

## HYDROGENATION OF LEVULINIC ACID TO $\gamma$ -VALEROLACTONE ON Ni-MODIFIED ZEOLITE

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### ABSTRACT

The hydrogenation of levulinic acid to  $\gamma$ -valerolactone in vapor-phase is economically more viable route if compared to reaction in liquid-phase. To improve the  $\gamma$ -valerolactone yield in the vapor-phase reaction, the optimization of nickel modified zeolite as bi-functional catalyst (Ni/HZSM-5) was studied. Ni/HZSM-5 materials with fixed Al/Si molar ratio of 0.04 and different nominal Ni/Si molar ratios (from 0.01 to 0.05) were synthesized without the use of organic template and with the most affordable sources of silica and alumina. Materials were characterized by X-ray powder diffraction, SEM-EDX, TEM-EDX, pyridine TPD and DRIFTS, H<sub>2</sub>-TPR, N<sub>2</sub>physisorption and isoelectric point. Increasing the nickel content in the catalysts leads to a progressive decrease of Brønsted acid sites and concomitant increase of Lewis acid sites. When Brønsted acid sites/Lewis acid sites is approaching to 1 and at the same time the amount of NiO reducible active sites is around 80 %, the bi-functional Ni/HZSM-5-3 catalyst (Ni/Al = 0.59) leads to 99 % conversion of levulinic acid and 100 % selectivity to  $\gamma$ -valerolactone at 320 °C. This catalyst also shows stable levulinic acid hydrogenation to  $\gamma$ -valerolactone in 3 reaction cycles conducted at 320 °C.

Keywords: Ni/HZSM-5, vapor-phase hydrogenation, levulinic acid conversion,  $\gamma$ -valerolactone selectivity, biomass valorization.

### INTRODUCTION

Nowadays, global climate change and world energy crisis are among the most concerned problems. These issues are mainly due to the fast industrialization, population growth and increased use of fossil fuels [1]. Replacement or supplementation of fossil fuels with alternative energy sources could help address this problem. Lignocellulosic biomass is a promising inexpensive renewable material that could satisfy society's requirements for chemicals and fuels. Lignocellulosic biomass can be hydrolyzed into a mixture of cellulose, hemicellulose and lignin. Further hydrolysis of the hemicellulose and cellulose leads to the formation of C5 and C6 monosaccharides. Levulinic acid can be derived from lignocellulosics *via* acid-catalyzed hydrolysis processes and can be utilized as a platform molecule for the production of valuable products including biofuels precursors such as  $\gamma$ -valerolactone.  $\gamma$ -valerolactone can be used as a solvent, fuel additive, and intermediate in the production of diverse value-added chemicals [1,2].

In the present study, we describe the application of Nifunctionalized HZSM-5 catalyst for vapor-phase hydrogenation of levulinic acid to  $\gamma$ -valerolactone with 100 % yield, where the catalytic properties of the catalysts are regulated by Ni/Al molar ratio. In this way, the requirement for additional metal to attenuate the acidity of the catalyst was avoided, which makes the synthesis of the catalysts simpler and more economic. A template-free ZSM-5 zeolite was synthesized, which is considered as a green and sustainable process, avoiding the use of any organic structure-directing agents (templates) [3].

## EXPERIMENTAL

*Materials:* sodium aluminate, sodium aqueous glass NaVS3M, sulphuric acid, ammonium sulfate and nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were provided by Sigma Aldrich. Sodium hydroxide was provided by Merck. ZSM-5 crystallization seeds were provided from Zeolyst (CBU2314,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$ ).

*Synthesis:* ZSM-5 was prepared by seed-assisted synthesis following a procedure previously reported [4]. ZSM-5 crystallization seeds (CBU2314, Zeolyst,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23$ ) were dissolved in distilled water (solution A). Sodium aqueous glass (NaVS3M, Silkem,  $\text{Na}_2\text{O} = 8.62\%$ ,  $\text{SiO}_2 = 27.83\%$ ) was added to solution A during stirring at room temperature with the aqueous solution of sodium aluminate (Silkem,  $\gamma(\text{Na}_2\text{O}) = 170.19$  g/L,  $\gamma(\text{Al}_2\text{O}_3) = 148.46$ )—solution B. Aqueous solution of sulphuric acid (Sigma Aldrich, 96 %) was slowly added to the solution B and stirred for 10 min in order to regulate the pH value at 11. Hydrogel was aged for 30 min and then transferred to 1 L reactor (Parr) for crystallization at 180 °C for 24 h during continuous stirring. The obtained product was filtered, washed with water, and dried at 60 °C overnight. Acidic zeolites were prepared by  $\text{NH}_4^+$  exchange. Ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ , Sigma Aldrich,  $\geq 99.0\%$ ), distilled water and zeolite (ZSM-5) were used as the main components in the molar ratio of 1:1:20 and mixed at 30 °C for 2 h. The exchanged product was filtered, washed with distilled water, dried overnight at 105 °C and calcined in air at 500 °C for 2 h. The Ni containing HZSM-5 catalysts were obtained by incipient wetness impregnation method using ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma Aldrich, purity = 99.999 %) with the theoretical molar ratios of Ni/Si = 0.01, 0.03, and 0.05. Finally, the products were calcined in air at 500 °C for 2 h, to obtain the corresponding metal oxide. The products were denoted: Ni/HZSM-5-1 (Ni/Si = 0.01), NiHZSM-5-3 (Ni/Si = 0.03), NiHZSM-5-5 (Ni/Si = 0.05).

