



Deactivation of Ni/TiO₂ catalyst in the hydrogenation of nitrobenzene in water and improvement in its stability by coating a layer of hydrophobic carbon

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ABSTRACT

Water as a green solvent to replace the conventional organic solvent presents many advantages in the organic synthesis. The hydrogenation of nitrobenzene in water has been investigated by using Ni/TiO₂ catalyst in this work, and our main purpose was focused on the Ni/TiO₂ catalyst activity and its stability improvement. The experimental results and analysis from the data of XRD, XPS, ICP revealed that the formation of nickel hydroxide from metallic nickel reacting with water caused a rapid deactivation of Ni/TiO₂ catalyst. Based on these, we designed a catalyst with hydrophobic property to prevent the nickel active species to contact with water; thus, a hydrophobic carbon layer was coated on the surface of Ni/TiO₂. As expected, the hydrophobic carbon was successfully coated on Ni/TiO₂ catalysts by a hydrothermal method and they presented higher reactivity and improved stability in the present aqueous reaction system; nickel hydroxide was not detected on the used and water treated carbon-coated Ni/TiO₂ samples. The improved abilities were attributed to the increased hydrophobicity of catalysts modified by carbon, which not only prevents water to contact with nickel catalytic species, but also protects the metallic nickel to be oxidized as it exposed to air.

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1. Introduction

As a solvent, water bears a number of attractive physicochemical properties over the traditional organic solvents. It is non-flammable, non-toxic, and non-carcinogenic, and in addition, water is probably the least expensive and most easily accessible solvent, and if a biphasic reaction system is used, organic substrates could be isolated by a simple phase separation [1]. Water also has a high specific heat capacity, enabling the more facile control of an exothermic reaction, and a network of hydrogen bonds which can influence the reactivity of substrates [2]. Therefore, the use of water as a reaction medium instead of organic solvents has been an important theme of current research in response to calls for sustainable chemistry in these years [1,3,4]. It was reported that the organic reactions exhibited improved reaction rates and product selectivity in water with comparing to the reactions in organic solvents. For example, the reaction rate was enhanced largely when the hydrogenation of *t*-butylbenzene with rhodium nanoparticles encapsulated in a porous carbon shell was performed in water compared with the results in octane, acetone, and ethanol [5].

Moreover, the addition of appropriate amounts of water could increase the reaction rate, like the transfer hydrogenations of styrene and nitrobenzene over Pd-based catalyst in methanol was increased from 26.3% and 7.1% to 100% and 31.9%, respectively, when the molar ratio of water to methanol increased from 0 to 1 [6], and the reaction rates for the selective hydrogenation of *p*-chloronitrobenzene in ethanol over the supported catalysts such as Ru/SiO₂, Fe/SiO₂, Co/SiO₂, Ni/SiO₂, Cu/SiO₂, and Ag/SiO₂ were also enhanced dramatically with the addition of water [7]. Furthermore, it was also reported that the reaction rate increased with water content and became the highest in pure water for the hydrogenation of *p*-nitrophenol in water–ethanol and water–dioxane [8]. In our previous work, the conversion of *o*-chloronitrobenzene in water was about three times larger than that in ethanol over Au/TiO₂ catalysts [9]. The promoting effect of water might be partially attributed to the H-bond interaction of interfacial water with reactant or transition state intermediates [10]. Most recently, we found that the hydrogenations of water-insoluble nitrobenzene and chloronitrobenzene could be performed selectively and efficiently in H₂O–CO₂ system over the supported Ni catalysts at 35–50 °C without using any harmful organic solvents [11]. It was found that the N–O bond of *N*-phenyl-hydroxylamine (PHA) was activated through interactions with water, possibly via OH···O and OH···N bonding. Water could promote the reaction step of hydrogenation of PHA to aniline, the rate-determining step in organic solvents

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[11]. Hydrogenation of nitro-compounds in $\text{H}_2\text{O}-\text{CO}_2$ is an environmental benign process for the production of anilines, the important chemicals in producing the polyurethanes, dyes, herbicides, pesticides, pharmaceuticals, etc., due to the high reaction rate, high product selectivity, lower temperature, easy product separation, and cheap and clean solvents of $\text{H}_2\text{O}-\text{CO}_2$.

