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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Preparation of 20%Co/SiO₂-ZrO₂ catalysts by the incipient wetness impregnation method are shown as follows.

Reagent: - Cobalt (II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$]

Molecular weight = 291.03 g

- Nano-SiO₂ support
- Nano-ZrO₂ support
- Micron-SiO₂ support
- Micron-ZrO₂ support

Example calculation for the preparation of 20%Co/Si-0-Zr-100

Based on 100 g for catalyst used, the composition of the catalyst will be as follows:

Cobalt = 20 g

ZrO₂ = 100-20 = 80 g

For 5 g of catalyst

Cobalt required = $1 \times (20/80)$ = 0.2 g

Cobalt 0.2 g was prepared from $Co(NO_3)_2 \cdot 6H_2O$ and molecular weight of Co is 58.93

$$\begin{aligned} Co(NO_3)_2 \cdot 6H_2O \text{ required} &= \frac{MW \text{ of } Co(NO_3)_2 \cdot 6H_2O \times \text{cobalt required}}{MW \text{ of } Co} \\ &= (291.03/58.93) \times 0.2 = 0.99 \text{ g} \end{aligned}$$

Since the pore volume of the pure zirconia support is 0.402 ml/g for ZrO₂. Thus, the total volume of impregnation solution which must be used is 0.803 ml for ZrO₂ by the requirement of incipient wetness impregnation method, the de-ionized water is added until equal pore volume for dissolve Cobalt (II) nitrate hexahydrate.

APPENDIX B

CALCULATION FOR TOTAL H₂ CHEMISSORPTION AND DISPERSION

Calculation of the total H₂ chemisorption and metal dispersion of the catalyst, a stoichiometry of H/Co = 1, measured by H₂ chemisorption is as follows:

Let the weight of catalyst used	=	W	g
Integral area of H ₂ peak after adsorption	=	A	unit
Integral area of 45 μl of standard H ₂ peak	=	B	unit
Amounts of H ₂ adsorbed on catalyst	=	B-A	unit
Concentration of Co (by AAS)	=	C	%wt
Volume of H ₂ adsorbed on catalyst	=	$45 \times [(B - A) / B]$	μl
Volume of 1 mole of H ₂ at 100°C	=	28.038	μl
Mole of H ₂ adsorbed on catalyst	=	$[(B - A) / B] \times [45 / 28.038]$	μmole

$$\begin{aligned} \text{Total H}_2 \text{ chemisorption} &= [(B - A) / B] \times [45 / 28.038] \times [1 / W] \text{ μmole/g of catalyst} \\ &= N \text{ μmole/g of catalyst} \end{aligned}$$

$$\text{Molecular weight of cobalt} = 58.93$$

$$\begin{aligned} \text{Metal dispersion (\%)} &= \frac{2 \times H_{2 \text{ tot}} / \text{g of catalyst} \times 100}{\text{No } \mu\text{mole Co}_{\text{tot}} / \text{g of catalyst}} \\ &= \frac{2 \times N \times 100}{\text{No } \mu\text{mole Co}_{\text{tot}}} \\ &= \frac{2 \times N \times 58.93 \times 100}{C \times 10^6} \\ &= \frac{1.179 \times N}{C} \end{aligned}$$

Table B.1 H₂ chemisorption results for various percent SiO₂ with ZrO₂ supported Co catalysts samples.

Sample	Total H ₂ chemisorption ($\mu\text{mol /g cat}$)	
	N	M
Co/SiO ₂	1.21	5.26
Co/Si-80-Zr-20	1.26	1.12
Co/Si-60-Zr-40	2.44	2.34
Co/Si-40-Zr-60	3.90	1.12
Co/Si-20-Zr-80	6.12	2.97
Co/ZrO ₂	2.01	0.84

APPENDIX C

CALIBRATION CURVES

This appendix showed the calibration curves for calculation of composition of reactant and products in CO hydrogenation reaction. The reactant is CO and the main product is methane. The other products are linear hydrocarbons of heavier molecular weight that are C₂-C₄ such as ethane, ethylene, propane, propylene and butane.

