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Cesium exchanged tungstophosphoric acid supported on tin oxide: An efficient solid acid catalyst for etherification of glycerol with tert-butanol to synthesize biofuel additives

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Graphical abstract

Cesium exchanged tungstophosphoric acid supported on tin oxide: An efficient solid acid catalyst for etherification of glycerol with tert-butanol to synthesize biofuel additives



The research highlights:

- > Cs exchanged TPA catalysts are selective for glycerol etherification.
- > Glycerol etherification activity depends on the acidity of the catalysts.
- > Acidity of the catalysts depends on amount Cs exchanged with TPA and support
- Surface-structural properties depend on the amount of CsTPA on SnO₂.

Abstract

Cesium exchanged tungstophosphoric acid (CsTPA) supported on tin oxide catalysts were prepared and their physio-chemical properties were derived from X-ray diffraction, FT-IR, laser Raman spectroscopy and temperature programmed desorption of NH₃. The catalysts activity was evaluated for etherification of glycerol with tert-butanol. The characterization results of the catalysts revealed that the primary Keggin structure remained intact during the exchange of TPA protons with Cs⁺ ions. The activity results showed that etherification activity depended on the amount of the CsTPA over SnO₂ and the catalyst with 20 wt% CsTPA supported on SnO₂ showed high catalytic activity with 90% glycerol conversion with 44% selectivity towards higher ethers. The activity of the catalyst depends on amount of surface acidic sites and dispersion amount of CsTPA over SnO₂. The etherification reaction was carried at different reaction parameters and optimum reaction conditions were established. The catalysts were recyclable and showed constant activity up on reuse.

Key words: Glycerol, tert-butanol, etherification, cesium exchanged tungstophophoric acid, tin dioxide.

1. Introduction

The development of environmental friendly process with the use of renewable resources has gained much attention in recent times. Glycerol, one of the renewable resources is obtained as a by-product in manufacturing biodiesel by transesterification of vegetable oils with alcohols [1, 2]. Unfortunately, the current application of glycerol is mainly confined to pharmaceuticals and cosmetics, hence the demand is somewhat limited [3]. It is necessary to find new outlets to convert the surplus glycerol into high-value-added products in order to increase the economy of biodiesel manufacture [4]. Selective oxidation of glycerol to glyceric acid, dihydroxyacetone, mesoxalic acid, etc. [5-7], dehydration to acrolein [8], hydrogenolysis to propylene glycol [9], carbonylation to glycerol carbonate [10-12], synthesis of hydroxyquinoline and quinolone by Skraup synthesis [13-15] and acetylation to esters [16] are some of the possible alternative routes to convert glycerol to valuable products. One interesting option is the catalytic etherification of glycerol with alcohols or short-chain olefins to obtain mono, di- and tri alkyl ethers of glycerol. The mono alkyl glyceryl ethers are highly valuable chemicals since they exhibit a wide range of application as intermediates in the pharmaceutical industry, agrochemicals and as non-ionic surfactants [17, 18]. The di and tri alkyl ethers of glycerol (higher ethers) constitute excellent oxygenated additives with a large potential for diesel and biodiesel reformulation. When these higher ethers are incorporated into standard 30-40% aromatic containing diesel fuel, emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes reduced significantly [19]. Thus, synthesis of higher ethers has gained lot of interest in recent times.

Glycerol etherification with tert-butanol or isobutylene has been studied in the presence of acid catalysts [20-24]. When isobutylene (IB) was used as an etherification agent, better conversion and selectivity to higher ethers were obtained [25]. However, it should be noted that

IB produced by steam cracking of high boiling petroleum fractions or mixture of saturate hydrocarbons [26]. Therefore, the use of tert-butanol as etherifying agent, in substitution of IB, avoids both the need of solvents (i.e., dioxane, dimethyl sulfoxide) and the mass transfer limitation phenomena related to the complex three-phase system [27]. Moreover, TBA is a by-product of the large-scale propylene oxide production and it also can be produced from bio-sources, like starch or lignocellulosic biomass [28].

