

Deep oxidative desulfurization with a microporous hexagonal boron nitride confining phosphotungstic acid catalyst

Haiyan Ji^a, Jia Sun^a, Peiwen Wu^b, Bilian Dai^c, Yanhong Chao^c, Ming Zhang^d, Wei Jiang^d, Wenshuai Zhu^{c,*}, Huaming Li^{d,*}

^a School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013 China

^b School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013 China

^c School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013 China

^d Institute for Energy Research, Jiangsu University, Zhenjiang 212013 China

ARTICLE INFO

Article history:

Received 1 March 2016

Received in revised form 21 June 2016

Accepted 22 June 2016

Available online 23 June 2016

Keywords:

Hexagonal boron nitride

Phosphotungstic acid

Heterogeneous catalyst

Confining catalysis

Oxidative desulfurization

ABSTRACT

Hexagonal boron nitride (h-BN), a layer structure material, has gained increasing attentions as a support. Herein, a few-layer h-BN is constructed and employed as an interlayer confining support for heterogenization of phosphotungstic acid (HPW/h-BN). The obtained HPW/h-BN is applied in oxidative desulfurization (ODS) and a ~100% of sulfur removal can be achieved. Detailed experiments show that porous structure of h-BN, functioned as confining sites, contributes to the remarkable catalytic activity. Besides, aromatic hydrocarbon and olefin are further applied as chaff interferent in ODS showing no obvious effects, suggesting a promising prospect. This catalyst presents preferable recyclability in ODS, which can be recycled 6 times without noticeable decrease in reactivity. Moreover, the reaction mechanism and resultant are instantly detected by gas chromatography-mass spectrometry.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the past a few decades, due to the rapid development of industry, protection of environment hereupon gains increasing attentions. Among all environmental issues, reduction of emission of oxysulfides (SO_x) has been proved to be an urgent one around world. To regulate source of SO_x, many countries have taken a lot of efforts in minimization of sulfur contents in gasoline [1]. Among which, hydrodesulfurization (HDS) has been proved to be an efficient one in industrial application. Whereas, harsh reaction condition and low activity to aromatic sulfur compounds have become a barrier to its further development. Thereupon, many researchers turn to hunting for substitutes to HDS. To date, some fungibles including adsorptive desulfurization (ADS) [2,3], extraction desulfurization (EDS) [4], oxidative desulfurization (ODS) [5–10], *etc.* have been developed. Within all these substitutes, ODS has come to the fore due to its mild reaction condition and high activity to aromatic sulfur compounds [10–16]. A central topic in ODS is to cast about for a prominent and high active catalyst.

Recently, heteropoly acids, represented by phosphotungstic acid (H₃PW₁₂O₄₀, denoted as HPW), have gained increasing attentions due to their excellent performance in organic catalysis [17–22]. Nowadays, owing to the mature manufacturing technique of HPW, it has turned to be commercial available, which results in its wide applications. Nevertheless, its applications are seriously limited by its solubility in many solvents. Thus, heterogenization of HPW has become a most common pathway for its enlargement of applications [23–25]. Generally, silicon-based materials and metal-organic frameworks (MOFs) are most ordinary supports [19,26–30]. However, those supports struggle from some inevitable deficiencies. For silicon-based materials, its poor alkali resistance, low mechanical strength and easy sintering reunion, leading to its poor performance in harsh condition [31]. While for MOFs, their high costs and complex synthesis process are also barriers to their large-scale applications. Seeking for a proper support with special structure and low cost in oxidative desulfurization is thus in urgent need [32].

More recently, hexagonal boron nitride (h-BN), as an analogy to graphene, has gained increasing attentions [33,34]. Compared with graphene, h-BN shows some additional advantages, including excellent resistance to chemical attack, remarkable thermostability, wide band gap, and excellent thermal conductivity, *etc.* [35–40]. These properties drive h-BN an outstanding material in

* Corresponding authors.

E-mail addresses: zhuws@ujs.edu.cn (W. Zhu), lihm@ujs.edu.cn (H. Li).

