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Synthesis and characterization of the catalysts of hydrolytic hydrogenation of lignocellulosic biomass

Lignocellulosic biomass is cheap and renewable feedstock for the production of biofuels and a wide range of platform chemicals. The use of biomass as a source of energy alternative to fossil fuel should lead in the future for the production of fuels and valuable chemical compounds independently on the natural oil and gas reserves. However, biomass conversion usually requires the use of catalyst, which would allow achieving the highest yields of desired products.

Therefore, the aim of my PhD thesis is development of an efficient catalyst for hydrolytic hydrogenation of lignocellulosic biomass towards γ- valerolactone (which can be used as biofuel additive), possessing high stability and resistance to coking.

The first part of my PhD thesis consists of literature review focused on the structure of lignocellulosic biomass and methods of its pre-treatment. In addition the hydrolysis and hydrogenation of lignocellulosic biomass and intermediates formed during its conversion and the role of the catalyst in these processes were discussed.

In the experimental part cellulose pre-treatment methods that were used during the studies, synthesis methods of zirconium oxides, which were chosen as the active phase of Ru catalysts, as well as procedure of the introduction of ruthenium on the zirconia surface were described. Moreover, commercial homogeneous and heterogeneous catalysts used in the experiments and a short description of the analytical techniques used for characterization of investigated materials were presented . The conversion of cellulose to γ-valerolactone was carried out in two stages. The first step was focused on the optimization of the conditions of the hydrolysis of cellulose to levulinic acid and selection of the most effective catalyst of this process. Both heterogeneous and homogeneous catalysts were tested in the mentioned reaction. It was found that the production of levulinic acid in the presence of heterogeneous catalysts is possible, however results in the formation of low

amount of this product. The performed experiments demonstrated that significantly higher yields of levulinic acid were obtained using homogeneous catalysts .

Levulinic acid formed in the first step of the lignocellulosic biomass conversion process was converted to γ-valerolactone using ruthenium catalysts supported on a series of zirconium oxides synthesized by different methods. The analysis of physicochemical properties of Ru/ZrO_2 catalysts allowed to determine the correlation between the activity of the catalysts and their specific surface area and the size of crystallites of active phase. The performed investigations revealed that the highest activity in the hydrolytic hydrogenation of biomass to γ-valerolactone was obtained for the catalyst with relatively small size of Ru crystallites and a large specific surface area, with zirconium oxide possessing tetragonal phase.

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