Synthesis, characterization and application of Y3Fe5O12 nanocatalyst for green production of NH3 using magnetic induction method (MIM)

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Citation: AIP Conf. Proc. **1482**, 633 (2012); doi: 10.1063/1.4757548
View online: http://dx.doi.org/10.1063/1.4757548
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1482&Issue=1
Published by the American Institute of Physics.

Synthesis, Characterization and Application of $Y_3Fe_5O_{12}$ Nanocatalyst for Green Production of NH_3 using Magnetic Induction Method (MIM)

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Abstract. $Y_3Fe_5O_{12}$ (YIG) was prepared through sol-gel technique and sintered at three different temperatures (1000-1200°C). Various characterizations on the morphological and structural properties of produced YIG have been done as to understand the potential of this unique magnetic type nanomaterial to be used in the catalyst application for ammonia synthesis at ambient or green production environment. YIG catalyst exposed under magnetic induction of 0.1 T produced about 242.56μmol/h.g-cat yield of ammonia (NH_3) at freezing reaction temperature of 0°C. About 95.88% improvements of NH_3 yield is produced in comparison with the absence of magnetic induction reaction condition (10μmol/h.g-cat). Synthesis at 25°C yielded reduction about 0.90% lower than the synthesis at 0°C temperature. Thus, it is proven that the temperature engaged the dominant roles in affecting the catalytic effect of YIG catalyst for NH_3 production. Further parametric studies should be conducted as to explore the robustness of YIG catalyst for new route of ammonia production until the commercial scale-up could be achieved.

Keywords: YIG; garnet; sol-gel; different calcinating temperature; ammonia; magnetic induction method.
PACS:81.07. Bc Nanocrystalline Material

INTRODUCTION

The premise / objective of this work focuses on vigorous and systematic investigation on the garnets having a general chemical formula of $Y_3Fe_5O_{12}$ prepared by the sol gel method in promoting the yield of ammonia (NH_3) under the magnetic induction method (MIM) at different reaction temperature and magnetic field strength. Nanoparticles garnets demonstrate unique engineering and physical properties that can be widely used as efficient catalyst, considering the factor of small size effect, large surface contact effect and quantum tunnel effect. In recent years, wet-chemical routes such as sol-gel, co-precipitation and glycothermal approaches have been developed to circumvent the synthetic difficulties to prepare fine particles of pure garnet powders. Sol-gel method has been used in this work due to the advantage of inexpensive precursors, a simple preparation method and resulting nanocrystalline powders [1].

The garnets have the chemical formula $3M_2O_3.5Fe_2O_3$, where for this case M is Yttrium. All cations in garnets are trivalent and as a result there is no possibility of electron hopping through the material, and the resistivity of garnets is extremely high. The garnets are rather weakly ferromagnetic. The Yttrium does not have a magnetic moment, since it does not have any free electron, so the net moment is due entirely to the unequal distribution of Fe^{3+} ions in up- and down-spin sites. The antiferromagnetic super-exchange interaction results in three up-spin electrons for every two down-spin electrons, and the net magnetic moment of 5 μB per formula unit. Since the formula unit is very large, this leads to a small magnetization per unit volume [2]. The ferromagnetic garnet has been popularly used in very high frequency (microwave), telecommunication and data storage applications due to their interesting magnetic and magneto-optic properties [2,8] and also widely used in electronic devices as isolators, circulators, transmitter, and transducers of acoustic energy [3,7]. The selection of Fe based catalyst for any chemical reaction under the magnetic induction strategy is based on the ferromagnetic nature of substance due to the way of inner unpaired electron are aligned in their crystal lattices (unpaired 3d electron). Fe has maximum five unpaired 3d electron that offer

International Conference on Fundamental and Applied Sciences 2012
AIP Conf. Proc. 1482, 633-638 (2012); doi: 10.1063/1.4757548

spontaneous magnetism due to positive exchange energy by parallel alignment of magnetic moment. YIG nanoparticles provide another advantage of wide surface area and larger magnetic moment [4].

However, a comprehensive understanding of their engineering, intrinsic and extrinsic properties is required as to fully utilize the potential of this nanomaterial for new uses as catalyst especially for the chemical reaction driven by the magnetic field induction method.

