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Decomposition of crude oil absorbed into expanded graphite/TiO_2 /NiO composites

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ABSTRACT

Expanded graphite/TiO_2/NiO (EG/TiO_2/NiO) or EG/TiO_2 composites were prepared by abruptly heating a mixture mainly consisting of expandable graphite, titanium isopropoxide and nickel containing compound or a mixture mainly consisting of expandable graphite and titanium isopropoxide at around 1000 °C, respectively. The products were characterized by X-ray diffractiometer (XRD) and scanning electron microscope (SEM). The decomposition degree of the crude oil absorbed into the EGs was evaluated by FT-IR spectroscopy. Results show that the crude oil absorbed into pure EG, EG/TiO_2/NiO and EG/TiO_2 all could be decomposed under UV irradiation, and the sequence of decomposition degree of the absorbed crude oil in the three cases could be concluded as: EG/TiO_2/NiO > EG/TiO_2 > pure EG.

1. Introduction

In recent years, using expanded graphite (EG) for removing spilled oils in water has attracted great attention of researchers due to its high sorption capacity of heavy oils [1–4]. It is reported that 1 g of EG could absorb more than 80 g heavy oil and the sorption could occur very rapidly [5]. However, the reproducibility of the EG as an absorbent is unsatisfactory, which has become one of the main factors obstructing its practical application. In order to improve the reproducibility of EG, the oil absorbed in the EG must be removed as completely as possible. By a simple compression on the absorbed EG, about 80% of the absorbed heavy oil could be squeezed out [6]. However, compression could lead to serious demolishment for the characteristic pore texture of the EG, which is the key factor determining the high sorption capacity of EG. In addition, about 70% of the heavy oil in EG also could be recovered by a filtration with suction at room temperature and the recovered oil had the same nature as the original, but the sorption capacity of EG decreased markedly with its recycling [7].

The photo-catalytic activity of TiO_2 is of a continuous interest and it has the ability to decompose oil in soil [8], or in water [9]. In 2002, M. Toyoda [10] and T. Tsumura [11] have loaded TiO_2 catalyst on EG. They found that loading TiO_2 on EG could accelerate markedly the decomposition of heavy oil in EG. Recently, there has been an increase in the research on photo-catalytic activity of TiO_2/NiO system photo-catalyst, and some significant results of experimental study were reported [12–14]. However, up to now, none of these studies has been focused on the photo-catalytic activity of TiO_2/NiO for oils. In present work, therefore, we attempted to investigate into the effect of TiO_2/NiO-loading on the decomposition rate of the crude oil absorbed in EG.

2. Experimental

2.1. Materials

Natural flake graphite (35 mesh, 99 purity) was provided by Qingdao Tianhe Graphite Company, China. Sulfuric acid (98%) (CAS: 7664-93-9), hydrogen peroxide (30%) (CAS: 7722-84-1), tetrabutyl titanate (CAS: 5593-70-4), Ni $(NO_3)_2 \cdot 6H_2O$ (CAS: 13478-00-7), ammonia (CAS: 1336-21-6), polyethylene glycol (CAS: 25322-68-3) and other chemicals used in the experiments were of analytically pure grade and provided by Qinhuangdao Chemical Reagent Company, China. Crude oil (density of 837 kg/m^3, viscosity of 0.602 Pa s, asphaltenes of 1.2 wt.%, sulfur of 0.49 wt.%) was provided by Qinhuangdao Port Office.

2.2. Preparation

Tetrabutyl titanate (6 mL) was dissolved in isopropyl alcohol (30 mL) at room temperature, stirred for 1 h, forming solution A. In a 200 mL beaker, Ni $(NO_3)_2 \cdot 6H_2O$ (1.2 g) and Polyethylene glycol (0.19 g) were dissolved in distilled water (60 mL) and stirred for 1 h. Afterwards ammonia (0.45 mL) was added slowly into the beaker, stirred at 80 °C for 1 h, forming solution B.

Expandable graphite was prepared from natural flake graphite (6 g) by chemical intercalation using sulphuric acid (10 mL) as intercalation agent and hydrogen peroxide (1.0 mL) as oxidant, washing and drying. The detailed preparation process of expandable graphite was described in reference [1]. Expanded graphite (EG) could be obtained by abruptly heating the expandable graphite at 1000 ° for 20 s.

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Table 1
Expanded volumes and sorption capacities of EG and the composites.

Sample	Expanded volume (ml/g)	Sorption capacity for crude oil (g/g)
Pure EG	250	70
EG/TiO_2	200	55
EG/TiO_2/NiO	205	56

EG/TiO_2/NiO was prepared as follows: expandable graphite was mixed with solutions A and B, placed at 30–40 °C for 3 days and dried at 70 °C for 24 h, finally heated at 1000 °C for 20 s. The preparation process of EG/TiO_2 was similar to that of EG/TiO_2/NiO. EG/TiO_2 was obtained by mixing the expandable graphite only with solution A instead of solutions A and B. The theoretical TiO_2 content in EG/TiO_2 thus prepared was 16 wt.%, while the theoretical contents of TiO_2 and NiO in EG/TiO_2/NiO thus prepared were 13 and 3 wt.%, respectively. The expanded volumes and sorption capacities for crude oil of EG, EG/TiO_2 and EG/TiO_2/NiO were shown in Table 1.

