Selective etherification of glycerol with tert-butanol over 12-tungstophosphoric acid catalysts supported on Y-zeolite

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Selective etherification of glycerol with tert-butanol alcohol has been investigated over tungstophosphoric acid (TPA) supported on Y-zeolite. The catalysts have been characterized by FT-IR spectroscopy, X-ray diffraction, scanning electron microscopy and temperature-programmed desorption of NH₃. The catalytic activity varies with the content of TPA on the support and the catalyst with 20 wt.% TPA shows the high activity. The catalytic activity is found to depend on the acidity which varies with the dispersion of TPA over zeolite. The etherification activity of catalysts has been correlated with the structural aspects and the acidity. Various parameters such as reaction temperature, reaction time, catalyst concentration and molar ratio of tert-butanol-to-glycerol have been studied to optimize the reaction conditions.

Keywords: Catalysts, supported catalysts, Etherification, Glycerol, Butanol, Tungstophosphoric acid, Zeolite

Biodiesel, a renewable and eco-friendly alternative fuel has been produced by transesterification of vegetable oil or animal fat with low carbon alcohol.¹-³ The main co-product of this process is glycerol which is 10 wt.% of the total amount of biodiesel obtained.⁴ Several catalytic reactions have been investigated for the conversion of glycerol into value added chemicals by hydrogenolysis,⁵ oxidation,⁸ dehydration,¹⁰-¹² carbylation¹³ and esterification.¹⁴ In addition, glycerol can be used as a fuel additive to improve the properties of biodiesel.¹⁵ Glycerol on etherification with isobutene or tert-butanol forms mono-tert-butyl ethers of glycerol (ME), di-tert-butyl ethers of glycerol (DE) and tri-tert-butyl ether of glycerol (TE).¹⁶-²³ These ethers are reported to have very high octane numbers and are considered as alternatives to gasoline additives such as methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE).²⁴,²⁵ It is reported that glycerol ethers have good combustion properties with reduced pollutant and particulate matter emissions when blended with biodiesel or petrodiesel.²⁶ Etherification of glycerol with isobutene or tert-butanol has been studied in the presence of acid catalysts. A wide variety of catalysts like silicotungstic acid,²⁷ acid ion-exchange resins (Amberlyst type),²⁸,²¹,²⁶ sulfonated peanut shell,²⁸ several supported acid catalysts like acid-functionalized mesostructured silicas²⁹,³⁰ and wide pore zeolites (HY, Hβ)²⁰,³¹ have been used for the etherification of glycerol. p-Toluenesulfonic acid as a homogeneous catalyst and ion exchange resin as a heterogeneous catalyst have shown good activity.¹⁰ However, homogeneous catalytic processes are not favorable due to difficulty in separating the catalysts from the reaction mixture. The ion exchange resins, even though they are solid catalysts, have limited thermal stability.

In recent years, solid heteropolyacids (HPAs) are known to be active acid catalysts due to their strong Bronsted acidity as compared to homogeneous catalysts such as H₂SO₄, HCl, AlCl₃, etc.³² The major disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area (5–8 m²/g) and solubility in polar media.³³ HPAs can become ecofriendly insoluble solid acid catalysts with high thermal stability and high surface area by exchanging their protons with metal/alkali metal ion³⁴,³⁵ or supporting them on suitable supports.³⁶,³⁷ Zeolites are considered to be a potential substitute for strong acid ion exchange resins due to their outstanding properties, such as tetrahedral framework, high thermal stability and tunable acidity. Y-zeolites, with uniform pore size and high specific surface area are considered as a good material to support and stabilize HPAs.³⁸-⁴¹

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In the present work, an attempt has been made to support the well-known Bronsted acidic tungstophosphoric acid on Y-zeolite to derive a highly acidic catalyst for the etherification of glycerol. The surface-structural properties of the catalysts derived from different spectroscopic methods are correlated with the glycerol etherification activity.

