การศึกษาผลกระทบของความเข้มข้นของเอธานอลต่อปฏิกิริยาการปฏิรูปเอธานอลด้วยไอน้ำ บนตัวเร่งปฏิกิริยา Co/SiO_2

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บทคัดย่อ

เอธานอลที่ได้จากกระบวนการหมักของชีวมวล สามารถถูกปฏิรูปด้วยไอน้ำเป็นไฮโดรเจน เมื่อมีตัวเร่งปฏิกิริยาที่เหมาะสม ตัวเร่งปฏิกิริยาโคบอลต์บนตัวรองรับซิลิกา โดยมีปริมาณโคบอลต์ 10 เปอร์เซ็นต์โดยน้ำหนัก ถูกใช้ในการศึกษานี้ เพื่อหาความเข้มข้นที่เหมาะสมของเอธานอล ในการทำปฏิกิริยาปฏิรูปด้วยไอน้ำ ที่ความเข้มข้นของเอธานอล 15%, 20% และ 25% โดยปริมาตร ที่อุณหภูมิ 450 °C และความดันบรรยากาศ ผลการทดลองแสดงให้เห็นว่า ถึงแม้ว่าไฮโดรเจนที่ผลิตได้มีปริมาณเพิ่มขึ้นเมื่อเพิ่มความเข้มข้นของเอธานอล ในรูปของผลผลิตกลับมีค่าลดลง นั่นคือสัดส่วนของเอธานอลที่ถูกเปลี่ยนเป็นไฮโดรเจนมีค่าลดลง ซึ่งแสดงให้เห็นในรูปของค่าการเลือกของไฮโดรเจนที่ลดลง ในทางตรงข้าม ค่าการเลือกของคาร์บอนมอนนอกไซด์ มีค่าค่อนข้างคงที่กับความเข้มข้นของเอธานอล ดังนั้นในเชิงคุณภาพของผลิตภัณฑ์ และผลผลิตของไฮโดรเจน ความเข้มข้นของเอธานอลที่ 15% โดยปริมาตรดูเหมือนเป็นสภาวะที่ดีที่สุดในการปฏิรูปด้วยไอน้ำของเอธานอล ผลการทดลองนี้สื่อเป็นนัยว่า เอธานอลที่ได้จากการหมักชีวมวลสามารถนำไปใช้ได้โดยตรง โดยไม่ต้องผ่านกระบวนการกลั่น นอกจากนั้น การพิจารณาดีกรีการใช้ประโยชน์ของตัวเร่งปฏิกิริยาเป็นอีกสิ่งหนึ่งที่น่าสนใจ ค่าความถี่ในการหมุนเวียนที่สูงขึ้นเมื่อเพิ่มความเข้มข้นของเอธานอล หมายความว่าตัวเร่งปฏิกิริยาถูกใช้ประโยชน์มากขึ้น เมื่อเพิ่มปริมาณโคบอลต์เป็น 20% โดยน้ำหนัก ผลการทดลองพบว่าคุณภาพของผลิตภัณฑ์ดีขึ้น นอกจากนั้น ความถี่ในการหมุนเวียนของตัวเร่งปฏิกิริยา 10% และ 20% Co/SiO_2 ที่สภาวะเดียวกัน มีค่าเท่าๆ กัน ดังนั้นปฏิกิริยาการปฏิรูปด้วยไอน้ำของเอธานอลจึงเป็นปฏิกิริยาที่ไม่ไวต่อโครงสร้างของตัวเร่งปฏิกิริยา เนื่องจากไม่ขึ้นกับขนาดอนุภาคของตัวเร่งปฏิกิริยา และที่อุณหภูมิเดียวกัน ความว่องไวของจุดกัมมันต์ของโคบอลต์เปลี่ยนแปลงกับความเข้มข้นของเอธานอลเท่านั้น ผลการทดลองในการศึกษาการเสื่อมสภาพของตัวเร่งปฏิกิริยา หลังจากใช้ในปฏิกิริยาเป็นเวลา 6 ชั่วโมง ไม่พบการรวมตัวของตัวรองรับซิลิกาจากความร้อน แต่พบการลดลงเล็กน้อยของปริมาตรรูพรุน และขนาดรูพรุนซึ่งเป็นไปได้ว่าเกิดขึ้นเพราะการก่อตัวของโค้กภายในรูพรุนขนาดกลาง

