# รายงานวิจัยฉบับสมบูรณ์

## โครงการ การพัฒนาวิธีการสังเคราะห์โลหะออกไซด์จำพวก

## $MAl_2O_4$ และ $MTi_2O_5$

## Thermolytic Molecular Precursor Route to Mixed-Metal Oxides of the Types $MAl_2O_4$ and $MTi_2O_5$

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30 มิถุนายน 2551

สัญญาเลขที่ MRG4980037

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สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

## บทคัดย่อ


**รหัสโครงการ :** MRG4980037

**ชื่อโครงการ :** การพัฒนาวิธีการสังเคราะห์โลหะออกไซด์จำพวก $MAl_2O_4$ และ $MTi_2O_5$

**ชื่อนักวิจัย :** จงกล จารุภัทรากร ปัณณพัฒน์ โชคมงคลทรัพย์ และ มนัส พรหมโคตร

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ทั้งอลูมินาและแมกนีเซียได้ถูกนำไปใช้ในอุตสาหกรรม เป็นทั้งตัวเร่งปฏิกิริยา, ตัวรองรับสำหรับตัวเร่งปฏิกิริยา และตัวดูดซับ อลูมินามีคุณสมบัติเป็นได้ทั้งกรดและเบส ในขณะที่แมกนีเซียมีคุณสมบัติเป็นเบส อลูมิเนียม -แมกนีเซียมมิกซ์ออกไซด์จึงมีความน่าสนใจในการใช้เป็นตัวเร่งปฏิกิริยากรด-เบส นอกจากนี้ วัสดุที่ความพรุนสูงมีความสำคัญในการเร่งปฏิกิริยา เนื่องจากเพิ่มประสิทธิภาพในการแพร่ผ่านของสารที่เข้ามาทำปฏิกิริยากับพื้นผิวของตัวเร่งปฏิกิริยา และถ้ายิ่งมีพื้นผิวที่สูงทำให้สามารถเพิ่มการสัมผัสของสารได้มากยิ่งขึ้นด้วย Cetyltrimethyl ammonium bromide (CTAB) เป็น structure-directing agent ที่นิยมใช้สำหรับการสังเคราะห์วัสดุที่มีรูพรุน ในงานวิจัยนี้ได้ใช้ aluminum isopropoxide และ magnesium nitrate เป็นสารตั้งต้นผสมกับ CTAB ในสภาวะที่เป็นกรด เพื่อเตรียมอลูมินา แมกนีเซีย และอลูมิเนียม-แมกนีเซียมมิกซ์ออกไซด์ และเปรียบเทียบคุณสมบัติของสารที่เตรียมได้ในการเป็นตัวเร่งปฏิกิริยา จากนั้นตัวอย่างออกไซด์ที่ได้มาจะนำไปโดปด้วย KI หรือ $KNO_3$ เพื่อเพิ่มความเป็นเบส เทคนิคที่ใช้ในการวิเคราะห์สารที่สังเคราะห์ได้ได้แก่ PXRD, IR, DTA-TGA, TEM, $N_2$ adsorption-desorption measurement, XRF และ acid-base strength measurement สารทุกตัวอย่างได้ถูกนำไปทดสอบประสิทธิภาพในการเร่งปฏิกิริยาทรานสเอสเทอริฟิเคชั่นของน้ำมันถั่วเหลืองกับเมทานอลที่อุณหภูมิ 80 องศาเซลเซียส สำหรับร้อยละของผลิตภัณฑ์สามารถหาได้โดยใช้เทคนิค $^1$H NMR โดยเฟสของอลูมิเนียม-แมกนีเซียม มิกซ์ออกไซด์เป็นเฟสผสมของ $\gamma$-$Al_2O_3$ และ periclase (MgO) หรือเฟสผสมของ hydrotcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) และ periclase ขึ้นอยู่กับอัตราส่วนของอลูมินัมและแมกนีเซียม อลูมิเนียม-แมกนีเซียมมิกซ์ออกไซด์ที่สังเคราะห์ได้มีโครงสร้างรูพรุนในลักษณะของ mesoporous และมีพื้นที่ผิวแบบ BET อยู่ในช่วง 96-266 $m^2 g^{-1}$ อลูมิเนียม-แมกนีเซียมมิกซ์ออกไซด์ที่อัตราส่วนโดยโมลของอลูมินัมต่อแมกนีเซียมเท่ากับ 1:4 และโดปด้วย KI จะมีความแรงของเบสอยู่ในช่วง $9.8 \le pK_{BH^+} \le 15$ และมีประสิทธิภาพในการเร่งปฏิกิริยาทรานสเอสเทอริฟิเคชั่นสูงสุด ในการศึกษาครั้งนี้ โดยให้ร้อยละผลิตภัณฑ์สูงถึงร้อยละ 90 ภายหลังจากการเร่งปฏิกิริยา 8 ชั่วโมง



**คำหลัก :** วัสดุรูพรุน, ตัวเร่งปฏิกิริยาแบบวิวิธพันธ์, ปฏิกิริยาทรานสเอสเทอริฟิเคชั่น

## Abstract

**Project Code :** MRG4980037

**Project Title :** Thermolytic Molecular Precursor Route to Mixed-Metal Oxides of the Types $MAl_2O_4$ and $MTi_2O_5$



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**Project Period :** 1 July 2006 – 30 Jun 2008 (2 yr)



Both alumina ($Al_2O_3$) and magnesia (MgO) are commonly used in the chemical industry as catalysts, catalyst supports, and adsorbents. Since alumina is amphoteric while magnesia is basic, the Al-Mg mixed oxides are interesting as bifunctional acid-base catalysts. Moreover, porous materials are important for catalytic reaction because the diffusion property of these materials enhances interaction between the substrates and the surface of the materials due to higher surface area and greater accessibility of the pores. Cetyltrimethylammonium bromide (CTAB) is one of the structure-directing agents for synthesizing several porous materials. In this work, alumina, magnesia and Al-Mg mixed oxides were prepared from aluminum isopropoxide and magnesium nitrate in the presence of CTAB in an acidic media to compare their properties as catalysts. The oxide samples were also doped with KI or $KNO_3$ to increase the base strength. The synthesized materials were characterized by PXRD, IR, DTA-TGA, TEM, $N_2$ adsorption-desorption measurement, XRF, and acid-base strength measurement. All samples were tested for activities in transesterification of soybean oil with methanol at 80 $^{o}$C. Percentage yields of fatty acid methyl ester (FAME) were characterized by $^{1}$H NMR. The phases of the Al-Mg mixed oxides are the mixture of $\gamma$-$Al_2O_3$ and periclase (MgO) or the mixture of hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) and periclase depending on the Al:Mg ratio. The Al-Mg mixed oxides have mesoporous structure with surface areas of 96-266 $m^2g^{-1}$. The calcined KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 has base strength in the range of $9.8 \leq pK_{BH^+} \leq 15$ and has the highest catalytic activity in transesterification of approximately 90 % yield of FAME after 8 h. This suggest that of the catalyst tested the calcined KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 is the most efficient catalyst for use in biodiesel production.