Materials and Methods

Preparation and characterisation of catalysts

TPA supported on Y-zeolite catalysts were prepared by impregnation method. In a typical procedure, the calculated amount of TPA was dissolved in minimum amount of water and this solution was added to the support while stirring. The excess water was removed on a water bath. The catalyst masses were dried in an oven at 393 K for 12 h and finally calcined at 573 K for 2 h. The amount of TPA deposited onto the surface of the zeolite was varied from 10-25 wt.%. The catalysts are denoted as xTZ, where x correspond to the content of TPA on zeolites and T and Z are abbreviations of TPA and zeolite, respectively.

BET surface area of all the samples were obtained by N₂ adsorption at liquid N₂ temperature on an Autosorb-1 (Quantachrome) instrument. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Siemens D-5000 diffractometer using nickel-filtered Cu Ka radiation with a scan speed of 2° min⁻¹ and a scan range of 5–80°. FT-IR spectra of catalysts were recorded on a Biorad Excalibur spectrometer adopting the KBr disc method.

Temperature-programmed desorption (TPD) of NH₃ was carried out in a laboratory-built apparatus equipped with a gas chromatograph using a TCD detector. In a typical experiment, about 0.1 g of the oven dried sample was taken in a quartz tube. The catalyst sample was initially activated at 573 K for 2 h under flowing helium (He) gas (99.95%, 50 mL/min) and after cooling to 373 K in the same medium, the adsorption study was carried out by replacing He with a mixture of 10% NH₃ balance He over the catalyst for 1 h. The sample was then flushed with He again, to drive off any physisorbed NH₃. TPD of the catalysts was then carried out in He flow in the temperature range of 353–973 K with a ramp of 283 K/min. The amount of NH₃ desorbed was calculated from the peak area of calibrated TCD signal.

Glycerol etherification

Etherification of glycerol was carried out in an autoclave (80 ml haste alloy Parr 4843 autoclave) at autogenous pressure. In a typical experiment, the required quantities of glycerol, tert-butanol and catalyst were taken. The reactor was flushed twice with nitrogen in order to displace the air inside. The set point temperature inside the reactor was reached within 20 min after the reactor was introduced and this time has been considered as the starting point of the reaction.

After completion of the reaction, the autoclave was cooled and the gas products were collected in a Teflon bag, while the liquid products were separated from the catalyst by filtration. The liquid products were analyzed by gas chromatography (Shimadzu 2010) using a flame ionization detector by separation on an Innowax capillary column. The products were identified by using GC–MS (Shimadzu, GCMS-QP2010S) analysis. The gas phase products were analyzed using a gas chromatograph equipped with a Porapak Q column and a thermal conductivity detector.

The glycerol conversion and selectivity to glycerol ethers is defined as

\[
\text{Conv. of glycerol (mol\%) = \frac{\text{Total amt of glycerol ethers (mol)}}{\text{Amt of glycerol taken (mol)}} \times 100}
\]

\[
\text{Sel. of glycerol (mol\%) = \frac{\text{Amt of corresponding glycerol ether (mol)}}{\text{Total amt of glycerol ethers (mol)}} \times 100}
\]

Results and Discussion

BET surface area of TPA/Y-zeolite catalysts

The physicochemical properties of the catalysts are reported in Table 1. The specific surface area of support (YZ) was found to be 550 m²/g. The surface area of the catalysts decreased with increase in the content of TPA on support. This decrease is presumably a result of pore blockage by the crystallites of Keggin ion \([\text{PW}_{12}\text{O}_{40}]^{3-40}\).
X-ray diffraction

The XRD patterns of the catalysts along with the support are shown in Fig. 1. The TPA/Y-zeolites did not reveal any diffraction peaks other than that of support, which indicates that TPA was well dispersed on the support. The XRD patterns of 25 wt.% TZ catalyst, on the other hand, showed small crystalline peaks of TPA at 20 of 10°, 25° and 35°. This indicates the attainment of bulk nature of TPA at higher loadings. The intensities of the diffraction peaks increased slightly after loading of TPA along with a marginal shift in the peaks towards higher angle. This is because of the strong interaction of TPA with the surface of zeolite that stabilizes the TPA phase.