Based on the requirements of industrial application, water is a promising reaction medium. Herein, the hydrogenation of nitrobenzene in neat water over the Ni/TiO_2 catalyst was investigated. We focused our attention on the mechanism of the Ni/TiO_2 catalyst deactivation and development of a new strategy to improve the catalyst stability. Based on the cause of the deactivation, we designed a catalyst with hydrophobic property by coating a hydrophobic carbon layer on the surface of Ni/TiO_2 catalyst via a hydrothermal method, and the catalytic performance of the carbon modified catalyst has been discussed.

2. Experimental

2.1. Catalyst preparation and characterization

Ni/TiO_2 was prepared by incipient wetness impregnation using anatase TiO_2 (specific surface area $120 \text{ m}^2 \text{ g}^{-1}$, Nanjing High Technology Nano Material Co. Ltd., China) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. After dried at 120°C , the samples were calcined at 450°C for 4 h in air. Before the hydrogenation run, the calcined samples were reduced under H_2 flow at 450°C for 2 h.

Carbon-coated Ni/TiO_2 catalysts were prepared via hydrothermal approach. Glucose and sodium chloride were dissolved in 10 mL of distilled water in the Teflon-lined stainless steel autoclave. Then, the reactor was charged with a certain amount of the unreduced catalyst Ni/TiO_2 . The reactor was then sealed and put into an oil bath and heated to 180°C for 24 h under stirring. The products were filtered off and washed several times, first with water and then ethanol and finally dried in air for 5 h. The catalysts were reduced under H_2 flow at 450°C for 2 h. The as-made catalysts were labeled as $(\text{Ni}/\text{TiO}_2)\text{@C-X}$ (X refers to the carbon content in the catalyst). The carbon content in the catalyst was analyzed using Thermogravimetric analysis (the TGA results were shown in the Fig. S1).

Ni loading on the catalysts was measured by inductively coupled plasma-optical emission spectrometry (ICP-MS, Thermo Scientific ICAP6000, USA) after the extraction of metal species from the support by aqua regia. The nickel content in the Ni/TiO_2 catalyst was 16%.

Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffract meter with a Cu K α source at 40 kV and 40 mA. 2θ scans were performed from 10° to 90° at a $4^\circ/\text{min}$ speed.

Transmission electron microscopy (TEM) study was carried out in a JEOL JEM-2010 instrument operating at an accelerating voltage of 200 kV. The TEM samples were prepared by dispersing the catalyst powder in ethanol under ultrasonic for 5–10 min and then the resulted solution was dropped on a carbon film of copper grid.

Hydrogen temperature-programmed reduction (H_2 -TPR) was carried out in a tubular quartz reactor, into which a 50 mg catalyst was loaded. The reduction was conducted in a 10% H_2/N_2 flow at a heating rate of $10^\circ\text{C}/\text{min}$. Hydrogen consumption was determined using a thermal conduction detector (TCD).

X-ray photoelectron spectroscopy (XPS, VG Microtech 3000 Multilab) was used to examine the electronic properties of Ni on the surface of the Ni/TiO_2 and carbon-coated Ni/TiO_2 catalysts. The C 1s peak at 284.6 eV arising from adventitious carbon was used as reference. This reference gives binding energy values with a precision of $\pm 0.02 \text{ eV}$. The surface composition of the samples was determined from the peak areas of the corresponding lines

using a Shirley type background and empirical cross section factors for XPS.

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 40°C to 800°C in the air atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

2.2. Nitrobenzene hydrogenation

Prior to reaction, the catalyst was freshly reduced in a quartz tube at 450°C with hydrogen flow $30 \text{ mL}/\text{min}$ for 2 h; then, the hydrogen was changed to nitrogen and the quartz tube was cooled down to room temperature. The reduced catalyst was then transferred into a 100-mL stainless steel autoclave reactor in which 6 mL nitrobenzene and solvent was added. It was noted that the catalysts should be put into the solvent directly without exposing to atmosphere. The reactor was then added the reactant, sealed, and flushed with H_2 more than three times to remove the air and placed into a water bath preset to the reaction temperature for 15 min. Then, H_2 (6.5 MPa) was introduced into the reactor, and the reaction was started at 80°C with continuously stirring. When the reaction was finished, the reactor was cooled to room temperature in ice-water bath and then vented hydrogen to ambient pressure. The liquid product was extracted with 10 mL diethyl ether and analyzed with a gas chromatograph (Shimadzu GC-2010, Rtx-5 capillary column) using a flame ionization detector. The conversion and selectivity were calculated using the following equations

