Materials Science and Engineering B 217 (2017) 49–62

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

The enhancement of the magnetic properties of α-Fe_2O_3 nanocatalyst using an external magnetic field for the production of green ammonia

Bilal Alqasem, Noorhana Yahya *, Saima Qureshi, Muhammad Irfan, Zia Ur Rehman, Hassan Soleimani

Department of Fundamental and Applied Science, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia

ARTICLE INFO

Article history:
Received 1 October 2016
Received in revised form 27 November 2016
Accepted 22 December 2016

Keywords:
α-Fe_2O_3 nanocatalysts
Nanowires
Electrical resistive heating
Singlet to triplet conversion
Ammonia synthesis
Magnetic induction

ABSTRACT

Hematite nanocatalysts with improved magnetic properties were synthesized using electrical resistive heating under the presence of a magnetic field and a gaseous environment containing oxygen and nitrogen. The synthesis temperature was varied from 500–850 °C in the absence and presence of a static magnetic field of 0.25 T. VSM hysteresis results showed that there is a clear improve in the magnetic properties of the nanocatalysts when an external magnetic field was used during the synthesis. It also showed that the nanowires amongst other shapes hold the highest saturation magnetization value. The produced α-Fe_2O_3 nanocatalysts were used for ammonia synthesis under an external magnetic field strength ranging between 0.4–2 T. Correspondingly, (24.174 mmol h^{-1} g cat^{-1}) ammonia was yielded by applying an external magnetic field of 1.2 T and using the α-Fe_2O_3 nanowires synthesized at 700 °C with the highest saturation magnetization value of 189.43 emu/g.

1. Introduction

Hematite (α-Fe_2O_3) is known to be the most stable oxide of iron present under ambient conditions with significant technological importance. It is a nontoxic material that is also environment friendly with a low processing cost. Not to mention that it is highly resistant to corrosion and can be easily obtained or manufactured. α-Fe_2O_3 is an antiferromagnetic material with an n-type semiconductor (Eg = 2.1 eV) [1,2]. Hematite also bears interesting chemical and magnetic properties. As such, a significant effort has been focused on the synthesis of hematite nanostructures given its wide range of usage's and vast potential applications in both industrial and commercial sectors. Such applications can be found in gas sensors [3–7], catalysts [8–12], ferrofluids [13], photocatalysts [14], printing ink [15], water splitting and treatment [16,17], fabrication of transistors [18] and Li-ion batteries [19]. Most of these applications depend mainly on the morphology and structure of the semiconductor materials. Several geometrical morphologies of α-Fe_2O_3, such as nanorods [20], nanowires [21], nanobelts [22], nanocages [23], nanoflakes [24], nanotubes [25], nanotube arrays [26], nanofibers [27], nanodendrites [28], nanocubes [29], nanorings [30], nanospheres [31], nano-hollow spheres [32] and nanoparticles [33] were synthesized successfully using various techniques and methods. These techniques include the vacuum pyrolysis method [9] electric arc discharge [34], sol–gel method [35], an excimer laser ablation [36], annealing method [37] and modified methods.

A wide range of studies were conducted by various researchers to synthesize hematite's nanostructure. Hsu and Li reported that, hematite nanowires were fabricated using a thermal oxidation method at 350 °C for 10 h [38]. Similarly, nanotubes have been prepared under vacuum at 60 °C for 6 h using a hydrothermal method by Song et al. [39]. The hydrothermal method was also used for nanoparticles synthesis at 200 °C for 12 h by Hua and Gengsheng [40]. Colombo et al. studied different sizes and shapes of hematite nanoparticles prepared by the hydrothermal method at 100 °C for 0.2–6 h [41]. Multilayered hematite nanosheets were prepared at 400 °C and 500 °C for 2 h respectively, using thermal oxidation of iron foil by [42]. In another study by Liang et al., a hierarchical 3D α-Fe_2O_3 microstructure was prepared through a urea-assisted hydrothermal synthetic route at 150 °C for 12 h [43]. Wang et al. reported a new hollow hematite non-spherical structure using the stepwise influences of fluoride and phosphate anions at 220 °C for 48 h [44]. Patra et al. developed a new green chemical approach for the shape-controlled synthesis of single-crystalline hematite nanocrystals in aqueous medium in the range of 25–200 °C using different time 36 h and 72 h. The authors reported the growth and shape of nanocrystals strongly depended on the synthesis temperature. The synthesis process showed that it is possible to control the size, shape, and facets of the nanocrystals simply by tuning the reaction temperature [45]. Li et al. synthesized hematite nanowires

