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# Stability of mixed-phase alumina catalysts for ethanol dehydration reaction

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***Abstract*— Dehydration reaction is an important and basic technology for converting ethanol into ethylene product which temperature is less than pyrolysis reaction. It is also considered as alternative energy for future. Many researches improve and modify catalyst in order to obtain high selectivity. The selectivity factor mostly depends on acidity on a catalyst and temperature, which is catalytic early degradation.**

**In this present study, the mixed gamma and chi crystalline phases of alumina catalyst calcined at 600 °C was employed for ethanol dehydration to ethylene. The mixed γ- and χ-crystalline phase alumina was prepared by solvothermal method. The catalyst was performed for ethanol dehydration reaction under atmospheric pressure at temperature of 200-400 °C in a fixed-bed reactor. They exhibited both high conversion and high selectivity to ethylene more than 90% of interval temperature 350-400 °C. The catalyst was characterized by several techniques. However, the stability of these catalysts will be further investigated by reaction test at the specified temperature (300-400 °C) within time-on-stream (TOS) around 6 hrs. The coke formation will appear on the surface of spent catalysts. After TOS 12 hrs., the coke content reaches very high level, which affects to catalyst deactivation. Therefore, the operating condition (such a TOS and temperature) leads to generate coke deposited on the catalysts significantly. The different characteristics of the fresh and spent catalysts will be compared and discussed further.**

***Keywords*— Deactivation, Ethanol dehydration reaction, Mixed-phase alumina, Optimum temperature, Stability**

## I. INTRODUCTION

Ethylene is an important preliminary product of petrochemical industry and many requirements in the world. Because ethylene is mostly used in reactant for produced a variety of polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and so on. Moreover, it is also used as intermediate compounds of ethylene dichloride, ethylene oxide and ethyl benzene as well as fibres and other organic chemicals [1]-[3]. However, these products are launched on consumer markets such as the packaging, transportation, electrical/electronic, textile and construction industries as well as consumer chemicals, coatings and adhesives.

Normally, ethylene is produced in the petrochemical industry by steam thermal cracking of hydrocarbon such as naphtha, liquefied petroleum gas and gas oil. The steam thermal cracking or pyrolysis method requires high thermal temperature around 750-900°C because of its endothermic reaction [4]. Nowadays, crude oil petroleum is concerned about non-renewable resource and limited consumer. Therefore, a new wave of produced ethylene is being created from definition of "Green chemical process technologies". The classified of green process based on natural bioethanol which produced from fermentation of sugar cane or corncob, avoiding the use of food products. Ethylene is obtained by dehydrating bioethanol vapor using a catalyst containing a mixture of magnesium oxide, alumina, silica and so on that can reduce the thermal energy, cost and also friendly environment to enhance yield in chemical process development.

The main catalysts which are used for ethanol dehydration reaction are based on γ-$Al_2O_3$ and HZSM-5 zeolite. Generally, the former required higher reaction temperature and lower product selectivity than zeolite. However, zeolite catalyst rapidly deactivated by coke formation. Therefore, researchers concentrate on alumina modification because γ-$Al_2O_3$ catalyst has excellent thermal stability, fine particle size, high surface area in adsorb and inhibit side reaction.

The objective of this research is to study stability of mixed γ- and χ-crystalline phase alumina for optimal operating condition via ethanol dehydration reaction that related to temperature and time on stream. The result is investigated physicochemical properties by using several techniques which were X-ray diffraction (XRD), $N_2$ physisorption (BET), $NH_3$-temperature programmed desorption ($NH_3$-TPD), thermogravimetric analysis (TGA), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX).

## II. MATERIALS AND METHODS

### A. Materials

Aluminum isopropoxide : $AIP[(CH_3)_2CHO]_3Al$ (Aldrich 98%), Toluene($C_6H_5CH_3$) (Merck 99%), 1-Butanol($C_4H_{10}O$) (Merck 99%), Methanol($CH_3OH$) (Merck), Ultra high purity nitrogen gas (TIG 99.99%), and Ethanol $C_2H_5OH$ (J.T.Baker 99.99%).

