

CHAPTER III METHODOLOGY

3.1 Materials and Equipments

3.1.1 Chemicals

- Silicon dioxide (SiO_2) with surface area $380 \text{ m}^2/\text{g}$ from Jebsen & Jessen Chemicals (T)., Ltd.
- Rhodium(III) chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$) crystalline, $\geq 99.9\%$ trace metals basis from S.M. Chemical Supplies Co., Ltd.
- $\text{HBr}/\text{H}_2\text{O}$ (48 wt% in water) from Ligand Scientific Co., Ltd.
- Distillated water

3.1.2 Gases

- Methane (99.995% Purity)
- N_2 (99.99% , HP grade, Purity)
- O_2 (99.99% , HP grade, Purity)
- H_2 (99.99% , HP grade, Purity)
- He (99.99% , HP grade, Purity)
- Air Zero (99.99% , HP grade, Purity)

Methane and oxygen were utilized as raw materials while nitrogen was used as carrier gas. The utility gases for GC are hydrogen, nitrogen, helium and air zero. Methane was purchased from Praxair (Thailand) Co., Ltd and other gases were purchased from Thai Industrial Gas, Co., Ltd.

3.1.3 Equipments

- Quartz-tube reactor filled with quartz sand
- Temperature controller equipped with a thermocouple (Type K)
- Gas chromatography (Agilent 7820A) with GS-GasPro column

3.2 Experimental Procedures

3.2.1 Catalyst Preparation

Catalyst preparation of Rh/SiO₂ was prepared by the incipient wetness impregnation method as described below.

3.2.1.1 Support Preparation of SiO₂

SiO₂ was prepared by calcinations in furnace (at 400 °C in atmospheric pressure for 4 h by using heating rate 5 °C/min) to get rid of moisture.

3.2.1.2 Catalyst Preparation of Rh/SiO₂

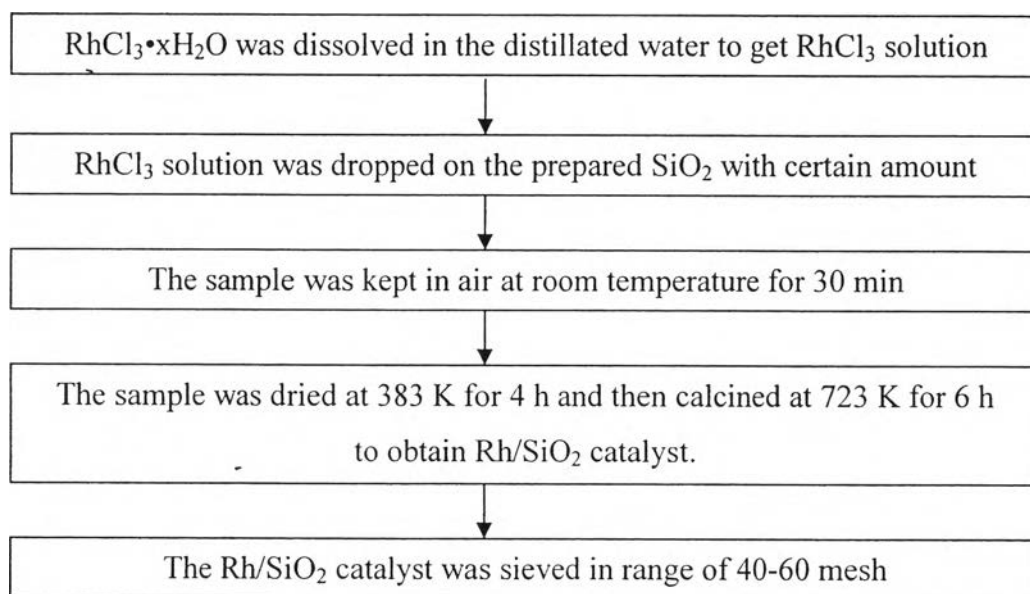


Figure 3.1 Catalysts preparation flow scheme.

3.2.2 Catalyst Characterization

The catalyst characterization techniques applied in this research are surface area analysis (BET), Temperature-Programmed Reduction (TPR), X-ray diffraction (XRD), Scanning Electron Microscopy and Energy Dispersion X-ray Spectroscopy (SEM-EDX).

