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Hydrogenation of m-Chloronitrobenzene over Different Morphologies Ni/TiO₂ without Addition of Molecular Hydrogen

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Abstract: Ni/TiO₂ catalysts with different morphologies (granular, sheet, tubular and spherical) were prepared. Hydrogen was generated from ethanol aqueous-phase reforming over Ni/TiO₂ in a water-ethanol-*m*-chloronitrobenzene reaction system and directly applied into *m*-chloronitrobenzene catalytic hydrogenation. Thereby, in-situ liquid-phase hydrogenation of *m*-chloronitrobenzene over Ni/TiO₂ without addition of molecular hydrogen was successful. Compared with granular, sheet and spherical Ni/TiO₂, the nanotubular Ni/TiO₂ prepared from one-step hydrothermal reaction had larger specific surface area, smaller and uniformly-distributed pore sizes and more Lewis acid sites. In-situ liquid-phase hydrogenation of *m*-chloronitrobenzene experiments showed the nanotubular Ni/TiO₂ had the highest catalytic activity, which was ascribed to both catalyst morphology and acid sites. Firstly, the nanotubular structure endowed the catalysts with a nanoscale confinement effect and thereby high catalytic performance. Secondly, the Lewis acid sites not only accelerated water–gas shift reaction, enhancing the ethanol aqueous-phase reforming activity for hydrogen generation, but also promoted the adsorption and hydrogenation of –NO₂ on the active sites of the catalysts.

Keywords: Ni/TiO₂; morphology effect; in-situ hydrogenation; aqueous-phase reforming; *m*-chloronitrobenzene

1. Introduction

Armatic haloamines are important intermediates in the synthesis of various organic compounds, such as dyes, drugs, and pesticides [1]. The reduction reaction of chloronitrobenzene (CNB) for the preparation of chloroaniline (CAN) (Scheme S1) can be divided into iron powder reduction [2], alcali sulphide [3] or hydrazine hydrate reduction [4], electrochemical reduction [5] and catalytic hydrogenation [6–10]. In particular, catalytic hydrogenation featured by environmental friendly, atom economy, high product purity and high yield is the most promising clean technique in the industry.

However, the dominant method of hydrogenation reaction in catalytic hydrogenation techniques depends on the addition of molecular hydrogen. Hydrogen in industrial applications is mainly obtained from recovered byproducts of fossil energy hydrogen generation, electrolysis water hydrogen generation, and petrochemical production [11,12]. However, these techniques are limited by the shortage of fossil energy, non-renewability, high electricity consumption, and unsafety in hydrogen storage and transport, which bring about inevitable challenges for the catalytic hydrogenation techniques that depend on addition of molecular hydrogen.



Recently, much attention has been paid to hydrogen preparation from reforming reactions starting from methanol [13–15] and especially ethanol [16–18], which has a 1.5-fold higher hydrogen concentration per mole than methanol. Moreover, the biomass Ethanol-water solution (8–15% v/v) or crude distillation of concentrated solution (15–50% v/v) generated from biomass conversion can be directly used for reforming reaction for hydrogen generation. This method is capable of biomass resource utilization and shows broad application prospects. The aqueous-phase reforming (APR) reaction proposed by Dumesic et al. [19–21] is a hydrogen generation technique starting from renewable biomass and water, and is featured by renewability and closed CO₂ circulation (no net emission of CO₂) [22].