METHODOLOGY

YIG Preparation and Characterization

The garnet nano-crystals were prepared by innovative sol-gel technique [3-4]. The starting solution was a mixture of iron nitrate $Fe(NO_3)3.9H_2O$ and yttrium nitrate $Y(NO_3)3.6H_2O$. All the starting powders were dissolved in an aqueous solution of nitric acid. The mixtures were stirred continuously at about 150 rpm at room temperature until the formation of gel was observed. Later, the gel was dried at 110°C in an oven. The dried powders were sintered at different temperatures (1000°C, 1100°C and 1200°C) for 4 hours in the normal furnace air. It was then dry crushed using an agate and mortar for 1 hour to obtain the fine YIG nanoparticles powder. The phase and crystal structure of the prepared samples were identified by using X-ray diffraction analyzer (Model PW 1830 Generator, Philips and PW 3210 MPD control, Philips). FESEM (Philips XL30, Environmental FESEM) images were captured and the Raman spectra (MultiSpectro Horiba Jobin Yvon) were taken as to reveal the surface morphology of the samples. The best YIG from the characterization will be selected for further investigation on its efficacy as magnetic nanocatalyts material under the magnetic induction reaction environment.

Ammonia Synthesis by MIM using YIG Catalyst

The synthesis of ammonia begins by placing 0.2g of catalyst inside the cylindrical acrylic chamber at room temperature (25°C) setting and flowing the hydrogen and nitrogen gas with 3:1 volume ratio for 30 minutes. Later, the magnetizer is switched on into the required magnetic field strength of 0.1 and 0.2 T and samples collection will be done after the 30 minutes of reaction period. Figure 1 shows the magnetic equipment that applied in this work. The experiment was then repeated for temperature of 0°C as to investigate the temperature effect of reaction by YIG catalyst.

Kjeldahl Method for Ammonia Quantification

Kjeldahl method is a method to quantify the amount of nitrogen in chemical substance [5]. A titration process was done to trace the amount of ammonia produce [6].

$HCl_{reacted} + NH_{3(g)} \rightarrow NH_4Cl$
$NaOH + HCl_{excess} \rightarrow NaCl + H_2O$
$HCl_{total} = HCl_{reacted} + HCl_{excess}$
Amount of $HCl_{reacted}$ = Amount of NH_3
Amount of HCl_{excess} = Amount of NaOH

Ammonia detection was done by dissolving the gas in 2.5ml of 0.01M HCI (in excess) to produce NH_4Cl. The amount of excess HCl was determined by titration with 0.01 M $NaOH_{(aq)}$. The amount of NH_3 produced is equal to the amount of HCI reacted.

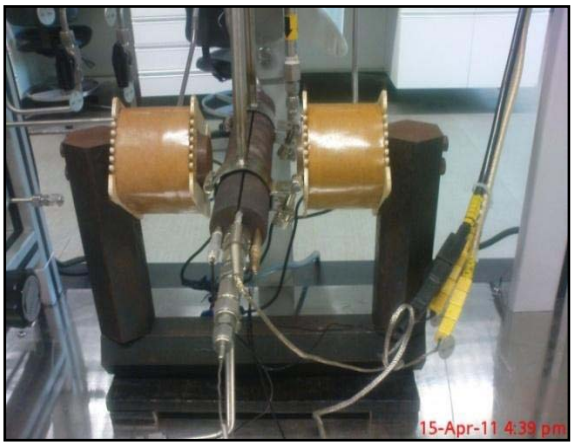

FIGURE 1. Magnetic Induction Reaction Zone

RESULT AND DISCUSSION

X-Ray Diffraction (XRD) Analysis

X-ray diffraction with CuKα radiation Kα = 0.89 and a wavelength λ = 1.54056 Å was used to determine the crystal structure of yttrium iron garnet produced at different temperatures. $Y_3Fe_5O_{12}$ was synthesized by sol-gel method and annealed at 1000°C, 1100°C, and 1200°C for 4 hours. The unit cell size and geometry of the YIG nanocatalyst were resolved from the angular positions of the diffraction peaks, whereas arrangement of atoms within the unit cell is associated with the relative intensities of these peaks [7]. The crystallite size can be measured from X-ray diffraction patterns by using Scherer equation [8].

$$D = \frac{K\lambda}{\beta \cos \alpha} \quad (1)$$

$K = 0.89$

θ = maximum peak

β =Full width at half maximum (FWHM)

λ = wavelength of incident radiation

Figure 2 shows the XRD pattern for $Y_3Fe_5O_{12}$ at three different annealing temperatures and it was found that the major peak obtained for [420] plane. The sharp peaks observed indicate high crystalline of the samples and the similar highest peak at [420] also found by previous researchers [7]. It is obvious that the correct calcinating temperature is one of the main factors affecting the formation of the garnet phase for all the produced samples.