$$\text{NB conversion}(\%) = \left(1 - \frac{m_{\text{NB}}}{m_{\text{AN}} + m_{\text{NB}} + m_{\text{By-products}}} \right) \times 100\% \quad (1)$$

$$\text{AN selectivity}(\%) = \left(\frac{m_{\text{AN}}}{m_{\text{AN}} + m_{\text{By-products}}} \right) \times 100\% \quad (2)$$

where m_{AN} , m_{NB} , and $m_{\text{by-products}}$ represent the amount of aniline, nitrobenzene, and by-products in the mixture.

3. Results and discussion

3.1. Catalytic performances of Ni/TiO_2 catalyst

When the hydrogenation of nitrobenzene was carried out in the organic solvents, several intermediates such as nitrosobenzene (NSB), N-phenylhydroxylamine (PHA), azoxybenzene (AOB), azobenzene (AB), and hydrazobenzene (HAB) are frequently produced and accumulated during the reaction [12–16]. Interestingly, these intermediates were less produced when nitrobenzene hydrogenation was catalyzed by Ni/TiO_2 catalyst in water, as the results shown in Fig. 1. The selectivity to aniline was higher than 98.5% through the whole reaction process and improved with the reaction time prolonged, no undesired intermediates accumulated during the reaction, while the conversion of nitrobenzene increased very slowly after 4 h (63%), indicating the activity of catalyst decreased during the reaction. Moreover, after reaction, the color of the Ni/TiO_2 catalyst changed from black to gray, which strongly suggested that the catalyst deactivation occurred during the reaction. By comparison, the catalyst presented a good stability for the reaction in ethanol (Fig. S2), the nitrobenzene was converted 70% within the first 1 h, and it increased near 100% after reaction for 2 h. but the selectivity to aniline was very low for the formation and accumulation of the intermediates like NSB, PHA, AOB, AB, HAB as ascribed in literature [12]. In general, the deactivation of supported metal catalysts may result from (a) sintering, (b) poisoning, and (c) loss of active species [17]. Hardacre et al. proposed that formation of $\text{Ru}(\text{OH})_x$ surface species was the main cause of Ru/SiO_2 catalyst deactivation in the liquid-phase hydrogenation of

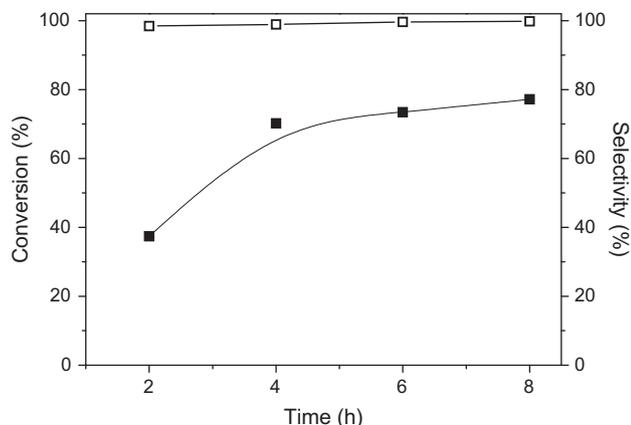


Fig. 1. Changes of conversion and selectivity of nitrobenzene hydrogenation over Ni/TiO₂ in water. Reaction conditions: NB: 6 mL, H₂O: 6 mL, H₂: 6.5 MPa, T: 80 °C, NB/Ni = 312/1 (molar ratio) (■) conversion of NB, (□) selectivity to AN. In this paper, NB refers to nitrobenzene and AN to aniline.