Ni-based catalysts are widely used in the catalysis field and can be used in ethanol APR reactions for hydrogen generation [23–25] and in CNB catalytic hydrogenation [26,27]. Since the conditions of these two types of hydrogen reactions are similar, researchers can simultaneously conduct ethanol APR for hydrogen generation and CNB catalytic hydrogenation on the same catalyst. In heterogeneous catalysis, the support is mainly used to disperse the active component resulting in larger specific surface area and improving its performance. TiO₂-based nanomaterials are widely used as support in heterogeneous catalysis because of its low cost, non-toxicity and environmental friendliness [28,29]. It is noteworthy that the morphology of titanium dioxide support has great influence on the activity of catalysts [30,31]. Based on this idea, we prepared a series of morphology-varying Ni/TiO₂ catalysts according to the references [31–33], and then in a water-ethanol–*m*-CNB reaction system and sent the hydrogen from ethanol APR directly into *m*-CNB catalytic hydrogenation. In this way, we succeeded in in-situ liquid-phase hydrogenation of *m*-CNB over Ni/TiO₂ catalysts. Moreover, the effects of catalyst morphology and reaction conditions on the catalytic performance were studied.

2. Results and Discussion

2.1. Catalyst Characterization

Figure 1 depicts the scanning electron microscopy (SEM) images of the catalysts. Ni/TNP exhibits a granular morphology and the granules are well agglomerated with uniform sizes of tens of nanometers (Figure 1a). After hydrothermal treatments, the unique nanosheet-like structures were obtained in Ni/TNS (Figure 1b), indicating raw P25 nanoparticles were stripped into nanosheets. Ni/TNT is tubular–shaped with diameters of 10–15 nm (Figure 1c). Ni/TMS shows a spherical structure with diameters of 2–4 μ m, and some TiO₂ spheres were broken (Figure 1d). The inset of Figure 1d shows a hierarchical structure with well-defined pyramid-shaped crystal facets.



Figure 1. Scanning electron microscopy (SEM) images of (**a**) Ni/TNP; (**b**) Ni/TNS; (**c**) Ni/TNT and (**d**) Ni/TMS.

Figure 2 depicts the transmission electron microscope (TEM) images of the catalysts. The Ni particles of Ni/TNP are unevenly distributed and obviously aggregated. Ni/TNS shows a layered sheet-like structure, but after hydrothermal treatment with alkaline water, this sheet-like structure was obviously curled. In comparison, the Ni/TNT shows hollow tubes, rather than solid nanolines, and its external diameter is 10–15 nm with very thin tube walls, and the nanotube length and external diameter

are both uniformly distributed. Compared with Ni/TNP and Ni/TNS, Ni/TNT could efficiently inhibit the aggregation of Ni particles. The numerous TiO_2 microspheres in Ni/TMS adhered mutually to form a large particle group, but the TiO_2 microspheres are uniformly-sized (average particle size of 4 μ m). The high resolution transmission electron microscope (HRTEM) image of Ni/TMS shows that the TiO_2 microspheres have crystal lattice stripes (Figure S1), indicating the TiO_2 microspheres resulted from the orderly and tight stacking of microcrystals.



Figure 2. Transmission electron microscope (TEM) images of (a) Ni/TNP; (b) Ni/TNS; (c) Ni/TNT and (d) Ni/TMS.

The microstructural characteristics of catalysts were investigated with the N₂ adsorption–desorption analysis (Figure 3). As shown in Table 1, Ni/TNS has larger Brunauer–Emmett–Teller (BET) surface area and pore volume than Ni/TNP. Generally, alkaline hydrothermal reaction can yield larger surface area products [34]. The BET surface area and pore volume of Ni/TNT are both the largest among different TiO₂-supported Ni-based catalysts, while those of Ni/TMS are both the smallest. In addition, Ni/TNS has type IV isotherms, with a hysteresis loop of type H₃ at high relative pressure, which suggests the existence of mesoporous structures [35]. The mesoporous structures with diameters from 5 to 30 nm are mainly attributed to the aggregation of TiO₂ nanosheets. Ni/TNT gives a narrow pore size distribution ranging from 3 to 12 nm with a peak at about 5 nm corresponding to the inner diameter of the nanotubes. Ni/TMS exhibits a type IV-like isotherm with a clear type H₃ hysteresis [35].



Figure 3. (**a**) N₂ adsorption–desorption isotherms and (**b**) pore size distribution curves of Ni/TNP, Ni/TNS, Ni/TNT and Ni/TMS.

