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APPENDICES

APPENDIX A

CALCULATION OF CATALYST PREPARATION

Calculation of the preparation of the zinc gallate and zinc aluminate.

In this study, zinc gallate and zinc aluminate were prepared in each organic solvent have 3 different charged Zn/Ga or Zn/Al atomic ratios, Zn/Ga or Zn/Al = 0.33, 0.50 and 1.00.

Zinc acetate and gallium acetylacetonate are used as the reactants.

For the preparing of zinc gallate powder.

1. Gallium acetylacetonate ($\text{Ga}(\text{acac})_3$, $[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_3\text{Ga}$) has molecular weight (M.W.) of 367.05 g/mol.
Gallium (Ga) has M.W. of 69.72 g/mol.
2. Zinc acetate ($(\text{CH}_3\text{COO})_2\text{Zn}$) has M.W. of 183.46 g/mol.
Zinc (Zn) has M.W. of 65.37 g/mol.

Example A1: Calculation of preparation of zinc gallate with Zn/Ga= 0.5 is shown as follow:

Gallium acetylacetonate 5 g were used for preparation of all Zn/Ga atomic ratios.

The reagent 5 g were consisted of gallium equal to:

$$\text{Gallium} = (69.72 / 367.05) \times 5 \text{ g} = 0.9497 \text{ g} = 0.0136 \text{ mole}$$

zinc equal to :

$$\text{Zinc} = 0.5 \times 0.0136 = 0.0068 \text{ mole} = 0.4452 \text{ g.}$$

From zinc = 0.4452 g, zinc acetate is used equal to :

$$\text{So, weight of zinc acetate} = (183.46 / 65.37) \times 0.4452 \text{ g.} = 1.2460 \text{ g.}$$

The results of calculation of all Zn/Ga atomic ratios are shown in Table A1.

Table A1. Reagents used for the synthesis of zinc gallate.

Zn/Ga atomic ratio	Gallium acetylacetonate	Zinc acetate
0.33	5 g	0.8330 g
0.50	5 g	1.2496 g
1.00	5 g	2.4991 g

Similarly, the calculation of the preparation of the zinc aluminate is shown as follow:

Zinc acetate and aluminium isopropoxide (AIP) are used as the reactants for the preparing zinc aluminate powder.

1. Aluminium isopropoxide (AIP, $[(CH_3)_2CHO]_3Al$) has M.W. of 204.25 g/mol. And purity >98%.

Aluminium has M.W. of 26.98 g/mol

2. Zinc acetate $((CH_3COO)_2Zn)$ has M.W. of 183.46 g/mol.

Zinc (Zn) has M.W. of 65.37 g/mol.

Example A2: Calculation of preparation of zinc aluminate with Zn/Al = 0.5 is shown as follow:

Aluminium isopropoxide 15 g were used for preparation of all Zn/Al atomic ratio.

The reagent 15 g were consisted of aluminum isopropoxide more than :

$$\text{Aluminium isopropoxide} = (98/100) \times 15 = 14.70 \text{ g.}$$

So, aluminium isopropoxide 14.70 g were consisted of aluminium equal to:

$$\text{Aluminium} = (26.98/204.25) \times 14.7 \text{ g} = 1.9418 \text{ g} = 0.0720 \text{ mole}$$

So, Zn/Al = 0.5 has zinc equal to :

$$\text{Zinc} = 0.5 \times 0.0720 = 0.0360 \text{ mole} = 2.3524 \text{ g.}$$

From zinc = 2.3524 g., zinc acetate is used equal to :

$$\text{So, weight of zinc acetate} = (183.46/65.37) \times 2.3524 = 6.0619 \text{ g.}$$

The results of calculation of all Zn/Al atomic ratios are shown in Table A2.

Table A2. Reagent used for the synthesis of zinc aluminate.

Zn/Al atomic ratio	Aluminium isopropoxide	Zinc acetate
0.33	15 g	4.4012 g
0.50	15 g	6.6019 g
1.00	15 g	8.9821 g

APPENDIX B

CALCULATION OF CRYSTALLITE SIZE

Calculation of crystallite size by Scherer equation

Crystallite size was calculated from the half-height width of the diffraction peak of zinc gallate and diffraction peak of zinc aluminate using the Scherer equation. The value of the shape factor, K was taken to be 0.9 and KCl was used to be internal standard.