คำสำคัญ : ปฏิรูปเอธานอลด้วยไอน้ำ / ตัวเร่งปฏิกิริยา Co/SiO_2 / ผลจากความเข้มข้นของเอธานอล

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The Study on the Effect of Ethanol Concentration on Co/SiO_2 Catalyst for the Steam Reforming of Ethanol

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Abstract

Ethanol obtained from the fermentation process can be steam reformed to hydrogen in the presence of suitable catalyst, to be further used in fuel cells. In this study, the 10%Co/SiO_2 catalyst was studied to determine the suitable concentration of ethanol during the steam reforming. The ethanol concentration was varied from 15%, to 20% and 25% by volume at 450 °C reaction temperature and atmospheric pressure. The results showed that although the amount of hydrogen generated increased with ethanol concentration, in term of hydrogen yield it decreased. It implied that smaller fraction of ethanol was converted to hydrogen at higher ethanol concentration, as shown by the decrease in hydrogen selectivity. On the other hand, the selectivity toward carbon monoxide was nearly constant with ethanol concentration. Thus, in term of product quality and hydrogen yield, 15% ethanol by volume seems to be the best condition for ethanol steam reforming. This result implied that bio-ethanol from fermentation process can be directly used without distillation. The degree of utilization of the catalyst can be shown in term of turnover frequency (TOF). It showed that higher TOF was obtained at higher ethanol concentration meaning that catalyst was more utilized at higher ethanol concentration. When increasing the cobalt loading to 20%, it was found that the product quality was improved. In addition, the TOFs of the 10% and 20% Co/SiO_2 were approximately the same at the same reaction condition, thus, the steam reforming of ethanol is the structural insensitive reaction. It suggested that at the same reaction temperature, site activity of cobalt metals varies only with the concentration of ethanol, not the percent loading. Results from the deactivation study after 6 hours of reaction showed no sintering of silica support but a slight decrease in pore volume and pore size was observed, probably by a slight coke formation inside the mesopores.

Keywords : Ethanol Steam Reforming / Co/SiO_2 Catalyst / Ethanol Concentration

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1. Introduction

Main fuels used at present come from crude oil refinery. This energy source is limited and will be extinguish within a few decades. This necessity forces researchers to look for other alternative fuels. Fuel derived from biomass is an environmental friendly alternative. Its high availability makes it more attractive especially in agricultural countries like Thailand. The fermentation process can be incorporated to produce ethanol, which can be steam reformed to hydrogen and then further used in fuel cells. The overall process from biomass production to fuel cell operation has zero net carbon dioxide generation.

The main reaction of ethanol steam reforming is:

$$C_2H_5OH + 3H_2O \longrightarrow 6H_2 + 2CO_2 \qquad \textbf{(1)}$$

Other side reactions such as reverse water gas shift generate undesired byproducts. The most important one is carbon monoxide. Carbon monoxide can poison the fuel cell electrode and inhibit the oxidation reaction taking place on the anode. Many types of fuel cells have limited CO tolerance even with more advanced anode catalysts. There are many factors that can affect carbon monoxide content in the product stream of steam reforming process. Reaction conditions, feed conditions, types of catalysts are examples. Another alternative is to incorporate a downstream process such as selective oxidation prior to fuel cell.

Metals found active to ethanol steam reforming are Pd, Rh, Ni, and Co [1-4]. These metals have been studied after being dispersed on different supports. Over a wide range of metals supported on alumina, it was found that cobalt was the most selective one at temperature around 400 ^{o}C [5]. In addition, the product composition can be adjusted by varying the reaction conditions [6]. The acidity of support is also another factor to consider. Ethylene production is promoted by support acidity [5]. This ethylene is the precursor of carbon that deposits on catalyst surface and makes it deactivates [5].

This study focused on the activity of Co/SiO_2 catalyst with varying ethanol concentrations. Co/SiO_2 was chosen because it was cheaper than other metals with comparable activity. The effect of ethanol concentration (ethanol/water ratio) was investigated. Information from this study can be used to control the extent of fermentation process.