### B. Synthesis of mixed-phase alumina catalysts

The mixed gamma and chi crystalline phases of alumina were prepared via the solvothermal method. Aluminum isopropoxide (AIP) 25g was suspended in 100ml mixed solution (50ml toluene and 50ml 1-butanol) in a test tube. After that bring it in a 300ml autoclave and then added 30ml

solvent (15ml toluene and 15ml 1-butanol) in the gap between the test tube and the autoclave wall. The mixture is purged with nitrogen at pressure 20 bar. The operating condition is heated up to 300°C at 2.5°C/min heating rate and holding for 2 hrs. After it cooled down to room temperature, the resulting powder was washed with methanol several times by centrifugal machine at 20 rpm for 5 minutes and air drying overnight. The catalyst powder was calcined in a tube furnace for temperatures at 600°C with a heating rate 10°C/min and holding in the air for 6 hrs.

### C. Catalytic characterization

*1) X-ray diffraction (XRD):* The bulk crystal structure and X-ray diffraction (XRD) patterns of the catalysts will be determined by the SIEMENS D5000 X-ray diffractometer connected with a personal computer with Diffract ZT version 3.3 programs for fully control of the XRD analyzer. The experiment will be carried out by using Cu Kα radiation source with Ni filter in the 2θ range of 20 to 80° with a resolution of 0.02°. The mean crystallite size was calculated from the Scherrer equation [5].

*2) Nitrogen physisorption:* The BET surface area, pore volume and pore diameter of catalysts will be determined by nitrogen gas adsorption at liquid nitrogen temperature (-196°C) using Micromeritics ChemiSorb 2750 Pulse chemisorption System instrument. Before characterization, the sample will be thermally treated at 150°C for 1 hr.

*3) Temperature programmed adsorption ($NH_3$-TPD):* The acid properties of catalysts will be investigated by temperature programmed adsorption of ammonia ($NH_3$-TPD) equipment by using Micromeritics chemisorp 2750 Pulse Chemisorption System. In an experiment, a packed quartz wool and 0.1 g of catalyst will be loaded in a quartz tube and pretreated at 500°C under helium flow. The sample will be saturated with 15%$NH_3$/He. After saturation, the physisorbed ammonia will be desorbed under helium gas flow about 30 min. and then the sample will be heated from 40°C to 800°C at heating rate 10°C.min$^{-1}$. The amount of ammonia in effluent will be measured via TCD signal as a function of temperature.

*4) Thermal gravimetric analysis (TGA):* The spent mixed-phase alumina catalysts will be subjected to the thermal gravimetric analysis (Diamond Thermogravimetric and Differential Analyzer, TA Instruments SDT Q600) to determine the carbon content in the sample, as well as their thermal behaviors in the range of 30 to 800°C. The analysis will be performed at heating rate of 10°C.min$^{-1}$ in 100ml.min$^{-1}$ flow of air.

*5) Scanning electron microscopy and Energy X-ray Spectroscopy (SEM-EDX):* Scanning electron microscopy was observed the morphologies of catalysts after TGA checked by using JEOL JSM-35 CF model. The elemental dispersion over the catalysts surface were determined by energy x-ray spectroscopy (EDX) which it was perform on Link Isis Series 300 program.

### D. Catalyst tests in ethanol dehydration reaction

This experiment use 0.05 g. catalyst which was packed in a continuous down-flow fixed-bed reactor with an inner diameter size 0.7 mm. at 200°C under ambient pressure. The catalyst was placed on 0.01 g. quartz wool in the middle of a borosilicate glass reactor. Previous in situ activation was performed under argon (50 ml.min$^{-1}$) for 1 hr. at 200°C and 190 volt. The gas flow was kept during reaction, while absolute ethanol was fed into the reactor. The reaction was detected at temperature 300°C, 350°C and 400°C for mixed-phase alumina.