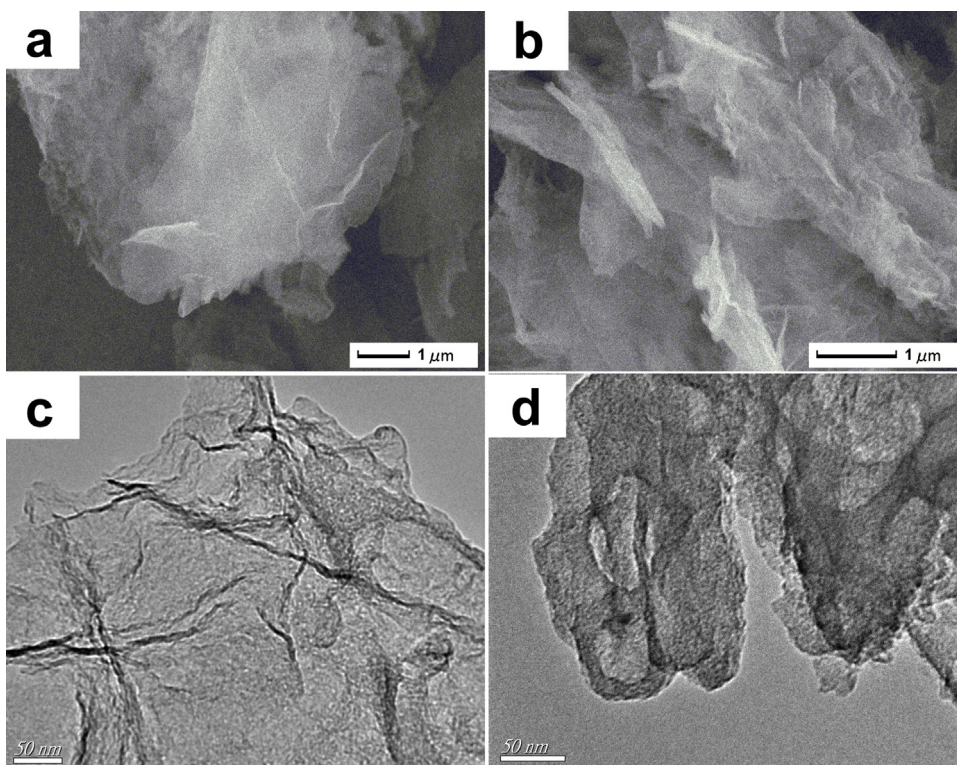


Fig. 1. SEM (a, b) and TEM (c, d) images of samples. (a) and (c): h-BN; (b) and (d): HPW/h-BN.

water-cleaning [41,42], adsorption [43], hydrogen storage [44], etc. Additionally, h-BN has been proved to be an outstanding support in preparation of catalysts to lessen consumption of catalytic center (such as ionic liquids, metal, etc.) [45,46]. Seeking for a proper immobilization method has a great effect on final catalytic activity and recycling achievement.

In the past few years, since the birth of the concept of confine effect by Bao's Group, confining catalysis has turned out to be an increasingly important concept in the field of catalysis [47–49]. Confinement usually regards to using a support (the most common is carbon nanotube) to stabilize active sites inside the tube, leading to a promising catalytic and recycling performance. Thus, we consider introducing the concept into construction of supported catalyst. A porous h-BN with numerous micropores is prepared, afterwards, the micropores function as confining sites for dispersion and stabilization of HPW to obtain HPW/h-BN with a high-activity for ODS. Detailed characterizations provide evidences of uniform distribution, promising stabilization and remarkable confinement of HPW. When the confined catalyst is applied in ODS, a ~100% of sulfur removal can be acquired. Experimental conditions are optimized from the point of economical consideration. Further researches show that the ODS system with the prepared catalyst holds a high resistance to olefins and arenes, showing a potential industrial prospect.

2. Experimental section

2.1. Materials

Tetradecane ($n\text{-C}_{14}\text{H}_{30}$, 99%), dibenzothiophene (DBT, 98%), benzothianaphthene (BT, 99%), 4,6-dimethyldibenzothiophene (4,6-DMDBT 97%) are marketed by Sigma-Aldrich. Phosphotungstic acid hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, denoted as HPW, A.R. grade), Diboron trioxide (B_2O_3 , A.R. grade), urea ($\text{CO}(\text{NH}_2)_2$, A.R. grade), ethanol ($\text{C}_2\text{H}_5\text{OH}$, A.R. grade), n -octane (C_8H_{18} , A.R. grade), toluene

($\text{C}_6\text{H}_5\text{CH}_3$, A.R. grade), cyclohexene (C_6H_{10} , A.R. grade), commercial bulk boron nitride (BN, 98%), hydrogen peroxide (H_2O_2 , 30 w.t.%) are acquired from Shanghai Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of catalysts

2.2.1. Synthesis of h-BN

At room temperature, 0.01 mol of B_2O_3 and 0.2 mol of urea are added to a beaker with 40 mL of ultrapure water. Then the mixtures are transferred to oil bath at 60°C and stirred persistently to evaporate the solvent absolutely. Afterwards, the mixtures are transferred to a tube furnace and heated at $5^\circ\text{C}/\text{min}$ from room temperature to 550°C and then kept for 2 h, and then the tube furnace is further heated to 1000°C with a heating ratio of $5^\circ\text{C}/\text{min}$ in N_2 atmosphere and maintained for another 2 h at 1000°C .

2.2.2. Preparation of HPW/h-BN

0.03 g of HPW is dissolved in 10 mL of ethanol and then stirred constantly for 30 min to dissolve completely. Subsequently, 0.17 g h-BN is then added and continued stirring for another 30 min at room temperature. After stirring, the mixtures are transferred to an autoclave and heated for 6 h at 150°C . Until naturally cooled to room temperature in autoclave, the mixtures are transferred to the beaker and dried for 12 h at 110°C to desiccate the mixture thoroughly. The collected h-BN immobilized with HPW denotes as HPW/h-BN.

The other catalyst HPW/commercial-BN is prepared by replacing h-BN with commercial bulk BN.

The synthesis procedure of HPW@h-BN without confining effect is similar to that of HPW/h-BN, only excepting the reaction of HPW and h-BN in the autoclave. 0.03 g of HPW is dissolved in 10 mL of ethanol and then stirred constantly for 30 min to dissolve completely. 0.17 g h-BN is then added and continued stirring for another 30 min at room temperature. After stirring, the mixtures are transferred to the beaker and dried for 12 h at 110°C to desiccate the

Download English Version:

<https://daneshyari.com/en/article/64541>

Download Persian Version:

<https://daneshyari.com/article/64541>

[Daneshyari.com](https://daneshyari.com)