

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

##### 3.1.1 Studied Catalysts

The bimetallic catalysts used in this work were prepared at the University of Michigan by incipient wetness impregnation. For Ru-Au/SiO<sub>2</sub>, the support was the colloidal silica (Davision 951N) having a BET surface area of 600 m<sup>2</sup>/g. The precursor compounds were RuCl<sub>3</sub>·H<sub>2</sub>O (Rudi Pont, commercial hydrated ruthenium trichloride) and HAuCl<sub>4</sub>·3H<sub>2</sub>O (Carlo Erba RPE, yellow gold trichloride). The support was impregnated with a freshly prepared aqueous solution about 1.6 cm<sup>3</sup> solution/ g support. The salt concentration in the solution was such to yield a total (Ru+Au) metal content of about 4-5 wt% in the catalysts. The impregnated support was dried at room temperature for 4 hours and at 383 K for 16 hours. The catalysts were then reduced by a purified hydrogen stream (20 cm<sup>3</sup>/min) for 2 hours at 573 K and 2 hours at 673 K.

Each catalyst was signed a code letter: "R" for Ru, "S" for the support material, SiO<sub>2</sub> and a three-digit number representing the approximate atomic percentage of Ru. The metal content of the catalysts was determined by atomic absorption spectroscopy. The Ru metal dispersion in the bimetallic sample was determined by H<sub>2</sub> and O<sub>2</sub> chemisorption at room temperature. A summary of these characterization data is presented in Tables 3.1 and 3.2. (Galvagno *et al.*, 1981)

**Table 3.1 Chemical composition, average particles size of the Ru-Au/SiO<sub>2</sub>**

Catalyst code	Ru(%wt)	Au(%wt)	Particle size of Au (A°)
RS100	3.86	-	-
RS091	3.32	0.61	448
RS048	1.66	3.47	257
RS014	0.39	4.65	237
RS000	-	4.69	276

**Table 3.2 Chemisorption data for Ru-Au/SiO<sub>2</sub>**

Catalyst Code	Chemisorption				
	H <sub>2</sub> Uptake*	O <sub>2</sub> Uptake*	H/Ru	O <sub>2</sub> /Ru	d(A°)
RS100	1.11	2.40	0.26	0.28	34
RS091	1.08	2.08	0.29	0.28	-
RS048	0.42	1.03	0.23	0.28	-
RS014	0.13	0.28	0.30	0.32	-
RS000	-	0.061	-	-	240

\* In cm<sup>3</sup>(STP)/g cat.

The other ruthenium catalysts were Ru/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, Ru-Au/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, Ru/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

### **3.1.2 Studied Gases and Oxygenated Compounds**

High purified (HP) hydrogen and nitrogen were commercially obtained from Thai Industrial Gas Public Co., Ltd. (TIG). Synthetic air (Air Zero) was supplied from PRAXAIR. 5% hydrogen balance in nitrogen and 5% oxygen balance in helium were used for the temperature-programmed reduction study. The oxygenated compounds used was methyl alcohol ( $\text{CH}_3\text{OH}$ ) procured as AR grade from J.T. Baker.

## **3.2 Catalyst Characterization**

### **3.2.1 BET Surface Area**

The BET surface area of the bimetallic catalysts was determined by nitrogen physisorption at 77 K with Quantachrome Autosorb-1. The catalyst sample was outgassed at 423 K for 16 hours before measuring the surface area.

### **3.2.2 Scanning Electron Microscopy (SEM)**

Electron micrographs were taken on the JOEL 5200 scanning electron microscope. The accelerating voltage was 5 kV and the magnification was 100X. Samples were prepared by splitting a pellet on the brass stubs. The samples were gold coated to prevent specimen charging.

### **3.2.3 X-ray Diffraction Measurement (XRD)**

A Rigaku X-ray diffractometer system equipped with a RINT2000 wide angle goniometer and a Cu tube for generating a  $\text{CuK}\alpha_1$  radiation ( $\lambda$

=1.54 Å) was used to obtain the XRD patterns at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the  $K_{\beta}$  filter. The goniometer parameters were divergence slit =  $1^{\circ}(2\theta)$ ; scattering slit =  $1^{\circ}(2\theta)$ ; and receiving slit = 0.3 mm. The catalyst samples were compacted on a glass slide, firmly pressed by hand. A scan speed of  $5^{\circ}(2\theta)/\text{min}$  with a scan step of  $0.02^{\circ}(2\theta)$  was used during a continuous run in the  $5$  to  $90^{\circ}(2\theta)$  range. The digital output of the proportional X-ray detector and the goniometer measurements were sent to an on-line microcomputer for storage and subsequent data processing.

