CATALYTIC ACTIVITY OF CLINOPTILOLITE –BASED CATALYSTS IN THE ESTERIFICATION OF LEVULINIC ACID

Jelena Pavlovic[1], Margarita Popova[2], Magdolna Mihalyi[3], Matjaz Mazaj[4], Gregor Mali[4], Janez Kovač[5], Hristina Lazarova[2], Nevenka Rajic[6]

[1]Innovation Centre of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia, [2]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Science, Acad. G. Bonchev, bl. 9, 1113 Sofia, Bulgaria, [3]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudosokkorutja 2, Budapest 1117, Hungary, [4]National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia, [5]Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia, [6]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
E-mail: jelena.pavlovic@tmf.bg.ac.rs

ABSTRACT

Natural zeolite – clinoptilolite loaded with SnO_2 (TOHCLI) or sulfated SnO_2 (STOHCLI) was studied inthe esterification of levulinic acid (LA) with octanol and ethanol. TOHCLI showed a high activity (55 %) in the conversion of LA into octyllevulinate (OLA) and a moderate activity (22 %) in the conversion to ethyl levulinate (ELA). Total conversion of LA to OLA and ELA was achieved by STOHCLI which is explainedby the presence of Brönsted and Lewis acid sites in the STOHCLI.

Keywords: clinoptilolite, sulfated SnO_2, levulinic acid, levulinate esters.

INTRODUCTION

LA is one of the most important sustainable platform chemicals which can be easily obtained from biomass and converted to many valuable products including levulinate esters (LE). Due to their specific physicochemical properties, LE are used as biofuels and biolubricants, green solvents, plasticizers and fragrances [1]. Usually, LE are produced by the esterification of LA with alcohols in the presence of strong mineral acidssuch as concentrated sulphuric acid. Although the esterification in the presence of sulphuric acidproceedsthrough a short reaction time and with a high conversion rate, many efforts have been done for replacement of corrosive and non-environmentally friendly sulphuric acid by a „green" catalyst. Various solid acid catalystssuch as heteropoly acids, sulfated oxides (SO_4-ZrO_2, SO_4-Nb_2O_5, SO_4-TiO_2, SO_4-SnO_2), ion-exchange resins, as well as synthetic zeolites (HUSY, HBEA, HMOR, HZSM-5, HMCM-22) have been tested. Generally, all these solids suffer from low catalytic activity and/or non-recyclibility [2-4].

The aim of this reaserch was preparationof an efficient „green" catalyst for the esterification of LA based on natural clinoptilolite.

EXPERIMENTAL

In this study clinoptilolite-rich zeolitic tuff (CLI) was obtained from Slanci deposit (Belgrade, Serbia). A semi-quantitative X-ray powder diffraction analysis (using the Rietveld refinement and the Topas Academic v.4 software [5]) showed that the CLI mainly consisted (wt.%): clinoptilolite - 80, feldspars -16 and quartz - 4.The cation exchange capacity (CEC) determined by a standard procedure [6] was160 mmol M^+/100 g.

Preparation of catalysts: A three steps procedure was applied [7] including: 1) conversion of CLI to H-form of CLI (HCLI), 2) loading of HCLI with 5-12 wt.% SnO_2(TOHCLI), and 3) sulfation of TOHCLI to sulfated TOHCLI (STOHCLI) using a slightly modified method given by Matsuhashi and Sowmiya [8,9]. The obtained TOHCLI

and STOHCLI were denoted as *x*TOHCLI and *x*STOHCLI (x=5, 9 and 12) where *x* refers the content of Sn in wt. %.

*Catalysts characterization:*A powder X-ray diffraction analysis (PXRD), thermal analysis (TG/DTG), energy dispersive X-ray spectroscopy(EDS), X-ray photoelectron spectroscopy (XPS), UV/VIS diffuse reflectance spectroscopy (UV/VIS DRS), solid state NMR spectroscopy (NMR), N_2 physisorptionat −196 ^{o}C (BET) and Fourier-transform infrared spectroscopy (FTIR) were used for characterization of the prepared catalysts.

*Catalytic experiments:*Esterification of LA was performed in a batch reactor with magnetic stirrer under reflux. Firstly, the catalyst was pre-treated *ex-situ* in an oven forat 1 h at 200 °C. Then, the reactor was charged with 1.0 cm^3 LA, 7 cm^3 ethanol (or octanol) and 0.2 g catalyst. The reactor was placed in an oil bath, heated under stirring at 100 °C for 5 h. Product samples were analyzed using HP-GC with a flame ionization detector equipped with a WCOT FUSED SILICA 25m x 0.25mm COATING CP-SIL 43CB column. The LA conversion rate was determined using the LA/OLA or LA/ELA area ratio.

