the same characteristic peak. This difference may be due to the difference in synthesis method for the catalysts. Further in both the cases, there is no change in XRD pattern for the fresh as well as calcined materials indicating stability of the TSA onto the surface of the supports.

3.1. Acid catalyzed reactions

3.1.1. Esterification

$$\text{R-OH} + \text{R}'\text{-COOH} \xrightarrow{\text{H}^+} \text{R-COOR}' + \text{H}_2\text{O}$$

The esterification is a straightforward reaction subject to general Bronsted acid catalysis. The yield of the ester can be increased by increasing the concentration of either alcohol or acid. For economic reasons, the reactant that is usually the less expensive of the two is taken in excess. In the present study all corresponding acids were used in excess.

3.1.1.1. Esterification on *n*-butanol. The esterification of *n*-butanol (7.4 g) with acetic acid (6 g) using whole series of catalyst was carried out with molar ratio of alcohol to acid, 1:2 and 1:4.4 with different amount of catalysts. The %yield of butyl acetate (BA) is reported in Figs. 3 and 4. It is seen from the figures that TSA₃/A (yield is 62%) is the best among all. Further, the esterification of *n*-butanol was carried out with formic acid (4.6 g) and propionic acid (7.4 g) by taking molar ratio of alcohol to acid (1:4.4) with different amount of the best catalyst, TSA₃/A. The %yield of butyl formate (BF) and butyl propionate (BP) is shown in Fig. 5.

3.1.1.2. Esterification of *iso*-butanol, 2-butanol and cyclohexanol. The esterification reaction of *iso*-butanol (7.4 g), 2-butanol (7.4 g) and cyclohexanol (9.9 g) was carried out with acetic acid in 1:4.4, 1:4.4 and 1:3 mole ratio, respectively, over TSA₃/A catalyst. The %yield of *iso*-butyl acetate (*i*-BA), 2-butyl acetate (2-BA) and cyclohexyl acetate (CA) are shown in Fig. 5.

The optimum conditions for all reactions using TSA₃/A are as follows:

- amount of the catalyst = 0.25 g;
- temperature = 80 °C;
- reaction time = 4 h.

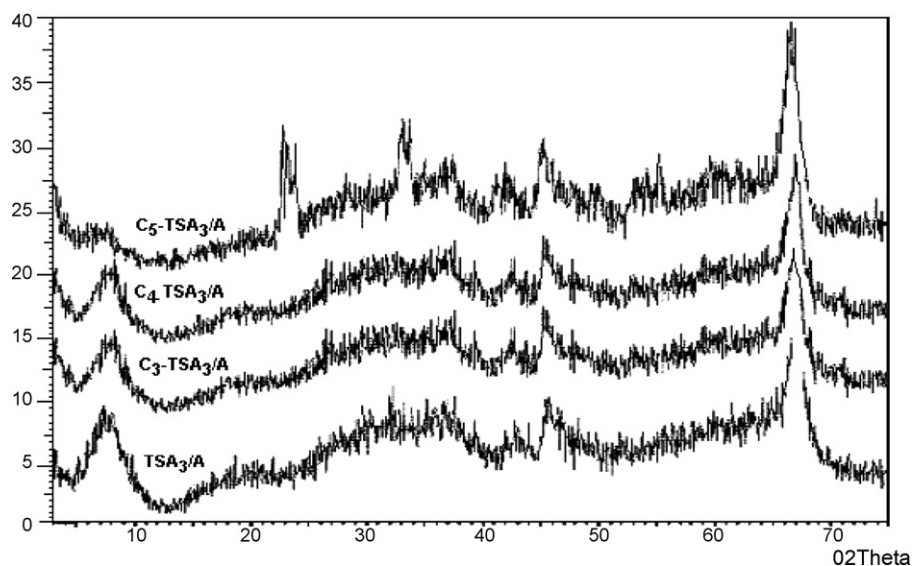


Fig. 1. The XRD pattern of TSA₃/A, C₃-TSA₃/A, C₄-TSA₃/A and C₅-TSA₃/A.

