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Mixture of fuels for solution combustion synthesis of porous Fe_3O_4 powders

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ABSTRACT

The solution combustion synthesis of porous magnetite (Fe_3O_4) powders by a mixture of glycine and urea fuels was investigated concerning the thermodynamic aspects and powder characteristics. The adiabatic combustion temperature and combusted species were thermodynamically calculated as a function of the fuel to oxidant molar ratio (ϕ). The combustion behavior, phase evolution, porous structure and magnetic properties were characterized by thermal analysis, X-ray diffractometry, N_2 adsorption–desorption, electron microscopy and vibrating sample magnetometry techniques. Nearly single phase Fe_3O_4 powders were synthesized by the mixture of fuels at ϕ values of 0.75 and 1. The as-combusted Fe_3O_4 powders at $\phi = 1$ exhibited porous structure with the specific surface area of 83.4 m^2/g. The highest saturation magnetization of 75.5 emu/g and the lowest coercivity of 84 Oe were achieved at $\phi = 1$, due to the high purity and large crystallite size, inducing from the highest adiabatic combustion temperature.

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1. Introduction

Magnetite (Fe_3O_4) has attracted considerable interest due to its remarkable properties for a wide field of technological applications. The high magnetization, oxidation resistance and biocompatibility of Fe_3O_4 make it very suitable for biomedical applications such as magnetic hyperthermia, magnetic resonance imaging and magnetic drug delivery [1,2]. Moreover, among the transition metal oxides, Fe_3O_4 nanoparticles are more suitable for application as anode materials in supercapacitors, due to high theoretical capacity and high electronic conductivity [3].

Magnetite has a cubic inverse spinel structure and consists of a cubic close packed array of oxide ions where all of the Fe^{2+} cations occupy half of the octahedral sites and the Fe^{3+} cations are equally distributed between the octahedral sites and tetrahedral sites [4,5]. Magnetite has unique electric and magnetic characters, ascribing to electron exchange between Fe^{2+} and Fe^{3+} in the octahedral sites [6]. It is evident that the electric and magnetic performance are very sensitive to the cation distribution, particle size and morphology which strongly depend on the synthesis method [7]. Up to now, several methods like high energy ball milling, coprecipitation, sol–gel, hydrothermal, thermal decomposition of different precursors, spray pyrolysis, carbothermal reduction and solution combustion are applied to synthesize the magnetic Fe_3O_4 powders

with high surface area, small particle size, narrow size distribution and good magnetic properties [8–15]. However, some of these approaches exhibit disadvantages such as complicated equipment, long preparation time, multiple processing steps or environmental pollution, which make them unsuitable for large-scale production economically, or because of environmental concerns [16]. Among the various methods, solution combustion synthesis (SCS) has attracted significant attention due to its simplicity, energy- and time-saving, environmentally friendliness and homogeneous products [17]. SCS involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g. metal nitrates) and fuels (e.g. urea, glycine and hydrazine) [18]. The short process duration and exhausting of various gaseous products during SCS inhibits particle growth and favors the synthesis of powders with high specific surface area [19].

The physicochemical properties of the solution combusted powders such as surface area, particle size distribution, and agglomeration depend on the flame temperature and the amount of released gaseous products, which in turn depend on the nature of fuel and fuel to oxidant ratio [19]. Mixture of fuels approach facilitates the reduction in particle size compared to the product formed using single fuel by a good control over flame temperature and the type and amount of released gaseous products [20]. Deshpande et al. [21] utilized a mixture of the hydrazine and glycine fuels to produce α and γ-Fe_2O_3 powders with high surface area (65 m^2/g). Naveenkumar et al. [22] also reported that the combination of the citric acid, oxalic acid and glycine fuels for

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the synthesis of SrFeO$_{3-\delta}$ catalysts prevents agglomeration of the particles, which in turn leads to decrease in the crystallite size and increase in the specific surface area of the catalysts.

