



Synthesis of Oxygenated Fuel Additives via Acetylation of Bio-Glycerol over H₂SO₄ Modified Montmorillonite K10 Catalyst



Kakasaheb Y Nandiwale^{1,2}, Prashant S Niphadkar¹ and Vijay V Bokade^{1*}

¹*Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, India*

²*Center for Environmentally Beneficial Catalysis, Department of Chemical and Petroleum Engineering, University of Kansas, USA*

***Corresponding author:** Vijay V Bokade, Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, India; Ph: +91-20-25902458; Fax: +91-20-25902634; Email: vv.bokade@ncl.res.in

Submission: 📅 December 21, 2017; **Published:** 📅 January 22, 2018

Abstract

Growing global biodiesel production demands valorization of bio-glycerol derived from biodiesel, which is crucial to make bio refinery process economical. Hence, a series of H₂SO₄ modified sulfonated Montmorillonite K10 catalysts were synthesized, characterized and evaluated for acetylation of bio-glycerol with acetic acid to produce mono acetin (MAG), di acetin (DAG), tri acetin (TAG) and di-glycerol tri-acetate (DGTA), which are the oxygenated fuel additives and facilitate the economic viability of biodiesel production so the bio refinery. The synthesized catalysts were characterized by compressive suite of characterization techniques such as powder X-ray diffraction (XRD), low temperature N₂ physisorption, temperature programmed ammonia desorption (TPAD) and Fourier transform infrared (FTIR). The glycerol conversion and product distribution results were found to correlate with the acidity and textural properties of the catalyst. 20% (w/w) SO₄/K10 was revealed to be a promising catalyst for glycerol acetylation with 99% glycerol conversion and with respective yield towards MAG, DAG, TGA and DGTA of 23%, 59%, 15%, and 2%. Moreover, 20% (w/w) SO₄/K10 catalyst was found to maintain the stable catalytic activity for three reaction cycles. However, the partial catalyst deactivation was observed after third reaction cycle, partly due to deposition of coke and loss of active sites during the reaction.

Keywords: H₂SO₄, Sulfonated MontmorilloniteK10, Glycerol, Acetylation, Fuel additives

Introduction

Currently, stringent environmental regulations for reducing air pollution have spurred tremendous attention to develop alternative energy source [1-3]. Biodiesel produced from transesterification of vegetable oil or animal fat with low carbon alcohol is regarded as sustainable alternative to fossil fuels [3-6]. However, the glycerol is an inevitable by-product (~10 wt. %) of biodiesel production [6]. By 2024, the global biodiesel production is expected to reach almost 39 billion liters, which would generate surplus glycerol leading an oversupply crisis worldwide [7-9]. Glycerol as such has low solubility and poor thermal stability hence, cannot be directly added to biodiesel fuel [2,10]. Therefore, valorization of redundant glycerol to value added fuel additives is crucial to facilitate the economic viability of biodiesel production. As such utilization of biodiesel is limited due to its low stability and need to add oxygenate fuel additives to improve its stability and fuel efficiency.

In this vain, several glycerol valorization processes such as esterification [1], carbonylation [11,12], etherification [13], hydrogenolysis [14-16], acetylation dehydration, oligomerization, dehydrogenation, and glycerol reforming [5,17] have been proposed. Among all of these processes, upgrading glycerol by catalytic acetylation has received tremendous research attention,

because it produces commercially valuable esters, namely, mono acetin (MAG), di acetin (DAG), and tri acetin (TAG) [4,7]. All of the glycerol acetylation products are widely used in the manufacture of dyes, softening agents and plasticizers [4,18]. In particular, DAG and TAG find extensive application as oxygenated fuel additives that can enhance the engine efficiency, improve the cetane number and the anti knocking properties and reduce the particulate emission and the noxious gas emission [18-20]. Moreover, TAG blended fatty acid methyl ester has similar physicochemical properties as that of biodiesel fuel, hence it could attain 100% atom efficiency in diesel engines [1,2,5].

