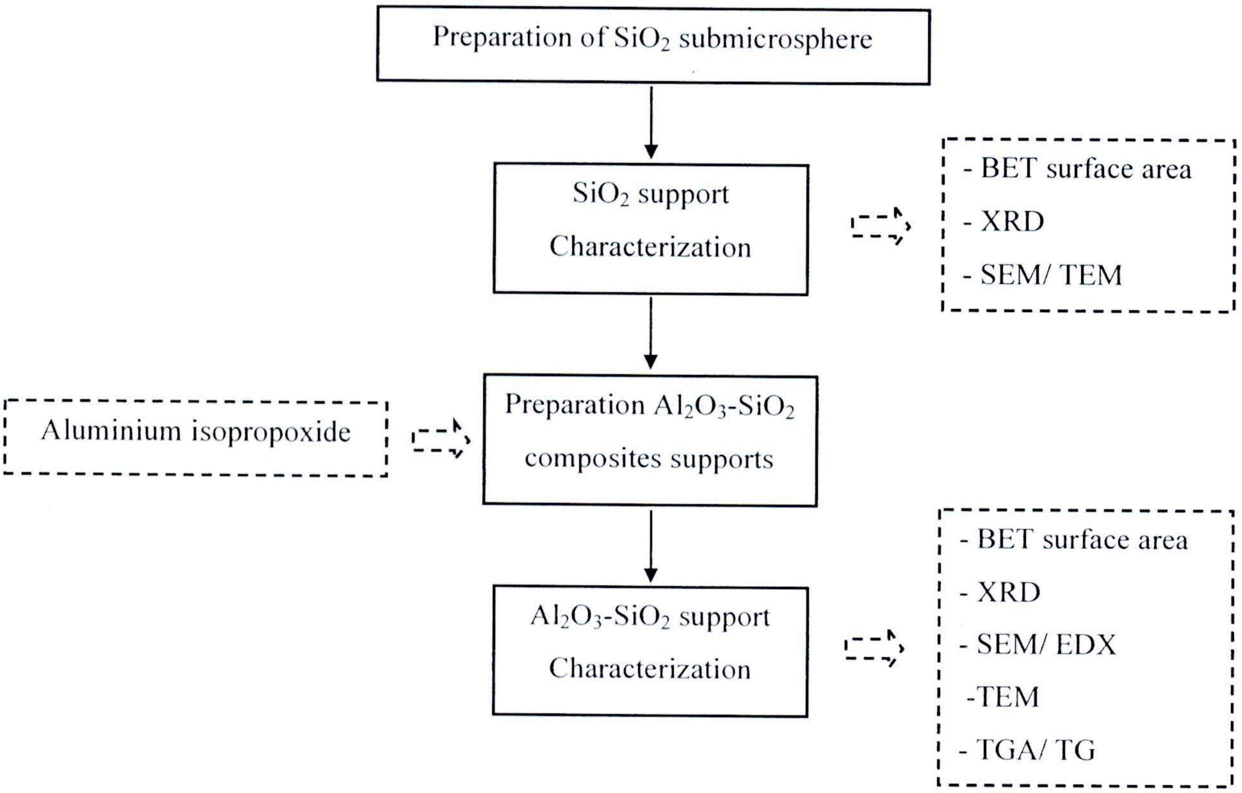
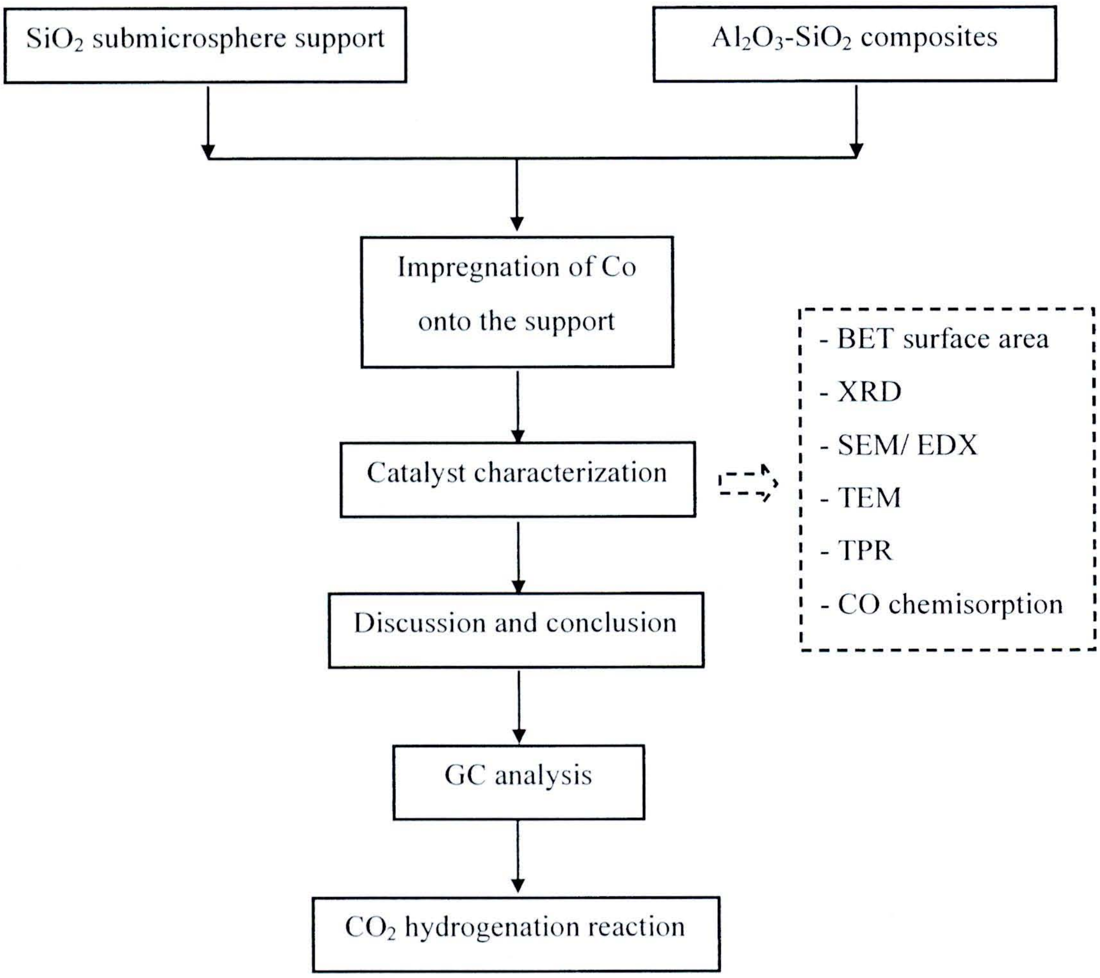
CHAPTER IV

