CHAPTER IV

EXPERIMENTAL

This chapter is the explanation about the experimental system and the experimental procedures that were used in this work. The chemical used in the preparation of metal oxides are presented in section 4.1. The lists of experimental apparatus are shown in section 4.2. In section 4.3 and 4.4 the metal oxides preparation and characterization are presented respectively.

4.1 Chemicals

The lists of chemical used in this experiment are shown in the following

1. Titanium (IV) tert-butoxide (TNB, $Ti[O(CH_2)_3CH_3]_4$), Aldrich Chemical Company, USA., (97%)

2. Iron (III) acetylacetonate ($Fe[CH_3COCH=C(O-)CH_3]_3$) , Aldrich Chemical Company , USA., (97%)

3. Zinc (II) acetylacetonate ($Zn[CH_3COCH=C(O-)CH_3]_2$) , Merck Co. , Ltd. , Germany. , (95%)

4. Tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) , Aldrich Chemical Company , USA. , (98%)

5. 1,4 – Butanediol (1,4-BG, $HO(CH_2)_4OH$) , Aldrich Chemical Company , USA. , (99%)

6. Toluene ($C_6H_5CH_3$) , Carlo Erba Reagent, (99.5%)

7. High purity nitrogen gas (99.99%vol.), Thai Industrial Gas Co.Ltd.

Table 4.1 Reagents used for the synthesis of metal oxides.

Metal Oxides	Reagents	Weight or Volume
Titanium oxide	Titanium tert-butoxide, TNB	15 g
	Tetraethyl orthosilicate, TEOS	
	For Si/Ti = 0	0 g
	Si/Ti = 0.005	0.0457 g
	Si/Ti = 0.08	0.7313 g
Iron Oxide	Iron (III) acethylacetonate	15 g
	Tetraethyl orthosilicate, TEOS	
	For Si/Fe = 0	0 g
	Si/Fe = 0.005	0.0436 g
	Si/Fe = 0.08	0.6973 g
Zinc Oxide	Zinc (II) acetyl acetonate	15 g
	Tetraethyl orthosilicate, TEOS	
	For Si/Zn = 0	0 g
	Si/Zn = 0.005	0.0574 g
	Si/Zn = 0.08	0.9184 g
	Organic Solvents (1,4-butanediol, toluene)	
	In the synthesis mixture	100 cm^3
	In the gap	30 cm^3

[a] Calculation of catalyst preparation, Appendix A

4.2 Instruments and apparatus

4.2.1 Autoclave reactor

The autoclave is made of stainless steel with 1000 cm^3 volume and 10 cm inside diameter. There are the iron jacket which used to reduce the volume of autoclave to be 300 ml and the beakers were used to contain the reactant. 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 the autogeneous pressure, which gradually increased as the temperature was raised. The autoclave reactor is shown in Figure 4.1.

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 established a set point at any temperature within the range of 0 to 350° 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 350° C at voltage of 200 volts.

4.2.4 Gas controlling system

High purity nitrogen gas is equipped with a pressure regulator (0-150 bar) and needle valves were used to release gas from autoclave. The schematic diagram of the reaction apparatus is shown in Figure 4.2.
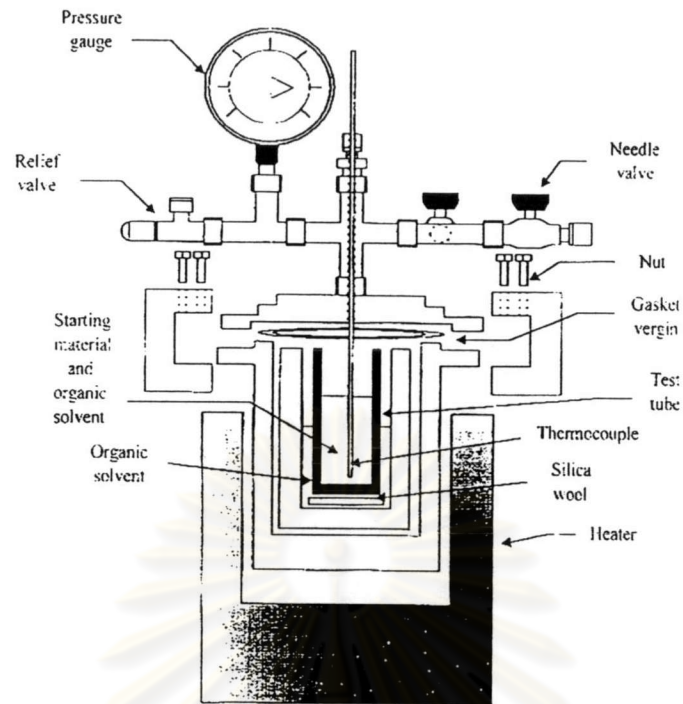
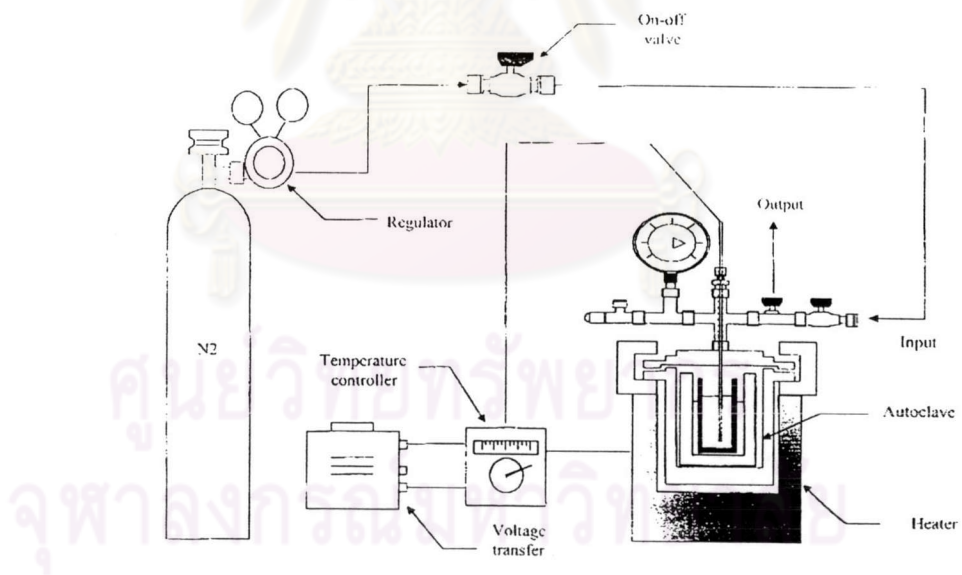**Figure 4.1**   Schematic diagram of the autoclave reactor.