The thermal conductivity detector, gas chromatography Shimadzu model 8A was used to analyze the concentration of CO by using Molecular sieve 5A column.

The VZ10 column are used with a gas chromatography equipped with a flame ionization detector, Shimadzu model 14B, to analyze the concentration of products including of methane, ethane, ethylene, propane, propylene and butane. Conditions uses in both GC are illustrated in Table C.1.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of CO, methane, ethane, ethylene, propane, propylene and butane are illustrated in the following figures.

Table C.1 Conditions use in Shimadzu modal GC-8A and GC-14B.

Parameters	Condition	
	Shimadzu GC-8A	Shimadzu GC-14B
Width	5	5
Slope	50	50
Drift	0	0
Min. area	10	10
T.DBL	0	0
Stop time	50	60
Atten	0	0
Speed	2	2
Method	41	41
Format	1	1
SPL.WT	100	100
IS.WT	1	1

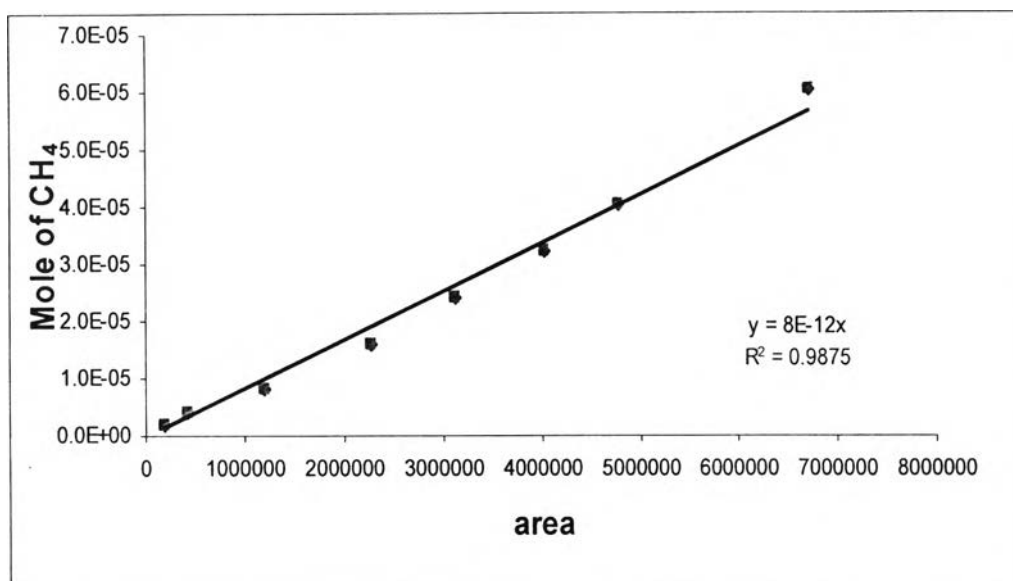


Figure C.1 The calibration curve of methane.