From Scherer equation :

$$t = \frac{0.9\lambda}{B \cos \theta_B} \quad (\text{B.1})$$

where t = crystallite size

K = shape factor = 0.9

λ = X-ray wave length, Cu K : = 1.5418 Å

B = the Bragg angle

$$B^2 = B_M^2 - B_S^2$$

B_M = the measured peak width in radians at half peak height.

B_S = the corresponding width of a standard material.

ExampleB1: The crystallite size of pure zinc gallate prepared in 1,4-butanediol is calculated as follow:

$$\begin{aligned} \text{From } B^2 &= B_M^2 - B_S^2 \\ &= 0.00902^2 - 0.00402^2 \\ &= 0.0000652 \\ B &= 0.008076 \text{ rad} \\ \theta_B &= 18.06^\circ \end{aligned}$$

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APPENDIX C

CALCULATION OF CHEMICAL COMPOSITION

Calculation of Zn/Ga and Zn/Al atomic ratio of as-synthesized zinc gallate and zinc aluminate

M.W. of Zn	=	65.39
M.W. of Ga	=	69.72
M.W. of Al	=	26.98

Example C1: The calculation of the as-synthesized sample at starting Zn/Al atomic ratio equals to 0.50 in 1,4-butanediol.

The data of the product at Zn/Al = 0.50 in 1,4-butanediol obtained by XRF analysis:

Percent by weight of Zn	=	53.3 %
Percent by weight of Al	=	44.9 %

Then, the mole of Zn is equal to:

$$\text{mole of Zn} = 53.3 / (100 \times 65.39)$$

and the mole of Al is equal to:

$$\text{mole of Al} = 44.9 / (100 \times 26.98)$$

So, the Zn/Al atomic ratio of the as-synthesized product is

$$\begin{aligned} \text{Zn/Al} &= [53.3 / (100 \times 65.39)] / [44.9 / (100 \times 26.98)] \\ &= 0.489 \end{aligned}$$

Example C2: The calculation of Zn/Ga of the as-synthesized products at starting Zn/Ga atomic ratio equals to 0.50 in 1,4-butanediol.

The data of the product at starting Zn/Ga = 0.50 obtained in by XRF analysis.

Percent by weight of Zn	=	35.9 %
Percent by weight of Ga	=	63.1 %

Then, the mole of Zn is equal to:

$$\text{mole of Zn} = 31.1 / (100 \times 65.39)$$

And the mole of Ga is equal to:

$$\text{mole of Ga} = 64.1 / (100 \times 65.37)$$

So, the Zn/Ga atomic ratio of the as-synthesized product is

$$\begin{aligned} \text{Zn/Ga} &= [31.1 / (100 \times 65.39)] / [64.1 / (100 \times 65.37)] \\ &= 0.489 \end{aligned}$$