Figure 4 shows the X–ray diffractometer (XRD) patterns of the catalysts. For Ni/TNP, the peaks at $2\theta = 25.3^{\circ}$, 37.9° and 48.0° correspond to anatase TiO₂; the peak at $2\theta = 27.4^{\circ}$ corresponds to rutile TiO₂, indicating the TiO₂ of Ni/TNP is in a mischcrystal of anatase and rutile. Moreover, the peak at $2\theta = 44.5^{\circ}$ corresponds to metal Ni; the peaks at $2\theta = 33.2^{\circ}$, 35.8° and 54.0° correspond to NiTiO₃, which resulted from a solid-state reaction between TiO₂ and NiO during the calcination process [36], indicating Ni of Ni/TNP existed in form of both metal Ni and NiTiO₃. Compared to Ni/TNP, in

Ni/TNS prepared from alkaline hydrothermal treatment, the peak of metal Ni was enhanced, but the peaks of anatase TiO₂ and rutile TiO₂ were significantly weakened, while the peaks at $2\theta = 24.4^{\circ}$, 32.9° and 47.3° are ascribed to Na_{0.23}TiO₃, the major component of nanosheets. The peaks of anatase TiO₂ and rutile TiO₂ disappeared in Ni/TNT, and besides the peak of Ni, the peaks at $2\theta = 10.2^{\circ}$, 24.5° , 28.4° and 48.5° also appeared, which correspond to the mineralogical composition of scrolled titanate nanotubes (such as H₂Ti₂O₅·*x*H₂O and H₂Ti₃O₇·*x*H₂O) [37,38]. Huang et al. [39] found the crystal structure of titanate nanotubes is similar to that of H₂Ti₂O₅·*x*H₂O. Under hydrothermal conditions and strong base NaOH, the Ti–O bond of TiO₂ was fractured, forming layered fragmented sheets of hydrated sodium titanate. During acid washing, an exchange reaction between H⁺ and Na⁺ occurred, forming hydrated titanium acid, followed by the formation of curled nanotubes. The Ni/TMS only shows the characteristic peaks of anatase TiO₂ and metal Ni. The sizes of Ni particles calculated from Scherrer's equation rank in different samples as: Ni/TMS > Ni/TNP > Ni/TNS > Ni/TNT.

Table 1. Physicochemical properties of different catalysts.

Catalyst	S _{BET} (m²/g)	V _{pore} (cm ³ /g)	D _{pore} (nm)	Ni Loading (wt.%)	H ₂ Consumption ¹	Surface Atomic Ratio ²	
					(mmol/g-cat)	Ni/Ti	Ni ⁰ /Ni ²⁺
Ni/TNP	17.9	0.15	34.1	20.7	3.37	18.1/81.9	11.3/88.7
Ni/TNS	71.3	0.20	11.0	19.1	3.07	17.1/82.9	44.1/55.9
Ni/TNT	126.4	0.34	10.3	18.6	0.88	16.6/83.4	53.7/46.3
Ni/TMS	14.5	0.08	21.9	19.5	3.17	17.8/82.2	39.3/60.7

¹ Calculated by hydrogen temperature-programmed reduction (H_2 –TPR); ² Calculated by X-ray photoelectron spectroscopy (XPS).



Figure 4. X-ray diffractometry (XRD) patterns of P25, Ni/TNP, Ni/TNS, Ni/TNT and Ni/TMS.