Reaction products were continuously monitored by online gas chromatography using a Shimadu GC8A gas chromatography equipped with FID detector connected to DB-5 capillary column at 150°C every 1 hr. for cycle.

## III. Results and Discussion

### A. Catalytic characterization

*1) X-ray diffraction (XRD):* *Transitional* alumina phase was characterized by using X-ray diffraction technique in order to prove and identify the structure of catalysts. XRD patterns of mixed-phase alumina catalysts synthesized via solvothermal method of AIP compound in 50:50 solution between toluene and 1-butanol were obtained. The catalysts were properly calcined at 600°C. The characteristic peaks of alumina reflect γ-phase at $2\theta$ = 32°, 37°, 39°, 45°, 61° and 66° and χ-phase at $2\theta$ = 37°, 40°, 43°, 46°, 60° and 67° confirms the transformation of mixed-phase as shown in Figure 1 [6].

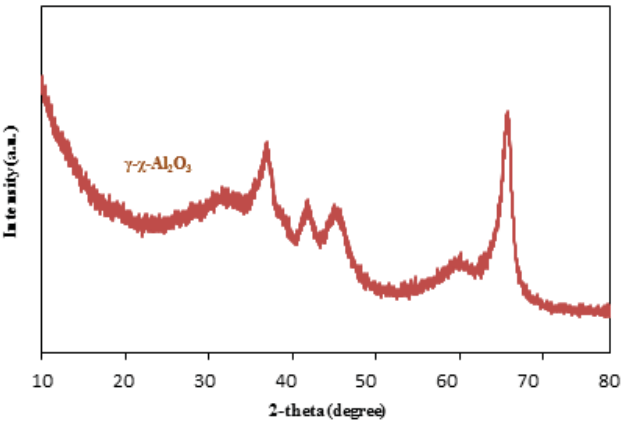


Fig. 1 XRD patterns of mixed γ- and χ-crystalline phase alumina

*2) Nitrogen physisorption:* The pore structure and the BET surface area of γ-χ $Al_2O_3$ sample were analysed on the basis of nitrogen adsorption-desorption isotherms as shown in Fig. 2, exhibited IV-type isotherms, indicating the existence of well-developed mesopores [7]. The pore diameter (D) is divided into three categories; macropores (D > 50 nm), mesopores (2 nm < D < 50 nm) and micropores (D < 2 nm) [8]. Therefore, the pore size distribution curve of the sample confirms to sort of unimodal with mesopores as shown in Fig. 3 (2-28 nm). The pore structure parameters of the γ-χ $Al_2O_3$ sample are listed in Table I.

TABLE I
BET SURFACE AREA, PORE VOLUME AND PORE SIZE DIAMETER OF THE MIXED Γ- AND X-CRYSTALLINE PHASE ALUMINA CATALYSTS.

| Sample | BET surface area | Pore volume | Pore size diameter |
|---|---|---|---|
| | $S_{BET}$ ($m^2$/g) | $P_V$ ($cm^3$/g) | $P_d$ (nm) |
| γ-χ $Al_2O_3$ | 200 | 0.69 | 8.26 |

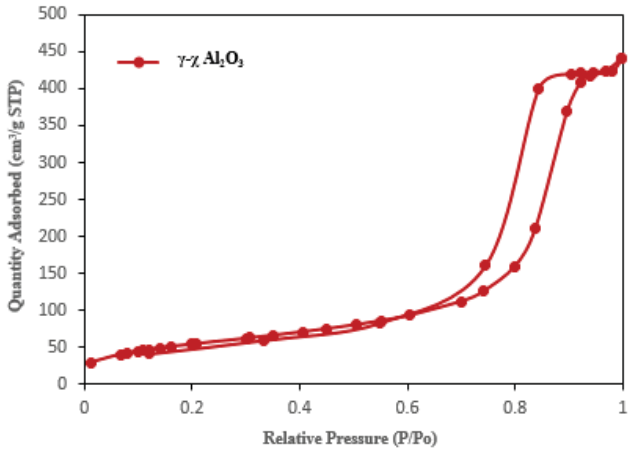


Fig. 2 The $N_2$ adsorption–desorption isotherms of mixed γ- and χ-crystalline phase alumina catalysts with calcined 600°C