In the present work, the structure, specific surface area and magnetic properties of the iron oxide powders synthesized using the modern fuel-mixture approach (urea and glycine) were reported. Previous works utilized the mixture of urea and glycine at stoichiometric ratio for synthesis of the multicomponent oxide products [20,23], while we investigated the effect of the fuel to oxidant molar ratio (ϕ). Our results showed nearly single phase Fe$_3$O$_4$ powders with a high surface area can be achieved at the low ϕ value of 0.75.

2. Experimental procedure

The required amounts of iron nitrate (Fe(NO$_3$)$_3$.9H$_2$O), glycine (C$_2$H$_5$NO$_2$) and urea (CO(NH$_2$)$_2$) were dissolved in the distilled water. After homogenization, the mixture was poured into a round bottom flask and heated till to transform into a gel while by further heating up to a certain temperature, ignition reaction started from a point and propagated spontaneously. The combustion gases were bubbled in a large beaker filled with water [24]. The obtained powders were hand-crushed with a pestle.

Thermal decomposition of the dried gel at 80 °C was examined by simultaneous differential thermal and thermogravity analysis (DTA/TGA) in air with the heating rate of 5 °C/min on the STA BäHR 503 instrument.

The phase evolution was analyzed by Philips X'pert X-ray diffractometer (XRD) using monochromatic CuKα radiation. The average crystallite size of the samples was also calculated from the width (2 2 0) peak using Scherrer's equation. The XRD patterns were also submitted to a crystal structure analysis by the Rietveld method using MAUD software. The morphology and microstructure of the particles were observed by TESCAN Vega II field emission scanning electron microscopy (FESEM).
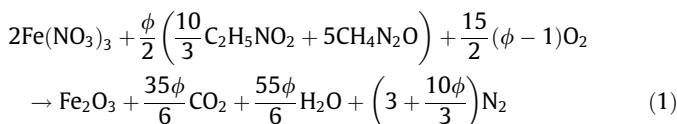
The Brunauer–Emmett–Teller (BET) specific surface area of the powders was measured by the nitrogen gas adsorption technique using a PHS-1020 instrument at 77 K, after the samples were degassed at 250 °C for 5 h. BJH (Barrett–Joyner–Halenda) cumulative volume of pores was calculated from the adsorption branch of the isotherms.

A vibrating sample magnetometer (Meghnatis Daghigh Kavir Co., Iran) was also employed to measure the magnetic properties at room temperature.

The thermodynamic calculations were performed using the FactSage 6.1 software. The equilibrium of adiabatic system including of 2 mol Fe(NO$_3$)$_3$, 10ϕ/6 mol C$_2$H$_5$NO$_2$ and 5ϕ/2 mol CO(NH$_2$)$_2$ was calculated at the various ϕ values (0.25 ⩽ ϕ ⩽ 3) with the initial condition of 298.15 K and 1 atm by Equilib module.

3. Results and discussion

The combustion behavior, oxidation state, morphology and specific surface area of the combusted powders mainly depend on the fuel type and fuel to oxidizer molar ratio, ϕ [25]. The redox processes that are taking place during combustion reactions can be written as follows on the base of the propellant chemistry:

$$2Fe(NO_3)_3 + \frac{\phi}{2}\left(\frac{10}{3}C_2H_5NO_2 + 5CH_4N_2O\right) + \frac{15}{2}(\phi - 1)O_2$$
$$\rightarrow Fe_2O_3 + \frac{35\phi}{6}CO_2 + \frac{55\phi}{6}H_2O + \left(3 + \frac{10\phi}{3}\right)N_2 \quad (1)$$

Here, $\phi = 1$ (stoichiometric) means that the initial mixture does not require atmospheric oxygen for complete fuel oxidation, while $\phi > 1$ (or <1) corresponds to fuel-rich (or lean) conditions.