Homogeneous and heterogeneous catalysts are employed for etherification of glycerol with tert-butanol [29, 30]. In spite of several advantages, homogeneous catalysts have some problems which include recovering the catalyst and separation of the products. Therefore an effective and environmentally benign solid heterogeneous catalyst is required. To date, very few heterogeneous catalysts such as commercial ion-exchange resins (Amberlyst 15 and 35) [31], wide-porous zeolites (ZSM-5, H–Y and H–Beta zeolites, etc.,) [26], sulfonated carbon [32], Nafion on amorphous silica [33] and heteropolyacids [34] were reported for etherification of glycerol. Very recently, M.D. Gonalez et al. [35] reported that fluorinated beta zeolites generated higher amounts strong Brønsted acid sites, which enable high glycerol conversion (75%) and selectivity to higher ethers (37%). Even though all of these catalysts reported high glycerol conversion, the overall selectivity towards higher ethers is limited and requires long reaction times.

The Keggin type heteropolyacids (HPA) have attracted a lot of attention due to their strong Bronsted acidity and environmental friendliness [36, 37]. However, its low surface area ($<10 \text{ m}^2\text{g}^{-1}$) and high solubility in polar solvents limit its potential catalytic performance. HPAs can be made heterogeneous by exchange of its protons (H⁺) with metal ions [38, 39] and/or supporting them on suitable supports [40, 41]. The support plays an important role in enhancing

the acidity, thermal stability and surface area of the final catalyst. Very recently, Frusteri et al [33] investigated cesium exchanged phosphotungstic acid (TPA) supported on silica catalysts and tested for etherification of glycerol with tert-butanol. However the catalyst was less selective towards higher ethers. Cs-containing phosphotungstates are well-known as a water insoluble strong Brønsted acid and a versatile solid acid catalyst possessing high thermal stability (\geq 500 °C) and water tolerance [42]. However, they have the tendency to form milky colloid in polar solutions which can be overcome by stabilizing them on suitable supports [43]. Tin oxide, SnO₂, has been used wide range of applications in sciences, technologies and industries, such as catalysis, conductivity, gas sensing, ceramics, plastics, and antistatic coating [44, 45]. Thus it is of interest to study the novelties of supported tin oxide catalysts for etherification of glycerol with tert-butanol.

In the present study, tungstophosphoric acid was modified by exchanging its protons with Cs⁺ ions and dispersed on tin oxide support. The catalysts were evaluated for etherification of glycerol with tert-butanol. The reaction was tested under different reaction parameters to yield higher ethers. The catalyst performance was discussed with the observed physico-chemical properties derived from different characterization methods.

2. Experimental

2.1 Catalyst preparation

Cs exchanged TPA supported on tin oxide catalysts were prepared in two steps. In the first step, the required quantity of TPA was dissolved in water and this solution was added drop

wise to support, tin oxide. After stirring for 30 min, the excess water was removed on water bath and the samples were calcined at 300 °C for 2 h. In the second step, calculated amount of cesium nitrate dissolved in distilled water was added drop wise to the TPA supported SnO₂ samples. The TPA content on support is varied from 10 - 30 wt %. The final catalyst are denoted as Y wt. % Cs_1TPA/SnO_2 (YC₁TS) where Y = 10, 15, 20, 25 and 30.

2.2 Catalysts characterization

BET surface area of the catalyst samples were obtained by N₂ adsorption at liquid N₂ temperature on Autosorb-1 (Quantachrome) instrument. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex diffractometer using CuK α radiation (1.5406 Å) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045° with an account time of 0.5 s and in the 2 θ range of 10-80°. FT-IR spectra of catalysts were recorded on a Biorad Excalibur spectrometer adopting the KBr disc method. The elemental analysis of the samples was measured by Agilent 7700 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

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 oven dried sample was taken in a quartz tube. The catalyst sample was initially activated at 300 °C for 2 h under flowing helium (He) gas (99.995%, 50 ml/min) to clean the surface of the catalyst. After cooling the sample to 100 °C the sample was exposed to 10% NH₃ balanced He gas for 1 h. The sample was then flushed with He to drive off physisorbed NH₃. TPD of the catalyst was then carried out in He flow at a rate of 30 ml/min, in the temperature range of 100–700 °C and with a ramp of 10 °C/min. The amount of NH₃ desorbed was calculated from the peak area of the already calibrated TCD signal.

