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Research Article

Preparation and Its Adsorptive Property of Modified Expanded Graphite Nanomaterials

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Modified expanded graphite (MEG) samples were prepared by strong acid treatment modification. As-prepared MEG samples were characterized by the means of FE-SEM, XRD, FT-IR, N_2 physical adsorption measurements, and TG-DTA. The influences of expanded volume and oil viscosity on adsorptive property of MEG samples were investigated. The results suggest that MEG samples have high crystallinity. The pores of MEG samples can be divided into three levels from FE-SEM images. All of the functional groups of MEG samples are nonpolar. The expansion temperature of modified expansible graphite starts at about 700°C. The sorption capacity of MEG increases gradually with expanded volume and oil viscosity increase. When the expanded volume of MEG samples is 320 mL/g, its maximum sorption capacity is up to 84.681 g/g for gear oil with the highest viscosity.

1. Introduction

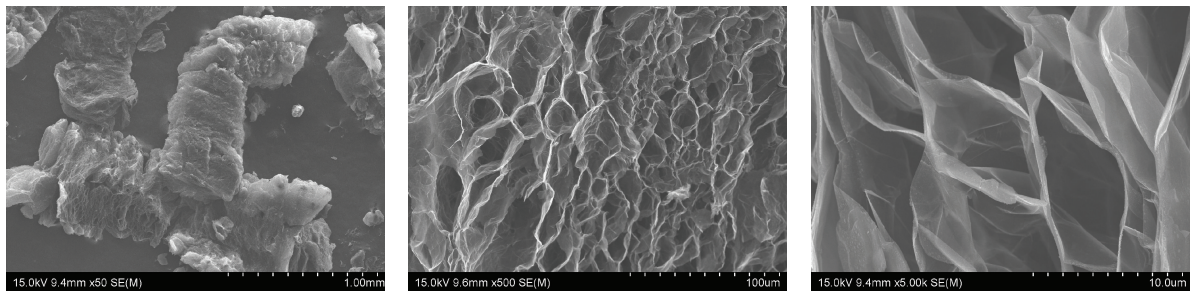
In recent years, the spill oils pollutions have caused extensive and widespread concerns. Spill oils not only severely pollute the marine environment but also threaten the human lives. The expanded graphite (EG) with a majority of macropores [1–3] and nonpolar surface make it as an excellent material for absorbing nonpolar and macromolecular compounds, especially for various kinds of oils. EG has been usually prepared through the sequential intercalating, washing, drying, and puffing from the natural flake graphite [4, 5]. Many scholars have paid more attention to research the relationships between the preparation conditions, pore structure, and its sorption capacities [6–8]. Furthermore, EG has also been widely applied in waste gas removal [9], catalysts carrier [10–12], medical materials [13], and many other fields [14–16]. However, EG has some disadvantages such as fragile, light mass and low expanded ratio by one step processing, so that a lot of studies have been focused on its modification researches [17–25]. The modification methods for EG mainly include strong acid treatment modification, in-situ modification, surfactant modification, and surface coating modification [26, 27].

In this paper, H_2O_2 was used as the oxidant, concentrated H_2SO_4 was used as the intercalator, and the MEG samples were prepared by strong acid treatment modification. The MEG samples were characterized by FE-SEM, XRD, FT-IR, N_2 physical adsorption measurements, and TG-DTA. Six kinds of industrial oils such as gasoline, kerosene, diesel oil, machine oil, crude oil, and gear oil were used as sorbents to investigate the sorption capacity of MEG samples.

2. Experimental

2.1. Materials. 3599-flake graphite, concentrated H_2SO_4 (98 wt.%), H_2O_2 solution (30 wt.%), distilled water, gasoline, kerosene, diesel oil, machine oil, crude oil, and gear oil were used.

2.2. Preparation. Weighed 2 g of expansible graphite was put into a beaker, and then it was mixed with concentrated H_2SO_4



(a) (b) (c)

Figure 1: FE-SEM images of the MEG samples.

and H_2O_2 solution (volume ratio 10 : 1.5) and was stirred with them until it formed an even mixture. Then, the beaker was put in the water bath at 45°C, and the mixture was stirred vigorously for 90 min. After the mixture was washed and dried, the expansible graphite was obtained. Weighed 2 g of expansible was put graphite into a beaker, and then the expansible graphite was mixed with concentrated H_2SO_4 and H_2O_2 solution (volume ratio 10 : 1.25) again, and the obtained mixture was also stirred vigorously at 45°C for 90 min. After the mixture was washed and dried and calcined at 900°C for 15 s in a muffle furnace, the preparation of MEG samples was accomplished.

