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Short communication

Photoinduced structural transformation of $SrFeO_3$ and $Ca_2Fe_2O_5$ during photodegradation of methyl orange

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Abstract

Photodegradation of methyl orange solution under UV light irradiation have been studied over photocatalyst perovskite $SrFeO_3$ and brownmillerite $Ca_2Fe_2O_5$. XRD and FTIR analysis show that both $SrFeO_3$ and $Ca_2Fe_2O_5$ transform to carbonates during the photodegradation process of methyl orange. This result indicates that UV light irradiation induce a photochemical reaction between photocatalysts and CO_2 released from the photodegradation of methyl orange. The photochemical reaction between photocatalysts and CO_2 is responsible for the transformation of the structures. The fact that $SrFeO_3$ has better photocatalytic property and endures serious transformation than $Ca_2Fe_2O_5$ is due to existence of unstable Fe (IV) in the perovskite structure of $SrFeO_3$. Such kind of Fe (IV) makes perovskite structure unstable and sensitive to ambient (especially sensitive to UV light irradiation).

Keywords: Photocatalysis; Brownmillerite; Structural transformation

1. Introduction

Perovskite oxide with the general formula of ABO_3 is a kind of frequently encountered structure in inorganic chemistry. An ideal perovskite structure has an ABO_3 stoichiometry and a cubic crystal structure which is composed of a three-dimensional framework of corner-sharing BO_6 octahedra. In this structure BO_6 octahedron is often considered as the basic cell of perovskite structure [1]. Furthermore most of the properties of perovskite oxides are related to the network of BO_6 octahedra [2] and the state of B-site cations [3,4]. Whereas brownmillerite ($A_2B_2O_5$) is a kind of oxygen-deficient perovskite structure that is composed of perovskite-like three-dimensional framework of corner-sharing BO_6 octahedra alternating with slabs containing rows of corner-sharing BO_4 tetrahedra which are formed by the deficiency of oxygen during the formation of the structure [5–7]. In other words, the structure of brownmillerite oxides can be described as the perovskite structure with 1/6 of the oxygen missing in ordered rows [8].

Both perovskite and brownmillerite have been studied widely. For example perovskites have been used as catalysts for controlled partial hydrocarbon oxidation [9], gaseous pollutant removal [10,11], oxidative dehydrogenation of alkanes [12] and photocatalysis [13] and that $SrFeO_3$ has been extensively studied as ferromagnet and antiferromagnet [14]. Whereas brownmillerites have been widely studied about their structural phase transitions under changing temperature conditions [15,16] and the structural transformation from perovskite structure to brownmillerite structure [17,18]. Due to their sensitivity to changing oxygen pressure and ambient temperature brownmillerite including $Ca_2Fe_2O_5$ exhibit attractive feature for oxygen sensors, oxygen pumps and oxygen permeable membranes [19,20]. The oxygen nonstoichiometry of brownmillerite also changes with oxygen partial pressure and temperature. This is the basis of using brownmillerite as a sorbent for a new high sorption process for air separation and partial oxidation of hydrocarbons [21].

Recently perovskite and brownmillerite have been studied extensively as a kind of promising photocatalyst due to their narrower band gap [22] (often less than 3.0 eV) which can be easily

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excitated under visible light or UV light irradiation. In this paper we discuss the photocatalytic properties and stabilities of photocatalyst perovskite $SrFeO_3$ and brownmillerite $Ca_2Fe_2O_5$ under UV light irradiation. This research will help us make further understanding about perovskite and brownmillerite photocatalysts.

2. Experiment

2.1. Materials

For the preparation of $SrFeO_3$ and $Ca_2Fe_2O_5$, Ferric nitrate (A.R.98.5%), strontium nitrate (A.R.99.5%), calcium nitrate (A.R.99.5%), citric acid (A.R.99.8%), ammonia solution (A.R.25.0%–28.0%) and deionized water were used. And methyl orange (A.R.) was used in photocatalytic experiment.