2.3 Experimental procedure

Etherification of glycerol was carried out in a 100-ml haste alloy PARR autoclave. Etherification of glycerol with tert-butanol were carried at autogenous pressure. Required quantities of glycerol (0.02 mol), tert-butanol (0.12 mol) and catalyst (1.3 mmol) were introduced in to the autoclave and purged three times with N₂. After the purge, the reactor was heated to desired reaction temperature and stirring was fixed for all experiments at 500 rpm to avoid external diffusion limitations. During the reaction, pressure was developed autogenously. After the reaction, the gas phase products were collected in a gasbag and the liquid phase products were separated from the catalyst by filtration. Liquid products were analyzed using a gas chromatograph (Shimadzu 2010) equipped with FID using capillary Inno wax (0.25 mm×30 m, DF=0.25) column. The products were confirmed by GC–MS (Shimadzu, GCMS-QP2010) analysis also. The gas products were analyzed by using a gas chromatograph (Porapak Q column) equipped with a thermal conductivity detector. In addition, the products were comparatively confirmed with the assistance of the characterization data reported by Jamróz et al [46].

3. Results and discussion

3.1 Catalysts characterization

Table 1 summarizes the physico-chemical properties of Cs salt of TPA supported over SnO₂ catalysts. The variation in the Cs₁TPA content over SnO₂ resulted a decrease in the BET

surface areas compared with their parent support. The decrease in the surface area of the catalyst is due to the pore blockage of the surface with Cs_1TPA . However, the supported catalysts surface areas were still much higher than the bulk TPA.

Fig. 1 shows the X-ray diffraction patterns of the catalysts. The peaks at 20 values of 26.1, 33.3, 51.4, 54.4, 61.5, and 65.6° were correspond to (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0), and (3 0 1) reflection planes of tetragonal structure of SnO₂ respectively [47]. The patterns showed the Keggin ion of Cs₁TPA at 20 of 23.7, 30.1, 37.6, and 45.8°. These characteristic peaks were observed for all the catalysts. The particle size of the catalysts calculated from Fig. 1 and the results suggest that increase in particle size with increase in CsTPA content on support.

FT-IR spectra of the catalysts are shown in Fig. 2. An IR spectrum of tungstophosphoric acid is shown in the inset of Fig. 2 for the sake of comparison. The spectra shows bands at 1080, 981, 889, 796, and 595 cm⁻¹ related to asymmetric vibrations of P - O_a, W = O_t, W-O_b-W and W-O_c-W and the bending mode of O_a- P - O_a, respectively [48]. Cs exchanged TPA supported on SnO₂ catalysts showed less intense IR bands. The shift of W–O_b-W band from 982 cm⁻¹ to 986 cm⁻¹ compared to TPA in all the samples reveals that the Keggin unit of TPA strongly interacted with SnO₂ surface through corner-shared oxygen. In addition, the typical vibration of 986 cm⁻¹ was spitted into two (987 and 995 cm⁻¹) for 20C₁TS suggesting the existence of direct interaction between the [PW₁₂O₄₀]³⁻ anions and Cs⁺ cations [48, 49].

The nature of acidic sites of the catalysts were determined by temperature programmed desorption of ammonia. The classification of acid site strength is depended on the NH_3 desorption temperature [50]. TPD profiles of the catalysts are presented in the Fig. 3. The Cs_1TPA/SnO_2 catalysts showed the desorption peaks related to medium and strong acidic sites.

Catalyst with 20 wt% Cs1TPA/SnO₂ showed a strong desorption peak centered at 580 °C related to strong acidic sites. The strong desorption band intensity decreased for the catalysts with above 20 wt% Cs1TPA content. The decrease in acidity at higher loadings of Cs1TPA might be related to the attainment of bulk nature on the support.

3.2 Activity measurements

3.2.1 Effect of Cs1TPA loading on SnO2 for etherification of glycerol

The catalysts with varying Cs1TPA content on SnO2 were evaluated for etherification of glycerol with tert-butanol and the results are presented in Table 2. The amount of Cs present in the catalysts was evaluated by using ICP-MS analysis. Amount of cesium present in the catalysts are found to be equal to their nominal values. The catalytic activity of the support SnO₂ and 20% TPA/SnO₂ were also studied for comparison. The support, SnO₂ showed 10% glycerol conversion with 100% selectivity towards monoethers and no selectivity for higher ethers. By loading 10 wt% of Cs1TPA over SnO2 glycerol conversion increased to 74% with 24% selectivity towards higher ethers. Further increase in Cs1TPA loading over tin oxide, conversion of glycerol increased and reached about 91% for the catalyst with 20 wt% Cs1TPA on SnO2. Above this loading there was no appreciable variation in the conversion. The loadings 15 and 20 wt% of Cs1TPA on SnO2 showed similar activity, but 20 wt% Cs1TPA showed high selectivity for higher ethers. The difference in selectivity for higher ethers might be due to the well dispersion of Cs1TPA on tin oxide and higher amount of stronger acidic sites. Acidity results of TPD of ammonia (Fig. 3) are also in good agreement with the observed catalytic activity. The 15 and 20%Cs1TPA/SnO2 showed acidity values as 0.122 and 0.196 mmol respectively. The increase in activity for 20%Cs1TPA/SnO2 is related to its high acidity which in turn related to the

