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Monodispersed nickel and cobalt nanoparticles in desulfurization of thiophene for in-situ upgrading of heavy crude oil

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ABSTRACT

Monodispersed nickel (Ni) and cobalt (Co) nanoparticles (NPs) with different sizes are synthesized via the thermal decomposition of organometallic precursors by controlling the reaction temperature and surfactant amount. X-ray diffraction analysis of the as-prepared NP samples shows the formation of cubic Ni metal phases with good crystallinity, while the cubic Co metal samples are semi-amorphous. Transmission electron microscopy characterization further confirms that two Ni NP samples with average sizes of 9 and 27 nm, and Co NPs with an average size of 6 nm are successfully prepared with a narrow size distribution. Furthermore, catalytic performance of these monodispersed NPs towards the hydrodesulfurization (HDS) reaction, which plays a pivotal role in the upgrading of heavy crude oil, is evaluated under reservoir-relevant conditions using thiophene as a sulfur-containing model compound. Different parameters including particle size, catalyst dosage, hydrogen donor ratio, temperature, and reaction duration are systematically studied to optimize the catalytic HDS performance. The morphology and size of the spent NP catalysts after the reaction are also analyzed. The results show that the 9 nm Ni NPs exhibit the best HDS activity and stability compared with other catalysts, which suggests that such well-dispersed Ni NPs are promising candidates for the in-situ upgrading and recovery of heavy crude oil from underground reservoirs.

1. Introduction

To address the challenges of ever-increasing energy demand and declining crude oil reserves, research in both academia and industry is devoting more attention to unconventional oil, which includes heavy and extra-heavy oils. Compared with conventional oil, the exploration and production of heavy crude oil is a challenging task due to its special physicochemical properties. More specifically, heavy oil is characterized by high viscosity or poor mobility, high fraction of asphaltenes and resins with large molecules, and considerable amounts of heteroatoms, including sulfur, nitrogen, oxygen and metals [1–9].

So far, numerous technologies for the exploration and production of heavy oil have been reported, such as thermal injection [10], chemical injection [11–14], and biological degradation [15]. Among them, thermal injection is regarded as the most effective one and has been widely implemented. This technique is, however, energy-intensive because external energy needs to be supplied by combustion of natural gas to generate steam with high temperature and pressure. In addition, this process causes the emission of large amounts of greenhouse gases and needs additional water separation and recycling facilities. It is therefore necessary to improve this technique to reduce the environmental footprint. Since the discovery of aquathermolysis reactions between injected steam and crude oil in 1980s [16], the concept of in-situ catalytic upgrading and recovery of heavy crude oil has been proposed and developed [3,7]. Extra catalysts are introduced into the reservoirs to facilitate the aquathermolysis reactions, which include a series of hydrocracking, hydrodesulfurization (HDS), hydrodenitrogenation, hydrodeoxygenation and hydrodemetallization reactions. Due to these reactions, large hydrocarbon molecules are cracked into small derivatives and the viscosity and oil quality are thus improved [17]. The reservoir is turned into an underground refinery to ease the extraction and production of heavy crude oil.

With regard to catalysts in aquathermolysis reactions, metallic nanoparticle (NP) has emerged to be a competitive alternative compared to other water-soluble, oil-soluble, amphiphilic, minerals and zeolites, and solid superacids catalysts [1,3,7]. Owing to the inherent catalytic activity, high specific surface area and accessibility of active sites, metallic NPs are reported to give rise to high viscosity reduction of