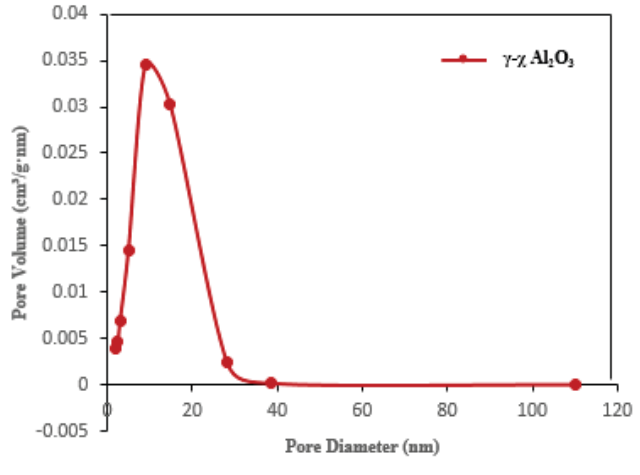


Fig. 3 Pore size distribution of mixed γ- and χ-crystalline phase alumina catalysts with calcined 600°C

*3) Temperature programmed adsorption ($NH_3$-TPD):* $NH_3$-TPD is one of the powerful techniques for characterizing surface acidity of heterogeneous catalysts. The higher desorption temperature identifies to strong acid site, corresponding to amount of $NH_3$ desorbed from under $NH_3$–TPD peak as shown in Table II. In Fig. 4, Mixed-phase alumina shows two peaks at 100-220 °C and 220-800 °C. The former indicates weak and the latter presents medium to strong acid site, consecutively. They are typically known as Lewis acid sites [9]. Moreover, the acid site was important to catalytic activity for ethanol dehydration into ethylene.

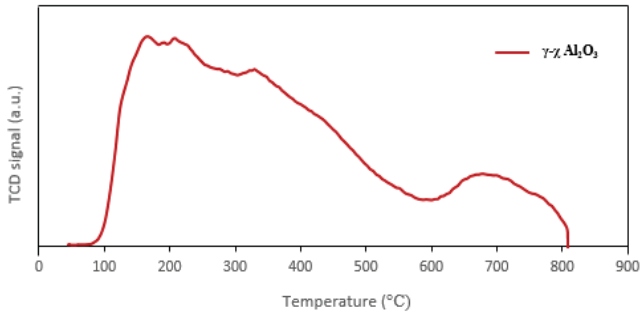


Fig. 4 $NH_3$-TPD of mixed γ- and χ-crystalline phase alumina catalysts

TABLE II
AMOUNT OF $NH_3$ DESORBED MEASURED BY AREA UNDER THE PEAK IN DIFFERENT TEMPERATURE RANGE IN THE $NH_3$-TPD PROFILES OF MIXED Γ- AND X-CRYSTALLINE PHASE ALUMINA CATALYSTS

| Sample | $NH_3$ desorption (mmol $NH_3$/g cat.) | | Total acidity (mmol $NH_3$ /g cat.) |
|---|---|---|---|
| | weak | medium to strong | |
| γ-χ $Al_2O_3$ | 2.71 | 6.20 | 8.91 |