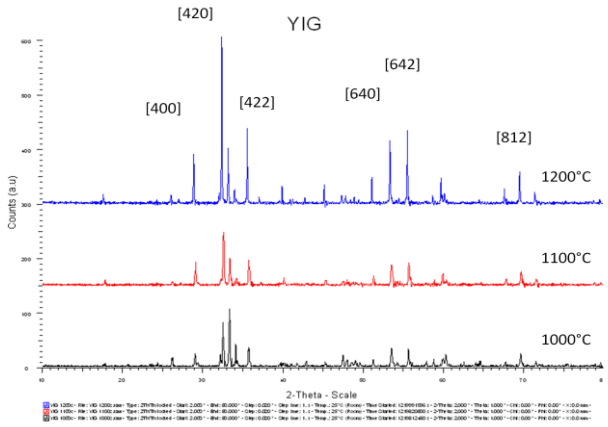

FIGURE 2. Diffraction pattern for YIG sintered at various temperatures (1000°C, 1100° and 1200°C)

XRD pattern clearly depicts the single phase garnet and crystallization had completely occurred at 1200°C. The average crystallite size of the single phase powders were determine, using the X-ray broadening of the [420] diffraction peak by Debye Scherer's formula. The average crystallite size of YIG sample is 95.1nm, 102.1nm and 114.9nm, respectively for 1000°C, 1100°C and 1200°C. It is clearly found that the peak intensity increased with the increasing of calcinating temperature. This suggests that the temperature of 1200°C gives dominant characteristic of YIG where high crystalline behavior could be achieved with the obvious increased of crystalline size. YIG sintered at higher temperature more than the range studied shows melted characteristic whereby not representing the particle in the powder form. This interesting phenomenon should be further studied as to seek the reason behind it. In overall, from this study, the perfect cubic crystal is obtained from the YIG produced considering a=b=c lattice distance which confirm the nature of garnets that have eight formula units in cubic unit cell with approximately the same lattice constant in the order of 12 Å [8]. Table 1, summarized the entire findings from XRD analysis.

TABLE 1. X-Ray Diffraction correspond to [420] peak for YIG sintered at three different temperatures

YIG Sample	XRD correspond to [420] peak						
	Intensity (Counts)	FWHM (2theta°)	d-spacing (Å)	Crystallite size (nm)	a	b	c
1000	183	2.70	0.17	95.1	12.375	12.375	12.375
1100	116	2.76	0.16	102.1	12.375	12.375	12.375
1200	136	2.76	0.14	114.9	12.376	12.376	12.376

Field Emission Scanning Electron Microscopy (FESEM) Observations

Morphology of $Y_3Fe_5O_{12}$ characterized by FESEM is depicted at Figure 3. The measurement was taken at 15K magnification. The averaged particle size from this result is 222 nm, 244 nm, and 301 nm in average. By increasing the annealing temperature, the particle size getting larger and less agglomeration could be observed. Growing of particle sizes may due to the factor of inter-particles diffusion during the calcinating temperature. Extensive diffusion at higher temperature contributed to the YIG particle size increment.

The FESEM images clearly depicts the cubical microstructure for all YIG sintered at different temperatures. However, there is significant different between them in term of particles size and the tendency of agglomeration or quality of dispersion between the neighboring particles. YIG sintered at 1200°C shows bigger particles size compared than YIG sintered at 1100°C, and this automatically will gives the advantage of less agglomeration or better dispersion of YIG inter-particles that sintered at higher temperature. This phenomena technically contributed by the factor of cumulative nanoparticles surface energy due to van der Waals force attraction that absolutely higher for smaller size of nanomaterials. However, most particles stuck to each other and form agglomerates or lumps due to their surface energy [9]. It is clearly found that the average particle size measured by FESEM is obviously bigger than the crystallite size measured by XRD applying the Scherrer's formula.

