

Chapter 3

Methodology

Catalysts preparation

Cu-Zn based catalysts over Al_2O_3 were prepared by incipient wetness impregnation methods. Three types of catalysts were made by using three different Cu-Zn salt aqueous solutions, which are the metal solution with urea (CZU), without urea (CZ) and with NaOH (CZNa). The catalysts prepared with urea (CZU) were synthesized by impregnating the aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%, Fluka) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Fluka) with an addition of urea (99%, Carlo Erba) over Al_2O_3 (98%, Riedel-de Haën). Two mole ratio, 1 mole of urea: CZU1 and 2 moles of urea: CZU2, were prepared to study the effect of the amount of urea in catalyst preparation to the activity of catalysts. The catalysts prepared without urea (CZ) were synthesized by impregnating the aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ over Al_2O_3 . The activity of Cu-Zn catalyst using NaOH instead of urea was also tested in order to study the effect of basicity of the metal salt solution to the activity of the catalyst. The catalyst prepared with NaOH (CZNa) was synthesized by impregnating the aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the addition of NaOH ($\geq 98\%$, Sigma-Aldrich) over Al_2O_3 . The pH of metal salt solution was adjusted using NaOH to be equivalent with the pH value of metal salt-urea solution. The impregnated samples were dried in air at 373 K for 12 hrs and then calcined at 573 K for 3 hrs. The commercial catalyst used for comparison was Cu/Zn/ Al_2O_3 prepared by precipitation method from Süd-Chemie AG (München, Germany). The compositions of the catalysts in this study and their abbreviations are shown in Table 2.

Table 2 The compositions of Cu-Zn catalysts for methanol reforming

Catalyst	Composition (Cu/Zn/ Al_2O_3) (% wt)	Urea (mole/mole _{Cu})
10CZ	5 / 5 / 90	0
10CZU1	5 / 5 / 90	1
10CZU2	5 / 5 / 90	2
20CZ	10 / 10 / 80	0
20CZU1	10 / 10 / 80	1
20CZU2	10 / 10 / 80	2
20CZNa	10 / 10 / 80	0
Commercial	40 / 30 / 30	0

