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Expanded graphite applied in the catalytic process as a catalyst support

Wei Li *, Chong Han, Wei Liu, Minghui Zhang, Keyi Tao

Department of Materials Chemistry, Nankai University, Tianjin 300071, PR China

Abstract

An amorphous NiB supported on expanded graphite (EG) catalyst was prepared as an example to show the superior characteristics of EG as a novel carbon support material. EG and the prepared catalysts were characterized by mercury porosimetry, inductively coupled plasma spectrometer (ICP), scanning electronic microscopy (SEM), transmission electron microscope (TEM) and selected area electron diffraction (SAED). The catalytic activities of prepared catalysts were investigated by the hydrogenation of sulfolene to sulfalone and the selective hydrogenation of *p*-chloronitrobenzene (p-CNB) to *p*-chloroaniline (p-CA). We showed that the prepared Ni-B/EG catalyst exhibited very high catalytic activity.
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Keywords: Amorphous NiB; Expanded graphite; Catalyst

1. Introduction

Recently, amorphous alloys have received great attention [1–4] due to their special structures and promising properties, and in particular, their superior catalytic activity in hydrogenation. In a previous study, we investigated the possibility of developing amorphous alloys supported catalyst to replace the Raney Ni catalyst in the hydrogenation catalysis process [1,2,5,6], as the Raney Ni catalyst is toxic to the environment. However, it is difficult to find the ideal support material to prepare the amorphous alloys supported catalyst as the catalyst is prepared in an intensely alkali solution, and therefore, Al_2O_3 and SiO_2 are not suitable for use. As a result, heavy MgO demonstrated the best performance in our previous studies [1,2,5,6]; however, MgO is not an ideal support due to its low surface area and the fact that is unstable in aqueous solution. In addition, all the supports mentioned above are not easy to separate from production at the end of the reaction. Thus, a suitable support to speed up the development process of amorphous alloy supported catalysts is required.

Carbon materials have long been used in heterogeneous catalysis as they satisfy most of the characteristics required for a suitable support: chemical inertness (resistance to both acidic and basic media), porosity, large surface area and facility in recovery of metals, especially precious metals by support burning. Several types of carbon materials have been used to prepare carbon-supported catalysts (activated carbon, activated carbon fiber, graphite, carbon black, graphite intercalation compounds, etc.) [7,8]. Recently, new carbon forms such as carbon nanotubes and magnetically separable carbon materials have generated an intense effervescence in the scientific community [9–12]; however, their high cost has limited their practical utility in industrial catalysis. Herein, we report a new carbon support material—expanded graphite (EG) that demonstrates good performance in the preparation of supported amorphous alloys catalyst.

Graphite is the most stable allotrope of carbon in STP conditions, and there is a vast amount of natural graphite mined worldwide, however, very little graphite is currently used as a catalyst support due to its low surface area. However, the special sandwich structure and long distance between the carbon layers have made it easy to insert atoms or molecules between the carbon layers; heating the graphite intercalation compounds induces the vaporization of the intercalated species and hence, a significant expansion of the material along the crystallographic *c*-axis occurs, and porous expanded graphite is obtained. The morphology and pore structure of EG can be modified by altering preparation conditions, and there are many reports on preparation procedures, pore structure and application of EG [13–18]. Although EG has been widely used in gasketing, adsorption, electromagnetic interference shielding, vibration damping, electrochemical applications, stress sensing

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* Corresponding author. Tel.: +86 22 23508662; fax: +86 22 23508662.
E-mail address: weili@nankai.edu.cn (W. Li).

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and thermal insulator, relatively few reports concerning the use of EG as catalyst support can be found in the literature [19]. Therefore, in the present paper, we will illustrate the superior properties of EG and discuss its performance as a novel catalyst support.

2. Materials and methods

Expanded graphite was prepared from flake graphite. Flake graphite, concentrated sulfuric acid and potassium permanganate were mixed in a flask at a weight ratio of 5:30:1, with stirring at 318 K for 30 min. The filtrated product was then dried at 393 K for 2 h after washing thoroughly with distilled water. Expansion occurred in a laboratorial microwave oven (NJL07-3) at 750 W. After approximately 10 s microwave irradiation, the wormlike expanded graphite was obtained. The simple mechanism of the preparation process and the micrograph of flaky graphite and EG are shown in Fig. 1. The prepared wormlike EG was broken up in shorter fragments by Supperfine Homegenizers (FLUKO FA25), the sample was washed with NaOH (0.1 mol/l) aqueous solution and distilled water to remove the remaining acid on EG and the filtrated specimen was dried at 393 K for 6 h, and then sieved to 200 μm. The surface area and the pore size distribution of the sample were measured by mercury porosimetry (Thermo-Finnigan PASCAL 440).

