

POSSIBILITY OF USING A NEWLY-SYNTHESIZED LDH-BASED OXIDE CATALYST FOR CATALYTIC BIO-ETHANOL CONVERSION

Napatsorn Makoknoi^a, Sirirat Jitkarnka^a

^aThe Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

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ABSTRACT

Bio-ethanol is a renewable energy that can be produced by crop and biomass fermentation process. Nowadays, bio-ethanol is used as an additive for blending in engine fuels such as gasohol, E10, E20, and E85. Moreover, ethanol can be converted to valuable chemicals such as hydrogen, hydrocarbon, C3-C4 olefins, and other chemicals (acetaldehyde, crotonaldehyde, butyraldehyde, crotyl alcohol, 1-butanol, 1,3-butadiene, and 1-hexanol). The aim of this research work was to study the conversion of bio-ethanol to valuable chemicals using a newly synthesized Mg₄Al-LDH derived oxide catalyst prepared by co-precipitation method. The catalyst was characterized by using XRD, XRF, BET, NH₃-, and CO₂-TPD, and tested in a plug flow fixed bed U-tube reactor at 400 °C, 9.468 gEtOH/gcat·h and atmospheric pressure. The liquid product (non-aqueous phase) was analyzed using GC-TOFMS. The gaseous product was analyzed using GC-FID for the concentration of hydrocarbons (C1-C4). As a result, it was found that Mg₄Al-LDO gave 62.4 % conversion of bioethanol. The major components in the gaseous and non-aqueous product were ethylene and 1-butanol, respectively, meaning that the MgAl-LDO catalyst can drive both ethanol dehydration and dehydrogenation pathways.

*Sirirat.j@chula.ac.th

INTRODUCTION

Bioethanol is a renewable energy that can be produced from crop or biomass fermentation process. It can be used as a feedstock for producing valuable chemicals via ethanol dehydration and ethanol dehydrogenation pathways. The acidic catalysts such as HSM-5, SAPO-34, and modified zeolites (Inaba *et al.*, 2006) have been employed in the catalytic dehydration of ethanol to ethylene and diethyl ether. In fact, the catalytic conversion of ethanol produces both gaseous and liquid products. The gaseous products are composed of C1-C4 hydrocarbons. The liquid product contains HCs and oxygenated compounds, such as aromatics, alcohols, aldehydes, esters, ethers, acids, and ketones. Layered double hydroxide was one type of layered materials, which is well-known as hydrotalcite-like layered clays. The general formula of LDH was $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ where M^{II} is a cation with the oxidation a state of 2+ and M^{III} is a cation with the oxidation a state of 3+. The cations stay on the octahedral position in the brucite-like layer (Mg (OH)₂), and A is an anion that locates in the layer of brucite-like layer. In general, LDHs have been mostly used in the fields of catalyst support precursors, anion exchangers, acid residue scavengers, flame retardants and polymer stabilizers. The LDHs are composed of hydroxyl group in the structure, which is located at the tetrahedral alumina representing a basic site. Moverover,

the relative amount of Lewis and Bronsted basic sites depends on anion-exchange the interlayer of LDHs. Normally, conventional LDH synthesis results in low specific surface area. In 2015, a newly-synthesized LDH method has been developed (Chen *et al.*, 2015). It was found that the novel LDHs have a significantly-higher specific surface area (up to $365\text{m}^2\text{g}^{-1}$). After an LDH is calcined, an LDH-based mixed oxide is formed. Mg and Al mixed oxides have been studied for the catalytic conversion of ethanol to n-butanol (Carvalho *et al.*, 2012). It was found that the increasing concentration of Mg suppressed ethanol conversion. The highest Mg/Al ratio gave about 24% ethanol conversion. In summary, the catalytic conversion of bio-ethanol to value chemicals required the different site of catalysts. Therefore, the layered double oxide was expected to enhance ethanol conversion because of its properties. The aim of this work was to investigate the catalytic performance of the newly-synthesized LDH based oxide catalyst for the conversion of bio-ethanol and product distribution.

