

Utilization of Ni-based Bimetal Oxide Catalysts for the Synthesis of γ -valerolactone via Catalytic Transfer Hydrogenation

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Abstract— γ -Valerolactone (GVL) is an organic compound that shows its great potential in the energy and polymer industries. Previously, Raney-nickel was employed as an effective catalyst for producing GVL from various types of levulinate esters. However, the high temperature required for the synthesis of Raney-nickel (about 1000 °C) and its complex pretreatment and storage steps are the main drawbacks of this catalyst. In this study, GVL can be produced via catalytic transfer hydrogenation from methyl levulinate on Ni-based bimetallic oxide catalysts which are used instead Raney-nickel. These bimetallic oxide catalysts are prepared at lower temperatures and do not require pretreatment before their use. Among different bimetallic oxide systems, nickel-copper oxide catalyst shows the best catalytic performance with 100% methyl levulinate conversion and more than 95% GVL yield. The study of the influences of the catalyst-supporting material indicates that the supporting materials significantly affect to catalytic behavior of nickel-copper oxide catalysts which can maintain the catalytic ability although the catalyst content was reduced. Nevertheless, all supporting materials includes Al₂O₃, SiO₂, and MgO affect the similar ability of nickel-copper oxide catalysts even though the surface area of a supported catalyst were significantly different according to SEM results.

Keywords—GVL, methyl levulinate, catalytic transfer hydrogenation, bimetallic oxide catalysts

I. INTRODUCTION

Nowadays, energy and fuel issues are currently a major problem due to the demand for large amounts of fuel for living and economy. However, because of the limited availability of fuel, which is in direct conflict with the growing demand for energy, the shortage of energy in the near future can have a major impact. The energy sources that are used today are of two types. The first type is the conventional energy source, which is the energy derived from the natural accumulation of organic matter such as petroleum, coal, and natural gas. This type of energy source is the main source that has been used from the past to the present. As a result of this use, the amount of these sources is gradually reduced and may be out of stock soon. The second type of energy source is renewable energy, which is energy from natural sources for example hydropower, wind power, solar energy, geothermal energy, and biomass. Among all the renewable energies mentioned above, Biomass is considered to be a powerful and attractive renewable energy source. It can be applied to a variety of applications. Moreover, it can be produced consistently, in large quantities, and cheaply.

γ -Valerolactone (GVL) is an organic chemical derived

from biomass that can be applied to the energy industry. It can be consumed to enhance the properties of fuel for example used as an additive in fuel to be enlarged octane booster and combustion performance such as filled-into gasoline replaced ethanol [1], transformation of GVL was getting a derivative compound which has properties like gasoline, diesel, and jet fuel [2, 3]. Moreover, it can be used as a starting material for the production of eco-friendly polymers [4] and applied as a green solvent which biodegradable, nontoxic, and renewable [5]. Levulinate ester is a starting material for GVL production. It is a derivative of biomass which is normally used in the food and perfume industries [6, 7]. In this study, Methyl Levulinate (ML) was selected as a precursor for GVL production from various types of levulinate esters. GVL can be obtained by hydrogenation reaction which the Catalytic Transfer Hydrogenation (CTH) process was selected to replace conventional hydrogenation which demands to press H₂ gas and be a high exothermic reaction [8]. CTH uses solvent as proton donors and is a lower exothermic reaction. Raney nickel was required as a catalyst in this reaction in the other past study. Although it gives high performance to catalytic activity it requires a high temperature for synthesis (about 1000 °C) and must be kept in solvent to maintain performance [9]. Ni-based bimetal oxide catalysts were studied to replace Raney-nickel. It uses lower calcination temperatures for synthesis such as Nickel-promoted copper-silica nanocomposite catalysts [10] but the catalysts in this research are many take time and have a complex process for catalyst synthesis. The purpose of this study is to synthesize Ni-based bimetal oxide catalysts at low temperatures and easy conditions which contain the high performance for GVL production, moreover, this research also needs to study the effect of support materials on the properties and catalytic behavior of catalysts.

II. MATERIALS AND METHODS

A. Synthesis of Bimetal Oxide Catalysts

Nitrates salt of Ni, Cu, Co, Cr, and Fe were mixed into ceramic crucibles. Then, DI water was filled and blended for harmonization. The mixtures were calcined in a muffle furnace at 700 °C. An effect of support materials (Al₂O₃, SiO₂, and MgO) on catalysts was studied by loading the catalyst into support materials for about 50% by weight and DI water was filled for blending. All catalysts were calcined for 5

hours and cooled down overnight. Finally, all catalysts were milled and kept in a dry cabinet.