The Scherrer equation relates the breadth,  $B$ , at half peak height of an XRD line due to a specific crystalline plane to the size of the crystallites,  $l$ : shown in equation (3.1)(Bond, 1987).

$$B = \frac{k\lambda}{l \cos \theta} \quad (3.1)$$

where

$\lambda$  = X-ray wavelength

$\theta$  = diffraction angle

$k$  = a constant , usually equal to 1.

### **3.2.4 Temperature-Programmed Desorption (TPD) and Temperature-Programmed Reduction (TPR)**

TPD and TPR experiments were carried out with the Micromeritics TPD/TPR 2900 instrument. The temperatures of thermal conductivity detector (TCD), valve, and loop were maintained at 373 K, 373 K, and 348 K respectively. The carrier gas was UHP nitrogen with a flow rate about 50 ml/min. The detector current was set at 50 mA. The schematic diagram of the TPD/TPR 2900 is shown in Figure 3.1.

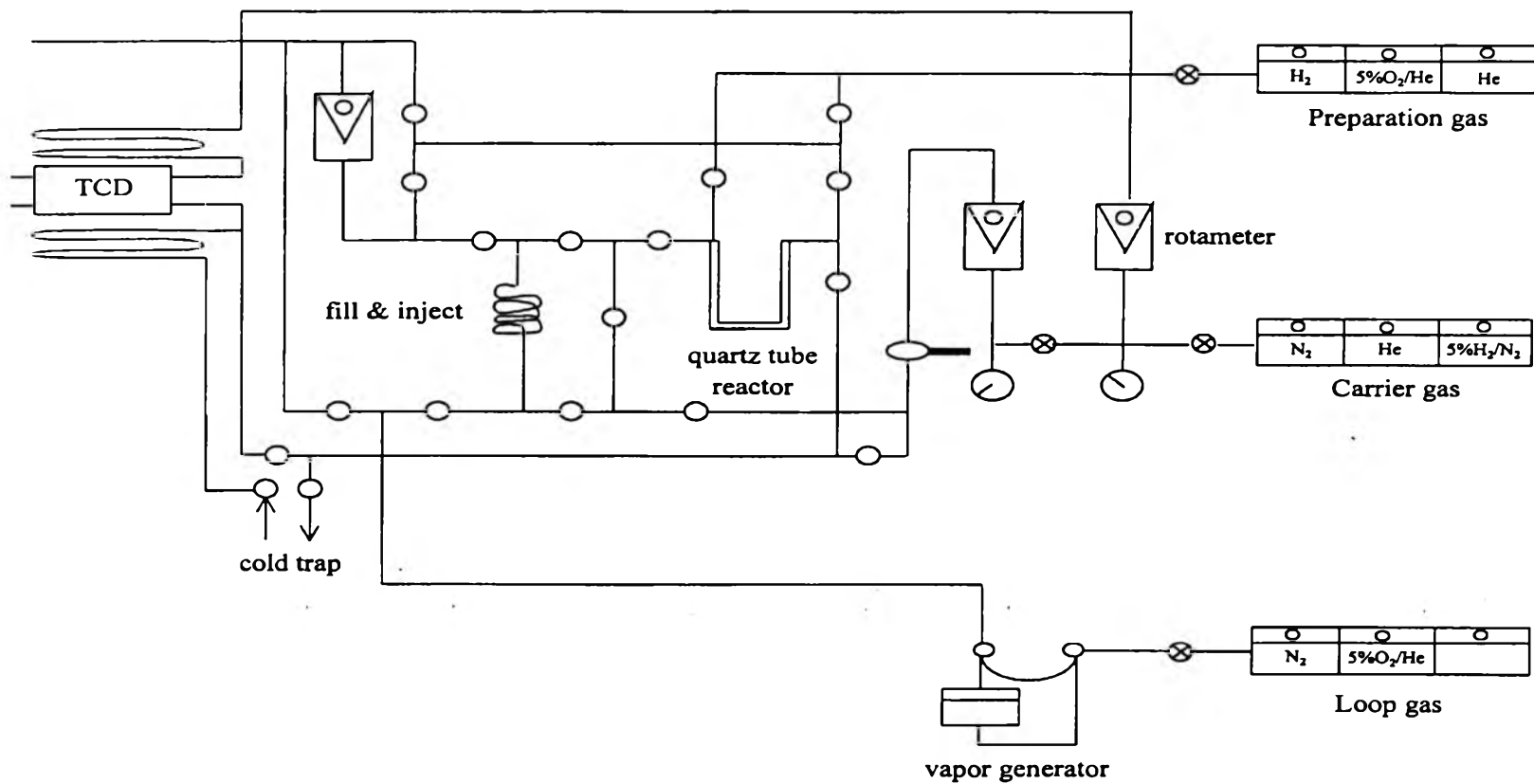


Figure 3.1 Schematic diagram of TPD/TPR 2900 instrument for TPD and TPR experiments

