Catalytic transformation of levulinic acid and C6-carbohydrates to γ-valerolactone over Zr- and Sn-containing BEA zeolites obtained by green ultra-fast synthesis

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The depletion of non-renewable carbon resources including petroleum and natural gas intensifies investigations concerning valorisation of lignocellulosic biomass into bio-fuels and value-added chemicals. Multi-stage catalytic transformation of the main components of this biomass, such as cellulose and hemicellulose, allows obtaining γ-valerolactone (GVL). This lactone has potential application as a bio-based solvent in organic reactions, an intermediate in the production of polymers and various chemicals, food additives, bio-fuels and fuel additives. The pathway of cellulose transformation to GVL includes cellulose-to-glucose hydrolysis, the dehydration of glucose to 5-hydroxymethylfurfural, hydrolysis of this aldehyde to levulinic acid and hydrogenation of acid to GVL (Fig. 1) [1]. For the individual stages of cellulose transformation to GVL, the various heterogeneous catalysts have been proposed. The stages up to obtaining levulinic acid are catalyzed by Brønsted acids, while the conversion of levulinic acids may proceeds *via* Meerwein-Ponndorf-Verley (MPV) reduction in the presence of Lewis acids and secondary alcohol as H-donor. Zr- and Sn-containing BEA zeolites are the most active and selective catalysts for the MPV reduction of levulinic acid and its esters to GVL. The high activity of these zeolites is explained by the enhanced surface area, water tolerance of their Lewis acid sites and the ability of Zr- and Sn- sites to coordinate and strongly polarise the carbonyl group of aldehyde, facilitating the transfer of two hydrogen atoms from the alcohol to a carbonyl group.

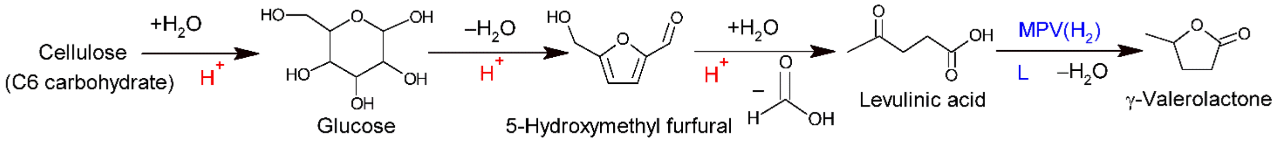

Figure 1

The reaction pathway for obtaining γ-valerolactone from cellulose over Brønsted (H^+) and Lewis (L) catalysts

The analysis of the literature data points to two mains approached used today for the Zr-BEA and Sn-BEA synthesis: 1) post-synthesis modification [2] and 2) direct hydrothermal synthesis [3]. The first approach is rather easy to accomplish, but it results on materials with large amount of defects, which prevent its application in many chemical reactions. The second procedure, based on hydrothermal synthesis leads to formation of crystals without defects. However, this procedure is rather difficult to commercialize at the industrial scale since it requires very long synthesis times and involves harmful reagents (HF). Therefore, new synthetic approaches are needed to overcome the drawbacks of existing procedures. An interesting alternative is steam-assisted crystallization (SAC). This approach allows to reduce synthesis time, use less water and template, produce less waste and increase the yield of the solid phase. Herein we report on the novel method for Zr-BEA, Zr-Al-BEA,Sn-BEA and Sn-Al-BEA synthesis based on modified SAC method and on their application in the conversion of levulinic acid, butyl levulinate and glucose into GVL.

The synthesis of Zr- and Sn-containing BEA zeolites was carried out using a new approach based on the crystallization of a wet precursor gel, which differs from the classical SAC method, in which dry gel and water are physically separated. The molar ratio of starting reagents in the wet precursor was as follows: $1\ SiO_2 : x\ Zr(Sn)O_2 : 0.5\ TEAOH : 0.5\ NH_4F : y\ H_2O$, where x was within 0.005 – 0.008, whereas y was varied within 0.5 – 4.5. The important aspect of the developed procedure was the replacing of harmful HF as a source of fluoride ions by NH_4F.

