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Cyclohexylation of Resorcinol with Cyclohexanol Catalyzed by Tungstophosphoric Acid Supported Zirconia Catalysts

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We demonstrate a highly active and reusable heterogeneous catalyst system, tungstophosphoric acid (TPA) supported on zirconia (ZrO_2), for the cyclohexylation of resorcinol by cyclohexanol to produce value added chemicals such as 2-cyclohexyl resorcinol, 4-cyclohexyl resorcinol and 3-Hydroxy cyclohexyl phenyl ether under liquid phase reaction condition. TPA/ZrO_2 catalysts prepared with different TPA loadings (5–30 wt.%) by wet impregnation method and calcined in the temperature range of 650–850 °C were characterized by Nitrogen sorption analysis, XRD, FTIR, DTG and DTA, and ^{31}P MAS NMR spectroscopy. Among the catalysts studied, 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C gave the highest conversion of resorcinol (51.2%) with the selectivities for 3-Hydroxy cyclohexyl phenyl ether (53.9%) and 2-cyclohexyl resorcinol and 4-cyclohexyl resorcinol together (46.1%) under optimum reaction conditions. However, the selectivity of the products were controlled by varying the reaction conditions. At higher conversion of resorcinol (78.9%), only C-alkylated products were formed at 200 °C with 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C. The combination of TPA and ZrO_2 coupled with calcination temperature offered an excellent platform for the conversion of resorcinol into O- or C-alkylated products.

Keywords: Resorcinol, Cyclohexanol, 15%TPA/ZrO_2, Cyclohexylation, Keggin TPA.

1. INTRODUCTION

Sterically hindered mono alkyl substituted resorcinol compounds are of great interest as they exhibit excellent antiseptic, anthelmintic, bacterial and germicidal properties, and are used in various therapeutic, agricultural and organic synthesis applications. These derivatives are generally prepared by condensing aliphatic carboxylic acids with resorcinol to produce acyl derivatives first and then reducing the resulting ketones with zinc amalgam.[1] Resorcinol is a phenolic compound having two hydroxyl groups in the benzene structure located at the 1 and 3 positions. Therefore, resorcinol can undergo electrophilic substitution reactions similar to phenol and the two hydroxyl groups present in the resorcinol molecule could strongly activate the ortho- and para- positions of the benzene ring as shown in Scheme 1.

Electrophilic substitution reactions with the resorcinol molecule can occur at the 2-, 4- and 6-positions. The 4- and 6-positions are located at the *ortho*- and *para*-positions (*o*–, *p*–) and 2-positions of *ortho*- and *ortho*-(*o*–, *o*–) with respect to both hydroxyl groups of the resorcinol molecule. Because of this, all the three positions of resorcinol molecule are doubly activated by the hydroxyl groups. In addition, the reaction usually takes place much faster than that of other phenol derivatives due the rational orientation of hydroxyl groups in the resorcinol. However, the composition of products is determined by the steric hindrance due to the OH groups. Cyclohexylation of resorcinol by cyclohexanol produces mainly; 2-cyclohexyl resorcinol, 4-cyclohexyl resorcinol and 3-Hydroxy cyclohexyl phenyl ether as shown in the Scheme 2.

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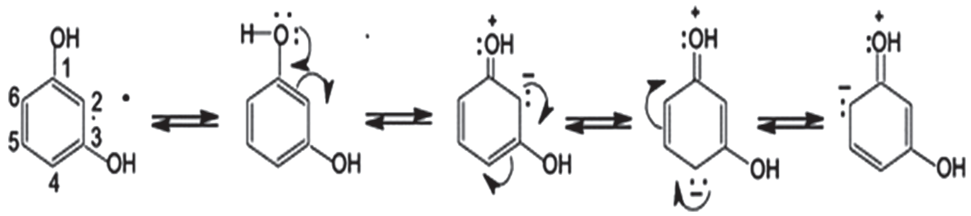


Scheme 1. Resonant forms of resorcinol.

