

# Liquid phase cyclohexylation of phenol with cyclohexene using 12-tungstosilicicacid supported onto different supports

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## Abstract

Alkylation of phenol with cyclohexene as an alkylating agent was carried out in liquid phase by varying different parameters such as temperature, time, mole ratio of phenol to cyclohexene and amount of the catalyst over 30% 12-tungstosilicicacid supported onto hydrous zirconia and neutral alumina. The present catalysts show high activity towards the %conversion and %selectivity, especially for 2-cyclohexyl phenol, an important product used as intermediate in dyestuff preparation as well as in preparation of 2-phenyl phenol which is used as disinfectant and fungicides. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Alkylation; Phenol; Cyclohexene; 12-Tungstosilicicacid; Hydrous zirconia; Neutral alumina

## 1. Introduction

Alkylation of phenol is very valuable because several of the organic intermediates are produced through alkylation of phenol. The alkylated phenol products are used as pesticides, herbicides, phenolic resins, antioxidants, polymerization inhibitors, fragrances, surfactants, plastics, paints, etc. Cyclohexylation of phenol leads to 2-cyclohexylphenol, 4-cyclohexylphenol, 2,4-dicyclohexylphenol, 2,6-dicyclohexylphenol and cyclohexylphenyl ether. These products have importance at both levels, at industries as well as at academic. These products have been used as perfumery compound and as precursors to a number of industrially important products.

Cyclohexylation reactions of phenol with various solid acid catalyst such as zeolite-H $\beta$  and various conventional Lewis and Bronsted acids [1–3], cationic ion exchange resins and acid treated clay [4], cesium salt of dodecatungstosilicic acid, sulphated zirconia [5] have been carried out by various groups. There is no literature available on the same using supported heteropolyacid.

Heteropolyacids are promising catalysts for the Friedel Craft reactions. They are stronger than many conventional acid catalysts. Supported heteropolyacids have been gaining impor-

tance as alkylating and acylating catalysts [6–10]. Since 12-tungstosilicic acid is the most stable HPA in keggin series, literature survey shows that 12-tungstosilicic acid supported on to different support [11–17] has been widely used as a catalytic system for different acid catalyzed reactions. Not much work has been reported on 12-tungstosilicic acid, the next acidic [16,18,19] and stable [18–20] HPA in the keggin series. So it was thought of interest to study the cyclohexylation reaction of phenol at liquid phase under mild conditions with excess of phenol over supported 12-tungstosilicic acid. Further all reported cyclohexylation reactions have been studied by taking alkylating agent in excess but no study is available for the reaction where substrate is taking in excess.

It is very interesting and important to note that support does not play always merely a mechanical role but it can also modify the catalytic properties of the HPAs. Since the supported catalysts are more active than the unsupported catalyst, it is important to understand the nature of the interaction between the HPAs and the supports. This interaction depends on the central and addenda atom of heteropoly anion, loading as well as dispersion of heteropolyacids on to the support, nature of the support and the pre-treatment [21]. The differences in the performance of the supported catalyst can be explained by considering the change in acidity as well as by evaluating their catalytic activity towards acid catalyzed reactions such as esterification, alkylation, acylation, etc. In the present study, two different supports have been

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used, acidic support and neutral support to see the effect of the support on the cyclohexylation of phenol.

In the present contributions the catalyst prepared of 30% 12-tungstosilicicacid (TSA) supported onto hydrous zirconia ( $ZrO_2$ ) and neutral alumina ( $Al_2O_3$ ). The supports and new amorphous catalysts have been characterised by various physico-chemical properties. Their catalytic properties were evaluated for the liquid phase alkylation of phenol with cyclohexene. Cyclohexylation of phenol was carried out by varying different parameters such as temperature, time, mole ratio of phenol to cyclohexene and amount of the catalyst to optimize the conditions. The stability of the catalysts was demonstrated by carrying out calcinations as well as by studying TGA, FT-IR and XRD.

## 2. Experimental

### 2.1. Materials

All chemicals used were of A.R. grade.  $H_4SiW_{12}O_{40} \cdot nH_2O$  (Lobachemie, Mumbai),  $ZrOCl_2 \cdot 8H_2O$  (SD Fine chemicals, Mumbai) were used as received. Neutral alumina, phenol and cyclohexene, were obtained from Merck and used as received.

