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Synthesis of bio-inspired N-doped SiC and investigation of its synergetic effects on Mo catalysts in oxidative desulfurization reaction

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ABSTRACT

Bio-inspired N-doped silicon carbide/Mo composites have been successfully synthesized through a facile method, combining magnesiothermic synthesis of biomorphic N-doped SiC by using gelatin biopolymer and embedded molybdenum composites forming in situ. The resulting composite materials contain MoO_2, Mo_2C, and $MoSi_2$ particles dispersed well on N-doped SiC matrix. The composites displayed superior catalytic properties in oxidative desulfurization of model fuel (99.6%). The comparison between catalytic activity of N-doped SiC, N-doped carbon and SiC without nitrogen dopants demonstrated that N-doped SiC composites are more promising for ODS reaction. Comparable catalytic activity, higher durability, and lower reaction time are the advantages make this composite a good ODS catalysts and a green and cost-effective alternative for practical desulfurization of fuel.

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1. Introduction

The removal of sulfur compounds in fuel is an important environmental concern [1–3]. Toxic sulfur compounds are released to the atmosphere and cause significant environmental and health problems [4,5]. Currently, hydrodesulfurization (HDS) process is widely used to reduce the sulfur content in the commercial fuels. However, HDS is cost-intensive process and less effective to remove thiophenic compounds [6]. Therefore, research is carried out to propose alternative technologies to obtain low-sulfur fuels. Among them, oxidative desulfurization (ODS) is considered as a promising approach because of its low-energy consumption [7,8]. In this method, thiophenic compounds are converted to related sulfones under mild condition which can be easily removed by adsorption or extraction [9,10]. The best results were achieved when transition metal oxides are used as catalysts; such as Mo, W, V, Ti, etc. [11–14]. Among them, MoO_3-based (Mo(VI)) catalyst has been widely used in ODS reaction, but little research has been reported on MoO_2-based (Mo(IV)) catalyst [15]. MoO_2 has been used as a catalyst for oxidation, alkane isomerization, metathesis, or reforming reactions [16–20]. MoO_2 has high density in the valence band energy than can enhance the catalytic activity [21–23]. Also, molybdenum carbide has been reported to show excellent catalytic properties in dry-methane reforming, steam-methane reforming, partial oxidation

of methane, and oxidative dehydrogenation [24,25]. But only few reports focused on using Mo_2C on ODS reaction [26]. Furthermore, alumina [27,28], silica [29] and activated carbon [30] are intensely used as catalyst supports in oxidation reactions of organosulfur compounds. However, silicon carbide, has never been employed as a catalyst in the ODS process. Besides the structural stabilization of the molybdenum carbide and oxide nanoparticles, the intrinsic structure and defect of the SiC support will also effect on product properties.

Silicon carbide has attracted attention due to its semiconducting properties, high mechanical strength, high thermal conductivity, good chemical inertness and excellent thermal shock resistance [31,32]. Thus, it widely has been used in electronic and optical devices, drug delivery, hydrogen storage, and catalyst support [33–35]. Silicon carbide can be synthesized by various methods [36,37]. The main disadvantages of these methods include high synthesis temperature, and expensive and not environmentally-friendly raw material precursors [38]. Addition, all the existing methods are unable to control the structure of the product [39]. Magnesiothermic reduction is a novel method, which synthesizes nanostructures at temperatures much lower than what was previously has been produced [39,40]. In general, for controlling structural properties of materials, including external shape, internal porosity and surface area, surfactants or polymers have been used as template [41]. But, most of polymers and surfactants used as templates are expensive and most often toxic and not suitable for ecosystems [42,43]. These problems are surmountable using renewable natural materials as templates [44]. Natural biopoly-

mers are nontoxic, biocompatible and biodegradable materials that can be selected here as good candidates for carbon template. Moreover they are an infinite source in nature and inexpensive materials.

In this work, we employed bio-inspired approaches for the preparation of N-doped SiC foam containing $MoO_2/Mo_2C/MoSi_2$ nanocomposites (designated as SiC-Mo). Gelatin as a natural material containing N species (a heterogeneous mixture of proteins) was selected as a suitable carbon source for synthesis of self-assembly N-doped silicon carbide. Also, sodium molybdate was used as molybdenum precursor. Furthermore, we evaluate the catalytic properties of the as-synthesized N-doped SiC-$MoO_2/Mo_2C/MoSi_2$ composites as oxidative desulfurization catalysts to obtain low sulfur fuel.

2. Experimental

2.1. Materials and methods

All chemicals and solvents used in the syntheses were reagent grade and used without further purification. Commercial gelatin was obtained from Merck chemical company. Magnesium powder (0.3–0.06 μm), Tetraethyl orthosilicate, ethanol, hydrochloric acid (37%) and hydrofluoric acid (40%) used for synthesis of SiC matrix. Dibenzothiophene (DBT), benzothiophene (BT), 4,6dimethyldibenzothiophene (4,6DMDBT), n-octane, hydrogen peroxide and molybdenum oxide were obtained from Merck. n-Dodecane was used as internal standard for the quantitative analysis of the product using gas choromatography and acetonitrile that was used as extractive solvent were also obtained from Merck.