butan-2-one in water [18]. In our previous work, the formation of carbonates, the oxidation of surface Au⁰, and the CO formation are proposed to be the possible factors for the deactivation of Au/TiO₂ in the hydrogenation of o-chloronitrobenzene in scCO₂ or H₂O/CO₂. In order to investigate the reasons for the deactivation of Ni/TiO₂, the experiments for the catalyst pretreatment and characterization were carried out. Ni/TiO₂ catalyst was pretreated with different solutions before reaction and the results are shown in Table 1. The conversion and reaction rate decreased largely for the catalysts pretreated in water or in the mixture of water and nitrobenzene (entries 4 and 5), while for the catalysts pretreated in aniline and nitrobenzene (entries 2 and 3), the conversions were a little higher than that of fresh Ni/TiO₂ catalyst (entry 1), which was probable because of the adsorption of aniline and nitrobenzene on the surface of Ni/TiO₂ catalyst forming a substrate (oil) adsorption film on the surface to lower the influence of water. These results indicated that water may be the most important factor to affect the activity of Ni/TiO₂ catalysts. Herein, the influence of water on the active species of catalyst has been investigated by using XRD and XPS. Fig. 2 shows the XRD patterns for the catalysts pretreated with different solution. For the fresh Ni/TiO₂ catalyst (Fig. 2a), besides the diffraction peaks of anatase TiO₂, diffraction of the metallic nickel peaks presented at 2θ of 44.5°, 51.8°, and 76.4° indicating only the metallic Ni presented on the surface of Ni/TiO₂ after reduced with hydrogen, and the average particle size of Ni was about 14.4 nm as calculated from the half-width of the Ni (111) diffraction peak with Debye–Scherrer equation. But two new diffraction

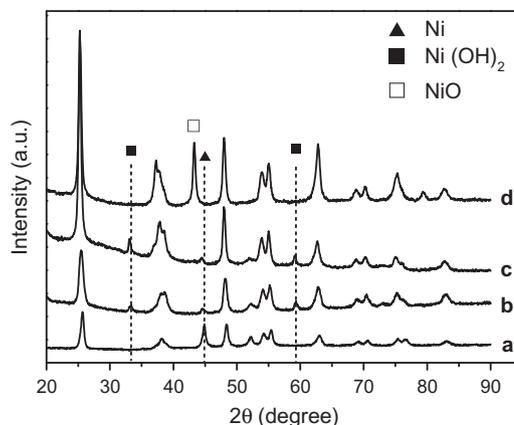


Fig. 2. XRD patterns of (a) fresh Ni/TiO₂ catalyst, (b) Ni/TiO₂ treated with water for 4 h, (c) used Ni/TiO₂ catalyst after reaction for 4 h, (d) NiO/TiO₂ treated with water for 4 h.

peaks of Ni(OH)₂ presented at 2θ of 33.2° and 59.3° for the Ni/TiO₂ pretreated with water and the used one (Fig. 2b and c), while the diffraction peaks of Ni(OH)₂ were not found for the water treated NiO/TiO₂ sample (Fig. 2d). This strongly suggested that Ni(OH)₂ was formed directly from the metallic nickel reacting with water during reaction or pretreatment in water, did not go through the step of metallic nickel oxidation to NiO and then formed Ni(OH)₂. Moreover, this result was further confirmed by using XPS. As the XPS spectra of Ni 2p shown in Fig. 3, for the fresh Ni/TiO₂ catalyst, a metallic nickel peak presented at binding energy of 851 ± 0.1 eV. It was noted that the binding energy (BE) of metallic nickel presented a little shift of 1.5 eV from the standard values (852.6 eV) which may account the strong interaction between metallic nickel and TiO₂ support [19,20]. The peaks at binding energies of 854.4 eV (Ni 2p_{3/2}) and 872.6 eV (Ni 2p_{1/2}) might be the satellite peak of NiO [21]. For the used and water-treated Ni/TiO₂ catalysts, besides the band at 855.6 eV and 873.2 eV of NiO, two peaks were found at binding energy of 861.3 eV and 880 eV, which are assigned to Ni²⁺ of Ni(OH)₂. This indicated that metallic nickel were converted to Ni(OH)₂ and NiO during the reaction or pretreatment. It should be noted that NiO was formed from the oxidation of metallic nickel by contacting air during the sample transfer and settlement, but which could not form during the reaction due to the reduction atmosphere of hydrogen. The XPS results demonstrated again the formation of Ni(OH)₂ in water was the main reason for Ni/TiO₂ deactivation, which is in agreement to the literature, that water promoted NiB/SiO₂ deactivation via the surface oxidation of Ni

Table 1
Results for the hydrogenation of nitrobenzene over Ni/TiO₂ catalysts pretreated in different solution.

