CHAPTER III

EXPERIMENTS AND ANALYSIS TECHNIQUE

Preparation of Adsorbents

Adsorbents used were Al_2O_3, Cu/Al_2O_3, Zn/Al_2O_3 and $CuZn/Al_2O_3$. These adsorbents were prepared by dry impregnation of neutral activated alumina (Aldrich) with a solution of copper nitrate and zinc nitrate (Fluka). Percent of copper and zinc loaded on support were varied at 2.5wt% and 5.0wt% in monometallic adsorbent. For bimetallic adsorbent, $CuZn/Al_2O_3$, weight ratio of copper to zinc was approximately 1:1 and total metal loading was fixed at 5.0% by weight. Apparatus for preparation was shown in Figure 3.1.

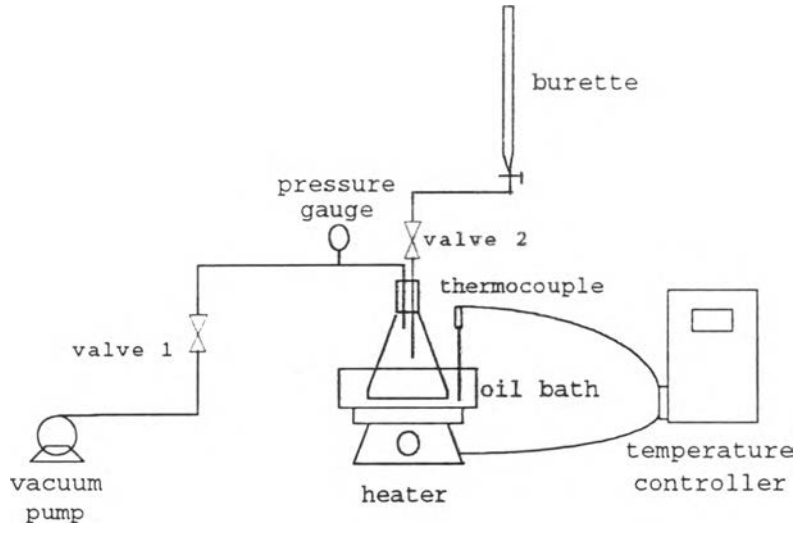

Figure 3.1 Apparatus for adsorbent preparation

Procedure:

Approximately 20.00 grams of neutral activated alumina was added to 250 mL conical flask. The flask was evacuated and kept at pressure of -28 psi and dried at temperature of 120 °C for 2 hr and 30 min. After that, the flask was cooled to room temperature. A 5.24 mL of appropriate concentration solution was impregnated on the dried alumina. The impregnated alumina was kept under vacuum pressure for 30 min and then, at atmospheric pressure for 6 hr. This alumina was then dried at 110°C for 12 hr and reduced with pure hydrogen gas at flow rate of 50 mL/min for 6 hr. Reduction temperature was 400°C for copper and zinc, respectively.

Alumina adsorbent:

Alumina support was calcined wih hydrogen gas at 400°C for 6 hr. The alumina adsorbent does not exactly contain copper and zinc content.

Copper adsorbent:

Alumina support was impregnated with copper solution (2.5wt% and 5.0wt%), then dried at 120°C and calcined at 400°C with hydrogen gas stream. The prepared adsorbent was referred as 2.5Cu and 5.0Cu, respectively.

Zinc adsorbent:

Alumina support was impregnated with zinc nitrate solution (2.5wt% and 5.0wt%), then dried at 120°C and calcined at 400°C with hydrogen gas stream. The prepared adsorbent was referred as 2.5Zn and 5.0Zn, respectively.

Copper-Zinc adsorbent:

Alumina support was first impregnated with 2.5wt% zinc nitrate solution, dried at 120°C and calcined at 400°C with hydrogen gas. After that, 2.5wt% of copper nitrate solution was impregnated, dried and calcined at the same condition. This bimetallic adsorbent was referred as CuZn.

Experiment

The experiments were conducted in a 300 mL batch reactor. All components of the reactor are made of 316 stainless steel to protect a system from a corrosion. This reactor was designed and constructed in order to withstand a maximum temperature of 350°C and a maximum pressure of 1000 psig. A schematic diagram of the system was shown in Figure 3.2. In this study, experiments were