## B. *Catalytic Activity*

The catalytic performances of mixed phase alumina in ethanol dehydration was investigated using different reaction temperature in the fixed-bed reactor and the results are given in Fig. 5, 6 and 7 respectively. Fig. 5 and 6 show the relationship of selectivity versus time on stream over mixed γ- and χ-crystalline phase alumina catalysts. The selectivity of ethylene almost keep constant over 90% in during test time 12 hrs. at 350°C and 400°C. On the contrary, at temperature 300°C, it is observed slightly inconsistent selectivity of product. It favours DEE selectivity more than main product at low temperature, corresponding with thermodynamic potential for ethanol dehydration reaction as shown below.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad \Delta H^{298} = +44.9 \text{ kJ/mole} \quad (1)$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \qquad \Delta H^{298} = -25.1 \text{ kJ/mole} \quad (2)$$

The enthalpy change (ΔH) is positive in endothermic reaction and negative in heat-releasing exothermic process. Therefore, the selectivity of DEE is high at low temperature, while selectivity of ethylene increases by rising temperature.

Fig 7 indicates the catalyst under different temperature, which shows a transient period before reaching a stable performance. The GC analysis was carried out at time on stream of 8 minutes and the ethanol conversion increased around within the first 2 hrs. of reaction time. As a result, the catalyst performance is considered at stable profile after the transient period. Therefore, the mixed γ- and χ-crystalline phase alumina catalysts need to pre-treat by the flowing gaseous reactants for activation before steady catalytic performance is reached.

In preliminary experiment results, the modification of mixed-phase alumina catalysts can improve activity to higher selectivity and conversion than main alumina catalyst ($\gamma$-$Al_2O_3$). Obviously, pure gamma alumina displays ethanol conversion around 70%. On the other hand, the mixed-phase alumina displays ethanol 85-90% of conversion which shift to more ethylene product.

*1) TGA of spent catalyst:* The TG analysis is performed in an oxidative atmosphere (air) with linear temperature ramp up. The maximum temperature is selected so that the sample weight is stable at the end of the experiment. Carbon is burn off leaving aluminium oxides. The removal of coke deposits on mixed-phase catalyst can be calculated into weight loss (%). During the temperature less than 200 °C, the weight loss is attributed to the physically adsorbed water in the porous materials. Moreover, the weight loss of the light coke and the heavy coke are attributed to desorption in temperature between 200–550 °C and 550–800 °C, respectively [10]. In Fig. 8, the TG expose two weight loss evident. The first evident represents water loss and the second evident represents coke content by two features in the derivative curve. The amount of coke deposition on spent catalysts tends to increase after rising temperature and also increased reaction time. We can summarize the coke content in Table III where T-400,12hrs. is the highest coke content among all condition.

TABLE III
SUMMARIZED THE AMOUNT OF COKE DEPOSITION ON SPENT MIXED Γ- AND X-CRYSTALLINE PHASE ALUMINA CATALYSTS

| Sample | Light coke weight loss (wt.%) | Heavy coke weight loss (wt.%) | Total weight loss (wt.%) |
|---|---|---|---|
| Temp = 300 °C TOS = 6 hrs. | 3.14 | 0.79 | 6.98 |
| Temp = 350 °C TOS = 6 hrs. | 3.72 | 0.88 | 8.2 |
| Temp = 400 °C TOS = 6 hrs. | 3.89 | 0.84 | 7.21 |
| Temp = 300 °C TOS = 12 hrs. | 3.18 | 0.79 | 7.01 |
| Temp = 350 °C TOS = 12 hrs. | 4.3 | 0.96 | 8.64 |
| Temp = 400 °C TOS = 12 hrs. | 6.43 | 0.94 | 9.63 |

*2) SEM-EDX of spent catalyst:* The Morphology of fresh and spent mixed phase alumina catalysts observed by SEM technique is shown in Fig. 9. As a result, the surface of spent catalyst after TG analysis affects the morphologies compared with a fresh catalyst. It possibly affects from coke formation after run reaction. The coke content can be detected using EDX technique and elemental composition of mixed phase alumina is listed in Table IV.