content of Cs_1TPA and its dispersion on SnO₂. Based on the above findings, plausible reaction mechanism was proposed (Scheme 1) for the etherification reaction. It is speculated that Bronsted acidic sites present on Cs_1TPA activates tert-butanol and Lewis acidic sites on support activates the glycerol and forms monoethers. Successive transformation of glycerol to higher ethers is attained due to the regeneration of acidic sites. The successive transformation of glycerol to higher ethers shows that the catalyst has no impact with the formed byproducts and water. These results indicate that Cs_1TPA/SnO_2 is a water tolerant acid catalyst [51].

The catalytic activity of the 20 wt% Cs1TPA/SnO2 was compared with 20 wt% TPA/SnO₂. The parent heteropolyacid supported on SnO₂ (20% TPA/SnO₂) showed about 85% conversion of glycerol and selectivity for monoethers and higher ethers was found to be 72% and 28% respectively. In the case of catalyst with Cs containing 20 wt% Cs1TPA/SnO₂, conversion of glycerol was 91% and selectivity towards higher ethers was 44%. The catalytic activity of Cs salt of TPA is higher than that of parent TPA supported on SnO₂. The main reason for the high activity of Cs salt of TPA is its high surface acidity *i.e.* the large number of strongly acidic protons on the surface. Moreover, the stability of the Cs1TPA/SnO2 catalyst is high compared to TPA/SnO₂. Okuhara et al. [52] have disclosed that alkali exchange with proton of TPA results in enhanced activity, better stability, and higher surface area of heteropoly acids. In order to know the efficiency of 20% Cs1TPA/SnO2 catalysts, turnover number (TON) were calculated by using complete catalyst weight as active component and the corresponding values are presented in Table 2. The TON was calculated by using the equation given below. The TON and conversion of glycerol depends upon the content of Cs₁TPA in the catalyst. The TON of 20% TPA/SnO₂ was low compared to 20% Cs1TPA/SnO2 catalysts. With the increase in content of Cs1TPA, the TON values increased and maximum value was obtained for 20% Cs1TPA/SnO2 catalyst.

$TON = \frac{(\% \text{ conversion of glycerol}) \times \text{moles of glycerol taken}}{\text{moles of the catalyst}}$

3.2.2 Effect of catalyst loading

The catalyst loading was varied in the range of 1.5 - 3.5 wt% and the results are presented in Fig. 4. The catalyst amount mainly influence the formation of higher ethers. At lower catalyst loading selectivity for monoethers are found to be maximum. With increase in the catalyst concentration, selectivity for higher ethers gradually increased and about 44% selectivity for higher ethers was obtained at a catalyst content of 2.5 wt%. The conversion of glycerol increased with an increase in catalyst loading due to the proportional increase in the number of active sites. When the catalyst amount was further increased there is marginal decrease in the conversion of glycerol and selectivity for monoethers increased. This decrease in the activity might be due to the continuously formation of water, which negatively affects the etherification equilibrium [53]. As the catalyst loading increased above 2.5 wt% there is substantial increase in the formation of by-products of isobutene was observed. Therefore, further reactions were carried out keeping catalyst loading as 2.5 wt% in all other experiments.

3.2.3 Effect of reaction time

Reaction time is an important parameter and long reaction times (>8 h) were adopted usually for glycerol etherification to obtain reasonable conversion [54]. The conversion of glycerol and selectivity to higher ethers at different reaction times was studied and the results are presented in Fig. 5.

