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

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**A B S T R A C T**

Monodisperse nickel nanoparticles (NPs) with different size were synthesized via the thermal decomposition approach using nickel acetylacetonate as precursors and trietylphosphine 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 N₂ 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.

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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 acetylacetone and oleylamine. Cordente et al. [4] synthesized nickel nanorods in tetrahydrofuran solution in the presence of hexadecylamine or trietylphosphine 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 trietylphosphine oxide and found that the size depended on the ratio of hexadecylamine to...
triocylphosphine 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 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 

## 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 (≥95%), hexane (≥99.5%), acetone (≥99.5%), and ethanol (≥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. N₂ 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 H₂ 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 stabilized for 30 min at determined 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.
Table 1
Detailed synthetic conditions of the single-factor experiment.

<table>
<thead>
<tr>
<th>Group</th>
<th>P:Ni</th>
<th>T(°C)</th>
<th>t(min)</th>
<th>OAm (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1:2</td>
<td>220</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>a</td>
<td>1:1</td>
<td>220</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>2:1</td>
<td>220</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>2:1</td>
<td>220</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>2:1</td>
<td>220</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>2:1</td>
<td>220</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>2:1</td>
<td>200</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>2:1</td>
<td>200</td>
<td>90</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>2:1</td>
<td>200</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td>d</td>
<td>2:1</td>
<td>200</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>d</td>
<td>2:1</td>
<td>200</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

T is the reaction temperature, t is the reaction time, P:Ni is the precursor ratio, OAm is the oleylamine quantity.

Fig. 1a–d was the XRD patterns of as-synthesized nickel NPs at different ratio of P: Ni precursor. It could be seen that the XRD patterns present the typical face-centered cubic (fcc) nickel signals (PDF#01-087-0712), the diffraction peaks at 2θ = 44.5°, 51.6°, and 76.4° were attributed to (111), (200), and (220) crystal faces of fcc nickel, and no extraneous peaks were exist, which indicated that as-synthesized nickel NPs were pure phase. No characteristic peaks of crystalline nickel oxides appeared, which indicated that the nickel NPs were stable enough in air atmosphere owing to the protecting effect of surfactant covering the particle surfaces probably. The XRD patterns of as-synthesized products at different temperature were shown in Fig. 1e–g. When the temperatures were 200 and 220 °C, the patterns presented the typical fcc nickel signal (PDF#01-087-0712). When the reaction temperature was further increased to 240 °C, Ni–P mixture was obtained, the diffraction peak was detected at 2θ = 44.5°, which was attributed to (111) crystal face of nickel, the diffraction peaks were detected at 2θ = 40.8°, 54.1°, and 80.9°, which were attributed to (111), (300), and (401) crystal faces of Ni3P (PDF#01-089-2742), the diffraction peak was detected at 2θ = 49.1°, which was attributed to (312) crystal face of Ni2P3 (PDF#00-022-1190). At the same time, the diffraction peaks were detected at 2θ = 47.1° and 74.6°, which were attributed to the overlap of Ni2P and Ni3P, respectively. These results indicated that TOP possibly decomposed at high temperature. Furthermore, Fig. 1h and i was the XRD patterns of as-synthesized nickel NPs at different OAm quantity. It could be seen that only the diffraction peak at 2θ = 44.5° could be observed, and the peak was extremely broad, which indicated that the NPs were nearly amorphous [9].

Fig. 2a–j was the morphology images and size distributions of as-synthesized nickel NPs at different P: Ni precursor ratio. TEM images illustrated that the as-synthesized nickel NPs exhibited monodisperse sphere-like morphology and had different size distribution with the changing of P:Ni precursor ratio. The typically spherical shape indicated that the growth of nickel NPs was isotropic. Decreased the molar ratio of P:Ni precursor resulted in an increase in the size of NPs. From Fig. 2a–h, one can observed that the size of NPs was from 18.97 ± 3.33 to 7.48 ± 0.52 nm when the molar ratio of P:Ni precursor was changed from 1:2 to 4:1. These results indicated that TOP can stabilize the particles by absorbing the surface of nickel NPs and limited the aggregation. However, increased the molar ratio of P:Ni precursor from 2:1 to 4:1, the size of as-synthesized nickel NPs was not changed, which indicated that the adsorption of TOP reached saturation state. These results were in accordance with the previous work [12]. The corresponding HRTEM image (Fig. 2i and j) of nickel NPs with size of 18.97 ± 3.33 nm exhibited different lattice fringes directions at various regions for a single particle, which indicated the polycrystalline nature of the NPs. Furthermore, the fringe spacing was about 2.05 Å, corresponding to the (111) lattice plane of fcc nickel (2.03 Å). The electron diffraction pattern (inset in Fig. 2j) showed four diffuse rings, corresponding to the (111), (200), (220), and (311) crystal faces of fcc nickel, which further confirmed the cubic phase structure of nickel NPs. In conclusion, P: Ni precursor ratio was an important factor in the control synthesis of nickel NPs.

