

CHAPTER IV

EXPERIMENTAL

This chapter describes the experimental systems and procedures used in this study. The chapter is divided into five sections. Section 4.1 and 4.2 is raw materials and equipments, respectively. Section 4.3 and 4.4 presents preparations of catalytic coke and catalytic coke/PP composites, respectively. Characterization of the products is presented in the last section.

4.1 Materials

4.1.1 Catalyst

An industrial steam reforming catalyst, Ni/SiO₂.MgO, was employed for the carbon dioxide reforming of methane in this research. More details of catalyst characteristics are shown in Table 4.1

Table 4.1 The specific properties of catalyst used in this study

Catalyst	N 185
Ni content	55 wt%
Support/co-catalyst	SiO ₂ , MgO
Surface area [m ² /kg]	1.23 x 10 ⁵
Ni Surface area [m ² /kg]	8.37 x 10 ³
Ni Diameter [nm]	44

4.1.2 Polypropylene

The polypropylene pellets (P602F) were obtained from CCC CHEMICAL COMMERCE CO.,LTD.. The melt flow index and density of PP are 1.0 g/10 min and 0.910 g/m³, respectively. The melting point is 165 °C.

4.2 Equipments

4.2.1 Part I : Preparation of catalytic coke

Flow diagram of a lab-scale gas phase carbon dioxide reforming of methane system is shown in Figure 4.1. The system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.2.1.1 Reactor

The reaction was performed in a conventional quartz tube (inside diameter = 11 mm) at atmospheric pressure. Two sampling points were located before and after the catalyst bed. Catalyst was placed over a quartz wool layer for supporting the weight of catalyst bed and coke which could be formed during the reaction.

4.2.1.2 Automatic temperature controller

This unit consisted of a magnetic solid state relay switch connected to a variable voltage transformer and a temperature controller connected to a thermocouple. Reactor temperature was measured by thermocouple which was placed in the furnace at the position of the catalyst bed. The temperature control set point was adjustable within the range of 0-1,000°C at the maximum voltage output of 220 V.

4.2.1.3 Electrical furnace

The furnace with 2 kW heating coil was connected with the automatic temperature controller to supply heat to the reactor. The reactor could be operated from room temperature up to 800°C at the maximum voltage of 220 V.

4.2.1.4 Gas controlling system

Each reactant gas was equipped with a pressure gas regulator (0-120 psig) and an on-off valve. A flow rate was controlled by adjusting a needle valve. For periodic operation, each reactant feed was switched between opening and closing periodically by using a solenoid valve (Flon industry, Japan) controlled by a multi timer (Sibata BT-3).

4.2.2 Part II : Preparation of catalytic coke/polypropylene composites

4.2.2.1 Digital hot plate stirrer

A Cole-Parmer digital hot plate stirrer was used for mixing the polymers with catalytic coke. This hot plate stirrer is programmable. All function can be set from digital panel and display their status on LCD. The plate temperature and time are controllable.

4.2.2.2 Hydraulic hot press

A local made hydraulic hot press was used in these experiments. The maximum working temperature of this machine is 600 °C and the maximum pressure is 5000 psi. This equipment was used for prepare the sample for tensile test.

