ISGC 2019
May 13rd - 17th

N°349 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Biomass conversion

Nickel-based catalysts: influence of chlorine presence and catalyst composition on their activity in the hydrogenation of levulinic acid to gamma-valerolactone.

AUTHORS

Emilia SOSZKA / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO 116, LODZ
Marcin JEDRZEJCZYK / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO 116, LODZ
Izabela RZEZNICKA / SHIBAURA INSTITUTE OF TECHNOLOGY, 3-7-5 TOYOSU, TOKYO
Jacek GRAMS / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO, LODZ
Agnieszka RUPPERT / LODZ UNIVERSITY OF TECHNOLOGY, ZEROMSKIEGO 116, LODZ

PURPOSE OF THE ABSTRACT

Lignocellulosic biomass is a source of many valuable chemicals like g-valerolactone (GVL) which thanks to its properties (low volatility, minimal toxicity, high stability) can be used as a green solvent or biofuel additive1. GVL can be obtain via levulinic acid hydrogenation with formic acid used as a hydrogen source. LA and FA are obtained in equimolar amount in the hydrolysis of cellulose, the challenge is related with the design of the catalysts which can be capable for selective FA decomposition and the same time active for LA hydrogenation.

In this work, various Ni based catalysts were studied in the LA hydrogenation with the FA used as hydrogen source. Influence of several factors like nickel loading (4-30% wt), addition of noble metal as dopant (M=Pd, Pt, Ru, Rh), catalyst composition and various synthesis method on the catalytic activity was investigated.

All Ni-based catalyst were tested in levulinic acid hydrogenation with formic acid as internal hydrogen source. Reactions were performed in liquid phase in a batch reactor at 190°C. Catalyst activity was also tested in independent reactions. Several different surface and bulk (ToF-SIMS, TEM, XPS, TPR, FTIR, XRD) techniques were used to explain the differences in the activity of the tested catalysts.

The activity of all Ni-doped the catalysts was higher in comparison to 4%Ni/g-Al_2O_3 monometallic counterpart. The lowest activity boost was noticed for the Ru-doped system, followed in term of FA conversion by Rh- and Pt-doped nickel based bimetallic catalyst (Table 1). The highest activity was obtained using Ni-Pd. In the following step, the influence of treatment method, composition of Ni:Pd and palladium precursor were investigated. High temperature of treatment promotes the interactions between two metals, improving the activity of catalysts. In the subsequent step the metal ratio was optimized, showing that the highest activity was reached with the system containing Ni:Pd 4:1 ratio. (Table 1).

The type of used precursor also affects the catalyst activity (table 2). The catalyst prepared from the chlorine precursor highly outperformed the one derived from the nitrate. Interestingly, despite the way the chlorine was introduce (from metal precursor or via HCl addition (axHCl)) the catalyst with the chlorine presence showed the highest activity. The presence of chlorine ions facilitates the reduction of Ni and Pd (TPR), and influences the distribution of the metals on the surface of the support (ToF-SIMS, SEM) allowing the highest dispersion of metals on the surface when chlorine precursor was used. Surface analysis using a transmission electron microscope (TEM) equipped with EDX showed the presence of small particles for catalysts prepared from chloride precursor. The analysis of EDX Ni-Pd(Cl)/g-Al_2O_3 revealed that small crystallites of Ni were located in very close proximity of Pd (Figure 1). In contrast to catalyst prepared from nitrate Ni-Pd(N)/g-Al_2O_3 where large Pd particles were noticed. This might be explained by a strong competitive adsorption of chlorine species on the alumina during the impregnation step, which further limits the affinity of the nickel precursor to the surface and prevents the formation of spinel. The positive role of palladium in bimetallic Ni/Pd catalysts is attributed to favorable hydrogen molecule dissociation and hydrogen spillover onto Ni. This, in turn, favors the NiO_x reduction at lower temperatures.