Theoretical value of atomic percent for Y, Fe and O are 15%, 25% and 60%. However, by referring to the

Table 2, it shows that the EDX results with the standard deviation may vary from sample annealed at 1000°C, 1100°C and 1200°C and a bit deviated from the theoretical amount of YIG. This could be due to the nature of mapping analysis by EDX which are not able to represent the whole observed system. It is clearly understood that, by referring to the Table 2, there are no impurities for the YIG sample that produced by three different calcinating temperatures due to the high purity starting materials of the sample composition and stringent control of the preparation procedures. The dominated atomic amount is on oxygen content, followed by iron and yttrium. The atomic % of iron to oxygen is a constant and compared to oxygen, the higher peak of oxygen in the spectrum indicated more concentration of oxygen comparing to the iron element as in the formula $Y_{3-x}Al_xFe_5O_{12}$.

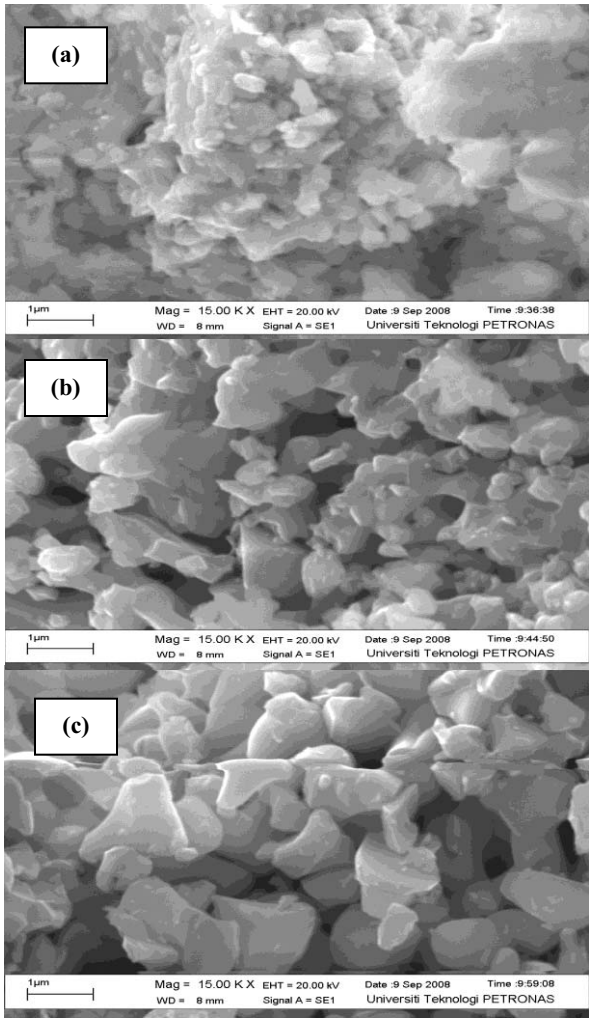

FIGURE 3. Morphology of YIG at a) 1000°C; b) 1100°C and c) 1200°C calcinating temperature (15 000X Mag.)

Raman Spectroscopy Results

Raman Spectra using the Horiba HR800 was used to see the vibration of the $Y_3Fe_5O_{12}$ atoms after being annealed at 1000°C, 1100°C and 1200°C for 4 hours. Figure 4 shows the value of Raman shift and the intensity for $Y_3Fe_5O_{12}$ produced by the sol gel method.

TABLE 2. Weight and Atomic Percent from EDX spectrum analysis of $Y_3Fe_5O_{12}$ sintered at various temperatures a) 1000°C; b) 1100°C and c) 1200°C

YIG Sample		Y	Fe	O
1000°C	Weight %	37.64	31.86	30.50
	Atomic%	14.60	19.67	65.73
	Std. Deviation %	2.67	21.32	9.55
1100°C	Weight %	34.77	40.21	25.02
	Atomic %	14.62	26.92	58.46
	Std. Deviation %	2.53	7.68	2.57
1200°C	Weight %	34.52	34.16	31.33
	Atomic %	13.13	20.68	66.20
	Std. Deviation %	12.47	17.28	10.33

