

## ปฏิกิริยาจัดน้ำของเอทานอลโดยตัวเร่งปฏิกิริยาอะลูมินาซิลิกาที่ปรับปรุงด้วยแลนทานัม

### Ethanol Dehydration over La-modified Alumina-silica Catalysts

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#### บทคัดย่อ

ตัวเร่งปฏิกิริยาอะลูมินาซิลิกาในอัตราส่วน 60:40 ที่ปรับปรุงด้วยแลนทานัมถูกเตรียมสำหรับปฏิกิริยาจัดน้ำของเอทานอลโดยทำการเปลี่ยนแปลงปริมาณแลนทานัมตั้งแต่ 0 ถึง 3 เปอร์เซ็นต์โดยมวล โดยมีแลนทานัมในเตรตเฮกซะไฮเดรตเป็นสารตั้งต้น การทดสอบตัวเร่งปฏิกิริยาถูกทำที่อุณหภูมิ 200-400 องศาเซลเซียสภายใต้ความดันบรรยากาศ เอทิลีนและไดเอทิลอีเทอร์เป็นผลิตภัณฑ์จากปฏิกิริยาเคมี จากการเติมแลนทานัมพบว่าค่าการเลือกเกิดของไดเอทิลอีเทอร์เพิ่มขึ้น ส่วนค่าการเลือกเกิดของเอทิลีนและร้อยละการเปลี่ยนของเอทานอลมีแนวโน้มลดลง ผลของการเพิ่มอุณหภูมิพบว่าค่าการเลือกเกิดของเอทิลีนและร้อยละการเปลี่ยนของเอทานอลสูงขึ้น ส่วนค่าการเลือกเกิดของไดเอทิลอีเทอร์ลดลงสำหรับทุกตัวเร่งปฏิกิริยา จากการวิเคราะห์คุณสมบัติพบว่าแลนทานัมกระจายตัวดีและไม่มีผลต่อโครงสร้างผลึก ความเป็นกรดอ่อนมีแนวโน้มเพิ่มขึ้น การเกิดคาร์บอนที่ผิวที่ตัวเร่งปฏิกิริยาแปรผกผันตามปริมาณการปรับปรุงแลนทานัมในตัวเร่งปฏิกิริยา ทั้งสเดนในแบบ โมโนทั้งสเดนได้ดี ส่งผลให้มีความเป็นกรดและความว่องไวสูง

**คำสำคัญ:** ตัวเร่งปฏิกิริยาอะลูมินาซิลิกา แลนทานัม ปฏิกิริยาการจัดน้ำ

#### Abstract

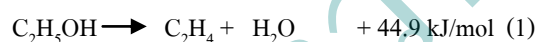
Lanthanum (La) modified alumina-silica catalysts (60:40) are prepared for ethanol dehydration by varying La loading from 0 to 3 wt% using  $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  as the precursor. Catalytic performance is tested at temperatures ranging from 200 °C to 400 °C under atmospheric pressure. Ethylene and diethyl ether are the main products from this reaction. From the reaction test, the addition of La can result in increased selectivity of diethyl ether. However, both ethylene selectivity and ethanol conversion were found to decrease. The effect of increasing temperature is that

ethylene selectivity and ethanol conversion continue to increase, but diethyl ether selectivity declines for all catalysts. Based on the characterizations, it was revealed that La was in a highly dispersed form without basic phase structure transformation. Weak acid tended to increase with La modification. Coke deposition decreased when the amount of La loading was increased.

**Keywords:** alumina-silica catalyst, lanthanum, dehydration

## 1. Introduction

Petroleum, as nonrenewable resource, continues to diminish rapidly. Thus, using alternative fuels instead has widely been investigated. Ethanol is potential substance which can be transformed into hydrocarbon easily by dehydration reaction. Moreover, ethanol can be obtained from industry and biomass like vegetable biomass, lignocellulosic waste and sugar-industry residues. Dehydration of ethanol can transform to ethylene, diethyl ether with followed reactions (1) and (2) by alumina, zeolite, carbon, silica and alumina-silica as well.



Ethylene, which is one of the essential primary intermediates for petrochemical industry, is used for producing a variety of products such as polyethylene, ethylene oxide, ethylene dichloride and ethyl benzene (Ciftci et al., 2012). In addition, diethyl ether (DEE) is typically used as additive for blending with diesel due to their high cetane number (Matachowski et al., 2012; Varisli & Dogu, 2009).

