

CHAPTER IV

EXPERIMENTAL

The synthesis of titanium (IV) oxide (TiO₂) by using organic solvents is explained in this chapter. The chemicals and reaction apparatus are shown in sections 4.1 and 4.2, respectively. In sections 4.3 and 4.4, the catalyst preparation and characterization are explained.

4.1 Chemicals

The synthesis mixtures are prepared with the following reagents:

1. Titanium (IV) tetra -tert -butoxide (TTB, Ti[O(CH₂)₃CH₃]₄) available from Aldrich, 97%
2. Tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) available from Aldrich, 98%
3. 1,4 Butanediol (HO(CH₂)₄OH) available from Aldrich, 99%
4. 2-Propanol (C₃H₈O) available from Merck, 99.7%
5. Toluene (C₆H₅CH₃) available from APS Finechem, 100%

Table 4.1 Reagents used for the synthesis of titanium (IV) oxide

Reagents	weight/volume
Titanium (IV) tetra -tert -butoxide, TTB	25 g
Tetraethyl orthosilicate, TEOS (Calculation of catalyst preparation, APPENDIX A)	
For Si/Ti = 0	0 g
Si/Ti = 0.05	0.7651 g
Si/Ti = 0.1	1.5303 g
Si/Ti = 0.2	3.061 g
Si/Ti = 0.3	4.591 g
Si/Ti = 0.5	7.652 g
Organic solvents (1,4 butanediol, 2-propanol and toluene)	
in the synthesis mixtures	100 cm ³
in the gap	30 cm ³

4.2 Instruments and apparatus

The schematic diagram of the reaction apparatus for the synthesis of titanium (IV) oxide is shown in Figure 4.1

4.2.1 Autoclave reactor: The autoclave is made of stainless steel with 1000 cm³ volume and 10 cm inside diameter. This consists of a pressure gauge within the range of 0 to 140 bar and a relief valve, which used to control pressure in the autoclave. This autoclave can be operated at high temperature and pressure. The reaction was carried out under autogenous pressure, which gradually increased as the temperature was raised. (Figure 4.2)

4.2.2 Automatic Temperature controller: This consists of a magnetic switch connected to a variable voltage transfer and a RKC temperature controller connected to a thermocouple with 0.5 mm diameter attached to the synthesis mixtures in autoclave. A dial setting establishes a set point at any temperature within the range 0 to 400°C

4.2.3 Electrical furnace (Heater): This supplied the required heated to the autoclave for the reaction. Autoclave can be operated from room temperature up to 300°C at voltage of 200 volts

4.2.4 Gas controlling system: Nitrogen are equipped with a pressure regulator (0 – 150 bar), and needle valves were used to release gas from autoclave.