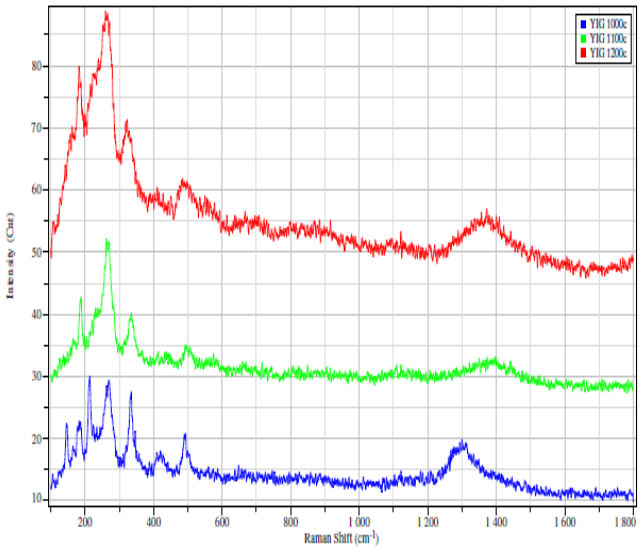

FIGURE 4. Raman shift for YIG sintered at various temperatures (1000°C, 1100° and 1200°C)

It has been observed that the major peak at 264 cm^{-1} for Raman shift (as depicted at Figure 4) is identical for all the three YIG sintered at three different temperatures. This clearly indicates the garnet phase and also confirmed the grain growth is successfully achieved at all these three temperature. In YIG crystal,

there are 16-octahedral lattice and 24-tetrahedral lattices. Fe^{+3} ion displacement may take place either at one of their lattices [3]. Thus, the combination of peaks observed identical at 160, 217, 264, 340, 369 and 489 cm^{-1} are from the vibrations of yttrium ions in the YIG sample. Identical shift around 1200 – 1500 for each YIG could be explained by the factor of different calcinating temperature which allow the arrangement of Fe^{+3} ion displacement in more random with increasing calcinating temperature.

Temperature Program Reduction (TPR) for YIG Catalyst

The reducibility of $Y_3Fe_5O_{12}$ was studied by using H_2-TPR result. Figure 5 reveals the H_2-TPR profiles for $Y_3Fe_5O_{12}$ prepared by sol-gel method. The temperature reduction and percentage hydrogen consume were summarized at Table 3.

TABLE 3. Temperature reduction and percentage hydrogen consume for $Y_3Fe_5O_{12}$

Temperature	%Hydrogen	MVs	µmol/g
489	40.66	556751.32	208.16505
692	8.15	111578.05	41.71818
806	51.20	701077.34	262.12744

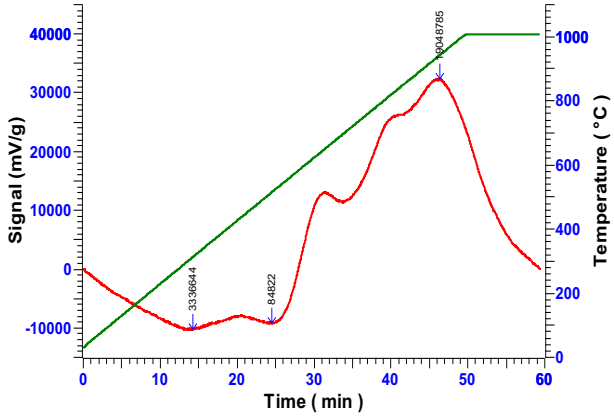

FIGURE 5. TPR Profile of $Y_3Fe_5O_{12}$ (YIG) Nanocatalyst sintered at 1200°C

Based from the Table 3, first reduction occurred at 489°C to reduce Fe_5O_{12} to FeO and YO_2. Second peak of reduction is at 692°C for reduction of FeO to Fe. The third peak occurred at 806°C which is the expected temperature to reduce all the oxide to metallic state. The mechanism of reduction for YIG is summarized at the Table 4.

TABLE 4. Reduction Mechanism of $Y_3Fe_5O_{12}$ (YIG)

Reaction	Temperature (°C)
$Y_3Fe_5O_{12} \rightarrow FeO+YO_2+O_2$	~ 489
$FeO \rightarrow Fe$	~ 692
$YO_2 \rightarrow Y_3$	~ 806

Ammonia Synthesis with Various Parametric Strategies

Ammonia Synthesis at Different Temperature with and without MIM using YIG as Catalyst

The synthesis of ammonia was conducted at temperature of 0°C using $Y_3Fe_5O_{12}$ (YIG) nanocatalyst. Firstly, the reactant gases were reacted with $Y_3Fe_5O_{12}$ (YIG) nanocatalyst under the magnetic induction method (MIM) applied at 0.1Tesla for 30 minutes duration. Later, the experiment was repeated by react the gases without the application of MIM. The yield of ammonia synthesis by using $Y_3Fe_5O_{12}$ (YIG) nanocatalyst with MIM is 242.56µmole/h.g-cat while only 10µmole/h.g-cat without the application of MIM. The results clearly shown that there are huge different between the reaction with and without MIM as the percentage different is about 95.88% when using YIG with the exposure of MIM. The reaction with magnetic induction is much higher than the reaction done without the magnetic induction since the presence of magnetic induction force the electron spin to align them properly. The reaction without the magnetic induction provides condition whereby the electron spin is random and the reaction is a bit hard to occur. Magnetic fields could alter the chemical reaction rate, conversion yield and product distribution of chemical reactions.