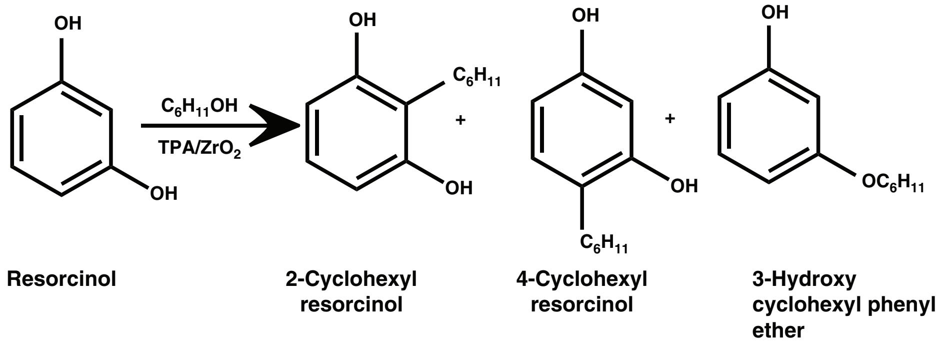
Alkylation of resorcinol has been carried out by Friedel Craft's alkylating agents using various solid acid and supported catalysts.[2–6] Yadav et al. reported the alkylation of resorcinol using heteropoly acid (HPA) supported on clays. Although clays offered solid support for the HPA, the poor textural characteristics of support significantly affect the activity of the HPA. Therefore, developing more efficient and alternate solid acid catalysts for the cyclohexylation of resorcinol is of prime interest to the researchers. Halligudi and his co-workers have been actively working on developing novel catalyst systems for alkylation of aromatics and has developed many solid acid catalysts based on HPA such as 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ (TPA), silicotungstic acid, $H_4SiW_{12}O_{40}$ (STA), molybdophosphoric acid, $H_3PMo_{12}O_{40}$ (MPA) etc. supported on zirconia, titania and mesoporous supports like MCM-41 and SBA-15. These substances are found to be highly efficient catalyst systems for catalyzing many acid catalyzed organic transformations.[7–34]

We reported that HPA's supported on zirconia are excellent catalysts for various acid catalysed organic transformations including alkylation, benzoylation, allylation of aromatics.[7–9] We have demonstrated that TPA/ZrO_2 as an efficient catalyst for *tert*-butylation of resorcinol, and *p*-cresol with *tert*-butanol. Zirconia supported TPA has also been used as an effective and active solid acid catalyst for the synthesis of linear alkyl benzenes.[10–12] Catalytic behaviour of these catalysts in liquid-phase veratrole benzylation has also been reported by our group.[13–16] Nano-sized zirconia supported TPA has been introduced inside the mesochannels of well-ordered porous structured SBA-15 materials and this was employed as a stable and versatile solid acid catalyst for the liquid phase veratrole acylation. It has been found that the mesoporous supports offered an excellent platform for the dispersion of these nanocatalysts and promoted the catalytic activity whereas zirconia helped to stabilize the HPA. Similar nanoparticle stabilized HPA supported mesoporous catalysts have also been used effectively for the intermolecular hydroamination of activated olefins.[22–34] Therefore, the choice of the perfect support for HPA is extremely important to achieve excellent performance in the acid catalysed organic transformation.[17–21] From these results, it is quite clear that there is a huge potential for the metal oxide supported HPA catalysts in the alkylation reactions. In this work, we report the results on tungstophosphoric acid (TPA) modified Zirconia based catalysts for cyclohexylation of resorcinol with cyclohexanol. It has been found that 15 wt.%TPA/ZrO_2 calcined at 750 °C catalyst gave the highest conversion of resorcinol and offered higher selectivity for O-alkylated product (3-Hydroxy cyclohexyl phenyl ether) than C-alkylated products (2-cyclohexyl resorcinol, 4-cyclohexyl resorcinol) under optimized liquid phase reaction conditions. However, higher conversions of resorcinol with the concomitant increase of the C-alkylated products are obtained with increase in reaction temperature and time.

2. EXPERIMENTAL DETAILS

2.1. Materials

Tungstophosphoric acid, resorcinol and cyclohexanol were supplied by Aldrich. Zirconium oxychloride was procured from Loba Chemie Ltd., Mumbai. Methanol was



Scheme 2. Cyclohexylation of resorcinol by cyclohexanol.

purchased from E. Merck India Ltd., Mumbai. All the above materials were used as received without further purification.