Figure 4.2   Schematic diagram of the reaction apparatus.

4.3 Metal Oxides preparation

The synthesis of metal oxide, 15g of metal acetylacetonate (Ti,Fe and Zn) was dissolved in 100 cm^3 of organic solvent (1,4-butanediol/toluene) , in a test tube

which was then set in an autoclave. In the gap between the test tube and autoclave wall was added with 30 cm^3 of organic solvent. The autoclave was purged with nitrogen, heated to the desired temperature (200-350°C) at a rate of 2.5° C/min and held at that temperature for 2 hours. Autogeneous pressure gradually increased as the temperature was raised. After the reaction was terminated, the autoclave was cooled to room temperature and the precipitate was separated from the solution via centrifugation, washed with methanol and dried at room temperature. Part of the products was calcined in a box furnace, the sample in a combustion boat was heated at a rate of 10°C/min to the desired temperature (900°C) and held at that temperature for 1 hour.

The synthesis of the silica-modified metal oxide were doing the same procedure with the used of 15g of metal acetylacetonate and an appropriate amount of tetracthyl orthosilicate, as shown in Table 4.1 in order to control the charged ratio of Si/Metal equal to 0.005 and 0.08 respectively

4.4 Characterization

4.4.1 X-Ray Diffraction (XRD)

In X-Ray Diffraction (XRD) a collimated beam of X rays, with wave length $\lambda \cong 0.5\text{-}2$ Å; is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law ($\lambda = 2d\sin\theta$, where d is the spacing between atomic planes in the crystalline phase) . The intensity of the diffracted X rays is measured as a function of the diffraction angle 2θ and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phase and to measure its structural properties, including strain (which is measured with accuracy), epitaxy and the size, and orientation of crystallites (small crystalline regions).

XRD pattern of the catalyst sample were determined by using Ni-filtered CuKα radiation in the 2θ range of 10 to 80° (SIEMENS XRD D5000, Center of Excellences on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University). The crystallite size was calculated from the half-height width of the line

broadening using the Scherrer equation (see Appendix B). The value of the shape factor, K, was taken to be 0.9 and α-Al_2O_3 was used to be internal standard to eliminate the broading effect attributed to the equipment.

4.4.2 Scanning Electron Microscopy (SEM)

In Scanning Electron Microscopy (SEM) method, an electron beam passing through an evacuated column is focused by electromagnetic lenses onto the sample surface. The low energy (<50eV) secondary electrons emitted from the surface of the sample provide the basis for a different type of imaging. The beam can be concentrated to a small probe (20 Å diameter) that may be deflected across the sample in a raster fashion using scanning coils. The secondary electron can be detected above the sample, and as image the intensity of secondary electron emitted from different parts of the sample can be displayed on a CRT. Difference in secondary emission results from changes in surface topography.

The morphology and size of secondary particle was observed by JEOL-5800LV scanning microscope at the Scientific and Technological Research Center (STREC), Chulalongkorn University

4.4.3 Surface Area Measurement

The multipoint BET surface area of the samples were measured by a micromeritics model ASAP 2000 using nitrogen as the adsorbate at the Analysis Center of the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. The operating conditions are as follows:

Sample weight	~0.3 g
Degas temperature	200°C for as-synthesized sample
	300°C for calcined sample
Vacuum pressure	<10 μmHg