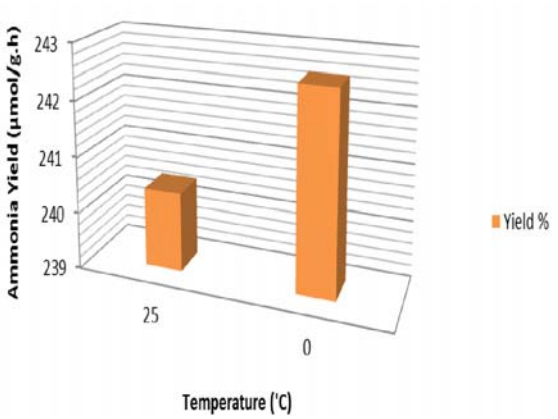

FIGURE 6. Trend of ammonia yield using YIG nanocatalyst at two different testing temperatures

The contribution of YIG as catalyst could be explain by the nature of YIG that have the magnetic ions which distributed over the three crystallographic sites with sub lattice magnetization Ma (octahedral site, 16 Fe^{3+} ions in a), Md (tetrahedral site, 24 Fe^{3+} ions in d) and Mc dodecahedral site, 24 R^{3+} ions in c. The interaction between the Fe^{3+} ions in (a) and (d) sites is strongly antiferromagnetic due to strong super-exchange interaction. The magnetic moment of the Yttrium ions in the (c) sub lattice couples antiparallel with the resultant moment of Fe^{3+} ions that absolutely caused no magnetic moment in YIG [8]. Thus, the net magnetic moment in YIG during the reaction in MIM is due to the unequal distribution of Fe^{3+} ions in the two different sub lattices of (a) and (d).

Next, the synthesis of ammonia was conducted at temperature of 25°C using $Y_3Fe_5O_{12}$ (YIG) nanocatalyst with magnetic induction of 0.1Tesla and the result obtained is compare with the ammonia synthesis at 0°C of reaction.

Figure 6 depicts the yield percentage of ammonia is 0.90% higher at 0°C temperature (242.56µmole/h.g-cat) in comparison with the yield obtained at 25°C reaction temperature (240.4µmole/h.g-cat). Raising the temperature of catalyst caused the increase of thermal vibrations which resulting the atomic magnetic moments free to rotate. This phenomenon allows the atoms to randomize the directions of any moments that may be aligned due to magnetic induction by the external field. With the increasing temperature, the saturation magnetization diminishes gradually and abruptly drops to zero at Curie temperature (T) of YIG which is at 550K. Hence, the lower the temperature, the higher the alignment of the electron spins in the atom and the better the yield could be produced. Increasing the temperature will disturb the direction of each spin and caused the spin to cancel out each other and it will not magnetize [10, 11].

CONCLUSIONS

It is concluded that the YIG nanoparticles were successfully synthesized by sol-gel technique. X-Ray diffraction analysis confirmed that the single phase of garnet structure has been formed at [420] plane. FESEM micrographs show that the YIG have cubical like microstructure with the average particle size 114.9 nm for YIG sintered at 1200°C. EDX analysis disables to represent the chemical elements fraction in comparison with the theoretical values. Identical shift around 1200 – 1500 by Raman spectroscopy indicates the arrangement of Fe^{+3} ion displacement in more random with increasing calcinating temperature. TPR analysis gives the clear idea of catalyst reduction behavior and catalytic activity at two different reaction temperatures indicates the dependency of chemical reaction under the magnetic environment. It is found that at 0°C of reaction temperature, the efficacy of magnetic effects on YIG nanocatalyst was more pronounced.

ACKNOWLEDGMENTS

We acknowledged with gratitude the financial support from Ministry of Higher Education (MOHE) of Malaysia under Long Term Research Grant Scheme (LRGS) for One-Baja project. The author would like to appreciate MOHE and UTeM for the study leave concession and scholarship granted to him

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