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Oil-soluble Ni-Mo sulfide nanoparticles and their hydrogenation catalytic properties

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Abstract: Oil-soluble bimetallic Ni-Mo sulfide nanoparticles (NiMoS) with narrow size distribution were successfully synthesized through a composite-surfactants-assisted- solvothermal process. The surface functionality and lipophilicity of the Ni-Mo sulfides were shown by transmission electronic microscopy, Fourier transform infrared and ultraviolet spectroscopy. The as-prepared Ni-Mo sulfides supported on activated carbon (NiMoS/AC) exhibited enhanced catalytic activity towards naphthalene hydrogenation instead of cracking. For comparison, CoMoS/AC and MoS_2/AC catalysts were also prepared through similar procedures, and it was found that their catalytic performance decreased in the order of NiMoS/AC>CoMoS/AC>MoS_2/AC. Furthermore, the activity of the bimetallic NiMoS nanocatalyst can be effectively tuned via variation of the atomic ratio of Ni/(Ni+Mo).

Key words: Bimetallic sulfide, activated carbon, hydrogenation, nanocatalyst, naphthalene

1 Introduction

The search for highly efficient hydrogenation (HYD) catalysts for the petrochemical industry is of great significance for energy saving and environmental protection. Moreover, conversion of aromatic compounds during hydrotreatment to avoid their negative effects on the cetane numbers has received significant attention (Ferraz et al, 2010; He et al, 2011; 2013; Mendez et al, 2013; Temel et al, 2010). Particularly, catalysts based on molybdenum sulfides have attracted much interest for HYD reactions (Bellussi et al, 2013; Daage and Chianelli, 1994). The performance of a sulfide catalyst in the hydrofining process is closely related to its particle size and dispersion in nonaqueous media. Therefore, synthesis of a HYD catalyst with high surface area and improved oil-solubility, to eliminate particle aggregations, and to enhance the HYD performance, is an important issue.

Generally, there are two ways to obtain sulfides with improved catalytic efficiency. One is to load the sulfide components onto different supports, such as titania (Azizi et al, 2013; Kibsgaard et al, 2009), alumina (Ju et al, 2012; Lu et al, 2012; Si et al, 2010; Yao et al, 2012; Zhang et al, 2012), zirconia (Al-Daous and Ali, 2012; Jia et al, 2005), activated carbon (AC) (de la Puente et al, 1999; Liu et al, 2011a; Shi et al, 2010), and zeolites with different Si/Al atomic ratios (Mendez et al, 2013; Yin et al, 2011). In such cases, the properties of the support, i.e., the porosity, surface area, acidity, and mechanical strength, will determine the characteristics and activities of the active sulfide phase, which is anchored on the support through the interactions of the sulfide phase and support at S-edge and metal-edge sites. Another method is to incorporate promoting elements, such as cobalt (Co) or nickel (Ni), into the sulfide nanoparticles (NPs) (Zhang et al, 2013; Zhou et al, 2012). The promoting elements of Ni or Co can weaken the edge anchoring of the active phase towards the supports. However, introduction of Co often encounters sintering and segregation (Eijsbouts et al, 2007; McCormick et al, 1989). Moreover, the Ni-Mo sulfides usually possess a high ratio of Brönsted to Lewis acid sites (Ferraz et al, 2010; Kibsgaard et al, 2009), which intensify the coordinative unsaturation of the transition metal atoms and their edge bonding effect (Kibsgaard et al, 2009; Yoosuk et al, 2010). Therefore, incorporation of Ni is more preferred in terms of the stability, activity, and cost reduction of catalyst. The synergetic effect between the promoting elements and the catalysts can significantly improve the activity of the composite sulfide catalyst. Consequently, integration of the support effect and the promoting effect of transition metals would be highly promising for designing a novel HYD catalyst (Kibsgaard et al, 2009).

As part of our group's continuing efforts to develop efficient HYD nanocatalysts, this paper reports the synthesis

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