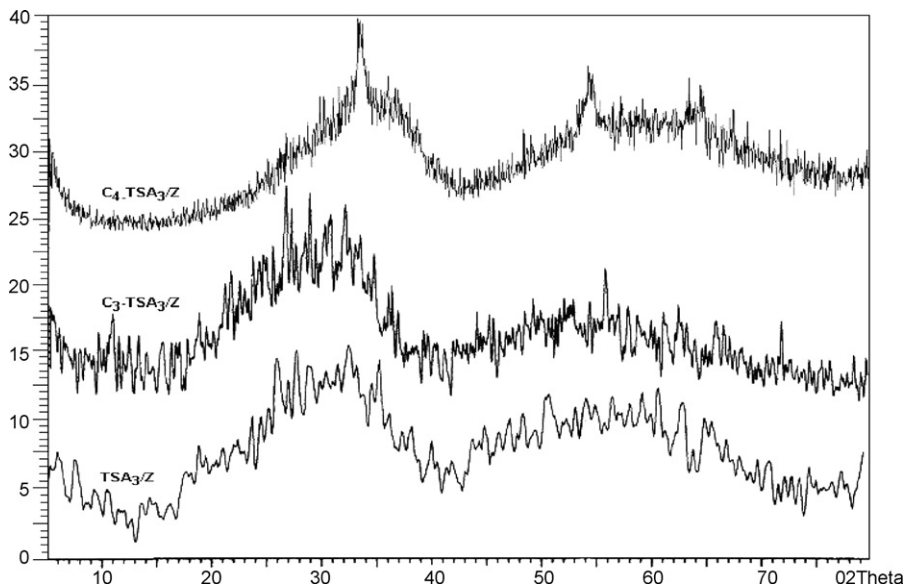
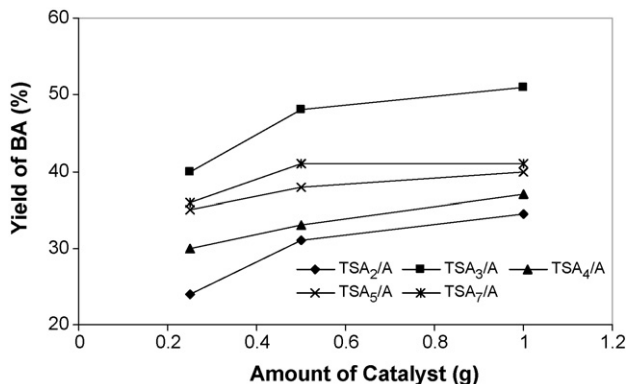
Fig. 2. The XRD pattern of TSA₃/Z, C₃-TSA₃/Z and C₄-TSA₃/Z.

Fig. 3. %Yield of BA with different amount of catalyst. %Yield is based on alcohol, molar ratio of alcohol to acid is 1:2.

To see any change in the structure of supported 12-tungstosilicic acid after reaction, the XRD of used catalyst was also recorded. Fig. 6 illustrates the XRD pattern of fresh catalyst as well as used catalyst. No difference in XRD pattern indicates stability of the used catalyst as well as absence of any degraded

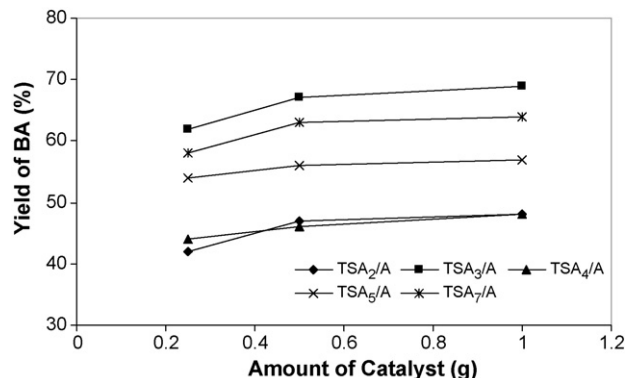
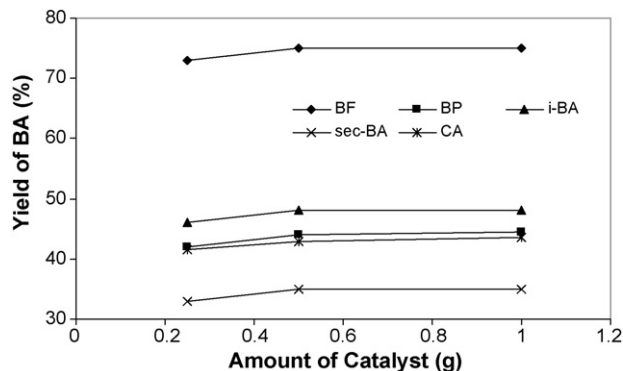


Fig. 4. %Yield of BA with different amount of catalyst. %Yield is based on alcohol, molar ratio of alcohol to acid is 1:4.4.

Fig. 5. %Yield of BF, BP, *i*-BA, *sec*-BA and CA with different amount of catalysts. %Yield is based on alcohols, catalyst used is TSA₃/A, molar ratio of alcohol to acid is 1:4.4.

heteropolyanion after the reaction. Same observation was found in case of TSA₃/Z (Fig. 7).

Further, to investigate the details of the deactivation, repeated use of the catalyst was examined. The catalyst was separated from the reaction mixture by simple filtration, washed with conductivity water till filtrate is free from acid, dried at 100 °C in oven for 5 h and charged for the further run. The results obtained are shown in Table 3. It is seen from the table that, in the regenerated catalyst the yield decreased by 5% approximately and

Table 3
%Yield of different esters with regenerated catalysts

Cycle	%Yield ^a					
	BF	BA	BP	<i>i</i> -BA	2-BA	CA
1	71	64	47	47	32	43
2	66	59	41	39	27	37
3	65	58	41	39	26	37
4	65	58	41	38	26	36

^a Amount of the catalyst = 0.25 g; temperature = 80 °C; reaction time = 4 h.