### 2.2. Synthesis of the catalyst (TSA/ $ZrO_2$ )

The support hydrous zirconia and the catalyst 30% loading of 12-tungstosilicicacid onto hydrous zirconia have been synthesized by following method reported by us earlier [22]. The synthesized catalyst has been calcined at 300 and 400 °C and designed as  $C_3$ -TSA/ $ZrO_2$  and  $C_4$ -TSA/ $ZrO_2$ , respectively.

### 2.3. Supporting of 12-tungstosilicicacid onto neutral alumina (TSA/ $Al_2O_3$ )

12-Tungstosilicicacid was supported on neutral alumina by impregnation method. A catalyst containing 30% of 12-tungstosilicicacid (TSA) were synthesized by impregnating 1 g of  $Al_2O_3$  with an aqueous solution of 12-tungstosilicicacid (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 TSA/ $Al_2O_3$ . The synthesized catalyst has been calcined at 300, 400 and 500 °C and designed as  $C_3$ -TSA/ $Al_2O_3$ ,  $C_4$ -TSA/ $Al_2O_3$  and  $C_5$ -TSA/ $Al_2O_3$ , respectively.

### 2.4. Characterization

Thermo gravimetric analysis of the samples was carried out on METTLER TOLEDO STAR SW 7.01 instrument. Differen-

tial scanning calorimetric of the samples was carried out on TA INSTRUMENTS DSC-2010 instrument. The FT-IR spectra of the samples (Fresh and calcinated) were obtained by using KBr wafer on Perkin-Elmer. The XRD pattern of fresh and calcinated samples were obtained by using PHILIPS PW-1830. The conditions used were: Cu  $K\alpha$  radiation (1.5417 Å), scanning angle from 5° to 60°.

### 2.5. Catalytic reaction

The 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. Cyclohexene to Phenol was taken in 1:10 ratio and catalyst was added in to the required amount. The resultant mixture was heated at 80 °C on magnetic stirrer for 1 h. Same reaction was carried out by varying cyclohexene to phenol mole ratio, amount of the catalyst, reaction time and temperature. Products formed after completion of reactions were analyzed on GC using SE-30 column and product identification was done by gas chromatogram–mass spectroscopy.

## 3. Results and discussion

Two series having 20–70% loading of 12-tungstosilicicacid on to hydrous zirconia as well as neutral alumina was synthesized in our laboratory and well characterized by us earlier [22]. From our earlier study, it was found that catalyst containing 30% loading of 12-tungstosilicicacid on to hydrous zirconia and neutral alumina are the best. In the present study we have made use of the best catalyst for carrying out alkylation reaction.

The main characterization of the support as well as catalysts like ion exchange capacity, surface area measurement, particle size distribution and total acidity obtained from temperature program desorption of  $NH_3$  for TSA/ $ZrO_2$  and TSA/ $Al_2O_3$  are presented in Table 1.

In order to check the stability, both the catalysts were studied for thermo gravimetric analysis. Further the FT-IR and XRD of fresh as well as calcinated catalysts were also recorded.

The TGA of  $ZrO_2$  indicates about 13% weight loss within a temperature range of 100–180 °C corresponding the loss of adsorbed/hydrogen bonded water molecules, after which there is no significant change in weight obtained till 600 °C. The TGA of 12-tungstosilicicacid shows 4–6% weight loss within a temperature range of 100–180 °C which is due to the loss of adsorbed water molecules. Further it shows 1–3% weight loss at 250–280 °C due to the loss of crystallization water molecules and 1–3% weight loss at 470–500 °C which is due to the decomposition of heteropolyacid and this is in good agreement with

Table 1  
Main characterization of 12-TSA/ $ZrO_2$  and 12-TSA/ $Al_2O_3$

Catalyst	Total acidity (mmol $NH_3$ /g)	Total surface area ( $m^2$ /g)	Average particle diameter ( $\mu m$ )	IEC (mequiv./g)
$ZrO_2$	0.64	170	112.15	0.16
$Al_2O_3$	0.47	81	114.0	0.0
TSA/ $ZrO_2$	0.72	208	69.6	0.45
TSA/ $Al_2O_3$	0.60	122	42.3	0.39

Table 2  
Experimental absorption bands of support, supported catalysts and tentative band assignments