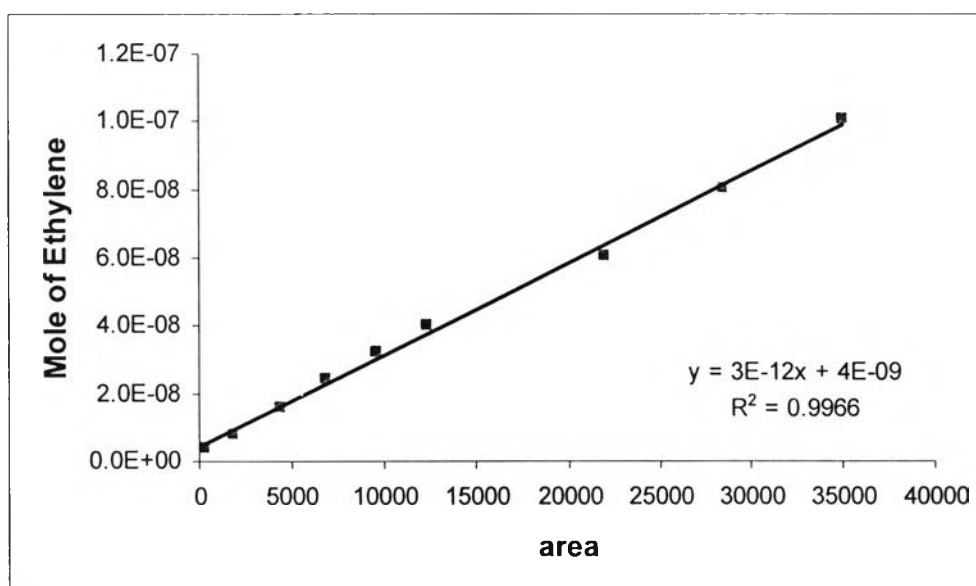


Figure C.2 The calibration curve of ethylene.

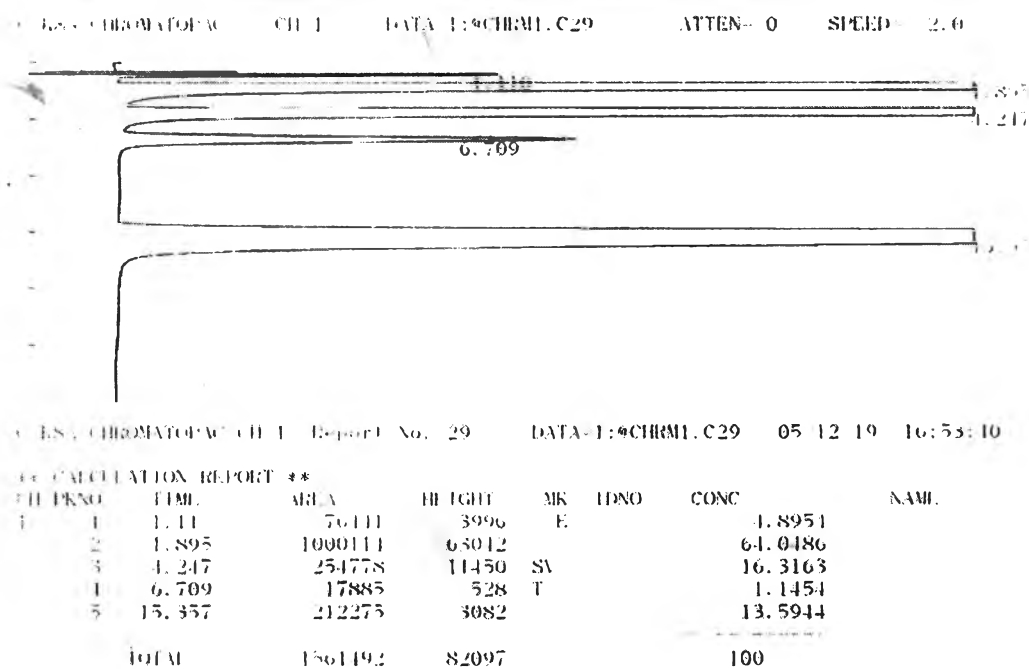


Figure C.3 The chromatograms of catalyst sample from thermal conductivity detector, gas chromatography Shimadzu model 8A (Molecular sieve 5A column).