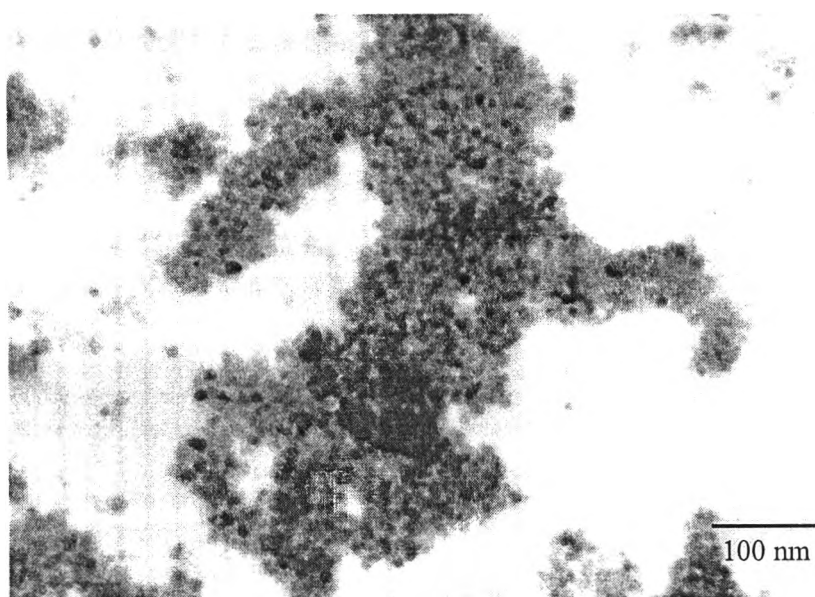
APPENDIX D

CALCULATION OF CRYSTALLITE SIZE FROM TEM PHOTOGRAPH

Calculation of crystallite size from TEM photograph

Crystallite sizes measured from TEM photograph of the as-synthesized product and calcined product of zinc gallate and zinc aluminate (d^c) (as shown in Table 5.1 to 5.7) were calculated as follows:

Example D1: The measurement of as-synthesized crystallite size of zinc gallate at starting Zn/Ga = 0.50 synthesized in 2-propanol.



At X150, 000 magnification, the scale is

$$\begin{aligned} 150 \text{ mm} &= 1 \mu\text{m} \\ &= 1000 \text{ nm} \end{aligned}$$

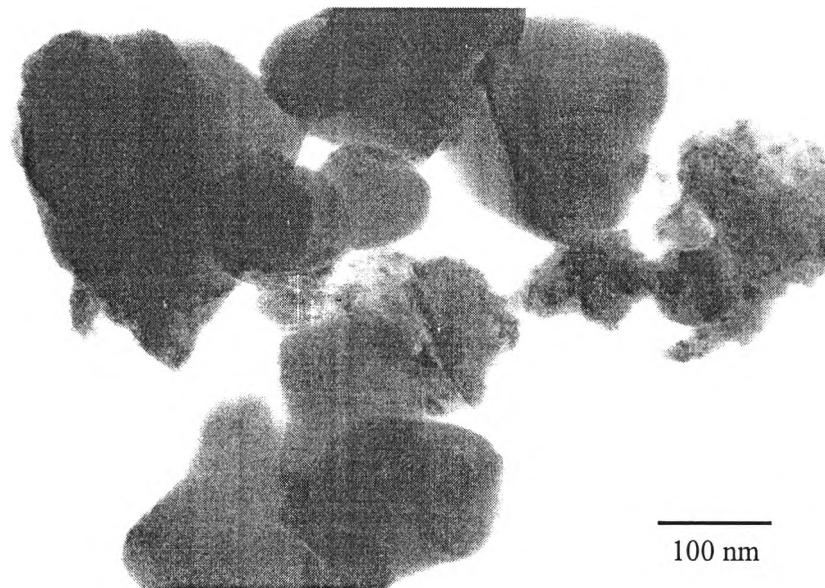
From TEM photograph, it was found that the crystallite size closed to each other and that was 1.2 mm.

So, the true crystallite size is equaled to

$$\text{true crystallite size} = (1000 \text{ nm} / 150 \text{ mm}) \times 1.2 \text{ mm}$$

$$= 8.00 \text{ nm}$$

Example D2: The measurement of as-synthesized crystallite size of zinc gallate at starting Zn/Ga = 0.50 synthesized in 1,4-butanediol calcined at 1100°C.



At x150,000 magnification, the scale is

$$\begin{aligned} 150 \text{ mm} &= 1 \mu\text{m} \\ &= 1000 \text{ nm} \end{aligned}$$

From TEM photograph, it was found that the distribution of crystallite size of the calcined product was broad so the true crystallite size was averaged.

The measured crystallite sizes in TEM photograph were 28, 25, 24, 21, 20, 19, 18, 15, 13, and 10 nm. So, the average measured crystallite size was equaled to:

$$\begin{aligned} \text{Average measured crystallite size} &= \frac{28 + 25 + 24 + 21 + 20 + 19 + 18 + 15 + 13 + 10}{10} \\ &= 19.3 \text{ nm} \end{aligned}$$

Thus the true crystallite size was:

$$\begin{aligned} \text{true crystallite size} &= (1000 \text{ nm} / 150 \text{ mm}) \times 19.3 \text{ nm} \\ &= 128.67 \text{ nm} \end{aligned}$$

VITA

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