Catalyst	Band frequency (cm <sup>-1</sup> )						
	O–H	H–O–H	O–H–O	Zr–O–H	W–O–W	W=O	Si–O
ZrO <sub>2</sub>	3400	1600	1370	600	NA	NA	NA
TSA/ZrO <sub>2</sub>	3400	1600	1370	600	799	970	916
C <sub>3</sub> -TSA/ZrO <sub>2</sub>	3400	1600	1370	600	803	970	908
C <sub>4</sub> -TSA/ZrO <sub>2</sub>	3400	1600	1370	600	803	970	899
TSA/Al <sub>2</sub> O <sub>3</sub>	–	–	–	NA	800	965	915
C <sub>3</sub> -TSA/Al <sub>2</sub> O <sub>3</sub>	–	–	–	NA	800	965	912
C <sub>5</sub> -TSA/Al <sub>2</sub> O <sub>3</sub>	–	–	–	NA	805	965	912

reported one [20]. The TGA of TSA/ZrO<sub>2</sub> and TSA/Al<sub>2</sub>O<sub>3</sub> show 14–16% and 6–9% weight loss within 100–180 °C temperature range which is due to loss of adsorbed water and there is no appreciable change in weight till 400 and 500 °C indicating increase in the stability of the HPA. This results in the decrease in percentage weight loss indicating the presence of chemical interaction between the support and HPA. This study indicates that 12-tungstosilicic acid supported onto neutral alumina is more stable than that of hydrous zirconia.

FT-IR spectra of 12-tungstosilicic acid supported on to hydrous zirconia and neutral alumina show that the 12-tungstosilicic acid keeps its Keggin type structure when supported onto supports. Further there is no appreciable shifting in the band position observed in the FT-IR of calcinated samples indicating that the 12-tungstosilicic acid keeps its keggin type structure up to 400 and 500 °C when supported on hydrous zirconia and neutral alumina, respectively.

The main bands of FT-IR spectra for fresh catalysts as well as calcinated catalysts are presented in Table 2.

The XRD pattern shows a broad diffraction peak appeared at  $2\theta=8^\circ$ , characteristic to solid state 12-tungstosilicic acid, is observed in case of TSA/Al<sub>2</sub>O<sub>3</sub>, C<sub>3</sub>-TSA/Al<sub>2</sub>O<sub>3</sub>, C<sub>4</sub>-TSA/Al<sub>2</sub>O<sub>3</sub> and C<sub>5</sub>-TSA/Al<sub>2</sub>O<sub>3</sub> (Fig. 1). In case of TSA/ZrO<sub>2</sub>, C<sub>3</sub>-TSA/ZrO<sub>2</sub> and C<sub>4</sub>-TSA/ZrO<sub>2</sub>, no any diffraction peak of HPAs is observed (Fig. 2). The difference in the XRD pattern for the same may be due to the difference in the synthesis methods as well as due to the nature of the support. It is also interesting

to note down that in both the cases, the XRD pattern remains same after calcinations, also indicating stability of the catalyst as well as no degradation of the supported HPA anion up to 400 °C when zirconia is used as support and up to 500 °C when neutral alumina is used as support.

### 3.1. Catalytic reaction

Alkylation of phenol results in a mixture of three different products. 2-Cyclohexylphenol (2-CHP), 4-cyclohexylphenol (4-CHP), 2,4-dicyclohexylphenol (2,4-DCHP) and 2,6-dicyclohexylphenol (2,6-DCHP) as shown in Scheme 1.

Alkylation reaction carried out using supports shows that the supports are inactive for the alkylation of phenol with cyclohexene. The mentioned reaction catalyzed by TSA/ZrO<sub>2</sub> and TSA/Al<sub>2</sub>O<sub>3</sub> give mainly two products: 2-cyclohexylphenol, 4-cyclohexylphenol. The products were conformed by gas chromatogram–mass spectroscopy.

### 3.2. Effect of mole ratio of cyclohexene to phenol and temperature

The reaction was carried out by varying mole ratio of cyclohexene to phenol with 0.5 g of the catalyst for 6 h at two temperature; ambient temperature and 80 °C. At ambient temperature, the %conversion is found to be 0. The results obtained at 80 °C are shown in Table 3. Further the reactions carried out