Among the numerous dehydration catalysts, alumina-silica has high specific surface areas, surface acidity and catalytic performance, but deactivation

easily occurred. Recently, Jia (Ouyang et al., 2009) reported that 3%La-HZSM-5 catalyst showed high reactivity and stability during dehydration. Zhang (Zhang et al., 2007) found that a few addition of La into catalyst could increase selectivity in propane dehydrogenation and stability of PtSnNa/ZSM-5 catalyst, but acidity diminished insignificantly. However, the effect of lanthanum addition into alumina-silica for ethanol dehydration has not been investigated.

In this work, we characterized the catalyst by XRD, SEM-EDX,  $\text{NH}_3$ -TPD and TGA techniques in order to study the effect of lanthanum doped alumina-silica composite catalyst (Al/Si = 60:40) (Chanchuey & Jongsomjit, 2013) in ethanol dehydration during 200-400 °C.

## 2. Objectives

The main purpose of this work is to characterize the lanthanum-modified alumina-silica catalyst, test catalytic performance and study the possibility of stability due to coke decomposition.

### 3. Material and Method

#### 3.1 Catalyst preparation

##### Spherical silica particle (SSP)

SSP was synthesized by hydrolysis method. (98%) tetraethoxysilane (TEOS), hexadecyltrimethylammonium bromide (CTAB), (30%) ammonia solution and (99.99%) ethanol were mixed by following molar ratio  $1\text{TEOS} : 0.3\text{CTAB} : 11\text{NH}_3 : 58\text{Ethanol} : 144\text{H}_2\text{O}$ . Then, the mixtures were stirred for 2 h. The resultant was separated by centrifuge, dried in a oven and calcined in air at  $550^\circ\text{C}$  for 6 h.

##### Alumina-silica composite catalyst (AlSSP)

60% AlSSP was prepared from (98%) aluminium isopropoxide, 2-propanol, (30%) ammonia solution and SSP. First, aluminium isopropoxide was dissolved in 2-propanol before prepared SSP was added. Secondly, the mixtures were stirred for an hour before  $\text{NH}_3$  solution with ratio of  $\text{H}_2\text{O}:\text{Al}(\text{OPr})_3 = 4:1$  was filled. Then, it was continuously stirred in ambient temperature for 20 h. After that, it was dried and calcined in air at  $650^\circ\text{C}$  for 2 h.

##### Lanthanide doped AlSSP (LaAlSSP)

LaAlSSP was obtained by incipient wetness impregnation method using lanthanum nitrate hexahydrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) as the precursor of lanthanide. The impregnated sample was evaporated, dried in an oven at  $110^\circ\text{C}$  for 6 hour and finally calcined in air at  $550^\circ\text{C}$  for 4 h. The nomenclature of catalysts are xLaAlSSP (where  $x = 0.5\%\text{wt}, 1\%\text{wt}, 2\%\text{wt}$  and  $3\%\text{wt}$ ).

#### 3.2 Catalyst characterization

Catalysts used in this work were characterized by using X-ray diffraction (XRD), energy X-ray spectroscopy (EDX), scanning electron microscopy (SEM), temperature programmed desorption of Ammonia ( $\text{NH}_3$ -TPD) and thermogravimetric analysis (TGA).

The crystal structure of all catalyst was studied by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  radiation with Ni filter. The diffraction intensity as a function of  $2\theta$  was measured in the range of  $10$ – $90$  degree.

Crystalline phase and distribution of element in catalyst were analyzed by scanning electron microscope (SEM)(JEOL mode JSM-5800LV) and energy X-ray spectroscopy techniques (EDX)(Link Isis Series 300 program).

$\text{NH}_3$ -TPD was performed with Micromeritics chemisorb 2750. The samples were pretreated at  $400^\circ\text{C}$  by helium before saturated with  $15\%\text{NH}_3/\text{He}$  at  $120^\circ\text{C}$  for 1 h. Then, physisorbed  $\text{NH}_3$  was removed by purging with helium. The TPD measurement was conducted by heating a sample from  $120$  to  $800^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  in helium stream. The desorbed ammonia was detected by thermal conductivity detector.

Coke deposition in spent catalyst was examined by thermogravimetric analysis (SDT Q600, TA instruments). 5 mg of sample was prepared. The temperature was heated under a  $100\text{ mL}/\text{min}$  air using a  $10^\circ\text{C}/\text{min}$  ramping from  $30$  to  $800^\circ\text{C}$ .