The reaction temperature was another important factor in controlling the size of nickel NPs. As one seen from Fig. 3, when the temperature was 200 °C, the nickel NPs not only exhibited monodisperse sphere-like morphology with an average size of 5.23 ± 0.72 nm, but also direction alignment, which indicated that the NPs were self-assembly in the process of synthesis. Increased the temperature from 220 to 240 °C resulted in an increase in the particles size from 7.12 ± 1.27 to 10.17 ± 1.52 nm, and the nickel NPs exhibited polydispersity, which were attributed to the aggregation of nickel NPs.

In addition, the effect of reaction time on particle size was further investigated. As shown in Fig. 4, only small clusters were observed after the reaction for 10 min (Fig. 4a), and the particles remained well dispersed, which suggested that the particles were possibly protected by a shell of ligands. When the reaction time reached 60 min (Fig. 4b), the size of particles increased but the monodispersity was very well. The size of particles increased gradually and the dispersity became lower after reaction for 90 min (Fig. 4c). When the reaction time further reached 120 min (Fig. 4d), the average size was not changed due to the adsorption of TOP reached saturation state but the dispersity was very poor, and most of the particles were aggregate and exhibited polydispersity.

In the experiments system, OAm acted as reductant to control the nucleation rate, which possibly affected the size of nickel particles. TEM analysis (Fig. 5) indicated that the size of the nickel NPs changed from 6.48 ± 0.69 to 5.53 ± 0.45 nm with the quantity of OAm changed from 2 to 10 mL, and the dispersity become better gradually. This is because the presence of excess OAm was in favor of the nucleation process, as well as limited the growth of particles. However, a small quantity of OAm, which reduced the nucleation rate of nickel clusters and aggregated easily in solution due to the high surface energy and intermolecular forces [38].

Generally, P:Ni precursor ratio, temperature, time, and OAm quantity all play important roles in controlling the size and morphology of nickel NPs, and high P:Ni precursor ratio, low temperature, short reaction time, and high OAm quantity were
Fig. 2. TEM images and size distribution of as-synthesized nickel NPs at different P:Ni precursor ratio of (a, b) P:Ni = 1:2; (c, d) P:Ni = 1:1; (e, f) P:Ni = 2:1; (g, h) P:Ni = 4:1. HRTEM images (i, j) and SAED pattern (insetted in image j) of nickel NPs at P:Ni = 1:2.
beneficial for forming the small particles. Of course, the temperature also impacted the crystal phase of particles, nickel NPs generated at low temperature but Ni-P mixture at high temperature.

3.2. Possible growth mechanism

The possible growth mechanism of nickel NPs with size-controlled monodisperse spherical morphology could be proposed according to the above experimental results. The formation process of nickel NPs consisted of three stages, nucleation, aggregation growth, and Ostwald ripening process. In the experimental system, OAm acted as solvent, as well as the reductant to control the nucleation rate, and the nucleation process mainly took place when the reaction temperature reached 200 °C. The small nanoclusters could be observed at short reaction time. Meanwhile, TOP acted as surfactant, which could adsorb on the surface of nickel NPs and inhibited the growth of nickel NPs. TOP also could realize

![Fig. 3. TEM images and size distribution of as-synthesized nickel NPs at different temperature of (a, b) T=200 °C; (c, d) T=220 °C; (e, f) T=240 ° C.](image-url)
the self-assembly process of nickel NPs. This is probably because that TOP molecules bound to the crystalline planes of nuclei and reached a balanced state in all direction. Meanwhile, the increase in OAm quantity was favorable to this nucleation process, which led to larger quantities of nuclei were formed in the solution. However, the small nanonuclei was unstable in solution due to the high surface energy and intermolecular forces [38], which led to the rapidly aggregation of nickel NPs. With increasing reaction temperature and time, the particle aggregation process increased correspondingly, which led to the formation of particles with broad size distribution and low dispersity. When the reaction time continues to be prolonged, the Ostwald ripening process occurred, the smaller particles dissolved, and the larger ones grew [12]. According to the above discussions, the possible growth mechanism of as-synthesized nickel NPs was summarized in Fig. 6.