2. Experimental

2.1 Catalyst preparation

Catalysts consisting of 10 wt% and 20 wt% Co supported on SiO_2 powder were prepared by incipient wetness impregnation. The support was first dried at 110 ^{o}C for 6 h to get rid of moisture before being impregnated at room temperature with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$. The catalyst was then dried overnight at 110 ^{o}C and calcined at 350 ^{o}C for 2 h under static dry air.

2.2 Catalyst characterization

BET surface area

The BET surface areas of prepared catalysts were measured by Quantachrome Instruments, AUTOSORB-1. Prior to the BET measurement, the sample was degassed by purging helium for more than 2 hrs. After that, the sample was moved to the analyzing port where it was kept at liquid nitrogen temperature (77 K). The amount of adsorbed N_2 at different pressures was measured and compared with that of standard at P_O (P_O ~ 760-770 mmHg). After the analysis was completed, the surface area (m^2/gram of catalyst), pore volume (cc/ gram of catalyst), pore size (Å) and adsorption isotherm were reported.

H_2-chemisorption

To determine the number of surface metal atoms, approximately 0.3 g of sample was placed in the pulse chemisorption instrument (Pulse ChemiSorb 2700). Before packing the catalyst sample into the sample cell, the pressure of inlet gases (N_2 and H_2) was adjusted to 760 mmHg. Then, the sample cell was purged with carrier gas (N_2) at 400 °C to removed moisture. After that, flow was switched to hydrogen to reduce sample at 400 °C for 2 hrs. After reduction, the sample was purged again with nitrogen to removed hydrogen inside the sample cell while it was cooled to adsorption temperature (100 °C). During the analysis, known amount of hydrogen was injected into the sample cell until the sample was saturated with hydrogen. This amount of hydrogen was reported by the value shown on the monitor. The stoichiometry of H_2 chemisorption on Co metal was assumed to be 1 hydrogen atom on 1 surface Co atom (H:Co = 1:1).

X-Ray Powder Diffraction (XRD)

To confirm that no cobalt nitrate was left in the catalyst samples after calcination, the x-ray powder diffraction was used to determine the crystalline phase of prepared catalysts. The analysis was performed in JEOL X-ray Diffractometer with $2\theta = 100^{\circ}$.

2.3 Reaction system

The ethanol steam reforming was carried out in a fixed-bed stainless steel reactor. Ethanol with different concentrations was fed to the preheater by the electromagnetic dosing pump (the LMI MILTON ROY model number A962-161S). Ethanol vapor and steam were flowing further through the reactor with the stream of helium. Helium was used as the carrier gas for both the reaction and the gas chromatography. The reactor outlet was connected with an ice bath to condense unreacted reactants and liquid products before the dry gas was collected in the sampling u-shape tube. The schematic diagram of this ethanol steam reforming system is shown in Fig. 1.

