Journal of Nano Research *Online: 2012-12-27*
ISSN: 1661-9897, Vol. 21, pp 131-137
doi:10.4028/www.scientific.net/JNanoR.21.131

$Y_3Fe_5O_{12}$ Nanocatalyst for Green Ammonia Production By Using Magnetic Induction Method

Noorhana Yahya[1, a] and Poppy Puspitasari [2,b]

[1]Fundamental and Applied Sciences Department, UniversitiTeknologi PETRONAS

[2]Electrical and Electronics Engineering Department, UniversitiTeknologi PETRONAS

Bandar Seri Iskandar, 31750, Tronoh, Perak DarulRidzuan, Malaysia.

[a]noorhana_yahya@petronas.com.my,[b]povopivi@gmail.com

Keywords: garnet; sol-gel; ammonia; magnetic induction method; spins

Abstract. Ammonia production is an energy-intensive industry as it requires high temperature (400-500^{o}C) and also high pressure (150-300bar). This motivates research to finding greener and lower energy process for ammonia synthesis. In this work, $Y_3Fe_5O_{12}$ (YIG) nanocatalyst that has large surface area was synthesized. Ammonia was produced at ambient environment by using the Magnetic Induction Method (MIM).The $Y_3Fe_5O_{12}$nanoparticles were prepared using the sol-gel technique and were sintered at three different temperatures (950-1150°C). The X-Ray Diffraction (XRD) patterns show the major peak at [420] plane with the value of a=b=c=12.38Åwhich indicates a cubic structure. The magnetic saturation (Ms) value of the samples is 16.6emu/g. The reducibility of the particles was described from the Temperature Program Reduction (TPR) profile at 806^{o}C where all the oxide phase is changed to metallic phase. Ammonia yield of 242.56μmole/h.g-cat was successfully obtained at 0^{o}C reaction temperature. It was observed that ammonia synthesis that was conducted at 0^{o}C temperature resulted in higher ammonia yield indicating a better spin alignment and hence improved catalytic activities.

Introduction

Ammonia is a chemical substance which has been used as an additive in various applications such as explosives and detergents. About 76% from the total production of ammonia has been applied in fertilizer industry. Unfortunately, the current production is only capable of producing only a 10-20% of ammonia yield. This major drawback is overcome by using nanotechnology and a magnetic method as a solution. Nanoparticles garnets demonstrate unique engineering and physical properties which can be used as an efficient catalyst, considering the factor of small size effect, large surface contact effect and quantum tunnelling effect. In recent years, wet-chemical routes such as sol-gel, self-combustion, co-precipitation and glycothermal approaches have been developed to circumvent the synthesis difficulties to prepare fine particles of pure garnet powders. The sol-gel method has been used in this work due to the advantage of inexpensive precursors, a simple preparation method and yet resulting in nanocrystalline powders [1].

Garnet has a chemical formula of $3M_2O_3.5Fe_2O_3$, where M is known as yttrium. All cations in garnets are trivalent and, as a result, there is no possibility of electron hopping through the material. The resistivity of garnets is extremely high and 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 [2,3] and also widely used in electronic devices as isolators, circulators, transmitter, and transducers of acoustic energy [4,5]. 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 electrons that offer spontaneous magnetism due to a positive exchange energy by parallel alignment of the magnetic moment. YIG nanoparticles provide another advantage of wide surface area and larger magnetic moment [6]. The objective of this work is to focus on a systematic investigation of $Y_3Fe_5O_{12}$ prepared by the sol-gel method in promoting the ammonia (NH_3) yield under the magnetic induction method (MIM). The ammonia synthesis was done at different temperatures, 0^oC and 25^oC in a 0.2 T reaction zone.