3.3. Surface state of as-synthesized nickel NPs

The FT-IR analysis was used to characterize the surface state of as-synthesized nickel NPs. The FT-IR spectra of synthetic products at various P:Ni precursor ratio were shown in Fig. 7. The absorption peak at 3430 cm$^{-1}$ was due to stretching vibration of N–H bond, the absorption peaks at 2928 and 2854 cm$^{-1}$ were attributed to the stretching vibration of C–H in methyl and methylene. The
absorption peak at 1620 cm\(^{-1}\) was attributed to the stretching vibration of C=O in OAm. The presence of two peaks at approximately 1050 and 988 cm\(^{-1}\) in spectra indicated the coordination of the TOP on the surface of the nickel NPs and confirmed the presence of phosphorous, and these results were in agreement with Sophie Carenco, etc. [12]. The absorption peaks from 720 to 560 cm\(^{-1}\) were attributed to the stretching vibration of long carbon chain. The FT-IR spectra confirmed that TOP and OAm acted as ligand coexisted on the surface of nickel NPs, which results in the excellent dispersibility of nickel NPs and protected the nickel NPs from being oxidized in air atmosphere.

### 3.4. Textural properties of as-synthesized nickel NPs

The textural properties (BET surface area, pore volume, and pore size) of as-synthesized nickel NPs with different size were shown in Table 2. It could be observed that the as-synthesized nickel NPs with the size of 18.97 ± 3.33 nm exhibited a lower BET surface area (37.3 m\(^2\)/g) than the other NPs, whereas nickel NPs with the size of 7.48 ± 0.52 nm had the highest BET surface area (53.4 m\(^2\)/g), which suggested that the surface area of nickel NPs increased gradually with decreasing size of nickel NPs. Meanwhile, the pore volume and pore size increased gradually with increasing size of nickel NPs. The \(N_2\) adsorption–desorption isotherms of the as-synthesized nickel NPs with different size were shown in Fig. 8. The isotherms belong to type IV which was typical for mesoporous material.

### 3.5. Size-dependent magnetic properties

To further investigate the magnetic properties of monodisperse nickel NPs, magnetic measurements of the as-synthesized nickel NPs with different particles size were carried out by measuring both the temperature-dependent magnetization (\(M-T\)) and hysteresis (\(M-H\)) curves. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were shown in Fig. 9I, and the hysteresis loops of the nickel NPs with different size measured at different temperature were shown in Fig. 9II and III, respectively. As one can see from Fig. 9I, a distinct magnetic cooling effect was observed, and the FC magnetization monotonically decreased when the temperature increased from 5 to 300 K. Meanwhile, the ZFC magnetization firstly increased with increasing temperature, then decreased slowly after the ZFC-FC magnetization curves reached a crossing point, which was called as blocking temperatures (\(T_B\)). The ZFC-FC curves showed that the \(T_B\) of nickel NPs were about 120 and 160 K for the size of 5.23 ± 0.72 and 7.12 ± 1.27 nm nickel NPs, respectively. These results indicated that \(T_B\) were lower than room temperature and increased gradually with increasing particle size. From Fig. 9II, the measured saturation magnetization (\(M_s\)) under a field of 10 kOe for nickel NPs with the size of 5.23 ± 0.72 and 7.12 ± 1.27 nm were 0.2369 and 0.3044 emu/g at 300 K, respectively. In addition, the coercivity (\(H_c\)) and remnant magnetization (\(M_r\)) values measured at 300 K of these two samples were negligible basically, and no hysteresis behavior was observed, which revealed that the as-synthesized nickel NPs had superparamagnetism characteristics at room temperature [31]. However, the \(M-H\) curve measurements at 5 K had different magnetic characteristics. From Fig. 9III, the measured \(M_s\) under a field of 10 kOe were 0.3145 and 0.4115 emu/g. The \(M_s\) values were about 0.0991 and 0.1299 emu/g, and the \(H_c\) values measured at 5 K were 317 and 284 Oe, respectively. Both samples presented a distinct hysteretic

### Table 2

Textural properties of as-synthesized nickel NPs with different size.