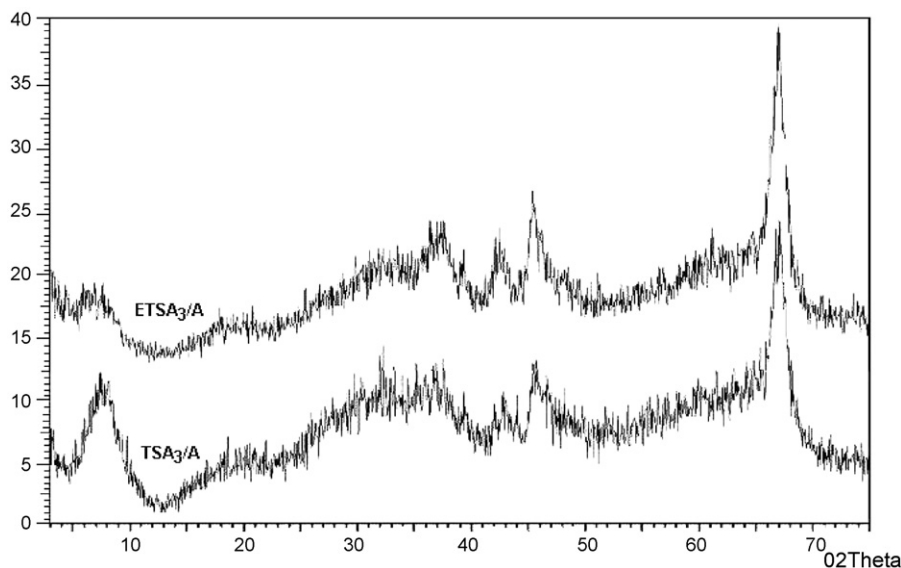


Fig. 6. XRD of fresh as well as used catalyst (TSA₃/A and ETSA₃/A). TSA₃/A: fresh catalyst, ETSA₃/A: used catalyst.

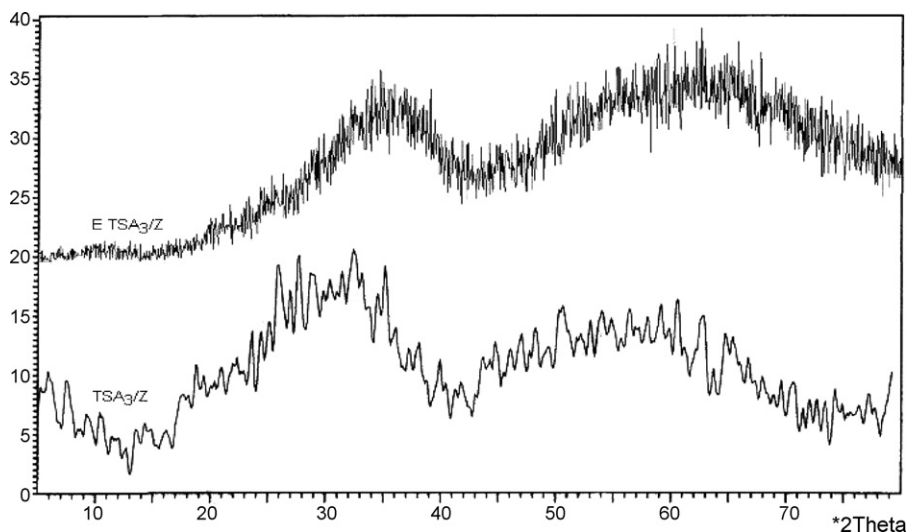


Fig. 7. XRD of fresh as well as used catalyst (TSA₃/Z and ETSA₃/Z). TSA₃/Z: fresh catalyst, ETSA₃/Z: used catalyst.

becomes constant on further regeneration. It was found by us earlier [27] that in the case of TSA₃/Z, also, the yield decreased by 5% for regenerated catalyst in first cycle and becomes constant on further recycling.

All calcined samples were also evaluated for esterification reactions under the optimized conditions and the obtained results are shown in Table 4.

It is seen from Table 4 that activity of the fresh catalyst is in the order of TSA₃/Z > TSA₃/A. This may be due to the nature of the support. As zirconia (Z) is an acidic support, catalyst supported onto zirconia is expected to be more active than the catalyst supported onto neutral alumina. The obtained results are as expected and further supported by the values of total acidity and ion exchange capacity of the TSA₃/Z and TSA₃/A (Table 2), which are greater for TSA₃/Z than that of TSA₃/A.

It is also interesting to observe the order of activity for fresh as well as calcined catalysts in both the cases.

