

Ni/ZSM-5 AS EFFICIENT CATALYST FOR THE SELECTIVE HYDROGENATION OF LEVULINIC ACID TO γ -VALEROLACTONE IN VAPOR PHASE

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ABSTRACT

In search for efficient and robust catalysts for the continuous vapor-hydrogenation of biomass-derived levulinic acid (LA) to γ -valerolactone (GVL), Ni supported on ZSM-5 zeolites were investigated. This study provides an insight into the correlations between the catalyst properties and catalytic activity in the LA hydrogenation in a packed-bed reactor. The preliminary results show that the acid properties play a role in the product selectivity of the hydrogenation of LA in *iso*-propanol. The GVL formation is favoured by catalysts with a high fraction of Brønsted acid sites in proximity of the Ni active sites.

Key words: vapor-phase hydrogenation, levulinic acid, GVL, Ni/ZSM-5, packed-bed reactor.

INTRODUCTION

Biomass valorization, i.e., transforming abundant carbon-containing resources into high-value chemicals, has been the topic of a large number of studies [1]. Among these, the hydrogenation of biomass-derived levulinic acid (LA) to γ -valerolactone (GVL) has gained increasing attention [2]. GVL is considered as a platform chemical and can be found in a plethora of industrial applications. The conversion of LA into GVL requires both the acid and redox properties. With respect to acid functionality, ZSM-5 zeolites with their intrinsic and tunable acid properties have been used as solid catalysts in many catalytic applications. Additionally, ZSM-5 zeolites also provide high specific surface area to support active metal sites and great (hydro)thermal stability. The latter is especially crucial for continuous heterogeneously-catalyzed processes in vapor phase. Thus, in the current study, catalysts consisting of zeolite ZSM-5 functionalized with Ni are employed in the vapor-phase hydrogenation of LA in a packed-bed reactor. The tunability of the acid properties of ZSM-5 zeolites by varying $n_{\text{Si}}/n_{\text{Al}}$ -ratio allows a systematic investigation of their correlation with the catalytic activity of Ni/ZSM-5 catalysts in the hydrogenation of LA. The obtained findings enable the tailoring of product selectivity and thus a higher yield of the target product (GVL) is obtained while maintaining high productivity. With that in mind, a series of ZSM-5 zeolites with different Si-to-Al molar ratios, i.e., 13, 21 and 28, were synthesized using a „green“ template-free method. The obtained zeolites were impregnated with Ni aiming at various Ni content ($\omega_{\text{Ni}} = 1, 3$ and 5 wt.%). To unveil the correlations between material properties and catalytic activity, the bifunctional Ni/ZSM-5 catalysts were characterized and tested in the vapor-phase hydrogenation of LA in *iso*-propanol.

EXPERIMENTAL

ZSM-5 zeolites with different $n_{\text{Si}}/n_{\text{Al}}$ were prepared using a “green” surfactant-template free method, which was published in a previous work [3]. Subsequently, the obtained zeolites were loaded with Ni via incipient-wetness impregnation using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aiming at different Ni content, i.e., 1, 3 and 5 wt.%. The obtained catalysts are labelled as $x\text{Ni}/\text{ZSM-5-y}$ with x refers to Ni content and y is Si-to-Al molar ratio ($n_{\text{Si}}/n_{\text{Al}}$).

The catalytic experiments were carried out in a Microactivity Reference reactor (PID Eng&Tech). In a typical experiment, 100 mg of catalyst were mixed with 100 mg of glass beads (both having particle size < 100 μ m), which were then sandwiched by quartz wool in a tubular reactor. The catalysts were first heated and treated at 400 °C under a N₂ flow ($Q_{N_2} = 30 \text{ ml min}^{-1}$) for 1 h. Subsequently, the gas stream was switched to H₂ ($Q_{H_2} = 30 \text{ ml min}^{-1}$) for catalyst reduction while holding at 400 °C. The reduction was performed for 2 h. Subsequently, the reactor was cooled down and kept at 250 °C. The reaction solution, i.e., 1 wt.-% LA in *iso*-propanol solvent, was fed at a flow rate of 0.03 g h⁻¹ using a Gilson HPLC pump. The liquid products were collected every hour after reaching the reaction steady state (approximately after 120 min). The liquid products were identified and quantified by a GC-MS (Shimadzu, QP 2010) using a ZebtronTM ZB-5MSi capillary column (60 m x 0.25 mm x 0.25 μ m). The concentrations of the reaction products, i.e., LA, γ -valerolactone (GVL), angelica lactone (AL), *iso*-propyl levulinate (PL), pentanoic acid (PA) and *iso*-propyl pentanoate (PP), were determined using calibration curves of commercial LA, GVL, AL and self-prepared PL, PP via external calibration technique. The relative errors of measured concentrations were below 3% (for LA, GVL, AL and PA) and below 5% (for PL and PP).

