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Influence of ZrO_2 on catalytic performance of Ru catalyst in hydrolytic hydrogenation of cellulose towards γ-valerolactone

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ABSTRACT

This work is focused on the study of the influence of the surface properties of different zirconia supports on the catalytic performance of ruthenium catalyst in hydrolytic hydrogenation of cellulose towards γ-valerolactone. The surface properties of the synthesized catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature-programmed reduction (TPR) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The reaction products were analyzed by high-performance liquid chromatography (HPLC). The obtained results evidenced that the presence of small ruthenium crystallites supported on the tetragonal zirconia phase was beneficial to achieve the highest γ-valerolactone yield in the studied reaction.

Introduction

Nowadays, chemicals and fuels are mainly produced from non-renewable fossil resources which leads to their fast depletion due to the intensive development of the civilization [1,2]. Taking this into account, lignocellulosic biomass is considered to be a very promising alternative feedstock for the production of bio-based chemicals. Moreover, the production of chemicals from plants generates lower greenhouse gases emission due to consumption of CO_2 during photosynthesis [3–5].

One of the most interesting biomass derived chemical compounds, which gains a special attention is γ-valerolactone (GVL). It can be used for the production of polymers, directly as a solvent or fuel additive. Moreover, it has a great potential to be upgraded to a variety of valuable chemicals, such as 1,4-pentanediol (PD), methyltetrahydrofuran (MTHF), pentanoic acid (PA), or its esters (PE) or fuels additives [6,7]. γ-Valerolactone can be produced from cellulose or

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sugars in several steps (Fig. 1). The first step is hydrolysis of cellulose towards glucose which then via dehydration is converted to hydroxymethylfurfural (HMF) and next to levulinic acid (LA). LA can further be hydrogenated towards GVL using metal catalysts [8].

Different metal catalysts (like Pt, Ni, Au) have been tested in hydrogenation of LA towards GVL, and the materials based on Ru have been identified among the most efficient ones [6,8,9]. Ru was used as well for LA hydrogenation with formic acid (FA) as a hydrogen source [10], the challenge in this reaction was however to limit its activity to side reactions of gaseous products in which Ru is also active [11]. The literature data demonstrated that the process of LA hydrogenation using ruthenium catalysts supported on different materials, such as TiO_2, C, Al_2O_3 or SiO_2 was conducted in a wide range of solvents, such as methanol, ethanol, 1-butanol [12], 1,4-dioxane [7,12], tetrahydrofuran (THF) [13], water [8,12,14] and mixtures: ethanol–water, methanol–water [12] or without any solvent [7,12] in both mild and harsh conditions. Interestingly, the activity of the Ru catalysts strongly depends on the reaction media, so the selection of an appropriate solvent is incredibly important. It was proved in our previous work that Ru catalysts in this case are more active in water than in aprotic organic solvent like THF [13]. It was explained by the fact that the presence of a H-bonded water molecule dramatically reduces the energetic span of the preferred reaction pathway for the hydrogenation of LA, consequently improving the catalytic activity. This behavior can be assigned to oxophilic metals, such as Ru and also Ni or Co [13]. In addition Palkovits et al. noticed that water in the reaction mixture raises an amount of GVL produced in the presence of Ru catalysts and observed that the GVL yield was higher in the presence of water (86%) than in ethanol (61%) as a reaction medium [12]. Promoting effect of water in hydrogenation of LA toward GVL was also described by Tan et al. [15].