Methodology

YIG Preparation and Characterization

The garnet nano-crystals were prepared by an innovative sol-gel technique [4-6]. 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 for about 12 hours. The dried powders were sintered at different temperatures (1000°C, 1100°C and 1200°C) for 4 hours in a furnace. 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 a X-ray diffraction analyzer (Model PW 1830 Generator, Philips and PW 3210 MPD control, Philips). Field Emission Scanning Electron Microscopy (Philips XL30, Environmental FESEM) images were captured to reveal the surface morphology of the samples. The best YIG from the characterization was 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 ammonia synthesis was done by placing 0.2g of catalyst inside the cylindrical acrylic chamber at room temperature (25°C) while allowing a continuous flow of hydrogen and nitrogen gas with 3:1 volume ratio for 30 minutes. This reaction was done in a magnetic field strength of 0.2 T. The resulting ammonia samples were collected after 30 minutes of reaction period. The experiment was then repeated at 0°C and comparative studies were made on the ammonia yield.

Results 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 the sol-gel method and annealed at 950^oC, 1050^oC, and 1150^oC 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 the Scherer equation [8].

$$D = \frac{K\lambda}{\beta \cos \alpha}$$

K = 0.89

θ = maximum peak

β =Full width at half maximum (FWHM)

λ = wavelength of incident radiation

Figure 1 shows the XRD pattern for $Y_3Fe_5O_{12}$ at three different annealing temperatures and it was found that the major peak was obtained for the (420) plane.

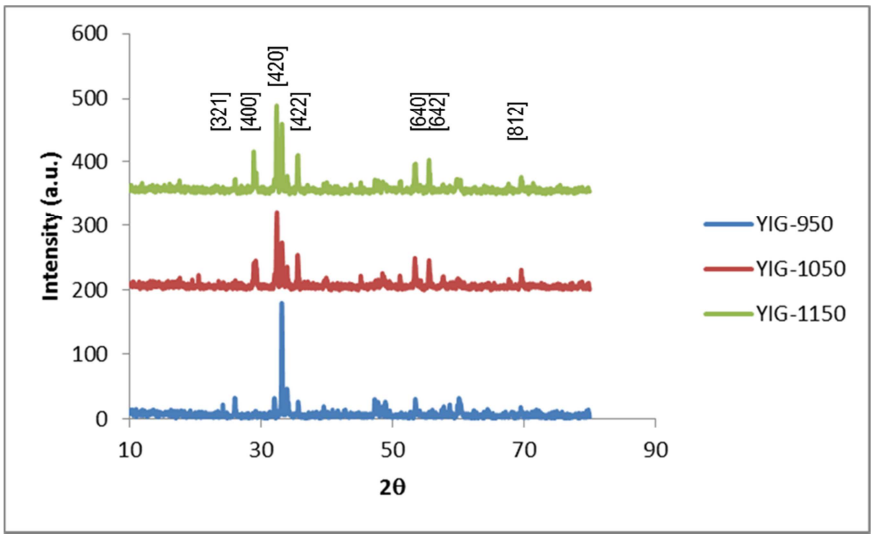

Fig. 1. XRD pattern for $Y_3Fe_5O_{12}$ nanocatalysts synthesized by the sol-gel method and annealed at 950°C, 1050°C, and 1150°C.

It was calculated that the particle size was in the range of 95 nm – 114 nm (Table 1). From the XRD patterns, single phase $Y_3Fe_5O_{12}$ was obtained at the annealing temperature of 950°C.

Table 1. Intensity, FWHM, d-spacing, crystallite size of $Y_3Fe_5O_{12}$ prepared by the sol-gel technique and annealed at 950°C, 1050°C and 1150°C.