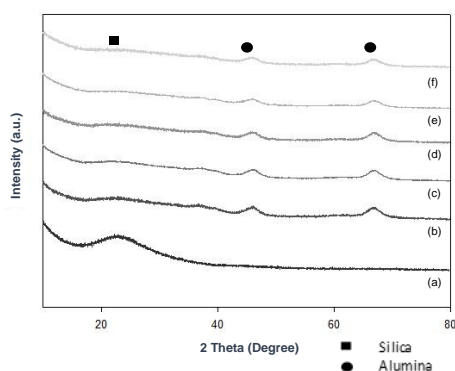
### 3.3 Catalytic performance

Vapor phase of ethanol dehydration was tested in a packed bed reactor under atmosphere pressure and temperature ranging from 200 - 400 °C. Approximately 0.05 g of the catalyst was supported by quartz wool and placed at the middle of the reactor that was installed in temperature-controlled furnace. The first step was preheated reactor with argon as carrier gas and followed by saturation of liquid ethanol. Each step was set at desired temperature for 1 h. After that, vaporized ethanol was fed into reactor by argon as carrier gas. Reactant and product samples were taken during 200-400 °C and analyzed by FID gas chromatograph, using DB5 capillary column.

## 4. Result and Discussion

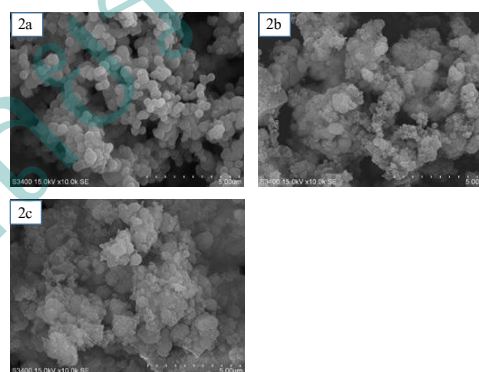
### 4.1 Textural properties

Figure 1 shows XRD patterns of SSP, AISSP and xLaAISSP. It is found that amorphous silica peak is at 21-24° (Zhan et al., 2010) and  $\gamma$ -alumina exhibits peaks at 46° and 67° (Phongsawat et al., 2012), but no peak of lanthanum can be observed for all loading due to uniform dispersion in surface and no effect to basic phase structure (Ouyang et al., 2009; Zhan et al., 2010).

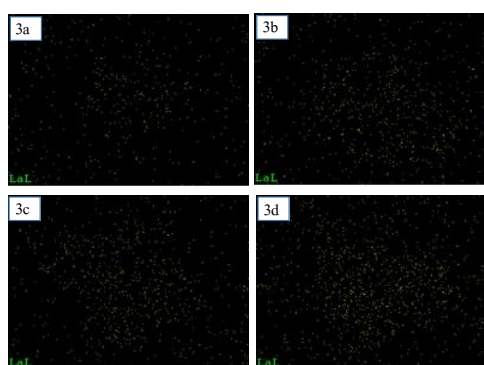


**Figure 1** XRD patterns of (a) SSP (b) AISSP (c) 0.5LaAISSP (d) 1LaAISSP (e) 2LaAISSP (f) 3LaAISSP

SEM images at an accelerating voltage of 15 kV and magnification of 10000 in SSP, AISSP and 3LaAISSP samples are shown in Figure 2. Figure 2a represents a spherical and flat in SSP and when adding alumina in SSP, there is a scraggly surface as shown on Figure 2b. After impregnated with 3% lanthanum, the morphology is shown in figure 2c. EDX analysis of all lanthanum loading in AISSP are presented in Figure 3a to 3d indicating good distribution.



**Figure 2** SEM picture of (a) SSP (b) AISSP (c) 3LaAISSP



**Figure 3** EDX mapping of lanthanum in (a) 0.5LaAISSP (b) 1LaAISSP (c) 2LaAISSP (d) 3LaAISSP

From temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD), the amount of weak and medium/strong acidity was classified by assigning the peak below 300 °C for weak acid and the above for

medium/strong acid sites (Ravenelle et al., 2011; Madeira et al., 2006). The result in Table 1 shows a medium-strong acidity has a tendency to decrease and weak acidity increases due to the addition of lanthanum.

**Table 1** Amount of acid strength in catalyst (mole/g catalyst)

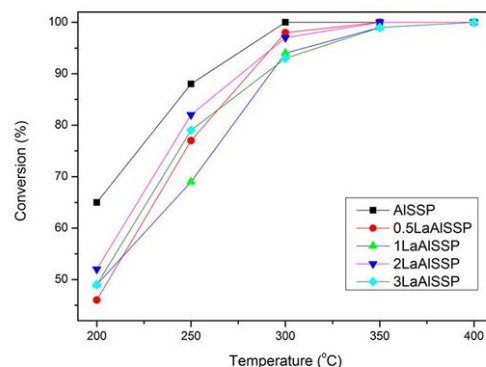
Acid strength	AlSSP	0.5LaAlSSP	1LaAlSSP	2 LaAlSSP	3 LaAlSSP
medium-Strong	0.055	0.055	0.045	0.045	0.031
Weak	0.003	0.009	0.004	0.009	0.008
W/MS ratio	0.056	0.154	0.082	0.200	0.248