METHODOLOGY

4.1 Research methodology



Scheme 4.1 Flow diagram of research methodology for support preparation.



Scheme 4.2 Flow diagram of research methodology for catalyst preparation and characterization.

4.2 Catalyst preparation

4.2.1 Chemicals

1. Tetraethoxysilane 98% (TEOS) available from Aldrich
2. Aluminium isopropoxide 98% ($Al(OPr^i)_3$) from Aldrich
3. Cetyltrimethylammonium bromide (CTAB) from Aldrich
4. Cobalt (II) nitrate hexahydrate 98% [$Co(NO_3)_2 \cdot 6H_2O$)] available from Aldrich
5. Ammonia 30% available from Panreac
6. Ethanol 99.99% available from J.T. Baker
7. Isopropanol available from QReC
8. De-ionized water

4.2.2 Preparation of spherical silica particle (SSP) [Liu et al., 2003]

1. The composition of the synthesis gel had following molar ratio: 1 TEOS : 0.3 C_{16}TMABr : 11 NH_3 : 58 Ethanol : 144 H_2O
2. The solution was further stirred for 2 h at room temperature.
3. The white precipitate was then collected by filtration and washed with distilled water.
4. Dried samples were calcined at 550°C for 6 h with a heating rate of 10 °C min^{-1} in air.

4.2.3 Preparation of the Al_2O_3-SiO_2 composites supports [Grzechowiak, 2008; Liu et al., 2009]

1. The desired amount of aluminium isopropoxide was dissolved in isopropanol (using 1:3 w/w of support: isopropanol).
2. The silica from 4.2.2. was added to the solution and stirred for 1 h.
3. Hydrolysis was performed by addition of ammonia (H_2O: $Al(OPr^i)_3$ = 4:1). The sol was further stirred for 20 h at room temperature. Then, the sample was dried at 110°C for 24 h.
4. Dried sample was calcined in air for 2 h at temperature up to 1000°C.

