Non-transition Metal Oxides Catalyst for Production of Gamma-valerolactone from Methyl Levulinate by Catalytic Transfer Hydrogenation

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Abstract

γ-Valerolactone (GVL) is an organic compound which shows its great potential in energy and polymer application. Normally, transition metal catalysts were employed as an effective catalyst for producing GVL from methyl levulinate (ML). However, non-transition metal oxides were usually used as support material for these catalysts, it provides catalyst to be higher dispersion and catalytic performance. In this study, non-transition metal oxides were directly used as catalyst and shows for interesting result that about 98% of ML conversion and almost 80% of GVL yield were appeared via use γ-Al_2O_3 as catalyst while others including $MgAl_2O_4$ and MgO shows the lower performance, respectively.

KEYWORDS: GVL; Catalytic transfer hydrogenation; Non-transition metal oxides

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Introduction

Today, increasing of fossil fuel consumption provides energy crisis via fuel sources were decrease, it is a reason that renewable energy was interested to study [1]. Among different alternative energy sources, Biomass is the most successful renewable energy source which shows the high potential [2]. Biomass derivatives were applied to many ways for solve the energy problems. One of the interesting biomass application is a high potential liquid which was generated from biomass derivatives named γ-valerolactone.

γ-Valerolactone or GVL is a cyclic structure organic compound which can be versatile chemical for energy and fuel industries [3]. Utilization of GVL for enhance fuel properties were mentioned in many ways such as use as fuel additive or fuel precursor [4 – 6]. Furthermore, it can use as green solvent and starting material of ecofriendly polymer [7]. In addition, it was show for other potentials by renewable low-toxic and biodegradable [8]. GVL can be produced from levulinate ester [9 – 10], a derivative from biomass which normally use in food flavoring and fragrance industries [11 – 12]. From the various alkyl levulinate, methyl levulinate (ML) was discovered to the higher ability for GVL production compared with other alkyl forms including ethyl, 2-propyl and butyl levulinate [13]. Transformation of methyl levulinate to GVL can be conduct by hydrogenation reaction. However, the conventional hydrogenation (CH) which directly use H_2 gas in the process was found that it had a high pressure in the system and it is exothermic. The other one kind, catalytic transfer hydrogenation (CTH) was selected for this study, this reaction is use solvent as hydrogen donor instead of directly press H_2 gas, so it shows more advantage as lower reaction pressure than CH and the system is an endothermic [13 – 14].

One of the important factor for the reaction is a catalyst. Normally, transition metals were a good accepted for using in hydrogenation reaction [15 – 20]. Nevertheless, they are required to complex process for synthesizes and need to dispersed on support material for enhance catalyst ability [21 – 22]. Commonly, non-transition metals were used as support material and discovered that their different acidity was affect catalyst performance [21, 23]. This work is purposed to production of GVL from methyl levulinate by

CTH reaction with easy condition via using of non-transition metal oxides which different acidity and were synthesized by non-complex process as directly catalysts.

Materials and Methods

Catalysts preparation

All starting materials including $Al(NO_3)_2 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were purchased from Ajax Finechem with minimum purity of 98.0% and 99.0%, respectively. γ-Al_2O_3 and MgO were obtained by calcination of the nitrate precursors following them species in muffle furnace at 800 ℃ for 5 h, composite catalyst $MgAl_2O_4$ was synthesized via mix of both starting materials in molar ratio of 1:1 and calcined in the same condition.

$$Conversion \ (\%) = \left(\frac{Number \ of \ mole \ of \ consumed \ methyl \ levulinate}{Number \ of \ mole \ of \ initial \ methyl \ levulinate} \right) \times 100 \qquad (1)$$

$$Yield \ (\%) = \left(\frac{Number \ of \ mole \ of \ GVL}{Theoretical \ number \ of \ mole \ of \ GVL} \right) \times 100 \qquad (2)$$

Catalysts characterization

Surface area and pore properties of all catalysts were observed by surface area and pore size analyzer (NOVA 2000e, Quantachrome instruments, USA), all samples were analyzed at –196 ℃. They were degassed at 250 ℃ for 4 h before analyze process. XRD pattern of catalysts were observed by X-ray diffractometer (D8-Advance, Bruker, USA) with handling 40 kV and 40 mA of Cu K_α radiation over 2θ in the range of 10º – 80º and step size of operation is 0.02º / s with 0.5 s of step time, crystallite size of catalysts were calculated by Scherrer equation. Scanning electron microscope (SU8030, Hitachi, Japan) was using to study of catalysts morphology with use 40 kV and 7 μA, all samples were coated by gold on their surface.

