CHAPTER 2

EXPERIMENTAL

2.1 Chemicals and Equipments

2.1.1 Zinc naphthenate ($2(C_{11}H_7O_2)Zn$), assay <8 wt%Zn, F.W. 319.71 g/mol, Sigma-Aldrich, Germany

2.1.2 Magnesium acetate tetrahydrate ($C_4H_6MgO_4{\cdot}4H_2O$), assay 99.0%, F.W. 214.45 g/mol, Merck, Germany

2.1.3 Absolute ethanol (C_2H_2OH), assay >99.8%, Scharlau, Barcelona, Spain

2.1.4 Methane gas (Pangas, Germany)

2.1.5 Oxygen gas (Pangas, Germany)

2.1.6 Syringe pump (Inotech, Germany)

2.1.7 Glass microfibre filters (Whatmann GF/A, 25.7 cm in diameter)

2.1.8 Vacuum pump (Busch, Seco SV 1040C, Germany)

2.2 Apparatus and Instrument

2.2.1 X-ray diffractometer (XRD), Bruker D8 advanced diffractometer, Germany

2.2.2 Scanning electron microscopy (SEM) & EDS, JEOL JSM-6335F, Japan

2.2.3 Transmission electron microscopy (TEM), JEOL JSM-2010, Japan

2.2.4 Brunauer-Emmett-Teller (BET), Quantachrome Autosorb 1 MP, USA

2.3. Precursors calculation

Table 2.1 presented the precursors calculation of the flame synthesis of pure ZnO and 5-20 wt%ZnO/MgO nanocomposites data. The precursor solutions consisted of zinc naphthenate (Sigma-Aldrich, <8wt% Zn) and magnesium acetate tetrahydrate (Merck, 99.0%) dissolved in ethanol (Scharlau, >99.8%). The precursor concentration was kept constant at 0.5 M for all experiments.