2.2. Preparation and Characterization of TPA/ZrO_2 Catalyst

The catalysts were prepared by wet impregnation method, following the procedure described in our earlier publications.[7, 16] Zirconium hydroxide obtained by the hydrolysis of zirconium oxychloride was added to a methanolic solution containing 5 wt.% TPA and then stirred well. The solvent was removed by evaporation to dryness and the resulting substance were calcined in air at different temperatures. Similarly, catalysts with different TPA loading (10, 15, 20, 25 and 30 wt.%) were prepared and calcined at different temperatures of 650, 750 and 850 °C. All TPA/ZrO_2 catalysts were characterized by Nitrogen sorption, XRD, FTIR, DTG and DTA, and ^{31}P MAS NMR spectroscopy to establish the integrity of the Kegin structure of TPA on ZrO_2 support. The characterization results using the above techniques has been published earlier by Halligudi et al. on TPA/ZrO_2 catalysts with different TPA loadings and at different calcination temperatures.[16] In this work, we have included only acidity data a crucial property of TPA/ZrO_2 catalysts with different loadings and calcined at different temperatures for the purpose of interpretation of catalytic data of the reaction cyclohexylation of resorcinol by cyclohexanol. As mentioned above, the physicochemical properties of TPA/ZrO_2 catalysts could be seen in our earlier publication.[16]

Acidity of the catalyst was measured by temperature programmed desorption (TPD) of NH_3. It is seen from the graph of acidity (NH_3 nm^{-2}) versus TPA loading (Fig. 1) that the acidity increased up to 15% and then decreased with further increase in TPA loading, which was due to monolayer coverage of TPA present in the Keggin form confirmed in our earlier work.[7, 16]

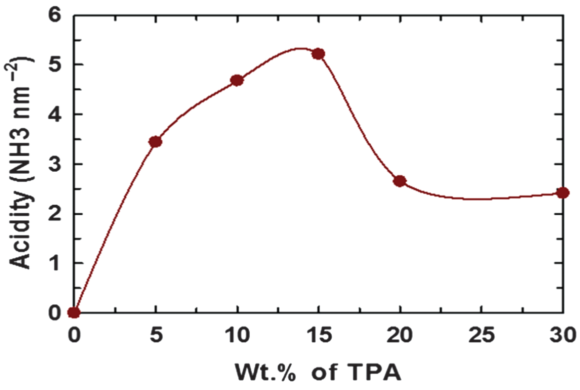


Figure 1. TPD of NH_3 for 5, 10, 15, 20 and 30 wt.% TPA loaded zirconia samples.

2.3. Experimental Procedure

Cyclohexylation of resorcinol with cyclohexanol was conducted in 100 ml Parr Autoclave (SS-316) in a batch mode. Known amounts of reactants and the catalyst were mixed and placed into the autoclave and was flushed with nitrogen with agitation prior to starting the reaction to ensure the removal of dissolved air. The autoclave was then pressurized to 400 psig with nitrogen and stirred at 800 rpm for all the experiments. The autoclave was heated to the desired temperature and the reaction was initiated. A sample (zero hour) of the reaction mixture was kept for analysis. After conducting the reaction for a fixed time interval, the autoclave was cooled to room temperature and the reaction mixture was analysed for the conversions of reactants and products distribution by Shimadzu 14B gas chromatograph equipped with a flame ionization detector using SE-52 packed column. The identity of the products were confirmed by GC-MS (Shimadzu QP-5000). Based on the analysis, the percentage of conversion with respect to either resorcinol or cyclohexanol and the distribution of products were calculated. Conversion of resorcinol (A) and Selectivity for the products (B) 3-Hydroxy cyclohexyl phenyl ether; (C) 2-Cyclohexyl resorcinol and (D) 4-Cyclohexyl resorcinol present in the reaction mixture were calculated as:

$$\begin{aligned}&\text{Conversion of A, (wt.\%)}\\&\quad=[((\text{wt.\% of A})\\&\qquad-(\text{sum of the wt.\% of B, C, and D}))\\&\qquad/(\text{wt.\% of A})]\times 100 \quad \text{and}\\&\text{Product selectivity (wt.\%)}\\&\quad=[(\text{wt.\% distribution of a product})\\&\qquad/(\text{sum of the wt.\% of all the products})]\times 100\end{aligned}$$

