Chapter IV

Experimental

The synthesis of zinc gallate ($ZnGa_2O_4$) and zinc aluminate ($ZnAl_2O_4$) 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. Zinc acetate ($(CH_3COO)_2Zn$) available from Aldrich, 99.9%
2. Gallium acetylacetonate ($Ga(acac)_3$, $(CH_3COCH=C(O-)CH_3)_3Ga$) available from Aldrich, 99.99%
3. Aluminium Isopropoxide (AIP, $[(CH_3)_2CHO]_3Al$available from Aldrich, 98%+
4. 1,4-Butanediol ($HO(CH_2)_4OH$) available from Aldrich, 99%
5. 2-Propanaol (C_3H_8O) available from Merck, 99.7%
6. Toluene ($C_6H_5CH_3$) available from APS Finechem, 100%

Table 4.1 Reagents used for the synthesis of zinc gallate

Reagents	Weight/Volume
Gallium acetylacetonate	5.00 g
Zinc acetate (Calculation of catalyst preparation, Appendix A)	
For Zn/Ga =0.33	0.8330 g
Zn/Ga =0.5	1.2496 g
Zn/Ga =1.0	2.4991 g

Table 4.1 (continued)

Reagents	Weight/Volume
Organic solvents (1,4-butanediol, 1-butanol and toluene)	
in the synthesis mixtures	88 cm^3
in the gap	40 cm^3

Table 4.2 Reagents used for the synthesis of zinc aluminate

Reagents	Weight/Volume
Aluminium isopropoxide (AIP)	15.00 g
Zinc acetate (calculation of catalyst preparation, Appendix A)	
For Zn/Al = 0.33	4.4012 g
Zn/Al = 0.50	6.6019 g
Zn/Al = 1.00	13.2037 g
Organic solvents (1,4-butanediol, 2-propanol, 1-butanol and toluene)	
in the synthesis mixtures	100 cm^3
in the gap	40 cm^3

4.2 Instruments and apparatus

The schematic diagram of the reaction apparatus for the synthesis of zinc gallate and zinc aluminate is shown in Figure 4.1.

4.2.1 Autoclave reactor**:** The autoclave is made of stainless steel with 1000 cm^3 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 autogeneous 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.

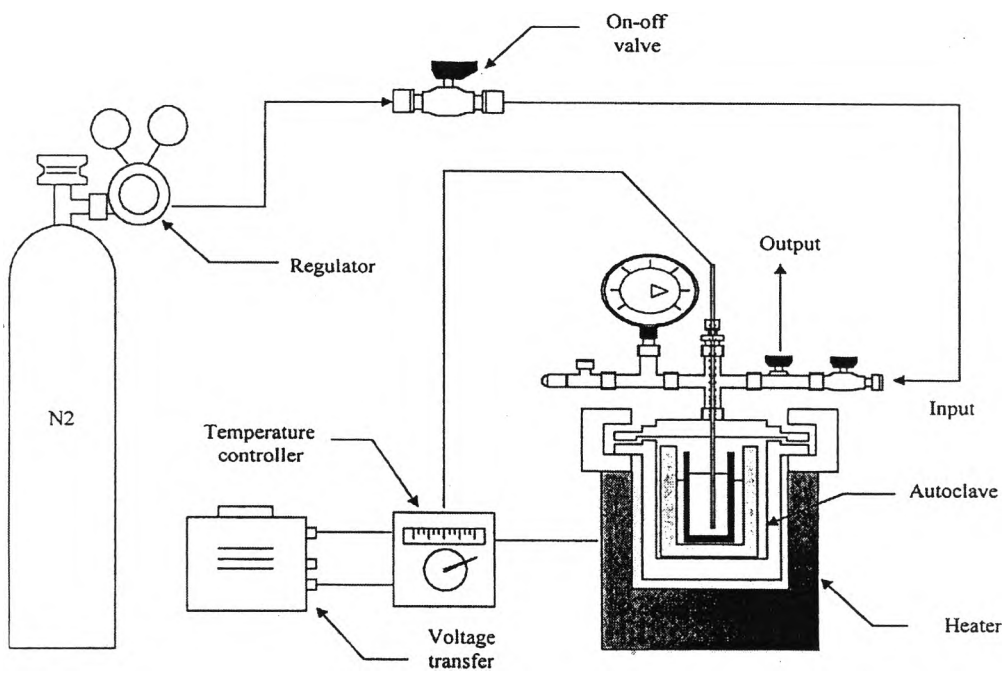

Figure 4.1 Schematic diagram of the reaction apparatus for the synthesis of zinc gallate and zinc aluminate.