Samples	X-Ray Diffraction (Correspond to [420] peaks)						
	Intensity [Counts]	FWHM [2θ]	d-spacing [Å]	Crystallite size [nm]	a [Å]	b [Å]	c [Å]
950	183	2.70	0.17	95.1	12.375	12.375	12.375
1050	116	2.76	0.16	102.1	12.375	12.375	12.375
1150	136	2.76	0.14	114.9	12.376	12.376	12.376

From the standard card SSNNNN 89-2609 (c), the structure of $Y_3Fe_5O_{12}$ is cubic garnet with the value of a=b=c=12.375Å. The particle size increases when the annealing temperature increases to 1150°C. The highest intensity and the smallest particle size are for sample $Y_3Fe_5O_{12}$which was annealed at 950°C in air for 4 hours.

Field Emission Scanning Electron Microscope (FESEM) Result

The morphology of the $Y_3Fe_5O_{12}$ nanoparticles were characterized by FESEM and showed at Fig.2. The particle size from this result is 222nm and 244nm in average. By increasing the annealing temperature, the particle size increases and less agglomeration occurred. Almost identical microstructure was observed for YIG sample and the individual particles seemed to be homogenous crystals structure with grain sizes below 1 μm. Most of the particles were agglomerated to each other in a regular and uniform manner to form a network-like structure and this is due to their high surface energy [7].

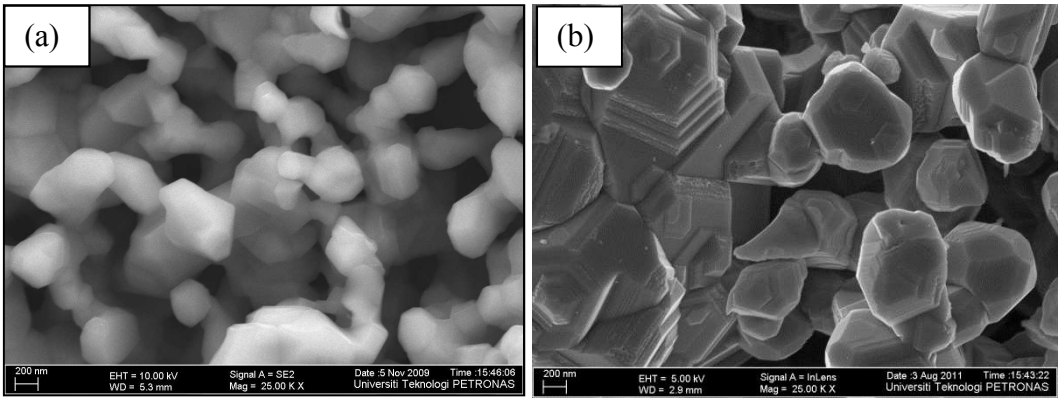

Fig.2 FESEM morphology for $Y_3Fe_5O_{12}$ annealed at (a) 950°C, and(b) 1050°C.

Temperature Program Reduction (TPR) Result

The reducibility of $Y_3Fe_5O_{12}$ was studied by using H_2-TPR result (Fig. 3). The temperature reduction and percentage hydrogen consumed are presented in Table 2.

Table 2 Temperature reduction and percentage of hydrogen consumed for $Y_3Fe_5O_{12}$.

Temperature	%Hydrogen	MVs	µmol/g
489	40.66	556751.32	208.17
692	8.15	111578.05	41.72
806	51.20	701077.34	262.13

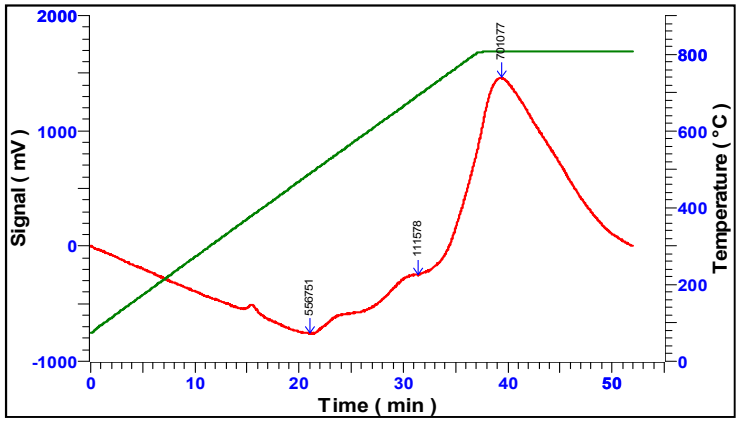

Fig.3 Temperature Program Reduction (TPR) profiles for $Y_3Fe_5O_{12}$prepared by sol-gel technique annealed at 950°C.