Entry	Pretreatment ^a	Conv. (%)	Sel. (%)	Reaction rate ^b (h ⁻¹)
1	–	73.4	99.6	36.7
2	AN	94.8	99.2	47.4
3	NB	81.2	98	40.6
4	H ₂ O	28.4	100	14.2
5 ^c	NB, H ₂ O	7.4	99.4	3.7

Reaction conditions: NB: 6 mL, H₂O: 6 mL, H₂: 6.5 MPa, T: 80 °C, NB/Ni = 312/1 (molar ratio), Reaction time: 6 h; NB and AN represents nitrobenzene and aniline, respectively.

^a The catalysts were treated at 80 °C for 4 h in different solution (6 mL).

^b Reaction rate was calculated by the moles of NB converted per mol Ni per hour.

^c The catalysts were treated at 80 °C for 4 h in the mixture of 6 mL NB and 6 mL H₂O.

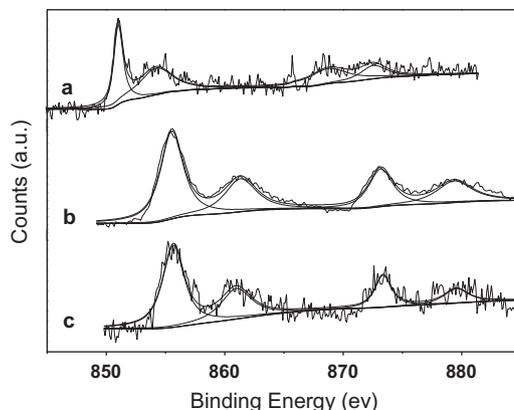


Fig. 3. Ni 2p XPS spectra for (a) fresh Ni/TiO₂, (b) used Ni/TiO₂, (c) Ni/TiO₂ treated with water for 4 h.

accelerated by forming $\text{Ni}(\text{OH})_2$ [22]. The leaching of the Ni species was also checked in this work. The concentration of nickel in the reaction solution was below 0.4 ppm from the inductively coupled plasma (ICP) analysis, suggesting the leaching of active species could be disregarded.

The above results confirmed that the formation of $\text{Ni}(\text{OH})_2$ during the reaction resulted in the deactivation of Ni/TiO_2 catalyst in water. Therefore, we designed a catalyst with a hydrophobic layer to prevent the contacting of H_2O with the active species. Nowadays, most studies are focused on the development of polymer or silica coatings to protect the nanoparticles from oxidation [23–25], for example, by using the co-functionalized silica supporters with aminopropyl and methyl groups, and the Ni–B amorphous alloy showed higher activity and selectivity owing to methyl could enhance the surface hydrophobicity and the B-content [26]. However, the approach of functionalized with groups exists poor chemical stability and it is difficult to quantitative functional groups on the support. More recently, carbon-protected nanoparticles are receiving more attention, because carbon-based materials have many advantages over polymer or silica, such as much higher chemical and thermal stability [27–31]. Herein, the Ni/TiO_2 catalysts were coated with a layer of hydrophobic carbon layer and the catalytic performance has been discussed in detail.

3.2. Preparation of carbon-coated Ni/TiO_2 catalysts and their catalytic performance

The carbon-coated Ni/TiO_2 catalysts were prepared via hydrothermal approach using glucose as the carbon source. The carbonization reaction took place in water at 180 °C, and the coated carbon content on the catalyst surface was in a range of 2%, 11%, and 19.3% as determined by TGA (shown in Fig. S1). $(\text{Ni}/\text{TiO}_2)@C-11\%$ catalyst was selected as research object to compare with original Ni/TiO_2 .

The typical TEM of the reduced Ni/TiO_2 and $(\text{Ni}/\text{TiO}_2)@C-11\%$ catalyst are shown in Fig. 4. For Ni/TiO_2 catalyst (Fig. 4a), Ni nanoparticles were well dispersed on TiO_2 , the average size of Ni particles was around 14 nm which was in a good agreement with the XRD results given above. For the as-prepared $\text{Ni}/\text{TiO}_2@C-11\%$ catalyst, the nickel particle size was about 12 nm which was smaller than that of Ni/TiO_2 catalyst (Fig. 4b). The chemical composition of $(\text{Ni}/\text{TiO}_2)@C-11\%$ catalyst was analyzed using an energy-dispersive X-ray spectrometer (EDX) attached to a high resolution electron microscope; it showed that carbon was contained on the catalyst surface (shown in Fig. S3). The results of TEM and EDX indicated that carbon was successfully coated on the Ni/TiO_2 catalyst, even though no obvious voids could be observed between the core and the shell from the TEM image (Fig. 4b).

