



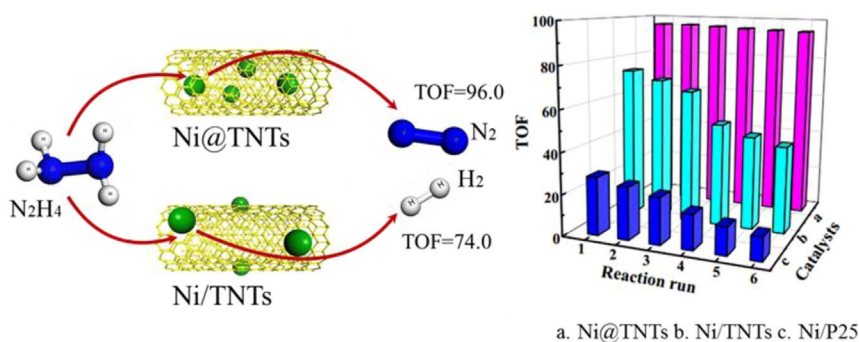
Ni nanoparticles encapsulated in the channel of titanate nanotubes: Efficient noble-metal-free catalysts for selective hydrogen generation from hydrous hydrazine



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GRAPHICAL ABSTRACT



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ABSTRACT

Ni nanoparticles were encapsulated in the channel of titanate nanotubes (TNTs) by the capillary forces under ultrasonic treatment (Ni@TNTs). The structure and properties of the catalyst were studied by scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), H_2 -temperature programmed reduction (H_2 -TPR), CO chemisorption and N_2 adsorption–desorption, respectively. The TEM, EDX and N_2 adsorption–desorption results demonstrated that Ni nanoparticles (NPs) were encapsulated in the channel of TNTs successfully. The results of XRD, H_2 -TPR and XPS indicated a strong metal-support interaction between Ni NPs and TNTs. Ni@TNTs exhibited a good catalytic performance for the decomposition of hydrous hydrazine which was due to the small nanoparticle size and high dispersion of Ni NPs after encapsulation in the channel of TNTs. The catalyst could be recycled six times without significant loss in catalytic activity, which was attributed that the confinement of TNTs prevents Ni NPs from leaching or aggregation. The design strategy for NPs confined in nanotubes may have potential applications in many heterogeneous reactions.

1. Introduction

Hydrogen is widely regarded as a clean energy carrier for sufficient and sustainable energy supplies [1]. However, the main technical

challenge for widespread hydrogen applications is the lack of safe and efficient approach for hydrogen storage and transmission [2]. Therefore, searching for effective hydrogen storage materials, which can release hydrogen conveniently under mild conditions, is extremely

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important [3–5]. Recently, hydrazine hydrate ($\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}$) has been considered to be a promising H_2 storage candidate owing to its high hydrogen density (8.0 wt%), easy recharging as a liquid, a relatively low cost and production of only nitrogen in addition to hydrogen via the complete decomposition reaction: $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$ (Eq. 1) [6–10]. However, the incomplete and undesired decomposition $3\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{NH}_3$ (Eq. 2) must be avoided [11,12].

Many efforts have been devoted on the development of efficient catalysts for H_2 generation from hydrous hydrazine. Noble-metal modified Ni catalysts, including Ni-M (M = Ir, Pt, Pd and Rh) were efficient for the selective decomposition of hydrous hydrazine owing to alloy synergy effect [12–19]. For example, noble-metal NiRh supported on graphene exhibited high catalytic activity and 100% selectivity to H_2 . The excellent catalytic performance might be attributed to the synergistic effect of the RhNi NPs and the graphene [20]. However, the limited resources and high costs of noble metal restricted their further application. Accordingly, the development of efficient non-noble metal catalysts has received considerable attention [21–28]. Generally, high dispersion of the NPs with more reactive sites could have good catalytic activity. Therefore, to obtain NPs during the preparation of nanocatalysts, various surfactants or supports has been used for the dispersion of NPs [21–26]. For example, Ni-Fe NPs were prepared by coreduction of nickel and iron chlorides in the presence of hexadecyltrimethylammonium bromide (CTAB), but the turnover frequency (TOF) of the catalyst is low (3.2 h^{-1}) in 0.5 M NaOH solution at 343 K. Alternatively, Ni NPs or alloy was supported on Al_2O_3 , MgO, and La(OH)₃. The TOFs of Ni/ Al_2O_3 [22], NiFe-alloy/MgO [23], NiMoB-La(OH)₃ [24] and Cu@Fe₃Ni₅ [25] were 3.2, 13.3, 16.5 and 35.3 h^{-1} , respectively. However, the NPs of the catalysts often undergo significant aggregation, which leads to poor catalytic activity due to a low surface-to-volume ratio after agglomeration. Recently, Iron-boron was supported on multiwalled carbon nanotube with a high H_2 generation rate ($34.2 \text{ L h}^{-1} \text{ g}^{-1}$) and 97.0% selectivity to H_2 at room temperature. But the deactivation of the catalyst is unavoidable due to the oxidation of B on the active surface of Fe-B [2]. From a practical point of view, the development of efficient non-noble-metal catalysts is still a challenge.