3. RESULTS AND DISCUSSION

3.1. Effect of TPA Loading

The catalysts with different TPA loading (10, 15 and 20 wt.%) on ZrO_2 and calcined at 750 °C were used in this study. The reactions were conducted in an autoclave at 130 °C for fixed reaction time of 2 h with catalyst 1.57 g, resorcinol = 15.7 g, cyclohexanol = 14.3 g, resorcinol/cyclohexanol = 1:1 mole. The results on the conversion of resorcinol and products distribution obtained in cyclohexylation are presented in Table I(A). Catalyst with 15 wt.% TPA loading was found to be the most active and gave 3-Hydroxy cyclohexyl phenyl ether (27.6 wt.%), 2-cyclohexyl resorcinol (7.0 wt.%) and 4-cyclohexyl resorcinol (16.6 wt.%) at a conversion of resorcinol (51.2 wt.%). These observations are in concurrence with the catalyst characterization, which indicated that 15 wt.% TPA loaded catalyst has the highest acidity

Table I. Results on cyclohexylation of resorcinol by cyclohexanol.

Catalyst	Products distribution (wt.%), w.r.t, A A	 B	 C	 D	Convn.w.r.t, A(wt.%)
A. Effect of TPA loading					
10 wt.%TPA/ZrO_2 calcined (750 °C)	94.3	3.9	1.8	–	5.7
15 wt.%TPA/ZrO_2 calcined (750 °C)	48.8	27.6	7.0	16.6	51.2
20 wt.%TPA/ZrO_2 calcined (750 °C)	71.2	15.7	3.7	9.5	28.8
B. Effect of catalyst calcination temperature					
15 wt.%TPA/ZrO_2 calcined (650 °C)	80.2	12.7	2.6	4.5	19.8
15 wt.%TPA/ZrO_2 calcined (750 °C)	48.8	27.6	7.0	16.6	51.2
15 wt.%TPA/ZrO_2 calcined (850 °C)	65.1	19.4	4.7	10.8	34.9

Notes: Reaction conditions for A and B: Catalyst = 1.57 g, resorcinol = 15.7 g, cyclohexanol = 14.3 g, resorcinol/cyclohexanol = 1:1 mole, temperature = 130 °C and time = 2 h, total wt. of reaction mixture = 30.0 g and total volume = 27 ml and *Legend*: (A) Resorcinol; (B) 3-Hydroxy cyclohexyl phenyl ether; (C) 2-Cyclohexyl resorcinol and (D) 4-Cyclohexyl resorcinol.

(Fig. 1) and hence gave the highest activity in the cyclohexylation of resorcinol by cyclohexanol. Interestingly, 10 wt.% TPA and 20 wt.% TPA loaded catalysts under the above conditions gave lesser conversion of resorcinol and also corresponding products compared to 15 wt.% TPA catalyst. The lesser activity could be attributed to the lower acidity of the 10 and 20 wt.% of TPA supported on ZrO_2. From these results, it is clear that the acidity of the catalysts play an important role in controlling the activity of the catalysts (Fig. 1). However, 30 wt.% TPA catalyst was not included in this study since it has poor acidity compared to others. It has been established in our earlier studies from ^{31}P MAS NMR spectroscopy that for lower loadings and at a calcination temperature of 750 °C, a broad signal above -20 ppm is observed, attributed to phosphorous (P–OH) in the Keggin unit and at higher loadings and at higher calcination temperatures, a new signal appears below -20 ppm, attributed to phosphorous oxide (P–O–P) resulting from the decomposition of the TPA.[16] Therefore, 15 wt.% of TPA/ZrO_2 calcined at 750 °C gave the best results and hence this catalyst was chosen for further studies to establish the effects of calcination temperature, catalyst weight and other reaction parameters to optimize reaction conditions for getting higher conversions of resorcinol and products distribution in the cyclohexylation of resorcinol by cyclohexanol.