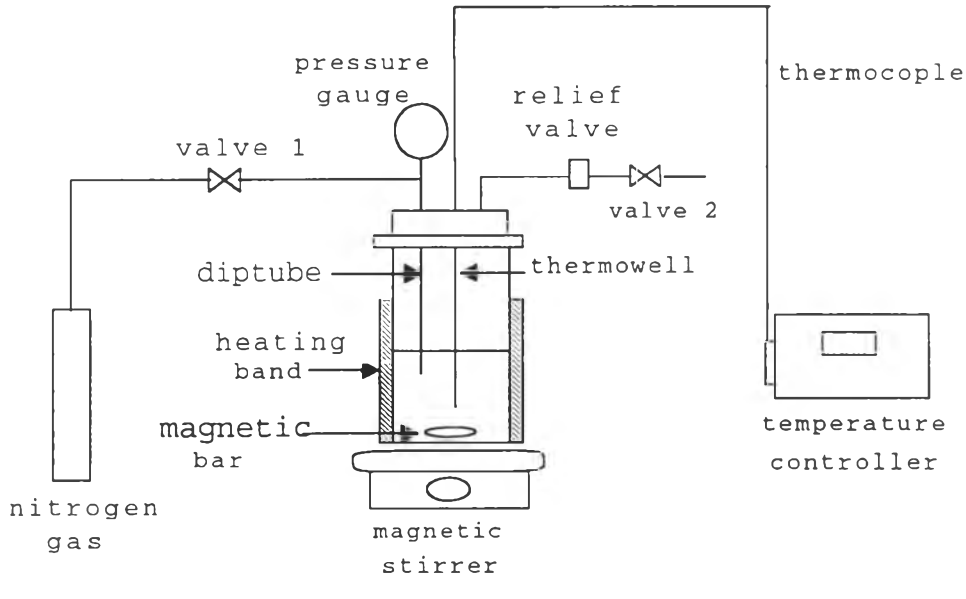

Figure 3.2 Schematic diagram of experimental apparatus

designed to study both adsorption and desorption experiment.

Liquid feed and adsorbent were added to a 200 mL beaker and then the beaker was placed in a bomb. Nitrogen gas was charged at the top through gas inlet valve (valve 1) into the bomb. The pressure in the bomb was measured by pressure gauge, usually 0-1000 psig, at the bomb head. A diptube was connected to the gauge and extended to imerse the liquid feed. A gas relief valve was connected to the gas outlet. This valve was intended to relief the bomb pressure before it reached a dangerous level. The bomb was set in the heating band which was connected to a temperature controller. A thermocouple, K(CA) type in a 1/8" diameter 316 stainless steel tube, was used for measuring the temperature inside the bomb. This thermocouple was inserted into the thermowell on the bomb head and connected to the temperature controller. The liquid feed was stirred by magnetic stirrer which was placed under the bomb. The gas release valve (valve 2) was used to discharge the gas in the bomb.

Adsorption procedure:

100 mL of toluene (Merck) containing 1000 ug/L of mercury were used as a liquid feed. Adsorbent, 1.0000 g, was added into the toluene in the beaker. The beaker was placed in the bomb. The bomb contains some oil which was used for transfer heat from reactor wall to the beaker. The reactor head was placed on the bomb to close the system. The system was operated at constant pressure of 200 psig which was supplied from nitrogen gas (TIG) and

at a various temperature of 30, 50 and 75°C. After 1 hr of contact time, the gas release valve was open carefully to reduce the pressure in the bomb. A Liquid product of each experiments was filtered and then kept before analysis.

Desorption Procedure:

Spent Adsorbent obtained from the adsorption experiment was mixed with 100 mL of pure toluene in the batch reactor at the same condition with adsorption experiment.

In this experiment, mercuric chloride, phenylmercuric acetate and diphenylmercury (Fluka) are used as mercury model compounds. Properties of these chemicals are shown in Tables 3.1 to 3.15.

Analysis Technique

Mercury by Cold Vapor Technique

Atomic Absorption Spectroscopy (AAS) was an effective method for determination of mercury. Since mercury shows poor sensitivity when it was determined by conventional flame AAS, cold vapor technique was used for determining trace amount of mercury for many years.

A characteristic of the cold vapor technique was that only inorganic mercury in the sample was measured. Organomercurials did not respond to this technique. As a consequence, organic mercury compounds must be converted

to inorganic mercury prior to determination. Otherwise, digestion of samples was necessary in order to obtain the ionic form and reduce analytical interferences. The sample digestion used in this study was based on ASTM D-3223 which is a standard method for determining of total mercury in water. To generate mercury vapor, the VGA-76 which was a hydride generation unit, was attached with Varian SpectrAA 300/400. The detection limit of this technique was 0.2 µg/L.