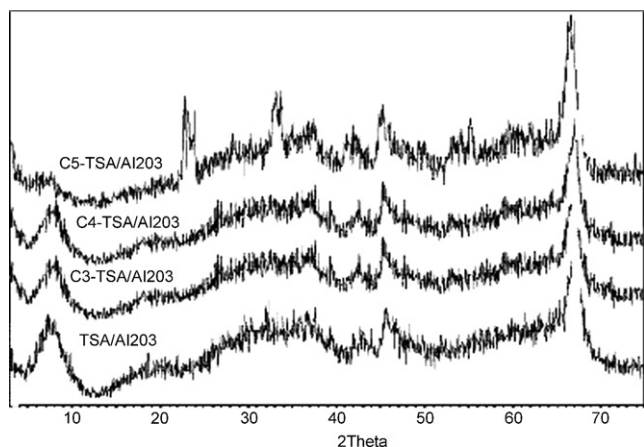


Fig. 1. XRD spectra of TSA/Al<sub>2</sub>O<sub>3</sub>, C<sub>3</sub>-TSA/Al<sub>2</sub>O<sub>3</sub>, C<sub>4</sub>-TSA/Al<sub>2</sub>O<sub>3</sub> and C<sub>5</sub>-TSA/Al<sub>2</sub>O<sub>3</sub>.

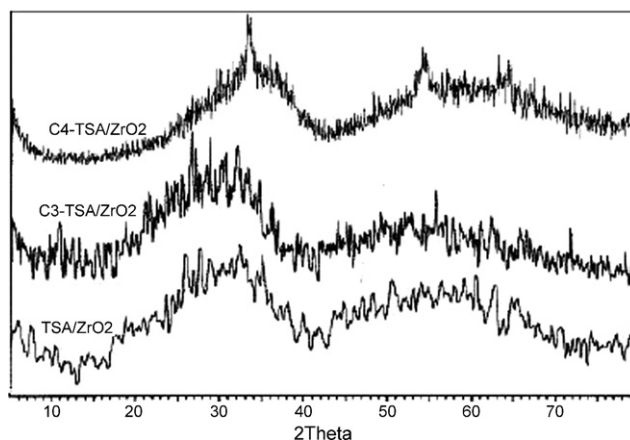
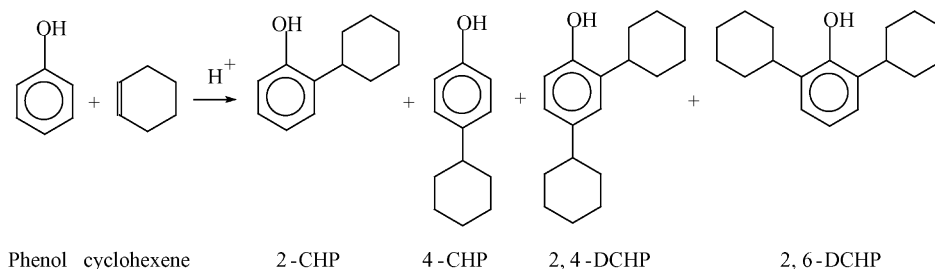


Fig. 2. XRD spectra of TSA/ZrO<sub>2</sub>, C<sub>3</sub>-TSA/ZrO<sub>2</sub> and C<sub>4</sub>-TSA/ZrO<sub>2</sub>.



Scheme 1.

by taking 0.0625 g (equivalent to the 0.25 g of supported 12-tungstosilicic acid) of unsupported 12-tungstosilicic acid shows 83% conversion with 32% and 68% selectivity for *o*- and *p*-isomer, respectively.

In both the cases, it is seen from the table that with increase the concentration of cyclohexene, there is decrease in the %conversion. The decrease in %conversion may be due to the steric hindrance of cyclohexene group. As number of cyclohexene molecules increases on the surface of the support, less site remain available on the surface of the support for the other reactant, phenol in the present case, and it is fact that if both the reactant was not in contact, reaction will not take place.

Further for 1:10 mole ratio of cyclohexene to phenol, only two products (2-CHP, 4-CHP) are obtained whereas with increasing in the mole ratio of cyclohexene to phenol, third product is also formed, *i.e.* 2,4-DCHP. This is because of the higher concentration of the alkylating agent in the reaction medium. Because of the higher concentration of the cyclohexene, more cyclohexene cation are available for reaction with 2-CHP and which results in the di-substituted product, *i.e.* 2,4-DCHP. The formation of 2,4-DCHP is more prominent for the mole ratio of 1:1.66 as expected in both the cases. The %conversion is 100% with 61% and 66% selectivity for *o*-isomer is found at 1:10 mole ratio with 0.25 g of the catalyst for TSA/ZrO<sub>2</sub> and TSA/Al<sub>2</sub>O<sub>3</sub>, 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 phenol to cyclohexene 10:1 for 6 h. The %conversion and %selectivity of different products is reported in Table 3. It shows 65% and 63% conversion with 0.15 g of the catalyst with TSA/ZrO<sub>2</sub> and TSA/Al<sub>2</sub>O<sub>3</sub>, respectively,

