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Size-controlled synthesis of monodisperse nickel nanoparticles and investigation of their magnetic and catalytic properties

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ABSTRACT

Monodisperse nickel nanoparticles (NPs) with different size were synthesized via the thermal decomposition approach using nickel acetylacetonate as precursors and trioctylphosphine as surfactant in oleylamine. The structure and morphology of as-synthesized nickel NPs were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and selected area electron diffraction (SAED). The surface states of as-synthesized nickel NPs were characterized by Fourier transform infrared (FT-IR) spectra. The textural properties of as-synthesized nickel NPs were characterized by N_2 adsorption–desorption. The size of as-synthesized nickel NPs was found to be easily controlled by changing synthetic conditions, including P:Ni precursor ratio, reaction temperature, reaction time and oleylamine quantity, and the possible growth mechanism of nickel NPs was proposed. In addition, the magnetic measurements showed that the as-synthesized nickel NPs exhibited superparamagnetism characteristics at room temperature, and the saturation magnetization increased significantly with the increase in nickel NPs' size. Finally, the size-dependent catalytic properties of nickel NPs for cyclohexane dehydrogenation reaction were studied. The results demonstrated that the catalytic activity can be enhanced by decreasing the size of NPs, which indicated that the dehydrogenation reaction of cyclohexane on nickel NPs was structure sensitive reaction.

1. Introduction

In recent years, increasing attention has been paid to the monodisperse nickel NPs because of their excellent physical and chemical properties and comprehensive applications in a variety of fields, such as magnetic materials [1–5], sensor materials [6], optical [7,8], and catalysts [9–11]. In comparison with the traditional Raney nickel, nanostructured nickel particles showed excellent catalytic activity, high stability, and could be synthesized easily, which indicated that the research of nickel NPs will become very attractive in the future [1]. Many studies suggested that the size of nickel NPs played an important role in the magnetic [12,13] and catalytic properties [14,15]. Therefore, the control synthesis of monodisperse nickel NPs with different sizes became a key problem for the exploration of new research and application fields. However, the synthesis process is complicated, the nickel nanoparticles agglomerated easily, and it was oxidized easily in air. All of these problems make it as a big challenge to control the size of monodisperse nickel NPs.

Nowadays, various methods have been attempted to synthesize monodisperse nickel NPs, such as thermal decomposition of organometallic precursor [16–18], hydrothermal or solvothermal [19,20], sol–gel methods [21,22], sonochemical reduction [23], microemulsion [24–26], and microwave synthesis [27]. Among these methods, thermal decomposition of organometallic precursor has the advantage of the easily achieved reaction, and the size and morphology of NPs could be well controlled by changing reaction conditions. In general, in this method, the presence of surfactant is necessary in order to prevent particle agglomeration, as well as controlling the size and morphology of NPs. For example, Peck et al. [28] synthesized the monodisperse nickel NPs with different size by changing the amounts of nickel acetylacetonate and oleylamine. Cordente et al. [4] synthesized nickel nanorods in tetrahydrofuran solution in the presence of hexadecylamine or trioctylphosphine oxide. Railsback et al. [29] reported that the solvent also played an important role in controlling the size of nickel NPs. Hou et al. [30] synthesized monodisperse nickel NPs in the presence of hexadecylamine and trioctylphosphine oxide and found that the size depended on the ratio of hexadecylamine to

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trioctylphosphine oxide. Wang et al. [31] reported that the size of NPs could be adjusted by changing the reactant ratio and reaction time, and the phase could be controlled by adjusting the reaction temperature. There are lots of reports on the synthesis of nickel NPs, but the influence of various reaction conditions on the particle size distribution was not studied systematically, and the formation mechanisms of nickel NPs were not clearly explained, as well.

As we all know, the dehydrogenation of cyclohexane was an important model reaction in petroleum refining and reforming processes, and noble metal catalysts were usually be used as dehydrogenation catalysts [32–34]. However, the high price of noble metal limited their application. Therefore, more and more researches focused on the development of non-noble metal catalysts [35–37]. Nickel catalyst was one of the non-noble metal catalysts which had good catalytic activity on dehydrogenation reaction, while most of researches were focus on supported nickel catalyst. Our previous work [36] had reported that nickel-based catalysts supported on alumina showed better catalytic performance on cyclohexane dehydrogenation and found that nickel agglomerated easily in high temperature and the particle size increased rapidly, which led to the decreased of catalytic activity. Therefore, the particle size played an important role in the heterogeneous catalytic reaction of nickel. However, the researches on size-dependent catalytic properties of nickel NPs for cyclohexane dehydrogenation reaction was scarce. According to this, in the present report, monodisperse pure phase nickel NPs were synthesized via the thermal decomposition approach using nickel acetylacetonate as precursors and trioctylphosphine as surfactant in oleylamine. The structure and morphology of as-synthesized nickel NPs were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and selected area electron diffraction (SAED). The surface states of as-synthesized nickel NPs were characterized by Fourier transform infrared (FT-IR) spectra. The textural properties of as-synthesized nickel NPs were characterized by N_2 adsorption–desorption. In addition, the effect of synthetic conditions such as P:Ni precursor ratio, reaction temperature, reaction time, and oleylamine quantity on size and morphology of nickel NPs were studied, and the possible formation mechanism was proposed. Finally, the size influences of nickel NPs on magnetic properties and catalytic activity for cyclohexane dehydrogenation reaction were also investigated systematically.