EXPERIMENTAL

A. Catalyst Preparation

The layered double hydroxide (LDH) was first synthesized using co-precipitation method. A solution of 0.3500 M magnesium nitrate and 0.0875 M aluminum nitrate were added dropwise by using a peristaltic pump into a well-stirred solution of 0.175 M Na_2CO_3 for 10 min. Next, the pH of the mixture was adjusted by slightly dropping NaOH (4M) until pH 10. The precipitate formed was aged under stirring for 16 h, washed with deionized water until pH 7. The wet LDH was dried at 65°C overnight (Mg4Al-LDH), and then calcined to the LDO at 500°C for 5 hours. After calcination, the LDO catalyst was pelletized and sieved to 20-30 mesh. This catalyst was labeled as Mg4Al-LDO.

B. Catalyst Activity Testing

The catalytic conversion of bioethanol was performed in a U-tube isothermal fixed bed stainless steel reactor at the atmospheric pressure (Kittikarnchanaporn and Jitkarnka, 2015). One gram of a catalyst was loaded in the U-tube reactor using quartz wool as a bed support above alumina ball. The U-tube reactor was heated by an electrical furnace. The bio-ethanol concentration was fixed at 99.5% in the feed. The 9.468 gEtOH/gcat·h of bioethanol was fed to the U-tube reactor by a syringe pump, and mixed with 30 ml/min of helium gas as a carrier gas through the catalyst bed. The product effluent coming out from the U-tube reactor was condensed in a condensing flask at -3°C in order to collect the condensable product whereas the non-condensable product was kept in the gas bag.

C. Product Analysis

The products from the reaction were condensed into two phases; that are, the gaseous and liquid phases. The gaseous components were analyzed by gas chromatography (Agilent Technologies 6890 Network GC system, using HP-PLOT Al_2O_3 S column: 25 m long x 0.32 mm ID and 8 μm film thickness, and DB-WAX column: 30 m x 0.32 mm diameter and 20 μm film thickness). The gas chromatograph was performed using the Flame Ionization Detector (FID), and the supporting gases were He, N_2 , H_2 , and air zero. The analytic conditions were set; namely, the initial temperature of 40°C , held for 10 min, the heating rate of $10^\circ\text{C}/\text{min}$ until 120°C held for 10 min, the heating rate of $10^\circ\text{C}/\text{min}$, and the

final temperature of 190°C held for 10 min. The liquid product accumulated during the catalytic reaction was condensed in the condensing flask at -3°C. CS₂ was used to extract organic compounds from the liquid product. The extracted phase was analyzed using gas chromatography-mass spectrometry, time of flight type (GC-TOFMS) using a non-polar Rtx®-5sil MS (30 m x 0.25 mm x 0.25 μm) column. The analytic conditions were set; namely, the initial temperature of 40°C held for 2 min, the heating rate of 5°C/min until the temperature was 150°C, the heating rate of 30°C/min, the final temperature was 250°C held for 2 min, and the split ratio was 1:25.

D. Catalyst Characterization

The morphology of Mg₄Al-LDH and Mg₄Al-LDO was analyzed by using XRD (Rigaku/Rint 2200 HV). To prepare a sample for XRD analysis, one gram of a catalyst powder was packed in a sample holder, and placed in sample plate inside the instrument. The analytic conditions were set; namely, a scanning rate of 10°/min with 2θ ranging from 5° to 70° using CuKα small radiation (1.5406 Å) operating at 40kV and 30 mA. The acidity and basicity of a catalyst were analyzed by using TPDRO/BEL Analyzer (BELCAT II model). For CO₂-TPD, a calcined sample (0.05 g) was pre-treated at the initial temperature of 450° for 90 min in He flow, and after that the sample was heated up to the final temperature of 950°C with the ramp rate 10°C/min, and then held for 60 min. For NH₃-TPD, the calcined sample (0.05 g) was pre-treated at the initial temperature of 300° for 105 min in He flow and after that the sample was heated up to the final temperature of 950°C with the ramp rate 10°C/min and then held for 60 min.