Fig. 5 shows the TPR profiles of the Ni/TiO_2 and $(\text{Ni}/\text{TiO}_2)@C-11\%$. In the profile of Ni/TiO_2 (Fig. 5a), the main reduction peak centered at about 419 °C that is assigned to NiO significantly interacting with

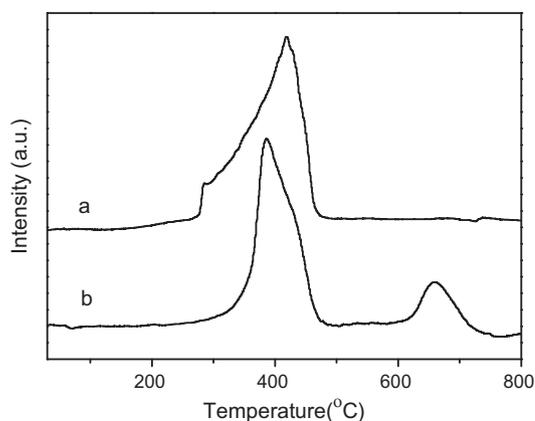


Fig. 5. H₂-TPR profiles for (a) Ni/TiO_2 and (b) $(\text{Ni}/\text{TiO}_2)@C-11\%$ samples.

the titania surface [32], while a shoulder peak at lower temperature (285 °C) which was comparable to bulk NiO without any interaction with titania surface [33]. $(\text{Ni}/\text{TiO}_2)@C-11\%$ sample presented two reduction peaks at 386 °C and 660 °C (Fig. 5b). The main reduction peak presented at 386 °C was attributed to the reduction of NiO, about 33 °C lower than that of Ni/TiO_2 , which indicated that NiO was much easier to be reduced through carbon modification; it may be attributed to the interaction between nickel and carbon and/or the reduction ability of carbon. The extra peak at 660 °C should correspond to the reduction of the surface-coated carbon due to the TGA results (Fig. S4) showed that the carbon content of the $(\text{Ni}/\text{TiO}_2)@C-11\%$ reduced at 660 °C is about 3% lower than that of the $(\text{Ni}/\text{TiO}_2)@C-11\%$ reduced at 450 °C; thus, it should be the reduction peak of carbon. Therefore, the first nickel species reduced at 386 °C might be the active species under the reaction conditions.

Their catalytic ability was studied. The results showed that the carbon coating could improve the activity of the catalyst as shown in Table 2; all the reaction rates for the carbon-coated $(\text{Ni}/\text{TiO}_2)@C$ catalysts were higher than that of the Ni/TiO_2 irrespective to the content of carbon. But the $(\text{Ni}/\text{TiO}_2)@C-11\%$ (containing 11% carbon in weight percent) presented the highest activity compared with $(\text{Ni}/\text{TiO}_2)@C-2\%$ and $(\text{Ni}/\text{TiO}_2)@C-29.2\%$, which may ascribe to the carbon content (2%, thin carbon layer) was too low to coat the surface uniformly and could not to efficiently prevent water to contact with Ni species, and the higher carbon content (29.2%, thick carbon layer) prevented the contacting of water with nickel, and simultaneously lowered the activity of Ni species. This also could be ascribed to the thicker layer of carbon blocking the catalytic sites on the surface or blocking the pores effectively compared with the 11% sample. Even at the high 29.2% coverage of carbon, the rate

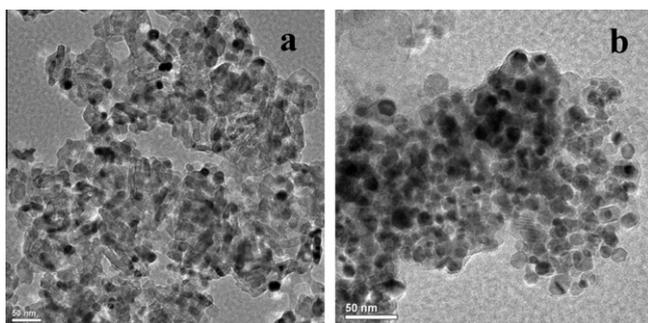


Fig. 4. TEM images for (a) Ni/TiO_2 and (b) $(\text{Ni}/\text{TiO}_2)@C-11\%$.

Table 2

The catalytic performance of carbon-coated nickel catalysts with different carbon contents.