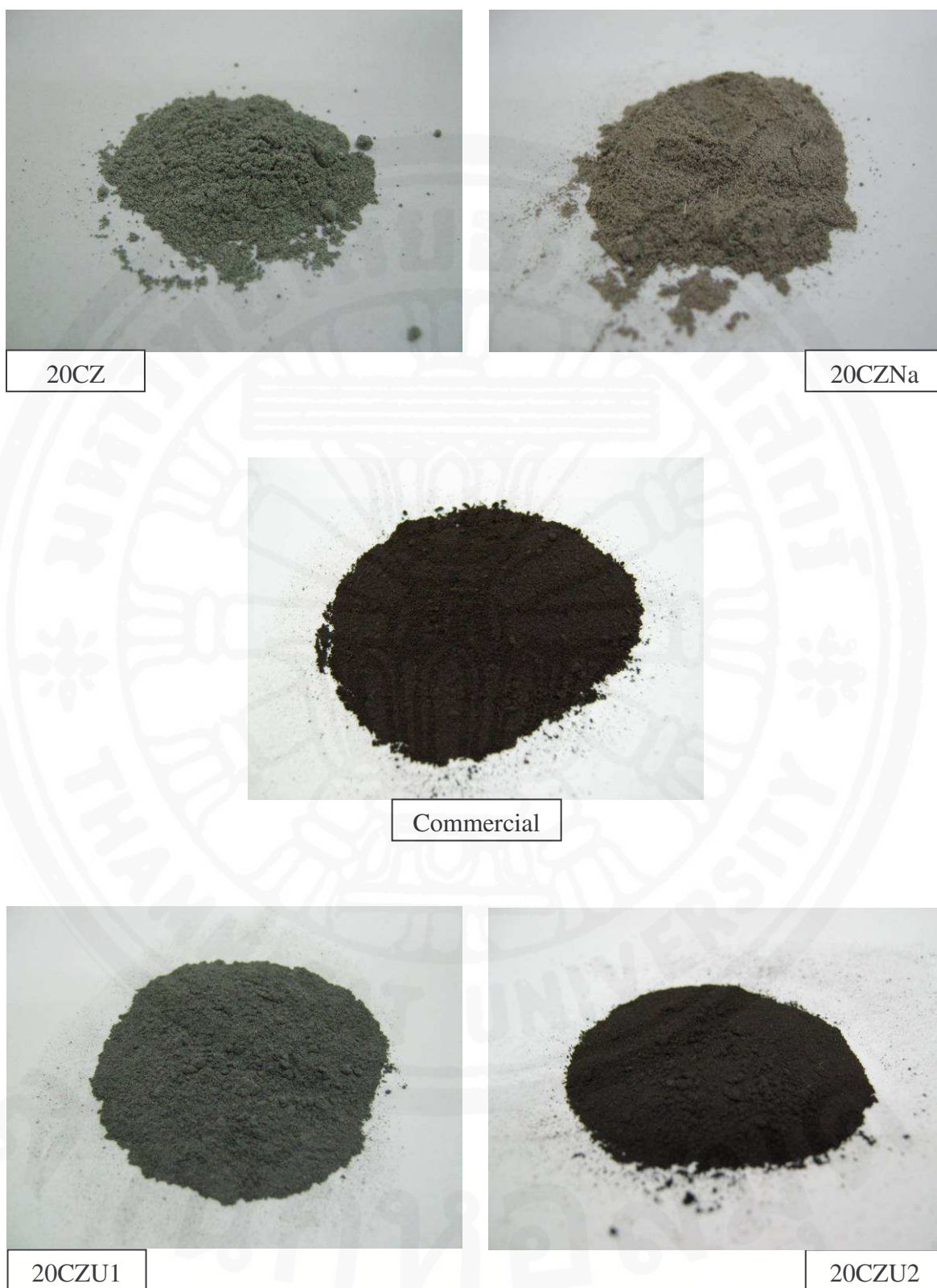


Figure 11 The impregnated catalysts and commercial catalyst

Methanol Reforming Reaction in Tubular Reactor

The methanol steam reforming reaction for the hydrogen production was studied on the prepared catalysts in a stainless steel tubular reactor which has an inside diameter of 1 cm. Two grams of catalyst were packed between quartz wool in the tubular reactor. The catalyst was reduced with 30 ml/min of 10% H₂: N₂ balanced at 453 K for 1 hr prior to the methanol reforming reaction test. The reactor was flushed with 30 ml/min N₂ flow at 453 K for 30 min to get rid of adsorbed hydrogen from the reduction process. The mixture of methanol and water solution was loaded into a saturator which was heated to 333 K. The compositions of methanol and water in the liquid phase are 0.125:0.875 molar ratios. The composition of solution was calculated by the Aspen Plus simulation program (Aspen Technology Inc., Burlington, Mass., USA) to ensure that the composition of the mixture in the vapor phase is a 1:1 molar ratio at the outlet from the saturator. The vapor of the mixture within the saturator was carried out at 20 ml/min N₂, and sent into the reactor at 453 K and 523 K in a continuous system. Therefore, the time spent in the packed bed reactor in a continuous mode was about 6 seconds. The product was collected and the production of hydrogen was determined via gas chromatography (GC).

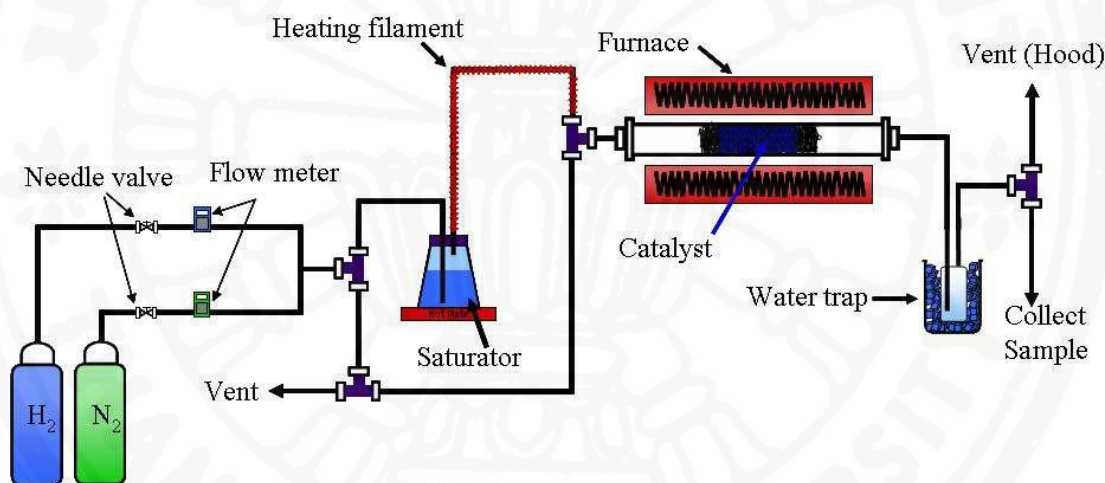


Figure 12 Schematic of methanol reforming process

Analysis Section

Gas Chromatograph

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, and the temperature.