2. Experimental

2.1. Materials

Nickel(II) acetylacetonate (Ni(acac)$_2$, 95%), trioctylphosphine (TOP, 90%), oleylamine (OAm, 95%) was obtained from Aladdin Chemistry Co. Ltd. Cyclohexane ($\geq$95%), hexane ($\geq$99.5%), acetone ($\geq$99.5%), and ethanol ($\geq$99.7%) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as-received without further purification. All reactions were carried out under argon atmosphere using standard air-free techniques.

2.2. Synthesis of nickel NPs

In a typical reaction, nickel acetylacetonate, OAm (2–10 mL) were placed in a four-neck flask and stirred magnetically under a flow of argon. The mixture was raised to 120 °C with a heating rate of 10 °C min^{-1} and kept at this temperature for 30 min to remove moisture and dissolved oxygen. After TOP was quickly injected into the solution, the mixture was heated to 200–240 °C rapidly and maintained for 10–120 min. The molar ratio of TOP to nickel acetylacetonate was typically kept at 0.5–4. The color of the solution changed from blue, green, dark green to black. After cooling to room temperature, the black precipitate was obtained from the solution by adding excess ethanol and separated by centrifugation (4000 rpm, 15 min), then the black precipitate was washed with the mixture of hexane and acetone, and precipitated by adding excess ethanol. This procedure was carried out three times at least to remove excess surfactant and organic solvent. Finally, the product was dried in vacuum at 60 °C for 24 h. The size and morphology of as-synthesized nickel NPs could be controlled by changing synthetic conditions, including P (TOP):Ni (Ni(acac)$_2$) precursor mole ratio, reaction temperature, reaction time, and OAm quantity.

2.3. Characterization

XRD was performed on a panalytical X'pert PROX-ray diffractometer with Cu Kα monochromatized radiation (λ = 1.54 Å) operated at 45 kV and 40 mA. The scan rate was 8° min^{-1} and the 2θ scan range was from 20° to 90°. TEM was performed on a JEM-2100 UHR microscope (JEOL, Japan) at an accelerating voltage of 200 kV. SAED was used to identify the crystalline phases. The samples for TEM analysis were prepared by sonicating the as-synthesized powers in hexane and depositing a drop on an amorphous carbon-coated copper grid, which was allowed to slowly dry at ambient condition. FT-IR spectrum was collected on a Nexus spectrometer (Nicolet, USA) in the range of 4000–400 cm^{-1} with 32 scans and the samples were prepared as KBr pellets. N_2 adsorption–desorption experiments were carried out on a ChemBET 3000 (Quantachrome, USA) instrument. The magnetic properties measurements of as-synthesized nickel NPs were carried out with a superconducting quantum interference device (SQUID) magnetometer (MPMS-5) in a temperature range of 5–300 K.

2.4. Catalytic properties assessments

The cyclohexane dehydrogenation reaction was performed in a pulse chromatographic microreactor. The main reactor was made of quartz glass tube equipped with a fine hole at the top for the injection of liquid reactant (cyclohexane). A carrier gas H_2 was introduced to the reactor with flow rate of 30 mL min^{-1}. The catalyst was heated using a heater and the reaction temperature was held at 350–420 °C using a temperature controller and thermocouple arrangement. The installation was stabled for 30 min at determinate temperature, and then pulse feed 0.2 μL each time. The products were analyzed by the on line gas chromatograph (Agilent GC-4890D) and flame ionization detector (FID). The conversion of cyclohexane was used to evaluate the activities of catalysts. The conversion was calculated from the ratio of converted cyclohexane and initial cyclohexane.

3. Results and discussion

3.1. Effect of synthetic conditions on particle size and morphology

In order to control the size and morphology of the as-synthesized nickel NPs, four groups of the single-factor experiment were carried out under different conditions, including P:Ni precursor ratio, reaction temperature, reaction time, and OAm quantity. Each effect of the four reaction parameters on the size of the as-synthesized nickel NPs was studied. The detailed synthetic conditions for each group were listed in Table 1. The crystal phase structure of as-synthesized samples at different synthetic conditions were characterized by XRD, and the corresponding results were shown in Fig. 1a(i). The size distribution and morphology were characterized by TEM analysis, and the results were shown in Figs. 2–5.