3.2. Effect of Catalyst Calcination Temperature

In order to know the effect of the calcination temperature on the catalytic activity in the cyclohexylation of resorcinol with cyclohexanol, the reaction was carried out using 15 wt.%TPA/ZrO_2 calcined at 650 °C, 750 °C and 850 °C in an autoclave under the same reaction conditions as used in Section 3.1 and the results are presented in Table I(B). It was found that 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C gave the higher conversion of resorcinol (51.2%) with products 3-Hydroxy cyclohexyl phenyl ether (27.6 wt.%), 2-cyclohexyl resorcinol (7.0 wt.%) and 4-cyclohexyl resorcinol (16.6 wt.%). These results show that the catalyst 15 wt.%TPA/ZrO_2 calcined at 750 °C has higher acidity compared to other two catalysts calcined at 650 °C and 850 °C, respectively. At higher calcination temperature (850 °C), the conversion of resorcinol decreased (34.9%) with decrease in corresponding products. This could be the fact that ZrO_2 calcined 750 °C has much higher crystallinity and surface area as compared to the samples calcined at 650 °C and 850 °C. The higher crystallinity affects the interaction between the TPA and the support and it is also evident from DTG and DTA studies that an exothermic peak at 607 °C due to the complete decomposition of the Keggin structure to form a mixture of oxides followed by its crystallization.[16] This could offer excellent monolayer coverage of TPA over ZrO_2 calcined at 750 °C which is directly related to the total acidity of the materials as they give free H^+ ions on the surface. To study the effect of reaction parameters such as catalyst weight, temperature and resorcinol/cyclohexanol mole ratio on the conversion of resorcinol and products distribution in the cyclohexylation reaction, the 15 wt.% TPA/ZrO_2 calcined at 750 °C catalyst has been used in further studies.

3.3. Effect of Weight of 15 wt.%TPA/ZrO_2 Catalyst Calcined at 750 °C

The effect of 15 wt.%TPA/ZrO_2 calcined at 750 °C catalyst weight on the conversion of resorcinol and products distribution in the cyclohexylation of resorcinol with cyclohexanol was studied by varying the catalyst weight from 0.78 g to 2.36 g keeping other reaction conditions same and the results are presented in Table II.

From the results presented in Table II, it is found that with an increase in catalyst weight from 0.78 to 2.36 g, the conversion of resorcinol increased from 34.3 to 65.2 wt.%. Due to higher conversion of resorcinol, the formation of O-alkylated (3-Hydroxy cyclohexyl phenyl ether) product is favoured compared to C-alkylated (2-, and 4-cyclohexyl resorcinol) products.

Table II. Effect of weight of 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C.

Cat.wt. (g)	Products distribution (wt.%), w.r.t, A A	 B	 C	 D	Convn.w.r.t, A (wt.%)
0.78	65.7	18.9	4.5	10.9	34.3
1.57	48.8	27.6	7.0	16.6	51.2
2.36	34.9	28.0	9.5	27.6	65.2

Notes: Reaction conditions: Resorcinol = 15.7 g, cyclohexanol = 14.3 g, resorcinol/cyclohexanol = 1:1 mole, temperature = 130 °C, time = 2 h, total wt. of reaction mixture = 30.0 g and total volume = 27 ml and *Legend*: (A) Resorcinol; (B) 3-Hydroxy cyclohexyl phenyl ether; (C) 2-Cyclohexyl resorcinol and (D) 4-Cyclohexyl resorcinol.

3.4. Effect of Reaction Temperature

It is observed that the rise in reaction temperature has a significant influence on both the conversion of resorcinol and products distribution. The reaction was carried out using the 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C and the temperature of the reaction was varied between 100 to 200 °C keeping other conditions same as given in Table III. From the results presented in Table III, it is seen that the performance of catalyst was significantly improved when the reaction temperature is increased. At 130 °C, maximum amounts of O- and C-alkylated products are formed, however, with further increase in the temperature, the conversion of resorcinol increased to 78.9% with the concomitant decrease in the formation of O-alkylated product resulting only in C-alkylated products. Further, it is also observed that C-alkylation is dominating above 150 °C in the cyclohexylation reaction.