**Keywords :** Mesoporous material, Heterogeneous catalyst, transesterification

## หน้าสรุปโครงการ (Executive Summary)

1. ความสำคัญและที่มาของปัญหา

High surface area metal oxides have great promise in applications as diverse as catalysis, separations, sensors, and electronics. Mixed-metal oxides of the type $MgAl_2O_4$ have found used as catalysts, supports, and precursors to new ceramics. The potential applications of these mixed-metal oxide materials stipulate the essential to develop an effective synthetic method, which can offer the desired compositions and structural architectures. We have applied the sol-gel method with the assistant of structural directing agent to obtain the Mg/Al mixed-metal oxides with well-defined compositions and good surface properties.

2. วัตถุประสงค์

To apply and develop the sol-gel method with the assistant of structural directing agent to obtain the mesostructured Mg/Al mixed-metal oxides

3. ระเบียบวิธีวิจัย

โครงงานวิจัยนี้ใช้เวลาทั้งสิ้น 2 ปี โดยประกอบด้วย 3 ขั้นตอนหลัก คือ

(1) พัฒนาการสังเคราะห์โลหะออกไซด์ $Al_2O_3$, MgO และ Mg/Al mixed oxide (ที่อัตราส่วน Mg/Al = 0.125-8) โดยใช้ structure directing agent 3 ชนิด คือ น้ำตาลกลูโคส cetyltrimethyammoniumbromide (CTAB) และ Pluronic 123

(2) วิเคราะห์คุณลักษณะและสมบัติทางเคมีของโลหะออกไซด์ที่สังเคราะห์ได้ โดยใช้เทคนิค XRD, IR, TGA/DTA, XRF, $N_2$ physisorbtion, และ TEM รวมถึงความเป็นกรด-เบสของโลหะออกไซด์

(3) นำโลหะออกไซด์ที่สังเคราะห์ได้ไปศึกษาการนำไปประยุกต์ใช้เป็นตัวเร่งปฏิกิริยาและตัวรองรับสำหรับตัวเร่งปฏิกิริยา ในปฏิกิริยา transesterification

4. แผนการดำเนินงานวิจัยตลอดโครงการ

แผนงานวิจัย ระยะเวลาโครงการ 2 ปี

| | ปีที่ 1 | | | | | | | | | | | | ปีที่ 2 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| - ศึกษาการสังเคราะห์โลหะออกไซด์โดยใช้ structure directing agent ชนิดต่างๆ | | | | | | | | | | | | | | | | | | | | | | | | |
| - ตรวจสอบสมบัติทางกายภาพและเคมีของโลหะออกไซด์ที่สังเคราะห์ได้ | | | | | | | | | | | | | | | | | | | | | | | | |
| - พัฒนา ปรับปรุง และสรุปวิธีการสังเคราะห์โลหะออกไซด์ที่เหมาะสมที่สุด | | | | | | | | | | | | | | | | | | | | | | | | |
| - วิเคราะห์สมบัติทางการยภาพและเคมี รวมถึงการวัดวิเคราะห์สมบัติในระดับจุลภาค | | | | | | | | | | | | | | | | | | | | | | | | |
| - ศึกษาการนำโลหะออกไซด์ที่เตรียมได้ไปใช้เป็นตัวเร่งปฏิกิริยา | | | | | | | | | | | | | | | | | | | | | | | | |
| - ศึกษาการนำโลหะออกไซด์ที่เตรียมได้ไปใช้เป็นตัวรองรับสำหรับตัวเร่งปฏิกิริยา | | | | | | | | | | | | | | | | | | | | | | | | |

5. ผลงาน/หัวข้อเรื่องที่คาดว่าจะตีพิมพ์

ปีที่ 2: ชื่อเรื่องที่คาดว่าจะตีพิมพ์ : Synthesis, Characterization, and Catalytic Activities of Mg/Al Mixed Oxides

ชื่อวารสารที่คาดว่าจะตีพิมพ์ : Microporous and Mesoporous Materials กำลังอยู่ในขั้นเตรียม manuscript

# เนื้อหางานวิจัย

Mixed-metal oxide systems are attractive to many researchers because such systems have the potential of exhibiting chemical properties that differ notably from those of the corresponding single component oxides. The mixed-metal oxide systems, whose initial components differ considerably in their acid-base properties, are especially interesting. γ-Alumina ($\gamma$-$Al_2O_3$) based catalysts are widely used in various industrial chemical processes. Alumina is amphoteric and its acid-base properties depend very much on the synthesis conditions. Magnesia (MgO), on the other hand, is unique in its basicity. Therefore, the Mg/Al mixed-metal oxides are of our interest. In addition to the oxide components, the physical properties such as surface area, pore distribution and volume have significant effect on the performance in applications. The use of structure directing agents or templates has provided the improvement to these properties in many metal oxides. Thus, we are interested in the synthesis and characterization of Mg/Al mixed-metal oxides using cetyltrimethylammonium bromide (CTAB) as a template. The application of these mixed-metal oxides in catalysis has also been explored.

**Objectives**

To synthesize mesostructured Mg-Al mixed-oxide catalysts

**Experimental**

*Synthesis of Mg/Al mixed-oxide samples*

The mixture of aluminum and magnesium precursors were added to the solution mixture of HCl, $H_2O$, $C_3H_7OH$ and CTAB and stirred at room temperature for 4 h. The molar composition of the synthesis mixture was as follows: Al:Mg:CTAB:HCl:$C_3H_7OH$ = 1-*x*:*x*:0.3:1.5:22:17. The reaction mixture was then evaporated at 80 °C for 2 h and dried at 110 °C for 15 h. The resulting solid was thermally treated in two steps: (i) heated under nitrogen flow to 550 °C and (ii) calcined at 550 °C under oxygen flow for 5 h.

*Preparation of potassium doped Mg/Al mixed-oxide samples*

The total of 1 g mixed oxide was ground with 2.1 mmol KI or $KNO_3$ and a small amount of water for 30 min. The mixture was then heated at 120 ºC in an oven overnight, followed by calcination in air at 550 ºC for 5 h (heating rate of 1 ºC/min).