In a GC analysis, a known volume of gaseous is injected into the entrance of the column, usually using a microsyringe. As the carrier gas sweeps the gas sample molecules through the column, this motion is inhibited by the adsorption of the gas molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the gas mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which they emerge from the column and by the retention time of the gas sample in the column. The area under a peak is proportional to the amount of analyte present in the chromatogram. The area of the peak can be calculated using the mathematical function of integration. The Concentration of the gas sample can be calculated using a calibration curve created from a standard gas.

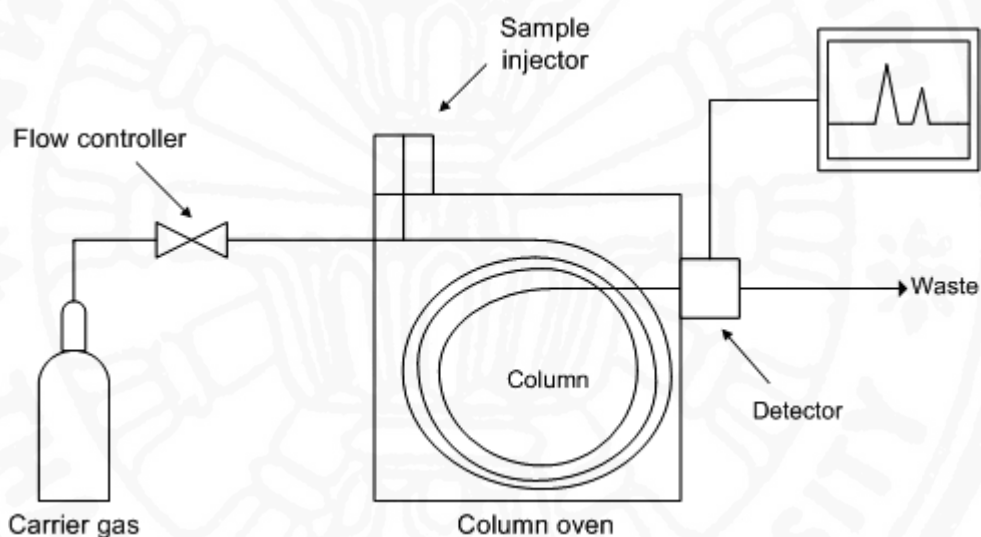


Figure 13 Schematic of gas chromatograph

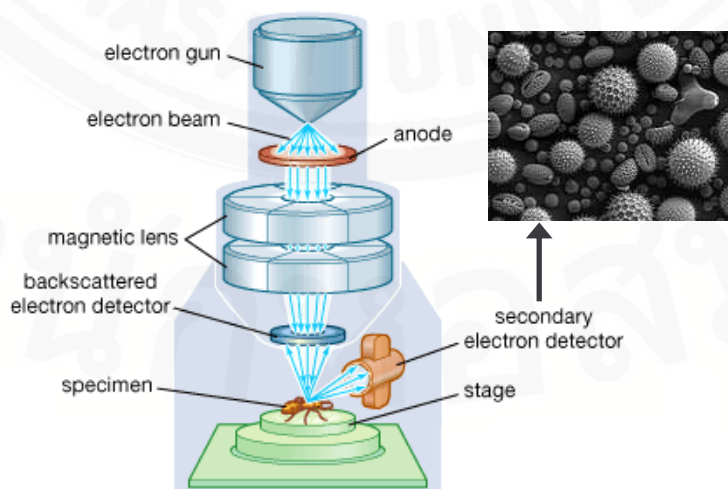


Figure 14 Gas chromatograph (Perkin Elmer- Autosystem XL)

A Perkin Elmer (Waltham, Mass., USA) Autosystem XL gas chromatograph with Porapak Q column (Supleco, Bellefonte, PA, USA) coupled with a thermal conductivity detector (TCD) was used to determine the amount of hydrogen production. The GC was linked to a computer for automatic determination of peak areas which could be converted to concentration.

Scanning Electron Microscope

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. The electron beam, which typically has an energy ranging from a few hundred electron volts (eV) to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube (CRT). The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image can be digitally captured and displayed on a computer monitor and saved to a computer's hard disc. X-rays, which are also produced by the interaction of electrons with the sample, may also be detected in an SEM equipped with energy dispersive spectroscopy.



