A facile synthetic route to flower-like NiO and its catalytic properties

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NiO with flower-like morphology has been synthesized via the simple homogeneous precipitation method by using nickel nitrate and urea at 115 °C for 1.5 h. The physicochemical properties of as-obtained NiO are characterized by X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, N2 sorption, and H2 temperature-programmed reduction. The results show that the flower-like NiO exhibits a larger surface area, higher reducibility and better catalytic activity for oxidative dehydrogenation of ethane to ethylene, compared to conventional particulate NiO.

Keywords: Nickel oxide, Precipitation, Homogeneous precipitation, Flower-like morphology, Dehydrogenation, Oxidative dehydrogenation, Ethane dehydrogenation, Ethylene

Due to their unusual physicochemical properties compared to bulk counterparts, highly ordered micro- and nano-structured materials have potential applications such as catalysts, drug delivery materials, photonic materials, and battery materials. In recent years, morphology-controlled synthesis of highly ordered nanostructured materials has become an increasingly interesting research topic. Amongst a variety of transition metal oxides, nickel oxide (NiO), is one of the most important promising materials and has attracted great attention due to its exotic properties and extensive applications such as positive magnetic materials, electrochromic films, fuel cell electrodes, gas sensors and catalysts.

Numerous chemical methods have been developed for the controlled synthesis of NiO nanostructures with novel morphologies because their properties and application are intimately related to the size and shape. NiO nanoparticles have been prepared by anodic arc plasma method, NiO nanowires and nanodisks have been successfully obtained via a wet chemical method under hydrothermal conditions using ethanol, NiO nanorolls can be selectively synthesized through a facile hydrothermal synthetic method, NiO nanowalls have been obtained by using a plasma assisted oxidation method and NiO nanotubes have been produced for the first time via an anodic aluminium oxide (AAO) template processing method. Recently, a few studies have reported on the synthesis of flower-like NiO nanostructures, which because of its special morphology and large surface area showed special properties. Ranga Rao and co-workers synthesized NiO powders with a flower spherical morphology by a hydrothermal technique using organic surfactants as templates and urea as the hydrolysis controlling agent, Zhu et al. have successfully synthesized NiO architectures through a microwave-assisted hydrothermal method using polyethylene glycol (PEG) as a surfactant while Lai et al. prepared 3D rose-like NiO under solvothermal conditions with sodium acetate (Na-Ac) and PEG-4000 and Al-Hajry and co-workers have obtained flower-shaped NiO structures composed of thin nanosheet networks via the aqueous solution route by using nickel chloride and ammonium hydroxide. To the best of our knowledge, however, in the reported studies the synthesis of flower-like NiO, were carried out either at higher temperature and pressure as well as for long reaction time or by using expensive instruments and chemicals. Thus, it is desirable to develop a facile and effective method for the synthesis of NiO nanostructures and to investigate their properties.

Herein, we report a simple, low-cost, and environmentally friendly preparation method, by which flower-like NiO nanostructures composed of nanosheet networks can be synthesized, without using hard/soft templates or other organic reagents. Catalytic activity of the flower-like NiO for oxidative dehydrogenation of ethane to ethylene (ODHE) has been compared with that of conventional particulate NiO.

Experimental

Typically, Ni(NO3)2·6H2O (0.08 mol) and urea (0.32 mol) were dissolved in 80 mL of deionized
water and then transferred into a 150 mL flask, which was subsequently sealed. The mixture was subjected to magnetic stirring at 115 °C for 1.5 h and then cooled to room temperature. The resulting greenish precipitate was centrifugated and washed three times each with deionized water and absolute ethanol. Then it was oven-dried at 110 °C for 24 h, followed by calcination at 400 °C for 1 h in air. The obtained NiO sample was denoted as NiO-F (F for flower-like). For comparison, NiO was also prepared by calcination of Ni(NO$_3$)$_2$·6H$_2$O under the same conditions and the obtained sample was denoted as NiO-N (N for nitrate).

Powder X-ray diffraction (XRD) patterns were recorded using a Philips PK 3040/60 powder diffractometer with Cu–K$_\alpha$ radiation ($\lambda$ = 0.1542 nm, 40 kV and 40 mA) and step scanning (0.2°) in the 2$\theta$ range of 10-90°. The average crystalline sizes were calculated by the Scherrer formula ($D = 0.89\lambda/\beta\cos\theta$).

The morphology of the samples was observed by a scanning electron microscope (SEM, Hitachi S-4800) operated at an acceleration voltage of 5 kV. Nitrogen sorption at 77 K was carried out with a Micromeritics Tristar Autosorb-1 3000 surface area and porosimetry analyzer to evaluate the porous properties and surface areas of the samples. Pore diameter distribution was evaluated by the Barrett-Joyner-Halenda (BJH) algorithm and the specific surface area was calculated by Brunauer-Emmett-Teller (BET) procedure.