*Characterization techniques*

Powder X-ray diffraction was carried out on a Bruker D8 Advance diffractometer with filtered Cu K$\alpha$ radiation ($\lambda$ = 1.54060 Å) operating at 40 kV and 40 mA; the counting time was 1 s in step of 2$\theta$ = 0.037º/s. FTIR measurements were carried out on a Perkin-Elmer system 2000 spectrometer (KBr pellet). Thermal analyses were preformed on a TA instrument STD 2690 simultaneous DTA-TGA; samples were heated at a heating rate of 10 ºC/min under air flow.

Nitrogen physisorption was conducted at 77 K on a Micromeritics ASAP 2020 surface area and porosimetry system; samples were degassed at 90 ºC for 60 min and 350 ºC for 240 min prior to measurement. The TEM images were obtained using a Phillips Tecnai-20 microscope, operating at 25 and 50 kV. The elemental analysis was determined by wavelength dispersive x-ray fluorescence spectrometer, The measurements were performed by using Bruker AXS Model S4 Explorer equipped with Rh K radiation operated at 50 kV and 20 mA.

The basic strength of the samples was determined using Hammett indicator method, according to literature protocols. The Hammett indicators used were bromothylmol blue ($pK_a$ ~ 7.2), phenolthalein ($pK_a$ ~ 9.8), 2,4-dinitroaniline ($pK_a$ ~ 15), and 4-nitroaniline ($pK_a$ ~ 18.4). Methanol was used as the solvent. The base strength was reported as being stronger than the weakest indicator which exhibits a color change, but weaker than the strongest indicator that produces no change.

*Catalytic activity tests*

The transesterification reactions were performed at 70 ºC in a 100 mL two-neck reaction flask equipped with a condenser by refluxing 10 mL of methanol (247 mmol) with 11.23 g of soybean oil (commercial edible grade, acid value < 0.4 mg KOH/g, saponification index = 185.6 mg KOH/g, and average molecular weight = 909 g/mol) and 0.56 g of catalyst (5 wt%). The catalyst was dried at 120 ºC overnight prior to use. A 0.5 mL aliquot was taken from the reaction mixture at various times in order to follow the product yield. Each aliquot was extracted in a hexane/water system. The hexane layer was then dried with anhydrous $Na_2SO_4$ and was purged with $N_2$ to remove hexane. The percentage yield of the fatty acid methyl ester (FAME) was determined by the integration ratio of the $^1$H NMR signal of the methoxy protons of FAME and the signal of the metylene protons of the triglyceride and FAME.

**Results and discussion**

The calcined products of the alumina and the magnesia were γ-$Al_2O_3$ and periclase (MgO), respectively. The PXRD patterns of the calcined products of the Al-Mg mixed oxides at Al:Mg ratios of 8:1, 4:1, and 2:1 showed mixed phases between γ-$Al_2O_3$ and periclase. The relative amount of the periclase phase in the Al-Mg mixed oxides increased with the increase of the magnesium content as seen in Figure 1. The Al-Mg mixed oxides at Al:Mg ratios of 1:1, 1:2, 1:3, 1:4, and 1:8 were the mixture between hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) and periclase. The amount of the hydrotalcite phase in the Al-Mg mixed oxides was the highest at the Al:Mg ratio of 1:3 which was the exact ratio of Al:Mg in the hydrotalcite. The relative hydrotalcite content decreased as the Al:Mg ratio deviated from 1:3. In addition, the Al-Mg mixed oxides had higher relative amount of periclase phase with the increase of the magnesia content as seen in Figure 2. The change in the relative amount of each phase was consistent with the molar ratio of Al:Mg in the samples. The PXRD results suggested that the $Al_2O_3$ and MgO phases of Al-Mg mixed oxides did not mix as a homogeneous solid solution and only hydrotalcite had the atomic mixture of Al-Mg. This was attributed to the differences in the hydrolysis rate of $Al(O^iPr)_3$ and $Mg(NO_3)_2$, as well as the condensation rate of Al and Mg intermediates during the synthesis of the as-synthesized Al-Mg mixed oxides.

Thermogravimetry analysis and differential thermal analysis (TGA-DTA) of the CTAB were studied. The TGA result indicated a two-step complete decomposition of CTAB. The first mass change occurred at above 200 $^{o}$C with a mass loss of over 90 % and the second mass change at above 400 $^{o}$C. The former mass change was attributed to the decomposition of CTAB, and the latter was to the decomposition of carbon residue.[1] The DTA of CTAB displayed one endothermic peak at 114 $^{o}$C and three exothermic peaks at 208, 324, and 492 $^{o}$C. The endothermic process was probably due to desorption of physisorbed water in CTAB. The first two exothermic peaks (at 208 and 324 $^{o}$C) were possibly associated with the decomposition of CTAB, as they were in the same temperature vicinity as the major mass loss (90 %). The last exothermic peak at 492 $^{o}$C was attributed to the combustion of the carbon residue. The TGA-DTA results of the as-synthesized alumina, Al-Mg mixed oxides at Al:Mg ratios of 2:1 and 1:2, and magnesia showed similar patterns. Nevertheless, the combustion of carbon residue in the as-synthesized Al-Mg mixed oxides took place at higher temperature (526 $^{o}$C and 537 $^{o}$C for the Al-Mg mixed oxides at Al:Mg ratios of 2:1 and 1:2, respectively) than the as-synthesized alumina (509 $^{o}$C) and the as-synthesized magnesia (501 $^{o}$C) samples. In addition, the decomposition of CTAB in the as-synthesized samples occurred at higher temperature than that of the CTAB itself. The DTA results revealed the exothermic decomposition at 343, 343, 330,

and 346 °C for the as-synthesized alumina, Al-Mg mixed oxides at Al-Mg ratios of 2:1 and 1:2, and magnesia, respectively, indicating the interactions between the oxides and CTAB. Furthermore, the exothermic peak at about 300 °C in the DTAs of the as-synthesized Al-Mg mixed oxides and that of the as-synthesized magnesia, which was absent in the DTAs of the CTAB and the as-synthesized alumina, was likely due to the dehydroxylation of $Mg(OH)_2$.[2]

