ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 4, pp. 926–929. © Pleiades Publishing, Ltd., 2015.

Synthesis of Fe_3O_4 Nanowires and Their Catalytic Activity towards Thermal Decomposition of Ammonium Perchlorate[1]

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Received April 17, 2014

Abstract—Uniform single-crystalline Fe_3O_4 nanowires have been prepared at 150°C via a simple hydrothermal route assisted by polyethylene glycol (PEG600). Morphology and molecular structure of the Fe_3O_4 nanowires have been studied by means of scanning and transmission electron microscopy, X-ray diffraction, and infrared spectroscopy. Fe_3O_4 nanowires have been studied as an additive promoting thermal decomposition of ammonium perchlorate; their catalytic performance has been investigated by thermal gravimetric analysis. Temperature of ammonium perchlorate decomposition decreases by about 50°C upon addition of Fe_3O_4 nanowires.

Keywords: ammonium perchlorate, catalytic activity, Fe_3O_4 nanowires, thermal decomposition

DOI: 10.1134/S1070363215040283

One-dimensional (1D) nanostructures such as nanotubes [1], nanofibers [2], nanowires [3], nanorods [4], etc have been paid increasing attention over the recent decades, owning to the unique properties and promising applications in various nanoscale devices [5]. Many papers have focused on preparation of nanoscale materials based on metals and metal oxides (e.g. Ag, Au, Pt, ZnO, SnO_2, TiO_2, MnO_2, Fe_2O_3, Fe_3O_4, etc.) showing novel electronic, optical, catalytic, and magnetic properties [6–9]. Among the 1D-structured materials, magnetite (Fe_3O_4) nanowires have attracted great interest in the magnetic materials field [10] in view of the potential applications as magnetic recording media [11], magnetic supports [12], catalyst [13], ferrofluids [14], etc.

Ammonium perchlorate (AP) is a common oxidizing agent used as component of various propellants [15], and features of its thermal decomposition are highly relevant to combustion behavior of the solid propellants. Extensive studies of AP thermal decomposition have revealed its efficient catalysis with many transition metal oxides [16]. In particular, certain 1D nanostructured metal oxides (e.g., ZnO [17], CuO [18], Fe_2O_3 [19], etc.) can promote AP decomposition.

In this paper, we report on catalytic activity of magnetite (Fe_3O_4) nanowires towards decomposition of AP as studied by TGA and DTG techniques.

Magnetite nanowires were prepared via a facile hydrothermal synthesis in the presence of polyethylene glycol PEG600. The product X-ray diffraction pattern (Fig. 1a) contained the six characteristic reflections at 30.1° (220), 32.3° (311), 43.2° (400), 54.1° (422), 57.5° (511), and 62.6° (440), their relative intensity matching well the reference data for bulk Fe_3O_4 (JCPDS No.190629) [20]. Hence, the crystal structure of the prepared Fe_3O_4 nanowires was confirmed. The product FT–IR spectrum contained an absorption band at 585 cm^{-1}, characteristic of Fe–O vibration [21]. The absence of other characteristic peaks evidenced about high purity of the magnetite material.

Morphology of the prepared samples was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Fig. 2). The samples contained a large fraction of Fe_3O_4 nanowires and a negligibly low fraction of nanoparticles of other shape. The nanowires were 0.19 μm in diameter at the average up to 8 μm long.

The catalytic activity of Fe_3O_4 nanowires was investigated by monitoring thermal decomposition of ammonium perchlorate containing various amounts of the metal oxide additive (0 to 5 wt %) at heating rate of

[1] The text was submitted by the authors in English.