The conversion of glycerol was high even at 30 min suggesting that high activity of the catalyst, but the selectivity for higher ethers was only 25%. As the reaction time increased from 30 min to 60 min glycerol conversion and selectivity towards higher ethers also increased, whereas the selectivity of monoethers decreased, because the di- and triether products are formed through consecutive etherification reactions [24]. Maximum conversion of glycerol and selectivity towards higher ethers were achieved within 60 min of reaction time. Further increase in the reaction time over 60 min there is no appreciable increase in conversion of glycerol and in the formation of higher ethers, on further increasing the reaction time selectivity for higher ethers remained constant indicating that the reaction reached equilibrium after 60 min. The higher selectivity to higher ethers even at longer reaction times reflects that the present catalyst was efficient to selective etherification to synthesize higher ethers.

3.2.4 Effect of reaction temperature

The effect of reaction temperature on conversion of glycerol was studied in the temperature range of 80–110 °C and the results are shown in Fig. 6. As expected, the conversion of glycerol increased with increase in reaction temperature. The glycerol conversion was only 66% at 80°C with 20% selectivity towards higher ethers. As the temperature increased to 100 °C the conversion of glycerol also increased up to 91% and selectivity to higher ethers were also increased from 27% to 43%. However, when the reaction was carried out above 110 °C, formation of polymeric products were observed. These byproducts might be formed by the dimerization of isobutene. It was also observed the presence of isobutylene in the gas phase at higher reaction temperatures (>110 °C). No polyglycerols were detected under these experimental conditions. These results suggest that the optimum reaction temperature is 100°C.

3.2.5 Effect of glycerol to tert-butanol mole ratio

Glycerol to tert-butanol molar ratio is an important parameter to obtain high glycerol conversion and selectivity towards higher ethers. Fig. 7 shows the effect of glycerol to tert-butanol mole ratio on the etherification reaction. The results suggest that, as the mole ratio of glycerol to tert-butanol decreased from 1:6 to 1:12, the glycerol conversion was increased from 75 to 91%. However, there was no significant increase in the conversion of glycerol with further decrease the mole ratio from 1:12 to 1:15. A marginal decrease in selectivity to higher ethers was observed at high mole ratios but evidenced the formation of isobutene dimers. The decrease in selectivity may be explained on the basis of the fact that the increase in the tert-butanol concentration hinders the etherification reaction by blocking the active sites on the catalyst surface [35]. Thus, there is a competitive adsorption of the tert-butanol on the acid sites with glycerol, which reduces the efficiency of the catalyst.

3.2.6 Comparison of the catalyst with other reported catalysts

In addition to the above study, the catalytic activity of the present catalyst was compared with activity of the reported catalysts for the etherification of glycerol with tert-butanol and the results were summarized in the Table 3. Among the reported catalysts, sulfonated clay exhibited high glycerol conversion (95 %) and selectivity for higher ethers (37 %) [28]. The highest yield for glycerol ethers (46%) was obtained with an amount of catalyst equivalent to 7.5 wt% A-15 catalyst with respect to the mass and reaction time of 50 h [33]. The present catalyst, 20%Cs₁TPA/SnO₂ exhibited high glycerol conversion (91%) and selectivity (44%) than the previously reported catalysts under mild conditions as shown in Table 4. The catalyst designed in the present work was prepared by non-toxic Cs metal ion with eco-friendly heteropolyacids as its backbone and made the synthesis of glycerol ethers, a green process.

3.27 Reusability

In order to assess the reusability of $20C_1TS$ catalyst for glycerol etherification, the catalyst was separated from the reaction system by centrifugation after the completion of each run. The catalyst was washed with methanol, dried at 100 °C and used for further reaction cycle under identical reaction conditions. As illustrated in Table 4, $20C_1TS$ catalyst exhibited constant activity until four reaction cycles without showing distinct decline in catalytic activity. These results have demonstrated that the $20C_1TS$ catalyst is rather durable and holds the potential for practical applications. Furthermore, the inherent heterogeneous nature of $20\% Cs_1TPA/SnO_2$ catalyst can favor to recover the catalyst as well as the reaction products.

4.0 Conclusions

Cesium salts of TPA supported on SnO2 catalysts were prepared with retention of Keggin ion structure. The characterization results suggest the presence of strong acidic sites, where acid strength depends on the exchangeable protons on TPA with Cs⁺ ions and TPA loading on SnO₂. The etherification activity was related to the acidity of the catalyst. The Cs-containing catalysts possess stronger acidic sites compared to the catalyst without Cs. The 20% CsTPA/SnO₂ catalyst exhibited 90% glycerol conversion with 44% selectivity for higher ethers. The glycerol etherification activity and selectivity not only depended on the nature of the catalyst but also on some reaction parameters such as temperature, time and mole ratio of glycerol to tertbutanol. The catalyst exhibited reusability with constant activity.