Entry	Catalyst	Time (h)	Conv. (%)	Sel. (%) ^a	Reaction rate (h^{-1})
1	Ni/TiO_2	6	73.4	99.6	38.2
2	$(\text{Ni}/\text{TiO}_2)@C-2\%$	6	81.2	98.1	42.2
3	$(\text{Ni}/\text{TiO}_2)@C-11\%$	3	97	94.8	100.9
4	$(\text{Ni}/\text{TiO}_2)@C-29.2\%$	5.5	97.9	90.9	55.5

Reaction conditions: NB: 6 mL, H_2O : 6 mL, H_2 : 6.5 MPa, T : 80 °C, NB/Ni = 312/1 (molar ratio).

^a The products was confirmed with GC–MS analysis. Some intermediates and by-products such as nitrosobenzene (NSB), N-phenylhydroxylamine (PHA), azoxybenzene (AOB) and azobenzene (AB) were identified.

Table 3
Comparison of the stability of Ni/TiO₂ and carbon-coated Ni/TiO₂ catalysts.

Catalyst	Runs	Time (h)	Conv. (%)	Sel. (%)	Reaction rate (h ⁻¹)
Ni/TiO ₂	1	6	73.4	99.6	38.2
	2	6	0.5	99.1	0.3
(Ni/TiO ₂)@C-11%	1	3.5	97.7	94.4	87.1
	2	5	98.7	94	61.6
	3	9.5	97.4	94.7	32
	4	20	83.1	97.9	13

Reaction conditions: NB: 6 mL, H₂O: 6 mL, H₂: 6.5 MPa, T: 80 °C, NB/Ni = 312/1 (molar ratio).

of reaction is still higher than the bare Ni/TiO₂ for its hydrophobicity is still effective to lessen the deactivation.

The catalyst stability of (Ni/TiO₂)@C-11% was also examined and compared with Ni/TiO₂; it was reused directly without any treatment after precipitated and separated from the reaction solution, and it was noted that the catalysts should be immersed in the solution during the recycling process to avoid the oxidation of active Ni species. As the results shown in Table 3, for Ni/TiO₂, the conversion reached ~80% at the first run and it dropped to <10% in the second run, indicating the catalyst deactivated significantly during the reaction. As expected, the stability of (Ni/TiO₂)@C-11% catalyst was improved largely, the conversions could reach >95% for the first three runs. Although the reaction rate presented a little decrease in the recycling, the reaction rate was about 2.3 times higher than that of the catalyst Ni/TiO₂, and the stability was improved significantly.

3.3. Discussion

The Ni/TiO₂ catalyst disperses in the aqueous phase (H₂O), but the (Ni/TiO₂)@C-11% disperses in the oil phase (NB) (Fig. S5). This indicated that the surface of Ni/TiO₂ catalyst was hydrophilic and it changed to hydrophobic after coated with carbon, which should contribute to the improvement of activity and stability due to the transformation of active nickel metallic species to Ni(OH)₂ via the reaction of Ni with H₂O was inhibited. For (Ni/TiO₂)@C-11% samples, only diffraction peaks of metallic Ni were detected for the fresh, used, and water-treated samples from XRD patterns in Fig. 6, and Ni(OH)₂ was not found for the used and water-treated samples, suggesting the Ni species was successfully prevented to contact with water. For all the samples, no obvious diffraction peak of carbon was found because that the formed carbon layer on the

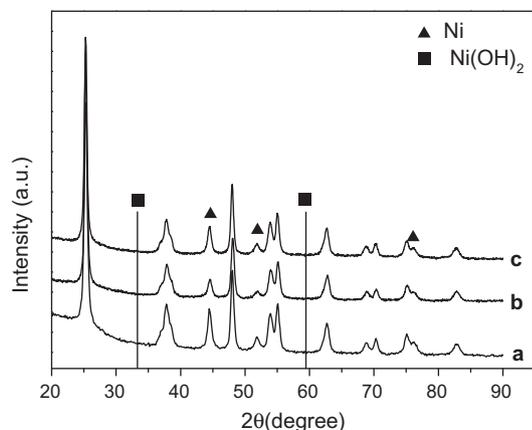


Fig. 6. (A) XRD patterns for (a) (Ni/TiO₂)@C-11% reduced at 450 °C under hydrogen for 2 h, (b) (Ni/TiO₂)@C-11% treated with water for 4 h, (c) (Ni/TiO₂)@C-11% after reaction for 3.5 h.