Results and Discussion

Catalytic result

Catalytic performance of all catalysts were shown in Fig.1. The highest of ML conversion and GVL yield about 98% and 80%, respectively were obtained by using γ-Al_2O_3 as catalyst. In contrast, MgO show the lowest catalytic activity via provide ML conversion around 21% and GVL

After catalyst were cooled down, they were ground by mortar and kept in dry cabinet.

Catalytic evaluation

All reactions were proceeded in 130 ml stainless steel batch reactor. 0.58 ml of methyl levulinate was using as feedstock and 24 ml of 2-PrOH was employed to be a hydrogen donor. 1 g of catalyst were consumed for the reaction via the catalyzing process (200 ℃ for 3 h). The reaction was stopped by suddenly quenched in an ice bath. All products were collected and analyzed by gas-chromatography with flame ionization detector (GC-2010 plus, Shimadzu, Japan). The conversion of ML and yield of GVL can be calculated following these equations.

yield less than 3%. It is noteworthy that the composite catalyst $MgAl_2O_4$ was shows for moderate catalytic performance by gave almost 90% of ML conversion and GVL yield close to 60%. The important role which can be explain to this effect is an acidity of catalyst. Lewis acid sites which contained on γ-Al_2O_3 surface [10, 15, 24] has a great potential for GVL production by CTH process [10, 15, 25] while MgO show the lower capability in this reaction [26].
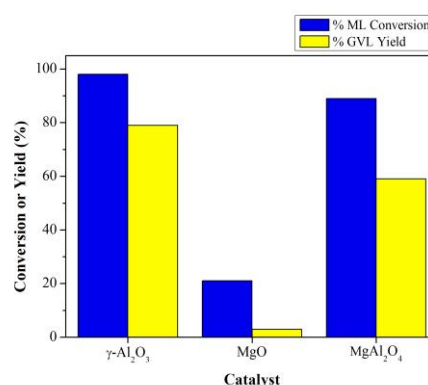

Fig. 1 Catalytic performance of non-transition metal oxide catalysts: 2-PrOH as hydrogen sources, 200 ℃ of reaction temperature, 3 hr of reaction time, 0.63 g of ML loading, 1.00 g of catalyst loading, atmosphere pressure.

Catalyst characterization
Surface area and pore properties of catalysts

The specific surface area and pore properties of all catalysts were offered in Table 1. This result shows that γ-Al_2O_3 is have the highest surface area and following by $MgAl_2O_4$ and MgO, respectively. Complied with the catalytic result, existence of MgO in the structure of composite catalyst $MgAl_2O_4$ makes the surface area of this catalyst decrease which was compared with γ-Al_2O_3. This property is a one of important factor which affect the catalytic performance of catalyst. However, other properties including pore volume and pore size are not significantly different.

Table 1 Surface area and pore properties of non-transition metal oxide catalysts.

Catalyst	Surface area (m^2 g^{-1})	Average pore volume (cc g^{-1})	Average pore diameter (nm)
γ-Al_2O_3	~ 96	< 1	~ 4
MgO	~ 2	< 1	~ 3
$MgAl_2O_4$	~ 70	< 1	~ 4

XRD pattern of catalysts

XRD pattern of γ-Al_2O_3 catalyst was shown in Fig. 2. This catalyst has a cubic structure. Their broad peaks and quite a lot of the noise can be told that this catalyst is have the low crystallinity by agreeable with crystallization result of the whole system via indicate for 59% of amorphous and 41% of crystallinity.
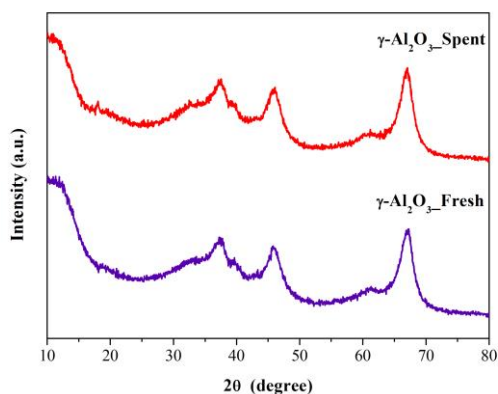

Fig. 2 XRD patterns of fresh and spent γ-Al_2O_3 catalyst.