The NiB/EG catalyst was prepared by metal inductive powder electroless plating (MIEP) method. Precursor Ag_2O/EG (2.3 g) (prepared by impregnation and loading of Ag at 2000 ppm) was added to an electroless plating solution containing $NiSO_4 \cdot 6H_2O$ (2.699 g), $NH_2CH_2CH_2NH_2$ (2.47 g), NaOH (6.9 g), KBH_4 (0.836 g) and H_2O (240 ml), with stirring for approximately 0.5 h at 318 K. After the plating was finished, the product was washed with distilled water and absolute alcohol orderly, then dried at 393 K for 0.5 h. A NiB/MgO catalyst was prepared using the same method for comparison purposes. The chemical composition of these catalysts was analyzed by inductively coupled plasma spectrometer (ICP) analysis on IRIS Intrepid. Surface morphology and dispersion of NiB clusters on EG were characterized by field emission scanning electronic microscopy (SEM) performed on a LEO 1530VP, and the high resolution transmission electron microscope (HRTEM, JEOL-2010 FEF) with a TOPCON 022B microscope operated at 160 kV. The selected area electron diffraction (SAED) pattern was obtained using a JEOL-2010 FEF operated at 80 kV (beam size, ~40 nm) to analyze the crystallinity of NiB alloys.

The catalytic activities of these catalysts were tested by the hydrogenation of sulfolene to sulfalone and selective hydrogenation of p-CNB to p-CA without diffusion effects. The Raney Ni is used in the hydrogenation process in industry. The hydrogenation reaction of sulfolene was performed at 318 K and 2.5 MPa of hydrogen pressure in a 100 ml stainless autoclave which contained 0.6 g catalyst, 30 g sulfolene and 30 ml distilled water. The mixture was stirred at 800 rpm for 2.5 h. Similarly, the hydrogenation reaction of p-CNB was carried out in a high stainless autoclave. Typical reaction conditions were: p-CNB 8.0 g, catalyst 0.8 g, 48 ml absolute