FT-IR spectra

FT-IR spectra of the bulk TPA sample appeared at 1082, 983, 890, 793, 595, and 521 cm\(^{-1}\) are assigned to the characteristic Keggin anion vibrations of \(\nu_{\text{as}}(\text{P–O})\), \(\nu_{\text{as}}(\text{W=O})\), \(\nu_{\text{as}}(\text{W–O}_b–\text{W})\), \(\delta(\text{O–P–O})\), and \(\nu(\text{W–O–W})\), respectively (Supplementary Data, Fig. S1). The subscripts b and c indicate corner-sharing and edge-sharing oxygen, respectively, and the W–O–W bridges belong to the \(\text{WO}_6\) octahedra and terminal oxygen. In FT-IR spectra of the catalysts, bands at 1082 and 983 cm\(^{-1}\) are masked by matching bands of asymmetric stretching of the tetrahedron \(\text{TO}_4\) of Y-zeolite support.\(^{43}\) The other characteristic band at 890 and 790 cm\(^{-1}\) were clearly assigned to the W–O\(_b–\)W stretching bands, and their relative intensity increased with increase in TPA content (Supplementary Data, Fig. S1). The FT-IR analysis suggests the presence of intact Keggin ion of TPA on Y-zeolite.

Temperature programmed desorption of ammonia

The amount and strength of the acid sites of the catalysts were studied by temperature-programmed desorption of ammonia (Fig. 2). The support and the 10TZ catalysts exhibited low temperature desorption peaks related to weak acid sites. The catalyst with 15 wt.% TPA showed a broad desorption peak at 800 K related to the presence of moderate to strong acidic sites. The 20 wt.% TPA catalyst also showed the NH\(_3\) desorption peaks related to moderate and strong acidic sites. The low temperature desorption peaks are mainly due to acidic sites of the zeolites, whereas the high temperature peak is related to the acidity associated with TPA present on support. The total acidity of the catalysts is expressed as the total amount of ammonia desorbed per gram of catalysts. The acidity of samples decreases in the following order: 20TZ > 25TZ > 15TZ > 10TZ (Table 1).

Catalytic activity

Effect of TPA content

The catalytic activity of TPA/Y-zeolite catalysts for the etherification of glycerol with tert-butanol was studied (Table 2). The reaction products obtained were ME, DE and TE. The support Y-zeolite showed glycerol conversion of 10% with near 100% selectivity towards ME. The etherification of glycerol over TPA/Y-zeolite catalysts leads to the formation of mainly ME with selectivities reaching ca. 88%. From Table 2, it can be seen that the etherification activity of the catalysts increased with TPA loading and maximum conversion of glycerol was obtained for the catalyst with 20% TPA and there was increase in
activity with further increase in TPA content. The 20TZ catalyst was more active and selective towards ME compared to other catalysts. The main reason for the high activity of 20 wt.% is because of its high acidity, which is due to the presence of well dispersed TPA on zeolite.

Effect of reaction time
In order to investigate the influence of the reaction time on glycerol conversion and selectivity, the reaction was carried at different reaction times. Conversion of glycerol increased with time and reached up to 85% of conversion within 60 min (Table 2). The selectivity of glycerol ethers was also affected by reaction time. It can be seen that the selectivity towards ME decreased obviously with time. With the increase of reaction time, maximum conversion of glycerol is reached and availability of glycerol is limited for further conversion. This situation favors the etherification of the largely available ME. Considering both glycerol conversion and selectivity to ME, the appropriate reaction time was 1 h.

Effect of catalyst weight
The conversion of glycerol increased upon increase in the catalysts amount from 0.1 to 0.5 g. About 84% of glycerol conversion with 85% selectivity for ME was obtained at a catalyst amount of 0.5 g. Further increase in the catalyst amount there was no considerable variation in glycerol conversion. At higher catalyst amount, the selectivity toward higher ethers increased as the available catalytic sites favor further etherification of ME.