The reduction behaviors of different catalysts were studied via hydrogen temperatureprogrammed reduction (H₂-TPR) experiments (Figure 5). For Ni/TNP, there was a strong broad hydrogen consumption at 878 K, which was assigned to the partial reduction of bulk NiTiO₃ [40,41]. Moreover, two shoulder reduction peaks appear at 625 and 700 K, which are ascribed to the reduction of bulk-phase NiO without interaction between the carriers, and to the highly-dispersed NiO interacting with the titania surface through the formation NiO–TiO₂ species [42], respectively. Compared with Ni/TNP, the reducing peaks of Ni/TNS at 664 and 763 K were strengthened, while that at 976 K was significantly weakened. Ni/TNT shows two weak reducing peaks at 573 and 728 K. Ni/TMS shows strong reducing peaks at 750 and 900 K, in addition to the weak reducing peak at 600 K. The H₂ consumption calculated from the H₂-TPR graphs ranks as Ni/TNP > Ni/TMS > Ni/TNS > Ni/TNT (Table 1). In particular, the H₂ consumption of Ni/TNT is far smaller than Ni/TNP, Ni/TNS and Ni/TMS, and its high-temperature H₂ consumption peak nearly disappeared. This result further confirms the ascorbic acid added into Ni/TNT preparation directly reduced Ni²⁺ into Ni⁰, this process can be regarded as one-step hydrothermal synthesis of Ni-based Ti nanotubular catalysts.



Figure 5. Hydrogen temperature-programmed reduction (H₂-TPR) profiles of Ni/TNP, Ni/TNS, Ni/TNT and Ni/TMS.

The X-ray photoelectron spectroscopy (XPS) spectra of Ni2p and Ti2p regions of the catalysts are shown in Figure 6, and the corresponding element compositions with different chemical states calculated from the peak areas are reported in Table 1. According to Ni2p3/2 spectra (Figure 6a), the Ni species existed in both elemental state (Ni⁰) centered at 851.8–852.2 eV and oxidized state (Ni²⁺) centered at 855.0–855.4 eV [43], along with a satellite around 5.0 eV above the Ni²⁺ species [44]. In comparison with the standard binding energy (BE) of pure Ni^0 (853.1 eV), the BE of elemental Ni shifted negatively in all catalysts of different morphologies, indicating some electrons transferred from TiO₂ to form electron-rich Ni. Among the four different catalysts, negative shift in BE is smallest in Ni2p3/2 of Ni/TNT (0.9 eV) and largest in Ni/TNP (1.2 eV). The strong metal-support interaction in different catalysts, especially the formation of NiTiO₃ in Ni/TNP, promotes the formation of an electron-rich Ni center, which is consistent with the H₂-TPR results. Compared with Ni/TNT, a significant negative shift is also observed for Ti2p in Ni/TNP, Ni/TNS and Ni/TMS (Figure 6b). One possible explanation is that a fraction of Ti⁴⁺ in the support is partially reduced into Ti³⁺ under H₂ flow, which results in the negative shift of Ti 2p3/2 for Ni/TNP, Ni/TNS and Ni/TMS. Meanwhile, electron-rich Ti³⁺ species can transfer electrons to Ni species [45]. On basis of the peak areas for reduced Ni⁰ and oxidized Ni²⁺, Ni/TNT contains more reduced Ni⁰ than the other catalysts (Table 1), which might be due to the easier reduced nickel species in the preparation of Ni/TNT and the unique confinement effect of nanotubes [6,46].



Figure 6. X-ray photoelectron spectroscopic (XPS) spectra of Ni/TNP, Ni/TNS, Ni/TNT and Ni/TMS. (a) Ni2p; (b) Ti2p.

2.2. In-Situ Liquid-Phase Hydrogenation of m-CNB

In-situ liquid-phase hydrogenation of *m*-CNB over different catalysts was investigated (Table 2). Under the same reaction conditions, different catalysts exhibited nearly the same selectivity towards

m-CAN, a slight amount of aniline (AN), and trace amounts of byproducts (e.g., halogenated hydroxylamine), indicating the slight effect of catalyst morphology on product distribution. However, the conversion of *m*-CNB was highly variable depending on the morphology of catalysts. The Ni/TNT with nanotubular structure showed the highest hydrogenation activity, with *m*-CNB conversion up to 97.5%. The catalytic activity of different morphological catalysts decreased in the order of Ni/TNT > Ni/TNS > Ni/TNS > Ni/TNP. This high hydrogenation activity of Ni/TNT can be attributed to the catalyst morphology and the mechanism of in-situ liquid-phase hydrogenation.