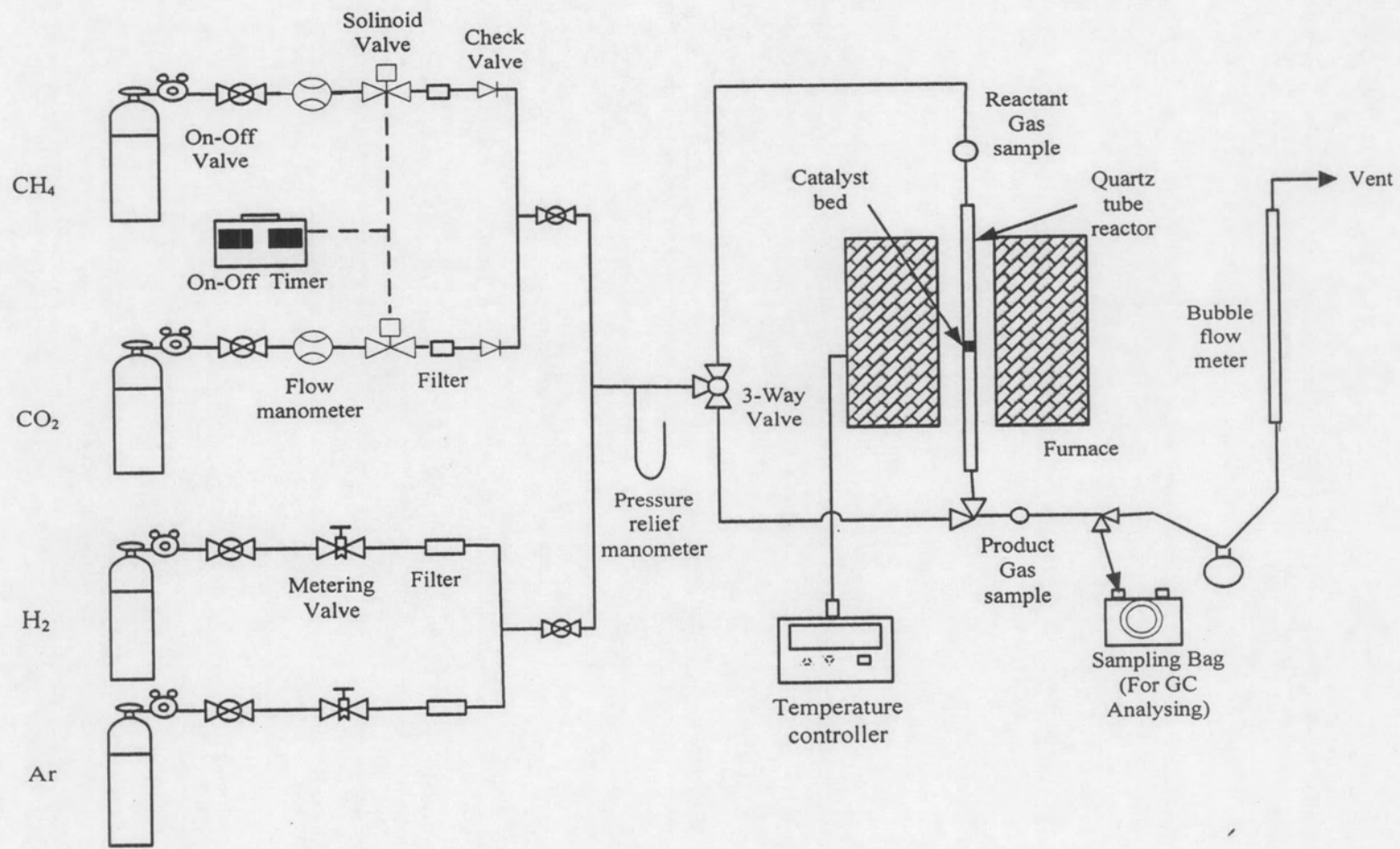


Figure 4.1 Schematic diagram of a lab-scale gas phase for carbon dioxide reforming of methane under periodic operation

4.2.2.3 Twin-screw extruder

Extrusion processing is defined as converting plastic powder or granules into a continuous uniform melt and forcing this melt through a die which yields a desired shape.

Powder or granular material is fed from the hopper, through the throat and on to the screw. Rotation of the screw transports the plastic along the cylinder through the first zone, where it is compacted and trapped air is expelled. Progressing down the cylinder, it is heated further by shear between the screw and cylinder wall, and by conduction of heat from the wall, so that the material is melted by the end of the zone. The final section of the extruder ensures the consistent and required output of molten polymer. The melt usually passes through a die, which defines a profile; this is cooled in air, or more frequently, in a cooling bath.

4.3 Preparation of Catalytic coke

The catalytic coke was synthesized by methane decomposition.

1. 55 wt% Ni/SiO₂.MgO (0.3 g) was packed in the middle of quartz tubular reactor located in the electrical furnace. Argon (30 cc/min) was fed to the reactor for purging reactant gases.

2. The reactor was heated up to 800 °C at a rate of 5 °C/min. At this temperature the argon gas was switched off and the catalyst was reduced under hydrogen flow (30 cc/min) for 1 h. After the catalyst reduction, the system was purged with argon for 10 min to remove hydrogen gas from the system.

3. Then the argon gas was switched to the methane gas at flow rate of 12.5 ml/min. Start to count the time for reaction by changing various reaction times as 60, 80 and 100 min.

4. Then the methane gas was switched to the argon gas. The reactor temperature was held at 800 °C for 10 min before the reactor was cooled down.

4.4 Preparation of catalytic coke/PP composites

Preparation of the catalytic coke/PP composites can be described in three steps.

The first step was preparation of a precursor material in the form of catalytic coke/PP composites. The procedure used to prepare the composites is shown schematically in Figure 4.2(a)-(d). The composites of PP and catalytic coke were prepared by using a digital hot plate stirrer at the compositions of 1.0, 2.0 and 3.0 percent by weight of catalytic coke. PP was weight in a beaker about 5.0 g and catalytic coke was weighted corresponding to the desired compositions. Each composite was mixed on the hot plate at 200 °C for 10 min. After that, the composites were compressed to form a thin plate and cut into small pellets, which was called the composite pellets.

The second step was to feed the prepared composite pellets into a twin-screw extruder (Rheocord 300p of Haake Inc.), as shown in Fig.4.2(e). The extruder system is composed of feeding unit, extruder, pelletizing unit. Diameter (D) of screw is 16 mm and its length (L) is 400 mm, which L/D is 25. Temperatures of six zones were set 150, 160, 175, 185, 195 and 210°C from die side, respectively. And screw speed was fixed around 60 rpm for all mixing experiments. The composite pellets were then extruded through a slit die to form a catalytic coke/PP. Composite pellets were dried at 100 °C for 1 h in an air oven.