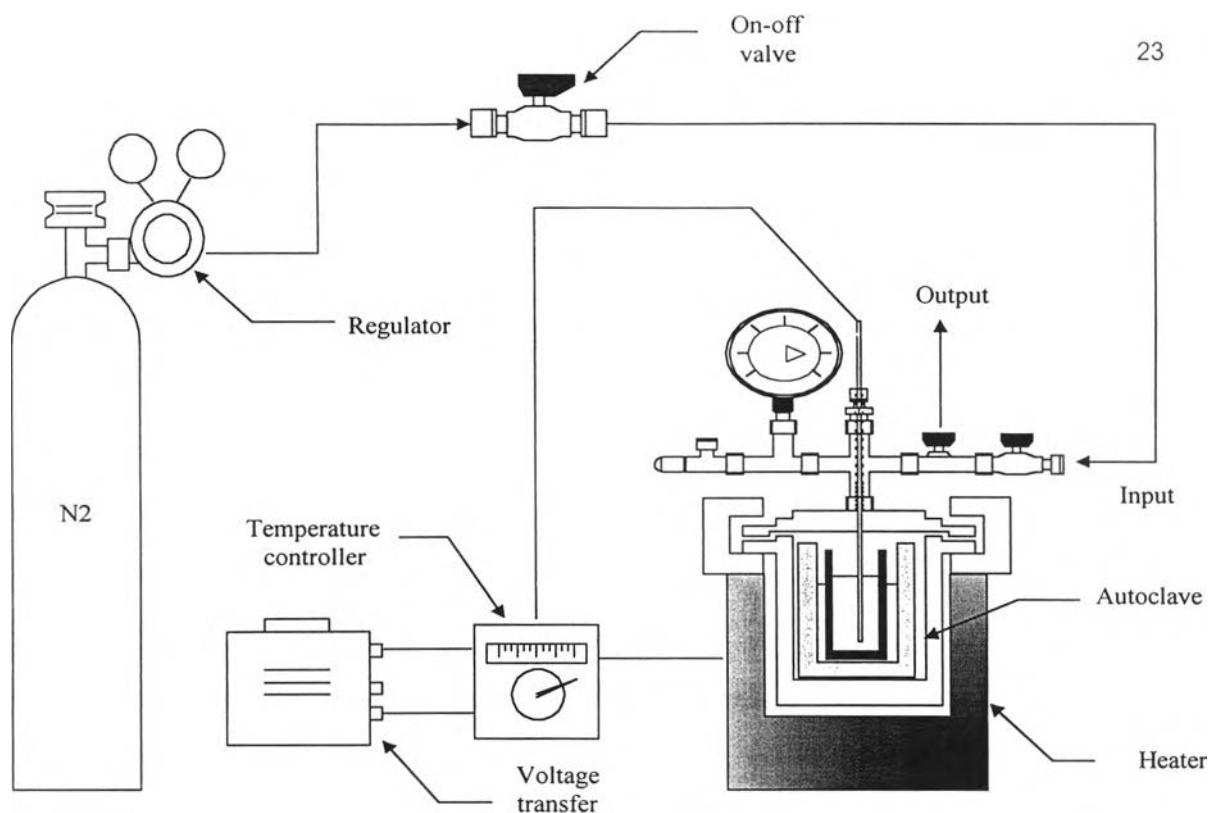


Figure 4.1 Schematic diagram of the reaction apparatus for the synthesis of titanium (IV) oxide