3.2.2.1 *Surface Area Analysis (BET)*

Surface area analyzer (AS-1-MP) was used to examine the surface area of the catalysts. The sample approximately 0.06-0.1 g was pressed into the dried glass tube, and then outgassed at 250 °C until the moisture completely desorbed which can identify by the desorbed molecule less than 20 $\mu\text{mol}/\text{min}$. The outgassed sample was weighed again to obtain the exact weight before introduce into the analysis station. The measurement was performed at the liquid nitrogen temperature (-196 °C), using relative pressure (P/P_0) in the range of 0.001 to 0.999 with a number of adsorption equal to 21 points and desorption 20 points. The surface area was calculated by using 7 points BET method with P/P_0 in the range of 0.05 to 0.3.

3.2.2.2 *X-ray Diffractometer (XRD)*

The X-ray diffraction patterns of the prepared is obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered $\text{CuK}\alpha$ radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mV. A catalyst sample is first pressed into a hollow of glass holder and held in place by a glass window. After that, it is scanned in the 2θ range from 5 to 90° in the continuous mode with the rate of 5°/min. The XRD results consist of peak parameters, including the centroid 2θ , the full line width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size will be calculated from the XRD data from X-ray line broadening, using the full line width at half maximum of intensity and the 2θ value and plugging them into the Debye-Scherrer equation.

3.2.2.3 Temperature Program Reduction (TPR)

The TPR experiments were carried out at ambient pressure in an apparatus. The experimental parameters are;

Flow rate = 11 ml/min

Heating rate = 10 °C /min

Reducible material = 5% H₂ balanced in N₂

TPR profile recorded range = 200-1000 K

The sample was weight around 0.05-0.1 g and placed into quartz tube that supported with quartz wool. The sample was pretreated in 20 ml/min nitrogen flow at 120 °C for 30 minutes with heating rate 10 °C/min. The TPR analysis process utilized 30 ml/min of 5% hydrogen balanced in nitrogen flow and detected the signal by TCD detector from 200-1000 K with heating rate 10 °C/min.

3.2.2.4 Scanning Electron Microscopy and Energy Dispersion X-ray Spectroscopy (SEM-EDX)

Field-Emission Scanning Electron Microscope (Hitachi, S4800) was used to examine the morphological structure of the catalyst. The samples were placed on the holder with an adhesive tape and coated with a thin layer of platinum using Hitachi E-1010 ion sputtering device for 180 second prior to observation under SEM. The scanning electron images were investigated by using an acceleration voltage of 5 kV with a magnification in the range of 250-10000x.

Energy Dispersion X-ray Spectroscopy was used to identify the elemental composition in the catalyst and also examine the elemental distribution. The sample preparation was the same as SEM, the acceleration voltage was using 20 kV with a magnification 9000x.

3.2.3 Catalytic Activity Testing

The oxidative bromination reaction was carried out in continuously-flow reactor under atmospheric pressure. The reaction procedure is shown below.