Procedure:

100 mL of liquid sample was transferred to 250 mL flat round flask. 5 mL of concentrated sulfuric acid and concentrated nitric acid were added and mixed after each addition. Then, 15 mL of potassium permanganate solution was added to each flask. The mixture was stirred virgously for at least 15 min. And, 8 mL of potassium persulfate was added to the flask. The flask at the top was equipped with a reflux condensor and subsequently heated in oil bath at 95°C for approximately 2 hours. After that the flask was removed from the oil bath and cooled to ambient temperature. 6 mL of sodium chloride-hydroxylmaine hydrochloride solution was added to the sample and shaken for a few seconds. The solution was transferred into 250 mL separating funnel and shaken virgously. After the water-phase separates from toluene-phase, the water-phase was added to a 100 mL volumetric flask. The solution in the funnel was still washed with 10 mL of distillated or deionized water. This water was also added to the flask until the flask is

filled up to the mark. Then the obtained aqueous solution was shaken and transferred to a sample bottle. The mercury content in the digested solution was determined and recorded.

Copper and Zinc Content in Adsorbents

The standard test method, ASTM D1977-91, which was intended for the determination of nickel and vanadium in catalysts was applied for determination of copper and zinc content in each adsorbents. In this experiment, the quantitative analysis of copper and zinc was carried out by using Varian SpectrAA 300/400 atomic absorption spectroscopy.

This test method was a process by which adsorbent samples were decomposed with hydrofluoric and sulfuric acid. After complete volatilization of the acids and cooling, the sulfate salts were diluted to the appropriate concentration range for analysis by flame atomic absorption.

Procedure:

Approximately 0.5 gram of adsorbent was weighed and transfer to a basin. 10 mL of 48% sulfuric acid, 10 mL of concentrated nitric acid and 10 mL of concentrated hydrofluoric acid were added to each basin. The solution in the basin was evaporated by heat on a hot plate to near dryness. After that, the basin was removed from hot plate and cool to ambient temperature. 20 mL of 19% hydrochloric acid and 30 mL of 3% hydrogen peroxide were

added and the basin was covered with watch glass and return to hot plate. The solution was heated to boiling and continue to boil until the salts were dissolved. After dissolution was complete, the basin was removed from hot plate and cool to ambient temperature. The watch glass was washed in the basin and transfer solution to a 100 mL of volumetric flask. The solution was diluted with water to a mark and mixed. This diluted solution was quantitatively analysed by flame AAS to determine the concentration of metal content in each samples.

Surface Area and Pore Volume

A Micromeritics model ASAP 2000 was used to determine surface area, pore volume and pore size distribution of each adsorbent. There are two operating step, the degassing step and analysis step.

Fresh and spent adsorbent in each experiment were analysed in order to study the variation of surface area, pore volume and also pore size distribution. The adsorbent first was heated and placed under vacuum to remove moisture and other contaminants. Temperature of degassing was carried out at 150°C and vacuum pressure of 10 mmHg for 3 hours. After this step, the catalyst was weighed and then the degassed sample was transfer from the degas port to the analysis port.

At the analysis port, the sample was analysed at vacuum pressure of 15 mmHg and liquid nitrogen was used

as a coolant. The nitrogen gas was used as analysis gas. The volume of adsorbed nitrogen on sample will relate with relative pressure (P/P_o).

Table 3.1 Properties of Toluene*

Formula	C_7H_8
Chemical Name	Toluene
Physical Properties	
Molecular Weight	92.13
Form	liquid
Colour	colourless
Boiling Poing (°C)	110.8
Melting Poing (°C)	-95
Specific Gravity	0.866
Solubility	soluble in ether and alcohol
Purity	> 99%
Supplier	Merck

*From Encyclopedia of Chemical Engineering

Table 3.2 Properties of Mercuric chloride*

Formula	$HgCl_2$
Chemical Name	Mercuric chloride
Physical Properties	
Molecular Weight	271.52
Form	solid
Colour	white
Melting Poing (°C)	277
Boiling Point (°C)	302
Specific Gravity	5.44
Solubility	soluble water
Purity	> 99%
Supplier	Carlo Erba

* From Merck Index

Table 3.3 Properties of Phenylmercuric Acetate*

Formula	$C_8H_8O_2Hg$
Chemical Name	Phenylmercuric acetate
Physical Properties	
Molecular Weight	336.74
Form	solid
Colour	white
Melting Poing (°C)	149
Boiling Point (°C)	-
Specific Gravity	5.44
Solubility	insoluble water but soluble in organic solvent
Purity	> 97%
Supplier	Fluka

* From Merck Index

Table 3.4 Properties of Diphenylmercury*

Formula	$C_{12} H_{10} Hg$
Chemical Name	Diphenylmercury
Physical Properties	
Molecular Weight	354.8
Form	solid
Colour	white
Melting Poing (°C)	121-124
Boiling Point (°C)	-
Specific Gravity	2.32
Solubility	moderately soluble in toluene
Purity	> 97%
Supplier	Fluka