However, the crystallite size of this catalyst is very small with about 5 nm. Contrast with MgO, a base catalyst which has a likewise cubic structure was shown sharp peaks by its XRD result in Fig. 3. This catalyst was had the largest crystallite size about 50 nm and show the highest crystallinity of the whole system by indicate for 93% of crystallinity and 7% of amorphous. Interestingly, XRD result of composite catalyst $MgAl_2O_4$ which was presented in Fig. 4 show 2 different phases and the both of them have a cubic structure. The pure MgO phase peaks were still presented at the 2θ of 42.9° and 62.3° which might because of normally synthesis of the completed $MgAl_2O_4$ is require to higher temperature [26 – 28].
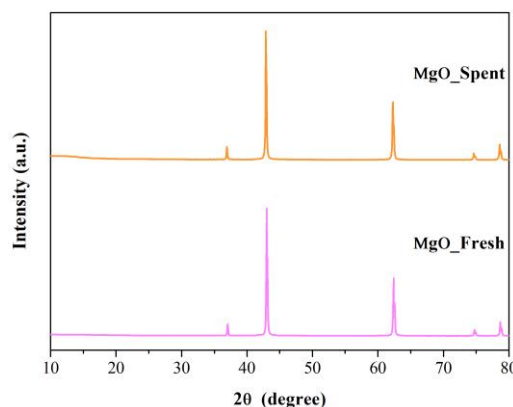

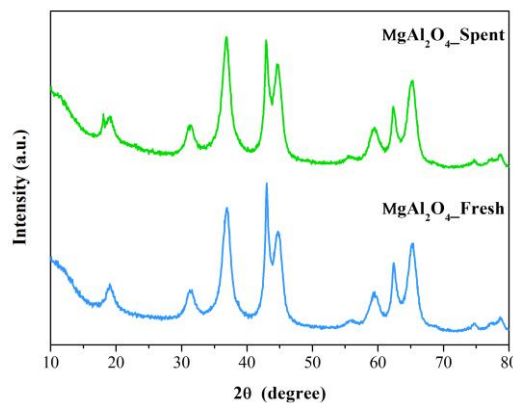**Fig. 3** XRD patterns of fresh and spent MgO catalyst.

Fig. 4 XRD patterns of fresh and spent $MgAl_2O_4$ catalyst.

Morphology of catalysts

SEM images of γ-Al$_2$O$_3$, MgO and MgAl$_2$O$_4$ catalysts were shown in Fig. 5(a – c), respectively. The morphology of γ-Al$_2$O$_3$ was demonstrated that it was be the large particles which about 13 μm and its shape is asymmetric. The particle size of MgO catalyst is very small which about 1 μm and its morphology is look like a dispersion of little spherical shape particles. Composite catalyst MgAl$_2$O$_4$ was shown to the morphology which can be related with XRD result, it was observed to the 2 different clusters. The small fluffy spherical shape of MgO particles were presented on the large particles of MgAl$_2$O$_4$, their particle sizes is about 2 μm and 12 μm, respectively. It can be confirmed that the remaining of MgO is a result of using of low temperature for synthesis this catalyst.
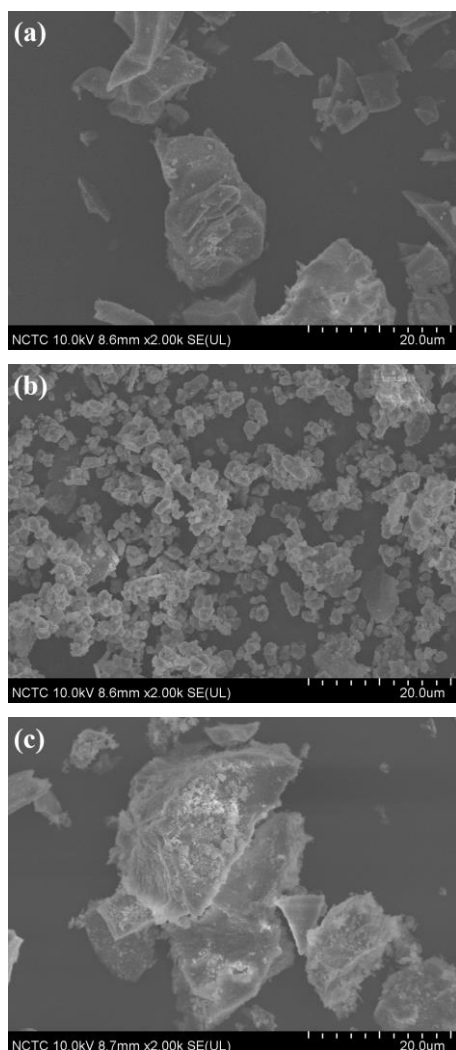

Fig. 5 SEM images of all catalysts. (a) γ-Al$_2$O$_3$, (b) MgO, and (c) MgAl$_2$O$_4$.

