Molecular Sieves as Green Heterogeneous Acidic Catalyst for Esterification Reaction

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Abstract: Molecular sieves and its acid-modified forms were examined for their performance as a solid acid catalyst in the esterification reaction of acetic acid with different alcohols. Particle size in terms of crystallite diameter via XRD, FTIR spectroscopy in order to study the surface functionality, surface acidity studies using pyridine adsorption method via FTIR spectroscopy was being carried out. It was found that Molecular sieves modified using Sulfuric acid gave highest yield for the esterification reaction.

Keywords: Molecular sieves, acid-modification, esterification, heterogeneous catalysis, green chemical proce

1. Introduction

Globally there is an urgent need for the chemical processes which are green. The prime area under investigation under the heading of green chemical processes is the use of solid acid catalysts as the heterogeneous catalysts. Heterogeneous catalysts are preferred over homogenous catalysts due to their corrosive nature and difficulty in separation. On the other hand, heterogeneous catalysts are non-corrosive, easy to handle, easy to separate and the most important feature is that they are ecofriendly and economical [1,20]. A variety of materials have been employed as the solid acid catalysts viz Zinc oxide, acidic resins, sulfamic acid, titanium pillered clay, zeolites, titanium dioxide; tin oxide, niobia, sulfated zirconia, heteropolyacids, sulfated metal oxides and so on [2-7, 21-25]. It is found that most of them exhibit a behavior of that of a Bronsted acid.

These solid acids are utilized in several reactions such as acylation, dehydration reactions, alkylation, esterification, etherification; etc [8-10]. From the literature it can be also seen that the acid-activation tends to increase the efficiency of these solids, along with dissolution of impurities, external layer dissolution; etc which becomes an additional advantage.[11-13]

In the present work, we have investigated the esterification reaction of various alcohols with acetic acid over molecular sieves. Esters are basically obtained as the product of the reaction between an alcohol and an acid [19]. Esterification is an important reaction as far as chemical industry is concerned. As it uses an efficient acid catalyst like corrosive mineral acids [14,15], solid acids can very well replace these mineral acids. In our investigation we have used molecular sieves and acid-modified molecular sieves as solid acid catalyst for the esterification reaction.

2. Experimental Details

In the present investigation Molecular sieves 4Å used were purchased from LOBA Chemicals, Sulfuric acid, hydrochloric acid, Methanol, ethanol, 1-butanol, isoamyl alcohol and glacial acetic acid were purchased from Thomas Baker Pvt Ltd. Molecular sieves (SM) were used as catalyst and also cation modified molecular sieves were used as the catalyst, which were synthesized as follows:

a) Untreated Molecular sieves (SM): Molecular sieves were grounded to a fine powder using a motor and pastle and were activated at 100°C and were used for the reaction.

b) Molecular sieves treated with sulfuric acid (SMS): Molecular sieves were refluxed with 2M Sulfuric acid for 2 hours and were given washing with hot distilled water till the filtrate gave negative sulfate test. The resulting solid was oven dried at 100°C and were used for the reaction.

c) Molecular sieves treated with hydrochloric acid (SMH):

d) Molecular sieves were refluxed with 2M hydrochloric acid for 2 hours and were given washing with hot distilled water till the filtrate gave negative sulfate test. The resulting solid was oven dried at 100°C and was used for the reaction.

The catalysts were characterized by:

- X-ray diffraction (XRD): XRD patterns were recorded using Rigaku Ultima IV diffractometer which employed CuKα radiation of wavelength 1.5406 Å with Ni filter. Using these patterns crystallite diameter and catalyst nature was determined.

- Fourier Transform Infrared spectroscopy: IR spectra were recorded by using IR Prestige 21 shimadzu spectrophotometer to investigate the surface functionalities of the samples.

- Pyridine adsorption studies: Pyridine adsorption studies were used to investigate the acidity of the catalyst surface by using IR spectroscopy. In this method 1g of the sample was activated at 110°C for 1hr and was exposed to pyridine vapors for 4hrs. Later, the samples was degassed at 110°C using an oven and IR spectra of the same were recorded.[2]

Catalytic activity: Catalytic activity was tested for Esterification of acetic acid with various alcohols. In our investigation, 25mL of glacial acetic acid preheated at 80°C was taken in a round bottomed flask and to it preheated
calculated 2 moles of alcohol was added to the flask containing the glacial acetic acid. 1 g of the catalyst was added to the reaction flask and refluxed for 4 hours using a magnetic stearer equipped with heating mantle at 80°C. The product was separated by using separating funnel followed by purification by simple distillation yield was calculated and boiling point was determined. Later, the product was characterized by FTIR spectroscopy.