B. Catalytic Test

2-PrOH, ML, and catalyst were filled into an autoclave reactor and the magnetic bar for stir. The reaction was run at 200 °C for 3 hours. Samples were collected every hour for 3 hours and analyzed by Gas chromatography with a mass spectrometer (GCMS-QP 2010 Ultra, SHIMADZU) and study gasses product by micro-GC (CP4900, Agilent Technologies).

C. Characterization

The H₂ temperature-programmed reduction technique (ChemBET Pulsar, Quantachrome INSTRUMENTS) was performed to study the reduction profile of Ni-based bimetal oxide catalyst. The X-ray diffractogram of all catalysts were analyzed to obtain the crystalline properties via an X-ray diffractometer (D8- Advance, Bruker). Then the morphology was diagnosed by scanning electron microscope (S3400N, Hitachi). Finally, a surface area and pore size analyzer (2000e, NOVA) was used for the study of surface area and pore properties of catalysts.

III. RESULT AND DISCUSSION

The catalytic potential of Ni-based bimetal oxide catalysts was presented in Fig. 1(a). NiCuO presented the highest catalytic ability by performing 100% of ML conversion and over 95% of GVL yield. This result corresponds to reaction pressure results in Fig. 1(b). The reaction using the NiCuO catalyst provides the highest pressure in the reaction at about 40 bar while other catalysts including NiCoO, NiCrO, and NiFeO allow a lower pressure at about 25 bar in the reaction, the pressure is from H₂ gas which is observed by micro-GC. The abovementioned result indicates that NiCuO was outstanding affects the releasing of H₂ atoms from 2-propanol and these H₂ gases were consumed in the reaction which was the important process in the hydrogenation reaction for GVL production from ML. Normally pure NiO and CuO lack catalytic performance in this reaction, but bimetal NiCuO catalysts have good catalytic efficiency. This phenomenon can be described as the hydrogen spillover effect which was promoted by Cu species led to a high amount of hydrogen atom extraction from 2-propanol and encouraged the reduction of the NiO phase to an active Ni metal phase, simultaneously in a catalytic activity [11]. According to the H₂ TPR profile of all Ni-based bimetal oxide catalysts in Fig. 2, the lowest reduction peak appeared in the case of the NiCuO catalyst. The front large peak (centered about 400 °C) indicated the reduction profile of the CuO phase in the catalyst content while the small peak (centered about 440 °C) that reduced at the higher temperature was related to the NiO phase. In the other catalysts includes NiCoO, NiCrO, and NiFeO, the above phenomenon can't be observed. The reduction peak of NiCoO and NiFeO were started at a higher temperature (centered about 440 °C and 480 °C, respectively) which made it predictable that the hydrogen spillover effect was not happening while the reaction was performed. Furthermore, although the center of NiCrO's first peaks was observed at a similar temperature to NiCuO, the reduction content was significantly lower which makes it possible to foresee that no

hydrogen spillover effect will occur as well [12].

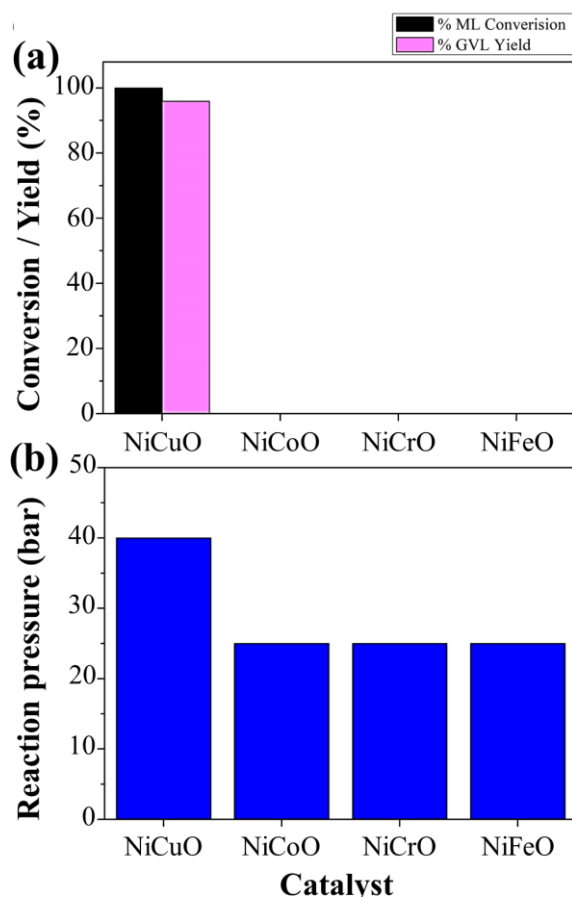


Fig. 1. Potential of bimetal oxide catalysts; (a) catalytic performance, (b) reaction pressure.