4.2.4 Cobalt loading

In this experiment, incipient wetness impregnation was the one method used for loading cobalt. Cobalt (II) nitrate hexahydrate $[Co(NO_3)_2 \cdot 6H_2O)]$ was used as precursor in this method.

The incipient wetness impregnation procedure was as follows:

1. The certain amount of cobalt (20 %wt loading) was introduced into the de-ionized water which its volume equals to pore volume of catalyst.
2. Spherical silica particle (SSP) and Al_2O_3-SiO_2 composites support were impregnated with aqueous solution of cobalt. The cobalt solution was dropped slowly to the spherical silica particle (SSP) and Al_2O_3-SiO_2 composites support, respectively.
3. The catalyst was dried in the oven at 110^oC for 12 h.
4. The catalyst was calcined in air at 500^oC for 4 h.

4.2.5 Catalysts nomenclature

The nomenclature was used for the catalyst samples in this study are as follows:

- CoSSPXXX
- CoAlSSPXXX (a:b)

CoSSPXXX refers to cobalt supported on spherical silica composites (CoSSP) was calcined at XXX ^oC.

CoAlSSPXXX refers to cobalt supported on alumina-spherical silica composites (CoAlSSP) was calcined at XXX ^oC.

a refers to the weight ratio of Al_2O_3

b refers to the weight ratio of SiO_2

4.3 Characterization

4.3.1 X-ray diffraction (XRD)

XRD was performed to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 programs for fully control of the XRD analyzer. The experiment was carried out by using CuK_α radiation with Ni filter in the 2θ range of 20-80 degrees resolution 0.04°. The crystallite size was estimated from line broadening according to the Scherrer equation and α-Al_2O_3 was used as standard.

4.3.2 N_2 physisorption

BET apparatus for the single point method, the reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas was adjusted by means of fine-metering valve on the gas chomatograph. The sample cell made from pyrex glass. The mixture gases of helium and nitrogen were flowed though the system at the nitrogen relative of 0.3. The catalyst sample (ca. 0.3 to 0.5 g) was placed in the sample cell, which was then heated up to 160°C and was held at this temperature for 2 hours. After the catalyst sample was cooled down to room temperature, nitrogen uptakes were measured as follows.

1. Adsorption step: The sample that set in the sample cell was dipped into liquid nitrogen. Nitrogen gas that was flowed though the system was adsorbed on the surface of the sample until equipment was reached.

2. Desorption step: The sample cell with nitrogen gas-adsorption catalyst sample was dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the sample. This step was completed when the indicator line was in the position of base line.

3. Calibration step: 1 ml of nitrogen gas at atmospheric pressure was injected though the calibration port of the gas chomatograph and the area was measured. The area was the calibration peak.

4.3.3 Scanning Electron Microscope: SEM and Energy Dispersive X-ray Spectroscopy (EDX)

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) was used to determine the morphology and elemental distribution of the catalyst particles. Model of SEM: JEOL mode JSM-5800LV and EDX were performed using Link Isis Series 300 program at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

4.3.4 Transmission Electron Microscope (TEM)

The particle size and distribution of catalyst samples were observed using JEOL-JEM 200CX transmission electron microscope operated at 100 kV.

4.3.5 Temperature Programmed Reduction (TPR)

TPR was used to determine the reducibility of catalysts. The catalyst sample 0.1 g was used in the operation and temperature ramping from 35°C to 800°C at 10 °C/min. The carrier gas will be 5% H_2 in Ar. During reduction, a cold trap was placed to before the detector to remove water produced. A thermal conductivity detector (TCD) was measured the amount of hydrogen consumption. The calibration of hydrogen consumption was performed with bulk cobalt oxide (Co_3O_4) at the same conditions.

4.3.6 Thermogravimetry Analysis (TGA)

TGA was used to determine the weight loss pattern and the reducibility of catalysts by Shimadzu TGA model 50. The catalyst sample of ca. 10-20 mg and temperature ramping from 35°C to 1000°C at 10°C/min were used in the operation. The carrier gas was H_2UHP.