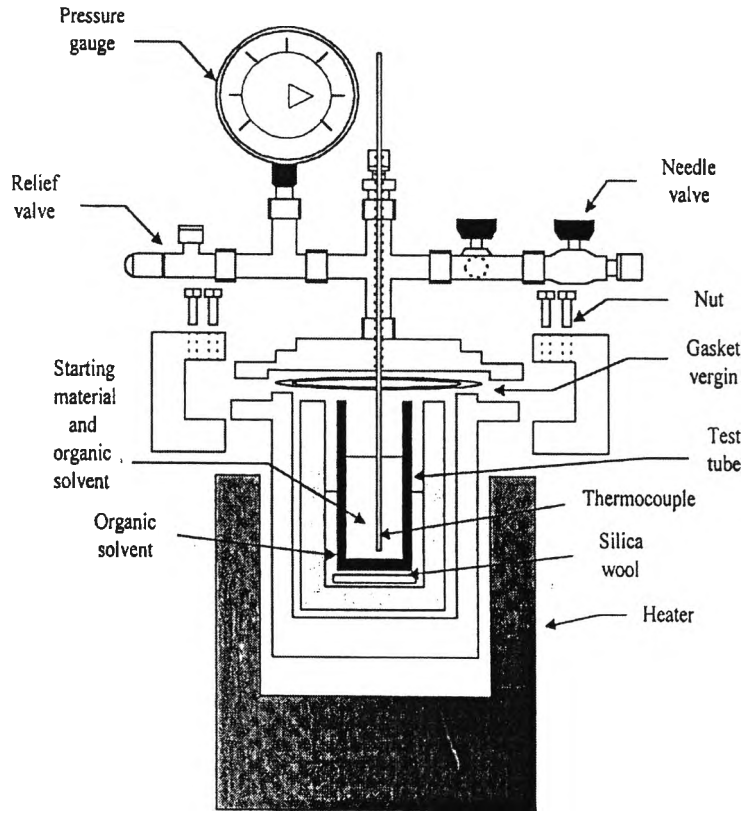

Figure 4.2 Autoclave reactor.

4.3 Catalyst preparation

For the synthesis of zinc gallate, gallium acetylacetonate, 5.0 g and an appropiate amount of zinc acetate (Zn/Ga molar ratio of 0.33, 0.5and 1.0) were dissolved in the 100 cm^3 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 cm^3 of organic solvent was added (Figure4.2). The autoclave was purged with nitrogen, heated to a desired temperature (300°C) at a rate 2.7°C min^{-1}, and held at this temperature for 2h. Autogeneous pressure during the reaction gradually increased as temperature was raised and depended on the kind of organic solvents. After the autoclave was cooled, the resulting products were washed repeatedly with methanol by centrifugation and dried in air. The calcination of

the thus-obtained product carried out in a box furnace. The product was heated at a rate of 10°C min^{-1} to a desired temperature (600, 800 and 1100°C) and held at that temperature for 1 h.

4.4 Characterization of the catalyst samples

4.4.1 X-Ray Diffraction (XRD)

In X-ray Diffraction (XRD) a collimated beam of X rays, with wave length $\lambda \approx$ 0.5-2 A°, 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 phases and to measure its structural properties, including strain (which is measured with great accuracy), epitaxy, and the size and orientation of crystallites (small crystalline regions).

X-ray diffraction (XRD) patterns of the catalyst samples were determined by using Ni-filtered Cu K radiation in the 2 range of 10 to 80 for zinc gallate and 20 to 80 for zinc aluminate (SIEMENS XRD D5000, Petrochemical Engineering Research Laboratory, Chulalongkorn University). The Crystallite size was calculated from line broadening of the 400 diffraction line of zinc gallate and zinc aluminate according to the Scherer 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

In transmission electron microscopy (TEM) a thin solid specimen ($\leq$ 200 nm

thick) is bombarded in vacuum with a highly-focused, monoenergetic beam of electrons. The beam is of sufficient energy to propagate through the specimen. A series of electrons are observed in the form a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of sample that contain contrast, due to several scattering mechanisms associated with interactions between electron images yields information about atomic structure and about defects present in the material.

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 BET Apparatus

Physical adsorption isotherms are measured near the boiling point of a gas (e.g., nitrogen, at 77 K). From these isotherms the amount of gas needed to form a monolayer can be determined. If the area occupied by each adsorbed gas molecule is know, then the surface area can be determined for all finely divided solids, regardless of their chemical composition.

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

Nitrogen physisorption data of the supports were obtained on a Micrometrics ASAP 2000 equipment.

4.4.4 X-ray fluorescence (XRF)

In X-Ray Fluorescence (XRF), an X-ray beam is used to irradiate a specimen, and the emitted fluorescent X rays are analyzed with a crystal spectrometer and scintillation or proportional counter. The fluorescent radiation normally is diffracted by a crystal at different angles to separate the X-ray wavelengths from the peak intensities.

The chemical composition of the products were determined by X-ray fluorescence (XRF)