## RESULTS AND DISCUSSION

The X-Ray patterns of the catalysts before the reaction are typical for a single crystalline phase with MFI structure. The crystalline structure of HZSM-5 is not affected by deposition of nickel, however, broad diffraction peaks belonging to NiO are detected, indicating on the formation of nanosized particles, located on the surface of zeolite crystals. The crystallite sizes of NiO are calculated using Scherrer's equation based on the selected diffraction peaks of the corresponding XRD pattern and it was found to be 21, 12, and 10 nm for Ni/HZSM-5-5, Ni/HZSM-5-3, and Ni/HZSM-5-1, respectively. No other crystalline phases are detected in the prepared catalysts. XRD patterns of the spent catalysts show the preservation of the ZSM-5 structure and the presence of the metallic Ni crystallites, having from 36 (Ni/HZSM-5-3) to 44 nm (Ni/HZSM-5-1 and Ni/HZSM-5-5) in size.

The measured by EDXS elemental analysis amount of nickel in the Ni/HZSM-5-1 and Ni/HZSM-5-3 materials corresponds approximately to the nominal values (1.18 and 2.22 wt.%), whereas it is significantly lower in the Ni/HZSM-5-5 sample (2.71 wt.%). The modification of HZSM-5 by nickel causes the specific surface area of the catalysts to decrease progressively with the increase of nickel content (from 400 to 345  $\text{m}^2/\text{g}$ ). This is most likely due to the deposition of NiO crystallites on the surface of zeolite crystals, which is in agreement with XRD results. Micropore surface area decreased due to  $\text{Ni}^{2+}$  exchanged Brønsted acid sites in micropores. The redox properties of the catalysts were analyzed with  $\text{H}_2$ -TPR indicating the presence of different reducible nickel containing phases. The TPR curves were deconvoluted into several contributions (bulk NiO,  $\text{Ni}^{2+}$  strongly interacting with the zeolite support and charge compensating  $\text{Ni}^{2+}$  cations), according to the temperature range where they occur, in order to estimate their contribution to the overall amount of  $\text{H}_2$  consumed (Figure 1).

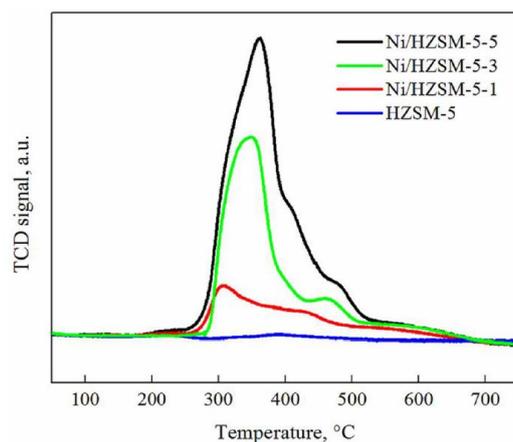


Figure 1. H<sub>2</sub>-TPR profiles of HZSM-5 and Ni/HZSM-5 catalysts containing 1, 2, and 3 weight % of nickel (Ni/HZSM-5-1, Ni/HZSM-5-3, Ni/HZSM-5-5).

It was found that the bulk NiO is the predominant phase in all analyzed materials, accounting for 61–83 % of all nickel. Temperature programmed desorption of the chemisorbed pyridine show that as nickel content increases, the acid site strength decrease. This is due to the fact that the newly formed Lewis acid sites (coordinatively unsaturated Ni<sup>2+</sup>), exhibit intrinsically weaker electrophilic character and consequently lower acid site strength compared to Brønsted acid sites. The sharp pyridine desorption peak recorded over Ni/HZSM-5-3 and Ni/HZSM-5-5 catalysts between 470 and 550 °C could only tentatively be ascribed to pyridine desorption from the Lewis acid sites due to the most abundant NiO phase present in these materials (Figure 2).

