DEHYDRATION OF GLYCEROL OVER HIGH SURFACE AREA
γ-ALUMINA SUPPORTED HETEROPOLY ACID CATALYSTS

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ABSTRACT
Dehydration of glycerol was performed over heteropoly acids (HPA), viz., silicotungstic acid (H-SiW), phosphotungstic acid (H-PW), and phosphomolybdic acid (H-PMo), supported high surface area γ-alumina (HSAI-S25) catalysts. Various physico-chemical studies of these supported catalysts indicate high dispersion of the active (HPA) species on the support surface. It was observed that the catalyst, H-SiW/HSAI-S25 show high activity, i.e., high glycerol conversion and combined acrolein and hydroxylacetone selectivity. On the other hand, the catalysts such as H-PW/HSAI-S25 and H-PMo/HSAI-S25 demonstrate low selectivity of the expected products owing to a very different acidity of the catalyst leading to side reactions like oligomerisation and carbonization of glycerol as well the formation of allyl alcohol.

INTRODUCTION
High surface area alumina, in particular γ-alumina (γ-Al₂O₃), is widely used as catalyst and catalyst support owing to their favorable textural properties and intrinsic acid-base characteristics (Pines et al., 1960). However, the preparation of alumina with high surface area and uniform pore size in a reproducible way is still a challenge. In this regard, recently, we have developed a facile route for preparation of high surface area γ-Al₂O₃ with desirable pore characteristics using aluminium salts and auxiliary chemicals such as ethylene glycol, n-butanol, etc. (Selvam et al. 2011). The textural properties could be tuned by substantially under varying experimental conditions, i.e., temperature, time, auxiliary chemical treatments, etc.

In the context of increased biodiesel production, by transesterification of vegetable oils, the availability of a large volume of undesired glycerol requires valorization. Since glycerol is a highly functionalized molecule and forms one of the building blocks as a key feedstock for several value added products and intermediates such as acrolein, hydroxyacetone, glycercic acid, epichlorohydrin, glyceraldehyde, lactic acid, tartronic acid, 1,2-propane diol and 1,3-propane diol, etc. Conversion of glycerol into such useful chemicals, in particular, acrolein, is one of the important reactions since it is an important intermediate in the preparation of polyester resin, polyurethane, propylene glycol, amino acid like DL-methionine and many other industrially important
chemicals. On the other hand, hydroxyacetone is used to prepare 1,2-propane diol, and many other industrially important compounds like geminal diols, acetal and ketal. Glycerol in the presence of solid acid catalyst reacts in two independent pathways gives acrolein and hydroxyl acetone as shown in Figure 1.

Various solid acid catalysts including metal oxides, mixed-metal oxides, sulphates (Chai et al., 2007), phosphates (Suprun et al., 2009) and zeolites (Corma et al., 2008) have been tested for the dehydration of glycerol in either gaseous or liquid state. However, one of the main disadvantages of these catalysts lie in the formation of a large amount of by-products (25–40%) and catalyst deactivation. On the other hand, heteropoly acids are strong Bronsted acids with tunable acidity but they lack thermal stability and have low specific surface area. In order to alleviate such problems heteropoly acids are often supported over acidic carriers like alumina (Atia et al., 2008), titania, zirconia (Chai et al., 2008), and silica (Tsukuda et al., 2007). Among the various heteropoly acids, silicotungstic acid (H-SW) is moderately strong acid with high water tolerant ability (Atia et al., 2008; Tsukuda et al., 2007). In this work, we have attempted to prepare high surface area γ-alumina (HSAI-S25) using aluminium salts (Selvam et al., 2011) and the same is employed as a support for the heteropoly acids such as silicotungstic acid (H-SiW), phosphotungstic acid (H-PW), and phosphomolybdic acid (H-PMo). These supported catalysts were employed for the dehydration reaction of glycerol.