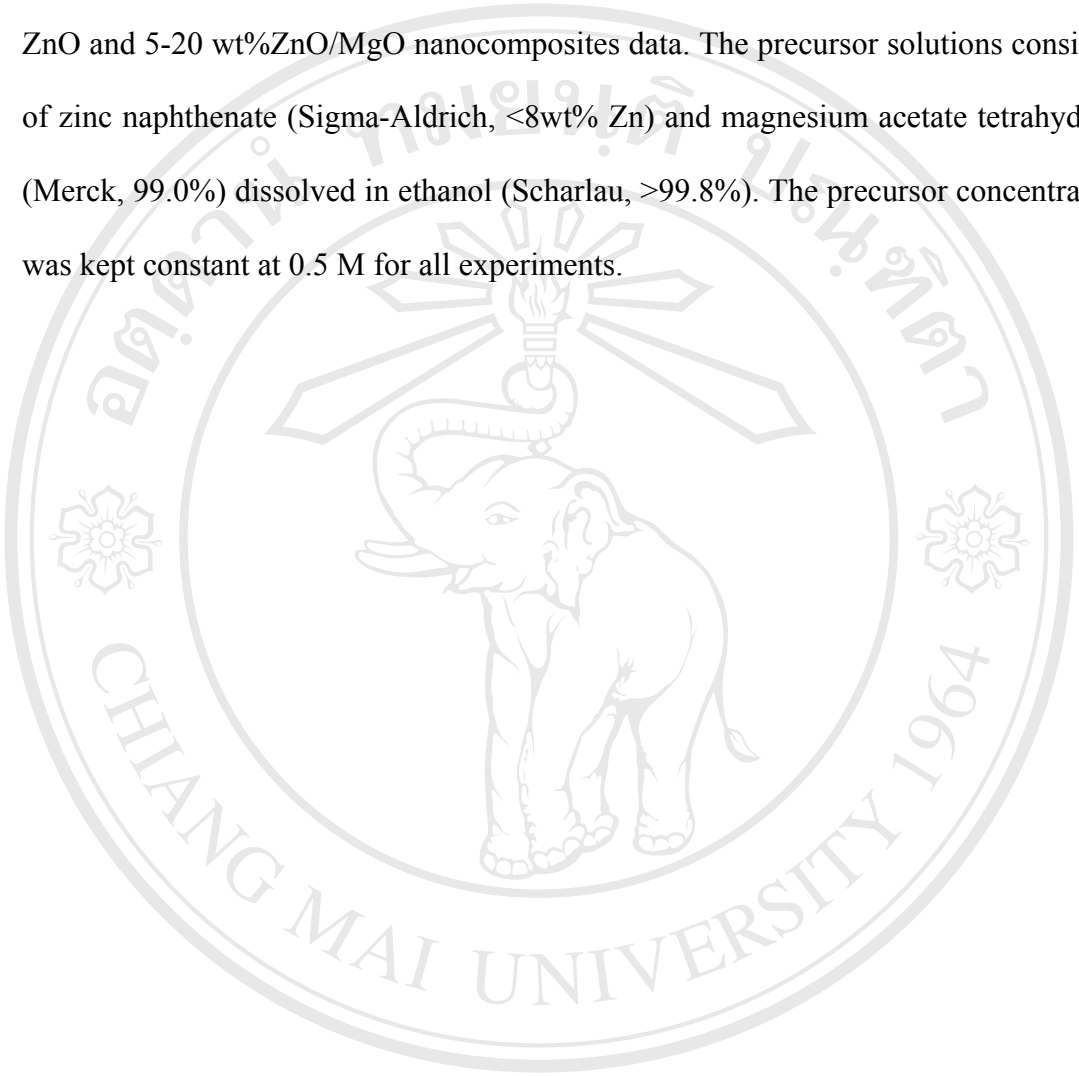

Table 2.1 Flame synthesis of pure ZnO and 5-20 wt% ZnOMgO nanocomposites data

Flame-made pure ZnO and 5-20 wt% ZnO/MgO Nanocomposites			
Precursor	**CAS No.**	**Density (g/cm^3)**	**Molecular weight (g/mol)**
Zinc naphthenate (8 wt%)	12001-85-3	0.962	-
Magnesium acetate tetrahydrate (99%)	16674-78-5	-	214.4
element		**molecular weight**	
Zn		65.38	
O		15.999	
Mg		24.31	
MgO		40.309	
ZnO		81.379	

No.	Sample	Precursor concentration (mol/L)	Starting materials, Dopant and Solvent						Fillter			Flame appearance	Powder appearance
			ZnO wt%	MgO wt%	Magnesium acetate tetrahydrate (g)	Zinc napthenate (ml)	Ethanol (absolute) (ml)	Total (ml)	On filter (g)	Collected (g)	Yield (%)		
1	Pure ZnO	0.5 M	100	0	0	21.24	28.76	50	2.03	1.36	67.00	yellowish-orange	light white
2	Pure MgO	0.5 M	0	100	5.4141	0.00	50.00	50	1.01	0.63	62.38	yellowish-orange	light white
3	5 wt% ZnO/MgO	0.5 M	95	5	0.5752	20.18	29.82	50	1.98	1.10	55.56	yellowish-orange	light white
4	10 wt% ZnO/MgO	0.5 M	90	10	1.2145	19.11	30.89	50	1.93	1.11	57.51	yellowish-orange	light white
5	15 wt% ZnO/MgO	0.5 M	85	15	1.9289	18.05	31.95	50	1.88	1.27	67.55	yellowish-orange	light white
6	20 wt% ZnO/MgO	0.5 M	80	20	2.7326	16.99	33.01	50	1.83	1.53	83.61	yellowish-orange	light white