2.2. Sample preparation

Both $SrFeO_3$ and $Ca_2Fe_2O_5$ were synthesized by citrate-nitrate combustion method. For preparation of samples stoichiometric amount of metal-nitrates (for $SrFeO_3$: ferric nitrate and strontium nitrate; whereas for $Ca_2Fe_2O_5$: ferric nitrate and calcium nitrate) were mixed and dissolved in deionized water to form 0.1 mol L^{-1} solution, and citrate acid were dissolved in deionized water to form 0.5 mol L^{-1} solution (the molar ratio of citrate/metal ions was a little more than 1). Then put the metal-nitrates mixed solution under constant stirring, followed by adding citrate acid solution drop by drop 30 min later. In order to combine citric acid with metal ions adequately ammonia solution was added to the mixed solution to keep the pH at 9 and heat the mixed solution at 70 °C. Constant stirring was used during the whole process. The mixed solution was then polymerized under infrared irradiation for more than 10 h till gel-like product was formed. After drying, this gel-like product was calcined at 450 °C for 2 h to let the product self-ignite and burn off the organic compound in the material, then at 800 °C for 4 h to form their final structure (for $SrFeO_3$: perovskite; whereas for $Ca_2Fe_2O_5$: brownmillerite).

2.3. Photocatalytic properties experiment

The photocatalytic experiment was conducted in homemade photochemistry reactor equipped with 250 W high pressure mercury lamp. In the experiment, the methyl orange solution was 20 mg L^{-1} and the samples used in the experiment were 0.01 g. The absorbencies of the samples were measured via UV-754 UV–vis spectrophotometer at 464 nm. The photocatalytic decoloration rates were computed via the formula: $d = (A_0 - A_i)/A_0$, where A_i is the absorbencies of methyl orange solution measured every 10 min in the process of photodegradation and A_0 is the absorbency of original methyl orange solution.

2.4. Measurement methods

X-ray diffraction measurements were performed on a Rigaku D/MAX 2500PC diffractometer (Cu/50 kV/250 mA, 2θ from 20° to 60°). The FTIR far-infrared spectra of the samples were measured by a Nexus-670 FTIR spectrometer.

3. Results and discussion

3.1. X-ray diffraction analysis

$SrFeO_3$ and $Ca_2Fe_2O_5$ have been synthesized by citrate-nitrate combustion method. Fig. 1 shows XRD patterns of $SrFeO_3$ before (Fig. 1(a)) and after (Fig. 1(b)) photocatalytic experiment. It can be seen from Fig. 1(a) that relative pure perovskite oxide is synthesized with little $SrCO_3$ in it which is regarded as inevitable in the process of synthesizing relevant oxides [23,24]. And from Fig. 1(b) we find that $SrFeO_3$ mostly transforms to $SrCO_3$ after photocatalytic experiment. As regard to such phenomenon, it is believed that during the photocatalytic experiment the whole reaction system is in active circumstances under the UV light irradiation and photochemical reactions are induced between photocatalyst and CO_2 released from the photodegradation of methyl orange. It is due to the fact that a large amount of CO_2 are released constantly during the process of photodegradation of methyl orange and that those CO_2 react with $SrFeO_3$ to form $SrCO_3$. As regard to the potential reactions happened in the whole process of photodegradation of methyl orange solution under UV light irradiation we list the some reactions as below:

$$\text{photocatalyst } SrFeO_3\ (Ca_2Fe_2O_5) + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$e^- + h^+ + H_2O + \text{methyl orange} \rightarrow \text{micromolecular substance} + CO_2 \quad (2)$$

$$\text{photocatalyst } SrFeO_3\ (Ca_2Fe_2O_5) + CO_2 \rightarrow SrCO_3\ (CaCO_3) \quad (3)$$

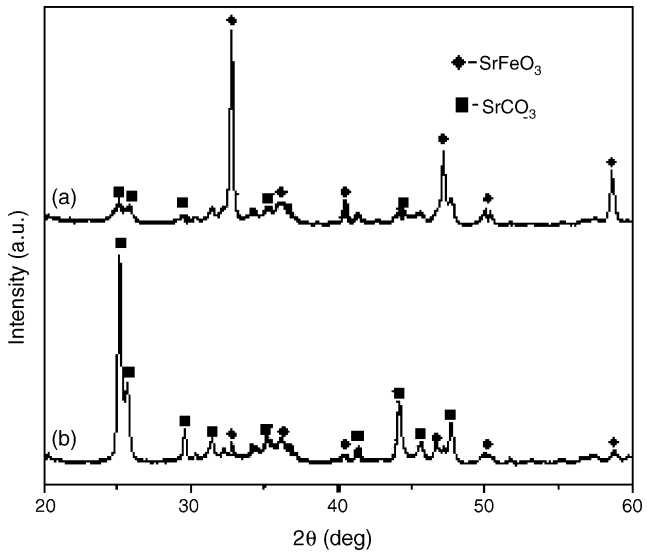

Fig. 1. The XRD patterns of $SrFeO_3$ before and after photocatalytic experiment ((a) before photocatalytic experiment; (b) after photocatalytic experiment; (♦) $SrFeO_3$ and (■) $SrCO_3$).