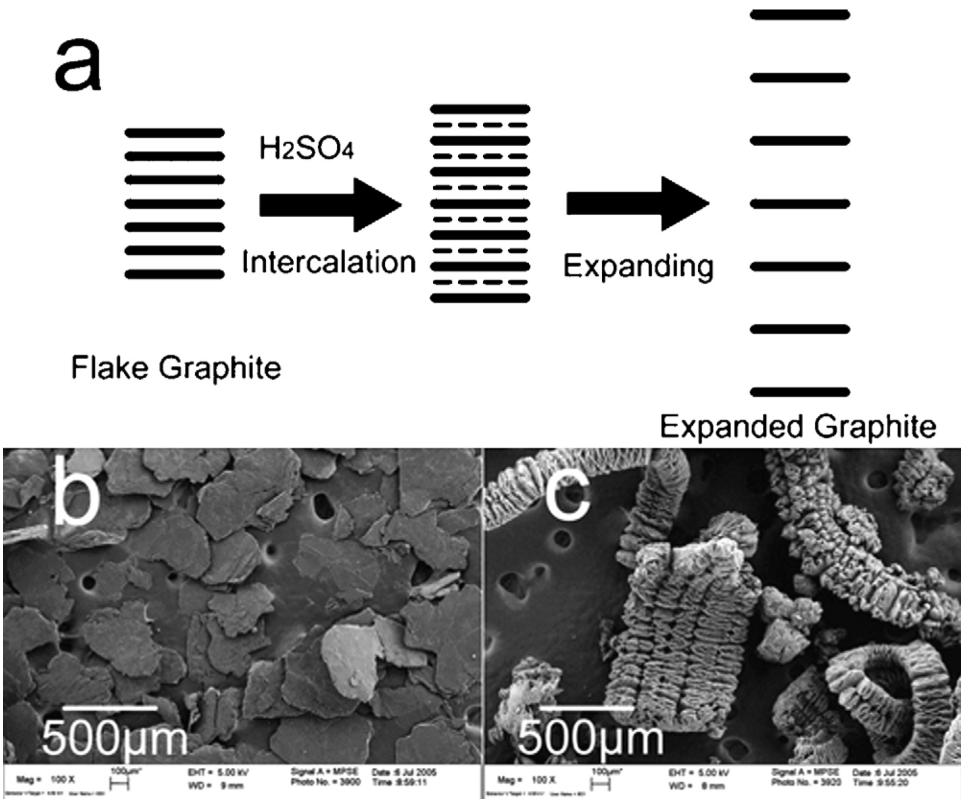

Fig. 1. (a) Mechanism of expanding process, (b) the SEM micrograph of flaky graphite and (c) the SEM micrograph of expanded graphite.

alcohol, 368 K, 800 rpm, 2.5 MPa H_2. The two hydrogenized products were both filtered to remove the solid catalyst and analyzed by a gas chromatograph (GC 7800) with a flame ionizatin detector (FID).

3. Results and discussion

The pore structure of EG was measured by mercury porosimetry (ThermoFinnigan PASCAL 440) and the surface area of EG obtained was 292.5 m^2/g (Fig. 2). The pore size distribution reveals that EG is a mesoporous material with a macroporous network structure, which can eliminate the effect of inward diffusion. As a result, EG can be used in the liquid phase reaction, and thus, it is very easy to separate the catalyst from the reactant and product. Furthermore, the wide pore size distribution enables EG to satisfy various demands.

The SEM micrograph of NiB/EG (Fig. 3) showed that the NiB clusters were well distributed on EG in a single layer, and that the size distribution was homogeneous. As shown in Fig. 4, the TEM micrograph revealed detailed information about the NiB clusters, which appeared snowflake-like with an average size of 40 nm. The halo diffraction pattern in the SAED image verified the amorphous structure of the NiB clusters. Their unique isotropic structure and high concentration of coordinated unsaturated sites result in superior catalytic activity and selectivity compared to their crystalline counterparts. In addition, NiB Alloy B preferentially absorbed O_2 and those in the bulk diffused to the surface when surface elemental boron was consumed, preventing nickel from oxidation. The mechanism regarding the formation of NiB clusters is very complex and is still being investigated.

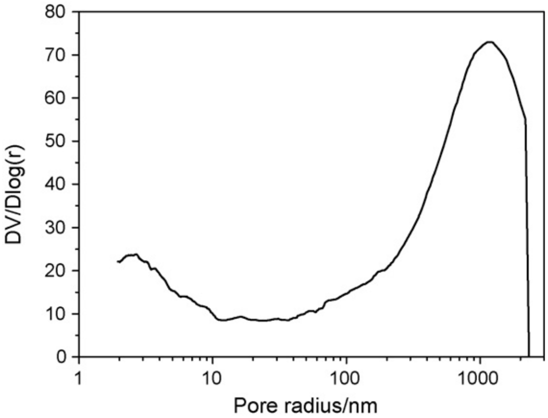

Fig. 2. The pore size distribution of EG.

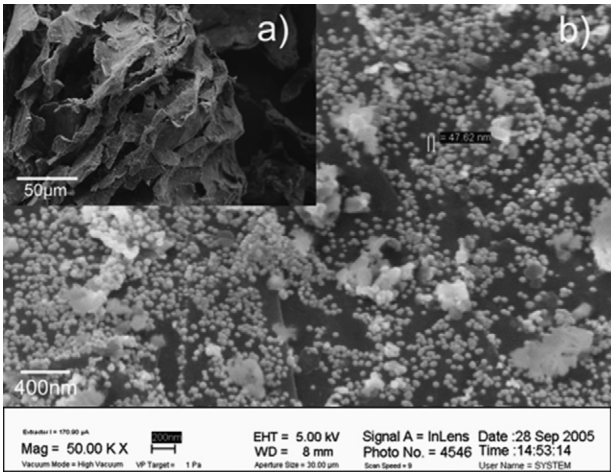

Fig. 3. The SEM micrograph of NiB/EG: (a) low magnification and (b) high magnification.