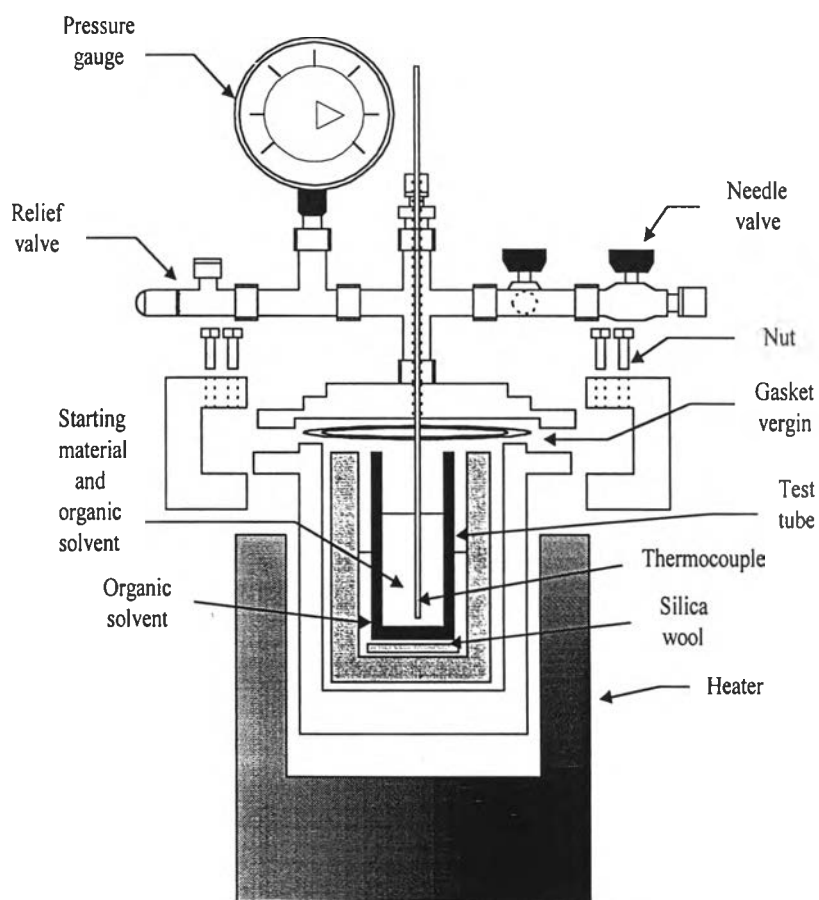


Figure 4.2 Autoclave reactor

4.3 Catalyst preparation

Titanium (IV) tetra-*tert*-butoxide (TTB), 25 g, and an appropriate amount of tetraethyl orthosilicate (TEOS, Si/Ti atomic ratio of 0 to 0.5) were dissolved in 100 cm³ of organic solvents in a test tube, which was then set in an autoclave. In the gap between the test tube and autoclave wall, 30 cm³ of organic solvent was added (Figure 4.2). The autoclave was purged with nitrogen, heated to a desired temperature (300 °C) at a rate of 2.5 °C min⁻¹, and held at this temperature for 2 h. Autogenous pressure during the reaction gradually increased as temperature was raised and depended on the kind of the organic solvents. After the autoclave was cooled, the resulting powders were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the thus-obtained product carried out in air in a box furnace. The product was heated at a rate of 10 °C min⁻¹ to desired temperature (600, 800 and 1000 °C) and held at that temperature for 1 h.

4.4 Characterization of the catalyst samples

4.4.1 X-Ray Diffraction Patterns (XRD)

X-Ray Diffraction (XRD) patterns of the catalyst samples were determined by using Ni-filtered Cu K α radiation in the 2 θ range of 10 to 80° (SIEMENS XRD D5000, Petrochemical Engineering Research Laboratory, Chulalongkorn University). Crystallite size was calculated from the half-height width of the 101 diffraction peak of anatase and 110 diffraction peak of rutile using the Sherrer equation. The value of the shape factor, K was taken to be 0.9 and KCl was used to be internal standard.

4.4.2 Morphology

Morphology of the catalyst samples was observed by a JEOL TEM-200CX transmission electron microscope (TEM), which operated at 100 kV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

4.4.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model impact 400 at Petrochemical Engineering Laboratory, Chulalongkorn University. Each sample was mixed with KBr with a ratio of sample to KBr equal to 1:200 before being formed into a thin wafer. Infrared spectra were recorded between 400 to 4000 cm^{-1} on a microcomputer.