3.5. Effect of Resorcinol/Cyclohexanol Mole Ratio

The activity of 15 wt.% of TPA/ZrO_2 calcined at 750 °C as a function of stoichiometric ratio between Resorcinol and Cyclohexanol was also investigated. In this study, only the mole ratio of Resorcinol/Cyclohexanol is varied from 1:1 to 1:3, keeping other reaction conditions same as given in Table IV. It is seen from the results that with increases in mole ratio of Resorcinol/Cyclohexanol, no significant change in the conversion of resorcinol and products distribution is observed. However, with the mole ratio of 1:1 at 170 °C only C-alkylation is favoured and further increase in mole ratio of Resorcinol/Cyclohexanol, both O- and C-alkylated products are formed. Any mole ratio of Resorcinol/Cyclohexanol could be used depending on the requirement of the desired alkylated products in the cyclohexylation reaction.

3.6. Effect of Reaction Time on Cyclohexylation

Under optimized reaction conditions (Resorcinol = 15.7 g, Cyclohexanol = 14.3 g, Catalyst = 1.57 g of 15 wt.%TPA/ZrO_2 calcined at 750 °C, Temperature = 130 °C, Total wt. of reaction mixture = 30 g and Total volume of reaction mixture = 27 ml), the reaction was carried out in autoclave and the samples were withdrawn at different time intervals and analysed for reactants and products. Conversion with respect to cyclohexanol and resorcinol as a function of time is shown in Figure 2(a). It is seen that the conversion of cyclohexanol is always on the higher side compared to that of resorcinol at all times. However, conversion

Table III. Effect of reaction temperature with 15 wt.%TPA/ZrO_2 calcined at 750 °C.

	Products distribution (wt.%), w.r.t, A				
°C	A	B	C	D	Conv.w.r.t, A (wt.%)
100	94.7	4.1	1.2	–	5.3
130	48.8	27.6	7.0	16.6	51.2
150	42.5	14.8	12.3	30.4	57.5
170	31.5	–	20.9	47.3	68.9
200	21.1	–	19.6	59.3	78.9

Notes: Reaction conditions: Wt. of the catalyst = 1.57 g, resorcinol = 15.7 g, cyclohexanol = 14.3 g, resorcinol/cyclohexanol = 1:1 mole, time = 2 h, total wt. of reaction mixture = 30.0 g and total volume = 27 ml and *Legend:* (A) Resorcinol; (B) 3-Hydroxy cyclohexyl phenyl ether; (C) 2-Cyclohexyl resorcinol and (D) 4-Cyclohexyl resorcinol.

Table IV. Effect of resorcinol/cyclohexanol mole ratio with 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C.

	Products distribution (wt.%), w.r.t, A				
Mole ratio	A	B	C	D	Convn.w.r.t, A (wt.%)
1:1	31.5	–	20.9	47.3	68.9
1:2	29.5	30.6	13.7	26.2	70.5
1:3	26.2	38.4	14.1	21.3	73.8

Notes: Reaction conditions: Wt. of the catalyst = 1.57 g, temperature = 170 °C, time = 2 h, total wt. of reaction mixture = 30.0 g and total volume = 27 ml and *Legend*: (A) Resorcinol; (B) 3-Hydroxy cyclohexyl phenyl ether; (C) 2-Cyclohexylresorcinol and (D) 4-Cyclohexyl resorcinol.