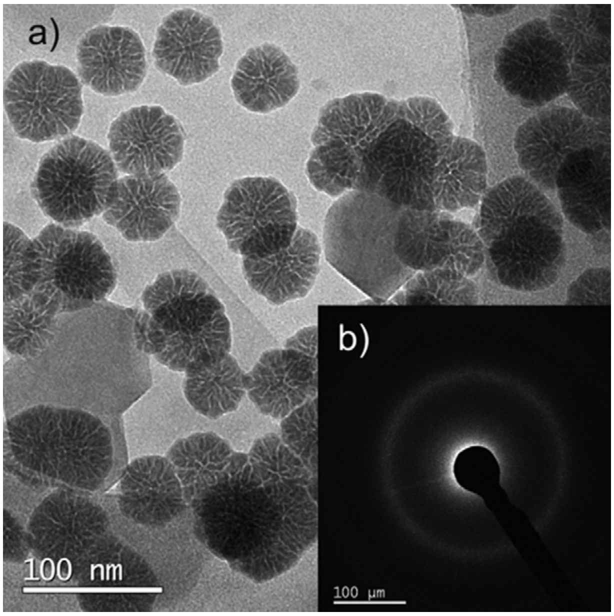

Fig. 4. (a) TEM micrograph of NiB/EG and (b) SAED image of NiB/EG.

To test the performance of the prepared catalyst, the hydrogenation of sulfolene to sulfalone was selected as a test reaction, which used Raney Ni as the catalyst in the industrial process. As shown in Table 1, the catalytic activity of NiB/EG exceeded that of Raney Ni and NiB/MgO (prepared using the same method as NiB/EG); the Ni loading of NiB/EG was only 14.2%. To obtain further information, hydrogen consumption was monitored as a measure of the progress of each catalytic reaction (Fig. 5). The initial rate of sulfulene hydrogenation

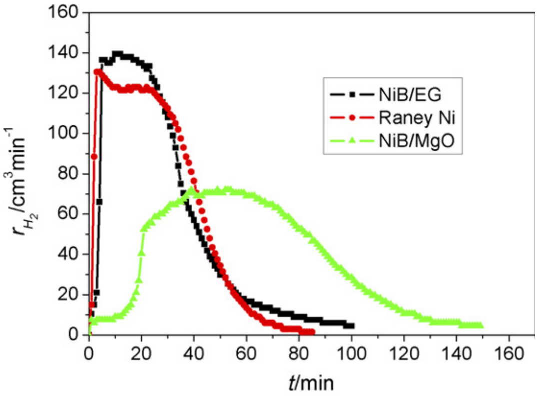

Fig. 5. Hydrogenation process of Raney Ni, NiB/EG and NiB/MgO, the consumption of H was measured by Mass Flow Meters (seven star D07-7B/ZM).

Table 1
Results of ICP analysis and catalytic performance

Catalyst	Ni (wt.%)	Hydrogenation of sulfolene		Hydrogenation of p-CNB[a]	
		Conversion of sulfolene (%)	Selectivity of sulfolane (%)	Conversion of p-CNB (%)	Selectivity of p-CA (%)
NiB/MgO	15.3	96.9	99.5	80.5	99.2
NiB/EG	14.2	98.5	99.6	99.5	99.5
Raney Ni	~100	98.2	99.5	99.6	98.5

[a] p-CNB, *para*-chloronitrobenzene; p-CA, *para*-chloroaniline.

for NiB/EG exceeded that for Raney Ni, and was almost twice that compared for NiB/MgO; however, at the end of the reaction, there was little difference in the yield of sulfalone for the two catalysts. The results of selective hydrogenation of p-CNB to p-CA supported the above points. It is clearly shown that amorphous NiB supported on EG exhibited much higher catalytic activity than MgO, and therefore, we believe that NiB/EG has the potential to replace the Raney Ni catalyst.

In summary, EG was successfully applied to the catalytic process as a novel carbon support material. Herein, the NiB/EG catalyst was prepared and showed very high catalytic activity. Compared with other supports, EG showed superior results regarding the preparation of supported amorphous alloy catalysts at a low cost. We predict that EG will play an important role in industrial catalysis as a novel carbon support material in the near future.

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