Catalytic acetylation of glycerol can be carried out with the acetylating agents such as acetic anhydride or acetic acid [21]. However, the glycerol acetylation with acetic anhydride is highly exothermic with negative Gibbs free energy, therefore the acetic acid having positive Gibbs free energy is a preferred acetylating agent [21]. The glycerol acetylation is an acid catalyzed reaction, it can be performed over homogeneous and heterogeneous catalysts. However, the homogeneous acid catalysts are toxic, hard to separate from the product mixture, cause environmental problems in disposal, containment, handling and equipment corrosion and result

in considerable energy consumption and material wastage [6]. In contrary, the use of heterogeneous catalysts remains the greenest approach, since they thwart reactor corrosion and can be easily separated from the product mixture by filtration or centrifugation [20,22]. In this context various heterogeneous catalysts such as bio-derived carbon [1], propylsulfonic functionalized mesoporous silica [6], arenesulfonic acid-functionalized Bentonite [10], sulfonic or phosphonic silica [22], sulphonic acid functionalized zeolite support [23], heteropolyacids [24], mixed oxide [25] and dealuminated clay [26] have been evaluated for glycerol acetylation.

This work is motivated by several factors. First, K10 catalyst has been reported to catalyze the glycerol acetylation [27]. Second, sulfonation method has been revealed to increase the catalytic activity by increasing active sites [28]. Therefore, we hypothesized that the sulfonation of K10 should improve the glycerol conversion and product yields. Furthermore, to the best of our knowledge, the sulfonated K10 catalysts have not been evaluated for glycerol acetylation so far. Hence, in present study we report the synthesis of series of Sulfonated K10 catalysts and their catalytic evaluation for Acetylation of bio glycerol with acetic acid to produce MAG, DAG, TAG and di-glycerol tri-acetate (DGTA). The catalytic activity and selectivity results were correlated with the acidity and textural properties of the catalyst, which were determined by the compressive suite of characterization techniques such as powder X-ray diffraction (XRD), low temperature N_2 physisorption, temperature programmed ammonia desorption (TPAD) and Fourier transform infrared (FTIR). The reusability of catalyst for glycerol Acetylation was also presented.

Experimental

Materials

Clay (Montmorillonite, K10), acetic acid (>99%) were obtained from S.D. Fine Chem. Ltd., Mumbai (India). Glycerol (>98%) was procured from Loba Chemie (India). All the chemicals were of analytical quality and used as received.

Catalyst synthesis

H_2SO_4 modified Sulfonated K10 catalyst was prepared as follows: 1 g of K10 was added to 50ml (5g of H_2SO_4 added in distilled water to make final volume of 50ml) solution of H_2SO_4 at 100 °C with constant stirring for 2h. The stirring was continued for one more hour after heating. After the treatment, the mixture was cooled; the product was filtered and washed with 1l distilled water to remove residual H_2SO_4 , if any. The obtained sample was dried at 120 °C for 1h and then calcined in air at 500 °C for 5h. The sample obtained after calcination was grounded into fine powder used in catalytic evaluation. The obtained powder is denoted as 10% $SO_4/K10$. Similar procedure was followed to synthesize 20-30% $SO_4/K10$ catalysts by varying the amount of H_2SO_4 .

Catalysts characterization

XRD patterns of the catalyst samples were recorded on X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) using Cu $K\alpha$ radiation at a scanning rate of 0.0671/s in the 2θ range

from 10-90 °C. The specific surface area of the catalyst samples was obtained from low temperature (-196 °C) N_2 physisorption measured with SA 3100 analyzer (Beckman Coulter, CA, USA). Total acidities of synthesized catalyst samples were calculated by TPAD with Micromeritics Auto Chem (2910, USA). FTIR studies of the catalysts were conducted by using a Bruker IFS-66 single channel Fourier transform spectrophotometer. Thin wafers were prepared by mixing 3mg of the catalysts with 50mg of KBr [29]. The wafers were subjected to 200 scans after which the spectra were recorded.