* From Supplier

Table 3.5 Properties of Nitric Acid*

Formula	HNO_3
Chemical Name	Nitric Acid
Physical Properties	
Molecular Weight	63.02
Form	liquid
Colour	colourless
Boiling Poing (°C)	83
Melting Poing (°C)	-41.59
Specific Gravity	1.502
Solubility	soluble in water
Purity	> 99%
Supplier	BDH

* From Merck Index

Table 3.6 Properties of Hydrogen Peroxide*

Formula	H_2O_2
Chemical Name	Hydrogen Peroxide
Physical Properties	
Molecular Weight	34.02
Form	liquid
Colour	colourless
Boiling Poing (°C)	151.4
Melting Poing (°C)	0.89
Specific Gravity	1.13
Solubility	soluble in water, acid and ether
Purity	35-35.6%
Supplier	Merck

* From Encyclopedia of Chemical Engineering

Table 3.7 Properties of Hydrofluorid Acid*

Formula	HF
Chemical Name	Hydrofloric Acid
Physical Properties	
Molecular Weight	20.01
Form	liquid
Colour	colourless
Boiling Poing (°C)	112.2
Melting Poing (°C)	-83
Specific Gravity	1.155
Solubility	soluble in water
Purity	48-51%
Supplier	Carlo Erba

* From Encyclopedia of Chemical Engineering

Table 3.8 Properties of Hydrochloric Acid*

Formula	HCl
Chemical Name	Hydrochloric Acid
Physical Properties	
Molecular Weight	36.47
Form	liquid
Colour	colourless
Boiling Poing (°C)	
Melting Poing (°C)	-15.35
Specific Gravity	1.05
Solubility	soluble in water and alcohol
Purity	37%
Supplier	Merck

* From Encyclopedia of Chemical Engineering

Table 3.9 Properties of Sulfuric Acid*

Formula	H_2SO_4
Chemical Name	Sulfuric Acid
Physical Properties	
Molecular Weight	98.08
Form	liquid
Colour	colourless
Boiling Poing (°C)	~290
Melting Poing (°C)	10
Specific Gravity	1.84
Solubility	soluble in water
Purity	> 99%
Supplier	Merck

* From Merck Index

Table 3.10 Properties of Copper nitrate*

Formula	$Cu(NO_3)_2.3H_2O$
Chemical Name	Copper nitrate trihydrate
Physical Properties	
Molecular Weight	241.60
Form	solid
Colour	blue
Boiling Poing (°C)	-
Melting Poing (°C)	114.5
Specific Gravity	2.32
Solubility	soluble in ether and alcohol
Purity	> 99%
Supplier	Fluka

* From Merck Index

Table 3.11 Properties of Zinc Nitrate*

Formula	$Zn(NO_3)_2.6H_2O$
Chemical Name	Zinc nitrate hexanitrate
Physical Properties	
Molecular Weight	297.48
Form	solid
Colour	white
Boiling Poing (°C)	-
Melting Poing (°C)	36
Specific Gravity	2.065
Solubility	soluble in water and alcohol
Purity	> 98%
Supplier	Fluka

* From Merck Index

Table 3.12 Properties of Potassium Permanganate*

Formula	$KMnO_4$
Chemical Name	Potassium Permanganate
Physical Properties	
Molecular Weight	158.03
Form	solid
Colour	dark purple
Boiling Poing (°C)	-
Melting Poing (°C)	-
Specific Gravity	2.71
Solubility	soluble water
Purity	> 99%
Supplier	Carlo Erba

* From Merck Index

Table 3.13 Properties of Potassium Persulfate*

Formula	K_2SO_8
Chemical Name	Potassium Persulfate
Physical Properties	
Molecular Weight	270.32
Form	solid
Colour	white
Boiling Poing (°C)	-
Melting Poing (°C)	-
Specific Gravity	-
Solubility	soluble in water
Purity	> 99%
Supplier	Calro Erba

* From Merck Index

Table 3.14 Properties of Hydroxylamin-Hydrochloride*

Formula	$NH_2OH.HCl$
Chemical Name	Hydroxylamine-Hydrochloride
Physical Properties	
Molecular Weight	69.49
Form	solid
Colour	white
Boiling Poing (°C)	58
Melting Poing (°C)	33
Specific Gravity	1.20
Solubility	soluble in water and ether
Purity	> 99%
Supplier	Carlo Erba

* From Merck Index

Table 3.15 Properties of Sodium Chloride*

Formula	$NaCl_2$
Chemical Name	Sodium Chloride
Physical Properties	
Molecular Weight	58.54
Form	solid
Colour	white
Boiling Poing (°C)	804
Melting Poing (°C)	-
Specific Gravity	2.17
Solubility	soluble in water,
Purity	> 99%
Supplier	Carlo Erba

* From Merck Index