Catalvete	Conversion $(9/)$	Se	$TOP^{2}(1-1)$			
Calalysis	Conversion (%)	<i>m</i> -CAN	AN	Others	10F - (h -)	
Blank ³	-	-	-	-	-	
Ni/TNP	20.1	97.9	1.9	0.2	0.07	
Ni/TNT	97.5	96.2	3.5	0.3	0.36	
Ni/TNS	67.7	97.2	2.7	0.1	0.25	
Ni/TMS	41.1	97.6	2.2	0.2	0.15	

Table 2. In-situ liquid-phase hydrogenation of *m*-CNB over Ni/TNP, Ni/TNS, Ni/TNT and Ni/TMS¹.

¹ Reaction conditions: 0.1 g catalyst, 0.5 mmol *m*-CNB, 3 mL H₂O, 7 mL C₂H₅OH, 3 MPa N₂, 473 K, 4 h; ² Turnover frequency (TOF), *m*-CNB mole consumption per mole Ni and per hour; ³ Blank experiment without catalyst;

Firstly, Ni/TNT has a larger specific surface area and pore volume, smaller and narrowerdistributed pore sizes than Ni/TNP, Ni/TNS and Ni/TMS. Noticeably, the nanotubular structure of Ni/TNT has a unique nanoscale confinement effect, which endows the catalysts with higher catalytic activity [6,46,47]. Secondly, the in-situ liquid-phase hydrogenation of *m*-CNB consists of ethanol APR for hydrogen generation (Figure S2 and Table S1) and *m*-CNB catalytic hydrogenation. The ethanol APR involves two steps of C–C fracture and CO water-gas shift (WGS) reaction. As reported, Ni-based catalysts showed high C–C breakage ability in ethylene glycol APR [48,49], and the subsequent CO WGS was the step-controlling reaction in ethanol APR for hydrogen generation [50,51]. Wang et al. [52] studied the WGS reaction of mesoporous Cu–Co–CeO catalysts and found that the catalysts contained more Lewis acid sites and Brønsted acid sites, which facilitates the adsorption and activation of CO and H₂ molecules and thus, remarkably improves catalytic activity in WGS reaction. Thus, the amount of acid sites on the catalyst would affect the WGS reaction. Pyridine-adsorbed Fourier Transform Infrared Spectroscopy (Py-FTIR, Figure 7) shows that Ni/TNT and Ni/TNS contain a lot of Lewis acid sites and Brønsted acid sites, respectively, but neither Ni/TMS nor Ni/TNP contain Lewis acid sites or Brønsted acid sites.



Figure 7. Pyridine-adsorbed Fourier Transform Infrared Spectroscopy (Py-FTIR) patterns of Ni/TNP, Ni/TNS, Ni/TNT and Ni/TMS.

Py–FTIR analysis of the catalysts acidity is shown in Figure 7. The peak at 1445 cm^{-1} is characteristic for pyridinium ions from pyridine adsorbed on Lewis acid sites and the peak at 1540 cm^{-1}

is attributed to pyridine adsorbed at Brønsted acid sites. Ni/TMS and Ni/TNP do not have evident Lewis acid sites or Brønsted acid sites, while Ni/TNS contains more Brønsted acid sites, but no Lewis acid sites. Ni/TNT contains more Lewis acid sites and fewer Brønsted acid sites. These results indicate the types and acidity of acid sites both differ among different morphologies.