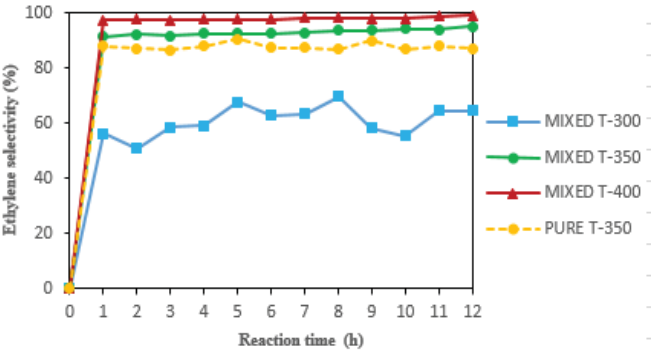


Fig. 5 Ethylene selectivity of mixed γ- and χ-crystalline phase alumina catalysts at 300°C, 350°C and 400°C for TOS 12 hrs.

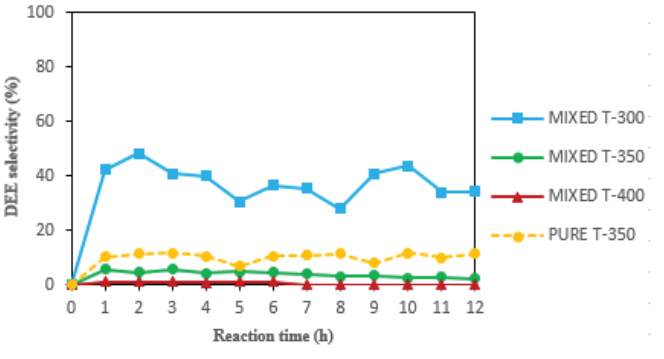


Fig. 6 DEE selectivity of mixed γ- and χ-crystalline phase alumina catalysts at 300°C, 350°C and 400°C for TOS 12 hrs

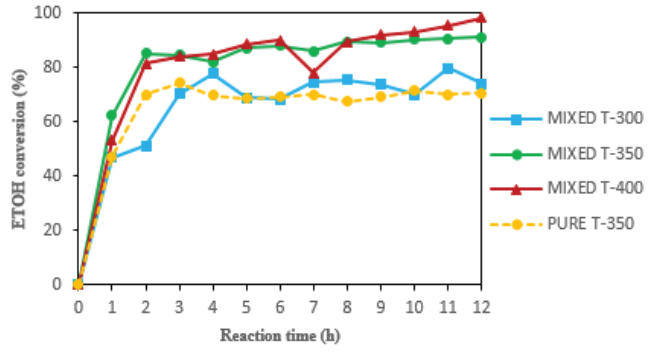


Fig. 7 Ethanol conversion of mixed γ- and χ-crystalline phase alumina catalysts at 300°C, 350°C and 400°C for TOS 12 hrs.