Scanning electron microscope (SEM) images were obtained on TESCAN, VEGA3. Crystalline phases were identified by X-ray diffraction (XRD) using filtered CuK$_\alpha$ radiation ($\lambda = 1.54060$ Å) in the range $2\theta = 5–80°$ (BrukerAxs, D8 Advance). Infrared spectra were measured on a Bruker, Vector spectrometer. Adsorption and desorption isotherms and were recorded by Belsorp mini instrument. Raman spectra were obtained with Bruker, Senterra micro-Raman with a laser wavelength of 785 nm. Catalytic tests were taken with GC-FID (Faraz Gostar, TG 2552).

2.2. Preparation of precursors

Sol-gel method was used for preparation of precursors. 5 g of gelatin was dispersed in 40 ml water under vigorous mixing. The mixture was then placed in boiling water bath with vigorous stirring for 2 h. After cooling down to room temperature, the gels were used as N-doped carbon precursor.

For synthesis of SiC/Mo composites, the prepared gelatin gel mixed with different amount of molybdenum salt (sodium molybdate): 0.5, 0.75, 1, and 1.25 g. Then the composites were sonicated for 15 min (120W) and used as N-doped carbon/molybdenum precursors.

The silica precursor was prepared using tetraethyl orthosilicate (TEOS) according to previous literatures. TEOS, ethanol and water were mixed together at 8: 4: 5.5 ratios under mild stirring for 1 h. After homogenization of the mixture, it was used as silica precursor for synthesizing the silicon carbide nanostructures.

2.3. Synthesis of N-doped silicon carbide

Porous N-doped SiC was synthesized by mixing carbon and silica precursors. After homogenization of the mixture with ultrasonic agitation, acetic acid solution was added by dropwise until the resulting sol had a pH in the range of 4–5. The mixture was then put in a drying oven, treated at 80°C for 12 h. The dried mixture was carbonized at 750°C for 1 h under argon atmosphere to form SiO_2/C composites. After that, the SiO_2/C composites were mixed with magnesium powder (SiO_2: Mg molar ratio of 1:2) and put in a ceramic crucible, heated in an electrical furnace to 750°C for 6 h with heating rate of 5°C/min in Ar. Finally, the mesoporous N-doped SiC was obtained after cooling to room temperature. To remove magnesia (MgO), the resulting powders were immersed in a 2 M HCl solution for 24 h at room temperature. Finally, the samples were exposed to a HF solution to remove any unreacted silica for 24 h. At last, the samples were washed with ethanol and water, and dried at 40°C for 4 h in a vacuum oven. Bio-inspired N-doped SiC was coded with GG.

2.4. Synthesis of SiC/Mo composites

For synthesis of SiC/Mo composites, the above procedures repeated for carbon/molybdenum precursors and silica gel. The obtained SiC composites were named as GG/Mo1, GG/Mo2, GG/Mo3, and GG/Mo4 corresponding to the 0.5, 0.75, 1, and 1.25 g of molybdenum salt, respectively.

2.5. Catalytic test

DBT was dissolved in n-octane to prepare model fuel solutions with 100, 250 and 500 ppm total sulfur. The catalytic experiments were carried out in a 25 ml flask, equipped with a magnetic stirrer at an atmospheric pressure and different constant temperature (25–60°C). In a typical catalytic process, 2 ml of model fuel, 2.5–7.5 mg of catalyst, 1 ml acetonitrile as extractive solvent and dodecane as internal standard was added to a reactor and stirred for 5 min. Then 0.5–1.5 μl of H_2O_2 was introduced. In each 10-min period, the oil phase was withdrawn and determined by GC to investigate the conversion percent of DBT. Also another model fuel with the mixture of BT, DBT and 4,6DMDBT (equal amount of each sulfur compounds with total sulfur of 500 ppm) was tested to evaluate the selectivity of catalysts.

3. Results and discussion

A bio-inspired approach was use for the synthesis of N-doped SiC foam embedded by $MoO_2/Mo_2C/MoSi_2$ composites. The gelatin has been selected as a carbon source with nitrogen species that has self-assembling capability to produce N-doped carbon skeleton [45–47]. The XPS analysis of prepared N-doped carbon has shown the presence of four types of N-containing groups: pyridine, pyrrole, graphite, and pyridine-N-oxide nitrogen species. Among them, the pyridinic and pyrrolic nitrogen contribute is predominant in the N-doped carbon product [47].

Using magnesiothermic method for synthesis of SiC helps us to achieve the nanoporous structure. In the presence of metal precursor, there are molecular interactions between the amine groups in gelatin matrix and molybdenum ions. So, it can result the homogenous distribution of the molybdenum precursor in the gelatin matrix. At high temperature, molybdenum precursor converted to MoO_2 and in the presence of carbon and Si, Mo_2C and $MoSi_2$ can achieve too.

3.1. Characterization

In order to study the surface characteristics of Si/Mo composites, FTIR analysis was carried out. FTIR spectra for N-doped SiC and four SiC/Mo composites are presented in Fig. 1. Corresponding peak to the Si-C bonds were observed in about 813–837 cm^{-1} for GG and its composites. The shoulder appeared in about 913–914 cm^{-1} are assigned to Mo-O stretching vibration in SiC/Mo composites. As Fig. 1 shows, there were small differences in Si-C bonds in GG-SiC and its composites due to molybdenum grafting.