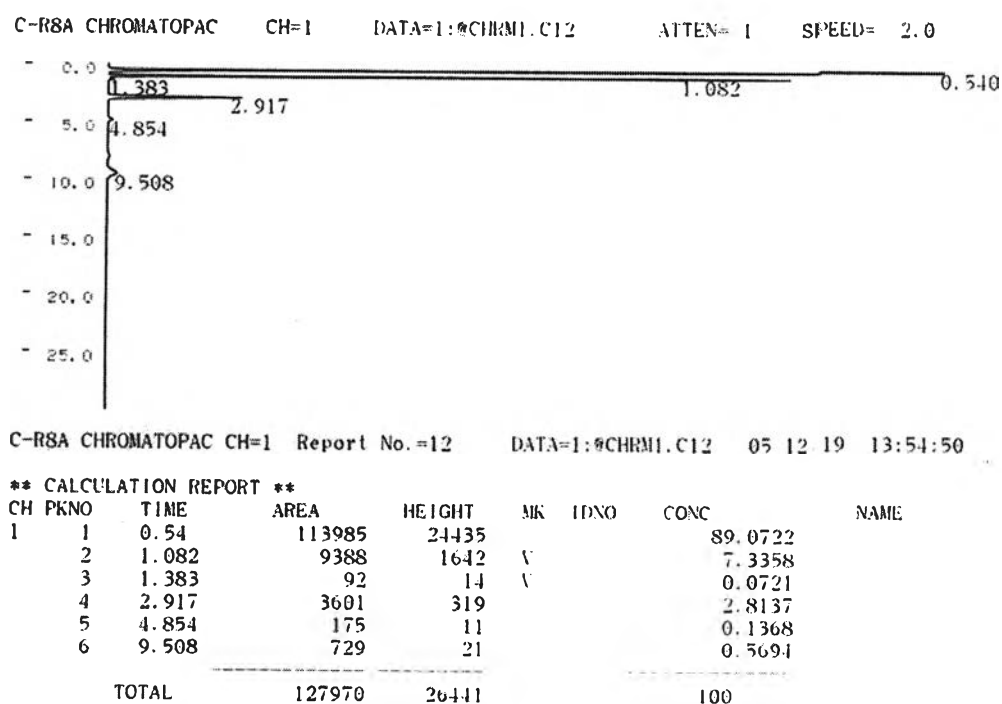


Figure C.4 The chromatograms of catalyst sample from flame ionization detector, gas chromatography Shimadzu model 14B (VZ10 column).

APPENDIX D

CALCULATION OF CO CONVERSION, REACTION RATE AND SELECTIVITY

The catalyst performance for the CO hydrogenation was evaluated in terms of activity for CO conversion rate and selectivity.

Activity of the catalyst performed in term of carbon monoxide conversion and reaction rate. Carbon monoxide conversion is defined as moles of CO converted with respect to CO in feed:

$$\text{CO conversion (\%)} = \frac{100 \times [\text{mole of CO in feed} - \text{mole of CO in product}]}{\text{mole of CO in feed}} \quad (\text{i})$$

Reaction rate was calculated from CO conversion that is as follows:

Let the weight of catalyst used	=	W	g
Flow rate of CO	=	2	cc/min
Reaction time	=	60	min
Weight of CH ₂	=	14	g
Volume of 1 mole of gas at 1 atm	=	22400	cc

$$\text{Reaction rate (g CH}_2\text{/g of catalyst)} = \frac{[\% \text{ conversion of CO} / 100] \times 60 \times 14 \times 2}{W \times 22400} \quad (\text{ii})$$

Selectivity of product is defined as mole of product (B) formed with respect to mole of CO converted:

$$\text{Selectivity of B (\%)} = 100 \times [\text{mole of B formed} / \text{mole of total products}] \quad (\text{iii})$$

Where B is product, mole of B can be measured employing the calibration curve of products such as methane, ethane, ethylene, propane, propylene and butane

$$\text{mole of CH}_4 = (\text{area of CH}_4 \text{ peak from integrator plot on GC} - 14B) \times 8 \times 10^{12} \quad (\text{iv})$$