In the final step, the catalytic coke/PP composites were placed between two aluminum plate, which was heated at 200 °C under the pressure of 1500 psi as shown in Figure 4.2(f) to form the thin catalytic coke/polypropylene composites.

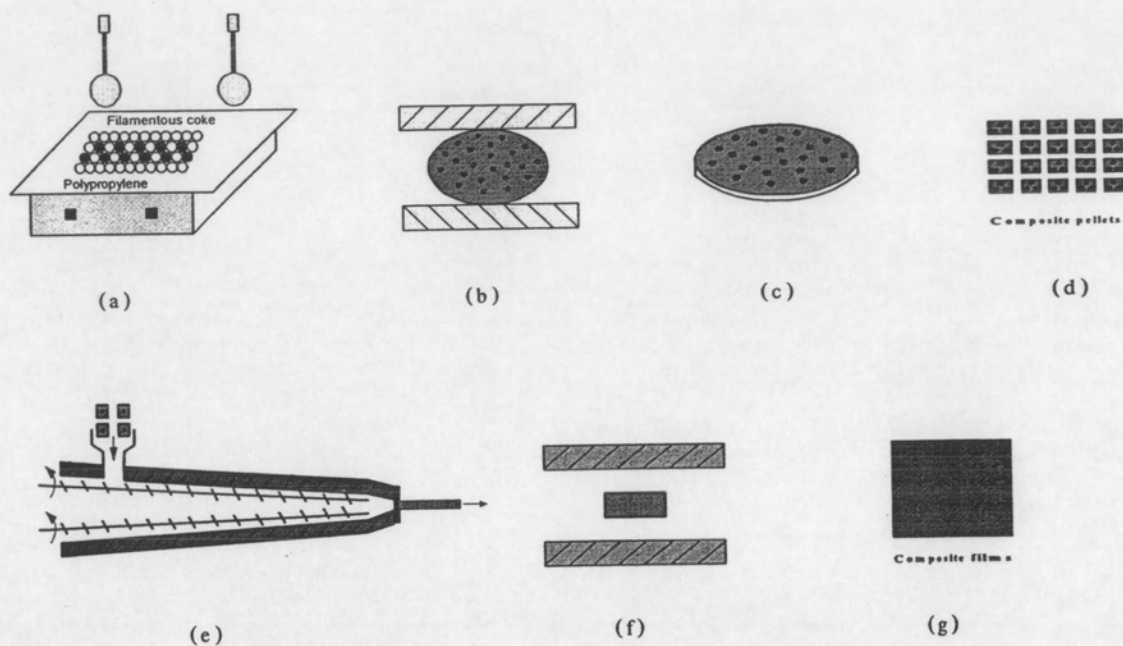


Figure 4.2 Procedures for preparing catalytic coke/polypropylene composites.

4.5 Characterization of the products

The obtained products were characterized using various techniques, as following:

4.5.1 Scanning Electron Microscopy (SEM)

The morphology of the catalytic coke, fresh catalyst and the fracture of the composites were examined by using a scanning electron microscope (JSM-5800LV, JEOL Co., Ltd.) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

4.5.2 Transmission Electron Microscopy (TEM)

The morphology of an individual grain in the samples was observed on a JEOL JEM-2100 Analytical Transmission Electron Microscope, operated at 80-200 keV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

4.5.3 X-ray diffraction (XRD)

Particle diameter of the product was determined from X-ray diffraction analysis, using a SIEMENS D5000 diffractometer with $\text{CuK}\alpha$ radiation. Each sample was scanned in the range of $2\theta = 10\text{-}80^\circ$ with a step size of $2\theta = 0.02^\circ$.

4.5.4 Thermogravimetric Analysis (TGA)

TGA was carried out under oxygen on a TA Instruments, Inc., apparatus. The catalytic coke/polypropylene composites were cut into small pieces. The catalytic coke/polypropylene composites were then machined using a mechanical grinder and 5-15 mg of the composites were used for TGA test. Next, the samples were heated from room temperature to 750°C at the heating rate of $10^\circ\text{C}/\text{min}$.

4.5.5 Surface Area Measurement

The single point BET surface area of fresh catalyst and spent catalyst were measured by using nitrogen as the adsorbate. The operating conditions are as follows:

Sample weight	~ 0.2 g
Degas temperature	200°C for as-synthesized sample

4.5.6 Differential scanning calorimetry (DSC)

DSC measurements were carried out on a Perkin Elmer differential scanning calorimeter. The samples of about 3-9 mg were heated from -40 to 200 °C at a rate of 40 °C/min in liquid N₂. Then, the samples were cooled down from 200 to -40 °C at a cooling rate of 40 °C/min. Subsequently, the melting point (T_m) was measured by raising the temperature to 200 °C at a rate of 40 °C/min.

4.5.7 Tensile testing

The tension test were performed at room temperature according to ASTM standard D882 in a model 5567 Instron 5567 Universal Testing Machine with a load cell of 1 kN, using a speed of 50 mm/min. The dimension of the test specimens were 100 mm x 20 mm x 0.8 mm.