

CHAPTER III

METHODOLOGY

3.1 Materials and Equipments

3.1.1 Chemicals

- Silicon dioxide (SiO_2) with surface area $172 \text{ m}^2/\text{g}$
- Barium nitrate ($\text{Ba}(\text{NO}_3)_2$)
- Ammonium Tungstate ($(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6$)
- Oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$)
- Tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$), TEOS
- $\text{HBr}/\text{H}_2\text{O}$ (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 barium oxide or tungsten oxide on silica were prepared by 2 technique

3.2.1.1 Incipient Wetness Impregnation Method

SiO₂ support 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.

Impregnation as described in flow diagram below.

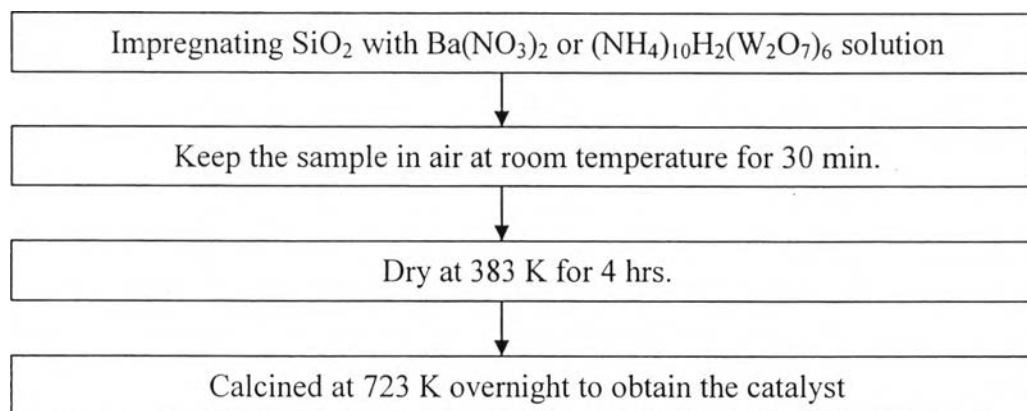


Figure 3.1 The catalyst preparation flow diagram of the incipient wetness method.

3.2.1.2 Sol-gel Method

Sol-gel method as described in flow diagram below.

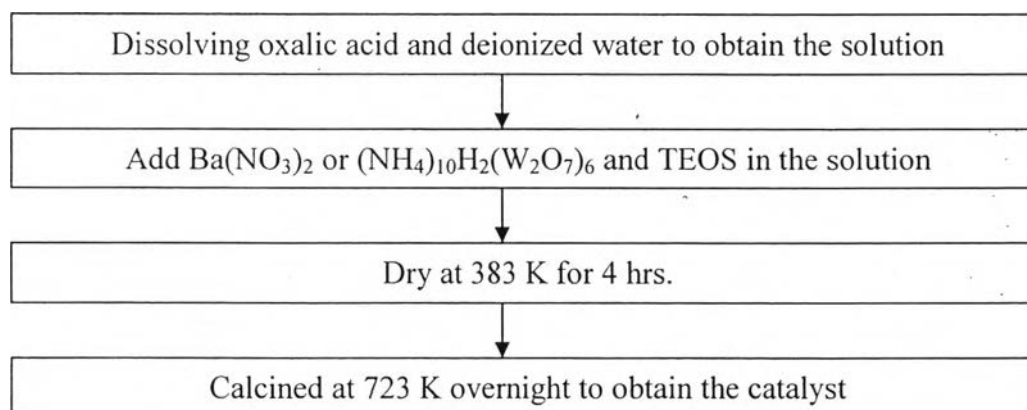


Figure 3.2 The catalyst preparation flow diagram of Sol-gel method.

To compare the activity of barium and tungsten metal on oxidative bromination of methane, metal loading of barium and tungsten were varied with equimolar of metal as shown in Table 3.1. The catalysts were sieved to particle size between 40 and 60 mesh and used hereafter without further treatments.

Table 3.1 Abbreviation of barium oxide or tungsten oxide on silica catalysts

Abbreviation	Mole of metal	%wt metal/SiO ₂
1Ba/SiO ₂	0.00293	0.40
1W/SiO ₂	0.00293	0.54
2Ba/SiO ₂	0.00486	0.67
2W/SiO ₂	0.00486	0.89
3Ba/SiO ₂	0.00971	1.33
3W/SiO ₂	0.00971	1.79

3.2.2 Catalyst Characterization

The catalyst characterization techniques applied in this research are surface area analysis (BET) and X-ray diffraction (XRD).

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 μmol/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 CuK α 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.