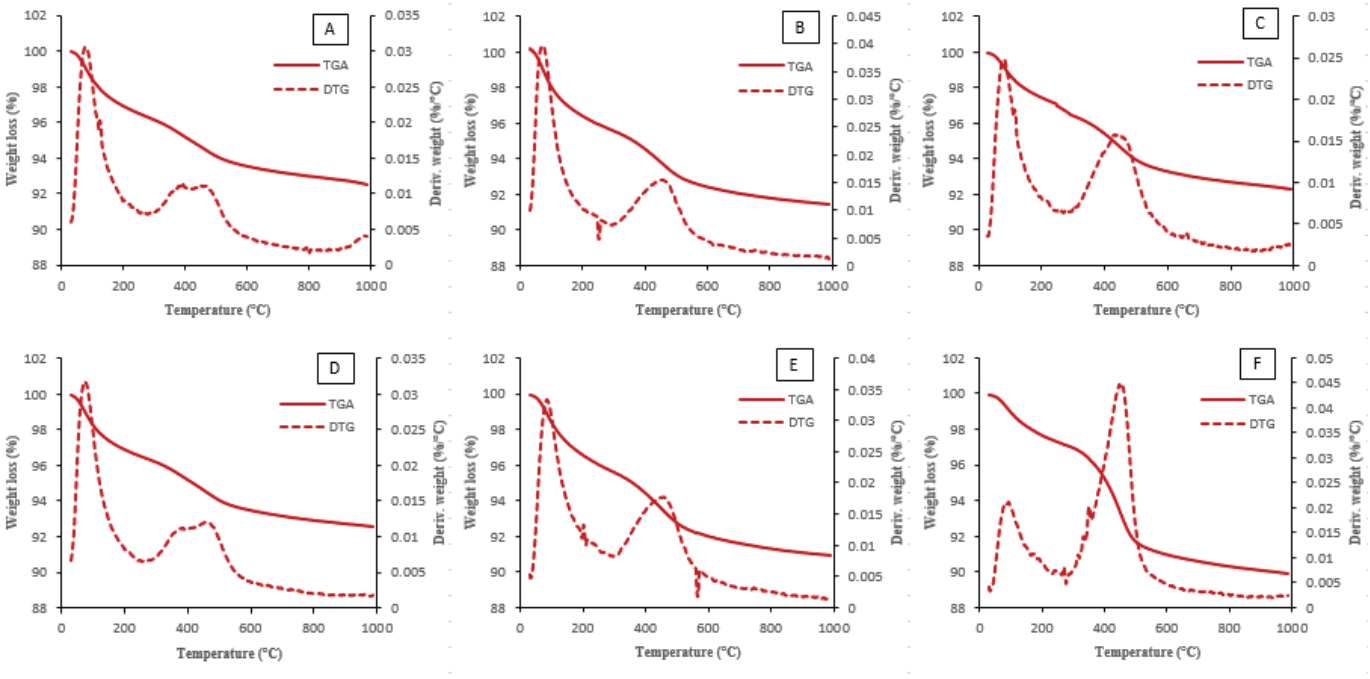


Fig. 8 TG profile of spent mixed γ- and χ-crystalline phase alumina catalysts in different reaction temperature: (A) T-300,6hrs., (B) T-350,6hrs., (C) T-400,6hrs., (D) T-300,12hrs., (E) T-350,12hrs. and (F) T-400,12hrs.

