Cyclohexylation of phenol over a solid acid catalyst comprising 12-tungstophosphoric acid and hydrous zirconia

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Received 23 February 2007; revised 29 January 2008

The Friedel-Crafts alkylation (cyclohexylation of phenol with cyclohexene) has been carried out over 12-tungstophosphoric acid supported on hydrous zirconia under mild conditions. The catalyst shows high activity and selectivity for 2-cyclohexylphenol, an important product used as intermediate in dyestuff preparation as well as in preparation of 2-phenylphenol which is used as disinfectant and fungicide. In addition, the catalyst can be recycled and reused.

IPC Code: Int. Cl. B01J21/06; B01J27/16

Friedel-Craft alkylation reactions are generally carried out with traditional Brönsted acids such as H$_2$SO$_4$, H$_3$PO$_4$ or by using Lewis acids such as AlCl$_3$, BF$_3$, FeCl$_3$ and ZnCl$_2$. Due to the known disadvantages of these acids, a number of solid catalysts such as zeolites, ion exchange resins and clays have been reported for the alkylation reaction of phenol aimed at achieving clean technology.

In recent years, heteropolyacids (HPAs) have been gaining importance as alkylating and acylating catalysts for the Friedel Craft reactions. Among them, Keggin type heteropoly acids, including 12-tungstophosphoric (TPA) supported onto different supports, have been used for the alkylation of various aromatic substrates because of their high acidity and thermal stability.

Literature survey shows that the cyclohexylation of phenol with various solid acid catalysts such as zeolite-Hβ and various conventional Lewis and Brønsted acids, cationic ion-exchange resins and acid treated clay, and cesium salt of dodecatunstophosphoric acid and sulphated zirconia are already reported. However, there is no report on the same using supported heteropolyacid. We have reported recently the cyclohexylation of phenol over supported 12-tungstosilicic acid, TSA. Keeping in view the encouraging results obtained therein, we report herein the use of supported TPA in liquid phase under mild conditions. 30% TPA supported onto hydrous zirconia (ZrO$_2$) has been evaluated as a catalyst for the liquid phase alkylation of phenol with cyclohexene. A detailed catalytic study of the reaction was carried out by varying reaction parameters such as temperature, run duration, mole ratio of phenol to cyclohexene and the amount of the catalyst to optimize the conditions.

Experimental

All chemicals used were of A.R. grade. TPA, H$_3$PW$_{12}$O$_{40}$·n H$_2$O (Lobachemie, Mumbai), Zirconium oxychloride, and ZrOCl$_2$·8H$_2$O (SD Fine Chemicals) were used as received. Phenol and cyclohexene were obtained from Merck and used as received.

30% TPA supported onto hydrous zirconia (ZrO$_2$) was synthesized and characterized by known methods.

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 and phenol were taken in 1:10 mole ratio and appropriate amount of the catalyst was added to it. The resultant mixture was heated at 80°C on magnetic stirrer for 1 h. Varying different parameters, the products were analysed on GC using SE-30 column. Product identification was done by gas chromatogram-mass spectroscopy.

Results and discussion

The main characterization of the support as well as catalysts, viz. ion exchange capacity, surface area measurement, particle size distribution and total acidity obtained from temperature programed desorption are given in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total acidity (mmol NH$_3$/g)</th>
<th>Total surface area (m$^2$/g)</th>
<th>Particle diameter (average µm)</th>
<th>IEC* (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>0.64</td>
<td>170</td>
<td>112.15</td>
<td>0.16</td>
</tr>
<tr>
<td>TPA/ ZrO$_2$</td>
<td>0.82</td>
<td>146</td>
<td>9.12</td>
<td>0.62</td>
</tr>
</tbody>
</table>

*Ion exchange capacity
Alkylation of phenol can result in a mixture of four different products, viz. 2-cyclohexylphenol (o-CHP) [1], 4-cyclohexylphenol (p-CHP) [2], 2, 4-dicyclohexylphenol (o,p-DCHP) [3] and 2, 6-dicyclohexylphenol (o-DCHP) [4] (Scheme 1).

Alkylation reaction carried out using the support alone showed that the support was inactive for the alkylation of phenol with cyclohexene. The mentioned reaction catalyzed by TPA/ZrO\(_2\) gives mainly two products: 2-cyclohexylphenol and 4-cyclohexylphenol. The products were confirmed by gas chromatogram-mass spectroscopy.

The reaction was carried out by varying mole ratio of cyclohexene to phenol (using 0.5 g of the catalyst) for 6 h at different temperatures, room temperature (30-40°C) and 80°C. At room temperature, the conversion is found to be zero. The results obtained at 80°C are given in Table 2. It is seen from the table that with increase the concentration of cyclohexene, there is a decrease in its conversion. However, the overall production of the alkylated products increases. This is generally observed in most bimolecular reactions.