Catalytic glycerol acetylation and analysis of products

The glycerol acetylation experimental runs were carried in 50ml round bottom flask. The thermostatic oil bath was used to heat the reaction mixture to the desired temperature and condenser was used to reflux of reactants. Once the desired temperature is attained the mixture was stirred with magnetic stirrer for desired reaction time. The flask was quenched in ice water for reaction to stop. Filtration was used to separate solid catalyst from the liquid products. The Acetylation reaction products were analyzed by GC-FID, Varian-CP-3800, SPB-5 (0.25mm I.D., 30m length and 0.25 μ m film thickness) and GC-MS (Agilent-5977-AMSD). The Acetylation products (MAG, DAG, TAG, and DGTA) were confirmed by GC-MS. The response factors and retention times of Acetylation products on GC-FID were obtained by external standard method. All products were quantified on GC-FID with an analytical error of $\pm 2\%$.

Results and Discussion

Catalyst characterization

The crystallinity and the phase purity of synthesized catalyst samples were analyzed by XRD. Figure 1 indicates the XRD patterns of the catalyst samples. The typical XRD pattern of parent K10 was well matched with the reported spectra [29]. It exhibits a diffraction band about $2\theta=17-19^\circ$ with a plateau inclining towards 17° . The XRD analysis confirmed that all the synthesized catalysts are well crystalline in nature. However, $SO_4/K10$ catalysts exhibited minor decrease in an intensity of peaks compared to the parent K10. This can be attributed to the decrease in the crystallinity during the process of sulfonation.

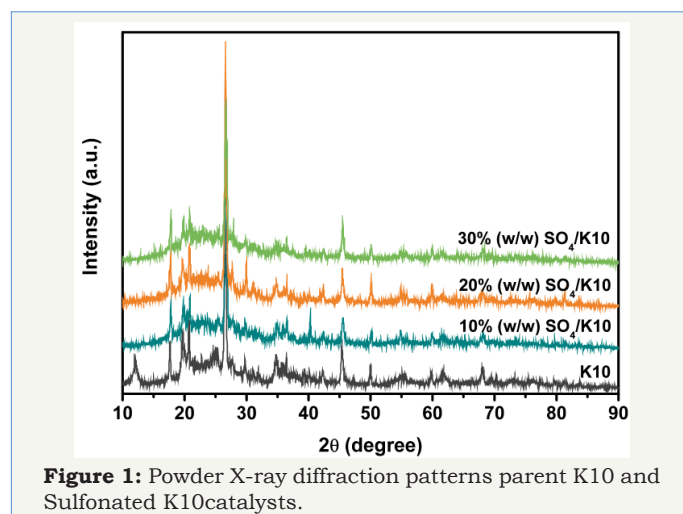


Figure 1: Powder X-ray diffraction patterns parent K10 and Sulfonated K10 catalysts.

Physico-chemical properties of synthesized catalysts are shown in Table 1. The sulfonated-K10 ($\text{SO}_4/\text{K10}$) catalysts exhibited lower BET surface area than the parent K10 (Table 1). Moreover, the BET surface area was found to be decreased with increasing the sulfonation from 10-30%. This is attributed to the blockage of the smaller pores by the active species of sulfonation.

Table 1: Physicochemical properties of the catalysts.

