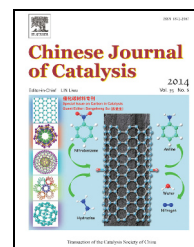


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Controllable synthesis and catalytic performance of graphene-supported metal oxide nanoparticles

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ABSTRACT

The size of nanoparticles plays a crucial role in their performance. In this article, three methods, i.e., direct impregnation, homogeneous oxidative precipitation with hydrogen peroxide, and ammonia-catalyzed hydrolysis, were applied to synthesize iron, cobalt, and nickel metal oxide nanoparticles supported on graphene. The influence of the three deposition methods on particle size distribution was investigated. Transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy were used to characterize the morphology and structure of the catalysts. The highest dispersion and the most uniform particle size distribution were obtained by the hydrogen peroxide homogeneous oxidative precipitation method. Hydrogen peroxide favors the maximization of the oxygen-containing groups on graphenes, thereby providing sufficient absorption and nucleation sites to give a high dispersion of nanoparticles. In contrast, ammonia accelerates the nucleation speed and results in the largest particle size and inhomogeneity. The catalytic properties of the graphene-supported metal oxide nanoparticles were tested with the oxidation of benzyl alcohol as a probe reaction. The reaction activity decreased in the following order: catalysts prepared by hydrogen peroxide-assisted deposition > direct impregnation > ammonia-catalyzed hydrolysis. The decrease in reaction activity was consistent with the order of increasing catalyst particle sizing shown in transmission electron microscopy images. The catalytic relevance of the particle size showed a necessity for the development of effective methods for size-controlled nanocatalyst synthesis on graphenes.

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1. Introduction

The size of nanoparticles (NPs) plays a crucial role in their performance. Smaller particle sizes offer higher surface-to-volume ratios, and thus, larger amounts of high energy sites on surfaces. For example, controlling the size of particles used in energy applications can lead to significantly enhanced surface-to-volume ratios and short transport lengths for the mobile charges [1]. Nano-sized NiO showed a higher capacity and

energy efficiency in lithium-ion batteries when compared with sub-micro-sized NiO [2]. The reduced particle size was responsible for the reduction in the charge-discharge hysteresis loop, and thus, higher reversible capacity and more stable cycle performance. Exceptional behaviors may also emerge at specific size ranges or in particular particle shapes [3]. For instance, it is well known that Au is highly active for low-temperature CO oxidation when the size of the Au particles is in the range 2–5 nm [4,5].

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Iron family metals (Fe, Co, Ni) are attracting more and more interest for their low prices and excellent performance in catalysis, such as hydrogenation [6], CO oxidation [7], alcohol oxidation [8], and electrochemistry [9]. The preparation of size-controllable Fe, Co, and Ni metal/metal oxide NPs can contribute much to the design of highly active non-noble catalysts. For Fe catalysts used in Fischer-Tropsch (FT) synthesis, the specific activity may increase 6 to 8-fold while the average iron carbide size decreases from 7 to 2 nm [10]. However, for Co catalysts, the specific activity of FT processes does not depend on the Co particle size when in the range 9–200 nm. For particles smaller than 7 nm, larger Co particles result in increased turnover frequency and C_5^+ selectivity [11]. Yang et al. [12] reported that Co NPs dispersed in the mesoporous carbon exhibited a higher selectivity with decreasing particle size in the CO hydrogenation reaction. Pina et al. [13] reported that the hydrodechlorination of aromatic compounds over Ni/SiO₂ catalysts was dependent on the Ni particle size. Larger particles favor the specific Cl removal, owing to the intrinsic electronic properties and metal/support interactions.

Graphene is widely used as an excellent support for highly dispersed metal nanocatalysts owing to its excellent electronic, thermal, and mechanical properties and high surface area [14–17]. Graphene oxide (GO), a derivative of graphene, possesses abundant oxygen-containing groups and defects, making it suitable for anchoring NPs. The resulting nanocomposites are promising in catalysis [18], energy conversion and storage [19,20], electronics and sensors [21,22]. A number of methods have been used to synthesize graphene-metal nanoparticle composites. The simplest approach is the direct growth from metal precursors on the surface of GO by electrostatic interaction at elevated temperatures [23]. The oxygenated functional groups anchor the metal ions for nucleation and GO is reduced during the depletion of the functional groups. In many cases, reducing agents, such as NaBH₄ [24], L-ascorbic acid [25], and hydrazine hydrate [26] were needed to reduce the ions to metal particles. NH₃·H₂O is commonly employed to aid the hydrolysis of metal ions [27,28], followed by reduction or decomposition of the metal hydroxide in a certain atmosphere to obtain metal/oxide-graphene composites. So far, efforts have been made to control the sizes of Fe, Co, and Ni NPs supported on graphenes by varying the starting precursor concentration [29], reaction time [30], annealing temperature [31], and the thickness of the additive agents [32]. However, the composites obtained by the above methods differ not only in the particle size, but also the metal loading, materials composition, and the reduction degree of GO.