3. Results and discussion

a) Structural properties of catalysts:
The XRD pattern of the catalysts showing partly sharp peaks reveal that SM, SMS and SMH are semi-crystalline in nature. (Fig. 1) The crystallite diameter were calculated for SM, SMS and SMH by using Debye-Scheerer formula and were found to be 36.12nm, 30.31nm and 33.55nm respectively. The peak at $2\theta=15^\circ$ reveals the presence of SiO$_2$[16] whereas, $2\theta=27^\circ$ can attributed to the presence of Al$_2$O$_3$ (JCPDS 16, 1312). A faint peak at $2\theta=48^\circ$ signifies the presence of anatase TiO$_2$[17].

Also, it can be observed that smaller particle size plays an important role in increasing the rate of the reaction as we know that smaller the particle size, larger will be the surface area which will lead to greater extent of adsorbtion on the catalytic surface and ultimately will felicitate a good yield.

It can be also be seen from the XRD patterns that initial crystallite behavior is broken down to the amorphous structure. It is reported in the literature that water loss from the structure results into a shift of octahedral AlO$_6$ units into tetracoordinated and pentacoordinated Al units. As Al units are more susceptible as well as reactive as compared to hexa-coordinated Al units to the acid leaching resulting in loss of some Al(III) sites which inturn enhances the formation of amorphous type of the structure.[8-10]

The IR spectra of all three catalysts (Fig. 2 (b)) viz SM, SMS and SMH show vibration frequencies at around 3000-3500 cm$^{-1}$ indicating the presence of O-H stretch due to the chemisorbed water. Peak at 1645 cm$^{-1}$ is due to C=O. Also there is a peak arising at 1011 cm$^{-1}$ which is due to C-O and that between 550-1200 cm$^{-1}$ can be attributed to M-O-M vibrations.[18]

From the pyridine adsorption studies, (Fig.2 (a)) infrared spectrum shows the peak at 3600 cm$^{-1}$ which may be due to the chemisorbed water. And the peak at 1366 cm$^{-1}$ is due to Lewis acid site and that at 1654 cm$^{-1}$ and 1477 cm$^{-1}$ is due to the combination of Lewis and Brosted acid sites.
Table 1: Percentage yield of esters of various alcohols with acetic acid

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Acid</th>
<th>Catalyst</th>
<th>Ester</th>
<th>% Yield</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoamyl alcohol</td>
<td>Acetic acid</td>
<td>SM</td>
<td>Isoamyl acetate</td>
<td>45.66</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMS</td>
<td></td>
<td>57.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMH</td>
<td></td>
<td>53.45</td>
<td></td>
</tr>
<tr>
<td>1-Butanol</td>
<td>Acetic acid</td>
<td>SM</td>
<td>1-Butylacetate</td>
<td>48.60</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMS</td>
<td></td>
<td>57.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMH</td>
<td></td>
<td>51.01</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>Acetic acid</td>
<td>SM</td>
<td>Methylacetate</td>
<td>46.20</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMS</td>
<td></td>
<td>55.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMH</td>
<td></td>
<td>50.67</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Acetic acid</td>
<td>SM</td>
<td>Ethylacetate</td>
<td>44.43</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMS</td>
<td></td>
<td>52.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMH</td>
<td></td>
<td>49.83</td>
<td></td>
</tr>
</tbody>
</table>

b) Catalytic studies

The esterification results are as summarized in the above table 1. From the table it can be seen that SMS gave a better yield than as compared to the SM catalyst and SMH catalyst. This may be due to more retention of the hydrides via adsorption which may be felicitating the esterification reaction in the forward direction thereby reducing the activation barrier in order to increase the rate of the reaction by yielding more amount of the desired reaction product i.e. ester. From the infrared spectra of the reaction products as shown in Fig. 3, it can be confirmed that the formed major products is ester which can be attributed to the presence of absorption peak at 1745.58 cm⁻¹ and 1741.72 cm⁻¹. (Fig.3)

Plausible reaction mechanism for the esterification reaction over acid modified molecular sieves is as follows:

4. Conclusions

From our investigation we can conclude that the SMS can be successfully utilized as solid acid heterogeneous catalysts in esterification reaction of acetic acid with various alcohols to produce considerable yield of esters as compared to SM and SMH as the catalysts. This is mainly due to the smaller particle size of the catalyst which exhibits a greater surface area for the reaction to take place effectively.

References