**EXPERIMENTAL**

The high surface area γ-alumina, designated as HSAI-S25, was prepared as per the procedure developed earlier (Selvam et al., 2011), and the supported catalysts were prepared as per the following procedure: An optimized amount of the heteropoly acid (HPA; 15 wt%) was supported on γ-alumina in two different ways, viz., a direct impregnation (Method 1) of the corresponding polyoxometallates, and an indirect approach of impregnation (Method 2), i.e., by impregnating appropriate amounts of the corresponding polyoxometallates with boehmite. All the supported samples were dried at 60°C for 12 h in vacuum and dried at 120°C for 2 h followed by calcinations at 450°C in presence of air for 4 h. These samples are designated as HPA/HSAI-S25 (M1) and HPA/HSAI-S25 (M2). The resulting supported catalysts were systematically characterized using various analytical techniques, viz., X-ray diffraction (XRD),
Results and Discussion

Figure 2 depicts the XRD patterns of γ-alumina (HSAI-S25) and various HPA supported HSAI-S25 catalysts. The diffraction patterns are typical of these materials. However, it is to be noted here that the supported catalysts show a diffused pattern owing to high dispersion of the active species as a consequence of the formation of very small crystallites (Atia et al., 2008).

The dehydration of glycerol was performed in a fixed-bed down-flow glass reactor under atmospheric pressure at 275°C. About 0.3 g of the supported catalyst was placed in the middle of the reactor tube and the catalyst bed was maintained at the desired temperature under nitrogen flow of 30 cm$^3$/min for 1 h. Aqueous glycerol (10 wt%) was fed into the reactor at the feed rate of 1.7 cm$^3$/h in flowing nitrogen. The liquid product collected in a dry ice-glycerol trap every hour was analyzed by gas chromatograph in hydrogen flame ionization detector (FID-GC, CHEMITO GC-1000) with a 30 m capillary column of HP-FFAP (30 m × 0.32 mm × 0.25 µm).

Figure 3 illustrates the BET isotherms of HSAI-S25, which show a type IV pattern typical characteristic of mesoporosity. A well-defined step occurs at a relative pressure of 0.4-0.5, corresponding to capillary condensation of nitrogen, indicative of the uniformity of the pores. Textural properties, viz., surface area, pore volume and average pore diameter, for HSAI-S25 and HPA supported on HSAI-S25 are...
summarized in Table 1. All the samples exhibit type-IV isotherms with H1 hysteresis loop indicating the mesoporous characteristics with cylindrical pores.

![Pore size distribution](image)

**Fig. 3.** \(\text{N}_2\) sorption isotherm and pore size distribution (inset) of HSAI-S25.

**Table 1 Textural properties of heteropoly acid (15 wt%) supported on \(\gamma\)-alumina.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}^a) (m(^2)/g)</th>
<th>(V_p^b) (cm(^3)/g)</th>
<th>(d_{\text{BJH}}^c) (nm)</th>
<th>Keggin anion density(^d) (HPA/nm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSAI-S25</td>
<td>272</td>
<td>0.30</td>
<td>4.2</td>
<td>---</td>
</tr>
<tr>
<td>H-SiW/HSAI-S25(M2)</td>
<td>228</td>
<td>0.24</td>
<td>4.1</td>
<td>0.14</td>
</tr>
<tr>
<td>H-PW/HSAI-S25(M2)</td>
<td>223</td>
<td>0.23</td>
<td>4.1</td>
<td>0.14</td>
</tr>
<tr>
<td>H-PMo/HSAI-S25(M2)</td>
<td>235</td>
<td>0.23</td>
<td>4.0</td>
<td>0.21</td>
</tr>
</tbody>
</table>

\(^a\)BET surface area (\(S_{\text{BET}}\)); \(^b\)Total pore volume (\(V_p\)); \(^c\)Average pore size (\(d_{\text{BJH}}\)); \(^d\)Keggin anion density = ((%HPA/100) \times 6.02 \times 10^5)/(\(S_{\text{BET}}\) cat \times Molecular weight of HPA).