2.3. Characterization. The morphology of MEG samples was studied by the field emission scanning electron microscopy (FE-SEM) of S4800. The crystal structure of the samples was determined by the X-ray powder diffractometer (XRD) of D/MAX-rB, which was radiated by Cu Kα with the pipe pressure of 40 mV, the wavelength (λ) is 1.54056 Å, and the diffraction angle is in the range of 10°–80°. The chemical functional groups in the samples were analyzed by the Fourier transformation-infrared spectroscope (FT-IR, EQUINOX55). The N_2 adsorption-desorption isotherms and pore size distribution plots were measured by NOVA4000e automatic physical adsorption apparatus, and the measurement was performed at 77 K, the outgas temperature was 250°C, and the BJH modeling was used for the pore size determination. Moreover, the thermogravimetric analysis and differential thermal analysis (TG-DTA) curves of the samples were carried out by CRY-2P and WRT-3P analyzer. The atmosphere set during the analysis was argon, and the heating rate was 10°C/min.

2.4. Adsorptive Property. A certain amount of seawater and some kind of industrial oils were added into the 200 mL beaker to simulate the spill oil on the sea. m g of MEG samples was immersed into the liquid mixture, and then MEG samples that absorbed oil and seawater mixture was put on the funnel covered with filter screen (mass m_0, g) until the MEG samples have reached the saturation adsorption amount and weighed MEG samples with filter screen (mass m_1, g) at that time. The sorption capacity (mass m_2, g/g) of the MEG samples can be calculated by the following formula:

$$m_2 = \frac{m_1 - m_0 - m}{m}. \quad (1)$$

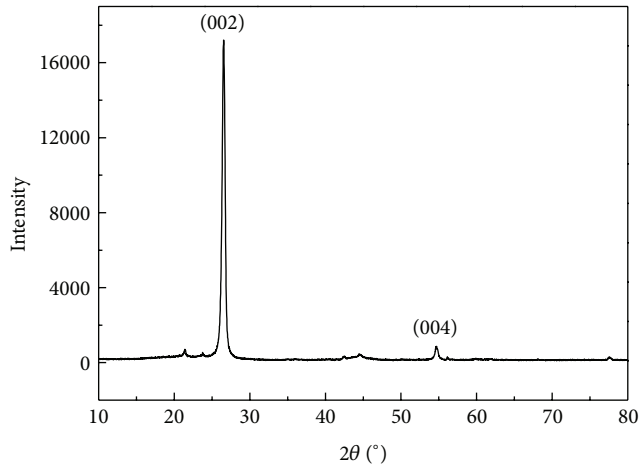


Figure 2: XRD pattern of the MEG samples.

3. Results and Discussion

3.1. FE-SEM Analysis. Figure 1 shows FE-SEM images of the MEG samples. The morphology of the MEG samples is worm-like as shown in Figure 1(a), and there are a lot of V-type pores that can also be observed on the surface. These V-type pores with dimension from several dozens of μm to several hundreds of μm are the I level pores, the willow leaf-type pores with dimension from several μm to several dozens of μm as shown in Figure 1(b) are ascribed to the II level pores. The pores with dimension from 0.1 μm to several μm as seen from Figure 1(c) come from the up and down on the pore walls of the II level pores and are assigned to the III level pores in the MEG samples. It is the particular loose and porous structures that would provide MEG samples with good adsorption property for the macromolecular compounds.

3.2. XRD Pattern. XRD pattern of the MEG is shown in Figure 2. There are two obvious characteristic diffraction peaks located at 2θ equal to 26.4° and 54.9°, which corresponded to the (002) and (004) crystal planes, respectively. Crystal phase composition of MEG samples is identified as graphite-2H phase according to the standard card of PDF number 41-1487. Thus, it can be inferred that the MEG samples still maintain the crystal structure of natural graphite itself [28], and it also belongs to the graphite crystal.

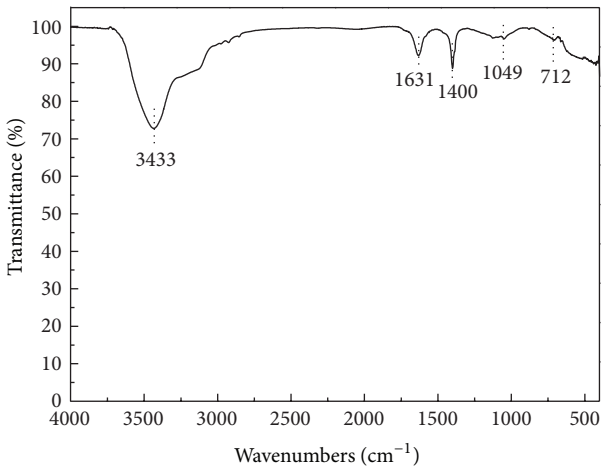


Figure 3: FT-IR spectra of the MEG samples.