Catalyst Name	Surface Area (m^2/g)	Total Acidity ($\text{NH}_3/\text{mmol/g}$)
K10	223	0.12
10%(w/w) $\text{SO}_4/\text{K10}$	210	0.15
20%(w/w) $\text{SO}_4/\text{K10}$	187	0.19
30%(w/w) $\text{SO}_4/\text{K10}$	185	0.2

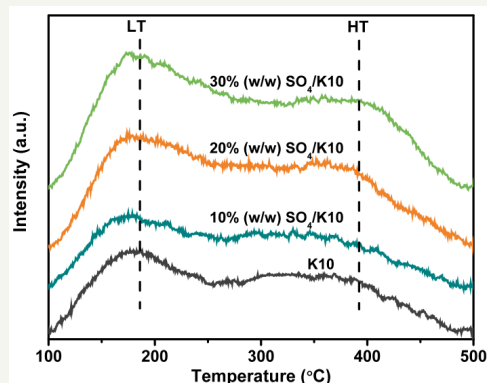


Figure 2: NH_3 -TPD profiles of parent K10 and Sulfonated K10 catalysts.

Figure 2 shows the acid site distribution of the catalyst samples with LT-peak representing weak acid sites (less than 350°C), while HT-peak representing strong acid sites (greater than 350°C). The total acidities of the sulfonated-K10($\text{SO}_4/\text{K10}$) catalysts was found to be higher than the parent K10. Moreover, the acidity was observed to be increased with increasing in sulfonation from 10-30%. Furthermore, weak acid sites (LT) were found to be increased with the increase in sulfonation from 10-30%. These results reveal that the strength of acid sites of Sulfonated K10 catalysts can be tuned by varying the SO_4 loading.

FTIR spectra of the K10 and the $\text{SO}_4/\text{K10}$ catalysts are presented in (Figure 3). The FTIR spectra of all catalyst samples exhibited a broad band centered at 1065cm^{-1} , which is characteristic of a stretching vibrational mode of a Si-O bond. A characteristic band at 925cm^{-1} can be assigned to Al-OH-Al deformation of aluminates. The bands at 520 are attributed to Si-O-Al bending vibrations and Si-O bending vibration separately. The bridging hydroxyl groups (3633cm^{-1}), and the hydroxyl groups in molecular water (1638cm^{-1}) are clearly observed. With the increase in concentration of the sulfuric acid, the band at 925cm^{-1} gradually disappears owing to damage of Al-OH-Al bond, which suggests that K10 was modified by sulfuric acid (Figure 3). Similar observation was reported by Xu et al. [30].

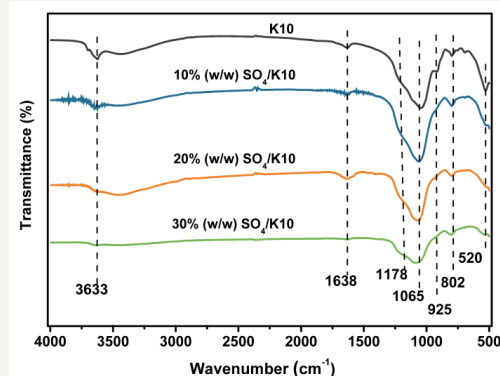


Figure 3: FTIR spectra of parent K10 and Sulfonated K10 catalysts.

Catalytic Performance

Glycerol acetylation is acid catalyzed reaction occurs consecutively with stepwise formation of MAG, DAG and TAG or DGTA, along with formation of water as a by-product. Parent K10 and different percent Sulfonated/K10 catalysts were evaluated for catalytic Acetylation of glycerol at an identical reaction conditions: molar ratio of 1:12 (glycerol: acetic acid), catalyst loading of 0.4g, 120°C and 5h. For comparison, the thermal (without catalyst) acetylation of glycerol was performed. Figure 4 represents comparative product distribution matrix for glycerol acetylation over thermal, K10 and Sulfonated/K10 along with the total acidities of the catalysts. The thermal run gave 41% glycerol conversion and the yields for MAG, DAG and DGTA were 32%, 6% and 3%, respectively, without formation of TAG.