Table 4
%Yield of esters with fresh as well as calcined samples

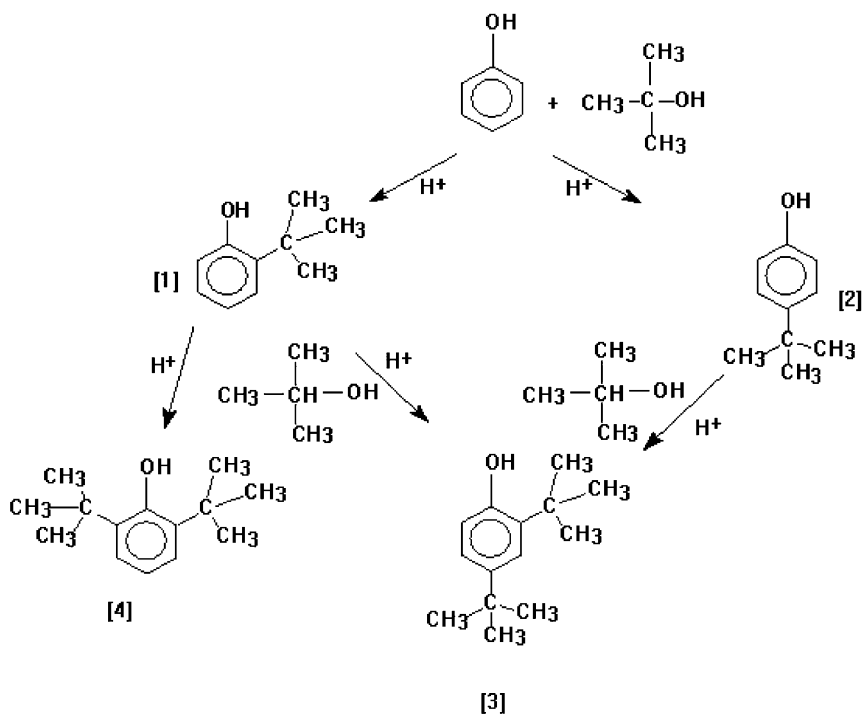
Catalyst	Ion exchange capacity (mequiv./g)	%Yield of esters ^a					
		BF	BA	BP	<i>i</i> -BA	2-BA	CA
H ₂ SO ₄	–	74 ^b	69 ^c	–	–	60 ^d	–
TSA	–	46	85	90	69	32	62
TSA ₃ /A	0.39	71	64	47	47	32	43
C ₃ -TSA ₃ /A	0.41	78	77	64	63	40	49
C ₄ -TSA ₃ /A	0.41	82	80	68	65	43	52
C ₅ -TSA ₃ /A	0.42	85	85	71	70	45	55
TSA ₃ /Z	0.45	61	81	83	75	57	68
C ₃ -TSA ₃ /Z	0.35	56	68	72	57	36	43
C ₄ -TSA ₃ /Z	0.35	54	67	71	56	36	42

^a Amount of the catalyst = 0.25 g; temperature = 80 °C; reaction time = 4 h.

^b Reaction time is 3–6 h.

^c Reaction time is 10 h.

^d Reaction time is 24 h, amount of H₂SO₄ taken is 1.5 ml.

Scheme 1. *tert*-Butylation of phenol.

In case of TSA₃/A, the trend for the %yield of the ester is, C₅-TSA₃/A > C₄-TSA₃/A > C₃-TSA₃/A > TSA₃/A. This can be explained by considering that as the calcinations temperature increases, Lewis acidity of the A also increases, which strengthens the Bronsted acidity. Hence an increase in the %yield of the ester is observed as expected. Since the esterification reactions are mainly catalyzed by the Bronsted acidity, increases in the %yield of esters is not that much high. These results are further supported by the value of ion exchange capacity, which is an indirect measurement of the Bronsted acidity only. It is seen from Table 4 that the increases in the values of ion exchange capacity is not appreciable.

In case of TSA₃/Z, the observed trend is TSA₃/Z > C₃-TSA₃/Z > C₄-TSA₃/Z. This trend can be explained on the basis of the structure of the hydrous zirconia. The structure of the hydrous zirconia contains crystalline water which is present in the form of H₃O⁺, H₂O or OH⁻. On heating at high temperature, these water molecules are lost and hence Bronsted acidity decreases. This is supported by the value of ion exchange capacity (Table 4). Table 4 shows a drastic change in the ion exchange capacity value, and hence decrease in the Bronsted acidity as well as in %yield of the esters.

Further, it is very interesting to note the order of catalytic activity for both the catalyst after calcinations. The order is found to be C₄-TSA₃/A > C₄-TSA₃/Z. In all cases, except in case of butyl propionate, the change in catalytic activity is appreciable. This may be totally due to the nature of the support. It is well known that Lewis acidity strengthen Bronsted acidity. As temperature increases, Lewis acidity on alumina also increases and resulting with an increase in the %yield of ester. This shows that at higher temperature, alumina works as a better support as compare to that of zirconia.

3.1.2. Alkylation of phenol with *t*-BA

Alkylation of phenol with *tert*-butyl alcohol is a typical Friedel-Craft alkylation and generally catalyzed by acid catalysts. Alkylation of phenol with *tert*-butyl alcohol results in a mixture of four different products: *o*-TBP, *p*-TBP, *o,p*-DTBP and *o*-di-*tert*-butyl phenol (*o*-DTBP) as shown in Scheme 1.

Literature survey shows that, the alkylating agent was taken in excess in most of the work reported up to the date. So it is interesting to study the effect of the concentration of the substrate on the %conversion by taking it in excess. Alkylation reaction carried out using supports, hydrous zirconia and neutral alumina, shows that the supports are inactive for the alkylation of phenol.

3.1.2.1. Effect of mole ratio of *t*-BA to phenol and temperature.

The reaction was carried out by varying mole ratio of *t*-BA to phenol 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 5. It is seen from the table that with increase the concentration of *t*-BA, there is drastic change in the %conversion. The decrease in %conversion may be due to the steric hindrance of *t*-BA group. As number of *tert*-butyl molecules increases on the surface of the catalyst, less site remain available on the surface of the catalyst for the other reactant, which is phenol, and it is fact that if both the reactant was not in contact, reaction will not takes place.