Ru catalysts are active not only in the hydrogenation of pure levulinic acid to GVL but also in reaction with real biomass feedstock, although its obtained yields are lower [2,4,16–18]. Galetti et al. [19] conducted two-steps (hydrolysis-hydrogenation) catalytic conversion of Giant Reed to GVL using ruthenium catalysts supported on an active carbon. The yield of GVL was low (16.6%) [19]. Twice higher yield of GVL (31%) was obtained by us in the similar two-steps conversion of biomass (delignified and air-dried pine wood in sheets) towards GVL using Ru/TiO_2 catalysts [8]. Wettstein et al. [20] carried out the conversion of cellulose in biphasic system using Ru–Sn/C catalysts and GVL and water as a solvents, however the GVL yield obtained in this case was lower than that observed in the hydrogenation of pure LA. The researchers pointed out several problems appearing in the conversion of biomass towards GVL for explaining the decrease in the reaction yield [17]. It was demonstrated that in the hydrolysis, a greater number of side products can be formed which may also undergo hydrogenation (e.g. to hydroxymethylfurfural or sugar alcohols). In consequence, it can lead to the production of humins (coke) which can deactivate the catalysts used in the reaction [21]. Moreover, hydrolysis is usually conducted in the presence of mineral acids (such as H_2SO_4) which results in poisoning of the catalysts by sulphur and consequently in the decrease in the GVL yield. It was proved that the activity of ruthenium catalysts can be reduced by the adsorption of sulfur present in the reaction mixture [8]. One of solutions is a neutralization or separation of H_2SO_4 from the mixture containing LA by solvents like sec-butylphenol or alkylphenol [17,22]. A nice alternative consist in the use of GVL as a green solvent. This method not only eliminates the need of the separation of impurities, but also limits the formation of humins [18,20].

An alternative way of the prevention of the reaction yield decrease is the design of proper stable and resistant catalysts for this reaction, which can be done by a support modification. The literature data showed several successful examples in which ZrO_2 has been applied as a support for the metal catalyst [4,23,24]. The research devoted to partial oxidation of methane to synthesis gas exhibited that the addition of ZrO_2 to mesoporous silica shell reduced the formation of carbon deposit [25]. A similar effect was observed in the case of the studies of hydrogen production by CH_4/CO_2 reforming. It was

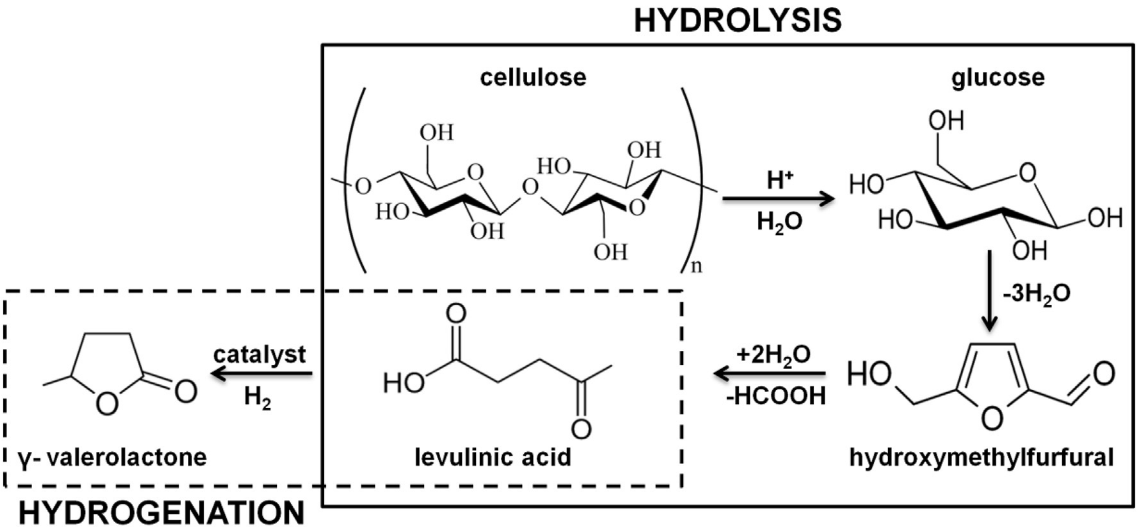

Fig. 1 – Simplified scheme of the hydrolytic hydrogenation of cellulose.

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