RESULTS AND DISCUSSION

A series of ZSM-5 zeolites with different Si-to-Al ratios, i.e., $n_{Si}/n_{Al} = 13, 21$ and 28 (determined by SEM-EDX), were successfully synthesized. All catalysts exhibit the MFI framework structure as confirmed by XRD. In terms of textural properties, a type I isotherm, which is typical for highly microporous ZSM-5 zeolites, was recorded regardless of Si-to-Al ratios and Ni content. Additionally, the N₂ sorption analysis results show that all employed catalysts possess comparable specific surface area (400 m² g⁻¹) and pore width (0.8 nm) despite various Ni content, i.e., $\omega_{Ni} = 0.8, 1.6$ and 3.4 wt.% (determined by SEM-EDX). This suggests a great preservation of the structural and textural properties of Ni/ZSM-5 after the introduction of Ni via incipient-wetness impregnation.

To investigate the catalytic activity, the bifunctional Ni/ZSM-5 catalysts were investigated in the vapor-phase hydrogenation of LA in a fixed-bed reactor under ambient pressure. The hydrogenation of LA into γ -valerolactone (GVL) underwent angelica lactone (AL) formation as suggested by the detection of AL in all catalytic experiments, i.e., $Y_{AL} = 1 - 7\%$, under investigated conditions ($T = 250 \text{ }^\circ\text{C}$, $c_{LA} = 1 \text{ wt.-%}$, $Q_{LA} = 0.03 \text{ g min}^{-1}$ and $Q_{H_2} = 30 \text{ ml min}^{-1}$). In addition to the target product GVL, the detection of *iso*-propyl levulinate (PL) confirms the occurrence of the competitive acid-catalyzed esterification between LA and the solvent *iso*-propanol regardless of the catalyst employed. Furthermore, the hydrogenated products of GVL and PL, i.e., pentanoic acid (PA) and *iso*-propyl pentanoate (PP), respectively, are also present in the products mixture. A proposed reaction pathway is displayed in Figure 1.

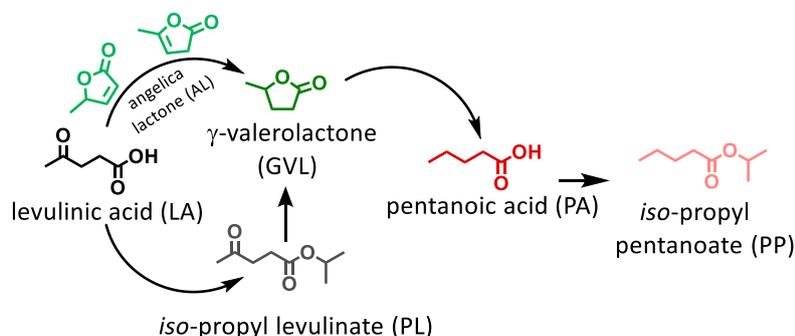


Figure 1. Proposed reaction pathway of the hydrogenation of LA in *iso*-propanol.

The catalytic results are depicted in Figure 2. With increasing the Ni content, a gradual gain in the yield of the target product GVL, i.e., from 2% to 37% and 43%, was obtained due to the higher hydrogenation activity (Figure 2, left). Additionally, no GVL was recorded in the hydrogenation of LA using ZSM-5-21 under identical conditions. These observations confirm the key role of Ni active sites, which is proportional to the hydrogenation activity of the catalysts, in the conversion of LA into GVL.