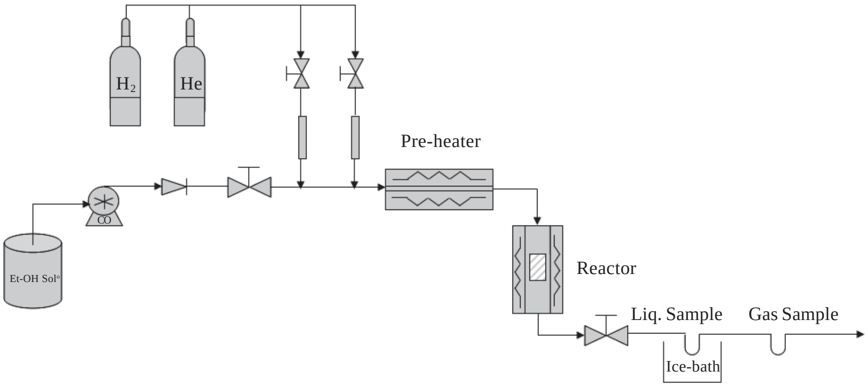

Fig. 1 Schematic diagram of the ethanol steam reforming laboratory system

2.4 Activity measurement

Prior to the activity measurement, approximately 1.0 g of catalyst sample was reduced in situ at 400 °C for 2 hrs in flowing hydrogen. The activity of the catalyst was measured under the following conditions: temperature = 450 °C, total pressure = 1 atm and gas hourly space velocity (GHSV) = 12,462 cc/g cat hr. To study the effect of ethanol concentration, the concentration was varied from 15% by volume to 20% and 25% for the 10% Co/SiO_2 catalyst. Dry gas products were analyzed by TCD gas chromatography (Shimadzu model 9A) using Carbosieve SII column. For the best product separation, the oven temperature was set at 35 °C for 5 min before ramping to 200 °C with 35 °C/min of ramping rate. Since the effluent from the reaction consisted mainly of only H_2, CO, CO_2 and CH_4, in this study, the percent ethanol conversion, hydrogen yield, hydrogen selectivity and carbon selectivity are defined as follows.

$$\%\text{Ethanol conversion} = \frac{\text{summation of CO, } CO_2, CH_4 \text{ (moles)}}{2 \text{ X amount of ethanol in feed (moles)}} \text{ X } 100\%$$

$$\%\text{Hydrogen yield} = \frac{\text{amount of hydrogen generated (moles)}}{6 \text{ X amount of ethanol in feed (moles)}} \text{ X } 100\%$$

$$\%\text{Hydrogen selectivity} = \frac{\text{amount of hydrogen generated (moles)}}{6 \text{ X amount of ethanol converted (moles)}} \text{ X } 100\%$$

$$\%\text{Carbon selectivity} = \frac{\text{amount of that species generated (moles)}}{2 \text{ X amount of ethanol converted (moles)}} \text{ X } 100\%$$

3. Results and Discussion

3.1 Catalyst Characterization

As shown in Table 1, results from the BET measurement showed high surface area of silica powder used as the support in this study. After cobalt was added, the total surface areas of the catalysts and catalyst pore volumes decreased as the percent metal loading increased. These indicate the possible blockage of silica pores by cobalt clusters. When considering the Co dispersion obtained from the total amount of H_2 chemisorption, it is quite low for both catalysts as expected for cobalt catalysts prepared by the incipient wetness impregnation method. Results from H_2 chemisorption can also be used to confirm the blockage of silica pores after the Co particle size was calculated. In general, metal particle sizes can be approximated from % dispersion using the following formula [7].

$$d = \frac{108}{\% D} \qquad \textbf{(2)}$$

where D : the dispersion (%)

d : average crystallite diameter (nm)

As shown in Table 1, the Co particle size was found to be 52.74 nm and 92.18 nm for 10%Co/SiO_2 20%Co/SiO_2, respectively. This large agglomeration of cobalt particles (57-92 nm) can completely block some of small mesopores of silica leading to the lower pore volume and surface area.

Table 1 Characteristics of Co/SiO_2 catalysts

Catalyst	**Surface area** (m^2/g)	**Pore volume** (cc/g)	**Pore size** (Å)	**Co Dispersion** (%)	**Metal particle size** (nm)
1) SiO_2 Powder	257	1.182	183.5	-	-
2) 10%Co/SiO_2	237	1.014	170.7	1.8706	57.74
3) 20%Co/SiO_2	199	0.829	166.8	1.1716	92.18

(c) X-Ray Diffraction (XRD)

Fig. 2 shows the comparison between the XRD patterns of two catalysts containing different metal loadings, 10%Co/SiO_2 and 20%Co/SiO_2.