The kinetics of crystallization at 180 °C showed that highly crystalline Zr-BEA material can be obtained already after 6 hours of crystallization, whereas in the case of Sn-BEA 37 hours was required for full crystallization, which is 25 or 7 times faster than using hydrothermal (HT) method. The crystals of the Zr – and Sn-BEA samples obtained by the SAC method had a bipyramidal octahedron shape, which is characteristic of the BEA materials obtained in a fluoride medium. However, the crystals obtained by novel procedure were smaller (about 4-8 μm) than the crystals of the materials obtained using the HT procedure (about 11 μm).

The crystallization mechanism of Zr- and Sn-BEA in a fluoride medium was investigated using ex-situ and in-situ approaches. It has been established that at the initial stage of gel precursor preparation a solid amorphous hydrogel is formed, which has a micro-mesoporous structure. During heating of the reaction mixture, interaction of R^+ and fluoride ions with the amorphous phase occurs, which is accompained by the formation of complexes of $R^+/Si[O]_4F$ type. These complexes are precursors of crystallization and initiate the formation of zeolite nuclei. The nucleation process is rapid and begins in the early stages with almost no induction period. Further transformations occur through aggregation and densification of nucleus-containing primary structures, which is a slower process. Solid-phase reorganization of the hydrogel determines the kinetics of crystallization and crystal growth.

The number and type of active sites were determined by IR spectroscopy of adsorbed CO in the case of Zr-BEA and by IR spectroscopy of adsorbed pyridine and acetonitrile in the case of Sn-BEA. It has been established that the significant degree of Zr and Sn incorporation is achieved after 120 hours of crystallization.

The active sites of Sn-BEA, obtained by the method developed, were also studied using MAS-NMR-DP-CPMG. The spectra showed the signals of tin atoms belonging to groups I, II and III. Group I corresponds to the crystallographic positions T9, T4 and T3 in the BEA structure (–420, –425 ppm); group II — T1, T2 and T8 (–435, –437 ppm); group III — T7, T5 and T6 (–443, –447 ppm) [4].

The conversion of levulinic acid using 2-pentanol as a solvent has been investigated in the liquid phase at 115 °C under atmospheric pressure and stirring. The initial rate of GVL formation was ~ 1 $mmol_{GVL}/g_{cat}h$ in the case of Zr-Al-BEA. An even higher initial rate of 2.3 $mmol_{GVL}/g_{cat}h$ is achieved over hierarchical Zr-BEA in the conversion of butyl levulinate since this ether does not block the basic framework oxygen of active Zr–O sites, as in the case of levulinic acid.

In conclusion, the novel method of Zr- and Sn- containing BEA zeolites synthesis based on steam assisted crystallization of wet precursor was proposed. The method does not require the separation of water at the bottom of the autoclave and allows for 25 fold reduction of the synthesis time with respect to hydrothermal synthesis in the case of Zr-BEA and 7 fold reduction in the Sn-BEA. Furthermore, it leads to 5 fold increase of the product yield as compared to conventional dry gel conversion method. Finally, the important aspect of the developed procedure is the replacing of harmful HF as a source of fluoride ions by NH_4F. The resulting materials show comparable physicochemical and catalytic properties to the sample synthesized using hydrothermal crystallization.

References

[1] R. Barakov, N. Shcherban, O. Petrov, D.N. Rainer, M. Kubů, J. Čejka, M. Shamzhy, and M. Opanasenko, *Catal. Today*, **426**, 114406 (2024).
[2] P. Dapsens, C. Mondelli, and J. Pérez–Ramírez, Chem. Soc. Rev., **V. 44**, P. 7025-7043 (2015).
[3] A. Yakimov, Y. Kolyagin, S. Tolborg, P. Vennestrøm, and I. Ivanova, New J. Chem., **V. 40**, P. 4367-4374 (2016).
[4] Y. Kolyagin, A. Yakimov, Tolborg S., P. Vennestrøm, and I. Ivanova, J. Phys. Chem. Lett., **V. 9**, P. 3738–3743 (2018).

Aknowledgment

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