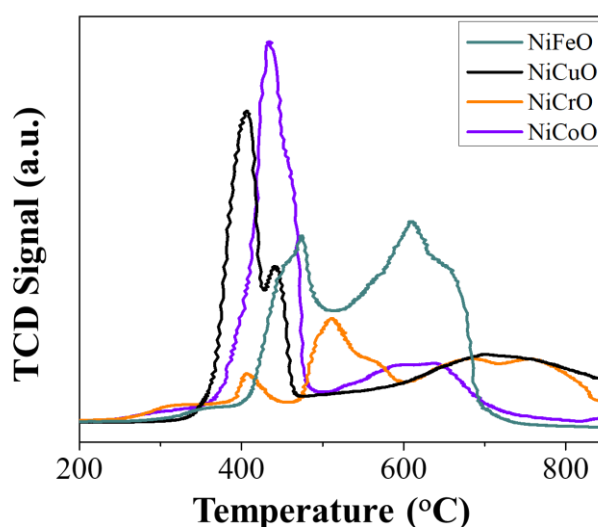


Fig. 2. H₂ TPR profile of Ni-based bimetal oxide catalysts.

The bimetal form of nickel-copper oxide represented new phases as shown in Fig. 3(a) which show better catalytic performance toward catalytic transfer hydrogenation reaction of ML to GVL compared to their host metal oxides which show their pure phase in Fig. 3(b). These new phases contain the same crystal structure of FCC and monoclinic as the nickel oxide-rich phase and copper oxide-rich phase, respectively.

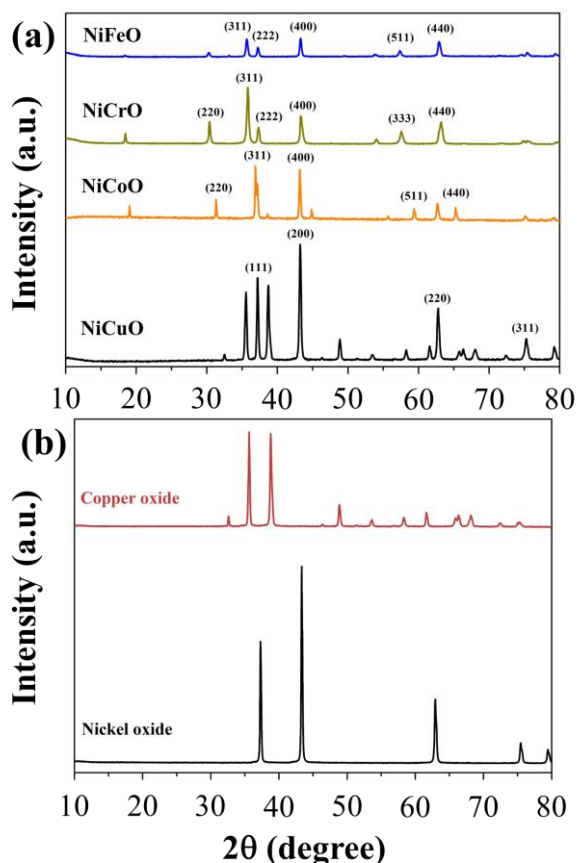


Fig. 3. XRD pattern of catalysts; (a) bimetal oxide catalysts, (b) pure nickel oxide and copper oxide.

The study of support material found that NiCuO dispersed on Al_2O_3 has the highest performance by giving 100% of ML conversion and about 95% of GVL yield as shown in Fig. 4(a). Catalysts supported by MgO and SiO_2 gave the catalytic performance decreased, respectively. Although the content of NiCuO in the total catalyst amounts was decreased by 50% by weight compared with NiCuO catalyst without support materials but the performance of catalysts is better than or as same as for pure NiCuO catalyst, so this was demonstrated that support materials provide a high performance of catalyst although pure catalyst contents were decreased. Fig. 4(b) presents the reaction pressure of NiCuO on support materials, this result shows NiCuO on Al_2O_3 furnishes the most H_2 pressure at about 40 bar while other support materials provide a lower at about 35 bar.

The morphology of all Ni-based bimetal oxide catalysts supported on the various support materials is shown in Fig. 5. With the magnification of 5,000x. An Al_2O_3 affects the high dispersion of bimetal oxide particles on the surface by its granular shape can be seen in the grain obviously and affected the most dispersion of NiCuO catalyst compared to other support materials as shown in Fig. 5(a) which resulted in the highest specific surface area. Furthermore, the Lewis acidity sites of Al_2O_3 led to the great potential for generating H_2 gas from 2-propanol to consume in the reaction.

MgO support material results in a catalyst to fluffy-like and had low dispersion by all particles were gathered in a group which presented in Fig. 5(b). Although the NiCuO catalyst on SiO_2 support material shows a granular shape and can see the evident grain, it had low dispersion which is the form of a grouping of catalyst particles as shown in Fig. 5(c).