Conclusion

The acidity and surface area have effect to catalysts behavior. The highest of ML conversion and GVL yield were obtained by using γ-Al$_2$O$_3$ as catalyst while MgO which is base and have the least surface area shows the lowest catalytic performance for this reaction. Furthermore, crystallite size of catalyst is might be affect catalyst activity. In addition, Mg species were act to interrupt of Al performance which was proved in a case of using MgAl$_2$O$_4$ as catalyst. However, all catalysts were the highly of crystal structure stabilities.

Acknowledgements

References

[1] D.M. Alonso, S.G. Wettsteinb, J.A. Dumesic, Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass, Green Chem. 15 (2013) 584 – 595.

[2] D.M. Alonso, S.G. Wettsteinb, J.A. Dumesic, Bimetallic catalysts for upgrading of biomass to fuels and chemicals, Chem. Soc. Rev. 41 (2012) 8075 – 8098.

[3] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Catalytic conversion of biomass to biofuels, Green Chem. 12 (2010) 1493 – 1513.

[4] I.T. Horváth, H. Mehdi, V. Faʹbos, L. Boda, L.T. Mika, γ-Valerolactone-a sustainable liquid for energy and carbon-based chemicals, Green Chem. 10 (2008) 238 – 242.

[5] Y. Zhao, Y. Fu, Q.X. Guo, Production of aromatic hydrocarbons through catalytic pyrolysis of γ-valerolactone from biomass, Bioresour. Technol. 114 (2012) 740 – 744.

[6] J.Q. Bond, D.M. Alonso, D. Wang, R.M. West, J.A. Dumesic, Integrated catalytic conversion of γ-valerolactone to liquid alkenes for transportation fuels, Science. 327 (2010) 1110 – 1114.

[7] C. Mochamad, Levulinic acid as a renewable source for novel polymers, Ph.D. Mathematics and Natural Sciences, University of Groningen, Groningen, 2012.

[8] D. Fegyverneki, L. Orha, G. Láng, I.T. Horváth, Gamma-valerolactone-based solvents, Tetrahedron. 66 (2010) 1078 − 1081.

[9] Z. Yang, Y.B. Huang, Q.X. Guo, Y. Fu, RANEY® Ni catalyzed transfer hydrogenation of levulinate esters to γ-valerolactone at room temperature, Chem. Commun. 49 (2013) 5328 − 5330

[10] J. He, H. Li, Y.M. Lu, Y.X. Liu, Z.B. Wu, D.Y. Hu, S. Yang, Cascade catalytic transfer hydrogenation cyclization of ethyl levulinate to γ−valerolactone with Al-Zr mixed oxides, Appl. Catal. A Gen. 510 (2016) 11 − 19.

[11] D. R. Fernandes, A.S. Rocha, E.F. Mai, C.J.A. Mota, V. Teixeira Da Silva, Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts, Appl. Catal. A Gen. 425 − 426 (2012) 199 − 204.

[12] K.C. Maheria, J. Kozinski, A. Dalai, Esterification of levulinic acid to n-butyl levulinate over various acidic zeolites, Catal. Letters. 143 (2013) 1220 − 1225.

[13] J. Geboers, X. Wang, A.B. De Carvalho, R. Rinaldi, Densification of biorefinery schemes by H-transfer with Raney Ni and 2-propanol: A case study of a potential avenue for valorization of alkyl levulinates to alkyl γ-hydroxypentanoates and γ-valerolactone, J. Mol. Catal. A Chem. 388 − 389 (2014) 106 − 115.

[14] E. Buckley, E.F.G. Herington, Equilibria in some secondary alcohol + hydrogen + ketone systems, Trans. Faraday. Soc. 61 (1965) 1618 − 1625.