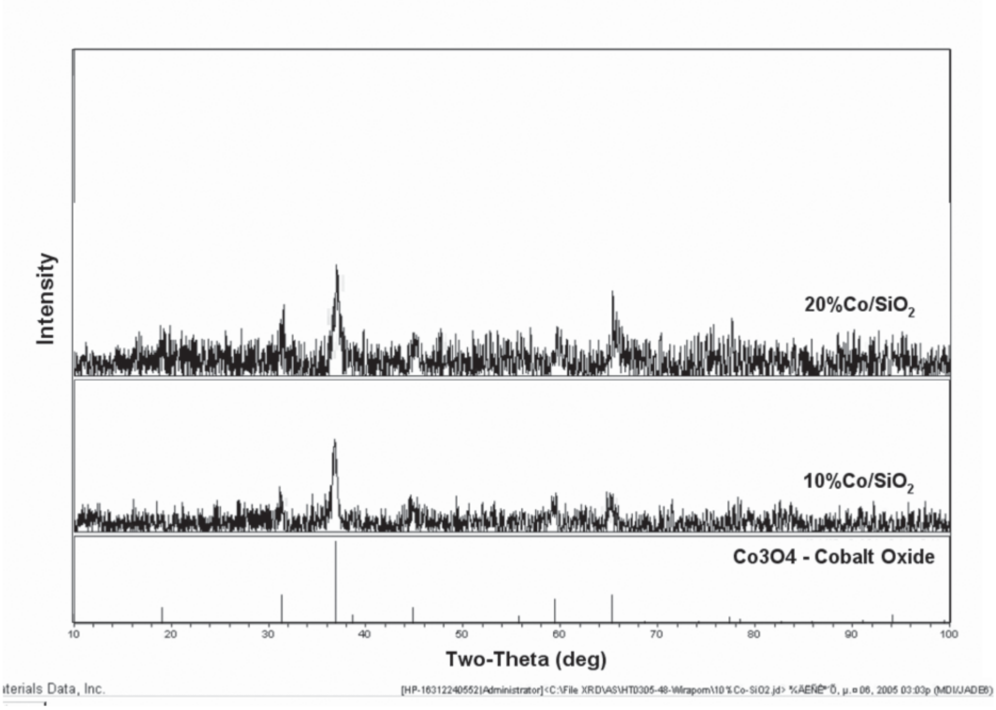

Fig. 2 The XRD pattern of 10%Co/SiO_2 and 20%Co/SiO_2 catalysts

From Fig. 2, both 10%Co/SiO_2 and 20% Co/SiO_2 catalysts have similar XRD patterns with the peak location matches with only cobalt oxide (Co_3O_4). Therefore, Co_3O_4 is the main component in these two catalysts and calcination at 350 ^{o}C for 2 hours in static air is enough to convert $Co(NO_3)_2$ into Co_3O_4.

3.2 Ethanol Steam Reforming Experiment

3.2.1 Effect of ethanol concentration

In all experiments in this study, only H_2, CO, CO_2, CH_4 and He were detected in dry gas product. Ethanol conversions were in the range of 75-98% in all cases. Fig. 3 shows the variation of the composition in dry gas product with ethanol concentration over 10%Co/SiO_2 catalyst. When the ethanol concentration increased, the percentage of all components in the product increased. In this study, the amount of CO generated was approximately 10-20% of hydrogen production, which is consistent with other works on Co/SiO_2 catalyst reported by Batista et al. [8] and Kaddouri and Mozzozhia [9] but at higher ethanol concentrations and lower temperatures. In addition, the amount of CH_4 and CO are approximately the same, which is also consistent with the results reported by Batista et al. [8] and Kaddouri and Mozzozhia [9], suggesting that the decomposition reaction of ethanol ($C_2H_5OH \longrightarrow CH_4+CO+H_2$) be responsible for the formation of both CO and CH_4. When comparing with reported work on 8%Co/SiO2 catalyst [9], at the same reaction temperature, %CO_2 in this work is quite high. This might be resulted from the higher oxidation capacity of 10%Co/SiO_2 to convert CO into CO_2. It is confirmed by the other work reported by Batista et al. [8] that the amount of CO_2 in the effluent gas increased and the amount of CO decreased when the metal loading was increased from 8 to 18% for Co/SiO_2 catalyst. See further discussion in section 3.2.2.