APPENDIX E**LIST OF PUBLICATIONS**

1. Sujitra Kittiruangrayub, Bunjerd Jongsomjit and Piyasan Praserthdam, "Characteristics of Mixed Nano SiO₂/ZrO₂-Supported Cobalt Catalyst", Proceedings of the Thai Institute of Chemical Engineering and Applied Chemical Conference 15th, Chonburi, Thailand, Oct., 2005, Ref. No.NA-13.
2. Bunjerd Jongsomjit, Sujitra Kittiruangrayub, and Piyasan Praserthdam, "Study of Cobalt Dispersion onto the Mixed Nano-SiO₂-ZrO₂ Supports and Its Application as a Catalytic Phase", Submitted to Reaction Kinetics and Catalysis Letters, Nov., 2005.
3. Bunjerd Jongsomjit, Sujitra Kittiruangrayub, and Piyasan Praserthdam, "Investigation of differences in characteristics of cobalt catalysts dispersed on micron- and nano-sized mixed SiO₂-ZrO₂ supports", Submitted to Applied Catalysis A: General, Mar., 2006.

Characteristics of Mixed Nano SiO₂/ZrO₂-Supported Cobalt Catalyst

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ABSTRACT

In the present study, characteristics of the mixed nano SiO₂/ZrO₂-supported cobalt catalysts were investigated. The various weight ratios of SiO₂/ZrO₂ were prepared by a physical mixing in toluene solution, then consequently impregnated with the cobalt precursor. After calcination, the various samples were characterized using XRD, SEM/EDX and TPR. In particular, it was found that cobalt dispersed on the mixed nano SiO₂/ZrO₂ supports can be reduced at lower temperatures. This was suggested that the strong interaction between cobalt and the support could be minimized using the mixed oxide supports as mentioned.

Keywords: cobalt catalyst, SiO₂, ZrO₂, nanoparticle, reducibility

1. INTRODUCTION

Many inorganic supports such as SiO₂ [1,2], Al₂O₃ [3,4], TiO₂ [5], ZrO₂ [6] and zeolites have been extensively studied for supported Co catalysts for years. Since the activity of Co catalyst apparently depends on the number of reduced Co metal dispersed on the support used, thus the nature of support can play important roles on such the phenomenon. It was found that the various supports could result in different activity and selectivity for supported Co catalyst as well. Besides the nature of support itself, mixed oxides such as Al₂O₃-SiO₂, SiO₂-ZrO₂, and SiO₂-TiO₂-supported Co catalysts can be used. It is clear that during the past years, the development in nanotechnology and nanoscience has been very impressive. Thus, it is very exciting to investigate how this nanosupport can do for the Co catalyst, especially in terms of the Co dispersion.

The main focus of this present study was to investigate characteristics of the mixed nano SiO₂/ZrO₂-supported cobalt catalyst. In this study, the mixed nano SiO₂/ZrO₂-supported cobalt catalysts were prepared by the incipient wetness impregnation method. Then, the catalyst samples were characterized using X-ray diffraction (XRD), temperature programmed reduction (TPR), and scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

2. EXPERIMENTAL

2.1 Materials

2.1.1 Preparation of nano SiO₂/ZrO₂ mixed oxide support

The nano SiO₂/ZrO₂ mixed oxide supports were prepared by the physical mixing. In particular, 1 g of the nano SiO₂/ZrO₂ mixed oxide support was physically mixed by dispersing in toluene (ca. 20 ml).

The mixture was stirred for 30 min, filtered, and then dried under vacuum. The nano $\text{SiO}_2/\text{ZrO}_2$ weight ratios were varied from 0/1, 2/8, 4/6, 6/4, 8/2, and 1/0.

The mixed supports were calcined at 500°C for 4 h.

2.1.2 Preparation of catalyst samples

A 20 wt% of $\text{Co}/\text{SiO}_2/\text{ZrO}_2$ mixed support was prepared by the incipient wetness impregnation. A designed amount of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] was dissolved in deionized water and then impregnated onto the mixed oxide supports obtained from 2.1.1. The catalyst precursor was dried at 110°C for 12 h and calcined in air at 500°C for 4 h.

2.2 Catalyst nomenclature

The nomenclature used for the catalyst samples in this study is following.