Titanate nanotubes with high specific surface area ($200\text{--}400 \text{ m}^2 \text{ g}^{-1}$), internal tube diameter between 3 and 10 nm and open mesoporous morphology [29,30] have attracted much attention in catalysis [31]. As supports for heterogeneous catalysis, the loading metal could be dispersed on TNTs due to strong metal-support interaction [32–34]. Moreover, the nanotubes structure can provide nanosized confined space (inner nanotubes) [35–38], which could prevent NPs growth by confining them in the nanochannel [39]. Recently, Pt NPs confined in TNTs exhibited higher photocatalytic activity for the oxidation of acetaldehyde than those of Pt NPs on the outside surface owing to the confinement effect of TNTs on the encapsulated Pt NPs [40]. Similar result was obtained in the case of TNTs confined CeO₂ catalyst [41]. However, to our knowledge, Ni NPs entrapped in titanate nanotubes as catalysts in hydrogen generation from hydrous hydrazine have not been reported.

Herein, Ni NPs were confined inside the TNTs channel using the capillary forces under ultrasonic treatment. Small nanoparticle size and high dispersion of Ni NPs were obtained after the encapsulation in the channel of titanate nanotubes. The results indicate that the Ni@TNTs exert nearly 100% selectivity to H_2 generation from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 333 K with a high TOF of 96.0 h^{-1} and Ni@TNTs could be recycled six times without significant loss in catalytic activity. This study provides an effective strategy for the preparation of Ni NPs confined inside the TNTs channel for H_2 generation from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in practical applications.

2. Experimental

2.1. Materials

All the reagents were analytical purity and were used as received.

P25 was purchased from Degussa Co., Ltd. Hydrochloric acid (37%) were obtained from Tianjin Institute of Chemical Agents China. Sodium hydroxide (NaOH, 98%), Nickel chloride hexahydrate ($\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, 98%) and NaBH_4 (98%) were obtained from Sinopharm Chemical Reagent Co., Ltd China. Other solvents, such as ethanol, acetone and xylene were supplied by Tianjin Feng Chuan Chem. Co., Ltd China.

2.2. Catalyst preparation

2.2.1. Preparation of TNTs

TNTs was prepared according to the similar method reported by Kasuga et al. [42,43]. Typically, titania nanotubes were synthesized by dissolving 2.0 g of P25 in 70 mL of 10 M NaOH solution and hydrothermally treated at 413 K for 24 h in a Teflon-lined stainless steel autoclave. After the thermal treatment, a white precipitate (sodium titanate) was centrifuged and washed with deionized water four times followed by 0.1 M HCl aqueous solution until the pH reached 1.0. Then, the sample was immersed in 0.1 M HCl aqueous solution for 12 h, and washed again with deionized water until the pH was neutral. Finally, the resulting nanotubes were dried at 343 K for 12 h.

2.2.2. Preparation of Ni NPs encapsulated in the channel of TNTs (Ni@TNTs)

The Ni@TNTs catalyst was prepared by introducing the nickel precursor into the TNTs channel using the capillary forces under ultrasonic treatment [44]. TNTs (0.1133 g) and NiCl_2 (0.081 g) were immersed in 3 mL acetone solution at 298 K. After ultrasonic treatment for 3 h, the mixture was stirred for 48 h at 298 K. Then, the mixture was heated to 383 K with a heating rate of 1 K min^{-1} and held at 383 K for 12 h. By this slow drying method, the catalyst precursor was introduced into the TNTs channel. The dried sample was reduced with the solution of sodium borohydride ($28 \text{ mg}\cdot\text{mL}^{-1}$) at 273 K for 1 h, and then the solid product was filtered, washed with deionized water, and dried at 313 K for 18 h under vacuum condition (-0.1 MPa).

2.2.3. Preparation of Ni NPs deposited on the outer surface of TNTs (Ni/TNTs)

The Ni/TNTs catalyst was prepared using xylene to block the TNTs channel [45]. TNTs (0.1133 g) were immersed in xylene (2.8 mL) at room temperature. After ultrasonic treatment for 3 h, NiCl_2 solution (2.0 mL , $0.17 \text{ mol}\cdot\text{L}^{-1}$) was added to the mixture. After stirred at 298 K for 12 h, the mixture was evaporated within 1 h by heated to 353 K under stirring for the preferential evaporation of water. Subsequently, the sample was heated to 383 K and held at 383 K for 12 h to remove xylene. Then the solid product is subjected to the same reduction treatment as Ni@TNTs.

2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on the D8 Discover (Bruker AXS Ltd) under ambient conditions using a $\text{Cu K}\alpha$ X-ray. The content of Ni was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on Opfima 7300V (Perkin Elmer). The chemisorption of CO was carried out on a Micromeritics Auto Chem II 2920 automated characterization system. 0.5 g of a reduced sample (Ni@TNTs or Ni/TNTs) was first pretreated in a mixture flow of 5% H_2/Ar at 423 K for 1 h. And then, the catalyst was cooled to room temperature and CO pulses were injected from a calibrated on-line sampling valve. CO adsorption was assumed to be completed after three successive peaks showed the same peak areas. H_2 -TPR was conducted on Micromeritics Auto Chem II 2920 automated characterization system. The reducibility of sample was studied by TPR in a mixture flow of 5% H_2/Ar ($50 \text{ mL}\cdot\text{min}^{-1}$) from 298 K to 973 K. XPS analysis was conducted on Escalab 250xi (Thermo Scientific Ltd.) with monochromated Al $\text{K}\alpha$ radiation. The shift of the binding energy due to relative surface charging was corrected using the C 1s level at 284.8 eV as

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