4.4.4 BET Surface Area Measurement

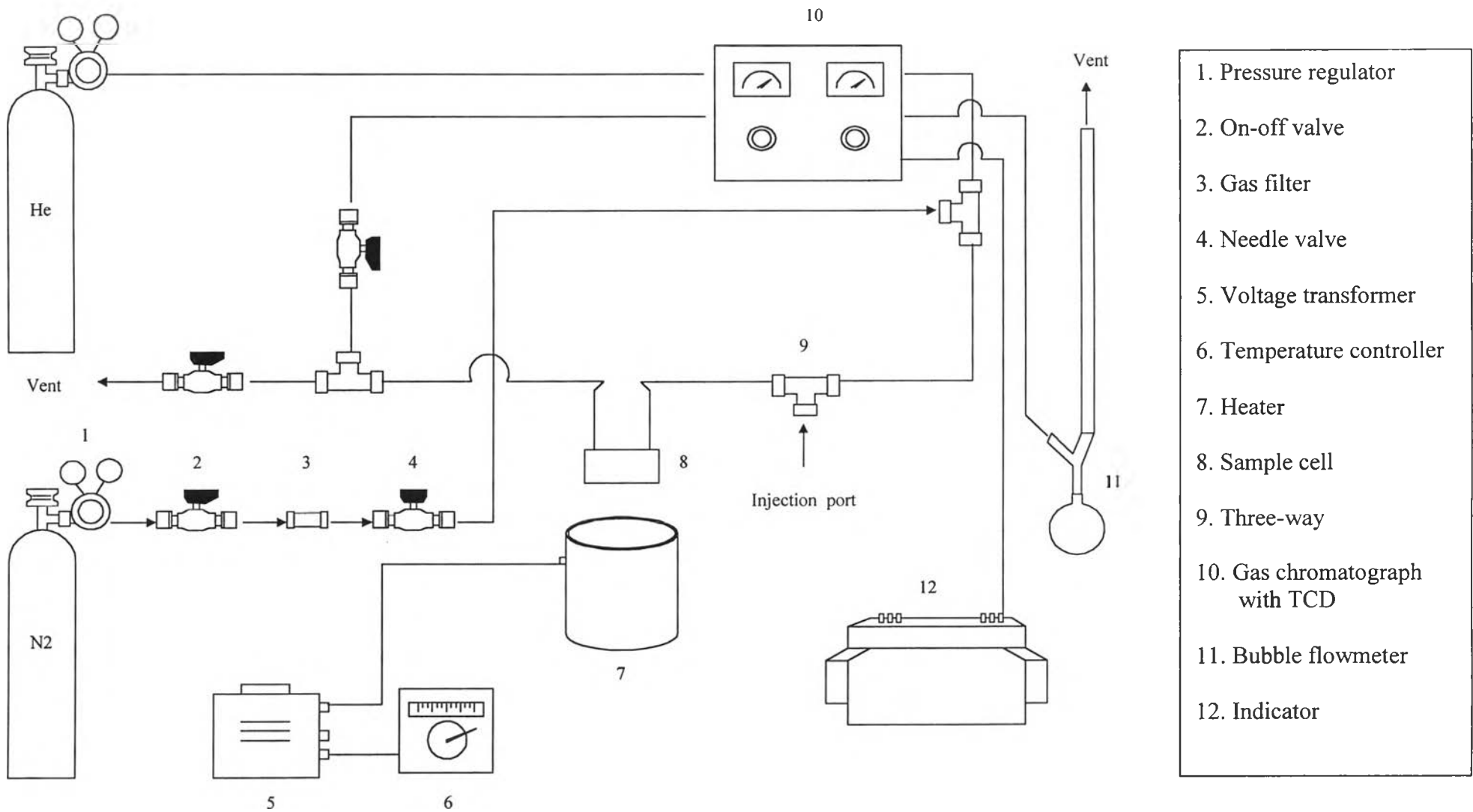
The specific surface area (S_{BET}) of the catalyst samples were calculated using the Brunauer-Emmett-Teller (BET) single point method on the basis of nitrogen uptake measured at liquid-nitrogen boiling point temperature equipped with a gas chromatograph.

4.4.4.1 BET Apparatus

The reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas was adjusted by means of fine-metering valve on the gas chromatograph. The sample cell made from pyrex glass. The schematic diagram of the reaction apparatus was shown in Figure 4.3 and the operation condition of gas chromatograph (GOW-MAC) is shown in Table 4.2

Table 4.2 Operation condition of gas chromatograph (GOW-MAC)

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml. min^{-1}
Detector temperature	80 °C
Detector current	80 mA



1. Pressure regulator
2. On-off valve
3. Gas filter
4. Needle valve
5. Voltage transformer
6. Temperature controller
7. Heater
8. Sample cell
9. Three-way
10. Gas chromatograph with TCD
11. Bubble flowmeter
12. Indicator

Figure 4.3 Schematic diagram of the BET specific surface area measurement

4.4.4.2 Measurement

The mixture gases of helium and nitrogen flowed through the system at the nitrogen relative pressure of 0.3. The catalyst sample was placed in the sample cell, ca. 0.3 to 0.5 g, which was then heated up to 160°C and held at this temperature for 2 h. The catalyst sample was cooled down to room temperature and was measured the specific surface area. There were three steps to measure the specific surface area.

Step (1) Adsorption step: The catalyst sample that set in the sample cell was dipped into the liquid nitrogen. Nitrogen gas that flowed through the system was adsorbed on the surface of the catalyst sample until equilibrium was reached.

Step (2) Desorption step: The sample cell with nitrogen gas-adsorbed catalyst sample was dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the catalyst sample. This step was completed when the indicator line was in the position of the base line.

Step (3). Calibration step: 1ml of nitrogen gas at atmospheric pressure was injected through the calibration port of the gas chromatograph and the area was measured. The area was the calibration peak. The calculation method is explained in APPENDIX B.