4.3.7 Carbon monoxide Chemisorptions

Static CO chemisorption at room temperature on the reduce catalysts were used to determine the number of reduced surface cobalt metal atoms. The total CO chemisorption was calculated from the number of injection of a known volume. CO chemisorptions was carried out following the procedure using a Micrometritics Pluse Chemisorb 2750 instrument at the Analysis Center of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. In an experiment, about 0.10 g of the catalyst sample was places in a glass tube. Prior to chemisorptions, the catalysts will be reduced at 350°C for 3 hours after ramping up at a rate of 10°C/min. After, carbon monoxide 30 microlite was injected to catalyst and repeated until desorption peak constant. Amount of carbon monoxide adsorption on catalyst is relative amount of active site.

4.4 Reaction study in CO_2 hydrogenation

4.4.1 Material

CO_2 hydrogenation was performed using 0.1 g of catalyst packed in the middle of the stainless steel microreactor, which is located in the electrical furnace. The total flow rate was 30 ml/min with H_2/CO_2 ratio of 10/1. The catalyst sample was re-reduced *in situ* in flowing H_2 at 350°C for 3 h prior to CO_2 hydrogenation. CO_2 hydrogenation will be carried out at 220°C and 1 atm total pressure. The effluent was analyzed using gas chomatography technique [Thermal conductivity detector (TCD), molecular sieve 5 °A was used for separation of carbon dioxide (CO_2) and methane (CH_4) and flame ioinization detector (FID), VZ-10 was used for separation of light hydrocarbon such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), etc.].

4.4.2 Apparatus

Flow diagram of CO_2 hydrogenation system was shown in Figure 4.1. The system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.4.2.1 Reactor

The reactor was made from a stainless steel tube (O.D. 3/8"). Two sampling points were provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

4.4.2.2 Automation Temperature Controller

This unit consisted of a magnetic switch connected to a variable voltage transformer and a solid-state relay temperature controller model no. SS2425DZ connected to a thermocouple. Reactor temperature was measured at the bottom of the catalyst bed in the reactor. The temperature control set point is adjustable within the range of 0-800^{o}C at the maximum voltage output of 220 volt.

4.4.2.3 Electrical Furnace

The furnace supplied heat to the reactor for CO hydrogenation. The reactor could be operated from temperature up to 800^{o}C at the maximum voltage of 220 volt.

4.4.2.4 Gas Controlling System

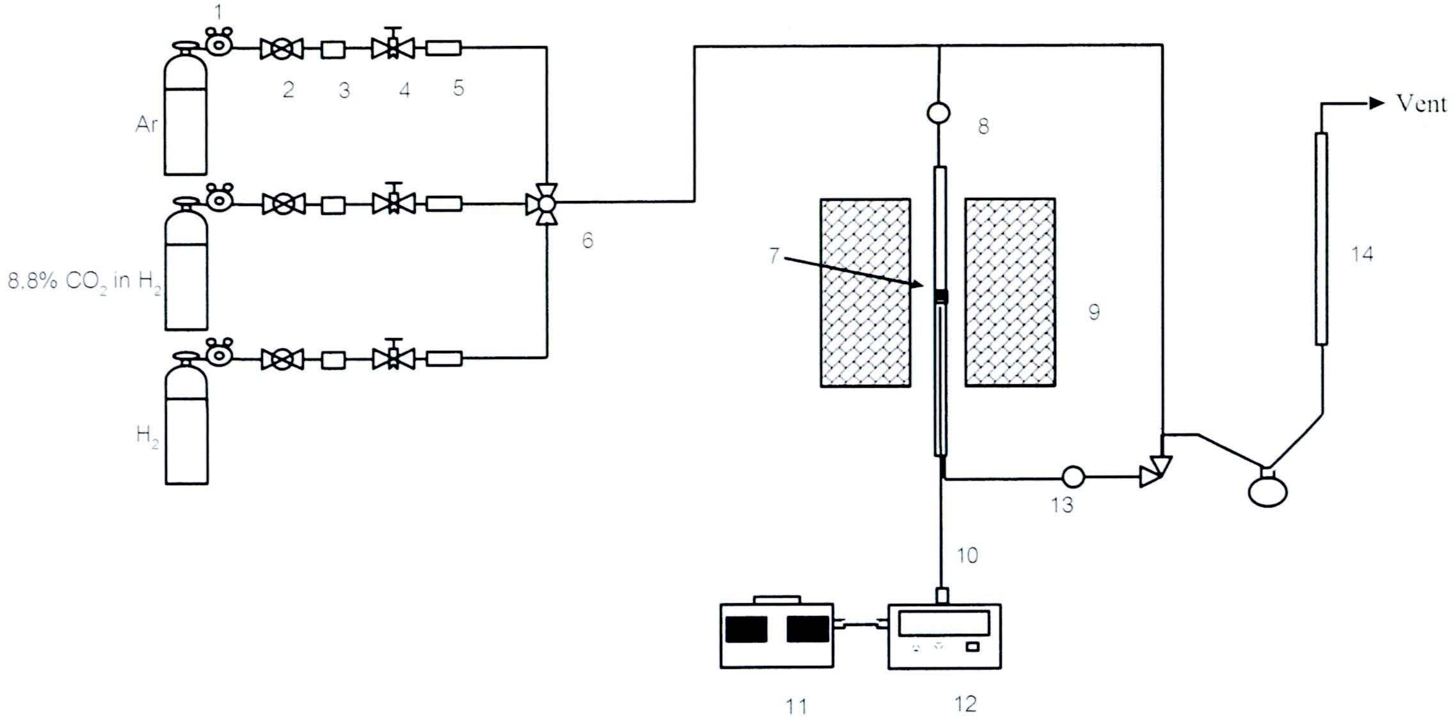
Reactant for the system was each equipped with a pressure regulator and an on-off valve and the gas flow rates were adjusted by using metering valves.