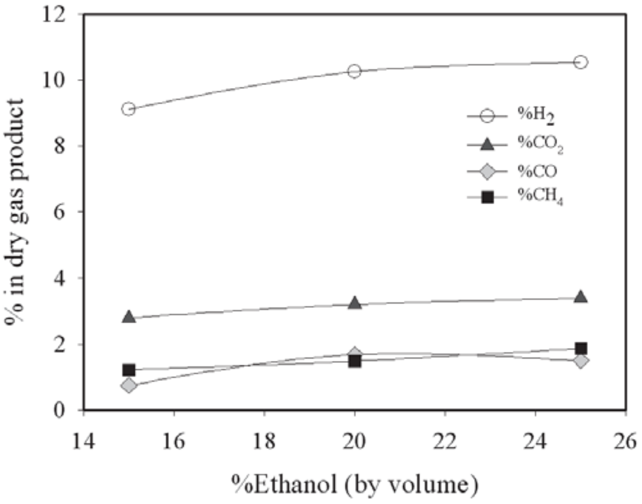

Fig. 3 The variation of the percentage in dry gas product with %ethanol in feed (balance He).

Although the amount of hydrogen in dry gas product increased with %ethanol, when considering the hydrogen yield as defined in section 2.4, it slightly decreased as shown in Fig. 4. From this point forward, in all figures, %E stands for %ethanol by volume, and %Co stands for %cobalt loading in silica-supported catalysts. Although, the time-on-stream behavior of the hydrogen yields at different ethanol concentrations and %Co loadings was quite fluctuated, it is clearly seen in Fig. 4 that the hydrogen yield decreased with ethanol concentration and increased with %Co loading. The decrease in hydrogen yield when increasing ethanol concentration might be due to the higher degree of coke formation at higher ethanol concentrations. The comparison between two metal loadings, 10 and 20% cobalt, at the same ethanol concentration showed a significant increase in hydrogen yield when increasing metal loading. Steady-state hydrogen yields were 57% and 84% for 10% and 20% cobalt loading, respectively. This result was not surprising since the 20% Co/SiO_2 catalyst has more surface metal atoms compared to the 10% Co/SiO_2 catalyst. The decrease of hydrogen yield with ethanol concentration was also observed for the ethanol steam reforming on other catalysts such as what was reported by Laosiripojana and Assabumrungrat [10] over Ni/Al_2O_3 and Rh/Al_2O_3 catalysts. When plotting the selectivities towards H_2, CO_2, CO and CH_4 with ethanol concentration, shown in Fig. 5, it is obvious that the selectivities towards H_2 and CO_2 decreased with ethanol concentration while that of methane increased and that of CO showed a maximum at 20% ethanol. The results obtained over Co/SiO_2 in this study were similar to the results reported when using Pd/Al_2O_3 [2], Ni/Al_2O_3 [3], Rh/Al_2O_3 [11] and Ni/Cu [12] catalysts. In addition, the effect of H_2O/EtOH ratio was less observable when H_2O/EtOH ratio is getting larger.

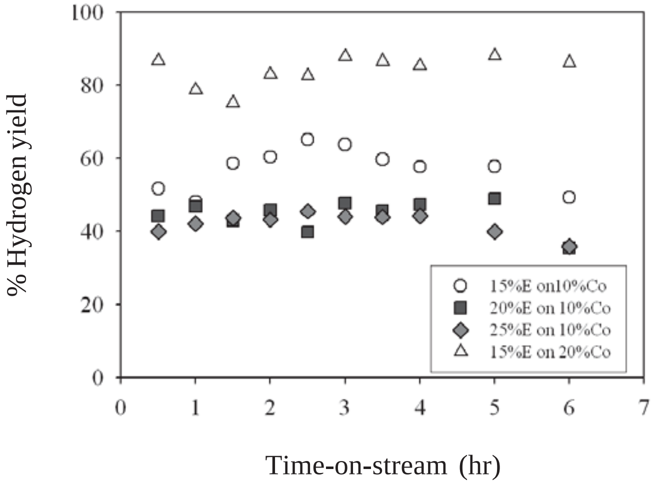

Fig. 4 The variation of hydrogen yield with ethanol concentrations on 10%Co/SiO_2 catalyst and at 15% ethanol concentration on 20% Co/SiO_2 catalyst.

