A comparative study on vapour phase glycerol dehydration over different tungstated metal phosphate acid catalysts

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Electronic Supplementary Information (ESI):

In the present study we also report the effect of tungsten oxide loading on the best support TiP and our results provide a basis mainly for correlating the catalyst acidity by varying the tungsten oxide content and the effect of reaction temperature in glycerol dehydration.

X-ray diffraction patterns of various WOₓ/TiP catalysts with tungsten oxide loadings ranging 5 to 25 wt% are shown in Figure S.1. For samples with low tungsten oxide (<15 wt%) loading, the XRD results did not show any reflections indicating that the tungsten oxide is present in a well dispersed amorphous state and the samples above 15 wt% loadings have shown crystalline peaks due to WO₃. Additional peaks are observed for samples with tungsten oxide loading of 15 wt % and above loadings in the 20 range of 23-25° [JCPDS-43-
1035] and these peaks can be assigned to monoclinic WO$_3$ micro crystallites. It has been suggested previously that the agglomeration of WO$_x$ species leads to WO$_3$ micro crystallites on the support surface when the tungsten oxide coverage exceeds that of a monolayer$^1$.

Figure S.1: X-ray diffraction profiles of various WO$_x$/TiP catalysts. (a) Pure TiP (b) 5 wt% WO$_x$/TiP (c) 10 wt% WO$_x$/TiP (d) 15 wt% WO$_x$/TiP (e) 20 wt% WO$_x$/TiP (f) 25 wt% WO$_x$/TiP.

Brunauer-Emmett-Teller (BET) surface area, average pore diameter, and pore volume for pure titanium phosphate support (TiP) and tungstated titanium phosphate (WO$_x$/TiP) materials were estimated from their respective adsorption isotherms and are given in Table S.1. All the isotherms are found to be typical of type IV hysteresis loops, suggesting the presence of mesoporous nature of these samples. The results further suggest that the surface area and pore volume decreases with WO$_3$ loading on the support. This is probably due to
crystalline nature of the samples at higher loadings. However, the pore diameter increases with the active phase loading on the support.

UV-Vis spectra of all the supported WOₓ samples are presented in Figure S.2., along with the spectrum of pure TiP support. The UV spectrum of TiP support is strongly modified by the WOₓ species. UV–visible diffuse reflectance spectroscopy was used to probe tungsten oxide species dispersed on TiP surface. The size effect can be reflected from the shift of the absorption edge. As the WOₓ loadings increases on TiP, the intensity of the charge transfer transition band at 300 nm is also increased, due to characteristic nature of crystalline WO₃.

![Figure S.2: UV-Vis spectra of various WOₓ/TiP catalysts. (a) Pure TiP  (b) 5 wt% WOₓ/TiP (c) 10 wt% WOₓ/TiP  (d) 15 wt% WOₓ/TiP  (e) 20 wt% WOₓ/TiP  (f) 25 wt% WOₓ/TiP](image-url)
The TPD-NH$_3$ profiles of all the WO$_x$/TIP catalysts are shown in Figure S.3 and the surface acidity was calculated as total acidity and expressed per mol of NH$_3$ desorbed per gram of catalyst [Table S.1].

It can be seen from the Figure S.3 that as WO$_x$ loadings are increasing, the intensity of the weak acidic region (50-150 °C) peaks are attenuating and the intensity of the moderate acidic region (150-400 °C) peak is increasing. The total acidity values of supported WO$_x$ on TiP support is increasing from 5 wt% to 15 wt% WO$_x$/TiP and further it is decreasing at higher loadings (above 15 wt% WO$_x$/TiP), this might be due to condensation of W–OH groups and formation of 3-D WO$_x$ clusters which reduce acidity at higher loadings [18]. However, in the all the samples ammonia is mainly desorbed between 200 and 400 °C, which suggest the presence of medium to strong acid sites. The acidity of the WO$_x$/TiP catalysts can be attributed to the P–OH groups also due to well dispersed WO$_x$ groups present on the surface are responsible for the acidity$^2$. TPD analysis suggests that the amount of acidity and strength of acidic sites are increasing upon addition of WO$_x$ to the TiP support.
Figure S.3: NH$_3$-TPD profiles of pure and tungstated TiP catalysts. (a) Pure TiP (b) 5 wt% WO$_x$/TiP (c) 10 wt% WO$_x$/TiP (d) 15 wt% WO$_x$/TiP (e) 20 wt% WO$_x$/TiP (f) 25 wt% WO$_x$/TiP.

Table S.1 B.E.T surface area, pore size distribution data and Temperature programmed desorption of NH$_3$ of pure and tungstated TiP catalysts.

<table>
<thead>
<tr>
<th>WO$_x$ Loads (wt%)</th>
<th>BET SA (m$^2$/g)</th>
<th>Total Pore Volume (cc/g)</th>
<th>Mean Pore Diameter (Å)</th>
<th>Total NH$_3$ Desorbed (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiP</td>
<td>248</td>
<td>0.31</td>
<td>84.1</td>
<td>3.51</td>
</tr>
<tr>
<td>5W-TiP</td>
<td>204.5</td>
<td>0.27</td>
<td>86.5</td>
<td>3.90</td>
</tr>
<tr>
<td>10W-TiP</td>
<td>187.3</td>
<td>0.24</td>
<td>87.4</td>
<td>4.49</td>
</tr>
<tr>
<td>15W-TiP</td>
<td>159.1</td>
<td>0.21</td>
<td>93.3</td>
<td>4.60</td>
</tr>
<tr>
<td>20W-TiP</td>
<td>101</td>
<td>0.14</td>
<td>94.3</td>
<td>4.03</td>
</tr>
<tr>
<td>25W-TiP</td>
<td>84</td>
<td>0.10</td>
<td>98.9</td>
<td>3.48</td>
</tr>
</tbody>
</table>

For characterizing the nature of surface acidic sites, we have employed ex-situ pyridine adsorbed FT-IR analysis. The FTIR spectra of pure TiP support and various WO$_3$/TiP catalysts are illustrated in Figure S.4. All the catalysts have shown IR bands at 1444 cm$^{-1}$ corresponding to Lewis sites and another IR band appeared at 1550 cm$^{-1}$ is attributed to Brønsted sites. It is interesting to note that with increasing WO$_x$ loadings on the support, the intensity of IR band at 1450 cm$^{-1}$ corresponding to the Lewis acidity decreases marginally. The intensity of IR absorption peak at 1498 cm$^{-1}$ is attributed to combination of both Brønsted (B) and Lewis (L) acid sites. This peak intensity is increased with increasing WO$_x$ loadings on the support up to 15 wt% WO$_x$/TiP. The pure TiP shows the band at 1550 cm$^{-1}$
due to Brønsted acidic sites. The Brønsted acidity of WO$_x$/TiP catalysts increases initially after that there is no great effect until 15 wt% WO$_x$/TiP. Furthermore, in 20 and 25 wt% WO$_x$/TiP a slight decrease of intensity of IR bands is noticed in both types of acidic sites.

**Figure 7.6:** FT-IR Pyridine adsorption profiles of pure and tungstated TiP catalysts.

(a) Pure TiP  (b) 5 wt% WO$_x$/TiP  (c) 10 wt% WO$_x$/TiP  (d) 15 wt% WO$_x$/TiP  (e) 20 wt% WO$_x$/TiP  (f) 25 wt% WO$_x$/TiP

References:
