Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2019

Manuscript ID: NJ-ART-08-2019-004484

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

Ginjupalli Srinivasa Rao,[*,a,b] Balla Putrakumar,[b,c] Shaik Hussain[b], Nekkala Nagaraju,[b] Ponnala Bhanuchander,[b] Mitta Hari shekar.[b]

(a) Basic Science and Humanities, Swarnandhra College of Engineering and Technology, Narsapur, India-534280

(b) Inorganic and Physical Chemistry, Catalysis division, Indian Institute of Chemical Technology, Hyderabad-500007

(c) State key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 - Zhong Shan Road – Dalian - 116023.

---

* Corresponding author: Ginjupalli Srinivasa Rao, Department of Chemistry, Swarnandhra College of Engineering and Technology, Narasapur, India. E-mail: gsrao260@gmail.com Tel: +91-9848088968

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 WO_x/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 WO_3. Additional peaks are observed for samples with tungsten oxide loading of 15 wt % and above loadings in the 2θ 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].

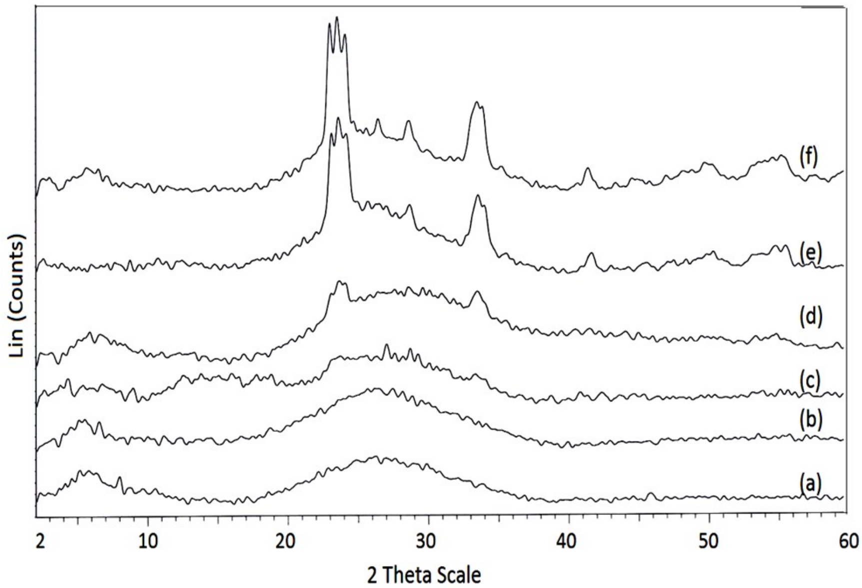

Figure S.1: X-ray diffraction profiles of various WO_x/TiP catalysts. (a) Pure TiP (b) 5 wt% WO_x/TiP (c) 10 wt% WO_x/TiP (d) 15 wt% WO_x/TiP (e) 20 wt% WO_x/TiP (f) 25 wt% WO_x/TiP.

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 WO_x 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 WO_x 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 WO_x loadings increases on TiP, the intensity of the charge transfer transition band at 300 nm is also increased, due to characteristic nature of crystalline WO_3.

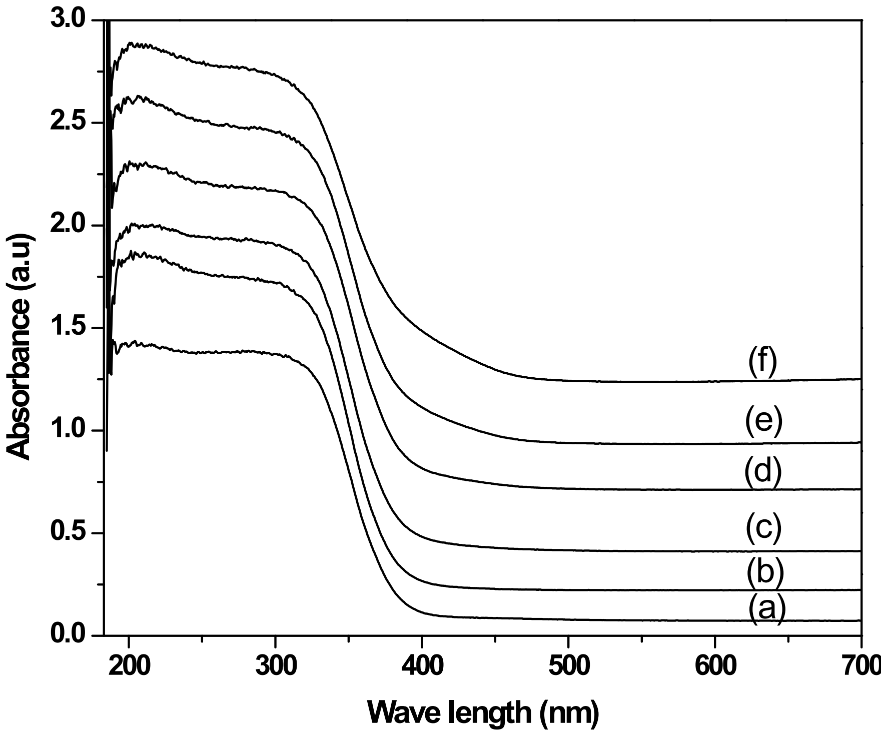

Figure S.2: UV-Vis spectra of various WO_x/TiP catalysts. (a) Pure TiP (b) 5 wt% WO_x/TiP (c) 10 wt% WO_x/TiP (d) 15 wt% WO_x/TiP (e) 20 wt% WO_x/TiP (f) 25 wt% WO_x/TiP

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.

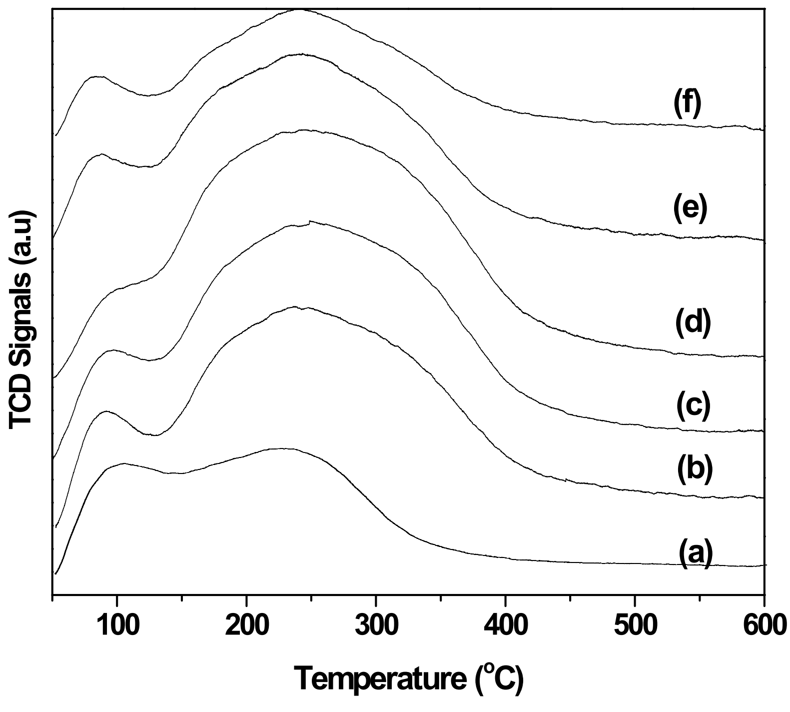

Figure S.3: NH_3-TPD profiles of pure and tungstated TiP catalysts. (a) Pure TiP (b) 5 wt% WO_x/TiP (c) 10 wt% WO_x/TiP (d) 15 wt% WO_x/TiP (e) 20 wt% WO_x/TiP (f) 25 wt% WO_x/TiP.

Table S.1 B.E.T surface are, pore size distribution data and Temperature programmed desorption of NH_3 of pure and tungstated TiP catalysts.

WO_x loadigs (wt%)	**BET SA (m^2/g)**	**Total pore volume(cc/g)**	**Mean pore diameter(Å)**	**Total NH_3 desorbed mmol/g**
Pure TiP	248	0.31	84.1	3.51
5W-TiP	204.5	0.27	86.5	3.90
10W-TiP	187.3	0.24	87.4	4.49
15 W-TiP	159.1	0.21	93.3	4.60
20 W-TiP	101	0.14	94.3	4.03
25 W-TiP	84	0.10	98.9	3.48

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.

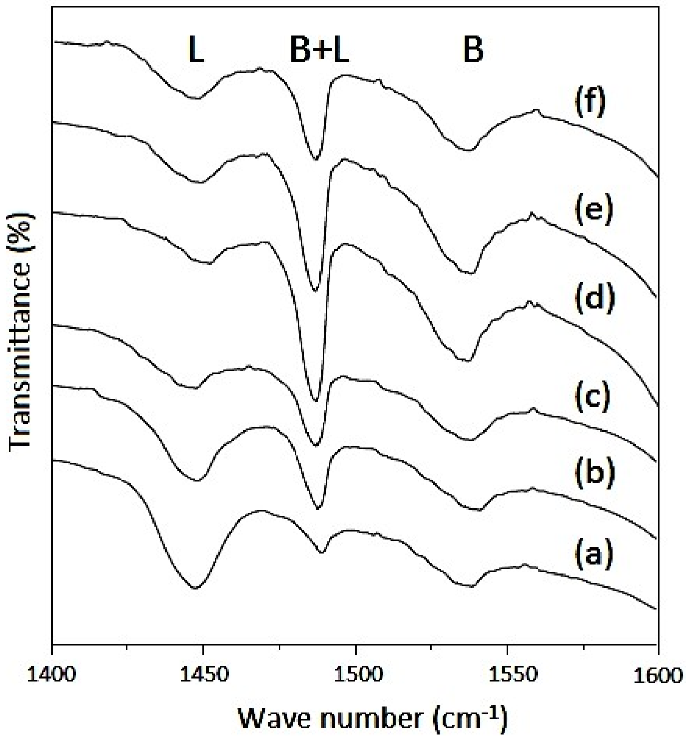

Figure 7.6: FT-IR Pyridine adsorption profiles of pure and tungstated TiP catalysts.

(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:

1. N. Liu, S. Ding, Y. Cui, N. Xue, L. Peng, X. Guo, W. Ding, Chem. Eng. Res. Des, 2013, **91**, 573.

2. T.Y. Kim, D.S. Park, Y. Choi, J. Baek, J.R. Park, J.Yi, J. Mater. Chem, 2012, **22**, 10021.