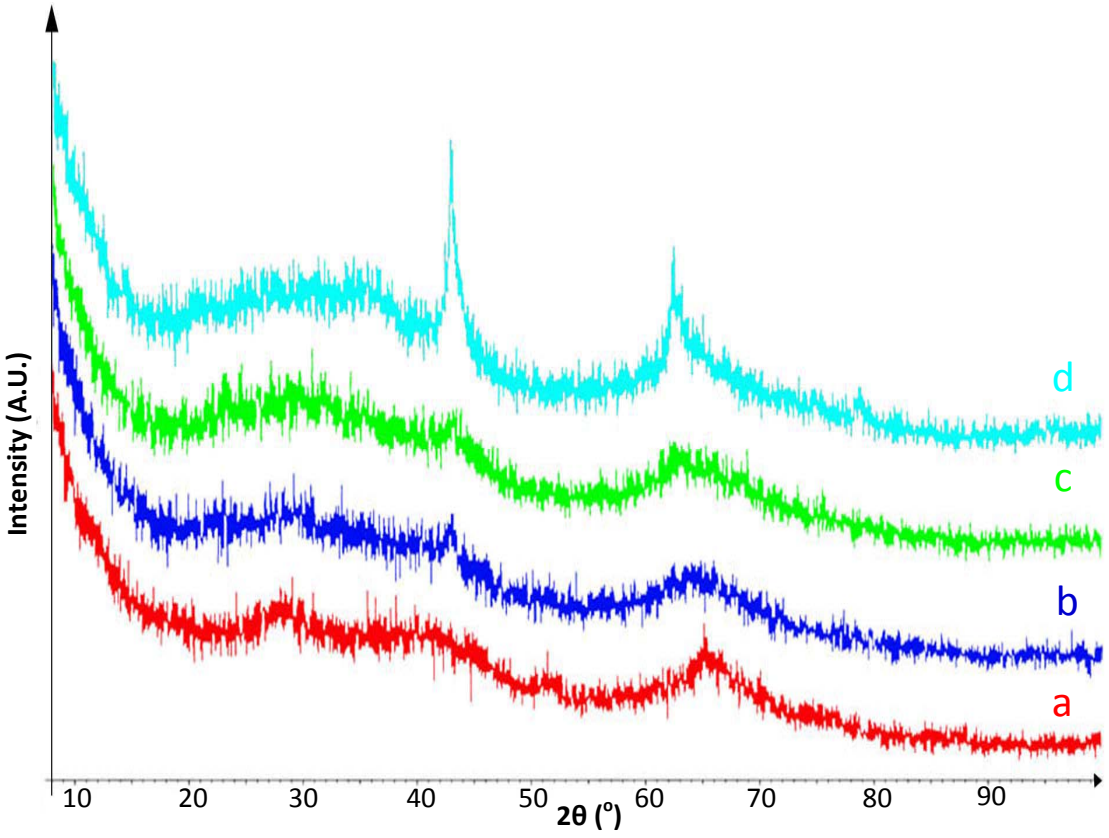


**Figure 1.** PXRD patterns of calcined products of (a) the alumina, the Al-Mg mixed oxides at Al:Mg ratios of (b) 8:1, (c) 4:1, and (d) 2:1.

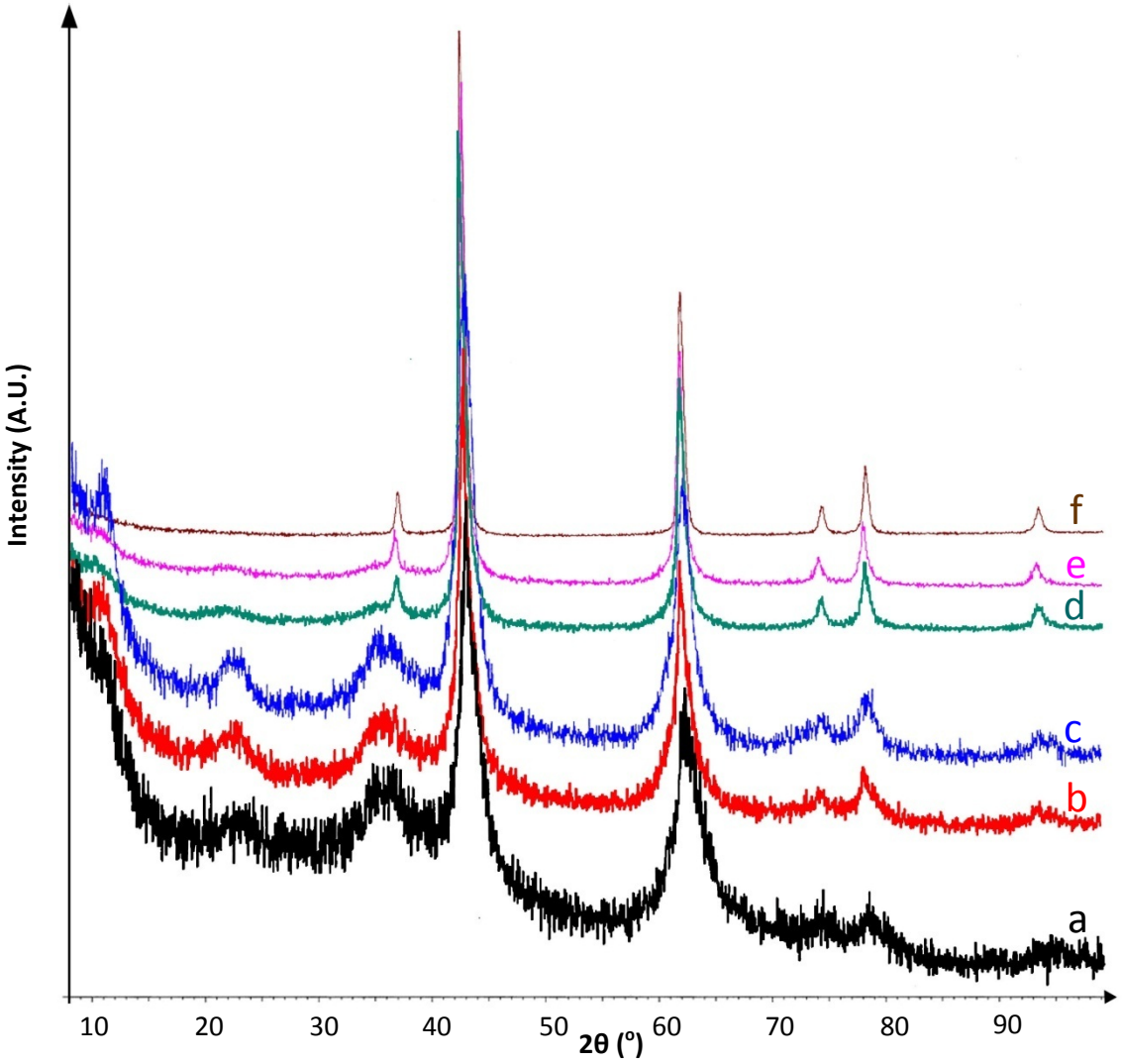


**Figure 2.** PXRD patterns of calcined products of the Al-Mg mixed oxides at Al:Mg ratios of (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4, (e) 1:8, and (f) the magnesia.