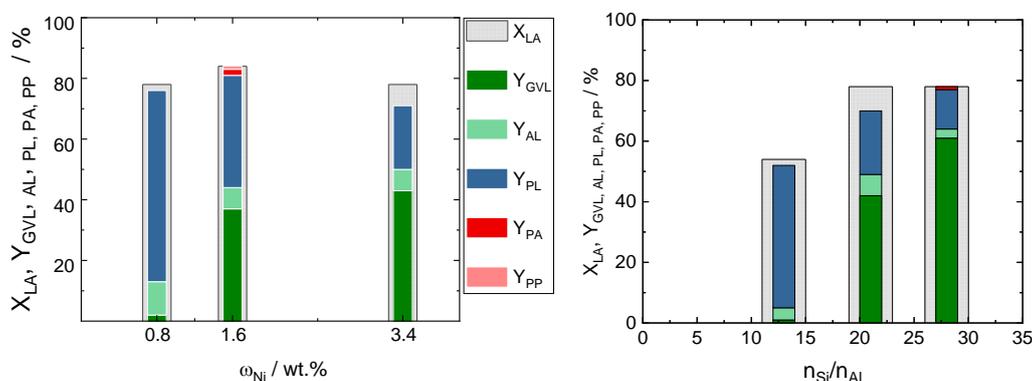


Figure 2. LA conversion (X_{LA}), yield (Y) of products (GVL, AL, PL, PA and PP) over the bifunctional catalysts x -ZSM-5-21 with $x = \omega_{Ni} = 0.8, 1.6$ and 3.4 wt.% (left) or 3.4 wt.% Ni supported on ZSM-5- y with $y = n_{Si}/n_{Al} = 13, 21$ and 28 (right). Reaction conditions: $m_{cat} = 100$ mg, $Q_{H_2} = 30$ ml min^{-1} , $c_{LA} = 1$ wt.-%, $Q_{LA} = 0.03$ g min^{-1} , 250 °C, 4 h.

To investigate the influence of acid properties in the hydrogenation of LA, a series of the bifunctional Ni/ZSM-5 catalysts with comparable Ni content ($\omega_{Ni} = 3.4$ wt.%) and importantly with different Si-to-Al molar ratios, i.e., 13, 21 and 28. Upon increasing the Si-to-Al molar ratios from 13 to 28, both LA conversion and GVL yield increase from 54% to 78% and from 1% to 61%, respectively. In addition to the gradual gain in the GVL formation, the yield of propyl levulinate (PL), the esterification product between LA and i-propanol solvent, decreases from 47% to 21% and further to 13%, respectively. It is noted that GVL can be formed via the hydrogenation of LA and PL via AL and propyl-3-hydroxyvalerate, respectively (Figure 2). The observed increase in the catalytic activity might be associated with the difference in the acid properties of the catalysts. At first, the increase in the hydrogenation activity seems to be associated with the gradual decrease in the acid site density of the catalysts from 518 to 448 and further to 329 $\mu mol\ g^{-1}$ as a result of increasing the Si-to-Al molar ratios from 13 to 21 and to 28, respectively. Further investigation in the acid site types reveals that the increased catalytic activity is proportional with the ratios of Brønsted acid sites-to-Lewis acid sites (n_{BAS}/n_{LAS}), which is 4, 9 and 11, respectively, which were calculated from DRIFTS with pyridine. It is suggested that the combination of surface Ni sites and a large amount of BAS in proximity facilitates the hydrogenation of LA to GVL and even to the further hydrogenated product pentanoic acid (PA). This is in good agreement with a previous study proposed that the LA hydrogenation occurs at the interface between Ni and acid sites of the catalysts [4].

CONCLUSION

The obtained results show that the hydrogenation of levulinic acid (LA) in iso-propanol over the bifunctional Ni/ZSM-5 catalysts entails various reaction pathways. Based on the composition of reaction mixtures, a reaction network was proposed. In addition to the hydrodeoxygenation into γ -valerolactone (GVL), LA also undergoes esterification forming iso-propyl levulinate or/and further hydrogenation of GVL into pentanoic acid. Regarding the

catalysts, Ni active sites are crucial in the hydrogenation of LA into GVL. By tailoring the catalyst properties via $n_{\text{Si}}/n_{\text{Al}}$, the hydrogenation is selectively driven into forming GVL. The hydrogenation of LA occurs at the interface of Ni and acid sites. The highest GVL yield obtained is 61% (LA conversion of 78%) recorded for Ni/ZSM-5 exhibiting the highest Brønsted acid sites-to-Lewis acid sites ratio ($n_{\text{BAS}}/n_{\text{LAS}} = 11$). Further investigation focusing on both the Ni and acid sites of catalysts will be conducted to disclose its relations with the catalytic activity in the vapor-phase hydrogenation of LA.

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