2.4 Nanoparticles synthesis

2.4.1 Flame-made Pure ZnO and ZnO/MgO nanocomposites

The experimental setup for the synthesis of pure ZnO and ZnO/MgO nanocomposites by flame spray pyrolysis was shown in Figure 2.1. In a typical run, the liquid precursor mixture was fed at 5 ml/min in the center of a methane (1.19 l/min)/oxygen (2.46 l/min) flame by a syringe pump (Inotech) and dispersed by oxygen (4.30 l/min), forming a fine spray. The pressure drop at the capillary tip kept constant at 1.5 bars by adjusting the orifice gap area at the nozzle. The spray flame was surrounded and ignited by a small flame ring issuing from an annular gap (0.15 mm spacing, at a radius of 6 mm). The flame height was observed approximately 10-11 cm, and was slightly increased with increasing the combustion enthalpy. The combustion enthalpies are directly depended on a solvent, starting materials, and dopants. All samples showed the yellowish-orange flame appearances as shown in Figure 2.2 (a)-(f) with increasing the MgO concentrations. The liquid precursor mixture was rapidly dispersed by a gas stream and ignited by a premixed methane/oxygen flame. After evaporation and combustion of precursor droplets, particles were formed by nucleation, condensation, coagulation, coalescence, and MgO deposited on ZnO support. Finally, the product nanoparticles were collected on a glass microfibre filters (Whatmann GF/A, 25.7 cm in diameter) with the aid of a vacuum pump.