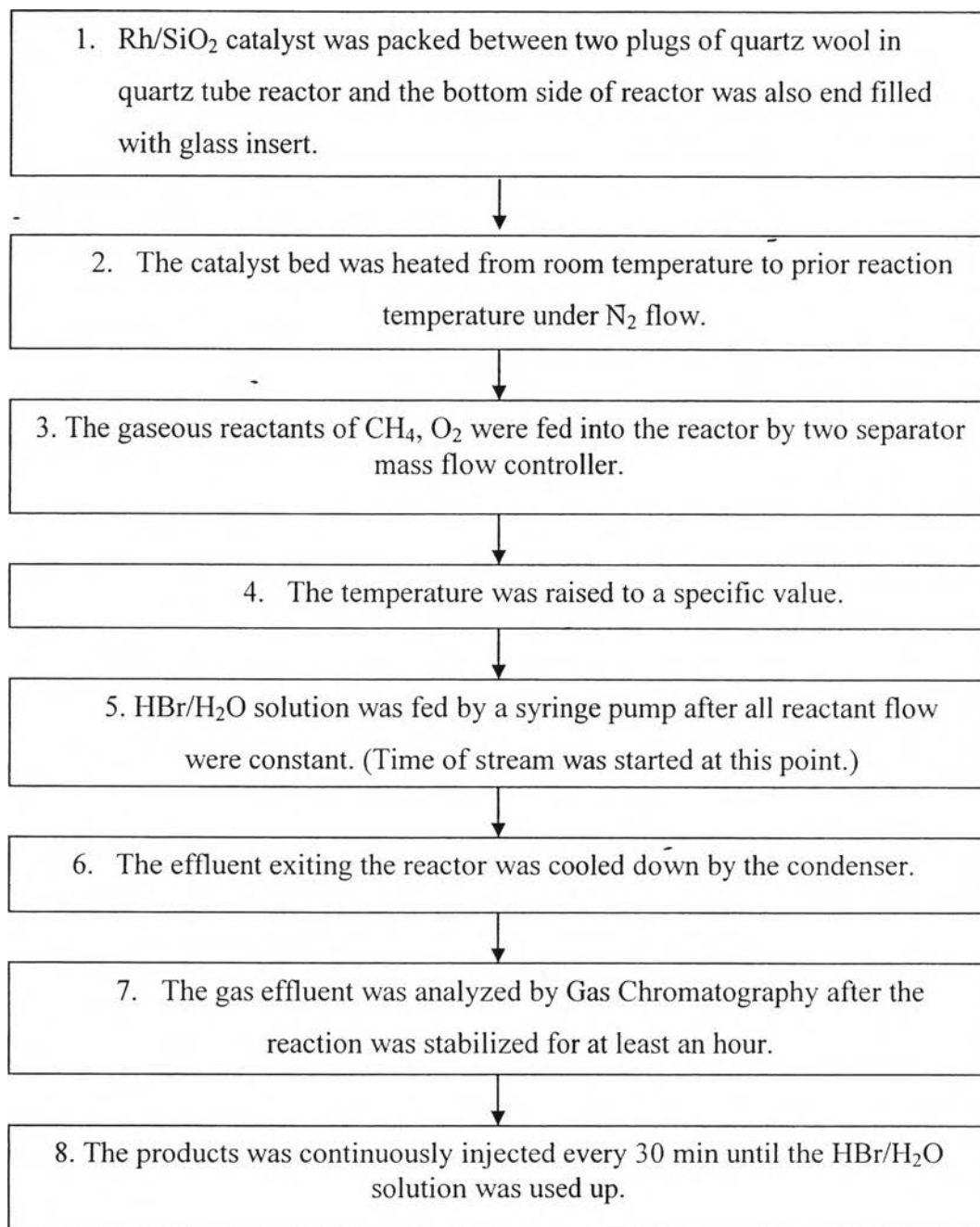


Figure 3.2 Procedure flow scheme for oxidative bromination of methane reaction.

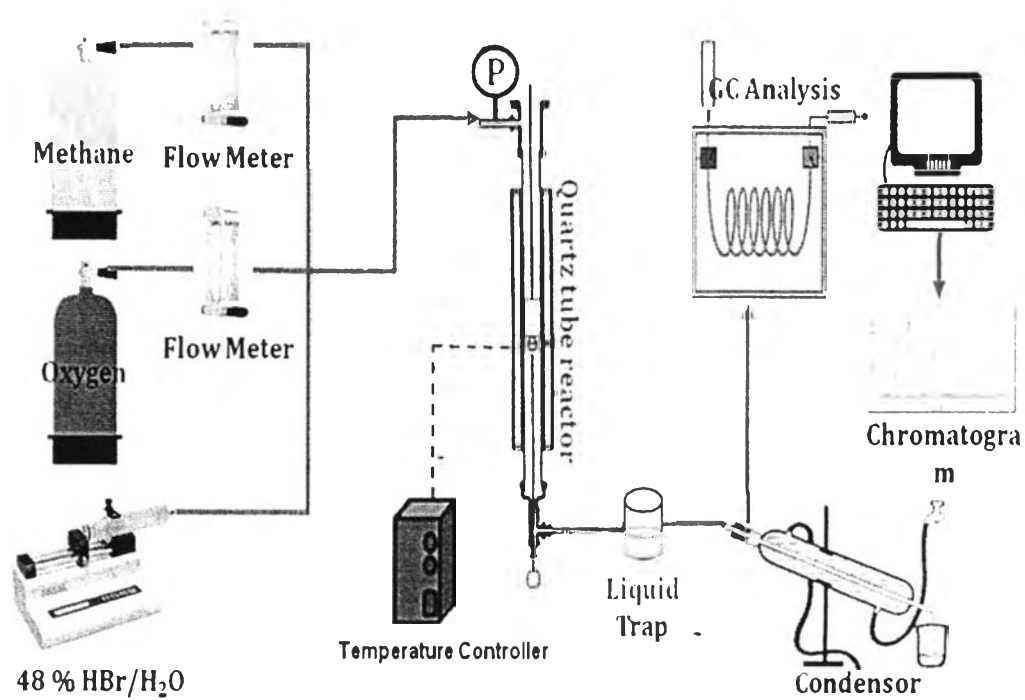


Figure 3.3 Experimental setup for oxidative bromination of methane reaction.