The *m*-CNB hydrogenation reaction obeys the Langmuir–Hinshelwood mechanism, and the corresponding reaction rate is decided by reactants of chemical adsorption and concentration of reactive hydrogen. As for the active center Ni⁰, firstly, the surface concentration of Ni⁰ is important for the activity of the catalysts. XPS and BET analysis (Table 1) show that the surfaces of Ni/TNT have the largest Ni⁰/Ni²⁺ ratio and specific surface area, and thus more catalytic active centers. Secondly, XPS shows Ni⁰ in under electron-rich state irrespective of catalyst shape, but higher electron density favors the activation of adsorbed hydrogen molecules and enhances the surface concentration of activated H species [53]. However, considering the high-temperature heat treatment (roasting and reduction) during preparation of Ni/TNP, Ni/TNS and Ni/TMS, we think this high heat treatment temperature would strengthen the interaction between Ni and TiO₂, and then reduce active specific surface areas and hydrogen adsorption quantity [54,55]. From the perspective of catalyst acidity, only Ni/TNT contained more Lewis acid sites. On one hand, Lewis acid sites would interact with the oxygen atoms on –NO₂, which is favorable of the adsorption of –NO₂ group on the surface of catalyst. On the other hand, Lewis acid sites could activate the N=O bond of –NO₂ which favors the attack by electron-enriched H atoms [56].

The effects of reaction conditions on the in-situ liquid-phase hydrogenation of *m*-CNB over Ni/TNT are illustrated in Table 3. The *m*-CNB conversion maximizes at a water/ethanol ratio of 3:7. This is because the increase of water/ethanol ratio would accelerate the ethanol APR for hydrogen generation and thereby promote *m*-CNB hydrogenation. When the water/ethanol ratio rises to a certain level (namely the water content rises to a certain level), further addition of water would rarely affect the chemical equilibrium of ethanol APR, and reduce the solubility of *m*-CNB in the water-ethanol system. Temperature rise contributes to accelerating the *m*-CNB conversion. This is because firstly, temperature rise contributes to the C–C bond fracture of ethanol and WGS reaction, thereby enhancing the ethanol APR reactivity, and secondly, since –NO₂ hydrogenation is an exothermic reaction, too, high reaction temperature is unfavorable for *m*-CNB hydrogenation. Thus, the catalytic activity was enhanced significantly with a temperature rise from 433 to 453 K, but was increased slowly with a further temperature rise to 493 K. The active hydrogen of *m*-CNB hydrogenation originated from ethanol APR, and its formation was not affected by N₂ pressure [57,58]. Thus, the variation of reaction pressure only slightly affected the in-situ liquid-phase hydrogenation of *m*-CNB.

H ₂ O/C ₂ H ₅ OH ²	Т (К) Р (М	$\mathbf{P}(\mathbf{M}\mathbf{P}_{2})$	Pa) Conversion (%)	Selectivity (%)			$TOF^{3}(1-1)$
		r (wra)		m-CAN	AN	Others	
1/9	473	3	69.7	97.7	2.1	0.2	0.26
2/8	473	3	88.1	96.5	3.4	0.1	0.32
3/7	473	3	97.5	96.2	3.5	0.3	0.36
4/6	473	3	78.3	97.5	2.1	0.4	0.29
3/7	493	3	98.2	94.7	4.5	0.8	0.36
3/7	453	3	91.3	95.8	3.7	0.5	0.33
3/7	433	3	66.9	96.8	3.0	0.2	0.25
3/7	473	4	95.2	96.1	3.6	0.3	0.35
3/7	473	2	94.6	96.6	3.3	0.1	0.35
3/7	473	1	93.9	97.2	2.6	0.2	0.34

Table 3. In-situ liquid-phase hydrogenation of *m*-CNB over Ni/TNT¹.

¹ Reaction conditions are similar to Table 2; ² Volume ratios of H₂O to C₂H₅OH; ³ *m*-CNB mole consumption per mole Ni and per hour.

The reusability of Ni/TNT was measured by repeating the catalytic experiment. As shown in Table 4, Ni/TNT showed no obvious loss of catalytic activity in the fourth cycle. The confinement

effect of nanotube can enhance the stability of Ni/TNT by preventing the loss and aggregation of Ni nanoparticles [6].