3.3. FT-IR Spectra. Figure 3 displays FT-IR spectra of the MEG. The peaks at 3433 cm^{-1} and 1631 cm^{-1} are described as stretching vibration absorption peak and deformation vibration absorption peak from water molecules, respectively. They may be derived of adsorbed water from MEG samples and potassium bromide crystal used for pressing pieces and the surface hydroxyl group. The strong peak at 1400 cm^{-1} is considered the absorption of the methylene fat hydrocarbon from graphitic carbon skeleton. A weak absorption peak at 1049 cm^{-1} belongs to stretching vibration of C–O–C. The weaker peak at 712 cm^{-1} corresponds to the absorption of SO_4^{2-}, and this may be related to inadequate expansion of modified expandable graphite under heat treatment. The results indicate that a large number of intercalator groups basically disappear after high temperature expansion, and MEG samples can be assigned to nonpolar materials.

3.4. N_2 Physical Adsorption Analysis. N_2 adsorption-desorption isotherms and pore size distribution plots of the MEG are illustrated in Figure 4. The adsorption-desorption isotherms correspond to the typical type II isotherms (IUPAC, 1985), suggesting the existence of macropores and showing an unobvious hysteresis between adsorption and desorption isotherms.

As shown in Figure 4, there is a small fraction of mesopores in the MEG samples, and the pore diameter is from 2 nm to 7 nm. These pores with nanometer scale within 100 nm are attributed to the III level pores of the MEG. Combining with FE-SEM analysis results, the present work divides the pores of MEG into three levels, and it is in agreement with reports [29–31] in the literature. In addition, according to the N_2 physical adsorption analysis results, the BET specific surface area of the MEG samples is 26 m^2/g, and the pore volume of the MEG samples is 0.069 cm^3/g by the BJH modeling.

3.5. TG-DTA Analysis. Figure 5 describes TG-DTA curves of modified expandable graphite. As shown in Figure 5, there is an endothermic peak at 60°C, and the corresponding mass loss appears in the TG curve, which inferred that some amount of absorbed water in the samples has been evaporated. Another endothermic peak appears at 225°C in the DTA curve, which is attributed to the dehydration of bound water. There is a broad and strong endothermic peak at 700°C in the DTA curve, and there is obvious mass loss in the TG curve accordingly. This could be ascribed to the decomposition of H_2SO_4-GICs (graphite intercalation compounds) and the burn of graphite, so some S–O and CO_x species diffuse out of graphite gallery. The results show that the onset expansion temperature of modified expandable graphite should be scheduled at 700°C by using muffle furnace.

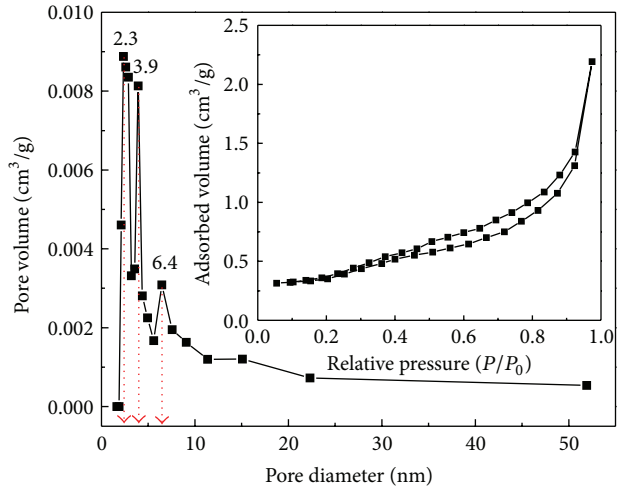


Figure 4: N_2 adsorption-desorption isotherms and pore size distribution plots of the MEG samples.

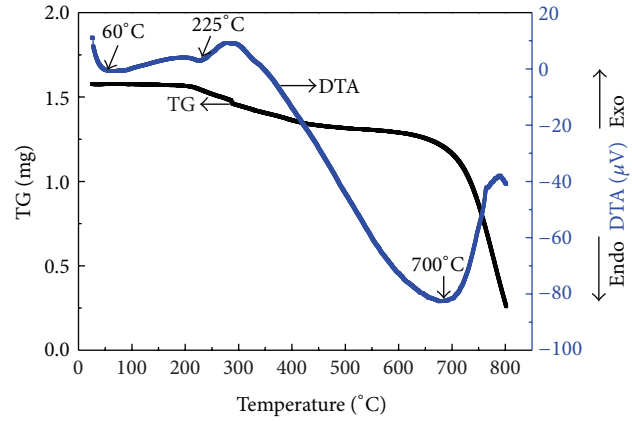


Figure 5: TG-DTA curves of MEG precursors.