* Corresponding author.
E-mail addresses: bilalalqasem@yahoo.com (B. Alqasem), noorhana_yahya@petronas.com.my (N. Yahya), saima_qureshi_25@yahoo.com (S. Qureshi), irfan-mohammad@hotmail.com (M. Irfan), zia545@hotmail.com (Z. Ur Rehman), hassan.soleimani@petronas.com.my (H. Soleimani).

http://dx.doi.org/10.1016/j.mseb.2016.12.002
0921-5107/

in dispersed and uniform modes using SBA-15 as hard templates by the nanocasting method heated at 550 °C for 6 h. The synthesized hematite nanowires were used in applications involving gas sensors [46]. Other researchers such An et al. studied the morphological effects on the magnetic properties of iron oxide (α-Fe_2O_3) core/shell composite hollow spheres fabricated by a facile hydrothermal method. The authors observed that when the shapes changed from spherical nanoparticles to disk-like nanopetals, the coercivity increased [47]. Hematite nanorods have been fabricated by pulse galvanostatic synthesis in the presence of external magnetic fields. The study showed that when an external magnetic field was used during the electrosynthesis process, a decrease in size and size distribution of particles was observed. In addition, the saturation magnetization of synthesized nanomaterials was improved [48].

The magnetic field is known to strongly influence the yield of chemical reactions due to the transitions from a singlet to a triplet state of reactants [49–51]. As such, the effect of external magnetic field on the rates of chemical reactions and related processes were studied intensely by scientists [52,53]. Green ammonia has been synthesized using a magnetic induction method at ambient conditions [54–57]. This study attempts to modify the magnetic properties of hematite using a novel method of synthesis conducted under the presence of an external magnetic field and a gaseous environment that includes both nitrogen and oxygen. The corresponding magnetically enhanced hematite is to be used as a nanocatalyst to improve the production rate of green ammonia.

2. Experimental

2.1. Synthesis and characterization of α-Fe_2O_3 nanocatalysts

An iron wire (1 mm diameter × 50 mm length) with a purity value of 99.99% (Aldrich) was used as, both a reagent and substrate for the α-Fe_2O_3 nanocatalysts. The growth of the nanocatalysts was carried out by applying a potential difference across ends of the iron wire that leads to its oxidation. Due to the applied DC voltage, the values of current passing through the wire were in the range of 12–20 A, which corresponds to a temperature range of 500–850 °C. An infrared thermometer (DT-1100A) was used to measure the synthesis temperatures. During the synthesis process, the wire was exposed to a 0.25 T external magnetic field in the presence of an oxygen and nitrogen environment as shown in Fig. 1. The gases were used to increase the density distribution of the nanowires. The flow rate of O_2 and N_2 was maintained to 20 sccm and 60 sccm respectively. The flow rate of O_2 and N_2 of (3:1) was chosen as Wen et al. concluded that using this ratio gave good growth results [22]. For the sake of comparison, the experiment was conducted again with absence of magnetic field.