The Keggin-anion density (HPA/nm\(^2\)) data is expressed as the number of Keggin anion per square nanometer of the support surface. This is calculated according to the actual HPA loading and the surface area of the sample. The Keggin anion density of all the catalysts are in the range of 0.14-0.21 suggesting that the catalyst is well below the theoretical monolayer coverage (0.6 HPA/nm\(^2\)). The lower values of our catalysts indicate that the HPA is highly dispersed over the alumina surface. On the other hand, the loading of HPA results in the decrease of surface area and pore volume due to covering and plugging of pores by the large Keggin anions (kinetic diameter \(\sim\) 1.2 nm).
Figure 4 depicts the TPDA profile of various catalysts. The traces can be viewed as a combination of several peaks which are assigned different acid strengths. Accordingly, they are classified and assigned (Yori et al., 2005) as weak (150-300°C), medium (300-500°C), and strong (500-650°C). It can be seen from this Fig. 4 that the TPDA traces can be considered as comprising of main peak and a shoulder which can be assigned to the Brönsted acid sites of medium and strong acidity, respectively. The maximum of the TPDA peak position in the low-temperature region decreased in the following order: 15 H-PMo/HSAI-S25 > 15 H-PW/HSAI-S25 > 15 H-SiW/HSAI-S25.

Fig. 4. TPDA profiles of: a) 15 wt% H-SiW/ HSAI-S25; b) 15 wt% H-PW/ HSAI-S25; c) 15 wt% H-PMo/ HSAI-S25; Inset: HSAI-S25.

Figure 5 shows the effect of contact time on glycerol conversion. Contact time is generally used to identify the more active catalyst in terms of conversion (Pattison, 1951). It can be seen from Fig. 5 that, in the case of 20wt% H-SiW/HSAI-S25 and 30wt% H-SiW/HSAI-S25 catalyst, the conversion increases steadily with contact time and a complete conversion is reached only at ~ 0.7 s. On the other hand, for 10wt% H-SiW/HSAI-S25 and 15wt% H-SiW/HSAI-S25, a complete conversion is reached within 0.2 s. Thus, it is clear that among the various loadings, the catalyst 15wt% SiW/HSAI-S25 is found to be better in terms of glycerol conversion possibly due to high dispersion of catalyst which is well supported from keggin anion density data.
Fig. 5. Effect of contact time on glycerol conversion: (■) 10 wt% SiW/HSAI-S25; (▼) 15 wt% SiW/HSAI-S25; (▲) 20 wt% SiW/HSAI-S25; (•) 30 wt% SiW/HSAI-S25. Reaction conditions: Reactant: 10 wt% glycerol; Catalyst mass: 10 mg; Reaction temperature: 275°C.

Table 2 presents the reaction results over various catalysts. It can be seen from this table that the catalysts prepared from Method 2, i.e., H-SiW/HSAI-S25(M2), is found to be superior to the catalyst prepared from Method 1, H-SiW/HSAI-S25(M1), in terms of acrolein selectivity. This may be due to high dispersion of active sites and the presence of additional surface hydroxyl groups in the support. Fig. 6 and Fig. 7 show the effect of time on stream over H-SiW and HSAI-S25, respectively. It is clear from these figures that H-SiW (Fig. 6) is deactivated rapidly due to its high acid strength and low surface area. On the other hand, HSAI-S25 (Fig. 7) shows good performance to glycerol conversion and reasonably product selectivity.

Table 2 Glycerol dehydration over various solid acid catalysts (15 wt%).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Acrolein</td>
</tr>
<tr>
<td>H-SiW</td>
<td>84.3</td>
<td>82.5</td>
</tr>
<tr>
<td>HSAI-S25</td>
<td>98.0</td>
<td>21.1</td>
</tr>
<tr>
<td>H-SiW/HSAI-S25(M1)</td>
<td>99.0</td>
<td>42.1</td>
</tr>
<tr>
<td>H-SiW/HSAI-S25(M2)</td>
<td>98.0</td>
<td>54.4</td>
</tr>
</tbody>
</table>