4.4.2.5 Gas Chromatography

The composition of hydrocarbons in the product stream was analyzed by a Shimadzu GC14B (VZ10) gas chromatograph equipped with a flame ionization detector. A Shimadzu GC8A (molecular sieve 5A) gas chromatography equipped with a thermal conductivity detector was used to analyze CO and H_2 in the feed and product streams. The operating conditions for each instrument were shown in the Table 4.1.

Table 4.1 Operating condition for gas chromatograph

Gas Chromatograph	**SHIMADZU GC-8A**	**SHIMADZU GC-14B**
Detector	TCD	FID
Column	Porapak Q	VZ10
- Column material	SUS	-
- Length	2 m	-
- Outer diameter	4 mm	-
- Inner diameter	3 mm	-
- Mesh range	60/80	60/80
- Maximum temperature	350°C	80°C
Carrier gas	He (99.999%)	He (99.999%)
Carrier gas flow	40 cc/min	-
Column gas	He (99.999%)	Air, H_2
Column gas flow	40 cc/min	-
Column temperature		
- Initial (°C)	60	70
- Final (°C)	60	70
Injection temperature	100	100
Detector temperature	100	150
Current (mA)	80	-
Analysed gas	Ar, CO, H_2	Hydrocarbon C_1-C_4



1. Pressure Regulator 2. On-Off Value 3. Gas Filter 4. Metering Valve 5. Back Pressure 6. 3-way Valve
7. Catalyst Bed 8. Sampling point 9. Furnace 10. Thermocouple 11. Variable Voltage Transformer
12. Temperature Controller 13. Heating Lin 14. Bubble Flow Meter

Figure 4.1 Flow diagram of CO_2 hydrogenation system

4.4.3 Procedures

1. Using 0.05 g of catalyst packed in the middle of the stainless steel microreactor, which was located in the electrical furnace.

2. A flow rate of Ar = 8 CC/min, 8.8% CO_2 in H_2 = 22 CC/min and H_2 = 50 CC/min in a fixed-bed flow reactor. A relatively high H_2/CO_2 ratio was used to minimize deactivation due to carbon deposition during reaction.

3. The catalyst sample was re-reduced *in situ* in flowing H_2 at 350°C for 3 h prior to CO_2 hydrogenation.

4. CO_2 hydrogenation was carried out at 220°C and 1 atm total pressure in flowing 8.8% CO_2 in H_2.

5. The effluent was analyzed using gas chromatograph technique. [Thermal conductivity detect (TDC) was used for separation of carbon dioxide (CO_2) and methane (CH_4) and flame ionization detector (FID) were used for separation of light hydrocarbon such as methane (CH4), ethane (C_2H_6), propane (C_3H_8), etc.]. In all case, steady-state was reached within 6 h.