 D	Conversion (%)	Se	$TOF^{2}(1-1)$		
Kun		<i>m</i> -CAN	AN	Others	10F ⁻ (n ⁻¹)
1	97.5	96.2	3.5	0.3	0.36
2	92.6	96.5	3.3	0.2	0.34
3	89.1	97.0	2.9	0.1	0.33
4	85.2	97.2	2.6	0.2	0.31

Table 4. Reusability of Ni/TNT in the in-situ liquid-phase hydrogenation of *m*-CNB¹.

¹ Reaction conditions are similar to Table 2; ² *m*-CNB mole consumption per mole Ni and per hour.

3. Materials and Methods

3.1. Chemicals

Commercial TiO₂ Aeroxide P25 was purchased from Evonik Degussa (Essen, Germany). Ascorbic acid, sodium citrate, ammonium hexafluorotitanate and boric acid were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Ni(NO₃)₂· $6H_2O$ was supplied by Beijing Shuanghuan Chemical Reagents Company (Beijing, China). NaOH and tetrabutyltitanate were obtained from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Sodium citrate, concentrated ammonia water (25–28%) and ethanol were purchased from Haerbin Chemical Reagent Co., Ltd. (Haerbin, China).

3.2. Catalyst Preparation

A total of 0.7 g of P25 was impregnated with 30 mL 0.1 mol/L Ni(NO₃)₂·6H₂O solution. Then, the mixture was dried at 343 K, roasted for 3 h at 873 K, and reduced under H₂ at 723 K for 3 h, forming granule-like Ni/TiO₂ catalysts, marked as Ni/TNP (Table S2). 1.6 g P25 was dispersed into 100 mL 10 mol/L NaOH solution, followed by dripping Ni(NO₃)₂· $6H_2O$ solution. The resulting mixture was ultrasonically dispersed for 0.5 h, and hydrothermally treated in a Teflon-lined stainless-steel autoclave at 403 K for 9 h. The products were filtrated, washed, dried at 343 K, and reduced under H₂ at 723 K for 3 h, forming nanosheet-like Ni/TiO₂ catalysts, marked as Ni/TNS. To 7 mL concentrated ammonia water, 0.752 g Ni(NO₃)₂·6H₂O, 2.4 g ascorbic acid and 4.2 g sodium citrate was successively added under stirring for 0.5 h. Then, 12.35 mL ethanol mixed with 2.65 mL tetrabutyltitanate was dripped under stirring for 0.5 h. Then, 52.5 mL 10 mol/L NaOH solution was added under stirring for 0.5 h, followed by hydrothermal treatment at 513 K in a Teflon-lined stainless-steel autoclave for 2 h. The products were filtrated, washed, and dried at 343 K, forming nanotube-like Ni/TiO₂ catalysts, marked as Ni/TNT. 3.86 g of (NH₄)₂TiF₆, 1.59 g H₃BO₃, and 1.91 g Ni(NO₃)₂·6H₂O were dissolved in 260 mL distilled water under stirring for 0.5 h, followed by hydrothermal treatment at 423 K in a Teflon-lined stainless-steel autoclave for 18 h. The products were filtrated, washed, dried at 343 K, and reduced under H₂ at 723 K for 3 h, forming microsphere-like Ni/TiO₂ catalysts, marked as Ni/TMS. The theoretical load of Ni in all catalysts was 20 wt.%.

3.3. Catalyst Characterization

The morphology of the catalysts was investigated by SEM and TEM (JEOL JEM-4000EX, Tokyo, Japan), respectively. The BET surface area, pore size, pore volume and N₂ adsorption/desorption of the catalysts were measured by a Micromeritics Tristar II 3020 surface area and porosity analyzer (Micromeritic, Atlanta, GA, USA). Ni loading was analyzed by means of an inductively coupled plasma spectrometer (ICPS-7510, Shimadzu, Tokyo, Japan). The crystal structure and phase composition of the catalyst were determined on a Rigaku D/max-2200 XRD (Tokyo, Japan) with Cu K α radiation. H₂-TPR was measured on a Chem BET 3000 chemical adsorption instrument by heating at a temperature