3.6. Adsorptive Property

3.6.1. Influence of Expanded Volume on Adsorptive Property of the MEG. The maximum sorption capacity of MEG with different expanded volume for kerosene, crude oil, and gear oil is shown in Figure 6. For the same kind of oil, the maximum sorption capacity of MEG increases gradually with the increase of the expanded volume. When the expanded volume of MEG varies between 100 mL/g, 150 mL/g, 190 mL/g, 250 mL/g, and 320 mL/g, the maximum sorption capacities

Table 1: The effect of oil viscosity on sorption capacity of the MEG.

Kinds	Gasoline	Kerosene	Diesel oil	Machine oil	Crude oil	Gear oil
Viscosity (Pa·s)	0.001	0.002	0.008	0.156	0.626	1.407
Oil absorption (g/g)	43.25	47.657	50.879	55.128	65.537	84.681

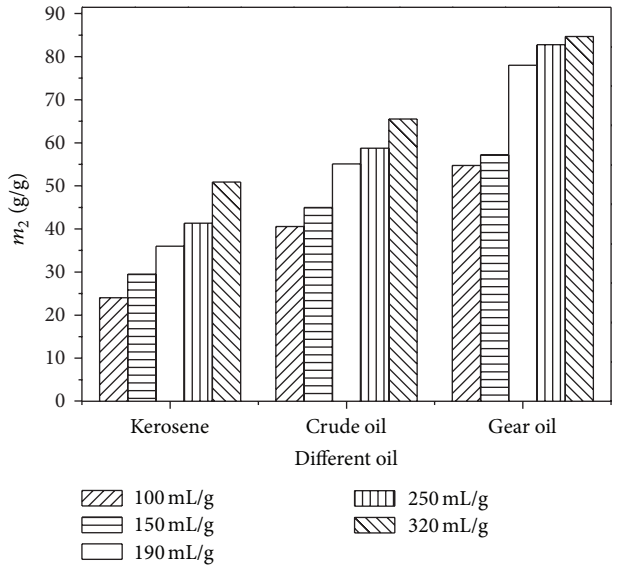


Figure 6: The effect of expanded volume on sorption capacity of the MEG samples.

for gear oil are 54.741 g/g, 57.192 g/g, 78.004 g/g, 82.802 g/g, and 84.681 g/g, respectively. Moreover, for the same expanded volume, the maximum sorption capacities arrange in the order of gear oil > crude oil > kerosene. When the expanded volume of MEG is 320 mL/g, the maximum sorption capacities of MEG samples are 50.879 g/g, 65.537 g/g, and 84.681 g/g for kerosene, crude oil and gear oil, respectively. The reasons are as follows: the I level V-type pores make the main contributions to the formation of MEG intertwining space, and the II level willow leaf-type pores constitute a unique internal storage space. So the synergy between the I level pores and the II level pores provides MEG samples with outstanding adsorptivity for several industrial oils [32]. Moreover, the number of the I and II level pores increases with expanded volume increase. So that with the expanded volume increasing, the sorption capacity of MEG samples for oils also increases obviously. The maximum sorption capacity of MEG samples for gear oil is up to 84.681 g/g.

3.6.2. Influence of Oil Viscosity on Adsorptive Property of the MEG. The effect of oil viscosity on sorption capacity of the MEG is listed in Table 1. The results show that the oil viscosity has a great influence on the sorption capacity of MEG, and the maximum sorption capacity of MEG increases gradually with the increase of the oil viscosity for the same expanded volume. For the low viscosity oil, such as gasoline, kerosene and diesel oil, the maximum sorption capacities of MEG are 43.25 g/g, 47.657 g/g and 50.879 g/g, respectively. For the high viscosity machine oil and crude oil, the maximum sorption capacities of MEG are 55.128 g/g and 65.537 g/g, respectively. And for the highest viscosity gear oil, the maximum sorption capacity of MEG can be up to 84.681 g/g. The main reason probably is that the higher viscosity oil has the higher glutinosity and density, and lower liquidity. In other words, high viscosity will be beneficial to the adhesion of MEG and oils.

4. Conclusions

To expand and develop the expanded volume of EG and MEG samples were prepared by the strong acid treatment modification. According to above characterization and experiment results, the MEG samples have high graphite crystallinity. The pores of MEG samples can be divided into three levels by FE-SEM. All of the functional groups of MEG samples are nonpolar. The expansion temperature of modified expansible graphite starts at about 700°C. The sorption capacity of MEG increases gradually with the expanded volume and oil viscosity increase. When expanded volume of MEG samples is 320 mL/g, the maximum sorption capacity is up to 84.681 g/g for gear oil with the highest viscosity. It is the property of multipores and worm-like structures that provide the MEG with high sorption capacity, and it will be a kind of promising adsorptive material in the future.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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