The above studies have explained the influence of many factors, thanks to which it is possible to obtain high catalytic activity in the tested reaction. This activity was related to the synergistic Ni-Pd interaction and to weakening the metal interaction with support, as well as high metal dispersion, which was observed in the case of chlorine-containing catalysts.

Acknowledgment

The authors gratefully acknowledge that this work was financially supported by a grant from the National Center of Science (NCN) in Krakow (Poland)

FIGURES

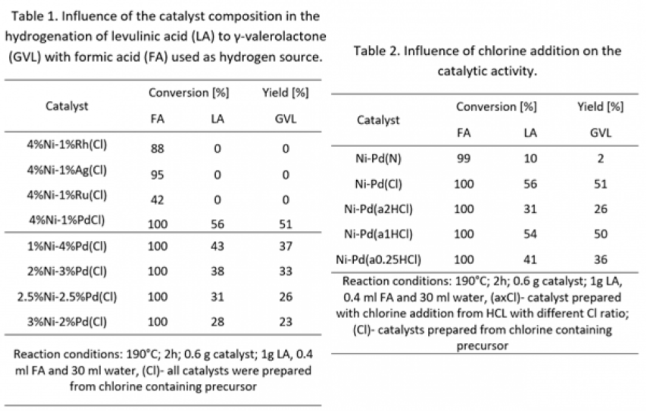


Table 1. Influence of the catalyst composition in the hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) with formic acid (FA) used as hydrogen source.

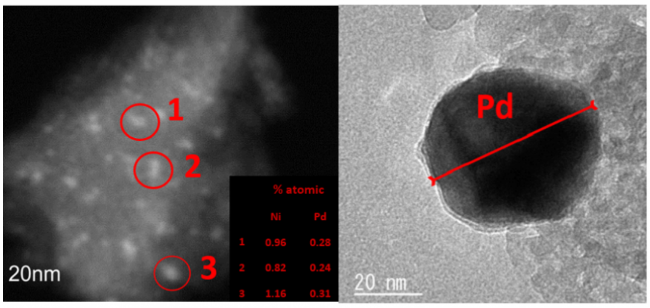
Catalyst	Conversion [%]		Yield [%]
	FA	LA	GVL
4%Ni-1%Rh(Cl)	88	0	0
4%Ni-1%Ag(Cl)	95	0	0
4%Ni-1%Ru(Cl)	42	0	0
4%Ni-1%PdCl)	100	56	51
1%Ni-4%Pd(Cl)	100	43	37
2%Ni-3%Pd(Cl)	100	38	33
2.5%Ni-2.5%Pd(Cl)	100	31	26
3%Ni-2%Pd(Cl)	100	28	23

Reaction conditions: 190°C; 2h; 0.6 g catalyst; 1g LA, 0.4 ml FA and 30 ml water, (Cl)- all catalysts were prepared from chlorine containing precursor

Table 2. Influence of chlorine addition on the catalytic activity.

Catalyst	Conversion [%]		Yield [%]
	FA	LA	GVL
Ni-Pd(N)	99	10	2
Ni-Pd(Cl)	100	56	51
Ni-Pd(a2HCl)	100	31	26
Ni-Pd(a1HCl)	100	54	50
Ni-Pd(a0.25HCl)	100	41	36

Reaction conditions: 190°C; 2h; 0.6 g catalyst; 1g LA, 0.4 ml FA and 30 ml water, (axCl)- catalyst prepared with chlorine addition from HCL with different Cl ratio; (Cl)- catalysts prepared from chlorine containing precursor



	% atomic	
	Ni	Pd
1	0.96	0.28
2	0.82	0.24
3	1.16	0.31

Figure 1. TEM images Ni-Pd(Cl)/γ-Al_2O_3 and Ni-Pd(N)/γ-Al_2O_3

FIGURE 1

Tables

Table 1, Table 2

FIGURE 2

Figure

TEM

KEYWORDS

nickel | bimetallic catalyst | gamma-valerolactone | levulinic acid

---

BIBLIOGRAPHY