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References

- [1] C.-H. Zhou, J.N. Beltramini, Y.-X. Fan, G.Q. Lu, Chem. Soc. Rev., 37 (2008) 527-549.
- [2] A. Corma, S. Iborra, A. Velty, Chem. Rev., 107 (2007) 2411-2502.
- [3] J. Izquierdo, M. Montiel, I. Palés, P. Outón, M. Galán, L. Jutglar, M. Villarrubia, M. Izquierdo, M. Hermo, X. Ariza, Renew. Sust. Energ. Rev., 16 (2012) 6717-6724.
- [4] C. Len, R. Luque, Sustainable Chemical Processes, 2 (2014) 1.
- [5] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. Int. Ed., 46 (2007) 4434-4440.
- [6] A. Tsuji, K.T.V. Rao, S. Nishimura, A. Takagaki, K. Ebitani, ChemSusChem, 4 (2011) 542-548.
- [7] W. Hu, D. Knight, B. Lowry, A. Varma, Ind. Eng. Chem. Res., 49 (2010) 10876-10882.
- [8] B. Katryniok, H. Kimura, E. Skrzynska, J.-S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul, F. Dumeignil, Green Chem., 13 (2011) 1960-1979.
- [9] M. Balaraju, V. Rekha, P.S.S. Prasad, B.L.A.P. Devi, R.B.N. Prasad, N. Lingaiah, Appl. Catal. A: Gen., 354 (2009) 82-87.

- [10] K. Jagadeeswaraiah, C.R. Kumar, P.S.S. Prasad, S. Loridant, N. Lingaiah, Appl. Catal. A: Gen., 469 (2014) 165-172.
- [11] V.S. Marakatti, A.B. Halgeri, RSC Adv., 5 (2015) 14286-14293.
- [12] G. Parameswaram, M. Srinivas, B. Hari Babu, P.S. Sai Prasad, N. Lingaiah, Catal. Sci. Technol., 3 (2013) 3242-3249.
- [13] H. Saggadi, D. Luart, N. Thiebault, I. Polaert, L. Estel, C. Len, Catal. Commun., 44 (2014)15-18.
- [14] H. Saggadi, D. Luart, N. Thiebault, I. Polaert, L. Estel, C. Len, RSC Adv., 4 (2014) 21456-21464.
- [15] H. Saggadi, I. Polaert, D. Luart, C. Len, L. Estel, Catal. Today, 255 (2015) 66-74.
- [16] J.M. Rafi, A. Rajashekar, M. Srinivas, B.V.S.K. Rao, R.B.N. Prasad, N. Lingaiah, RSC Adv., 5 (2015) 44550-44556.
- [17] F. Jérôme, Y. Pouilloux, J. Barrault, ChemSusChem, 1 (2008) 586-613.
- [18] A.M. Ruppert, A.N. Parvulescu, M. Arias, P.J.C. Hausoul, P.C.A. Bruijnincx, R.J.M.K. Gebbink, B.M. Weckhuysen, J. Catal., 268 (2009) 251-259.
- [19] M.P. Pico, S. Rodríguez, A. Santos, A. Romero, Ind. Eng. Chem. Res., 52 (2013) 14545-14555.
- [20] N. Ozbay, N. Oktar, G. Dogu, T. Dogu, Ind. Eng. Chem. Res., 51 (2012) 8788-8795.
- [21] J. Melero, G. Vicente, G. Morales, M. Paniagua, J. Moreno, R. Roldán, A. Ezquerro, C. Pérez, Appl. Catal. A: Gen., 346 (2008) 44-51.
- [22] K. Klepáčová, D. Mravec, A. Kaszonyi, M. Bajus, Appl. Catal. A: Gen., 328 (2007) 1-13.
- [23] R.S. Karinen, A.O.I. Krause, Appl. Catal. A: Gen., 306 (2006) 128-133.
- [24] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, Green Chem., 10 (2008) 13-30.