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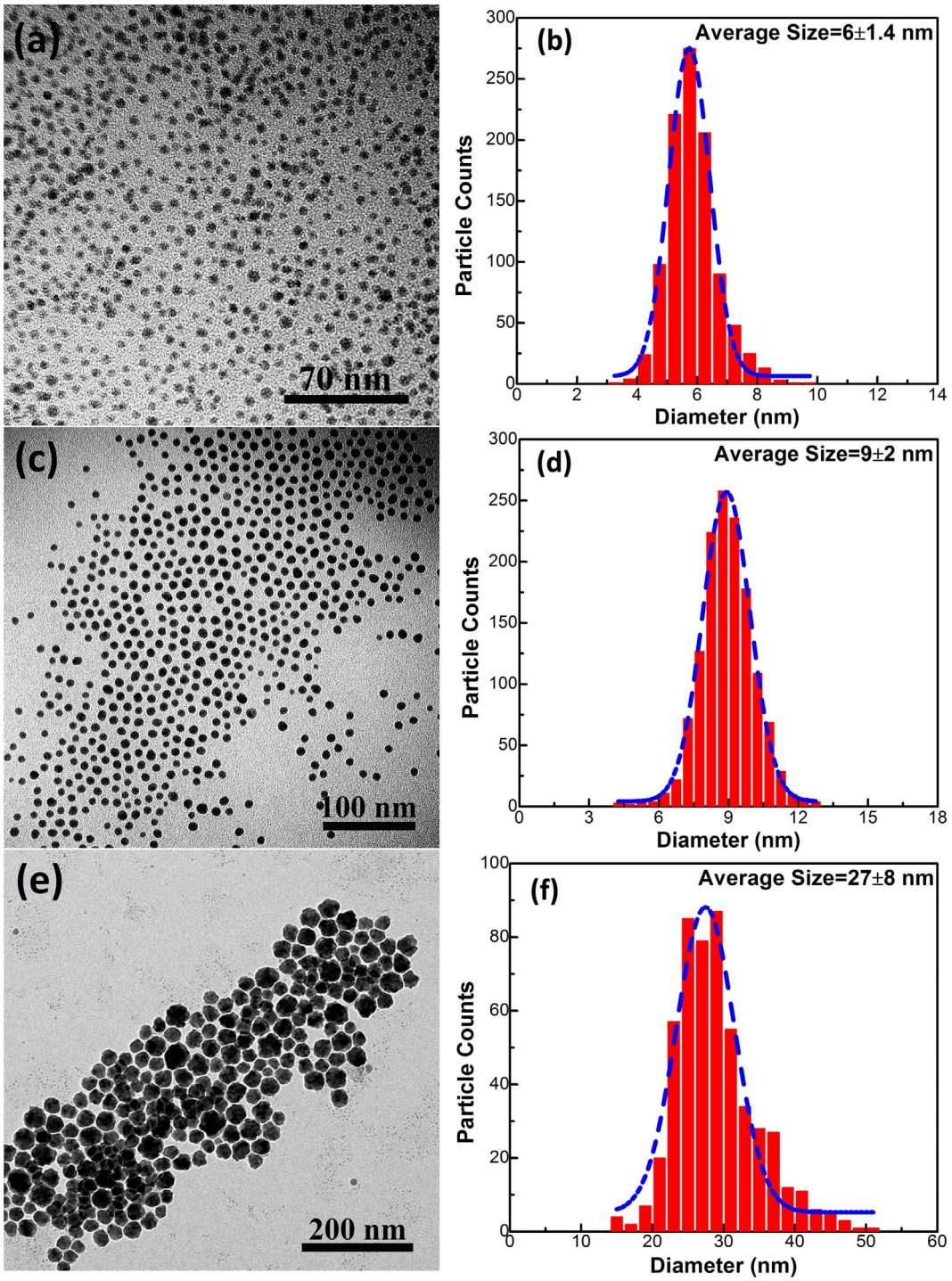

Fig. 1. TEM images and corresponding particle size distribution of the as-prepared Co NPs (a, b) and Ni NPs (c, d and e, f).

~90% at temperature of ~300 °C and pressure of > 3 MPa. Furthermore, the propagation of such NPs through porous rocks is demonstrated with little particle retention [18–21]. Nevertheless, the underlying mechanism behind the reactions remains largely unknown and further efforts are necessary to optimize the NP parameters in terms of metal type, particle size, suspension stability and structure design.

Previous work mainly uses commercially available metallic NPs or submicron particles, which have wide size distributions and can aggregate severely. Thus, it is difficult to fundamentally study the influence of individual property of the metal NPs on their catalytic activity. To this end, the preparation of monodispersed NP with narrow size distribution remains desirable. Besides, the size effect on catalytic activity is a frontier research topic in catalysis science. Despite smaller particle size entails higher metallic surface area-to-volume ratio and more active sites, the high surface energy of nanosized particles makes them tend to aggregate and thus lose the stability and activity. By precisely controlling the particle size in the synthesis process, numerous studies have reported the influence of particle size on the catalytic activity for different reactions [22–24]. To the best of our knowledge, the size-activity correlation for the aquathermolysis of heavy crude oil has never been investigated. Furthermore, current industrial catalysts for hydrotreating are prepared in the form of mixed metallic oxides, which need to be reduced to metallic states in the pretreatment process. Direct synthesis of metallic NPs can avoid the pre-reduction process,