Hydrolysis of Cellulose over NbO_x/ZrO_2 Solid Acid Catalysts in flow system

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Cellulose is a main component of renewable plant biomass what makes the polysaccharide a promising alternative to fossil resources for the production of valuable chemicals and fuel components. The presence of crystalline domains in the structure of the cellulose makes it insoluble in water and any organic solvents and prevents depolymerization of cellulose to any desired product. A promising solution seems to be cellulose processing over solid acid catalysts under high temperatures and pressures. Hydrolysis of cellulose produces value-added glucose product. Niobium oxide supported on zirconia (NbO_x/ZrO_2) shows considerable promise as the catalytic system for depolymerization of cellulose [1].

In this work we prepared the samples of $NbOx/ZrO_2$ with 0.9 - 9% content of Nb. Catalysts were characterized by XRD, N_2-adsoption, ICP, UV–vis DRS and tested in hydrolysis of activated microcrystal cellulose at 200 ºC in a flow reactor. The experiment were carried out in pure water without any additives.

In the presence of the catalyst containing 9% Nb, experiments with varying the loading of the catalyst were carried out to determine the optimal substrate-catalyst ratio. It was shown that the highest glucose yields (21%) were obtained with a substrate - catalyst ratio of 5: 1. With a larger value of the substrate - catalyst ratio, the yields were lower, which is associated with an insufficient number of active sites in the reaction system. On the other hand, when the ratio was 1: 1 and 2.5:1 the yields were lower due to catalyzing the rapid deep conversion of the target glucose product in a subcritical aqueous medium.

All the NbO_x/ZrO_2 catalysts were tested in the cellulose depolymerization under optimal conditions. Kinetic curves of glucose accumulation are shown in Figure 1. An analysis of the reaction mixtures by HPLC showed that in the presence of zirconium not doped with niobium oxide, the glucose yield was 20%. However, when using a catalyst containing 0.9% of Nb, the yield of the target product decreased to 13%. With an increase in the amount of the active component, glucose yields again increased to 21 and 26%, in the presence of catalysts containing 2 and 3% of a modifying additive (Fig. 1)

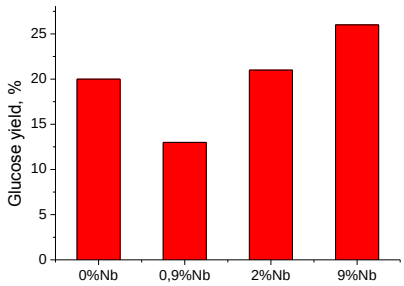

Figure 1. Glucose yield dependence on Nb content

A similar dependence of the catalyst activity on the niobium content was shown in our previous works [1]. A decrease in the activity of the $0.9\%Nb/ZrO_2$ catalyst is associated with the formation on of isolated NbO_4 clusters the ZrO_2 surface. That clusters do not carry acid sites which are active in the process under study. In addition, niobium oxide clusters lead to the isolation of acidic and basic centers of zirconium oxide and to the disappearance of the synergistic effect between them, responsible for the high activity of ZrO_2.

References

[1] Gromov, N.V., Taran, O.P., Semeykina, V.S., et al. Solid acidic $NbOx/ZrO_2$ catalysts for transformation of cellulose to glucose and 5-hydroxymethylfurfural in pure hot water. Catalysis Letters 147 (2017) 1485-1495.

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