TEM images of all calcined products of alumina, Al-Mg mixed oxides, and magnesia (Figure 3a-f) showed worm whole-like structure and they had less porosity with increasing magnesia content. The calcined magnesia sample displayed no feature of mesoporous structure (Figure 3f). Hence, the presence of the magnesia might lead to the collapse of the porous structure.

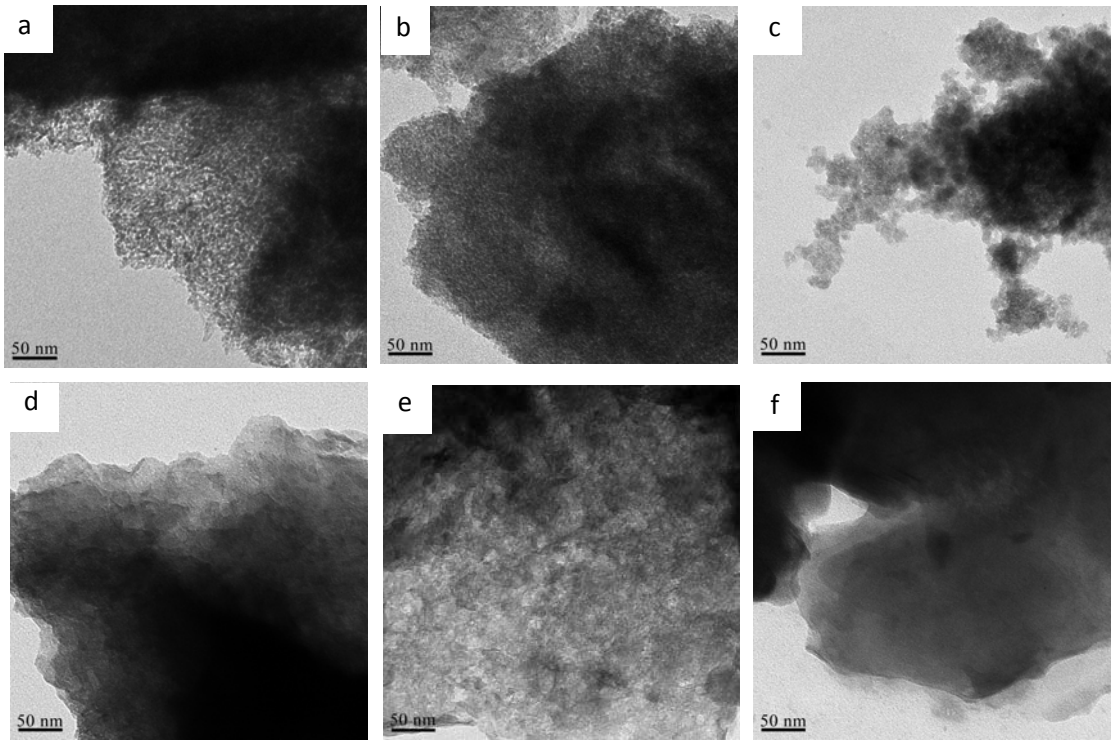


**Figure 3.** TEM images of the calcined products of (a) the alumina, (b) the Al-Mg mixed oxides at Al:Mg ratios of 4:1, (c) 2:1, (d) 1:2 , (e) 1:4, and (f) the magnesia. Bar scales in the images are 50 nm.

Textural properties of calcined products of the alumina, the Al-Mg mixed oxides, and the magnesia were summarized in Table 1. The BET surface areas of the alumina, the Al-Mg mixed oxides at Al:Mg ratios of 8:1, 4:1, and 2:1 were similar (211-230 $m^2g^{-1}$) and the BET surface areas of the Al-Mg mixed oxides decreased as the Al:Mg ratio changed from 2:1 to 1:1 and increased as the Al:Mg ratio changed from 1:1 to 1:4 and decreased again as the Al:Mg ratio changed from 1:4 to the pure magnesia. Likewise, the total pore volumes decreased as the Al:Mg ratio changed from 8:1 to 1:1 and increased as the Al:Mg ratio changed from 1:1 to the pure magnesia. Nevertheless, the average pore sizes exhibited no correlation with the Al-Mg content.

**Table 1.** The physico-chemical properties of the alumina, the Al-Mg mixed oxide, and the magnesia.

| Al:Mg ratio | BET surface area ($m^2 g^{-1}$) | Pore volume ($cm^3 g^{-1}$) | Average pore diameter (nm) |
|---|---|---|---|
| 1:0 | 230 | 0.27 | 4.7 |
| 8:1 | 216 | 0.32 | 5.9 |
| 4:1 | 224 | 0.32 | 5.8 |
| 2:1 | 211 | 0.27 | 5.1 |
| 1:1 | 127 | 0.09 | 4.7 |
| 1:2 | 172 | 0.13 | 5.2 |
| 1:3 | 252 | 0.18 | 3.8 |
| 1:4 | 266 | 0.19 | 3.9 |
| 1:8 | 205 | 0.25 | 7.2 |
| 0:1 | 96 | 0.38 | 16.3 |

The alumina and the Al-Mg mixed oxide at Al:Mg mixed ratio of 1:4 had narrow pore size distributions with average pore size of 4.7 and 3.9 nm, respectively. The other Al-Mg mixed oxides had similar pore size distribution curve, but the magnesia had a broad pore size distribution as shown in Figure 4. The $N_2$ adsorption-desorption isotherms of the alumina, the Al-Mg mixed oxides, and the magnesia (Figure 5) were similar and could be classified as the classical shape of type IV isotherm, indicating typical mesoporous solids. The hysteresis loop of the alumina displayed type E characteristic, indicating that the alumina had tubular or ink-bottom pores.[3] All Al-Mg mixed oxide samples had hysteresis loops of type B characteristic, indicating that the Al-Mg mixed oxides had capillary space between parallel plates or open slit-shaped capillary.[3] However, the isotherm of the magnesia indicated that the magnesia had spaces among particles instead of pores. This result agreed with the TEM image and the BJH pore size distribution, where less pore structure and broad pore size distribution were observed.