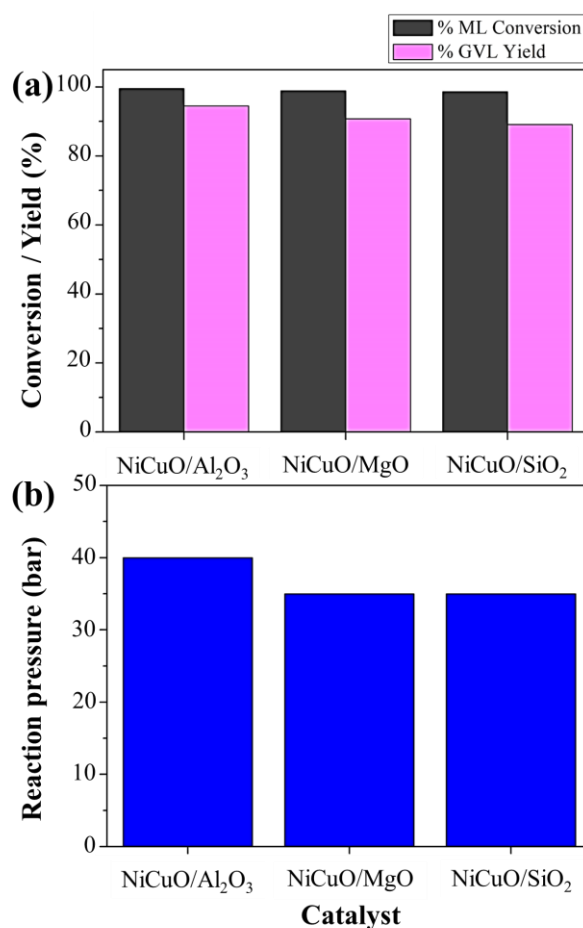


Fig. 4. Potential of bimetal oxide catalysts which synthesized on various support materials; (a) catalytic performance, (b) reaction pressure.

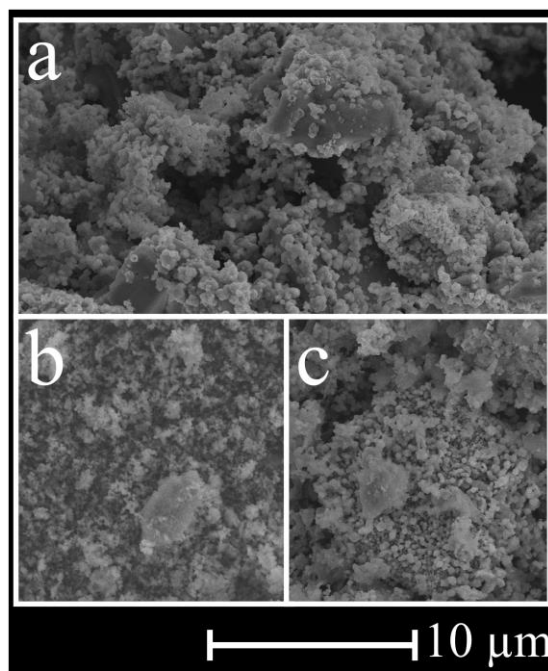


Fig. 5. SEM image of bimetal oxide catalysts which synthesized on various support materials; (a) Al_2O_3 , (b) MgO, and (c) SiO_2 .

Surprisingly, although Al_2O_3 provides the outstanding higher specific surface area of the catalyst compared to other support materials as presented in Table 1. and the greatest

catalytic ability was obtained, the catalytic behaviors of NiCuO on MgO and SiO₂ were not significantly worse.

Table 1. Surface area of catalysts on different support materials

Catalyst	Surface area (m ² ·g ⁻¹)
NiCuO/Al ₂ O ₃	72
NiCuO/MgO	6
NiCuO/SiO ₂	N/A

IV. CONCLUSION

Species of Ni-based bimetal oxide catalysts affect the catalytic activity of catalytic transfer hydrogenation reaction for the production of GVL from methyl levulinate. NiCuO is the best catalyst, it had the most appropriate phases to generate H₂ gas from 2-propanol and consume it in the reaction while other bimetal oxide catalysts includes NiCrO, NiCoO, and NiFeO were lacked of this property. Different support materials affected the shape and dispersion of catalysts which influenced the catalytic behavior. Al₂O₃ provides a catalyst to have the best catalytic performance followed by MgO, and SiO₂ respectively. However, although the surface properties of catalysts on different supporting materials were significantly different, the catalytic potentials were not shown to the notably contrasting.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

W. Tanwongwan performed the lab experiment and wrote the paper draft. All processes were designed, advised, and approved for the final version under the supervision of S. Kuboon, W. Kraithong, and A. Eiad-ua.

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