aReaction conditions: Catalyst weight = 300 mg; glycerol concentration = 10 wt%; temperature = 275 °C; feed flow rate = 1.68 ml/h; bInclude acetaldehyde, acetone, methanol, 1,2-propanediol, carbon monoxide and some unidentified products.
Table 3 presents the results of glycerol dehydration over various catalysts. The γ-alumina (HSAI-S25) catalyst showed excellent conversion with good acrolein and hydroxyacetone selectivity. On the other hand, with the loading of silicotungstic acid, the acrolein selectivity increased remarkably (54%) while the hydroxyacetone remained nearly the same (25%) which indicates the role of Lewis acidity in the supported system. The high catalytic activity could be attributed to moderately strong acidity of
the silicotungstic acid supported catalyst (Atia et al., 2011; Kim et al., 2010; Tsukuda et al., 2007). On the other hand, the other two catalysts, viz., H-PW/HSAI-S25 and H-PMo/HSAI-S25, show lower acrolein/hydroxyacetone selectivity owing to very different acidity of leading to side reactions such as oligomerisation and carbonization of glycerol as well the formation of allyl alcohol.

Table 3 Glycerol dehydration over various solid acid catalysts (15 wt%).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-SiW/HSAI-S25(M2)</td>
<td>98.0</td>
<td>54.4</td>
</tr>
<tr>
<td>H-PW/HSAI-S25(M2)</td>
<td>98.7</td>
<td>47.4</td>
</tr>
<tr>
<td>H-PMo/HSAI-S25(M2)</td>
<td>99.0</td>
<td>35.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Acrolein</th>
<th>Hydroxy acetone</th>
<th>Allyl alcohol</th>
<th>Ethylene glycol</th>
<th>Others b</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-SiW/HSAI-S25(M2)</td>
<td>54.4</td>
<td>25.0</td>
<td>7.5</td>
<td>4.2</td>
<td>8.9</td>
</tr>
<tr>
<td>H-PW/HSAI-S25(M2)</td>
<td>47.4</td>
<td>4.2</td>
<td>5.1</td>
<td>1.1</td>
<td>32.3</td>
</tr>
<tr>
<td>H-PMo/HSAI-S25(M2)</td>
<td>35.8</td>
<td>7.8</td>
<td>29.6</td>
<td>4.0</td>
<td>22.8</td>
</tr>
</tbody>
</table>

aReaction conditions: Catalyst weight = 300 mg; glycerol concentration = 10 wt%; temperature = 275 °C; feed flow rate = 1.68 ml/h; bInclude acetaldehyde, acetone, methanol, 1,2-propanediol, carbon monoxide and some unidentified products.

Figure 8 depicts the effect of time-on-stream over 15wt% H-SiW/HSAI-S25. It can be seen from this figure that that the acrolein selectivity has considerably increased from 54 to 64 % at 5 h which may possibly due to the conversion of some of the Lewis acid sites to Brønsted acid sites owing to the presence of steam (90%). On the other hand, as expected, hydroxyacetone selectivity is decreased from 25 to 12 %. The evaluation of the long term stability of the catalyst is in progress.

Fig. 8. Effect of time on stream over 15 wt% H-SiW/HSAI-S25.
CONCLUSIONS

For the first time, we have successfully used high surface area $\gamma$-alumina (HSAI-S25; > 250 $m^2$/g), prepared using low-cost aluminium sources, with high acidity for the preparation of supported heteropoly acid catalysts. The reaction results indicate that $\gamma$-alumina is promising support and that the supported heteropoly acid catalysts show promise for dehydration of glycerol. It is also evident from XRD and Keggin anion density that high dispersion of heteropoly acid on the surface is responsible for such high activity. Among the three different heteropoly acid supported catalysts, silicotungstic acid supported on $\gamma$-alumina (H-SiW/HSAI-S25) showed better performance for the dehydration of glycerol, i.e., high glycerol conversion (99 %) with a combined acrolein and hydroxyacetone selectivity of 80 %.

Acknowledgement

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References

BRIEF BIOGRAPHY OF PRESENTER

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