Influence of reaction temperature
The glycerol etherification was carried out in the temperature range from 373–413 K over 20TZ catalyst. The conversion of glycerol increased with increase temperature from 373–413 K; the highest glycerol conversion was obtained at 413 K after 1 h. However, the conversion of glycerol increased from 30% to 62% when the temperature increased from 373 to 383 K. The selectivity towards of higher ethers increased from 4% to 16% when the temperature was varied from 403 to 413 K. Based on the experimental results, 393 K was chosen as the optimum temperature, at which 84% glycerol conversion with 85% selectivity towards ME was obtained.

Role of glycerol:t-butanol mole ratio
In this study ME is the desired product in the glycerol etherification reaction. Thus, the stoichiometric molar ratio of glycerol:t-butanol for the glycerol etherification is at least 1:1. Since glycerol etherification is a reversible reaction, excess t-butanol promotes the formation of ME. The study on effect of glycerol:t-butanol molar ratio on the etherification reaction using three different ratios in the range of 1:9 to 1:15 shows that the glycerol conversion was considerably enhanced while the selectivity towards ME remained almost the same (Table 2). Although higher amounts of higher ethers are expected with

Table 2 – Effect of TPA loading, time and mole ratio on etherification of glycerol with tert-butanol

<table>
<thead>
<tr>
<th>TPA loading (%)</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Monoether</td>
</tr>
<tr>
<td>10</td>
<td>40.2</td>
<td>97.3</td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>95</td>
</tr>
<tr>
<td>20</td>
<td>84.2</td>
<td>85.5</td>
</tr>
<tr>
<td>25</td>
<td>83.1</td>
<td>81.3</td>
</tr>
<tr>
<td>Time (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>77.5</td>
<td>89.3</td>
</tr>
<tr>
<td>60</td>
<td>84.2</td>
<td>85.7</td>
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<tr>
<td>90</td>
<td>92.2</td>
<td>84.8</td>
</tr>
<tr>
<td>120</td>
<td>93.6</td>
<td>84.2</td>
</tr>
<tr>
<td>150</td>
<td>91.3</td>
<td>71.4</td>
</tr>
<tr>
<td>180</td>
<td>92.4</td>
<td>71.7</td>
</tr>
<tr>
<td>Mole ratio (glycerol:t-butanol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:9</td>
<td>73.9</td>
<td>85.9</td>
</tr>
<tr>
<td>1:12</td>
<td>84.2</td>
<td>85.7</td>
</tr>
<tr>
<td>1:15</td>
<td>85.4</td>
<td>89.1</td>
</tr>
</tbody>
</table>
increase in molar ratio of glycerol:tert-butanol, in the present case however, an increase in conversion was observed. This indicates that the selectivity mainly depends on the reaction time. These results suggest that the present catalysts are highly selective for the formation of monoethers of glycerol at mole ratio of 1:12.

Reusability of the catalysts
The reusability of 20TZ catalyst was studied by recovering the catalyst at the end of the reaction by filtration. The recovered catalyst was washed with methanol followed by drying at 373 K for 2 h and then reused. The catalytic activity of the recovered catalysts was comparable to that of fresh catalyst. Even after four cycles of reaction there was no appreciable variation in activity. The filtrate of the catalysts was reusable. The catalytic activity of the recovered catalyst was comparable to that of fresh catalyst. The recoverability of 20TZ catalyst was studied by recovering the catalyst at the end of the reaction by filtration. The optimized reaction conditions were established. The 20TZ catalyst is found to be reusable with consistent activity.

Conclusions
Selective etherification of glycerol with tert-butanol was carried out with TPA supported on Y-zeolite. The characterization results reveal the presence of highly dispersed intact Keggin ion of heteropolytungstate. The activity of the catalysts depended on the amount of TPA on support which directs the acidity of the catalysts. The 20TZ catalyst showed highest conversion (84%) with high selectivity (85%) towards ME. The optimized reaction conditions were established. The 20TZ catalyst is found to be reusable with consistent activity.

Supplementary Data
Supplementary data associated with this article, viz., Fig. S1, is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_53A(4-5)524-529_SupplData.pdf.

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