2.3. Characterization

The crystal phase composition of the composites was determined by X-ray diffractometer (D/max-rB, Rigaku, Japan) with a CuK_α ($\lambda = 0.15406$ nm) monochromatized radiation source, operated at 40 KV and 40 mA, and the morphology of EG/TiO_2/NiO was observed by means of a KY2828 type scanning electron microscope (SEM).

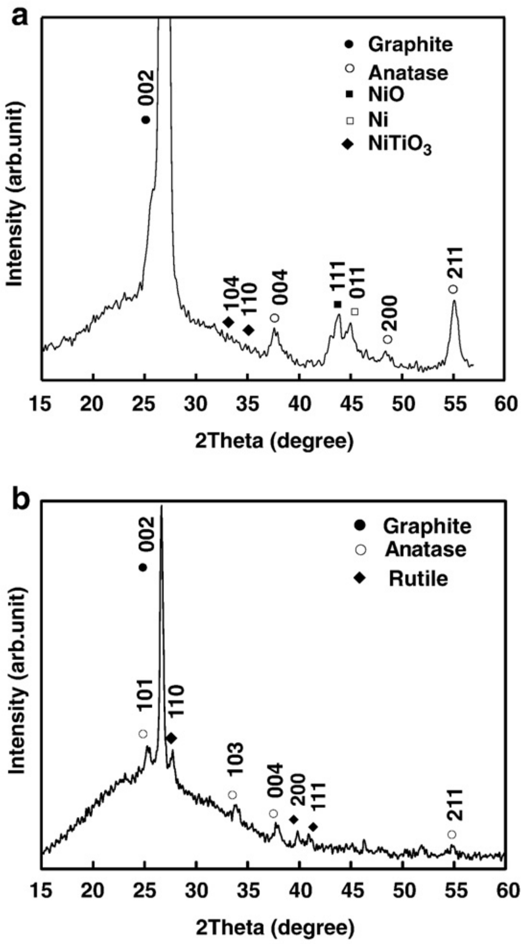

Fig. 1. XRD patterns of (a) EG/TiO_2/NiO and (b) EG/TiO_2.

2.4. Evaluation of decomposition of absorbed crude oil

100 mg of the composites was mixed with 2 ml of crude oil, which was much smaller than the maximum sorption capacity of the composites (Table 1). The resultant mixture was placed in a culture dish and irradiated by UV with the intensity of 20 W/m^2. At different irradiation times, the decomposition of the crude oil absorbed into pure EG, EG/TiO_2 and EG/TiO_2/NiO was evaluated, respectively, by using Fourier Infrared/Roman Spectrometer (E55 + FRA106, Germany).

3. Results and discussion

3.1. X-ray diffraction and SEM observation of the composites

Fig. 1 (a) and (b) presents the X-ray diffraction patterns of the EG/TiO_2/NiO and EG/TiO_2, respectively. In Fig. 1 (a) and (b), in addition to the graphite (002) diffraction peaks, the anatase-type TiO_2 diffraction peaks all can be clearly seen. It is well known that the (101) diffraction peak is strongest line for anatase, however, the anatase (101) peak is relative weak in comparison with the (103, 004 and 211) peaks on EG/TiO_2 (Fig. 1b) and hardly observed on EG/TiO_2/NiO (Fig. 1a). This indicates the anisotropic growth of the crystallites, and the similar phenomenon also can be observed in Ref. [10] and [11]. Several weak rutile-type TiO_2 diffraction peaks can be observed on EG/TiO_2, while

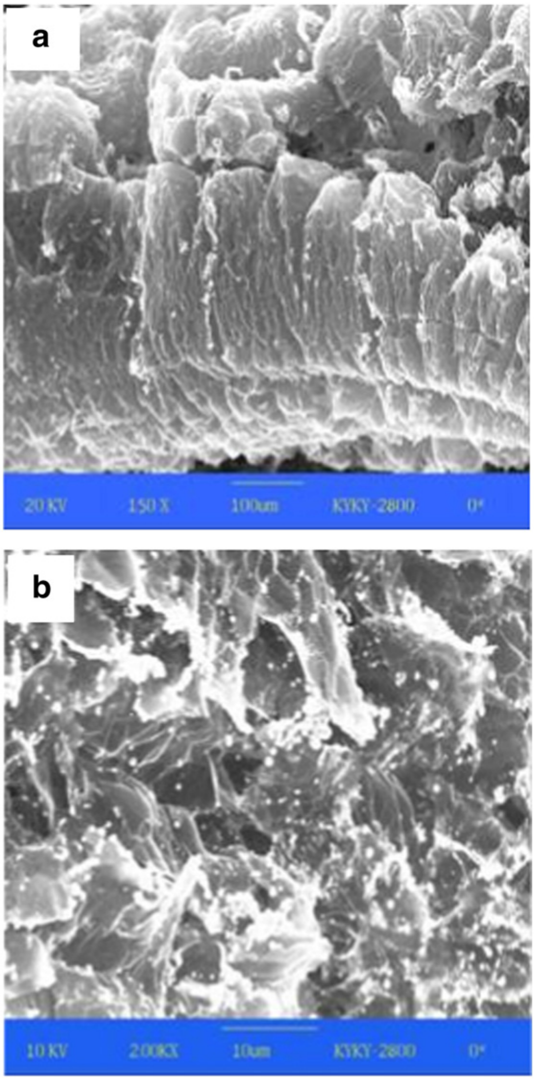

Fig. 2. SEM micrographs of EG/TiO_2/NiO: (a) 150×; (b) 2000×.