3.1.2.2. Effect of amount of the catalyst. The reaction was carried out with different amount of the catalysts keeping the mole ratio of *t*-BA to phenol 1:10 for 6 h. The %conversion and %selectivity of different products is reported in Fig. 8.

Table 5
Effect of mole ratio on %conversion and %selectivity

Catalyst	Mole ratio	%Conversion ^a	%Selectivity	
			<i>o</i> -TBP	<i>p</i> -TBP
TSA ₃ /A	1:10	100	5	95
	3:10	40	5	95
	6:10	12	4	96
TSA ₃ /Z	1:10	100	7	93
	3:10	42	9	91
	6:10	15	12	88

^a %Conversion is based on *t*-BA; amount of catalyst: 0.25 g; reaction temperature: 80 °C; reaction time: 6 h.

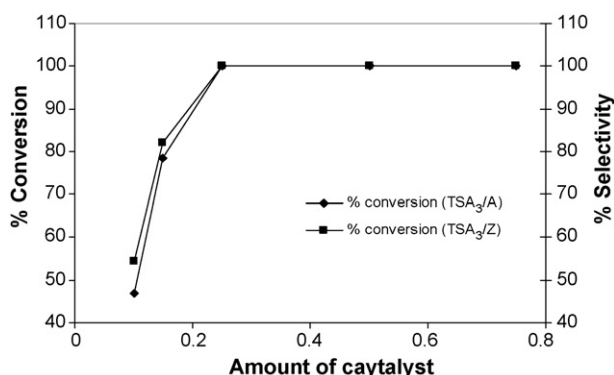


Fig. 8. Effect of the amount of the catalyst. %Conversion is based on *t*-BA, mole ratio of *t*-BA to phenol is 1:10, reaction temperature: 80 °C, reaction time: 6 h.

The activity increases with an increase in the amount of the supported heteropolyacids. The obtained results are in good agreement with the reported [31,32]. It is seen from the figure that TSA₃/Z shows more activity as compare to that of TSA₃/A. One hundred percent conversion was found with 0.25 g of both the catalysts with 95 and 93% selectivity for *p*-isomer for TSA₃/A and TSA₃/Z, respectively.

3.1.2.3. *Effect of reaction time.* The effect of reaction time on *tert*-butylation of phenol was studied at a mole ratio of 1:10 using 0.25 g catalyst. The results are presented in Fig. 9.

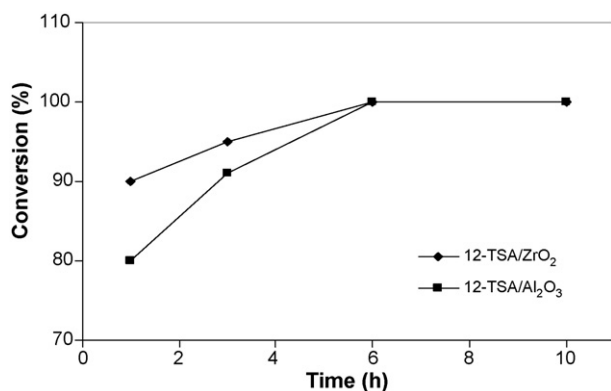


Fig. 9. Effect of reaction time on %conversion. %Conversion is based on *t*-BA, amount of catalyst: 0.25 g, mole ratio of *t*-BA to phenol is 1:10, reaction temperature: 80 °C.

Table 6
%Conversion and %selectivity for *tert*-butylation of phenol

Catalyst	%Conversion ^a	%Selectivity		TON
		<i>o</i> -TBP	<i>p</i> -TBP	
TSA	82	–	100	384
A	NA	–	–	–
TSA ₃ /A	80 ^b	4	96	375
R ₁ -TSA ₃ /A	80.0	18.0	82.0	375
R ₂ -TSA ₃ /A	80.0	19.4	80.8	375
C ₃ -TSA ₃ /A	85.0	17.0	83.0	399
C ₅ -TSA ₃ /A	84	17.5	82.5	394
Z	NA	–	–	–
TSA ₃ /Z	90 ^b	5	95	421
R ₁ -TSA ₃ /Z	76.0	24.8	75.2	356
R ₂ -TSA ₃ /Z	74.0	25.0	75.0	347
C ₃ -TSA ₃ /Z	78.0	20.2	79.8	366
C ₄ -TSA ₃ /Z	77.0	21	79	361

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

^b Time: 1 h.

Figure shows that the maximum conversion for TSA₃/Z and TSA₃/A is 90 and 80%, respectively only in 1 h, however time required for 100% conversion is 6 h in both the cases. It can also be seen that there is no change in %conversion even after 10 h, indicating the present catalysts do not deactivated even after 10 h.

The optimum conditions for the present reaction are as follows:

- mole ratio of *t*-BA to phenol = 1:10;
- amount of the catalyst = 0.25 g;
- temperature = 80 °C;
- reaction time = 6 h.

All calcined catalysts, C₃-TSA₃/A, C₄-TSA₃/A, C₅-TSA₃/A, C₃-TSA₃/Z and C₄-TSA₃/Z, were also evaluated for alkylation reaction under optimized conditions and result are shown in Table 6.