When GO is used as a support, the abundant oxygen-containing groups on its surface provides sufficient absorbing and nucleation sites for metal ions. Thus, the dispersion of the supported NPs can be controlled by adjusting the amount of the functional groups. Our previous studies showed that metal oxide NPs can be dispersed on carbon nanotubes (CNTs) by a H₂O₂ homogeneous oxidative precipitation (HOP) method [33,34], in which ultrafine oxide particles can be easily loaded on CNTs under mild conditions, without using any surfactants or corrosive reagents and without any emissions from the pro-

cess except water. Herein, we present Fe, Co, and Ni metal oxide NPs grown on reduced GO (RGO) with the H₂O₂ HOP method. By comparing with direct impregnation and ammonia-catalyzed hydrolysis, the influence of the deposition method on the particle size distribution was investigated and their catalytic performances were tested in the oxidation of benzyl alcohol.

As one of the most important reactions for the synthesis of valuable chemical intermediates, the aerobic oxidation of benzyl alcohol in the liquid phase has attracted much research interest. The most commonly used catalysts for this reaction are precious metals, such as Au, Pt, Ru, and Pd [35–37]. Some base transition metal (Fe, Co, Ni) catalysts were prepared to replace the noble metals [8,38–40]. The size and shape dependency of catalysts for reaction performance has been discussed [8], indicating that fine particle sizes (< 5 nm) is favored by the liquid phase benzyl alcohol oxidation. However, the preparation of size-controllable non-precious catalysts and the impact of size have not been investigated clearly and need further research. Therefore, in this paper, the influence of preparation conditions on the metal NP size and the size effect on the alcohol oxidation performance will be studied.

2. Experimental

2.1. Preparation of MeO_x/RGO (Me = Fe, Co, Ni) nanocomposites

Graphite oxide was prepared by a modified Hummers method with natural flake graphite as the carbon source (325 mesh, Alfa Aesar) [41]. First, 3 g of graphite was added to a solution of concentrated H₂SO₄ (30 mL), K₂S₂O₈ (10 g), and P₂O₅ (10 g) and heated at 80 °C for 4.5 h. After cooling to room temperature, the mixture was diluted with deionized (DI) water, filtered and dried. The pre-oxidized graphite was added to 120 mL of concentrated H₂SO₄. Fifteen grams of KMnO₄ was added slowly whilst keeping the mixture below 20 °C. The mixture was then stirred at 35 °C for 2 h, diluted with 250 mL of DI water and stirred for an additional 2 h. After adding 700 mL of DI water, 30% H₂O₂ solution (20 mL) was injected dropwise. The color of the solution turned to a bright yellow. The product was collected by filtration and washed by 1 L of H₂O/HCl solution (10:1, v/v). The product was then re-dispersed in DI water at 8 g/L and dialyzed for 1 week until the dialysate pH was neutral, to obtain graphite oxide. GO was prepared by exfoliating graphite oxide in DI water using sonication for 2 h. The concentration of the suspension was 1 mg/mL.

To prepare FeO_x/RGO, 15 mL of 12 mmol/L FeSO₄ aqueous solution was added into the GO/H₂O suspension dropwise while stirring. After ultrasonication for 2 h, the suspension was stirred at room temperature overnight for ion exchange. Subsequently, 1.6 mL of H₂O₂ aqueous solution (30 wt%) was added to the suspension dropwise, followed by stirring at 80 °C for 4 h to obtain the Fe(OH)_x/GO precursor. The solids, denoted here as Fe(OH)_x/GO-HP, were collected by centrifugation and lyophilization. For comparison, the impregnated sample, denoted as Fe(OH)_x/GO-I, was prepared without adding H₂O₂. We

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