3.2.3 Catalytic Activity Testing

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

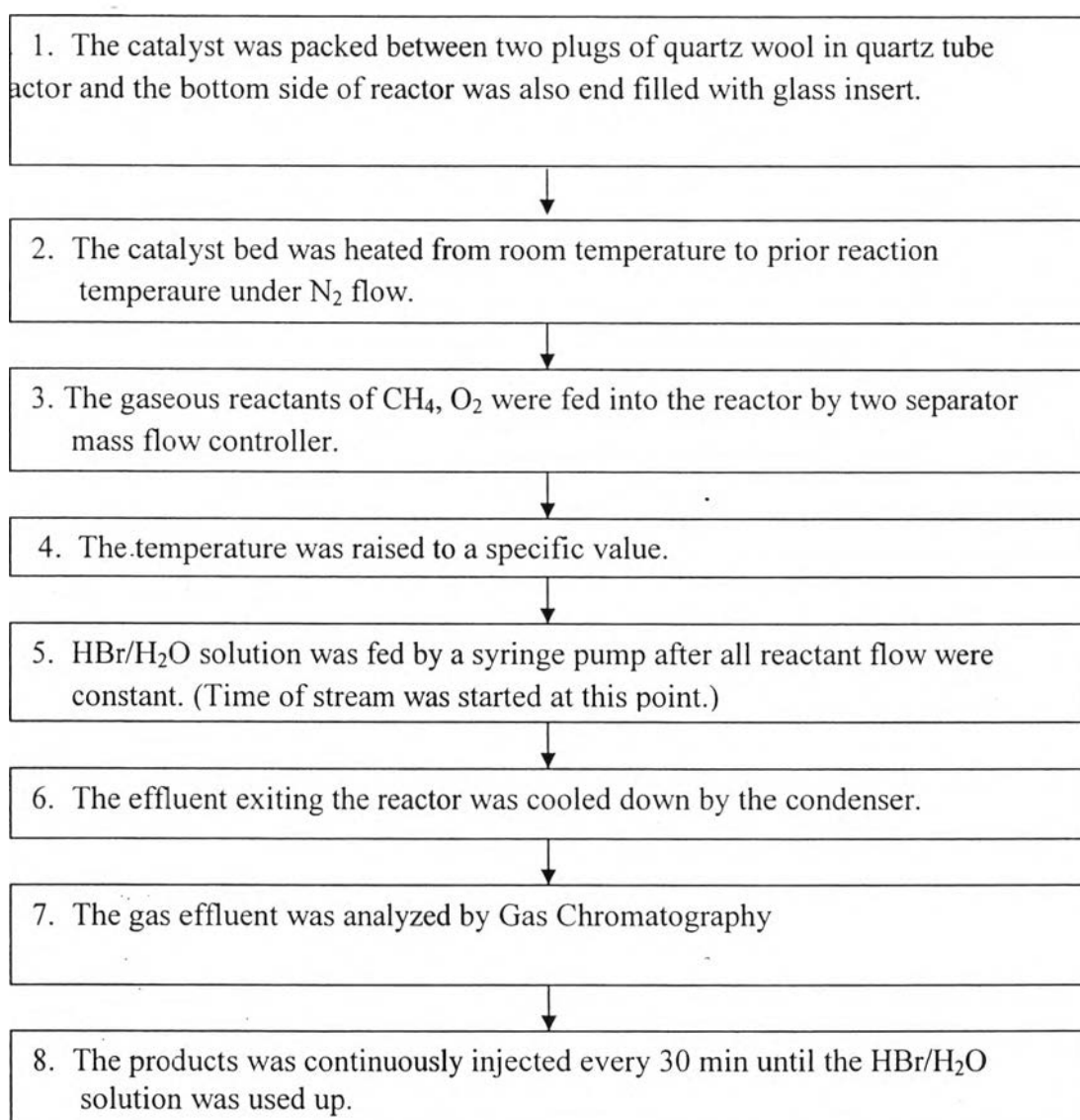


Figure 3.3 Procedure flow scheme for oxidative bromination of methane reaction.

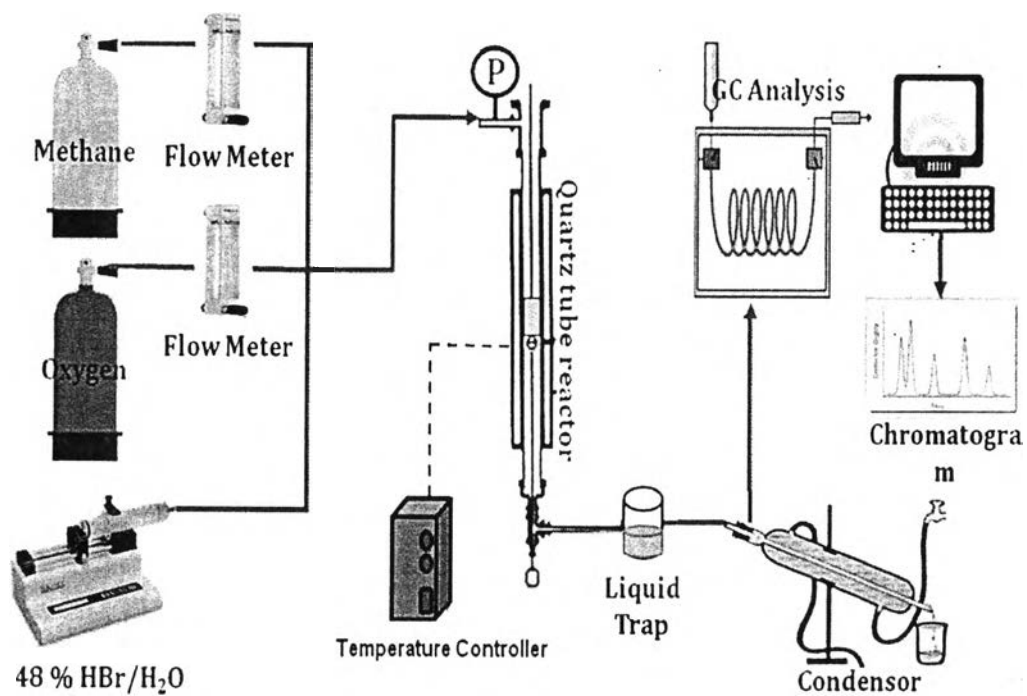


Figure 3.4 Experimental setup for oxidative bromination of methane reaction.