ramping rate of 10 K/min in a mixture of 5% H₂/Ar gas (Quantachrome, Boynton Beach, FL, USA). The X-ray photoelectron spectra measurements were performed using Thermofisher Scientific K-Alpha X-ray photoelectron spectrometer, using Al K α radiation as excitation source (Thermofisher, New York, NY, USA). Binding energies were adjusted with respect to the C1s binding energy of 284.8 eV. Py–FTIR was used to determine the amount of Lewis and Brønsted acid sites in Tensor 27 equipment (Bruker, Karlsruhe, Germany). The catalyst was treated at 613 K for 2 h under vacuum. Pyridine was then adsorbed to a 1.0×10^{-2} Pa equilibrium pressure at 313 K. FTIR spectra were recorded after consecutive evacuation at 423 K.

3.4. Catalytic Test

The in-situ liquid-phase hydrogenation of *m*-CNB over the catalysts was evaluated in a 50 mL high-pressure autoclave containing 0.1 g of catalyst, 3 mL of H₂O, 7 mL of ethanol and 0.5 mmol of *m*-CNB. The air inside the autoclave was substituted with N₂ six times. Then, the autoclave was ventilated with 3 MPa N₂ and heated to 473 K. After the stirring device was started, the reaction system went on for 4 h and then cooled to room temperature. The liquid products were analyzed with gas chromatography (Shimadzu GC-14C, FID, SE-30 capillary column) and identified by gas chromatography/mass spectrometry (GC/MS, Agilent 5890).

The conversion of *m*-CNB was calculated as:

$$\text{Conversion}_{m\text{-CNB}} = \frac{(n_m\text{-CNB})_{before} - (n_m\text{-CNB})_{after}}{(n_m\text{-CNB})_{before}} \times 100\%$$
(1)

where selectivity with respect to *m*-CAN was calculated as:

Selectivity_{*m*-CAN} =
$$\frac{(n_{m-CAN})_{after}}{(n_{m-CNB})_{before} - (n_{m-CNB})_{after}} \times 100\%$$
 (2)

the TOF was calculated as:

$$TOF = \frac{(n_{m-CNB})_{before} - (n_{m-CNB})_{after}}{(n_{Ni}) \cdot t}$$
(3)

additionally n_{m-CNB} and n_{m-CAN} are, respectively, the mole contents of *m*-CNB and *m*-CAN (mole); the subscripts *before* and *after* refer to the before and after reactions. n_{Ni} and *t* are, respectively, the mole content of Ni and the reaction time (h).

4. Conclusions

Ni/TiO₂ catalysts with different morphologies were prepared and used into ethanol APR for hydrogen generation and *m*-CNB catalytic hydrogenation. Thereby, the hydrogen generated from ethanol APR with Ni/TiO₂ catalysts was applied into in-situ liquid-phase hydrogenation of *m*-CNB. Compared with granular, sheet-like and spherical Ni/TiO₂, the nanotubular Ni/TiO₂ prepared from one-step hydrothermal method showed higher hydrogenation activity, which was attributed to its unique nanotubular structure and the Lewis acid sites. The hydrogenation reactivity was significantly enhanced by altering the water/ethanol ratio or by raising reaction temperature, but not by the change of reaction pressure.

Supplementary Materials: The following is available online at http://www.mdpi.com/2073-4344/8/5/182/s1, Figure S1: HRTEM image of Ni/TMS, Figure S2: Gas chromatogram of ethanol APR over Ni/TNT, Table S1: Volume fraction of gas products, Table S2: The catalysts and the corresponding abbreviations, Scheme S1: The hydrogenation reaction pathways of CNB.

Author Contributions: Feng Li, Cuiqin Li and Hua Song conceived and designed the experiments; Feng Li, Jinrong Liang and Wenxi Zhu performed the experiments; Keliang Wang and Cuiqin Li analyzed the data; Feng Li contributed reagents/materials/analysis tools; Feng Li and Cuiqin Li wrote the paper.

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