- **a/b** refers to the nano $\text{SiO}_2/\text{ZrO}_2$ mixed oxide support
- **Co_a/b** refers to the cobalt catalyst on the nano $\text{SiO}_2/\text{ZrO}_2$ mixed oxide support, where **a** = the weight ratio of SiO_2 and **b** = the weight ratio of ZrO_2

2.3 Catalyst characterization

2.3.1 X-ray diffraction:

XRD was performed to determine the bulk crystalline phases of catalyst. It was conducted using a

SIEMENS D-5000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54439 \text{ \AA}$). The spectra were scanned at a rate of 2.4 degree/min in the range $2\theta = 20\text{-}80$ degrees.

2.3.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy:

SEM and EDX were used to determine the catalyst morphologies and elemental distribution throughout the catalyst granules, respectively. SEM was carried out using a JEOL model JSM-5800LV. EDX was performed using Link Isis series 300 program.

2.3.3 Temperature-programmed reduction:

TPR was used to determine the reduction behaviors of the samples. It was carried out using 50 mg of a sample and a temperature ramp from 35 to 800°C at $5^\circ\text{C}/\text{min}$. The carrier gas was 5% H_2 in Ar. A cold trap was placed before the detector to remove water produced during the reaction. A thermal conductivity detector (TCD) was used to determine the amount of H_2 consumed during TPR [7-10].

3. RESULTS AND DISCUSSION

XRD patterns of the mixed nano $\text{SiO}_2/\text{ZrO}_2$ supports before impregnation with the cobalt precursor are shown in **Figure 1**. It was observed that the pure SiO_2 exhibited only a broad XRD peak assigning to the conventional amorphous silica. The pure ZrO_2

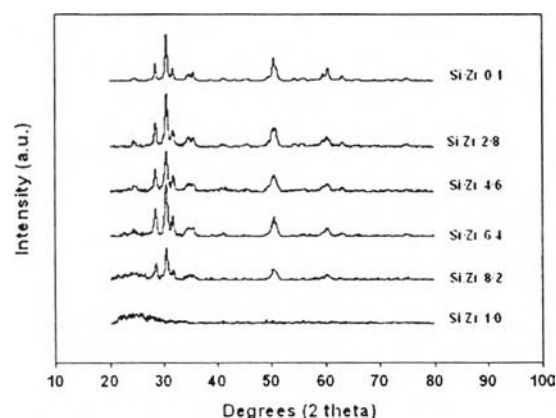


Figure 1 XRD patterns for various ratios of mixed nano $\text{SiO}_2/\text{ZrO}_2$ supports

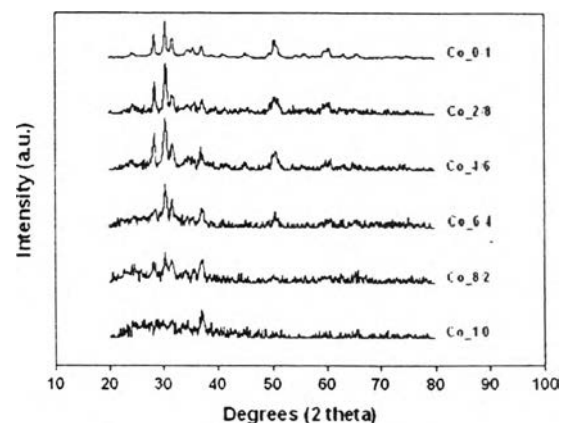


Figure 2 XRD patterns for the various mixed nano $\text{SiO}_2/\text{ZrO}_2$ -supported cobalt catalysts after calcination

exhibited the XRD peaks at 29.8° , 34.2° , 49.6° , and 59.5° assigning to the ZrO_2 in tetragonal phase. Besides, the XRD peaks at 28.2° , 31.5° , and 55.3° were also detected indicating the ZrO_2 in monoclinic phase [11].