If assuming that the number of active atoms equal the number of surface atoms as measured by H_2 chemisorption, the specific rate in term of turnover frequency can be calculated. As shown in Fig. 6, the turnover frequency increases when increasing the concentration of ethanol from 15% to 20% and 25% by volume. It suggests that at low ethanol concentration, Co surface atoms are not fully utilized. Lots of vacant surface atoms are still available for reaction. The specific reaction per gram of catalyst is thus dependent on the probability of surface atom contacting with ethanol molecule. If following the turnover frequency with time-on-stream, it can be seen that the turnover frequency does not change much. It can be concluded that the deactivation of this catalyst is not observable during 6 hr time-on-stream.

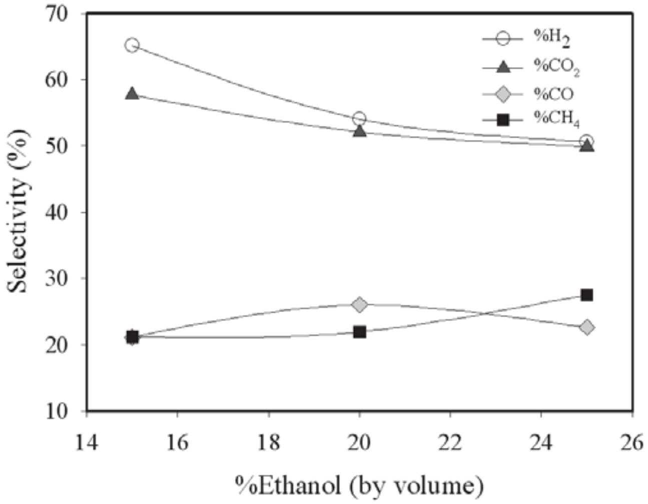

Fig. 5 Effect of %ethanol (by volume) on the selectivity of H_2, CO_2, CO and CH_4 obtained over 10%Co/SiO_2 catalyst at 450 ^{o}C.

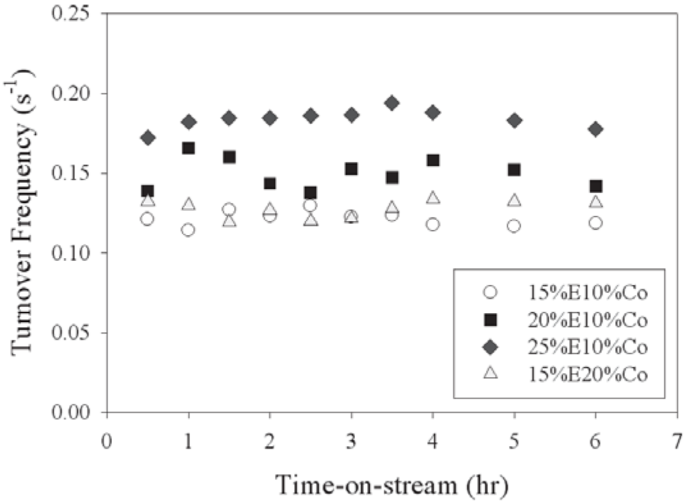

Fig. 6 Time-on-stream behavior of the turnover frequency of 10%Co/SiO_2 catalyst when varying ethanol concentrations and that of 20% Co/SiO_2 at 15% ethanol by volume at 450 °C.

3.2.2 Effect of metal loading

The effects of %Co loading on the selectivity of H_2, CO_2, CO and CH_4, and % ethanol conversion at 15% ethanol (by volume) are shown in Fig. 7. Since the reaction was operated at total conversion, the effect of %Co loading on ethanol conversion was only slightly even though %Co loading was doubled. From this figure, it is clearly seen that the selectivities towards H_2 and CO_2 were improved when using higher Co loading. The decrease in the selectivity towards CO and CH_4 accompanied by an increase in CO_2 selectivity implied that the rate of water-gas-shift reaction increased, and the rate of methanation, the undesired reaction, decreased at higher Co loading. These results are consistent with what was reported by Batista et al. [8] that smaller amount of methane was produced for the catalyst at higher Co loading. Although the increase in H_2 production yield when using 20%Co/SiO_2 is not twice that from 10% Co/SiO_2, it shows the advantage in using higher Co loading in terms of the quality of the product gas.