It was observed that the first reduction occurred at 489°C where Fe_2O_3 was reduced to Fe_3O_4. The second peak of reduction occurred at 692°C. In this profile, Y_2O_3 was reduced to YO and Fe_3O_4 to FeO, respectively. The third peak which occurred at 806°C is where all oxides were reduced to the metal metallic state [8].

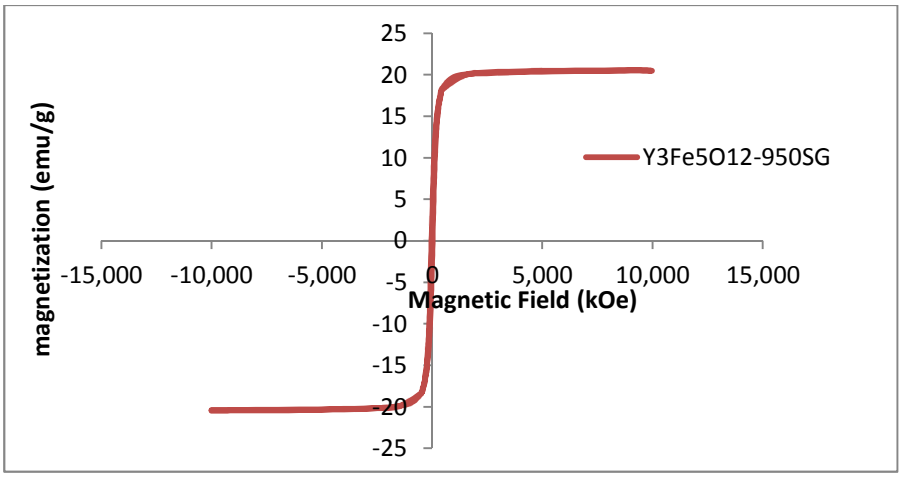

Fig. 4. Saturation Magnetisation (Ms) result for $Y_3Fe_5O_{12}$ by sol gel technique annealed at 950°C.

Fig.4 shows the Ms value of the magnetization curve that has average intensity of magnetic field which explains the soft magnetic nature of the $Y_3Fe_5O_{12}$ sample. It is also found that low values of Ms may be due to higher surface to volume ratio of the $Y_3Fe_5O_{12}$sample [9]. It has been studied that the variation of magnetic saturation Ms is due to the cation distribution in the spinel crystal lattice. The ratio of the MR to Ms of the samples is (0.945, 0.939), which shows the super paramagnetic behaviour of the $Y_3Fe_5O_{12}$ sample at room temperature [10].

It is speculated that the magnetic properties of the ferrites may be influenced due to thickness, shape of the samples and particle size [11]. The coercivity value of $Y_3Fe_5O_{12}$ is 24.3O e (Table 3).

Table 3 Hysteresis data for $Y_3Fe_5O_{12}$nanocatalyst prepared via sol-gel method.

Sample	Magnetic Saturation, Ms[emu/g]	Magnetic Remanence, Mr [emu/g]	Coercivity Force, Hc [Oe]
$Y_3Fe_5O_{12}$-950 SG	16.6	15.7	24.3

Ammonia Synthesis with Various Parametric Strategies

The synthesis of ammonia was conducted at 0°C and 25°C using $Y_3Fe_5O_{12}$ (YIG) nanocatalyst.