A catalyst sample about 0.05 g was placed into a quartz tube reactor which was externally heated by a tube furnace. For TPD of methanol and TPD of oxygen experiments, the catalyst sample was reduced by UHP hydrogen (in the preparation gas line) at 673 K, 20 cm<sup>3</sup>/min for 2 hours before pulse chemisorption of methanol. After that, the catalyst sample was cooled down to a room temperature in a stream of nitrogen. Then, UHP nitrogen carried the methanol vapor (in the loop gas line) through the vapor generator to be adsorbed on the catalyst sample. Methanol vapor injection was made in 2-minute intervals for 1 hour (controlled by fill and inject mode). For TPD of oxygen, 5% oxygen in helium was introduced to a sample by a loop gas in 2-minute intervals for 1 hour as well. The sample was then swept by UHP nitrogen in a programmed temperature rise at a rate of 10 K/min to 1073 K. The effluent gases were monitored using a thermal conductivity detector (TCD).

For TPR experiments, the catalyst sample was pretreated with 5% oxygen in helium at 473 K, 20 cm<sup>3</sup>/min for 2 hours before running TPR. After cooling the catalyst sample to a room temperature by UHP nitrogen, the catalyst sample was submitted to a programmed temperature rise with the rate of 10 K/min to 1073 K while a reducing gas mixture (5% hydrogen in nitrogen) was flowed over it (in the carrier gas line). The effluent gases were dried in a cold trap before reaching the TCD. The progress of the reduction was then simply monitored by the decrease in hydrogen concentration in the effluent gas. The catalyst sample was not pretreated with 5 % oxygen in helium for the next experiment.

### **3.3 Study of Methanol Oxidation Reaction**

#### **3.3.1 Equipment Set Up**

The catalyst sample about 0.05 g was packed into a Pyrex glass tube reactor between two plugs of quartz wool. The reactor was placed in an electrical heater equipped with a PID controller. The temperature was controlled by Yokogawa temperature controller with a thermocouple. All the reactant gases were first passed through a 7-micron filter in order to remove any small particles. The flow rate of each gas was controlled by Sierra Instrument mass flow transducers to achieve the desired feed stream composition. Check valves were installed to prevent the back flow. The pressure gauge was installed at the end of the lines near the needle valve. If there was a pressure drop in the system shown by the pressure gauge, it was released by the needle valve. So the reactor pressure was kept at atmosphere. The diagram of this study is shown in Figure 3.2.

### 3.3.2 Procedure of Oxidation Experiment

After loading the catalyst sample in the tube reactor, the catalyst bed temperature was raised to 673 K in helium stream at a flow rate 150 cm<sup>3</sup>/min. When the bed temperature reached 673 K, the hydrogen stream with a flow rate of 20 cm<sup>3</sup>/min was switched to the catalyst bed for 2 hours to reduce the catalyst sample. After completing the reduction step, the catalyst was then cooled down to the desired temperature by introducing the stream of helium. The methanol was then fed from a vapor generator that was immersed in a water bath. The temperature of water bath was kept constant at 278 K. The helium stream at flow rate about 5 cm<sup>3</sup>/min passed into the vapor generator (bubbler reactor) to carry the methanol vapor. The feed was a mixture of methanol, 99.7% oxygen, and helium. The total flow rate was 235 cm<sup>3</sup>/min at room temperature. The concentration of methanol vapor and oxygen in the feed stream were kept constant at 1000 ppm and 210,000 ppm (21% by