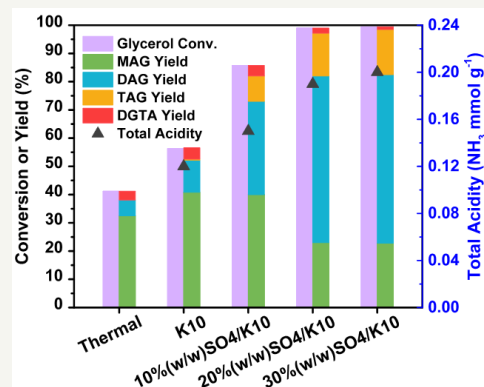


Figure 4: Glycerol conversion, product distribution matrix along with the total acidity of K10 and Sulfonated K10 catalysts at reaction conditions: molar ratio of 1:12 (glycerol: acetic acid), catalyst loading of 0.4g, 120°C and 5h.

The parent K10 catalyst gave about 56% glycerol conversion along with 41%, 11%, 0.4% and 4% yields towards MAG, DAG, TAG and DGTA, respectively. Glycerol conversion obtained over the Sulfonated K10 catalysts was higher than that of the parent K10. This is attributed to the increase in the total acidity by sulfonation (Table 1). Glycerol Acetylation being acid catalyzed reaction, the glycerol conversion increases with acidity. With just 10% sulfonation on K10 [10% (w/w) $\text{SO}_4/\text{K10}$], increases glycerol conversion from 56%-86%. Furthermore 20% (w/w) $\text{SO}_4/\text{K10}$ catalyst exhibited

99% glycerol conversion and the yields for MAG, DAG, TGA and DGTA of 23%, 59%, 15% and 2%, respectively. With increase in the sulfonation from 10 to 20%, the yield of MAG observed to be decreased while increasing the yields of DAG, TAG and DGTA. This implies that, the MAG is being used in subsequent reactions and the rate of reaction increases with the acid sites of the catalyst. However, there was subtle difference in product distribution matrix between 20% and 30% Sulfonated K10 catalysts. As indicated in Table 1, there was little increase in the acidity of the catalyst with increase in sulfonation from 20% to 30%. This may be due to multilayer formation of SO_4 on catalyst surface at higher loading of SO_4 . Hence, 20% (w/w) $\text{SO}_4/\text{K10}$ catalyst was found to be promising catalyst for glycerol acetylation.

Catalyst reusability

Reusability of 20% (w/w) $\text{SO}_4/\text{K10}$ catalyst was investigated for glycerol Acetylation at molar ratio of 1:12 (glycerol: acetic acid), catalyst loading of 0.4g, 120 °C and 5h. The catalyst was separated by filtration after each catalytic run and used in next catalytic cycle. Figure 5 depicts glycerol conversion and product distribution matrix obtained over 20% (w/w) $\text{SO}_4/\text{K10}$ in successive recycles. 20% (w/w) $\text{SO}_4/\text{K10}$ was found to be stable with identical catalytic activity for three catalytic runs. However, during fourth catalytic runs the decrease in catalytic activity was observed. This could be partly due to deposition of coke and loss of active sites during the reaction. The spent catalyst (K10) can be regenerated by calcination and can be reused after sulfonation in new batch of reactions.

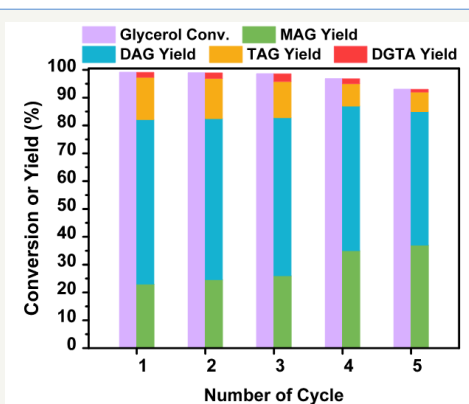


Figure 5: Reusability of 20% (w/w) $\text{SO}_4/\text{K10}$ catalyst for acetylation of glycerol at molar ratio of 1:12 (glycerol: acetic acid), catalyst loading of 0.4g, 120 °C and 5h.