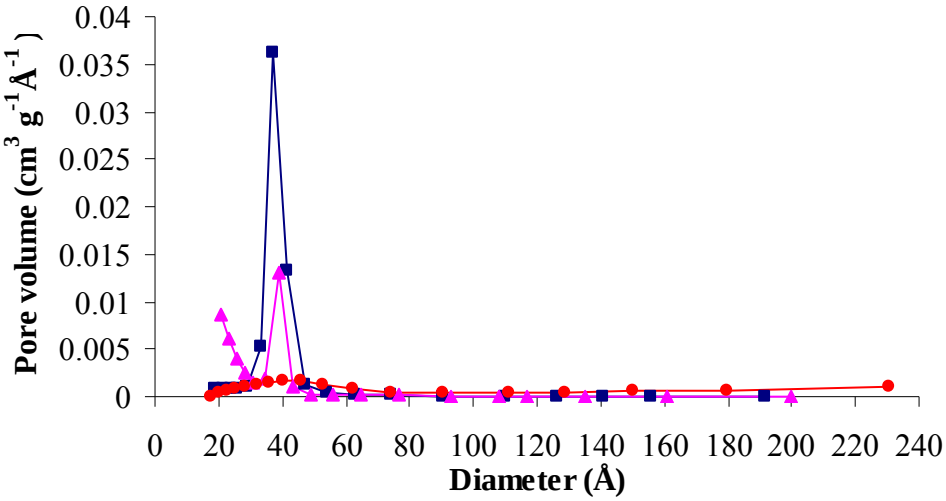


**Figure 4.** BJH pore size dritribution of (■) the calcined alumina, (▲) the calcined Al-Mg mixed oxide at Al:Mg ratio of 1:4, and (●) the calcined magnesia.

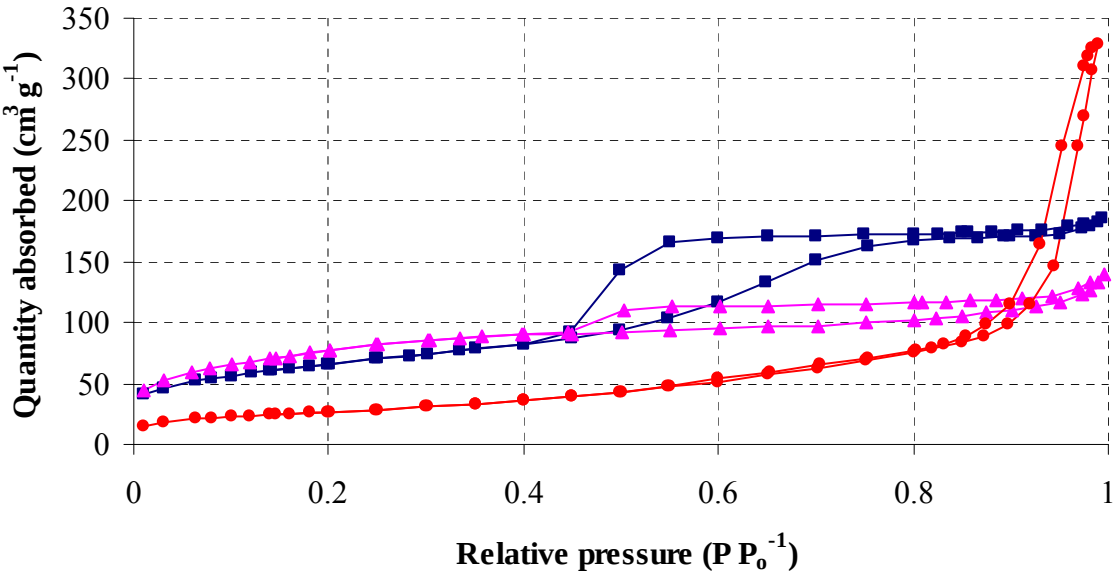


**Figure 5.** $N_2$ adsorption-desorption isotherms of (■) the calcined alumina, (▲) the calcined Al-Mg mixed oxide at Al:Mg ratio of 1:4, and (●) the calcined magnesia.

The Al:Mg atomic ratios in the calcined Al-Mg mixed oxides were measured by XRF spectrometry and shown in Table 2. The Al:Mg atomic ratio values in all samples were close to the values estimated from the amount of the starting materials.

**Table 2.** The Al:Mg atomic ratio values in the calcined Al-Mg mixed oxides.

| Sample | Al:Mg ratio (theoretical) | Al:Mg ratio (experimental) |
|---|---|---|
| Al-Mg mixed oxide at Al:Mg ratio of 8:1 | 1:0.125 | 1:0.094 |
| Al-Mg mixed oxide at Al:Mg ratio of 4:1 | 1:0.25 | 1:0.21 |
| Al-Mg mixed oxide at Al:Mg ratio of 2:1 | 1:0.5 | 1:0.47 |
| Al-Mg mixed oxide at Al:Mg ratio of 1:1 | 1:1 | 1:1.01 |
| Al-Mg mixed oxide at Al:Mg ratio of 1:2 | 1:2 | 1: 2.10 |
| Al-Mg mixed oxide at Al:Mg ratio of 1:3 | 1:3 | 1:3.35 |
| Al-Mg mixed oxide at Al:Mg ratio of 1:4 | 1:4 | 1:4.15 |
| Al-Mg mixed oxide at Al:Mg ratio of 1:8 | 1:8 | 1:8.06 |

The base strength of the alumina, the Al-Mg mixed oxides, and the magnesia increased with increasing magnesia content. Likewise, alkali doped samples had higher base strength with increasing magnesia content. Moreover, both KI and $KNO_3$ doped Al-Mg mixed oxides at the same Al:Mg ratio had the same base strength. Hence, the magnesia content could increase the base strength and the presence of alkali species (potassium) could also increase the base strength of the catalysts. The base strength of the alumina, the Al-Mg mixed oxides, the magnesia, and the alkali doped samples were shown in Table 3.

