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Fabrication of hierarchical porous ZnO and its performance in Ni/ZnO reactive-adsorption desulfurization

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Abstract: To investigate the effect of texture structure on the desulfurization performance in the Ni/ZnO reactive adsorption desulfurization (RADS) system, two kinds of ZnO porous materials with rod-shaped morphology were synthesized and their structure was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption/desorption. The formation mechanisms of hierarchical porous ZnO (ZnO with meso and macro pores) were also studied. Their application performance was evaluated in the RADS process over Ni/ZnO absorbent. Due to the difference in structure between the two kinds of ZnO, the two ZnO based adsorbents showed different desulfurization activity.

Key words: Ni/ZnO, reactive adsorption, desulfurization, texture structure, hierarchical pore

1 Introduction

With increasingly stringent environmental regulations, deep desulfurization for production of gasoline oil has become an important issue, and technologies for ultra-deep desulfurization of refinery streams have become an important subject of environmental catalysis studies worldwide (Song, 2003; Song and Ma, 2003; Brunet et al, 2005). Desulfurization should also be taken into consideration in processing of fuel for fuel-cells, which has a more rigorous requirement for sulfur content (e.g., <1 μg/g sulfur) than fuel for internal combustion engines. Approaches to deep desulfurization include hydrodesulfurization (HDS) and non-HDS processing. Although the development of high-performance catalysts for HDS processes can produce fuels with a sulfur content of <10–50 μg/g, this approach will result in unnecessary olefin saturation, excessive hydrogen cost and octane number reduction while removing sulfur species. Adsorption desulfurization (ADS) is achieved by using solid sorbents, which can adsorb organosulfur compounds from refinery streams, with excellent olefin control and reducing octane number loss (Babich and Moulijn, 2003; Fan et al, 2004). Recently, one novel method, reactive adsorption, has been implemented in S-Zorb desulfurization technology (Khare and Gyanesh, 2001). This technology can reduce the sulfur content of fuel to lower than 1 μg/g, meeting the requirement for sulfur content of fuel cells (Ma et al, 2005), and has been used on industrial scale in China. The sorbent, which consists of kieselguhr, alumina, zinc oxide and nickel, was developed by Sud-Chemie AG (Germany). This Ni/ZnO reactive adsorption desulfurization catalyst has an "auto-regenerative" mechanism (Siriwardane et al, 2000). Ni acts as the hydro-desulfurization site, while ZnO plays the crucial role in taking up generated H_2S, converting the H_2S into ZnS in the process. First, NiO in the adsorbent precusor is converted into reduced state Ni in H_2 atmosphere, and then the organosulfur reacts with Ni to form transition state sulfur species (NiS_x) due to its relative electronegativity. Second, the C-S bonds of the organosulfur compounds are broken under the influence of the strong adsorption potential. Finally, ZnS forms due to the reaction of ZnO with sulfur species, and NiS_x is converted back into Ni in a H_2 atmosphere, sulfur is immobilized onto the adsorbent in the form of ZnS while Ni remains in its reduced state. That is, Ni is "auto-regenerated" in the reaction (Ryzhikov et al, 2008; Mangnus et al, 1992; Bezverkhyy et al, 2008). Based on the mechanism, the regeneration rate of the nickel surface can determine the activity of the adsorbent. ZnO plays an important role in rapid conversion of NiS_x to Ni^0 on the nickel surface. Thus, the reaction rate of ZnO with H_2S or NiS_x is crucial as it determines the performance of the adsorbent. Conventional micron ZnO exhibits inferior reactivity with hydrogen sulfide because of its low surface area, topology and crystalline structure, so its sulfur-fixation capability and activity are limited. Recently, our research group has synthesized nano zinc oxide by a low-temperature solid-phase method, and the reactivity/performance of the corresponding Ni/ZnO

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