3.1.2.4. *Test for heterogeneity.* For the rigorous proof of heterogeneity, a test [33] was carried out by filtering catalyst from the reaction mixture at 80 °C after 1 h and allowed the filtrate to react up to 6 h, i.e. completion of the reaction. The reaction mixture of 1 h and filtrate was analysed by Gas Chromatogram. No change in the %conversion as well as %selectivity was found (Table 7) indicating the present catalyst fall into category C [33]. On the basis of these results, it can be concluded that there is no any leaching of the TSA from the support and the present catalysts are truly heterogeneous in nature.

3.1.2.5. *Recycling of the catalyst.* Both the catalysts, TSA₃/Z and TSA₃/A, were recycled for two times in order to test their activity as well as stability. The 1st recycling (R₁) was carried out after separating it from reaction mixture by filtration, washing with conductivity water, 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

Table 7
%Conversion and %selectivity for *tert*-butylation of phenol (with and without catalyst)

Catalyst	%Conversion ^a	%Selectivity	
		<i>o</i> -TBP	<i>p</i> -TBP
TSA ₃ /A (1 h)	80	5	95
Filtrate (6 h)	80	5	95
TSA ₃ /Z (1 h)	90	7	93
Filtrate (6 h)	90	6	94

^a %Conversion is based on *t*-BA; amount of catalyst: 0.25 g; mole ratio of phenol to *t*-BA is 1:10; reaction temperature: 80 °C.

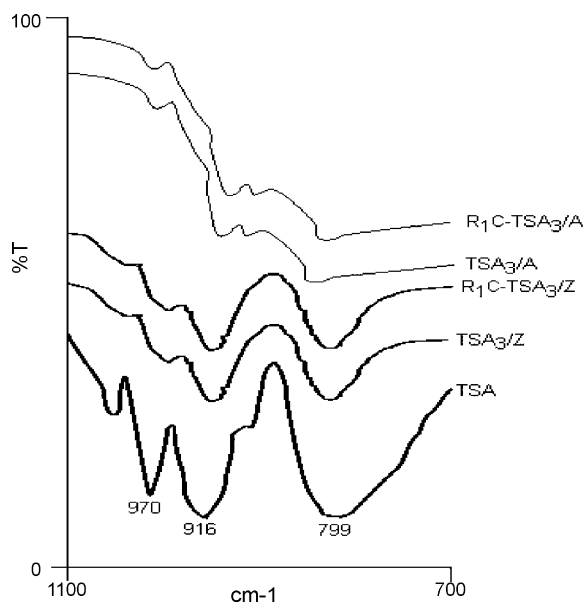


Fig. 10. FT-IR spectra of TSA₃/Z, R₁C-TSA₃/Z, TSA₃/A, and R₁C-TSA₃/A.

water and drying at 100 °C. In order to confirm the retention of the catalyst structure, after the completion of the reaction the FT-IR (Fig. 10) and XRD (Fig. 11) were run for the fresh catalysts and regenerated catalysts.

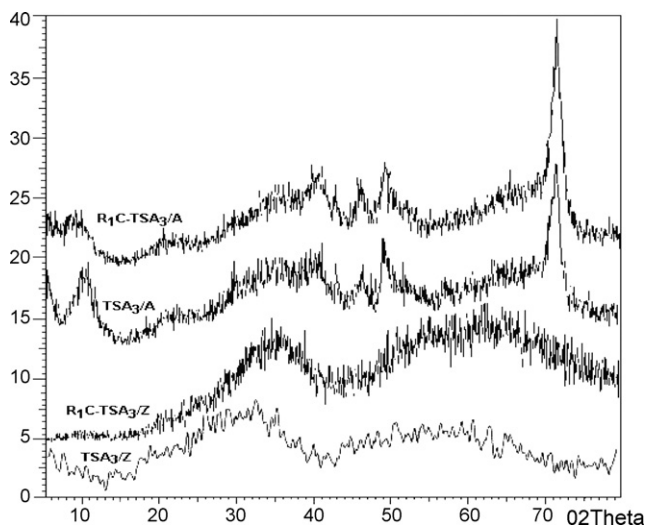


Fig. 11. XRD spectra of TSA₃/Z, R₁C-TSA₃/Z, TSA₃/A, and R₁C-TSA₃/A.

As mentioned earlier, FT-IR spectrum of TSA₃/A and TSA₃/Z shows characteristic bands of TSA at 970, and a shoulder at 916 and 799 cm⁻¹. No appreciable shift in the band position of regenerated catalyst indicates the retention of Keggin type TSA onto the supports. As seen from Fig. 11, there is no appreciable change in XRD spectra of fresh as well as regenerated catalysts indicate the stability of TSA after regeneration.

The above study confirms the retention of the catalyst structure.

The *tert*-butylation of phenol was carried out with regenerated catalyst under optimized conditions and the results are shown in Table 6.