- [25] J. Zhou, Y. Wang, X. Guo, J. Mao, S. Zhang, Green Chem., 16 (2014) 4669-4679.
- [26] N. Viswanadham, S.K. Saxena, Fuel, 103 (2013) 980-986.
- [27] T.S. Galhardo, N. Simone, M. Gonçalves, F.C.A. Figueiredo, D. Mandelli, W.A. Carvalho, ACS Sustain. Chem. Eng., 1 (2013) 1381-1389.
- [28] P.A. Celdeira, M. Gonçalves, F.C. Figueiredo, S.M. Dal Bosco, D. Mandelli, W.A. Carvalho, Appl. Catal. A: Gen., 478 (2014) 98-106.
- [29] A.D. Behr, H. Schmidke, C.D. Lohr, M. Schneider, in, Google Patents, 1994.
- [30] A. Behr, L. Obendorf, Eng. Lif. Sci., 2 (2002) 185-189.
- [31] K. Klepáčová, D. Mravec, M. Bajus, Chem. Pap., 60 (2006) 224-230.
- [32] M. Gonçalves, M. Mantovani, W.A. Carvalho, R. Rodrigues, D. Mandelli, J. Silvestre Albero, Chem. Eng. J., 256 (2014) 468-474.
- [33] F. Frusteri, F. Arena, G. Bonura, C. Cannilla, L. Spadaro, O. Di Blasi, Appl. Catal. A: Gen., 367 (2009) 77-83.
- [34] M. Srinivas, R. Sree, G. Raveendra, C.R. Kumar, P.S. Prasad, N. Lingaiah, Indian J. Chem., 53 (2014) 524-529.
- [35] M.D. González, Y. Cesteros, P. Salagre, Appl. Catal. A: Gen., 450 (2013) 178-188.
- [36] I.V. Kozhevnikov, Chem. Rev., 98 (1998) 171-198.
- [37] M.N. Timofeeva, Appl. Catal. A: Gen., 256 (2003) 19-35.
- [38] C.R. Kumar, N. Rambabu, N. Lingaiah, P.S.S. Prasad, A.K. Dalai, Appl. Catal. A: Gen., 471 (2014) 1-11.
- [39] K.-i. Shimizu, K. Niimi, A. Satsuma, Appl. Catal. A: Gen., 349 (2008) 1-5.
- [40] S. Rana, S. Maddila, R. Pagadala, K.M. Parida, S.B. Jonnalagadda, Catal. Commun., 59 (2015) 73-77.

- [41] E. Tsukuda, S. Sato, R. Takahashi, T. Sodesawa, Catal. Commun., 8 (2007) 1349-1353.
- [42] J.A. Dias, E. Caliman, S.C. Loureiro Dias, Microporous Mesoporous Mater., 76 (2004) 221-232.
- [43] G.D. Yadav, N.S. Asthana, Appl. Catal. A: Gen., 244 (2003) 341-357.
- [44] Y.-S. Cho, G.-R. Yi, J.-J. Hong, S.H. Jang, S.-M. Yang, Thin Solid Films, 515 (2006) 1864-1871.
- [45] A.I. Ahmed, S.A. El-Hakam, M.A.A. Elghany, W.S.A. El-Yazeed, Appl. Catal. A: Gen., 407 (2011) 40-48.
- [46] M.E. Jamróz, M. Jarosz, J. Witowska-Jarosz, E. Bednarek, W. Tęcza, M.H. Jamróz, J.C. Dobrowolski, J. Kijeński, Spectrochim. Acta, A Mol. Biomol. Spectrosc., 67 (2007) 980-988.
- [47] O. Lupan, L. Chow, G. Chai, A. Schulte, S. Park, H. Heinrich, Mater. Sci. Eng., B, 157 (2009) 101-104.
- [48] J.S. Santos, J.A. Dias, S.C.L. Dias, F.A.C. Garcia, J.L. Macedo, F.S.G. Sousa, L.S. Almeida, Appl. Catal. A: Gen., 394 (2011) 138-148.
- [49] K.M. Parida, S. Rana, S. Mallick, D. Rath, J. Colloid Interface Sci., 350 (2010) 132-139.
- [50] M. Misono, Chem. Commun., (2001) 1141-1152.
- [51] T. Nakato, M. Kimura, S.-i. Nakata, T. Okuhara, Langmuir : the ACS journal of surfaces and colloids, 14 (1998) 319-325.
- [52] T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, J. Mol. Catal., 74 (1992) 247.
- [53] F. Frusteri, F. Arena, G. Bonura, C. Cannilla, L. Spadaro, O. Di Blasi, Appl. Catal. A: Gen., 367 (2009) 77-83.