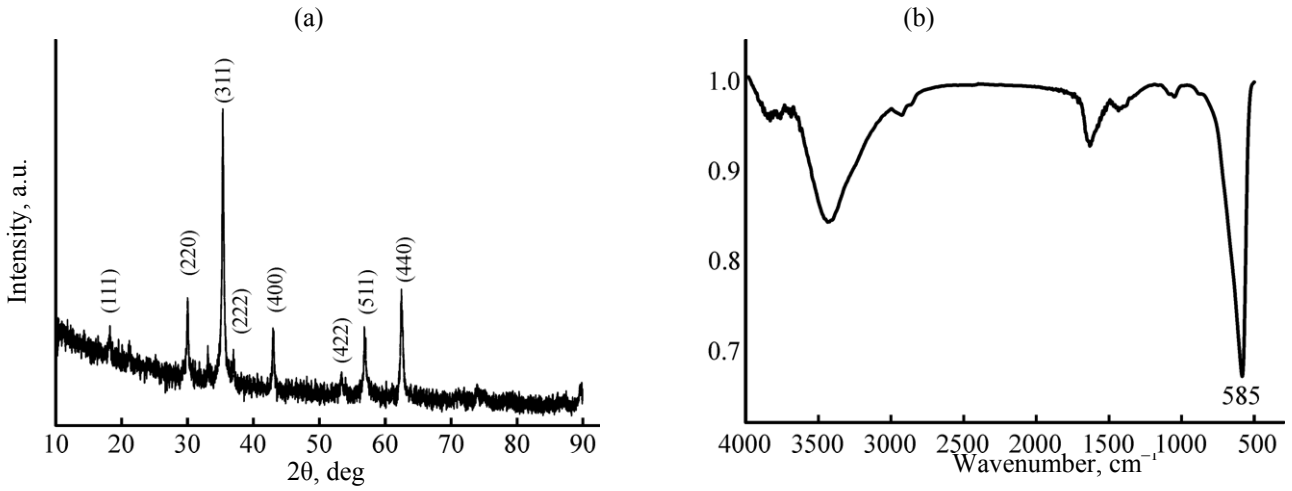

Fig. 1. (a) XRD pattern and (b) IR spectrum of the prepared Fe_3O_4 nanowires.

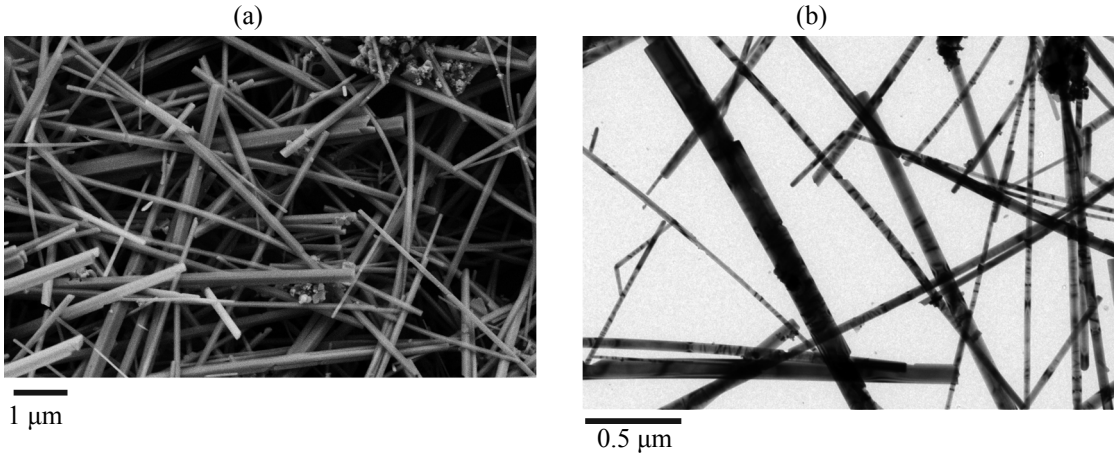

Fig. 2. (a) SEM and (b) TEM images of the Fe_3O_4 nanowires.

15 deg/min (Fig. 3). Thermal decomposition of pure AP occurred in two stages, the temperatures corresponding to the highest mass loss rate being of 345 and 434°C. The presence of Fe_3O_4 nanowires significantly promoted AP thermal decomposition, the corresponding temperatures of the fastest mass loss being of 320 and 405°C (1 wt% of the nanowires), 331 and 393°C (2 wt %), 329 and 391°C (3 wt %), 330 and 387°C (4 wt %), and 330 and 385°C (5 wt %). Noteworthily, temperature of the first stage of AP decomposition was the lowest with 1 wt % of the nanowire and remained somewhat higher and constant at the higher magnetite loadings. At the same time, the temperature of second stage of AP decomposition was steadily lowered with increasing fraction of the nanowires. Hence, the promoting activity of Fe_3O_4 nanowires towards thermal decomposition of ammonium perchlorate was obvious.

Of course, the above-discussed experiment can only demonstrate the catalytic effect qualitatively; however, elucidation of the kinetic parameters is not possible. One of the major reasons complicating the analysis is the additional effect of the heating rate. In particular, the experiment similar to that reported in Fig. 3 run at the variable heating rate (5–25 deg/min). The revealed decomposition temperatures of ammonium perchlorate are tabulated in the table.