Table 6 presents the results of *t*-butylation of phenol for various catalysts under optimised reaction conditions. In case of TSA₃/A, the regenerated catalysts as well as calcinated catalysts give almost same %conversion as that obtained by fresh catalyst in 1 h. This is in good agreement with IEC values which are almost same for TSA₃/A, C₃-TSA₃/A, C₅-TSA₃/A and R₁-TSA₃/A, i.e. 0.39, 0.41, 0.42 and 0.38 mequiv./g, respectively. In case of TSA₃/Z, the regenerated catalysts as well as calcinated catalysts show a decrease in %conversion. The observed loss in activity may be attributed to the decreases in the acidic strength of the catalyst, which can be co-related to the values of IEC. The IEC values for TSA₃/Z, C₃-TSA₃/Z, C₄-TSA₃/Z and R₁-TSA₃/Z are 0.45, 0.35, 0.35 and 0.35 mequiv./g, respectively. The appreciable decrease in the values of IEC may be due to the acidic nature (Bronsted acidity) of Zirconia.

It is interesting to note that in case of TSA₃/A, the %conversion is same for fresh as well as regenerated catalyst, however the time required to obtained same %conversion is different for fresh as well as regenerated catalyst. In case of TSA₃/Z, less %conversion is obtained with regenerated catalyst.

Further, the %selectivity for *o*-isomer is less in regenerated TSA₃/A as compared to that of regenerated TSA₃/Z. This may be due to the nature of the support. As it is proved that on heating at high temperature, Lewis acidity in alumina increases [34] which may strengthen the Bronsted acidity where as in case of zirconia, on heating at high temperature, loss of Bronsted acidity in terms of H₂O molecules is observed. This is supported by the ion exchange capacity values of the calcined samples (Table 4). As it is known that the weak acidity favours the *o*-substitution, the results are in good agreement.

This study demonstrates that the present catalysts can be used either as it is or after calcinations also. They are fairly stable, can be used for long time (10 h) and can also be reusable. It can also be concluded that neutral alumina is better support than zirconia from the viewpoint of stability, %conversion and %selectivity.

3.1.2.6. Comparison with reported catalysts. The superiority of the present catalysts lie in obtaining more %conversion and %selectivity. It is seen from Table 8 that 100% conversion was obtained with K-10 clay but the %selectivity for *p*-isomer was around 62%. Further with *p*-isomer, other products were also obtained which required tedious work up to separate. In case of Zeolite- β , 80.3% selectivity for *p*-isomer was obtained but %conversion is only 52.7%. With the present catalysts, the obtained results are very unique and outstanding for alkylation

Table 8

Comparison of %conversion of phenol and %selectivity for *p-tert*-butyl phenol of TSA₃/Z and TSA₃/A with other catalysts

Catalyst	Reference	Mole ratio ^a	Reaction condition ^b	%Conversion ^c	%Selectivity		
					<i>o</i> -TBP	<i>p</i> -TBP	<i>o,p</i> -DTBP
TSA ₃ /A	This work	10:1	353; 1; 250	80	5.0	95.0	–
TSA ₃ /Z	This work	10:1	353; 1; 250	90	6.0	94.0	–
K-10 clay	[35]	10:1	353; 6; 500	100	35.4	62.0	2.6
FeCl ₃ /K-10 clay	[35]	10:1	353; 0.5; 500	100	30.5	66.8	2.7
USY	[36]	10:6	343; 3; 200	52.7 ^c	63.0	23.0	13.1
Zeolite-β	[36]	10:6	343; 3; 200	54.2 ^c	18.3	80.3	1.4
Mordenite	[36]	10:6	343; 8; 200	28.8	48.1	49.1	2.8
TPA/MC M-41 ^d	[37]	1:2	333; 4; 282	44.8 ^c	29.0	49.0	21.2

^a Phenol:*t*-BA.^b Reaction temperature (K); reaction time (h); catalyst amount (mg).^c Conversion based on *t*-BA.^d TPA: 12-tungstophosphoric acid.^e Conversion based on phenol.

reaction with 95% selectivity for *p*-isomer in *tert*-butylation of phenol.

For *tert*-butylation of phenol, the study on recyclability has been carried out in detail. In spite of presence of *o*-isomer, our regenerated catalysts give high %selectivity for *p*-isomer than the other reported catalysts, which is novelty of the present work. 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. Thus the present catalysts are not only selective but also promising cleaner alternative to the environmentally hazardous traditional catalysts for liquid phase alkylation process.

4. Conclusion

FT-IR and DRS spectra show that 12-tungstosilicic acid keeps its Keggin type structure when supported on to neutral alumina. XRD study shows no any structural change of TSA upto 500 and 400 °C on neutral alumina and hydrous zirconia, respectively. Further, no any structural change takes place in reused catalysts indicating catalysts are very stable.

The catalysts are proved to be successful in the esterification of 1° and 2° alcohols under mild condition as compared with the traditional liquid acid catalyst. The obtained results for *tert*-butylation of phenol are very unique and out-standing 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.

More over in all reactions, removal of the catalyst consists of the single filtration and catalyst can be re-used after a simple work-up. Especially in *tert*-butylation reaction, the present contribution reports regeneration of the supported heteropolyacid catalyst at lower temperature, which is first report made ever. Thus the present catalysts are promising alternative to the traditional acid catalysts for liquid phase acid catalyzed reactions.