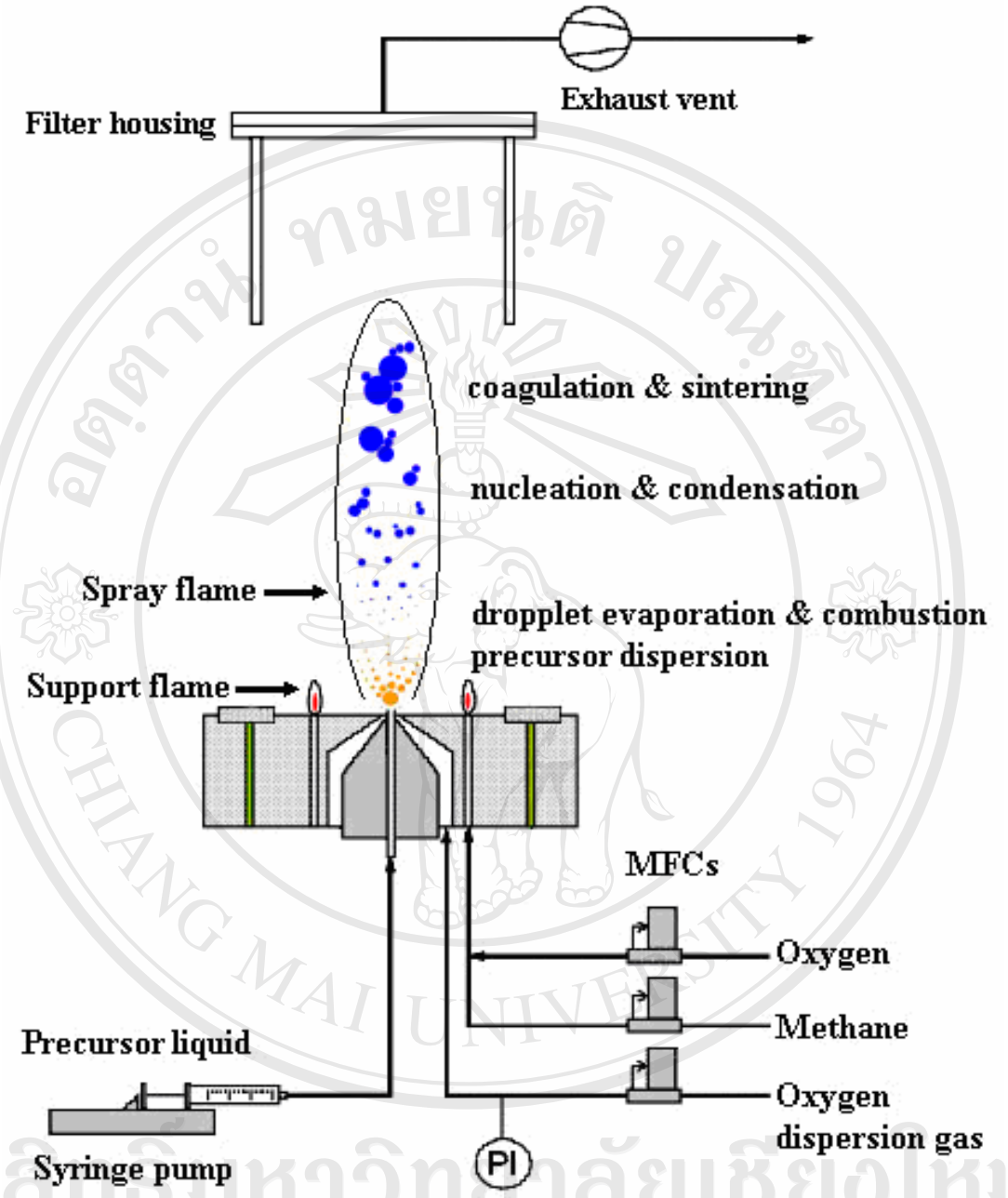

Figure 2.1 Schematic of the FSP experimental set up for the synthesis of ZnO and ZnO/MgO nanocomposites. The liquid precursor was dispersed by a gas stream and ignited by a premixed methane/oxygen flame [8].