The microstructures and morphology of α-Fe_2O_3 nanostructures were characterized by the X-ray Diffraction (XRD, Bruker D8 Advance, Germany), Field Emission Scanning Electron Microscopy (FE-SEM, Carl Zeiss AG-SUPRA 55VP, Germany) assisted with Energy Dispersive Spectroscopy (EDS), High-Resolution Transmission electron microscopy (HRTEM, Carl Zeiss AG-LIBRA 200FE, Germany) and Raman spectroscopy (Horiba Jobin Yvon-HR800, λ_{laser} = 514 nm) whilst the magnetic properties were verified by a vibrating sample magnetometer (VSM, Lakeshore-7400, USA). For the SEM test, the 5 cm wire sample was placed on the carbon tape pasted on the SEM sample holder. For a single sample five regions, evenly spaced between the two holding clip ends, were studied. The SEM instrument is operated at a voltage ranging between 0.1 kV and 30 kV and a pressure of 2–133 Pa. The images were taken at magnifications of 10, 30 and 50 KX.

To begin the TEM test, a cutter blade is used to scrap off the oxidized surface layer off the sample. After which, a few milligrams of oxide were dispersed in isopropanol solvent and sonicated for an hour. The mixture is then left to precipitate for another hour at room temperature. Correspondingly, two layers were formed consisting of a sediment and a clear solution. One drop of the clear solution was placed on a 300 mesh lacey formvar carbon-coated copper grid. The grid is then transferred to the TEM chamber for observation. A few nanowires and nanoflakes samples were chosen amongst many found within the sample. The samples were chosen based on the clarity. For Raman test, the whole sample was placed on sample holder and the scanning range was set from 100 cm^{-1} to 1800 cm^{-1}.

2.2. Synthesis of ammonia

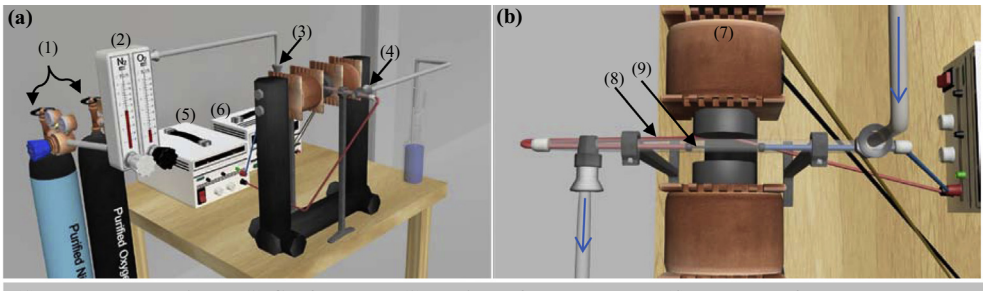
Ammonia was synthesized using the generated α-Fe_2O_3 as nanocatalyst in the presence of an external magnetic field. A special reactor was designed to synthesis ammonia (Fig. 2).

The reactor allows a mixture of pure hydrogen and nitrogen gases to pass over the α-Fe_2O_3 nanocatalyst which was placed between two DC electromagnetic coils. The chemical reaction takes place at an ambient temperature and pressure where the strength of applied magnetic field had corresponding values of 0.4, 0.8, 1.2, 1.6 and 2 T. The flow rates of hydrogen and nitrogen gases, with a ratio of 3:1, were 0.3 L/min and 0.1 L/min, respectively. The generated ammonia gas was collected for 30 min by diluting it in 0.01 M HCl, after which the Kjeldahl titration method was used to quantify the generated ammonia.

3. Results and discussion

3.1. Morphological and structural properties of hematite nanocatalyst

Fig. 3 shows the FE-SEM micrographs for the as-prepared samples obtained by the oxidation of iron wires in the presence and absence of external magnetic field. The morphology changed first from nanoflakes to nanowires, then finally to macro-porous



(1) N_2 and O_2 gas cylinders (2) Gas flow meter (3) The inlet of N_2 and O_2 gases (4) The outlet of N_2 and O_2 gases (5) Power supply (30A) (6) Power supply (10A) (7) Electromagnetic coil (8) Glass tube (9) Iron wire (sample)

Fig. 1. (a and b) front and top 3D schematic view of the experimental setup of nanocatalyst synthesis using O_2 and N_2 as gaseous environment in the presence of external magnetic field.