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References

- [1] T.A. Peters, N.E. Benes, A. Holmen, J.T.F. Keurentjes, *Appl. Catal. A* 297 (2006) 182.
- [2] F.T. Sejidov, Y. Mansoori, N. Goodarzi, *J. Mol. Catal. A* 240 (2005) 186.
- [3] J.H. Sepúlveda, J.C. Yori, C.R. Vera, *Appl. Catal. A* 288 (2005) 18.
- [4] L. Yang, Y. Qi, X. Yuan, J. Shen, J. Kim, *J. Mol. Catal. A* 229 (2005) 199.
- [5] S. Shanmugam, B. Viswanathan, T.K. Varadarajan, *J. Mol. Catal. A* 223 (2004) 143.
- [6] L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, *Appl. Catal. A* 256 (2003) 125.
- [7] M.J. Janik, R.J. Davis, M. Neurock, *J. Catal.* 244 (2006) 65.
- [8] Y. Kamiya, Y. Ooka, C. Obara, R. Ohnishi, T. Fujita, Y. Kurata, K. Tsuji, T. Nakajyo, T. Okuhara, *J. Mol. Catal. A* 262 (2007) 77.
- [9] L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, E.N. Alesso, M.R. Torviso, B. Lantaño, G.Y. Moltrasio, J.M. Aguirre, *Appl. Catal. A* 287 (2005) 1.
- [10] K. Usha Nandhini, B. Arabindoo, M. Palanichamy, V. Murugesan, *J. Mol. Catal. A* 223 (2004) 201.
- [11] G.D. Yadav, N.S. Doshi, *J. Mol. Catal. A* 194 (2003) 195.
- [12] J. Mao, Y. Kamiya, T. Okuhara, *Appl. Catal. A* 255 (2003) 337.
- [13] V.R. Sarsani, C.J. Lyon, K.W. Hutchenson, M.A. Harmer, B. Subramaniam, *J. Catal.* 245 (2007) 184.
- [14] G.D. Yadav, R.D. Bhagat, *J. Mol. Catal. A* 235 (2005) 98.
- [15] L.A.M. Cardoso, W. Alves Jr., A.R.E. Gonzaga, L.M.G. Aguiar, H.M.C. Andrade, *J. Mol. Catal. A* 209 (2004) 189.
- [16] C.D. Castro, J. Primo, A. Corma, *J. Mol. Catal. A* 134 (1998) 215.
- [17] I.V. Kozhevnikov, *Chem. Res.* 98 (1998) 171.
- [18] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199.
- [19] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [20] J.B. Moffat, in: M.V. Twigg, M.S. Spencer (Eds.), *Metal Oxygen Cluster, The Surface and Catalytic Properties of Heteropolyoxometalate*, Kluwer Academic Publisher, New York, 2001, p. 42, 146.
- [21] C. Hu, Y. Zhang, L. Xu, G. Peng, *Appl. Catal. A* 177 (1999) 237.
- [22] A. Molnar, C. Keresszegi, B. Torok, *Appl. Catal. A* 189 (1999) 217.
- [23] A. Bielanski, A. Lubanska, J. Pozniczek, A.M. Inicka, *Appl. Catal. A* 238 (2003) 239.
- [24] A. Biellanski, A. Lubanska, J. Pozniczek, A.M. Inicka, *Appl. Catal. A* 256 (2003) 153.

- [25] M.A. Schwegler, P. Vinke, M. Vijk, H. Bekkum, *Appl. Catal. A* 80 (1992) 41.
- [26] M.J. Verhoef, P.J. Kooyamann, J.A. Peters, H.V. Bekkum, *Micropor. Mesopor. Mater.* 27 (1999) 365.
- [27] N. Bhatt, A. Patel, *J. Mol. Catal. A* 238 (2005) 223.
- [28] I.V. Kozhevnikov, *Appl. Catal. A* 256 (2003) 3.
- [29] G.D. Yadav, V.V. Bokade, *Appl. Catal. A* 147 (1996) 299.
- [30] G.M. Varga, E. Papaconstantinos, M.T. Pope, *Inorg. Chem.* 9 (1970) 667.
- [31] V.M. Mastikhin, V.V. Tersskih, M.N. Timofeeva, O.P. Krivoruchko, *J. Mol. Catal. A: Chem.* 95 (1995) 135.
- [32] Y. Izumi, N. Natsume, H. Takamine, I. Tamaoki, K. Urabe, *Bull. Chem. Soc. Jpn.* 62 (1989) 2159.
- [33] A. Sheldon, M. Walau, I.W.C.E. Arends, U. Schuchardt, *Acc. Chem. Res.* 31 (1998) 485.
- [34] P. Sharma, S. Vyas, A. Patel, *J. Mol. Catal. A* 214 (2004) 281.
- [35] A.B. Shinde, N.B. Shrigadi, S.D. Samant, *Appl. Catal. A* 276 (2004) 5.
- [36] E. Dumitriu, V. Hulea, *J. Catal.* 218 (2003) 249.
- [37] Z.M.A. Judeh, C.B. Ching, Q.H. Xia, H.Y. Shen, *J. Mol. Catal. A* 212 (2004) 301.