<table>
<thead>
<tr>
<th>Nickel NPs size (nm)</th>
<th>BET surface area (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.48 ± 0.52</td>
<td>53.4</td>
<td>0.03</td>
<td>3.14</td>
</tr>
<tr>
<td>9.71 ± 1.49</td>
<td>41.1</td>
<td>0.04</td>
<td>4.49</td>
</tr>
<tr>
<td>18.97 ± 3.33</td>
<td>37.3</td>
<td>0.05</td>
<td>5.86</td>
</tr>
</tbody>
</table>

![Fig. 6. The possible growth mechanism of nickel NPs.](image)

![Fig. 7. FT-IR spectra of synthetic nickel NPs at different P: Ni precursor ratio of (a) P:Ni = 1:2; (b) P:Ni = 1:1; (c) P:Ni = 2:1.](image)

![Fig. 8. \(N_2\) adsorption–desorption isotherms of the as-synthesized nickel NPs with the different size of nickel NPs for (a) 7.48 ± 0.52 nm; (b) 9.71 ± 1.49 nm; (c) 18.97 ± 3.33 nm.](image)
behavior, which indicated that as-synthesized nickel NPs had the ferromagnetic characteristics at 5 K. We can also observe that with increasing particle size, the $M_s$ and $M_r$ of the samples increased rapidly, while $H_c$ decreased gradually. These results were in accordance with the previous report [13]. Moreover, the $M_r$ value of the two samples were far from the saturation value for bulk nickel (57.6 emu/g), which can be explained from the high specific surface area of nickel NPs [3].

3.6. Size-dependent catalytic properties

Particle size is one of the most important factors which could dominate catalytic activity [14]. The experiments on catalytic activity of the as-synthesized nickel NPs with different sizes were carried out in a pulse chromatographic microreactor, and the influence of reaction temperature on the conversion of cyclohexane and the selectivity of benzene were investigated. The results were presented in Fig. 10. It could be observed that: (1) the conversion of cyclohexane firstly increased, and then decreased gradually with increasing temperature until reached a maximum, especially for the larger particles. The selectivity of benzene decreased gradually for nickel NPs with a size of 18.97 ± 3.33 nm, while the small-size nickel NPs exhibited high selectivity of benzene and almost not changed with the increase in temperature. It is because that the dehydrogenation reaction of cyclohexane is an endothermic reaction in thermodynamics, and the increase in temperature was in favor of the reaction. However, when the temperature continued increasing, the conversions decreased, this is because the particle sintered seriously, which led to the increase of particles size and the decrease of active site density. (2) For nickel NPs with a size of 18.97 ± 3.33 nm, there is a low cyclohexane conversion. However, the conversion increased with the decrease of particle size, indicated a distinct size effect. The conversion of cyclohexane reached to the maximum of 79.77% with a size of 7.48 ± 0.52 nm at 390 °C. It is because that the smaller particles made the contact area larger, and the larger surface area (as shown in part 3.4) exposes more number of active sites. Furthermore, there exist reports on the activation energy of cyclohexene dehydrogenation also increased with the increase of catalyst size [14], which further confirmed that the dehydrogenation reaction of cyclohexane was favored for small size catalyst. Boudart proposed that catalytic reactions can be divided into structure sensitive reaction and structure insensitive reaction [39]. According to the above results, it can be concluded that the dehydrogenation reaction of cyclohexane on nickel catalyst was structure sensitive reaction, which was in accordance with the previous work on the dehydrogenation reaction of 2-methylpentane [40]. In addition, many research reported that the capping ligands which adsorbed on metal NPs also could affect the catalytic performance [41–45]. Chen et al. [47] reported that three properties of capping ligands have influences on the catalytic performance of metal NPs, including surface blocking effect, electronic effect and site-isolation effect. In our experiments system, on the one hand, TOP and OA0m acted as the capping ligands and coexisted on the surface of nickel NPs, which possibly decreased the number of
exposed active sites. On the other hand, the electronic effect also has influence on the catalytic performance because the capping ligands could donate electrons to Ni NPs.

4. Conclusion

Monodisperse nickel NPs with different size were synthesized via the thermal decomposition approach using nickel acetylacetonate as precursors and TOP as surfactant in OA. The effect of synthetic conditions on size and morphology of nickel NPs had been systematically studied. Generally, higher P: Ni precursor ratio, lower temperature, shorter reaction time, and higher OA quantity were beneficial for forming the small NPs. The formation mechanism of nickel NPs consisted of three stages: nucleation, aggregation growth, and Ostwald ripening process. The measurement results of magnetic properties indicated that the as-synthesized nickel NPs exhibited superparamagnetism characteristics at room temperature, and the saturation magnetization increased significantly with increasing nickel NPs size. The assessments of catalytic properties demonstrated that the catalytic activity could be enhanced by decreasing the size of NPs. The smallest nickel nanoparticle presented the best catalytic activity under the same conditions due to large surface area and high active site density. In addition, the surface-blocking effect and the electronic effect of the capping ligands which adsorbed on Ni NPs also possibly affect the catalytic performance. This study showed that the size is an important role to effect the magnetic and catalytic properties of nickel NPs. Further studies on the assembly of nickel NPs with support as well as its catalytic properties are in progress in our laboratories.

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