Table 3  
%Conversion and %selectivity with different mole ratio of cyclohexene to phenol

Catalyst	Mole ratio	%Conversion	%Selectivity		
			2-CHP	4-CHP	2,4-DCHP
TSA/ZrO <sub>2</sub>	1:10	100	61	39	–
	1:3.33	66	60	38.5	1.5
	1:1.66	47	16	24	60
TSA/Al <sub>2</sub> O <sub>3</sub>	1:10	100	66	34	–
	1:3.33	64	68	30	2
	1:1.66	43	14	20	66

%Conversion is based on cyclohexene; amount of the catalyst is 0.5 g; reaction time is 6 h.

which increases to 100% with 0.25 g of the catalyst which is as expected as increasing the amount of the catalyst, the %conversion is also increasing. But here 100% conversion is observed with 0.25 g of catalysts, so it is not possible to increase further. As it is well known that the alkenes are more reactive compounds, 100% conversion was found with 0.25 g of the catalysts for TSA/ZrO<sub>2</sub> and TSA/Al<sub>2</sub>O<sub>3</sub> with 61% and 65% selectivity for *o*-isomer, respectively. The %conversion and %selectivity of different products is reported in Table 4. The differences in the %selectivity for the products are because of the effect of the support.

### 3.4. Effect of reaction time

The effect of reaction time on cyclohexylation of phenol was studied at a mole ratio of 10:1 using 0.25 g catalyst. The results are presented in Table 5. It is seen from the figure that with increase in reaction time, the %conversion also increases. It is also seen from the table 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 cyclohexene consume in the reaction, less molecules are left in the reaction mixture and more time required generating the carbocation from the cyclohexene. 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:

Table 4  
%Conversion and %selectivity of cyclohexylation of phenol with different amount of catalyst

Catalyst	Amount of the catalyst	%Conversion	%Selectivity		
			2-CHP	4-CHP	2,4-DCHP
TSA/ZrO <sub>2</sub>	0.15	65	60	40	–
	0.25	100	61	39	–
	0.5	100	61.5	38.5	–
	0.75	100	62.5	37.5	–
TSA/Al <sub>2</sub> O <sub>3</sub>	0.15	63	63.4	36.6	–
	0.25	100	63	37	–
	0.5	100	63.5	36.5	–
	0.75	100	65	35	–

%Conversion is based on cyclohexene; mole ratio of cyclohexene to phenol is 1:10; reaction time is 6 h.

Table 5  
%Conversion and %selectivity of cyclohexylation of phenol with different reaction time

Catalyst	Time (h)	%Conversion	%Selectivity		
			2-CHP	4-CHP	2,4-DCHP
TSA/ZrO <sub>2</sub>	1	69.3	60	40	–
	3	83	60.4	39.6	–
	4	94.8	61	39	–
	5	96.5	60.9	39.1	–
	6	100	61	39	–
TSA/Al <sub>2</sub> O <sub>3</sub>	1	67.7	64.4	35.6	–
	3	82	63	37	–
	4	94	64.3	35.7	–
	5	96.3	63.6	36.3	–
	6	100	65	35	–

%Conversion is based on cyclohexene; mole ratio of cyclohexene to phenol is 1:10.

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

### 3.5. Repeated use of the catalyst

Both the catalysts were recycled for two times in order to test its activity as well as stability. Table 6 shows the results for the regenerated catalysts. There was not any change in selectivity, however, little decrease in %conversion is observed which shows that the catalysts are stable and can be regenerated for repeated use.