It is to be seen that increasing of the heating temperature not only shifted the decomposition to higher temperatures but also improved the apparent catalytic effect of the nanowires addition. Hence, the

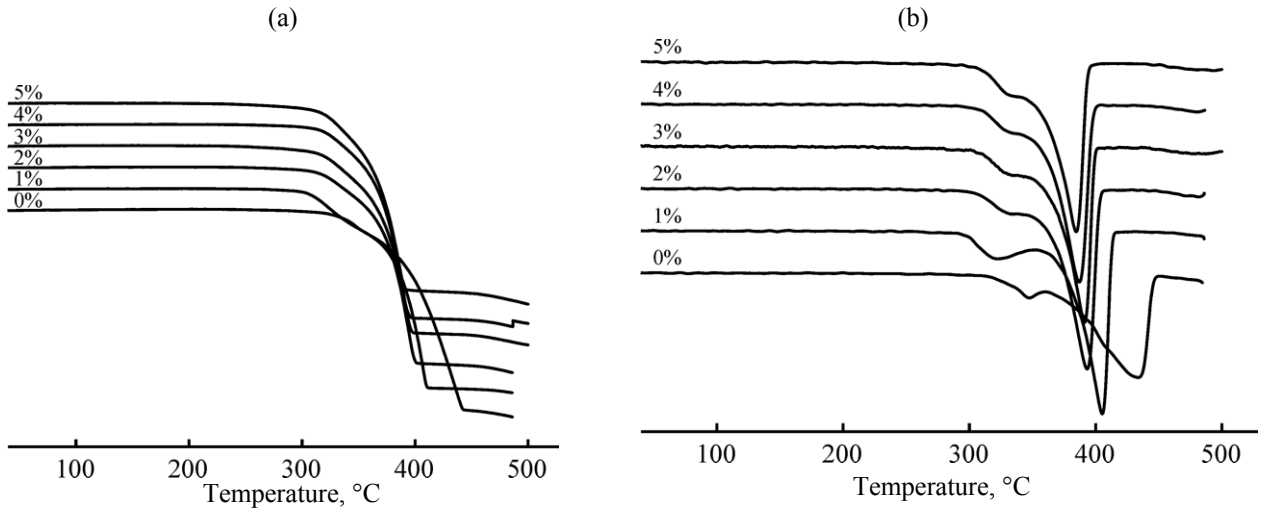

Fig. 3. (a) Loss of mass and (b) differential loss of mass of ammonium perchlorate containing various amounts of Fe_3O_4 nanowires (the mass fractions are shown above the corresponding curves). The curves are vertically shifted for better representation.

heating rate should be taken into account for accurate interpretation of the mass loss curves.

It has been earlier demonstrated that decomposition of AP includes three major processes: the crystal material transformation from orthorhombic into cubic phase (240–250°C), the first decomposition step of AP into NH_3 and $HClO_4$ accompanied with partial sublimation (300–330°C), and the second decomposition step to form N_2O, O_2, Cl_2, H_2O, and other products (450–480°C) [22]. Hence, we concluded that addition of Fe_3O_4 nanowires catalyses the second step of AP decomposition reducing its temperature. In view of the previously reported discussions [23] we proposed the probable mechanism of catalysis of AP thermal decomposition with the Fe_3O_4 nanowires. In detail, Fe_3O_4 provides a bridge for transfer of electrons from perchlorate ions to ammonium ions via the partially filled 3*d* orbital of iron atoms, thus decreasing of activation energy of thermal decomposition of AP.

EXPERIMENTAL

Magnetite nanowires were prepared via a hydrothermal route as described elsewhere [24]. In detail, iron(II) sulfate ($FeSO_4 \cdot 7H_2O$, 3.6 g, 12.8 mmol) and sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, 1.6 g, 6.4 mmol) were mixed, and added to 30 mL of PEG600–water (1 : 3 v/v) mixture. The so prepared solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. Lastly, NaOH (6.4 g, 160 mmol) was added into the autoclave. The autoclave was sealed, maintained at 150°C during 24 h, and then allowed to cool down to ambient. The product was separated via magnetic decantation, washed with deionized water and ethanol several times, and dried in vacuum at 40°C during 4 h.

Thermal decomposition of ammonium perchlorate (analytical grade) was studied by monitoring the mass and the differential mass loss over heating at 40–550°C under nitrogen atmosphere using a Pyris1 thermal analyzer (Perkin Elmer).

Morphology of the nanowires was observed via scanning electron microscopy (HITACHI S4800) and transmission electron microscopy (JEOL 1200EX). X-ray diffraction analysis was performed using a Bruker AXS D8 powder diffractometer (CuK_α radiation, 2θ of 10°–90°, continuous scanning mode). Infrared spectra of KBr pellets were recorded using a Perkin-Elmer IR spectrophotometer.

Decomposition temperatures of ammonium perchlorate

Heating rate, deg/min	Temperature of the fastest mass loss during the second stage of AP decomposition, °C		
	pure AP	AP + 4 wt % of the nanowires	Δ*T*
5	410	368	42
10	428	382	46
15	434	387	47
20	452	402	50
25	458	406	52

ACKNOWLEDGMENTS

This work was partly supported by the fund of Discipline Construction Project of Wenzhou University (no. 316406125020301) and Zhejiang Provincial Top Key Discipline of New Materials and Process Engineering (20110949).

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