XRD patterns of the mixed supports containing different weight ratios of SiO_2/ZrO_2 revealed the combination of SiO_2/ZrO_2 supports based on their content. After impregnation with the cobalt precursor, the catalyst samples were dried and calcined. The XRD patterns of the mixed SiO_2/ZrO_2 -supported Co catalyst are shown in **Figure 2**. Besides the observation of the characteristic peaks of the supports as shown in **Figure 1**, all calcined samples exhibited XRD peaks at 31° (weak), 36° (strong), and 65° (weak), which were assigned to the presence of Co_3O_4 . This indicated that the Co_3O_4 formed was highly dispersed.

SEM and EDX were also conducted in order to study the morphologies and elemental distribution of the samples, respectively. In general, there was no significant change in morphologies and elemental distribution of all catalyst samples after calcination. A

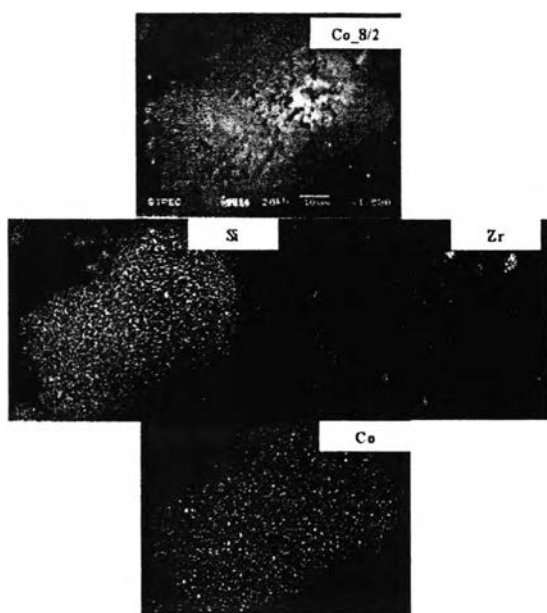


Figure 3 A typical SEM micrograph and EDX mapping of the calcined $Co_{8/2}$ catalyst sample

typical SEM micrograph and EDX mapping for $Co_{8/2}$ sample are illustrated in **Figure 3**. It can be seen that ZrO_2 was located on the outer surface of SiO_2 . It appeared that the distribution of Co was well on the surface of the support.

TPR was performed in order to determine the reduction behaviors of samples. The TPR profiles for all samples are shown in **Figure 4**. It was found that there was only one reduction peak, however, at different reduction temperatures for all calcined samples. The one reduction peak can be assigned to the overlap of two-step reduction of Co_3O_4 to CoO and then to Co metal [7,10]. Upon the TPR conditions, the two-step reduction may or may not be observed. Based on the TPR profiles, it indicated that Co oxides dispersed on the pure SiO_2 and ZrO_2 exhibited higher maximum reduction temperatures than those on the mixed SiO_2/ZrO_2 supports. It was suggested that using the mixed SiO_2/ZrO_2 supports could result in lowering the reduction temperature of Co oxides.

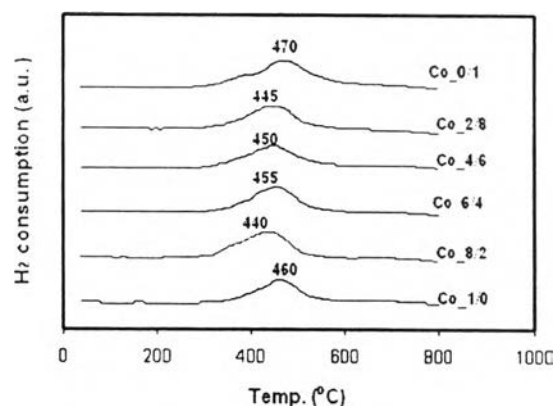


Figure 4 TPR profile of the various mixed SiO_2/ZrO_2 -supported cobalt catalysts after calcination

4. CONCLUSIONS

In this present study, the characteristics of mixed nano SiO_2/ZrO_2 -supported cobalt catalyst were revealed. It can be observed that Co was highly dispersed on the mixed supports. There was no

significant change in morphologies and elemental distribution of samples. However, based on the TPR results, it can be concluded that the presence of the mixed oxide supports in this study could facilitate the reduction of Co oxide species.

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VITAE

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