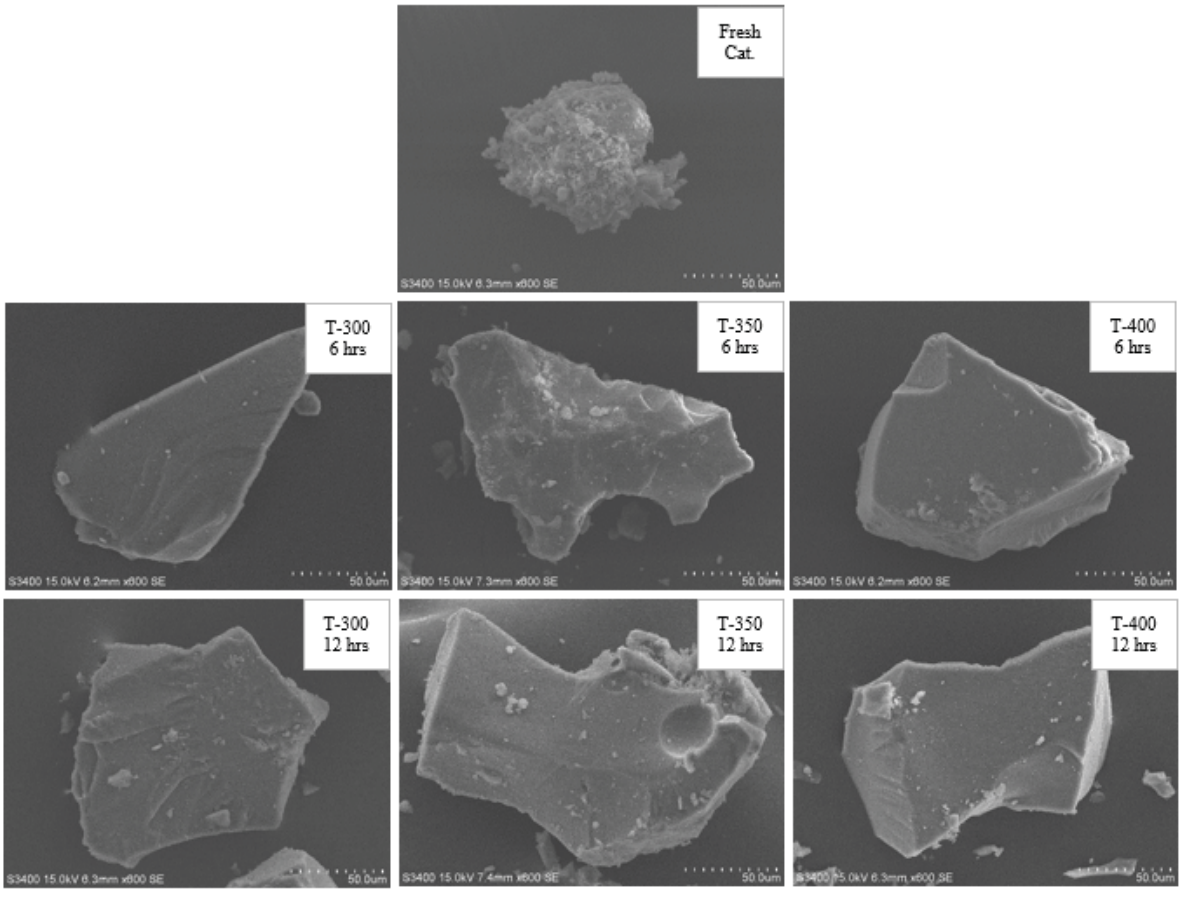


Fig. 9 SEM micrograph of fresh mixed γ- and χ-crystalline phase alumina catalysts and spent mixed γ- and χ-crystalline phase alumina catalysts after TGA

TABLE IV
EDX COMPOSITION ON SPENT MIXED Γ- AND X-CRYSTALLINE PHASE ALUMINA CATALYSTS AFTER TG ANALYSIS

| Sample | %Weight | | | %Atom | | |
|---|---|---|---|---|---|---|
| | Al | O | C | Al | O | C |
| Fresh γ-χ $Al_2O_3$ | 53.29 | 46.71 | - | 40.35 | 59.65 | - |
| Temp = 300 °C TOS = 6 hrs. | 67.84 | 29.56 | 2.60 | 54.91 | 40.36 | 4.73 |
| Temp = 350 °C TOS = 6 hrs. | 59.85 | 37.08 | 3.07 | 47.47 | 47.28 | 5.25 |
| Temp = 400 °C TOS = 6 hrs. | 59.28 | 37.32 | 3.40 | 45.65 | 48.47 | 5.88 |
| Temp = 300 °C TOS = 12 hrs. | 64.84 | 31.95 | 3.21 | 51.49 | 42.78 | 5.72 |
| Temp = 350 °C TOS = 12 hrs. | 65.34 | 30.93 | 3.73 | 51.91 | 41.44 | 6.65 |
| Temp = 400 °C TOS = 12 hrs. | 66.48 | 28.73 | 4.79 | 52.89 | 38.54 | 8.57 |

## IV. CONCLUSIONS

The catalytic performance for ethanol dehydration reaction revealed that the highest ethanol conversion and ethylene selectivity were around 90% and 98% in the stable period at T-400, respectively. On the contrary, stability of T-400 was less than T-350 because the spent catalysts were observed that coke formation increases with a function of temperature and time-on-stream condition. It affects to degrade catalyst rapidly. The ethanol conversion increased within the first 2 hrs. of reaction time after pre-treat catalysts. In all condition, the activity of fresh catalysts was maintained over 12 hrs. Therefore, the optimum condition of stability of mixed phase alumina catalyst is possibly suitable at T-350 and greater than pure gamma alumina catalyst.

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