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Synthesis, characterization and evaluation of unsupported porous NiS_2 sub-micrometer spheres as a potential hydrodesulfurization catalyst

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ABSTRACT

Nanostructured NiS_2 has attracted interest due to its wide applications and special properties. Synthesis of a pure phase NiS_2 in a single step has been a challenge. In this work, a new method for direct synthesis of uniform NiS_2/SiO_2 sub microspheres has been developed by ultrasonic spray pyrolysis. Colloidal silica was used as a sacrificial template to create the porous structure. After silica removal, hollow, porous NiS_2 nano spheres were obtained. The product was characterized by using scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction (XRD), transmission electron microscopy and N_2 adsorption/desorption isotherm. XRD confirmed the formation of single phase pyrite NiS_2. It was found that the porous spherical NiS_2 has a surface area of ca. 300 $m^2\,g^{-1}$. The HDS catalytic activity of NiS_2 was evaluated using a model compound, dibenzothiophene (DBT). It showed a first order reaction rate constant of $1.51 \times 10^{-4}\,s^{-1}\,g\,cata^{-1}$ at 320 °C for HDS of DBT, which is significantly promising for further exploration.

1. Introduction

Transition metal semiconductor chalcogenides are attracting wide interest because of their versatile optical [1], magnetic [2] and catalytic [3] properties. In nanometer scale, these properties are highly influenced by the size, shape and dimensionality of these materials [4,5]. Important transition metal sulfides such as cadmium sulfide [6], zinc sulfide [7,8], manganese sulfide [9], silver sulfide [9], iron sulfide [10], nickel sulfide [11,12] and many phases of copper sulfides [13] have been investigated extensively. These sulfides have broad field of potential applications including cathode materials in rechargeable lithium batteries [13], IR detectors [14], catalyst for photogalvanic cells [15], a possible transformation toughener [16], paramagnetic–antiferromagnetic phase-changing material [17], catalysts in the degradation of organic dyes [18] or hydrodesulfurization catalysts [19]. Among the family of metal sulfides, nickel sulfides also have attracted much interest as they can form various phases such as NiS, α-$Ni_{3+x}S_2$, β-Ni_3S_2, Ni_7S_6, Ni_9S_8, Ni_3S_4, and NiS_2. Kullerud and Yund [20] first reported the nickel sulfide system, followed by others [21–24]. NiS_2 in particular comes in two main phases, a triclinic phase [25] and a cubic phase [26]. Cubic pyrite NiS_2 possesses interesting electronic, optical and magnetic characteristics [27–29].

Heavy oil, extra heavy oil, and oil sands bitumen comprise of 70% of the world's total oil resources. These non conventional sources of oil are becoming more important as conventional oil reserves deplete rapidly [30]. However, non conventional oils contain high levels of contaminants including high sulfur content. High sulfur content is the main concern for nonconventional oil. To reduce the sulfur content to a regulated level, the hydrodesulfurization (HDS) process is indispensable in hydrotreating sulfur-containing fractions during petroleum refining and heavy oil upgrading. Nickel sulfide is an active component in hydrotreating catalysts, which improves the catalytic activity of MoS_2 by forming $NiMoS_x$. Catalytic activity of nickel sulfide alone was also investigated. Welters et al. [19] prepared sulfide NiNaY using ion-exchange followed by sulfiding, and found that the activity of the sulfided NiNaY depends on the preparation method and pretreatment conditions. They also found that the support affects the catalytic activity. Zeolite-Y supported Ni sulfide has a higher activity than its alumina supported counterpart, and performs comparably to its carbon supported

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