Reusability was tested using STOHCLI with 9 wt% Sn(9STOHCLI) in six reaction cycles. Between each cycle, the 9STOHCLI was separated by centrifugation, washed with acetone, dried at 60 ºC and calcined at 400 $^{°}$C in air for 3 h.

RESULTS AND DISCUSSION

PXRD analysis showed that the crystallinity of CLI is mainly preserved after all treatments. Conversion of CLI to HCLI increased the specific surface area from 32 to 60 m^2 g^{-1}. ^{27}Al NMR analysis of HCLI showed the presence not only of tetrahedrally coordinated Al characteristic for clinoptilolite structure but also 6- and 5- coordinated extra-framework Al species. EDS analysis confirmed the presence of Sn in TOHCLI andboth Sn and Sin STOHCLI samples.In these samples Sn content varied from about 5 to 12 wt.%.

XPS analysis revealed the presence of a novel Sn oxide phase at the surface and inside the zeolite lattice. UV/VIS DRS showed that this oxide phase belongs to SnO_2 (a strong adsorption at 263 nm characteristic for SnO_2 was evident in the DR spectrum). The SnO_2 covering slightly affects the specific surface area which increaseswith the Sn amount in TOHCLI samples (data are not shown).The trend was not evident for STOHCLI samples whichcan be explained by a partial pore blockage of the zeolite lattice caused by sulfate groups.

Acidity of the TOHCLI and STOHCLI samples was determined using pyridine adsorptionand FTIR analysis (Table 1).

Table 1. Acidity of the samples based on the FTIR spectra of the adsorbed pyridine.

Sample	Brönsted sites, μmol g^{-1}	Lewis acid sites, μmol g^{-1}
5TOHCLI	0	55.5
5STOHCLI	117.4	240.0
9TOHCLI	3.8	164.5
9STOHCLI	143.7	236.4

It is evident that amount of Lewis acid sites is higher than Brönsted ones for both TOHCLI and STOHCLI which could be ascribed to the coordinatively unsaturated Sn sites. For TOHCLI, increasing of Sn content increased amount of Lewis acid sites whereas Brönsted acid sites were not influenced significantly. For STOHCLI the amounts of Lewis and Brönsted acid sites are significantly higher than for TOHCLI, suggesting that sulfate species

contribute not only to Lewis acidity but also to Brönsted acid sites through formation of hydroxyl groups on the surface of SnO_2 particles.

Catalytic tests showed that all TOHCLI and STOHCLI are catalytically active in the conversion of LA to both OLA and ELA but the catalytic performance depends on type of alcohols (Figures 1 and 2). After 5 h, for all TOHCLI samples the esterification to OLA is about 55 % unaffected by Sn amounts (Figure 1). Relatively high catalytic activity of TOHCLI could be ascribed to the presence of high amounts of Lewis acid sites (Table 1). However, although the amounts of Lewis acid sites increase by increasing of the Sn content, the LA conversion rate remains constant suggesting that all acid sites in the TOHCLI are not available for the esterification to OLA. STOHCLI showed significantly higher catalytic activity leading to total conversion of LA. This can be explained by higher acidity of STOHCLI in comparison to TOHCLI suggesting that sulfate groups play an important role in the esterification process.
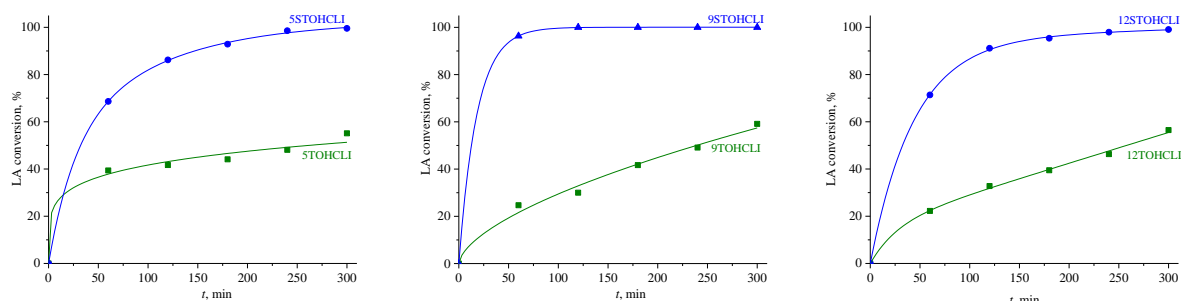

Figure 1. LA esterification with octanol (T=100 °C, LA:octanol=1:7, t=5 h).