The catalytic activities of NiO for oxidative dehydrogenation of ethane (ODHE) reaction were studied on a fixed-bed vertical-flow tubular quartz reactor (i.d. = 5 mm) packed with 0.1 g catalyst mixed with 0.2 g quartz particles. The feed gas consisted of ethane, oxygen, and nitrogen (C$_2$H$_6$/O$_2$/N$_2$ = 1/1/4), with a gaseous hourly space velocity (GHSV) of 18,000 mL h$^{-1}$ g$^{-1}$. The products were analyzed by an online gas chromatograph (GC-950) equipped with a thermal conductivity detector (TCD) attached with a Porapak Q and a 5A molecular sieve column.

**Results and discussion**

The phase structure of the precursor was examined by X-ray powder diffraction. As shown in Fig. 1, the as-synthesized material has both $\alpha$-Ni(OH)$_2$ and $\beta$-Ni(OH)$_2$ phases. The diffraction peaks corresponding to hexagonal $\alpha$-Ni(OH)$_2$ at 20 = 12.2°, 24.6° and 33.4° were assigned to (003), (006) and (101) crystal planes. The intensity of (003) peak is stronger than the others, indicating that (003) plane may be the preferred growth direction. The diffraction peaks corresponding to hexagonal structure of $\beta$-Ni(OH)$_2$ at 20 = 59.4° and 70.1° can be readily indexed as (110) and (103) crystal planes, respectively. The wide peaks and weak intensities imply the non-perfect crystalline structure of the precursor or the small crystalline size. The average crystalline size estimated by Sherrer’s equation is only 7.6 nm (calculated by the most intense (003) diffraction peak).

Figure 2 shows the morphology of the as-prepared Ni(OH)$_2$ precursor. The sample is composed of a large number of uniform flower-like microstructures with an average size of about 3 µm. Those flower-like architectures are built by several dozens of nanosheets with thickness of 10-20 nm and width of 0.2-0.3 µm, respectively.

The thermal behavior of flower-like Ni(OH)$_2$ nanostructures was examined with TG analysis (Supplementary Data, Fig. S1). The major weight loss occurred rapidly between 260 °C and 340 °C, indicating that the precursor with flower-like

![Fig. 1 – XRD pattern of the as-prepared Ni(OH)$_2$ sample.](image-url)
morphology is easily thermodecomposed. The total weight loss was measured to be about 25.6% which is larger than the theoretical value (19.4%) calculated according to the equation, Ni(OH)$_2$(endothermic) $\rightarrow$ NiO + H$_2$O. This may be attributed to the impurity of Ni(NO$_3$)$_2$ during the preparation process. Since the pyrolysis of the precursor was basically completed before 400 °C, we chose 400 °C as the decomposition temperature to obtain NiO in this study.

In the XRD patterns of NiO samples calcined at 400 °C all the reflections could be indexed to the cubic NiO phase (Fig. 3). The observed peaks at 20 = 37.2°, 43.2°, 62.8°, 75.2°, 79.3° were assigned to the (111), (200), (220), (311) and (222) crystal planes, respectively. Compared with NiO-N, the broader diffraction peaks of NiO-F suggest its small particle size and large surface area, which are consistent with the calculated results (9.1 nm for NiO-F, 36.5 nm for NiO-N) by the Scherrer formula.

The SEM micrographs of the NiO-F showed a flower-like hierarchical structure in the range of 20–30 µm (Fig. 4). Similar to the precursor Ni(OH)$_2$, NiO-F comprised of densely packed irregular sheets, with a thickness of 10-30 nm, which are assembled together. Moreover, no breakage in nanosheets was observed in these flower-like Ni(OH)$_2$ structures. Unlike the flower-like NiO-F, NiO-N is composed of large quantity of uneven bulk with an average size of about 150-300 nm.

Fig. 2—SEM images with different magnifications of the Ni(OH)$_2$ precursor. [(a) 10,000 times; (b) 110,000 times].

Fig. 3—XRD patterns of NiO with different morphology. [1, NiO-F; 2, NiO-N].

Fig. 4—SEM micrographs of (a) and (b) NiO-F, and, (c) NiO-N samples.
The surface textural characteristics of samples were further elucidated by N\textsubscript{2} sorption analysis (Fig. 5). The specific surface area of NiO-F was found to be about 85 m\textsuperscript{2}·g\textsuperscript{-1} as calculated by the Brunauer-Emmett-Teller (BET) method, which is much higher than that of NiO-N (7.4 m\textsuperscript{2} g\textsuperscript{-1}). Both NiO samples showed IUPAC type IV isotherms and H\textsubscript{3} type hysteresis. The samples have sorption isotherms with a hysteresis loop associated by capillary condensation starting at about \( p/p_0 \) 0.7 and extending almost up to \( p/p_0 \) 0.98, indicating that the pore size is relatively large. This is confirmed by the pore size distribution curve (inset of Fig. 5). The pore sizes of these two types of NiO are over a very wide range, especially NiO-F, and the peaks of the curves are 17.2 nm for NiO-F and 5.8 nm for NiO-N. The wider pore distribution of NiO-F as compared to NiO-N may be ascribed to the pore in NiO belonging to accumulated pore while in NiO-F there are large pores between the flowers and small pores between the nanosheets.