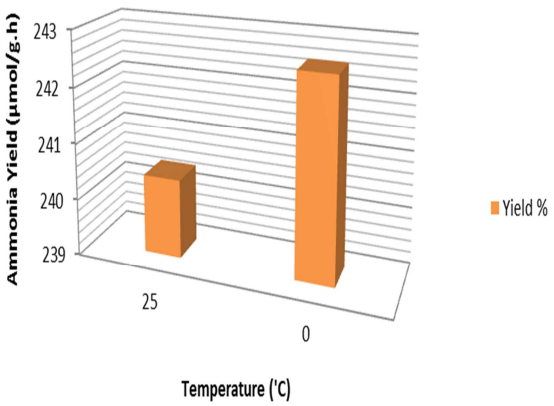

Fig. 5 Trend of ammonia yield using YIG nanocatalyst at two different testing temperatures

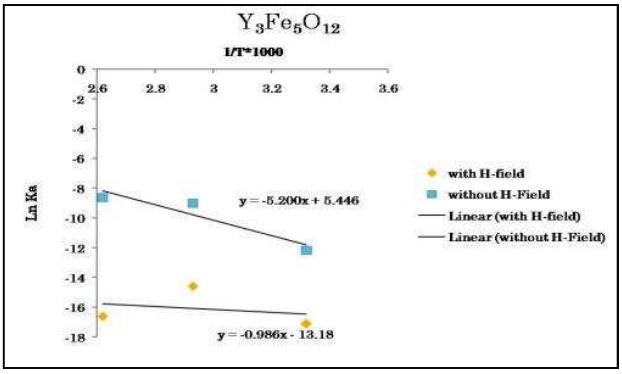

Fig. 6 Arrhenius plot for ammonia production for $Y_3Fe_5O_{12}$, T = 28°C-188°C, P = 1 atm, H-F = 0.2 T, Cat. = 0.2 g, GHSV = 12000 $cm^3/g_{cat}.h$, F = 40 cm^3/min, H_2:N_2 = 3:1

Fig.5 depicts the yield percentage of ammonia which is at 0°C and 25°C which resulted in 242.56 μmol/h.g-cat and 240.4 μmol/h.g-cat respectively. Raising the temperature of catalyst caused the thermal vibration to increase and resulting atomic magnetic moment free to rotate. This phenomenon allows the atoms to randomize the directions of moments that may be aligned by the external field. Increasing the temperature will disturb the direction of each spin and caused the spin to cancel out each other which resulted in a lower magnetization and thus reduced ammonia yield [12, 13]. Higher ammonia yield can also be speculated from the ortho-para hydrogen interconversion under the influence of the applied magnetic field [14]. The interconversion ortho-para hydrogen depends on the relative realignment of the two proton spins in the molecule. This interconversion will then affect the chemical reaction. A singlet-phased pair of spins can be induced to switch into a triplet if their individual precession frequencies differ [15]. The quantitative of the discussion can be written by using Hamiltonian equation (Eq.2) as follows [15]:

$$H = f_A.s_A + f_B.s_B = \frac{1}{2}(f_A + f_B).(s_A + s_B) + \frac{1}{2}(f_A - f_B).(s_A - s_B) \quad (2)$$

The term s_A - s_B will vanished if $f_A = f_B$ and this is the reason why the Larmor precession frequencies must be differ if singlet-triplet interconversion are to occur [14]. We also observed an endothermic-like behavior (Fig. 6). We speculate that more energy is needed for the conversion of ammonia dues to the three interpenetrating sub-lattices. We have yet to confirm this finding.

Conclusions

It is concluded that the YIG nanoparticles were successfully synthesized by sol-gel technique. Green ammonia was synthesized and a lower temperature resulted in higher ammonia yield by about 1.1 %.

Acknowledgement

We acknowledged with gratitude the financial support of Ministry of Higher Education (MOHE) of Malaysia under Long Term Research Grant Scheme (LRGS) for One-Baja project.