Conclusion

A series of Sulfonated Montmorillonite K10 catalysts were synthesized and evaluated for acetylation of bio-glycerol with acetic acid to produce oxygenated fuel additives for Biodiesel. Sulfonated K10 catalysts were found to have superior performance for glycerol acetylation than the parent K10, due to the increase in acid sites by sulfonation. 20% (w/w) $\text{SO}_4/\text{K10}$ catalyst has shown 99% glycerol conversion and the yields for MAG, DAG, TGA and DGTA of 23%, 59%, 15% and 2%, respectively. Moreover, 20% (w/w) $\text{SO}_4/\text{K10}$ catalyst was stable for three reaction cycles with identical activity. As per our knowledge, sulfonated K10 is not explored for this reaction so far, hence present study gives a new avenue as a

potential catalyst for the synthesis of oxygenated fuel additives, especially DAG and TAG.

References

- Okoye PU, Abdullah AZ, Hameed BH (2017) Synthesis of oxygenated fuel additives via glycerol esterification with acetic acid over bio-derived carbon catalyst. *Fuel* 209: 538-544.
- Cornejo A, Barrio I, Campoy M, Lázaro J, Navarrete B (2017) Oxygenated fuel additives from glycerol valorization. Main production pathways and effects on fuel properties and engine performance: A critical review. *Renewable and Sustainable Energy Reviews* 79: 1400-1413.
- Lee AF (2014) Catalysing sustainable fuel and chemical synthesis. *Applied Petrochemical Research* 4(1): 11-31.
- Arun P, Pudi SM, Biswas P (2016) Acetylation of Glycerol over Sulfated Alumina: Reaction Parameter Study and Optimization Using Response Surface Methodology. *Energy Fuels* 30(1): 584-593.
- Okoye PU, Abdullah AZ, Hameed BH (2017) A review on recent developments and progress in the kinetics and deactivation of catalytic acetylation of glycerol-A byproduct of biodiesel. *Renew Sust Energy Rev* 74: 387-401.
- Costa BOD, Decolatti HP, Legnoverde MS, Querini CA (2017) Influence of acidic properties of different solid acid catalysts for glycerol acetylation. *Catal Today* 289: 222-230.
- Kong PS, Aroua MK, Daud WMAW, Lee HV, Cognet P, et al. (2016) Catalytic role of solid acid catalysts in glycerol acetylation for the production of bio-additives: a review. *Rsc Adv* 6: 68885-68905.
- Lin YC (2013) Catalytic valorization of glycerol to hydrogen and syngas. *International Journal of Hydrogen Energy* 38(6): 2678-2700.
- Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE (2009) Glycerol acetylation over dodecatungstophosphoric acid immobilized into a silica matrix as catalyst. *Appl Catal B-Environ* 91(1,2): 416-422.
- Tangestanifard M, Ghaziaskar H (2017) Arenesulfonic acid-functionalized bentonite as catalyst in glycerol esterification with acetic acid. *Catalysts* 7(7): 211.
- Kondawar SE, Mane RB, Vasishta A, More SB, Dhengale SD, et al. (2017) Carbonylation of glycerol with urea to glycerol carbonate over supported Zn catalysts. *Applied Petrochemical Research* 7(1): 41-53.
- Srikanth A, Viswanadham B, Kumar VP, Anipindi NR, Chary KVR (2016) Synthesis and characterization of Cs-exchanged heteropolyacid catalysts functionalized with Sn for carbonolysis of glycerol to glycerol carbonate. *Applied Petrochemical Research* 6(2): 145-153.
- Nandiwale KY, Patil SE, Bokade VV (2014) Glycerol etherification using n-butanol to produce oxygenated additives for biodiesel fuel over h-beta zeolite catalysts. *Energy Technol-Ger* 2 (5): 446-452.
- Jiang T, Kong D, Xu K, Cao F (2015) Effect of ZnO incorporation on Cu-Ni/ Al_2O_3 catalyst for glycerol hydrogenolysis in the absence of added hydrogen. *Applied Petrochemical Research* 5(3): 221-229.
- Kumar VP, Beltramini JN, Priya SS, Srikanth A, Bhanuchander P, et al. (2016) Catalytic functionalities of nano Ru catalysts supported on $\text{TiO}_2\text{-ZrO}_2$ mixed oxide for vapor phase hydrogenolysis of glycerol to propanediols. *Applied Petrochemical Research* 6(1): 73-87.
- Jiang T, Kong D, Xu K, Cao F (2016) Hydrogenolysis of glycerol aqueous solution to glycols over Ni-Co bimetallic catalyst: effect of ceria promoting. *Applied Petrochemical Research* 6(2): 135-144.
- Okoye PU, Hameed BH (2016) Review on recent progress in catalytic carboxylation and acetylation of glycerol as a byproduct of biodiesel production. *Renewable and Sustainable Energy Reviews* 53: 558-574.
- Trifoi AR, Agachi PŞ, Pap T (2016) Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols. *Renewable and Sustainable Energy Reviews* 62: 804-814.
- Ramalingam RJ, Radhika T, Adam F, Dolla TH (2016) Acetylation of glycerol over bimetallic Ag-Cu doped rice husk silica based biomass catalyst for bio-fuel additives application. *Int J Ind Chem* 7(2): 187-194.