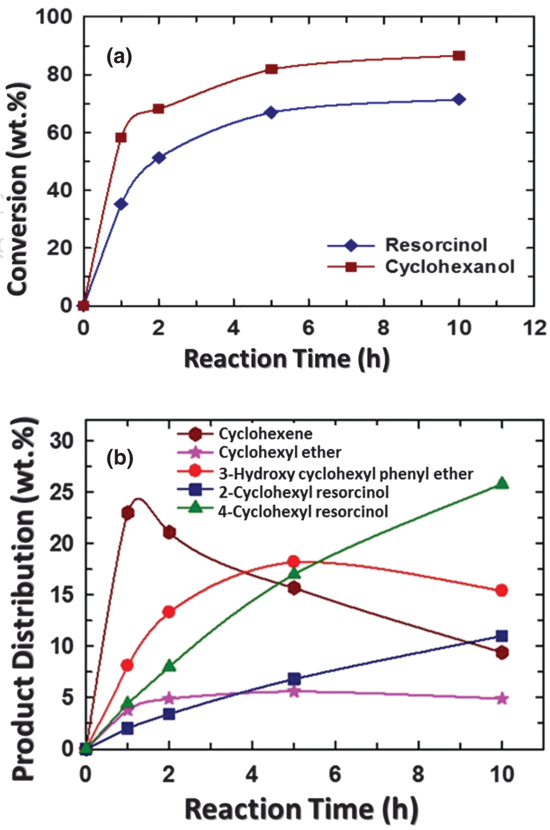


Figure 2. (a) Reaction time versus conversion of resorcinol. *Reaction Conditions*: Resorcinol = 15.7 g, cyclohexanol = 14.3 g, catalyst = 1.57 g of 15%TPA/ZrO_2 calcined at 750 °C, temperature = 130 °C, total wt. of reaction mixture = 30 g, total volume of reaction mixture = 27 ml. (b) Reaction time versus products distribution in cyclohexylation of resorcinol. *Reaction conditions*: Resorcinol = 15.7 g, cyclohexanol = 14.3 g, catalyst = 1.57 g of 15%TPA/ZrO_2 calcined at 750 °C, temperature = 130 °C, total wt. of reaction mixture = 30 g, total volume of reaction mixture = 27 ml.

of cyclohexanol increased from (81.9% to 86.6%), while resorcinol increased from (57.0% to 71.4%), in 5 h. Higher conversions of cyclohexanol could be due to the formation of cyclohexene via dehydration which is confirmed by the fact that only small amount remains in the reaction mixture after 10 h reaction. It shows that the cyclohexylation reaction is faster during first 5 h and later the rates are decreased, which could be due to the products inhibition. It is observed from Figure 2(b) that the products distribution varied as a function of time and the amounts of C-alkylated products (4-cyclohexyl resorcinol and 2-cyclohexyl resorcinol) increase continuously with increasing in the reaction time and reached maximum at 10 h. However, the selectivity for O-alkylated product (3-Hydroxy cyclohexyl phenyl ether) increases till the reaction time of 5 h and then decreases with further increase in time. Additionally, cyclohexene and cyclohexyl ether are also formed in the reaction along with the major products in the cyclohexylation reaction (Fig. 2(b)). However, initially more of cyclohexene is formed via dehydration of cyclohexanol during 1 h reaction and later decreased with further increase in time. Cyclohexyl ether is also formed as side product and its quantity is small compared to other products. From these results, it can be concluded that the reaction conditions play a significant role in controlling the activity of the catalyst and need to be optimized to get optimum amounts of desired products.

3.7. Reusability of the Catalyst

The most active 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C was used for its recyclability test in the cyclohexylation of resorcinol under optimized reaction conditions. In each cycle, the reaction was carried out in an autoclave using a reaction mixture containing known amount of catalyst, resorcinol/cyclohexanol mole ratio at 130 °C for 2 h and conversion of resorcinol and cyclohexanol and products distribution were estimated by GC analysis. In the second cycle, the used catalyst was separated by filtration and dried at 150 °C in air for 1 h and then reused in the reaction with fresh reaction mixture. Similarly, recycling of catalyst experiments were carried out for few more cycles. We found that there was no significant loss in the catalytic activity with respect to conversion of resorcinol or cyclohexanol and products distribution with 15 wt.%TPA/ZrO_2 catalyst calcined at 750 °C even after eight cycles. Hence, it is concluded that the reported catalyst sytem is recyclable and environmental friendly heterogeneous catalyst system, which could be used for any alkylation reactions.

4. CONCLUSIONS

Cyclohexylation of resorcinol by cyclohexanol has been efficiently catalyzed by ZrO_2 supported with different amount of TPA and calcined at different temperature under liquid phase conditions and it gave both C- and O-alkylated products. It has been found that the amount of TPA and calcination temperature which control the total acidity of the catalysts, played a critical role in controlling the activity of the catalyst in cyclohexylation of resorcinol by cyclohexanol. Among the catalysts studied, ZrO_2 calcined at 750 °C loaded with 15 wt.% of TPA found to be the best catalyst, registering high conversion of resorcinol and products. We also demonstrated that the products distribution can be tuned with a simple adjustment of the reaction time, catalyst weight, reactants mole ratio and temperature. It has also been found that at higher conversions of either cyclohexanol or resorcinol, electrophilic substitution shifts towards C-alkylation giving more of (4-cyclohexyl resorcinol and 2-cyclohexyl resorcinol) and less of O-alkylated product (3-Hydroxy cyclohexyl phenyl ether).

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