**Table 3.** Base strength of the catalysts.

| Catalyst | $pK_a$ |
|---|---|
| alumina | $pK_a \leq 7.2$ |
| Al-Mg mixed oxide at Al:Mg ratio of 8:1 | $pK_a \leq 7.2$ |
| Al-Mg mixed oxide at Al:Mg ratio of 4:1 | $pK_a \leq 7.2$ |
| Al-Mg mixed oxide at Al:Mg ratio of 2:1 | $7.2 \leq pK_a \leq 9.8$ |
| Al-Mg mixed oxide at Al:Mg ratio of 1:1 | $7.2 \leq pK_a \leq 9.8$ |
| Al-Mg mixed oxide at Al:Mg ratio of 1:2 | $7.2 \leq pK_a \leq 9.8$ |

| | |
|---|---|
| Al-Mg mixed oxide at Al:Mg ratio of 1:3 | $7.2 \leq pK_a \leq 9.8$ |
| Al-Mg mixed oxide at Al:Mg ratio of 1:4 | $7.2 \leq pK_a \leq 9.8$ |
| Al-Mg mixed oxide at Al:Mg ratio of 1:8 | $7.2 \leq pK_a \leq 9.8$ |
| magnesia | $7.2 \leq pK_a \leq 9.8$ |
| KI doped alumina | $7.2 \leq pK_a \leq 9.8$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 8:1 | $7.2 \leq pK_a \leq 9.8$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 4:1 | $7.2 \leq pK_a \leq 9.8$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 2:1 | $7.2 \leq pK_a \leq 9.8$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:1 | $9.8 \leq pK_a \leq 15$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:2 | $9.8 \leq pK_a \leq 15$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:3 | $9.8 \leq pK_a \leq 15$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 | $9.8 \leq pK_a \leq 15$ |
| $KNO_3$ doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 | $9.8 \leq pK_a \leq 15$ |
| KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:8 | $9.8 \leq pK_a \leq 15$ |
| KI doped magnesia | $9.8 \leq pK_a \leq 15$ |

*Catalytic activity*

The transesterification of soybean oil with methanol in the absence of catalyst essentially produced no fatty acid methyl ester (FAME) under the condition studied, while all KI doped catalysts were active for the reaction as shown in Figure 6 and 7. The KI doped alumina was more active than the KI doped Al-Mg mixed oxides with high aluminum content at the Al:Mg ratios of 1:2, 1:4, and 1:8. These samples had similar basic strength ($7.2 \leq pK_a \leq 9.8$) and similar surface area (211-230 $m^2 g^{-1}$), thus the difference in the transesterification is yet explained and further study is needed. One hypothesis now is the potassium species was better dispersed on the alumina compared to on the mixed oxides, as the XRD results showed no crystalline potassium species on the alumina, but KI and $KIO_3$ phases were observed on the mixed oxides. However, the KI doped Al-Mg mixed oxides at Al:Mg ratios of 1:1, 1:3 and 1:4 gave higher yield of FAME as the magnesium content increased as shown in Figure 7.

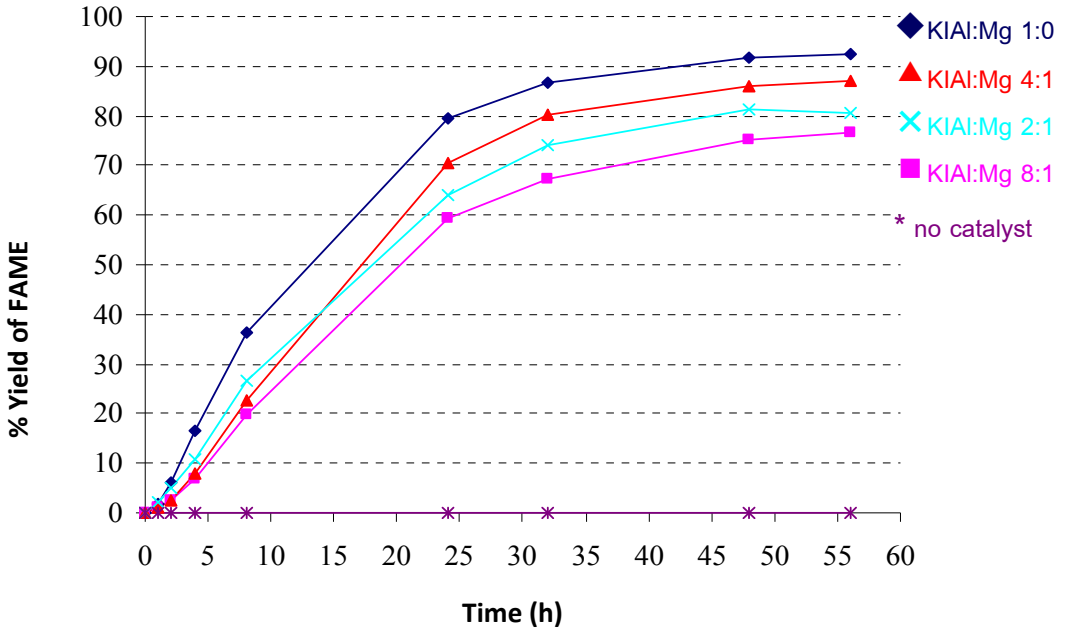


**Figure 6.** Percentage yields of FAME from transesterification of soybean oil using no catalyst, KI doped alumina, and KI doped Al-Mg mixed oxides at Al:Mg ratios of 8:1, 4:1, and 2:1 as catalyst.

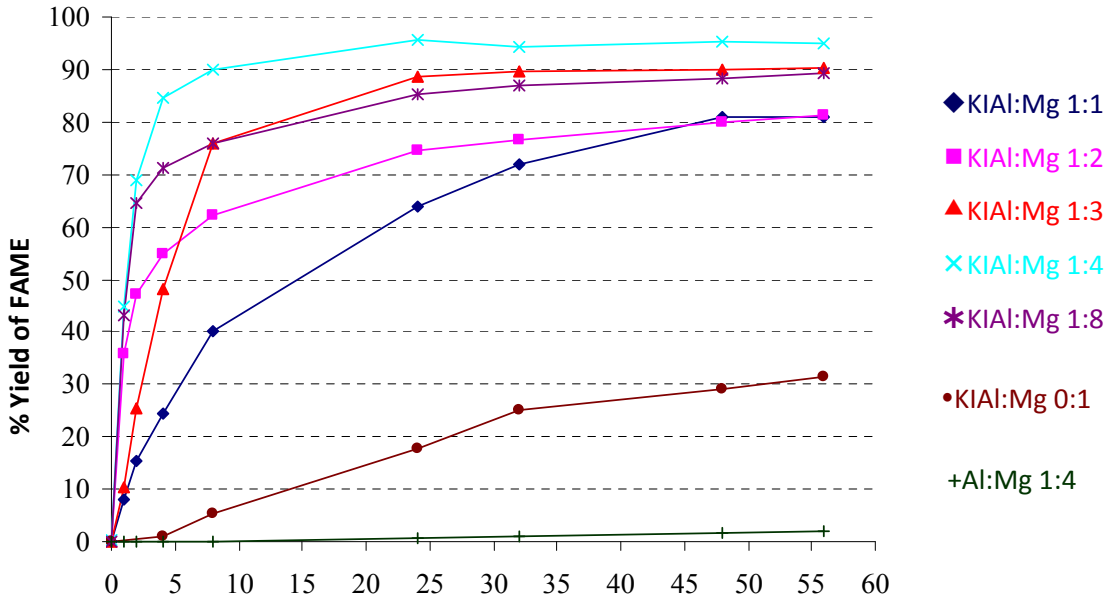


**Figure 7.** Percentage yields of FAME using KI doped Al-Mg mixed oxide at Al:Mg ratios of 1:1, 1:2, 1:3, 1:4, and 1:8, KI doped magnesia, and undoped Al-Mg mixed oxide at Al:Mg 1:4 as catalyst.