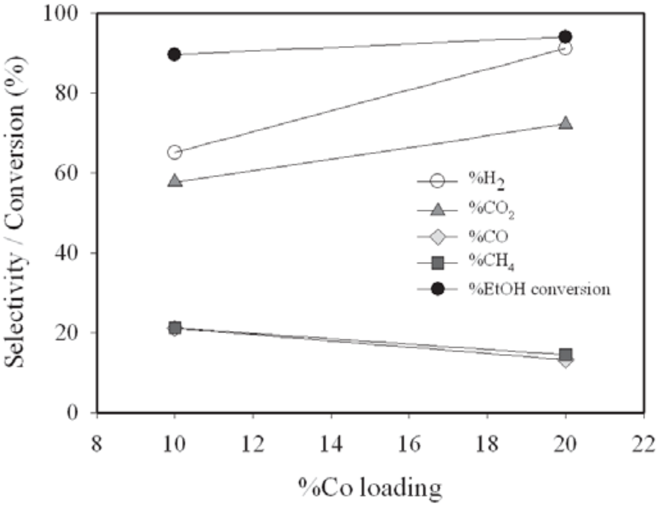

Fig. 7 Effect of %Co loading on the selectivity of H_2, CO_2, CO and CH_4, and %ethanol conversion obtained at 15% ethanol (by volume) and 450 ^oC.

Turnover frequency may differ significantly (factor of 2-1000) among catalysts of the same type because of (1) differences in surface structure in a structure sensitive reaction, (2) varying degree of metal-support or metal-promoter effects, and (3) differences in surface composition in a series of bimetallic or multi-metallic catalyst [7]. For the catalysts in this study, both 10% and 20% Co/SiO_2 catalysts exhibited the same turnover frequency (Fig. 6), which means that the intrinsic activity of both catalysts are approximately the same despite the different in metal particle size (Table 1). It implies that the steam reforming of ethanol is a structural insensitive reaction at the condition studied in this work.

3.3 Catalyst Deactivation

After 6 hours time-on-stream, the used catalyst was taken out from the reactor and characterized by using the BET technique. The results were then compared to the fresh catalyst as shown in Table 2. As can be seen in Table 2, the total surface of all catalysts after being used in the reaction remained approximately the same even though there was large amount of steam in the reactor. Although sintering can easily occur at this condition, the BET results show no reduction in the surface area of the support. However, pore volume and pore size of both catalysts reduced slightly probably by slight coke formation inside the mesopores.

Table 2 The BET results of catalysts after 6 hr time-on-stream compared to fresh catalysts.

Catalyst	% Ethanol	Surface area (m^2/g) Fresh/ used	Pore volume (cc/g) Fresh/ used	Pore size (Å) Fresh/ used
10%Co/SiO_2	15	237/250	1.014/0.890	170.7/141.8
	20	237/237	1.014/0.922	170.7/155.4
	25	237/228	1.014/0.884	170.7/154.5
20%Co/SiO_2	15	199/214	0.829/0.790	166.8/146.3

4. Conclusions

Low metal dispersion was observed for the 10% and 20% Co/SiO_2 catalysts prepared in study. It results in large agglomeration of Co particle and slightly lower BET surface area, pore volume and pore size. For 10% Co/SiO_2 catalyst, although the amount of all components in the product gas increased when increasing ethanol concentration, it decreased in terms of hydrogen yield. It suggested that less ethanol in feed was converted to hydrogen when increasing the concentration of ethanol. This is confirmed by the selectivity toward hydrogen which was decreased and accompanied by the increase in CH_4 selectivity with ethanol concentration. Although the degree of catalyst utilization of the 10% Co/SiO_2 catalyst was enhanced by increasing ethanol concentration, 15% ethanol by volume seemed to be the best concentration in term of the quality of product gas to be further used in fuel cell after pretreatment. Thus, bio-ethanol from the fermentation of biomass can be directly used to produce hydrogen without distillation step. The result on the effect of metal loading shows that high metal loading is preferable in term of hydrogen yield and the quality of product gas. However, it must be traded off with the price of metal being using to prepare the catalyst. In addition, despite a large amount of steam in the reactor, deactivation from support sintering was not observed during the entire reaction time for all cases in this study.

5. Acknowledgements

The authors would like to thank The Thailand Research Fund and The Commission on Higher Education for funding on this project.

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