RESULTS AND DISCUSSION

A. Characterization of XRD and BET techniques

The XRD patterns of Mg₄Al-LDH and Mg₄Al-LDO are displayed in Figure 1. The results show that the Mg₄Al-LDH sample gives peaks 2θ at 11.5°, 23.2°, 34.6°, 39.1°, 46.3°, 60.8°, and 62.2°. After the XRD peaks were matched with JCPD 37-0630, the characteristics of hydrotalcite are confirmed. After catalyst calcination, the peaks at 11.5°, 23.2°, 34.6°, 39.1° disappear, meaning that layered double hydroxide transformed successfully to the mixed oxide form. The surface area, pore volume, and pore diameter of Mg₄Al-LDH and Mg₄Al-LDO are shown in Table 1. The result shows that the LDO catalyst has a higher surface area and pore volume than its parent LDH.

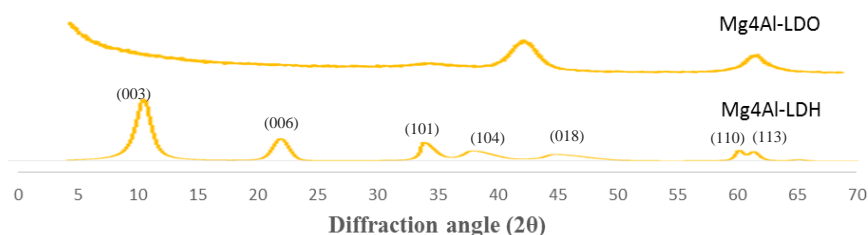


Figure 1 XRD patterns of Mg₄Al-LDH and Mg₄Al-LDO.

Table 1 Physical properties of Mg4Al-LDH and Mg4Al-LDO

Sample	Surface Area (m ² /g) ^a	Pore Volume (cm ³ /g) ^a	Pore Diameter (nm) ^b
Mg4Al-LDH	83.2	0.779	37.44
Mg4Al-LDO	377.7	2.571	19.49

^a determine using BET method
^b determine using B.J.H method

B. Characterization using NH₃- and CO₂-TPD techniques

The acidity and basicity of Mg4Al-LDO catalyst were investigated by using Temperature Programmed Desorption of ammonia and carbon dioxides, respectively. The total density of acid and base was calculated from the total area under a curve of NH₃ and CO₂-TPD profiles. The NH₃- and CO₂-TPD results are reported in Table 2. It is found that the total density of acid and base was 0.362 mmol/g and 0.393 mmol/g, respectively, meaning that the LDO catalyst possesses both acid and base properties.

Table 2 Total density of acid and base sites of Mg4Al-LDO catalyst, determined from TPD of NH₃ and CO₂

Catalyst (Mg : Al)	Total density of acid (mmol/g)	Total density of base (mmol/g)
4 : 1	0.362	0.393

C. Catalyst Activity Testing

The reaction was performed at 400°C, 9.468 gEtOH/gcat·h of WHSV, and the product sample was taken at 3 hours time-on-stream. The non-catalytic case and Mg4Al-LDO provide about 29.4 % and 62.4% conversion of bioethanol, respectively. In Figure 2, at 3 hours, Mg4Al-LDO catalyst enhances the yield of non-aqueous phase in the liquid product. The gas product obtained from the catalytic conversion of bio-ethanol at 400 °C contains C1, C2, C3, and C4 (isobutane, 1-butene, isobutene, trans-2-butene, cis-2-butene, and 1,3-butadiene) and others (such as methyl acetylene) as shown in Figure 3. As a result, it is seen that the majority of HCs concentration in the gaseous is ethylene. Moreover, Mg4Al-LDO catalyst can produce 23 wt% 1,3-butadiene in the gaseous product. The product distribution in non-aqueous phase is shown in Table 3, which is classified into two groups, based on two ethanol pathways; that are, ethanol dehydration and ethanol dehydrogenation. The results show that the non-catalytic case and LDO catalyst produce about 30.4 % and 69.5 % ethanol dehydrogenation products, respectively. As the result, the LDO catalyst prefers ethanol dehydrogenation to ethanol dehydration pathways. Moreover, the

concentration of each chemical group of oxygenated compounds in the non-aqueous phases is presented in Table 4.