Figure 2 shows that the catalytic activity of TOHCLI in the conversion to ELA is significantly lower than in the conversion to OLA and that the Sn content affects the activity. These suggest that the active sites for the esterification with ethanol and octanol mutually differ. STOHCLI samples showed better catalytic performance than TOHCLI ones supporting the role of sulfate groups in the esterification.
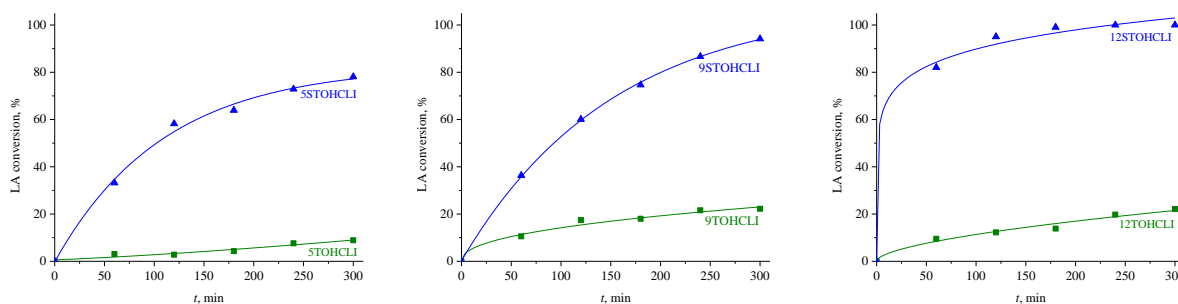

Figure 2. LA esterification with ethanol (T=100 °C, LA:octanol=1:7, t=5 h).

Reusability experiments showed that the catalytic performance slightly changes during recycling. The activity of 9STOHCLI decreased to 86 % in the conversion to OLA and to 66 % in the conversion to ELA. Pore blockage due to coke formation (which was evident from thermal analysis) during the conversion to ELA was found to be responsible for higher deactivation of the catalyst. This result suggests that the esterification with ethanol proceeds not only at the surface but also inside the lattice of the zeolite.
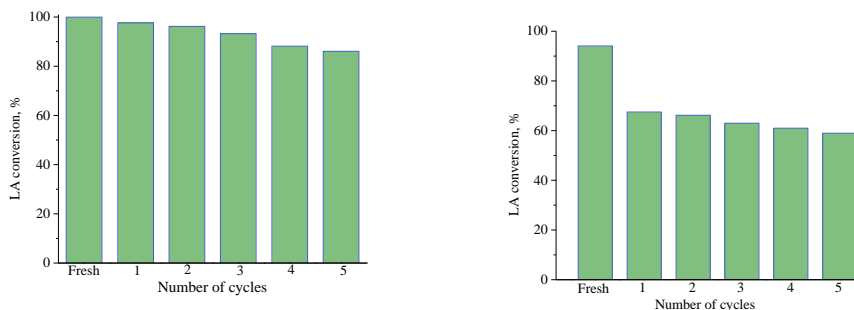
Figure 3. Reusability of the 9STOHCLI in LA esterification with a) octanol and b) ethanol. (T=100 °C, LA:octanol/ethanol ratio=1:7 and t= 5 h in 6 repeated reaction cycles).

CONCLUSION

The results showed that clinoptilolite-rich tuffloaded with SnO_2 or sulfated SnO_2 is catalytically active in the esterification of levulinic acid with octanol and ethanol. Total conversion of levulinic acid to the esters was achived in the presence of catalyst contained 9 wt% of sulfated SnO_2. This study shows that natural clinoptilolite is perspective zeolite for the preparation of a green catalyst for the esterification of levulinic acid.

ACKNOWLEDGEMENT

REFERENCES

[1] A. Démolis, N. Essayem and F. Rataboul, *ACS Sustain. Chem. Eng.,* 2014, **2**, 1338-1352.

[2] S. Dharne and V.V. Bokade, *J. Nat. Gas Chem*., 2011, **20**, 18-24.

[3] M. Popova, A. Szegedi, H. Lazarova, A. Ristić, Y. Kalvachev, G. Atanasova, N. Wilde, N. Novak Tušar and R. Gläser, *Micropor. Mesopor. Mat.,* 2016, **235**, 50-58.

[4] D.R. Fernandes, A.S. Rocha, E.F. Mai, C.J.A. Mota and V. Texeira da Silva, *Appl. Catal. A: Gen.,* 2012, **425-426**, 199-204.

[5] A. Coelho, TOPAS Academic 4.1, Coelho Software, Brisbane, Australia, 2007.

[6] D.W. Ming, J.B. Dixon, *Clay. Clay Miner., 1987*, **35**, 463-468.

[7] J. Pavlovic, M. Popova, R.M. Mihalyi, M. Mazaj, G. Mali, J. Kovač, H. Lazarova, N. Rajic, *Micropor. Mesopor. Mat.,* **279** (2019) 10-18.

[8] H. Matsuhashi, H. Miyazaki, Y. Kawamur, H. Nakamura and K. Arata, *Chem. Mater.,* 2001, **13**, 3038-3042.

[9] M. Sowmiya, A. Sharma, S. Parsodkar, B.G. Mishra, and A. Dubey, *Appl. Catal. A: Gen.,* 2007, **333**, 272-280.