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Figure 15 Schematic of scanning electron microscope



Figure 16 Scanning electron microscope (JEOL JSM-5410)

The surfaces of the catalysts were inspected by a scanning electron microscope (SEM) from JEOL JSM-5410, Jeol Inc., Tokyo, Japan). The elemental composition of the catalyst surface was determined by energy dispersive spectrometry (EDS, Oxford) which the SEM was equipped with.

X-ray Diffractometer

X-ray diffraction is a technique used to characterize the crystallographic structure, crystallite size, and preferred orientation in polycrystalline or powdered solid samples. The x-ray diffraction is commonly used to identify unknown crystalline substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. The peaks in an x-ray diffraction pattern are directly related to the atomic distances as described in the Bragg's Equation.

$$2d \sin \theta = n\lambda$$

In the equation, d is the distance between atomic planes in crystalline materials; θ is the scattering angle; n is an integer representing the order of the diffraction peak and λ is the x-ray wavelength. The x-ray diffraction can also be used for determining crystallite size in crystalline materials. An effect of the finite crystallite size can be seen as a broadening of the peaks in an X-ray diffraction as is explained by the Scherrer's Equation.

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

where τ is the mean crystallite dimension, K is the shape factor, λ is the x-ray wavelength, typically 1.54 \AA , β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the scattering angle. The dimensionless shape factor has a typical value of

about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to crystals larger than about 100 nm.

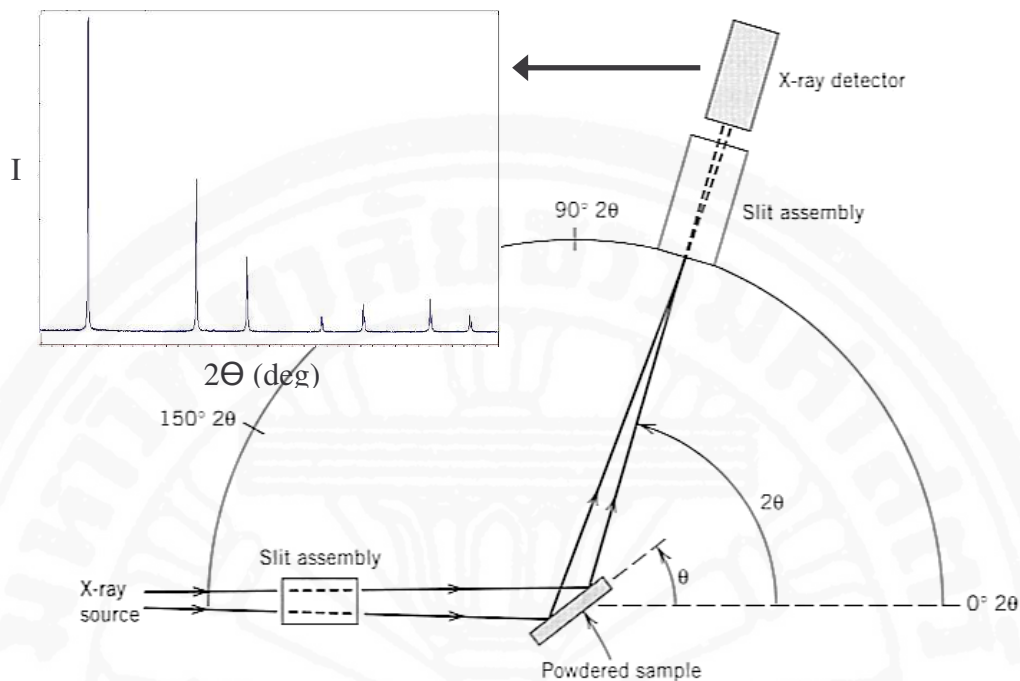


Figure 17 Schematic of x-ray diffractometer



Figure 18 X-ray diffractometer (JEOL, JDX-3530)

The catalysts were characterized by the X-ray diffraction technique (XRD, JEOL JDX-3530, Jeol Inc., Tokyo, Japan) using Cu $K_{\alpha 1}$ radiation, 30° - 41° 2-theta, 0.04° step size, 1 sec step time. JADE software (Jade Software Corporation Ltd., Christchurch, New Zealand) was used to determine the crystallite size of the CuO by using the broadening of peak at 38.8° 2-theta. JADE software was also used to identify phases of the catalysts before and after calcination with the references of X-ray diffractogram database from the International Centre for Diffraction Data (Newtown Square, PA, USA).