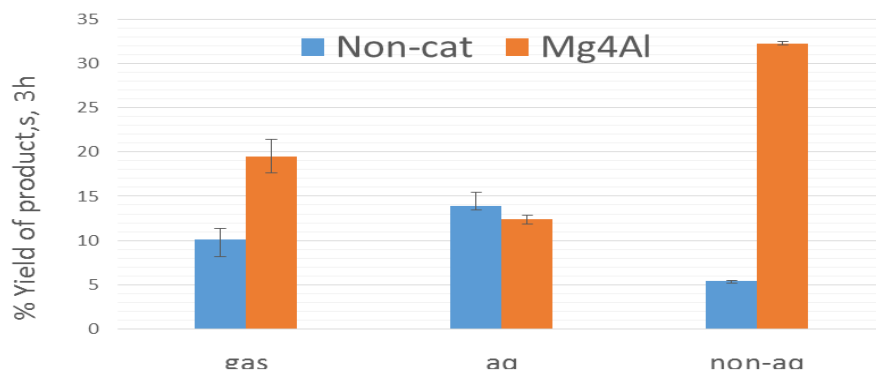


Figure 2 Product distribution using Mg4Al-LDO catalyst.

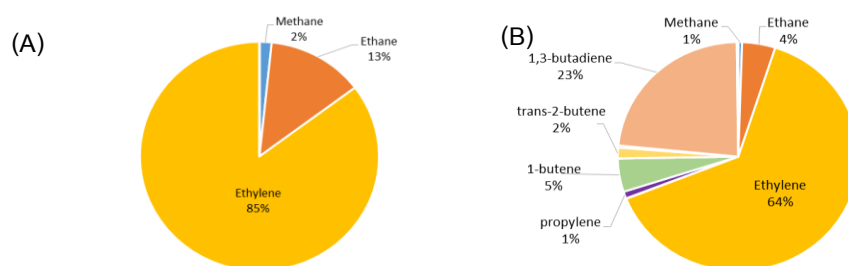


Figure 3 Concentration of HCs in gaseous product using Mg4Al-LDO catalyst : (A) Non catalyst, and (B) Mg4Al-LDO catalyst, at 3h TOS.

It is found that the non-catalytic case gives a big portion of aldehyde and ester groups whereas the LDO catalyst enhances the formation of alcohol group. As a result, both non-catalytic case and the LDO catalyst prefer dehydrogenation products, meaning that the reaction is driven to Pathway B in Figure 4, resulting in the increasing amount of oxygenated compounds such as alcohols, aldehydes, esters, ketones, and ethers.

Table 3 Selectivity of product groups in non-aqueous phase using Mg4Al-LDO catalyst

Sample	Dehydration* pathway (%)	Dehydrogenation* pathway (%)
Non-catalyst	44.9	30.4
Mg4Al-LDO	55.1	69.5

* liquid products were taken at 3 hours of time-on-stream

Table 4 Groups of oxygenated compounds in non-aqueous liquid phase obtained from using Mg₄Al-LDO catalyst

Product distribution* (%wt)						
Catalysts	Alcohols	Aldehydes	Esters	Ketones	Ethers	Acids
Non-cat	3.0	53.0	44.0	-	-	-
Mg ₄ Al-LDO	65.0	16.0	10.0	2.0	7.0	-

* liquid products were taken at 3 hours of time-on-stream

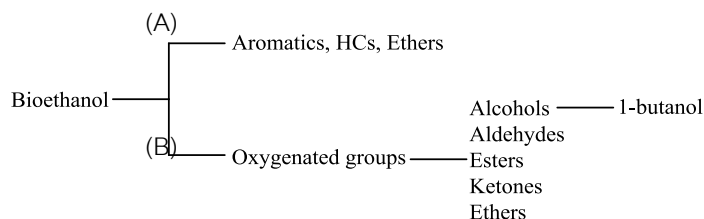


Figure 4 Transformation pathways of bioethanol using Mg₄Al-LDO catalyst : (A) Ethanol dehydration, and (B) Ethanol dehydrogenation.

CONCLUSIONS

In this work, the newly synthesized Mg₄Al-LDH derived oxide catalyst was investigated on the catalytic conversion of bioethanol to value chemicals. It can be summarized that the layered double oxide catalyst can highly enhance bioethanol conversion. The majority of component in gaseous and non-aqueous phases using Mg₄Al-LDO was ethylene, alcohols, aldehydes, esters, ethers and ketones groups, respectively.

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