To explain the formation of flower-like hierarchical Ni(OH)\textsubscript{2} and NiO nanostructures, a possible formation mechanism is proposed. The thermodynamic process may be formulated as follows:

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\begin{align*}
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} &\rightarrow 2\text{NH}_3 + \text{CO}_2\uparrow \\
\text{Ni}^{2+} + 6\text{NH}_3 &\rightarrow [\text{Ni(NH}_3\text{)}_6]^{2+} \\
\text{NH}_3 + \text{H}_2\text{O} &\rightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{Ni}^{2+} + 2\text{OH}^- &\rightarrow \text{Ni(OH)}_2 \downarrow
\end{align*}
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The special structure formation of Ni(OH)\textsubscript{2} comprised the formation of nanoparticles and its growth into nanosheets, and subsequent self-assembly into the flower-like structure. In solution, Ni\textsuperscript{2+} ions react with generated OH\textsuperscript{-} to form the Ni(OH)\textsubscript{2} nanoparticles rapidly. The freshly crystalline nanoparticles tend to aggregate due to their high surface energy, driven by the minimization of interfacial energy. For shorter synthesis time (0.5 h) mixed morphologies of nanoparticles and nanosheets are observed (Supplementary data, Fig. S2). During the process, NH\textsubscript{3}, which is released from the decomposition of urea, plays an important role as a capping agent\textsuperscript{23}. It can combine with Ni\textsuperscript{2+} to form a relatively stable complex \([\text{Ni(NH}_3\text{)}_6]^{2+}\) because of its strong affinity to Ni\textsuperscript{2+} at room temperature, which could help to regulate the formation direction. When the synthesis temperature was lowered (85 °C), the sample presents nanoparticles morphology (Supplementary data, Fig. S3), which can be ascribed to the slower decomposition of urea weakening the orienting function of NH\textsubscript{3}. Simultaneously, the primary nanosheets can assemble into 3D flower-like architecture due to the crystal-face attraction van der Waals forces and hydrogen bonds\textsuperscript{24,25}. The CO\textsubscript{2} decomposed from CO(NH\textsubscript{2})\textsubscript{2} can also act as soft template to induce self-assembly of the nanosheets on their surfaces, since no other templates/surfactants/emulsions were used in this work. The self-assembly and Ostwald ripening process may occur around the gas/liquid interface of CO\textsubscript{2} and water, and forming finally 3D flower-like hierarchical architectures. When the synthesis temperature is very high (145 °C), the fast escaping CO\textsubscript{2} cannot play the assembly-direction role, which is why nanosheets cannot be well organized to a flower-like structure (see Supplementary data, Fig. S4). Finally, after calcination the flower-like Ni(OH)\textsubscript{2} transforms into NiO with the morphology maintained by the removal of interlayer anions.

The H\textsubscript{2} temperature programmed reduction (H\textsubscript{2}-TPR) technique has been extensively used to characterize the reducibility of the catalysts. The NiO-F samples showed a large reduction peak centered at 331 °C, which is ascribed to the reduction of Ni\textsuperscript{2+} to metallic nickel (Supplementary data,
Fig. S5). The shoulder peak may be ascribed to the reduction of NiO with different sheet sizes. In contrast to NiO-F, the wider peak center of NiO-N is shifted to a higher temperature at 426 °C, indicating its less reducibility.

Figure 6 shows the catalytic performance for C$_2$H$_6$ oxidation dehydrogenation over the NiO samples with different morphologies. On flower-like NiO, ethane conversion increases rapidly with reaction temperature up to 330 °C, above which it increases slowly. At the same reaction temperature, NiO-F gives higher ethylene selectivity than NiO-N. The maximum ethylene yield of 47.5% could be obtained on flower-like NiO at 350 °C while the yield was only 9.9% on NiO-N. It is clear that NiO-F exhibits superior ODHE performance than NiO-N.

According to the SEM and BET results, NiO-F has special flower morphology built by lots of nanosheets with large surface area and wider pore distribution due to the accumulation of nanosheet or flowers. Thus, NiO-F showed better reducibility and consequently improve the catalytic activity for ODHE reaction, as compared to NiO-N. Meanwhile, the larger pore diameter is in favor of faster escape of the product ethylene, but not over-oxidation to CO$_2$, and hence the selectivity to ethylene on NiO-F is higher than that on NiO-N. Also, the used NiO-F catalyst shows similar morphology and phase (Supplementary data, Figs S6 and S7 respectively) as the fresh one, displaying good structure-stability of the as-prepared flower-like NiO.

In summary, flower-like NiO with thin nanosheets has been successfully synthesized via a simple aqueous solution route, which is template- and surfactant-free. Compared with conventional particulate NiO-N, NiO-F exhibits better catalytic performance for ODHE reaction due to the special morphology and higher reducibility.

**Supplementary data**

Supplementary data associated with this article, viz., Figs S1-S7, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(01)51-56_SupplData.pdf

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**References**


![Fig. 6—Catalytic performance as a function of reaction temperature. (a) yield of C$_2$H$_4$; (b) selectivity of C$_2$H$_4$; (c) conversion of C$_2$H$_6$. 1, NiO-F; 2, NiO-N.](image-url)