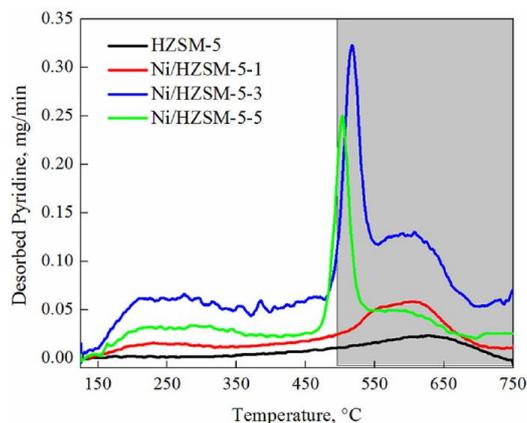


Figure 2. Desorption of pyridine as a function of temperature for Ni/HZSM-5 samples containing 1, 2, and 3 weight % of nickel (Ni/HZSM-5-1, Ni/HZSM-5-3, Ni/HZSM-5-5).

Catalytic results of the Ni/HZSM-5 catalysts in levulinic acid conversion to  $\gamma$ -valerolactone are compiled in Table 1. The only reaction products formed in measurable quantities are  $\gamma$ -hydroxyvaleric acid,  $\alpha$ -angelica lactone and  $\gamma$ -valerolactone. At 250 °C levulinic acid conversions between 53 and 82 % were achieved and  $\gamma$ -hydroxyvaleric acid,  $\alpha$ -angelica lactone and  $\gamma$ -valerolactone were registered products on all the studied samples. The highest levulinic acid conversion was registered for the Ni/HZSM-5-3 sample (82 %). The  $\alpha$ -angelica lactone was the predominant product with yields between 22 and 46 %, indicating that the dominant reaction is dehydration of levulinic acid over acid sites present at lower reaction temperature. The yield of  $\gamma$ -hydroxyvaleric acid was between 12 and 23 % and increased with nickel content. This directly shows that the hydrogenation of levulinic acid becomes increasingly prominent as the hydrogenation function (nickel content) of the catalyst increases.  $\gamma$ -valerolactone yields were relatively low, between 9 and 19 %. The increase of

reaction temperature to 300 °C led to a drastic rise in levulinic acid conversion (51–96 %) and change in product distribution:  $\gamma$ -valerolactone became the most abundant reaction product with yields between 31 and 93 %. The Ni/HZSM-5 catalyzed the reaction cascade all the way to the ultimate and desired reaction product:  $\gamma$ -valerolactone. The yields of  $\gamma$ -hydroxyvaleric and  $\alpha$ -angelica lactone were below 4 %, except for  $\gamma$ -hydroxyvaleric acid on Ni/HZSM-5-1, which remained relatively high at 16 %. No drastic changes in catalysis were observed at 320 °C: The Ni/HZSM-5-3 catalyst showed the highest levulinic acid conversion (99 %) and 100 %  $\gamma$ -valerolactone yield,  $\alpha$ -angelica lactone was produced in yields below 2 % on all catalysts. The catalytic activity of Ni/HZSM-5-1 catalyst was lower compared to Ni/HZSM-5-3 and Ni/HZSM-5-5 and  $\gamma$ -hydroxyvaleric acid yield remained relatively high at 19 %.

Table 1. Catalytic activity and product yields at different reaction temperatures for the studied samples.

T, °C	Catalyst	Yield of GVL, wt. %	Yield of $\gamma$ -hydroxyvaleric acid, wt. %	Yield of $\alpha$ -angelica lactone, wt. %	Conversion, %
250	ZSM-5-1Ni	18.8	11.7	22.5	52.9
	ZSM-5-3Ni	12.4	21.7	38.0	82.2
	ZSM-5-5Ni	9.0	23.4	45.6	77.9
300	ZSM-5-1Ni	31.4	16.5	3.3	51.2
	ZSM-5-3Ni	92.8	3.5	0	96.3
	ZSM-5-5Ni	90.2	3.2	1.3	94.7
320	ZSM-5-1Ni	57.5	19.3	1.5	78.3
	ZSM-5-3Ni	98.6	0	0	98.6
	ZSM-5-5Ni	95.3	1.4	0	96.7

## CONCLUSION

HZSM-5 zeolite was synthesized with Al/Si molar ratio of 0.04 without any organic template and was modified with different Ni content (approx. from 1 to 3 wt. %) by incipient wetness impregnation. Catalytic tests of levulinic acid conversion to  $\gamma$ -valerolactone revealed that the Ni/HZSM-5-3 (Ni/Si = 0.03) catalyst was the most active, and reached 99 % conversion of levulinic acid and 100 % selectivity to  $\gamma$ -valerolactone at 320 °C. Further increase of Ni content in Ni/HZSM-5-5 (Ni/Si = 0.05) does not lead to improved catalytic activity or selectivity. Ni/HZSM-5-3 catalyst shows also stable levulinic hydrogenation to  $\gamma$ -valerolactone in 3 reaction cycles carried out at 320 °C. The highest catalytic activity and stability of the Ni/HZSM-5-3 catalyst is achieved due to: (1) the metallic hydrogenation function and acidic dehydration have to be present simultaneously in the form of nickel metallic clusters and Lewis acid sites, (2) nickel aluminate phase on Brønsted acid sites having synergetic and stability effects on all active sites in the catalysts.

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