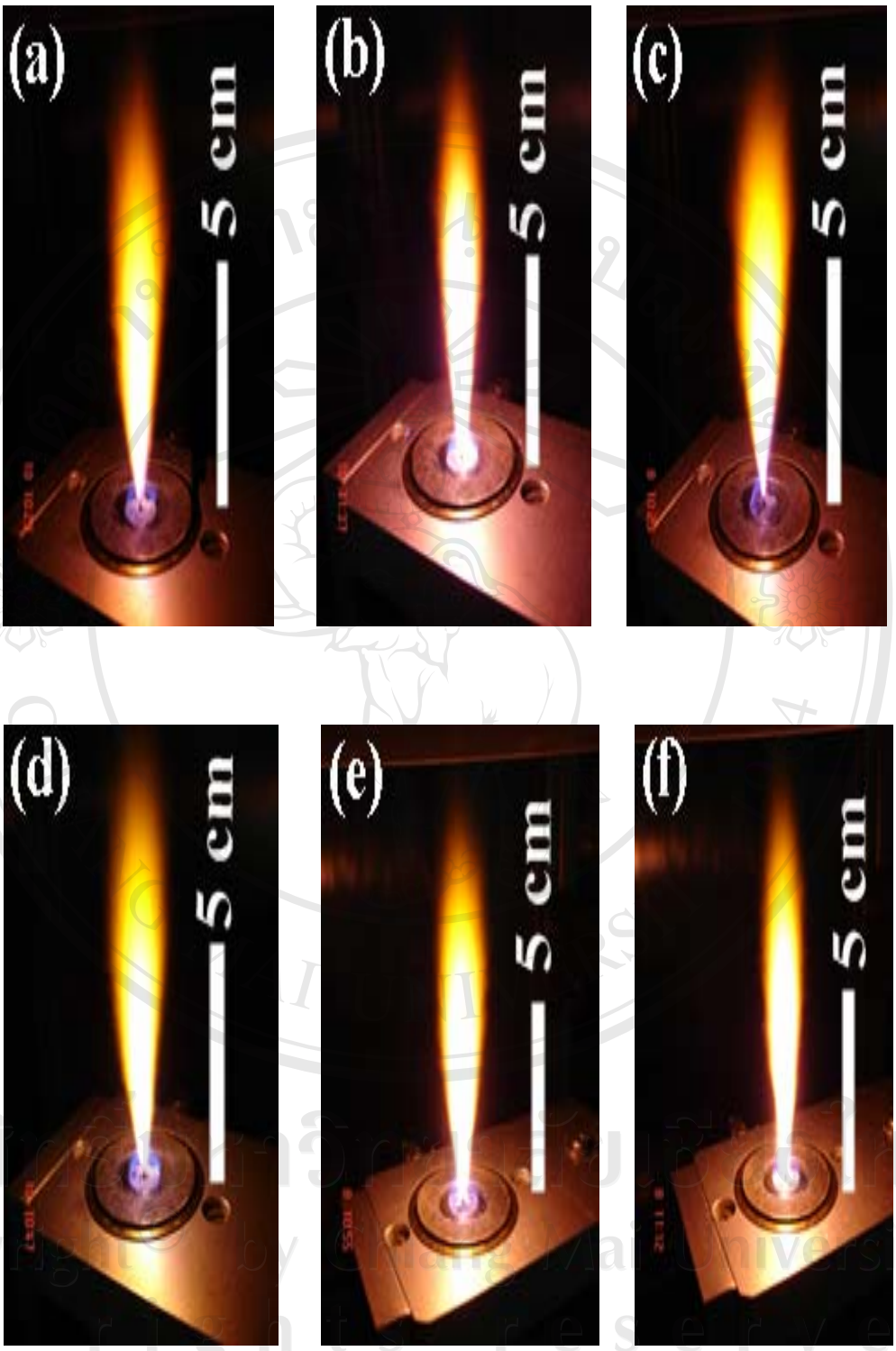

Figure 2.2 Spray flame (a) pure ZnO, (b) pure MgO, (c-f) 5-20 wt% ZnO/MgO nanocomposites. The flame heights were observed ranging from 10-11 cm

2.5 Sample characterization

In this work, pure ZnO and ZnO/MgO nanocomposites were characterized by using X-ray diffraction (XRD), nitrogen adsorption (BET) analysis, scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS) and transmittion electron microscopy (TEM). XRD was used to confirm the phase and crystalline structure of pure ZnO and ZnO/MgO nanaocomposites. BET was a method of choice to evaluate the specific surface area of pure ZnO and ZnO/MgO nanaocomposites. SEM and EDS were used to analyze morphology and chemical compositions of pure ZnO and ZnO/MgO nanaocomposites. TEM was selected to determine the accurate size and morphology.

2.5.1 X-ray Diffraction (XRD)

The phase and crystallinity of flame-made ZnO and ZnO/MgO nanocomposites were analyzed by XRD [Bruker D8 advance diffractometer, operated at 40 kV, 40 mA] using CuKα radiation at 2θ = 20-60° with a step size of 0.06° and a scanning speed of 0.72º /minute. Identification of crystalline phases was carried out by comparison of XRD patterns with JCPDS standards.

2.5.2 BET-Specific surface areas analysis (BET)

The specific surface areas (SSA_{BET}) of pure ZnO and ZnO/MgO nanocomposites were determined with 5-point nitrogen adsorption measurement applying the BET method at 77K (Quantachrome Autosorb 1 MP). All samples were controlled with degassing at 150°C for 1h prior to analysis. The diameter of particles can be calculated by $d_{BET} = 6/SSA_{BET} \times \rho_{sample}$, where ρ_{sample} are calculated from the

density of ZnO (ρ_{ZnO} = 5.61 x 10^3 kg/m^3) and the density of MgO (ρ_{MgO} = 3.58 x 10^3 kg/m^3) with the appropriate amount of both components.

2.5.3 Scanning Electron Microscopy (SEM)

The morphology of pure ZnO and ZnO/MgO nanaocomposites were analyzed by SEM [JSM-6335F, JEOL] and the elemental compositions of pure ZnO and ZnO/MgO nanocomposites were investigated by EDS [JSM-6335F, JEOL]. The powder samples were dispersed in ethanol using ultrasonic probe for 20 minutes. The suspension was dropped onto a copper conductive tape attached to the surface of the SEM brass stub. The stub was then coated with gold by plasma sputtering for 2 minutes, and an acceleration voltage of 20 kV was used.

2.4.1 Transmission Electron Microscopy (TEM)

The morphology and accurate particle sizes of pure ZnO and ZnO/MgO nanocomposites were analyzed by TEM [JSM-2010, JEOL] at an acceleration voltage of 200kV. The powder samples were dispersed in ethanol using ultrasonic probe for 20 minutes. The suspension was dropped onto carbon-copper grid. The deposit was dried in air prior to imaging.