The higher activity in this case might be a result of the higher magnesium content which led to the higher basicity of the sample. The undoped Al-Mg mixed oxide at Al:Mg ratio of 1:4 showed no activity after 8 h and has only 2% yield of FAME after 56 h because of low basicity of this catalyst ($7.2 \leq pK_a \leq 9.8$) as shown in Figure 7. KI doped magnesia catalyst was not as active as the KI doped Al-Mg mixed oxides. Even though the KI dope magnesia sample had similar base strength to those of the KI doped mixed oxides, the surface area of the magnesia support was much lower (96 $m^2 g^{-1}$). Therefore, the lower activity was obtained. In addition, the KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 had higher activity than that of the $KNO_3$ doped Al-Mg mixed oxide at the same Al:Mg ratio. This result was in good agreement with that reported by Xie.[4] Xie reported that the calcined KI doped alumina had higher activity than $KNO_3$ doped sample, with 87.4 and 67.4 % yield of FAME at 6 h, respectively. However, our KI doped Al:Mg mixed oxide at Al:Mg 1:4 exhibited higher activity (85 % yield at 4 h).

The leaching and reuse ability of the KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 were studied. Leaching test for the calcined KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 was carried out by filtering out the catalyst from the transesterification reaction mixture after 2 h. The result showed no change in the percentage yield of FAME after the catalyst removal. 10 mL of methanol was added to the reaction at 25 h to ensure that the loss of activity was not caused by methanol evaporation during the catalyst removal. After the addition of methanol, the yield of FAME remained relative unaffected, indicating that the Al-Mg mixed oxide at Al:Mg ratio of 1:4 was a heterogeneous catalyst without any soluble active species in the reaction. To study the reuse ability of the KI doped Al-Mg mixed oxide catalyst, recovered catalysts were washed with acetone and hexane, respectively, and dried at 120 $^{o}$C for 24 h, then either used without further treatment or treated by calcinations at 550 $^{o}$C for 5 h. The recovered catalyst with calcination treatment showed to be only half as active as the first catalyst (47 % vs 95 % yield at 24 h) for the calcined KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4. The recovered catalyst used without calcinations was even less active (10 % yield at 24 h). These results indicated that the reused catalysts were somehow deactivated or poisoned during the reaction.

**Conclusion**

The phases of the calcined alumina and the calcined magnesia were $\gamma$-$Al_2O_3$ and periclase, respectively. The phase of the calcined Al-Mg mixed oxides at Al:Mg ratios of 8:1, 4:1, and 2:1 were the mixture of $\gamma$-$Al_2O_3$ and periclase. On the other hand, the calcined Al-Mg mixed oxides at Al:Mg ratios of 1:1, 1:2, 1:3, 1:4, and 1:8 were the mixture of hydrotalcite

($Mg_6Al_2CO_3(OH)_{16}{\cdot}4H_2O$) and periclase (MgO). The phases of all samples remained unchanged after doping with KI or $KNO_3$, except the additional appearance of KI and $KIO_3$ phases in the calcined KI doped samples and of $KNO_3$ and $K_2O$ phases in the calcined $KNO_3$ doped samples.

The calcined alumina had mesoporous structure with tubular or ink-bottom pores. The calcined Al-Mg mixed oxides had capillary space between parallel plates or open slit-shaped capillary. The magnesia had only space among particles without mesopores in the material. The mesoporosity of the materials tended to decrease with the increasing magnesia content. BET surface area of alumina was 230 $m^2g^{-1}$. The calcined Al-Mg mixed oxides had BET surface areas varied between 127 and 266 $m^2g^{-1}$. The calcined Al-Mg mixed oxide at Al:Mg ratio of 1:4 had the highest BET surface area (266 $m^2g^{-1}$) and the calcined magnesia had the lowest BET surface area (96 $m^2g^{-1}$).

The base strength of the calcined alumina, the Al-Mg mixed oxides, and the magnesia increased with magnesia content.

The percentage yield of FAME using the calcined alkali doped alumina, Al-Mg mixed oxides, and the magnesia as catalyst were in range 5-90 % after 8 h of reaction. The calcined KI doped Al-Mg mixed oxide at Al:Mg ratio of 1:4 had the highest catalytic activity of approximately 90 % yield of FAME after 8 h and higher than the calcined $KNO_3$ doped Al-Mg mixed oxide at the same ratio (47 %). Moerover, There was no catalytically active species leaching from the calcined Al-Mg mixed oxide at Al:Mg ratio of 1:4, indicating that this catalytic system was heterogeneous. Nevertheless, the reused catalysts were inactive, indicating that the catalysts might be deactivated or poisoned during the reaction.

**Suggestion for further study**

Further characterization of the Al-Mg mixed oxides may reveal more information about the nature of the samples. Examples of these characterization techniques are x-ray photoelectron spectroscopy (XPS) and temperature program adsorption (TPD).

The catalytic parameters, such as K-loading, oil to methanol ratio, reaction temperature, may be studied to achieve the optimum transesterification conditions.

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## ผลลัพธ์ที่ได้จากโครงการ

1. กำลังอยู่ในขั้นเตรียม manuscript 1 เรื่อง ในหัวข้อ “Synthesis, Characterization, and Catalytic Activities of Mg/Al Mixed Oxides”
2. การเสนอผลงานวิจัยแบบปากเปล่า:
    - Synthesis and characterization of Mg-Al mixed oxides, Pure and Applied Chemistry International Conference ระหว่างวันที่ 30 มกราคม – 1 กุมภาพันธ์ 2551 ณ โรงแรมโซฟิเทล กรุงเทพฯ
3. การเสนอผลงานวิจัยแบบโปสเตอร์:
    - Synthesis and characterization of Mg-Al mixed oxides, The 5$^{th}$ PERCH Annual Scientific Congress V การประชุมวิชาการโครงการพัฒนาบัณฑิตศึกษาและการวิจัยทางเคมี ระหว่างวันที่ 6 – 9 พฤษภาคม 2550 ณ โรงแรงจอมเทียน ปาล์มบีช พัทยา ชลบุรี