- [54] F. Liu, K. De Oliveira Vigier, M. Pera-Titus, Y. Pouilloux, J.-M. Clacens, F. Decampo, F. Jerome, Green Chem., 15 (2013) 901-909.
- [55] M.D. González, P. Salagre, R. Mokaya, Y. Cesteros, Catal. Today, 227 (2014) 171-178.



Fig. 1. XRD patterns of (a) 10 C_1TS (b) 15 C_1TS (c) 20 C_1TS (d) 25 C_1TS and (e) 30 C_1TS . (\blacklozenge) TPA and (\blacklozenge) SnO₂



Fig. 2. FT-IR spectra of (a) $10 C_1TS$ (b) $15 C_1TS$ (c) $20 C_1TS$ (d) $25 C_1TS$ and (e) $30C_1TS$

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Fig. 3. Temperature programmed desorption of ammonia patterns of (a) $10 C_1TS$ (b) $15 C_1TS$ (c) $20 C_1TS$ (d) $25 C_1TS$ and (e) $30C_1TS$.



Fig. 4. Effect of catalyst loading on etherification of glycerol. Reaction conditions: glycerol (1.84 g), tert-butanol (17.84 g), reaction temperature (100 °C) and reaction time (1 h).



Fig. 5. Effect of reaction time on etherification of glycerol. Reaction conditions: glycerol (1.84 g), *tert*-butanol (17.84 g), catalyst weight (0.5g) and reaction temperature (100 °C).



Fig. 6. Effect of reaction temperature on etherification of glycerol. Reaction conditions: glycerol (1.84 g), *tert*-butanol (17.84 g), reaction time (1h) and catalyst weight (0.5g).



Fig. 7. Effect of glycerol to *tert*-butanol mole ratio on etherification of glycerol. Reaction conditions: Reaction time 1 h, Reaction temperature 100 °C and catalyst weight (0.5g).



Scheme 1. Plausible mechanism for etherification of glycerol with tert-butanol

Catalyst	Cs content (mg/L)	SBET (m^2/g)	Acidity (mmol/g) ^a	Particle size (nm) ^b
ТРА	-	9.5	-	-
SnO ₂	-	15.1	0.064	10.4
10%C1TS	0.45	14.1	0.112	23.2
15% C ₁ TS	0.68	13.8	0.122	62.2
20% C1TS	0.91	12.1	0.196	62.3
25% C1TS	1.08	10.4	0.141	97.2
30% C1TS	1.27	9.8	0.101	105.2

Table 1. Physio-chemical properties of the catalysts

^aAcidity measured using NH₃ TPD ^bParticle size calculated using Sherrer equation

Catalyst		Selectivity (%)			TON
	Conversion (%)	Monoethers	diether	triether	IUN
SnO ₂	5	100	-	-	-
20% TPA/SnO ₂	85	72	23	5	107
10C ₁ TS	69	74	17	9	93
15C ₁ TS	88	62	28	10	111
20C ₁ TS	91	56	33	11	115
25C ₁ TS	81	67	26	7	102
30C ₁ TS	80	61	30	9	101

Table 2. Effect of Cs1TPA content on etherification of glycerol

Reaction conditions: glycerol (1.84 g), *tert*-butanol (17.84 g), catalyst weight (0.5 g), reaction temperature (100 °C) and reaction time (1 h).

Catalyst	t (h)	T (°C)	X (%)	Selectivity (%)		References
				Monoethers	Higher ethers	
Sulfonated clay	5	120	95	60.3	38.6	[28]
Fluorinated beta zeolite	24	75	75	63	37	[35]
Black carbon	6	70	50	80	20	[55]
Amberlyst-15	50	70	93.6	54	46	[33]
20C1TS	1	100	91	56	44	Present work

Table 3 Literature about the etherification of glycerol with tert-butanol on solid catalysts

t: reaction time, T: reaction temperature, X: conversion of glycerol

Table 4. Reusability of the 20C₁TS catalyst

No: of cycles	Conversion (%)	Selectivity (%)			
		monoether	Diether	Triethers	
1	91	56	33	11	
2	88	52	35	13	
3	86	64	24	12	
4	85	64	25	11	

Reaction conditions: glycerol (1.84 g), tert-butanol (17.84 g), catalyst weight (0.5 g), reaction temperature (100 °C)

and reaction time (1 h).