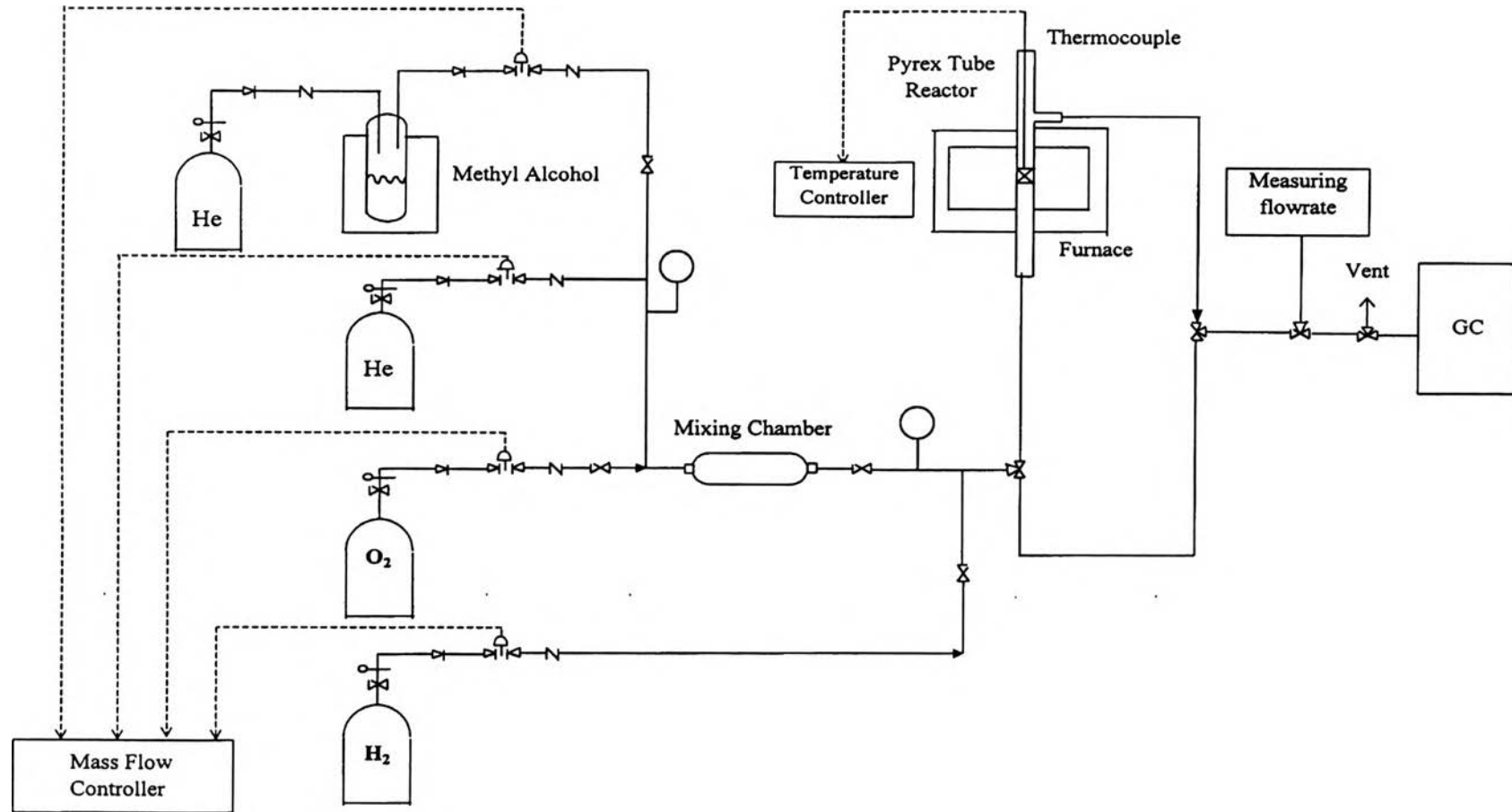


Figure 3.2 Flow diagram of the experiment of methyl alcohol oxidation



volume), respectively. The space velocity calculated from the total flow rate divided by the volume of catalysts was about  $93,000 \text{ h}^{-1}$  at room temperature.

The compositions of the reactants and reaction products were alternately analyzed by Autosystem Perkin Elmer ARNEL 5653V gas chromatography equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). The sample was injected into packed columns by 10-port valve with  $10 \mu\text{l}$  sampling loop. A 60/80 carboxen 1000 column to analyze oxygen, carbon dioxide, and carbon monoxide for TCD and a 80/120 carbopack column to analyze methanol for FID were both used at isothermal condition.

The methanol conversion can be evaluated from equation (3.2):

$$\% \text{ Methanol Conversion} = \frac{(\text{CH}_3\text{OH}_{\text{in}} - \text{CH}_3\text{OH}_{\text{out}})}{\text{CH}_3\text{OH}_{\text{in}}} \times 100 \quad (3.2)$$

where

$\text{CH}_3\text{OH}_{\text{in}}$  = The concentration of the methanol in influent

$\text{CH}_3\text{OH}_{\text{out}}$  = The concentration of the methanol in effluent.