[15] B. Putrakumar, N. Nagaraju, V.P. Kumar, K.V.R. Chary, Hydrogenation of levulinic acid to γ-valerolactone over copper catalysts supported on γ-Al$_2$O$_3$, Catal. Today. 250 (2015) 209 − 217.

[16] K. Yan, A. Chen, Efficient hydrogenation of biomass-derived furfural and levulinic acid on the facilely synthesized noble-metal-free Cu-Cr catalyst, Energy. 58 (2013) 357 − 363.

[17] K. Yan, A. Chen, Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu-Fe catalyst, Fuel. 115 (2014) 101 − 108.

[18] I. Obregón, E. Corro, U. Izquierdo, J. Requies, P.L. Arias, Levulinic acid hydrogenolysis on Al$_2$O$_3$-based Ni-Cu bimetallic catalysts, Chinese J. Catal. 35 (2014) 656 − 662.

[19] X. Long, P. Sun, Z. Li, R. Lang, C. Xia, F. Li, Magnetic Co/Al$_2$O$_3$ catalyst derived from hydrotalcite for hydrogenation of levulinic acid to γ-valerolactone, Cuihua Xuebao/Chinese J. Catal. 36 (2015) 1512 − 1518.

[20] K. Hengst, M. Schubert, H.W.P. Carvalho, C. Lu, W. Kleist, J.D. Grunwaldt, Synthesis of γ-valerolactone by hydrogenation of levulinic acid over supported nickel catalysts, Appl. Catal. A Gen. 502 (2015) 18 − 26.

[21] F. Dong, Y. Zhu, H. Zheng, Y. Zhu, X. Li, Y. Li, Cr-free Cu-catalysts for the selective hydrogenation of biomass-derived furfural to 2-methylfuran: The synergistic effect of metal and acid sites, J. Mol. Catal. A Chem. 398 (2015) 140 − 148.

[22] O.A. Abdelrahman, H.Y. Luo, A. Heyden, Y. Román-Leshkov, J.Q. Bond, Toward rational design of stable, supported metal catalysts for aqueous-phase processing: Insights from the hydrogenation of levulinic acid, J. Catal. 329 (2015) 10 − 21.

[23] A. Piskun, J. Winkelman, Z. Tang, H. Heeres, Support Screening Studies on the Hydrogenation of Levulinic Acid to γ-Valerolactone in Water Using Ru Catalysts, Catalysts. 6 (2016) 131.

[24] R. Feng, S. Liu, P. Bai, K. Qiao, Y. Wang, H.A. Al-Megren, M.J. Rood, Z. Yan, Preparation and Characterization of γ-Al$_2$O$_3$ with Rich Brønsted Acid Sites and Its Application in the Fluid Catalytic Cracking Process, J. Phys. Chem. C. 118 (2014) 6226 − 6234.

[25] V.V. Kumar, G. Naresh, M. Sudhakar, J. Tardio, S.K. Bhargava, A. Venugopal, Role of Brønsted and Lewis acid sites on Ni/TiO catalyst for vapour phase hydrogenation of levulinic acid: Kinetic and mechanistic study, Appl. Catal. A Gen. 505 (2015) 217 − 223.

[26] Y. Kuwahara, W. Kaburagi, T. Fujitani, Catalytic transfer hydrogenation of levulinate esters to γ-valerolactone over supported ruthenium hydroxide catalysts, RSC Adv. 4 (2014) 45848 − 45855.

[27] V.K. Singh, R.K. Sinha, Low temperature synthesis of spinel (MgAl$_2$O$_4$), Mater. Lett. 31 (1997) 281 − 285.

[28] T. Shiono, K. Shiono, K. Miyamoto, G. Pezzotti, Synthesis and characterization of MgAl$_2$O$_4$ spinel precursor from a heterogeneous alkoxide solution containing fine MgO powder, J. Am. Ceram. Soc. 83 (2000) 235 − 237.

[29] S. Zhang, D.D. Jayaseelan, G. Bhattacharya, W. E. Lee, Molten salt synthesis of magnesium aluminate (MgAl$_2$O$_4$) spinel powder, J. Am. Ceram. Soc. 89 (2006) 1724 − 1726.

[30] K. Yan, T. Lafleur, C. Jarvis, G. Wu, Clean and selective production of γ-valerolactone from biomass-derived levulinic acid catalyzed by recyclable Pd nanoparticle catalyst, J. Clean. 72 (2014) 230 − 232.