References

[1] S.H Vajargah, H.R. M. Hosseini, and Z.A. Nemati, Synthesis of NanocrystallineYttrium Iron Garnet by Sol Gel Combustion Process: The Influence of pH of Precursor Solution, Mat. Sci. & Eng. B 129 (2006) 211-215.

[2] N. Spaldin, Magnetic Materials: Fundamentals and Device ApplicationsCambridge University Press ISBN 0521816319, 119, 2003.

[3] R. Shaiboub, N.B. Ibrahim, M. Abdullah and F. Abdulhade,The physical properties of erbium-doped yttrium iron garnet films prepared by sol-gel method J. of Nanomat. 12, (2011) article ID 524903.

[4] N. Nasir, N. Yahya, M. Kashif, H. Daud, M.N. Akhtar, H.M. Zaid, A. Shafie, L.C. Teng, Observation of a Cubical-Like Microstructure of Strontium Iron Garnet and Yttrium Iron Garnet Prepared via Sol-Gel Technique, J. of Nanosci. and Nanotech, 10 (2010) 1-4.

[5] N. Yahya, R.M Al Habashi, K. Koziol, R.D. Borkowski, M.N. Akhtar, M. Kashif and M. Hashim Morphology and Magnetic Characterisation of Aluminium Substituted Yttrium-Iron Garnet Nanoparticles Prepared using Sol Gel Technique, J. of Nanosci. & Nanotech 11 (2011) 2652-2656.

[6] Y.Y.Xu,X.F.Rui, Y.Y.Fu, H. Zhang, Magnetic properties of a-Fe2O3 nanowires Chem. Phy. Lett. 410 (2005) 36-38.

[7] Z. Abbas, R. M. Al-Habashi, K. Khalid, M. Maarof, Garnet Ferrite ($Y_3Fe_5O_{12}$) Nanoparticles Prepared via Modified Conventional Mixing Oxides (MCMO) Method, European Journal of Scientific Research, ISSN 1450-216X, 36 (2)(2009) 154-160

[8] N. Yahya, P. Puspitasari, K. Koziol, G. Pavia, Chapter 17: Ammonia Synthesis, Carbon and Oxide Nanostructured, Springer, 2010.
[9] V. R. Cafarena, T. Ogasawara, M. S. Pinho, J. L. Capitaneo, Samarium-Iron Garnet Nanopowder Obtained By Co-Precipitation, Latin American Applied Research, 36 (2000) 136-140.
[10] R. Y. Hong, Y. J. Wu, B. Feng, Q. D. Di, H. Z. Li, B. Xi, Y. Z. Heng, D. G. Wei, Microwave-assisted Synthesis and Characterization of Bi-substited Yttrium Garnet Nanoparticles J. Magnetism and Magnetic Materials 321(8) (2009) 1106-1110.
[11] E.P. Sajitha, V. Prasad, S. V. Subrananyam, S. Eto, K. Takai, T. Enoki, Synthesis and characteristics of iron nanoparticles in a carbon matrix along with the catalytic graphitization of amorphous carbon Carbon 42 (2004) 2815-2825.
[12] M. Wang, J. Wang, K. Sun, Studies on the Relation between the Composition of Thermal Sensitive MnZn Ferrite and Curie Temperature J. Mater. Sci. Tech. 16 (2) (2010) 209-210,.
[13] J Pernicone, F Ferrero, Z Rosetti, L Forni, P Canton, P Rinello, G Fagherazzi, M Signorot, J Pinna, Wustite as a New Precursor for IndusrtialAmmonia Synthesis Catalyst, Applied Catalysis A: General 251 (2003) 121-129
[14] Information on www.yomiuri.co.jp/edu/chuo/dy/research/201008.htm.
[15] P.W. Atkins, T.P Lambert, The effect of a Magnetic Field on Chemical Reactions, available: http://pubs.rsc.org, doi:10.1039/PR9757200067.