#### 4.2 Catalytic performance of reaction

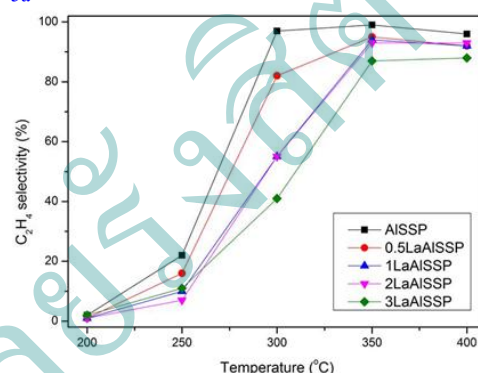
Ethanol conversion of lanthanum-doped catalyst has a tendency to decline slightly during 200-300 °C when comparing with AlSSP, but there is no significant difference at 350 and 400 °C as shown in Figure 4. The result in Figure 5a and 5b identify that an addition of lanthanum dramatically diminish ethylene selectivity and significantly increase diethyl ether due to acidity. Acid strength is an essential factor for dehydration and product distribution. The modification with lanthanum can increase weak acid site in catalyst, resulting in higher DEE selectivity more than AlSSP. Consistent with that weak acid sites are required for DEE route (Madeira et al., 2006). Temperature is a factor for reaction also. When temperature is increased, conversion and ethylene selectivity have tendency to increase significantly, but diethyl ether continue to decline for all catalysts as shown in figure 4 and 5.

**Figure 4** Effect of lanthanum on ethanol conversion

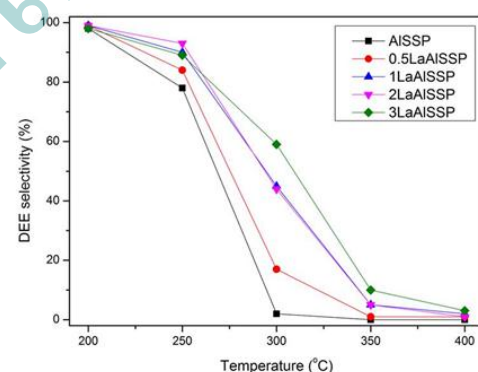
**Figure 5** Effect of lanthanum on (a) ethylene and (b) diethyl ether selectivity



5a



5b

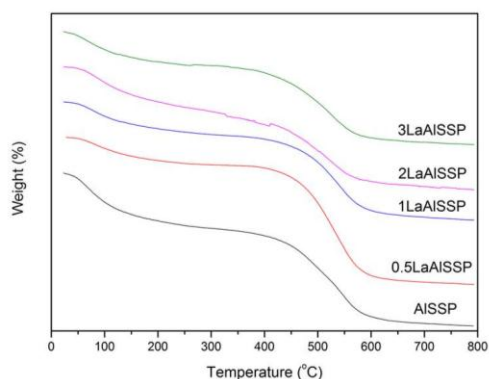


#### 4.3 Characterization of the spent catalysts

Thermogravimetric analysis was done to study carbon deposition. Figure 6 represents % weight loss of all catalysts as a function of temperature. The weight loss between 300 °C and 800 °C ascribed to coke and loss during 100-300 °C referred to volatile substance. Quantitative result as seen in Table 2 reveals that the addition of lanthanum could decrease coke deposition.

**Table 2** Quantitative result of coke deposition

Catalyst	Al-SSP	0.5LaAl-SSP	1LaAl-SSP	2 LaAl-SSP	3 LaAl-SSP
% coke	11.8	14.0	10.1	9.3	9.3

**Figure 6** TGA results of the spent catalysts (AlSSP and xLaAlSSP)

## 5. Discussion

From the study on the addition of lanthanum (0.5-3%wt) into AlSSP, it was found that lanthanum could decrease coke deposition which is an important cause of deactivation. It is possible that lanthanum-doped catalyst may have more stability than AlSSP, so catalytic performance with time on stream should be tested in order to assure an effect of lanthanum on stability of the catalyst.

## 6. Conclusion

From the various characterization techniques and ethanol dehydration study of lanthanum modified alumina-silica catalyst, we found that

- A modification was not affected on phase structure and a high dispersion of lanthanum was observed.
- Weak acid sites had a tendency to increase.

-Both ethanol conversion and ethylene selectivity diminished, but diethyl ether increased for lanthanum modification.

-After temperature was increased during reaction, not only ethanol conversion and ethylene selectivity increased for all catalysts, but diethyl ether continued to decline also.

-Coke deposition in spent modified catalyst decreased with lanthanum loading.

## 7. Acknowledge

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