20. Churipard SR, Manjunathan P, Chandra P, Shanbhag GV, Ravishankar R, et al. (2017) Remarkable catalytic activity of a sulfonated mesoporous polymer (MP-SO₃H) for the synthesis of solketal at room temperature. *New J Chem* 41: 5745-5751.
21. Liao X, Zhu Y, Wang S-G, Chen H, Li Y (2010) Theoretical elucidation of acetylating glycerol with acetic acid and acetic anhydride. *Applied Catalysis B: Environmental* 94(1, 2): 64-70.
22. Beejapur HA, La Parola V, Liotta LF, Testa ML (2017) Glycerol Acetylation over Organic-Inorganic Sulfonic or Phosphonic Silica Catalysts. *Chemistryselect* 2(17): 4934-4941.
23. Patel A, Singh S (2014) A green and sustainable approach for esterification of glycerol using 12-tungstophosphoric acid anchored to different supports: Kinetics and effect of support. *Fuel* 118: 358-364.
24. Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE (2011) Acetylation of glycerol over heteropolyacids supported on activated carbon. *Catalysis Communications* 12(7): 573-576.
25. Popova M, Szegedi A, Ristic A, Tusar NN (2014) Glycerol acetylation on mesoporous KIL-2 supported sulphated zirconia catalysts. *Catal Sci Technol* 4: 3993-4000.
26. Venkatesha NJ, Bhat YS, Prakash BSJ (2016) Volume accessibility of acid sites in modified montmorillonite and triacetin selectivity in acetylation of glycerol. *Rsc Adv* 6: 45819-45828.
27. Gonçalves VLC, Pinto BP, Silva JC, Mota CJA (2008) Acetylation of glycerol catalyzed by different solid acids. *Catal Today* 133-135: 673-677.
28. Tao ML, Guan HY, Wang XH, Liu YC, Louh RF (2015) Fabrication of sulfonated carbon catalyst from biomass waste and its use for glycerol esterification. *Fuel Process Technol* 138: 355-360.
29. Yadav GD, Bokade VV (1996) Novelities of heteropoly acid supported on clay: etherification of phenethyl alcohol with alkanols. *Applied Catalysis A: General* 147(2): 299-323.
30. Xu X, Zhang X, Zou W, Yue H, Tian G, et al. (2015) Conversion of carbohydrates to methyl levulinate catalyzed by sulfated montmorillonite. *Catalysis Communications* 62: 67-70.