It is seen from Table 1 that 12-tungstosilicic acid supported on to hydrous zirconia (TSA/ZrO<sub>2</sub>) poses large surface area compared to the neutral alumina (TSA/Al<sub>2</sub>O<sub>3</sub>). So TSA/ZrO<sub>2</sub> is supposed to be more active than compared to the TSA/Al<sub>2</sub>O<sub>3</sub>. But the results of the study shows that the surface area can not be correlated with catalytic activity. Hence it may be concluded that the 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 6  
%Conversion and %selectivity of cyclohexylation of phenol with fresh and regenerated catalyst

Catalyst	%Conversion	%Selectivity	
		2-CHP	4-CHP
TSA/ZrO <sub>2</sub>	100	61	39
R <sub>1</sub> -TSA/ZrO <sub>2</sub>	87	60	40
R <sub>2</sub> -TSA/ZrO <sub>2</sub>	86	59.8	40.2
TSA/Al <sub>2</sub> O <sub>3</sub>	100	65	35
R <sub>1</sub> -TSA/Al <sub>2</sub> O <sub>3</sub>	86	64.3	35.7
R <sub>2</sub> -TSA/Al <sub>2</sub> O <sub>3</sub>	84	64.1	35.9

%Conversion is based on cyclohexene; mole ratio of cyclohexene to phenol is 1:10; reaction time is 6 h.

Total acidity measurement study shows that TSA/ZrO<sub>2</sub> is more acidic than TSA/Al<sub>2</sub>O<sub>3</sub>. So TSA/ZrO<sub>2</sub> is supposed to be more active but the above study shows that the activities of both the catalysts are the same. Here support used, hydrous zirconia (ZrO<sub>2</sub>), is acidic in nature. So acidity of ZrO<sub>2</sub> is also contributing towards the measurement but the reactions carried out with support shows that the acidity of the support is not sufficient for the reactions as it is well known that alkylation reactions required strong acidity. So, the active species which is responsible for the reaction is 12-tungstosilicic acid only. In case of TSA/Al<sub>2</sub>O<sub>3</sub> also the active species is same, as alumina is also inactive for the alkylation reactions. It shows that activity is directly proportional to the acidity of the HPA. Since HPA is same the results are as expected.

It is interesting to note the difference in the selectivity of the products for both the catalysts. In case of TSA/ZrO<sub>2</sub>, the %selectivity for *p*-isomer is greater than that of TSA/Al<sub>2</sub>O<sub>3</sub>. It is well known that strong Bronsted acidic sites are responsible for *p*-isomer. It is also known that zirconia has some Bronsted acidity while that of alumina has only Lewis acidity, supported by the value of ion exchange capacity (Table 1) which is the indirect measurement of Bronsted acidity only. The values for total acidity as well as ion exchange capacity for TSA/ZrO<sub>2</sub> is greater than TSA/Al<sub>2</sub>O<sub>3</sub> as expected. The type of acidity of support may play a role towards the formation of *p*-isomer, however, the difference in %selectivity is not that much appreciable.

Alkylation reactions, especially where more than one product is possible required tedious work up procedure to separate them. All other works carried out on cyclohexylation reactions were end up with more than two products but in present work only two products are reports under optimized conditions. Literature survey shows that in reported cyclohexylation reactions, 2-CHP was obtained as a major product when cyclohexanol was used as an alkylating agent. The %conversion is 85% and 100% conversion and %selectivity for the mentioned product is 93% and 53% at 160 and 250 °C, respectively [23,4]. Here 93% selectivity was obtained but because of incomplete conversion of cyclohexanol, it required extra work up process to separate the reactant from reaction mixture to reuse. It was also found that ether was obtained as a major product when cyclohexene was used as an alkylating agent [5]. In the present study, 2-CHP was found as a major product with cyclohexene as an alkylating agent under mild condition. The uniqueness of the present work lies towards the 100% conversion of one of the reactant with 61% and 65% selectivity for 2-CHP.

Here both the catalysts are equally active for the reaction with the difference in the stability. TSA/ZrO<sub>2</sub> is stable only up to 430 °C where as TSA/Al<sub>2</sub>O<sub>3</sub> is stable up to 500 °C which shows that neutral alumina can be a better support than hydrous zirconia.

## 4. Conclusion

Thermal study shows that the supported HPA does not get disturbed up to 430 and 500 °C in TSA/ZrO<sub>2</sub> and TSA/Al<sub>2</sub>O<sub>3</sub>, respectively. FT-IR and XRD spectra of fresh and calcinated samples shows that the synthesized catalysts do not get disturb

up to 430 and 500 °C when supported on to hydrous zirconia and neutral alumina, respectively. The present paper also reports, liquid phase alkylation of phenol at low temperature. It provides remarkable economical advantage. Further, this method gives 100% conversion which is also one of the most important advantage of supported 12-tungstosilicic acid. Study shows that the catalysts are not ordinary surface type catalyst but it is pseudo liquid bulk type I catalyst.

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