Further, for 1:10 mole ratio of cyclohexene to phenol, only two products (o-CHP, p-CHP) are obtained while an additional product (o,p-DCHP) is also formed at larger cyclohexene concentrations. Because of the higher concentration of the cyclohexene, more cyclohexene cations are available for reaction with o-CHP and this results in the dissubstituted product, i.e. o,p-DCHP. The formation of o,p-DCHP is more prominent for the mole ratio of 1:1.66, as expected.

The reaction was carried out with different amounts of the catalyst keeping the mole ratio of phenol to cyclohexene 1:10 for 6 h. The conversion and selectivity for the different products are reported in Fig. 1. It shows 78% conversion with 0.15 g of the catalyst which increases to 100% with 0.25 g of the catalyst which is as expected.

The effect of reaction time on cyclohexylation of phenol was studied at a mole ratio of 1:10 using 0.25 g catalyst. The results are depicted in Fig. 2.

It is seen from the Fig. 2 that conversion increases with increase in reaction time. It is also seen from the
cyclohexanol was used as an alkylating agent in cyclohexylation reactions as a major product when the present studies. Two products, while only two products are reported in earlier work carried out on cyclohexylation reactions has reported more than one product is possible, require tedious work up procedure to separate them. Earlier work carried out after separating the catalyst from the reaction mixture by filtration. It was washed with conductivity water, dried at 100°C. The regenerated catalyst was designated as R₂-TPA/ZrO₂. The 2nd recycling (R₂) was carried out by separating R₁ from reaction mixture by filtration, washing with conductivity water, drying at 100°C and designating it as R₂-TPA/ZrO₂. There was no change in its selectivity; however, a little decrease in conversion was observed, showing that the catalyst is stable and can be regenerated and reused (Table 3).

Alkylation reactions, especially where more than one product is possible, require tedious work up procedure to separate them. Earlier work carried out on cyclohexylation reactions has reported more than two products, while only two products are reported in the present studies. o-CHP was obtained in cyclohexylation reactions as a major product when cyclohexanol was used as an alkylating agent. The conversion was 85 and 100 conversion and selectivity for the mentioned product was 93% and 53% at 160°C and 250°C, respectively. More selectivity (93%) could be attained in the present studies. But, due to incomplete conversion of cyclohexanol, separation of the reactant from reaction mixture was required. It was also found that ether was obtained as a major product when cyclohexene was used as an alkylating agent. In the present study, o-CHP has been found as a major product with cyclohexene as an alkylating agent under mild conditions. The uniqueness of the present work is the 100% conversion of cyclohexene with 69% selectivity for o-CHP. In all the reactions, removal of the catalyst as well as the products involves a simple filtration. The catalysts can be reused after a simple work up.

### Table 3—Influence of reuse of catalyst on conversion and selectivity of cyclohexylation of phenol with fresh and regenerated catalyst. [mole ratio cyclohexene:phenol, 1:10; reaction time, 6 h]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>o-CHP (%)</th>
<th>p-CHP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA/ZrO₂</td>
<td>100</td>
<td>69</td>
<td>31</td>
</tr>
<tr>
<td>R₁-TPA/ZrO₂</td>
<td>89</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>R₂-TPA/ZrO₂</td>
<td>86</td>
<td>64.5</td>
<td>35.5</td>
</tr>
</tbody>
</table>

figure that in the first hour itself, most of the reactant is converted into the product and after that the reaction becomes slow. This may be due to a kinetic effect arising from cyclohexene consumption and catalyst deactivation.

The optimum conditions for the present reaction are: mole ratio of cyclohexene to phenol (1:10); amount of the catalyst (0.25 g); temperature (80°C); reaction time (6 h).

The catalyst was recycled two times in order to test its activity as well as stability. The 1st recycling (R₁) was carried out after separating the catalyst from reaction mixture by filtration. It was washed with conductivity water, dried at 100°C and activated at 300°C. The regenerated catalyst was designated as R₁-TPA/ZrO₂. The 2nd recycling (R₂) was carried out by separating R₁ from reaction mixture by filtration, washing with conductivity water, drying at 100°C and designating it as R₂-TPA/ZrO₂. There was no change in its selectivity; however, a little decrease in conversion was observed, showing that the catalyst is stable and can be regenerated and reused (Table 3).

ACKNOWLEDGEMENT

The authors are thankful to Dr R V Jasra, CSMCRI, Bhavnagar for surface area analysis. Nikunj Bhatt, is thankful to Department of Science and Technology, New Delhi, for the financial assistance.

### References


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