However, the equilibrium combusted products are generally unknown. Thus, the equilibrium characteristics should be thermodynamically calculated by the free energy minimization method, which considers the contributions of Gibbs free energy for all the components present in the system for providing their concentrations [26]. The equilibrium should also be characterized in the adiabatic condition, no energy loss, on account of the rapid propagation combustion. The adiabatic combustion temperature (T_{ad}) and phase composition (solid, liquid, and gaseous) were calculated by FactSage software and are presented in Fig. 1. Fig. 1a shows the adiabatic temperature (T_{ad}) and the released gaseous products as a function of the fuel to oxidizer ratio (ϕ). The stoichiometric mixture ($\phi = 1$) shows the maximum adiabatic temperature of 2216 K which decreases steadily for either leaner or richer mixture because of the need to heat up either the excess reactants or products [27]. The released gaseous products are mainly CO$_2$, H$_2$O, N$_2$ and O$_2$ for $\phi < 1$ on account of the excess oxidants while the O$_2$ gas vanishes and the H$_2$ and CO gases appear due to the more fuel for $\phi > 1$. Furthermore, the amount of total released gaseous products increases with the increase of ϕ which can influence on the specific surface area. Fig. 1b also shows α-Fe$_2$O$_3$ is only equilibrium solid phase at $\phi < 0.5$ which reduced to Fe$_3$O$_4$ phase for 0.75 < ϕ < 1, and the FeO phase appears for $\phi > 1.25$.

DTA/TGA curves of the dried gel prepared by the mixture of the glycine and urea fuels at $\phi = 1$ are shown in Fig. 2. The vaporization of absorbed water and dehydration reaction lead to the weight loss of $\sim$9% in the temperature range of 25–180 °C. A sharp exothermic peak at 160 °C accompanied by $\sim$50% weight loss can be related to
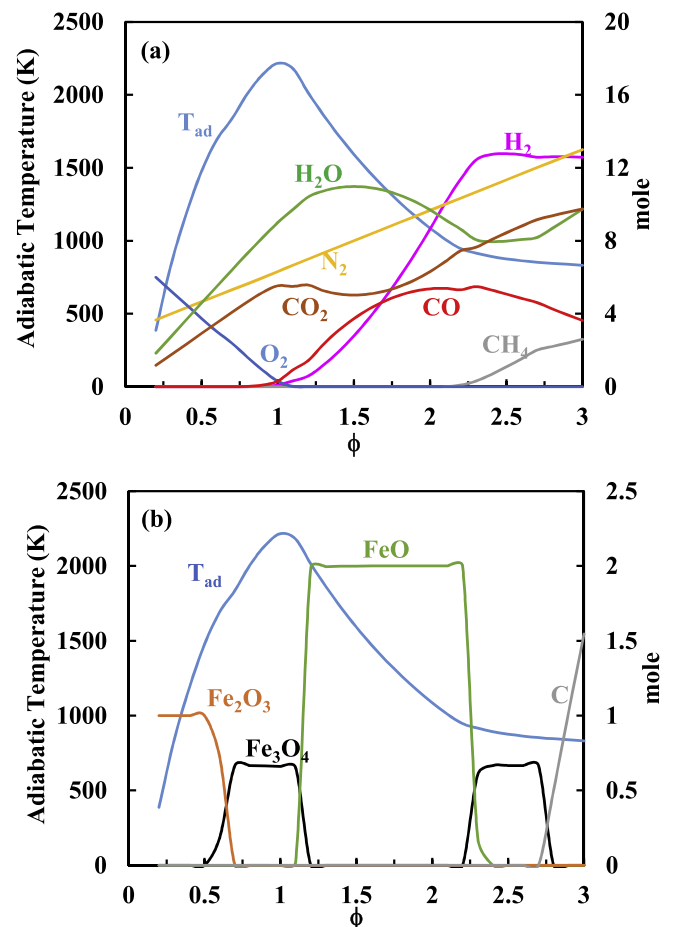

Fig. 1. Dependence of (a) the adiabatic temperature and the released gas species and (b) the equilibrium solid products after combustion by the mixture of glycine and urea fuel on the ϕ values.