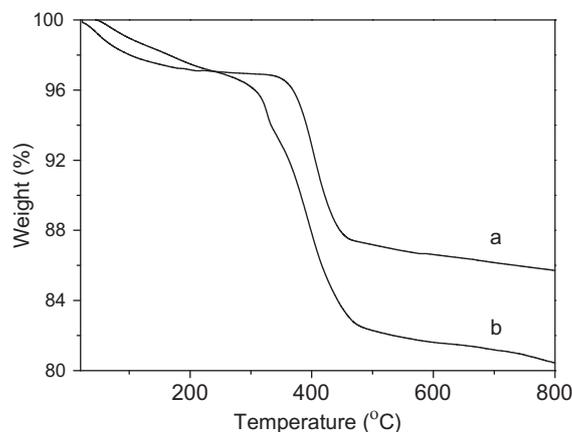


Fig. 7. TGA curves for (a) fresh reduced (Ni/TiO₂)@C-11%, (b) (Ni/TiO₂)@C-11% used for 3 times.

surface was composed with amorphous carbon (Fig. 6a) [28]. Okuhara and coworkers [34] reported that palladium-copper/hydrophobic active carbon was a highly active and selective catalyst for hydrogenation of nitrate in water. The catalyst using water-repelling agent polytetrafluoroethylene resulted in further enhancement; the activity was more than tripled. Ni–B amorphous alloy deposited on surface functionalized with aminopropyl and methyl groups that could enhance the surface hydrophobicity, which facilitated to the desorption of target product of p-chloroaniline, showed higher activity and selectivity in liquid-phase hydrogenation of p-chloronitrobenzene [26]. Thus, the surface hydrophobicity of the catalyst was very important for improving the catalytic activity and selectivity. However, the (Ni/TiO₂)@C-11% catalyst presented a gradual decrease in activity during recycling, which may ascribe to the adsorption of organic products due to the high adsorption ability of carbon. The TGA analysis results of the fresh and used (Ni/TiO₂)@C-11% samples are shown in Fig. 7. The mass-loss at <240 °C for both the samples was owing to the loss of the adsorbed water, for the fresh sample, a 11% mass-loss at 240–500 °C was due to the loss of carbon layer on the surface of the catalyst. By contrast, the mass-loss at 240–500 °C for the used sample was 14.9%, 3.9% higher than the fresh sample, strongly suggested additional organic compounds existed on the used samples. The above results indicated that bulky intermediate species should adsorb on the surface of the spent catalyst, resulting from the polymerization or/and condensation of reactant and/or product during the reaction. Corma et al. reported that the hydrogenation of nitrobenzene was a multi-step process, and there were some larger intermediate molecules produced during the reaction [35]. They may adsorb on the catalyst surface easily and then block the pores though these molecules can be converted to aniline, eventually. Moreover, they also can polymerize or/and condense to form much larger molecular intermediates. These intermediates would adsorb on the surface, block the pores (especially micropores), and cover the metal nickel, in turn, leading to the catalyst deactivation. Therefore, the decrease in activity of (Ni/TiO₂)@C-11% was a physical deactivation, and it is easy to recover by solvent washing or extraction. But for the Ni/TiO₂ catalyst, it is a chemical deactivation via the changes of the active species during the reaction, activity recover is complex.

4. Conclusions

In conclusion, the catalytic performance of Ni/TiO₂ catalyst and its stability improvement have been investigated for the hydrogenation of nitrobenzene in water. The results demonstrated that the

Ni/TiO₂ catalyst deactivated during the reaction, and the formation of nickel hydroxide from metallic nickel reacting with H₂O was the main reason, which was confirmed with the experimental results combined with the XRD, XPS, and ICP analysis. The further study showed that the activity and stability of Ni/TiO₂ catalyst were significantly improved after the catalyst was modified by a carbon coating. The carbon-coated catalyst (Ni/TiO₂)@C-11% presented an enhanced reactivity and stability because that the increased surface hydrophobicity of carbon-coated catalyst prevented water from contacting with nickel catalytic species. Even though the carbon-coated (Ni/TiO₂)@C-11% catalyst showed a gradual decrease in the activity during the recycling, which was coming from the physical adsorption of the organic intermediates or products, it is a physical deactivation and could be recovered easily.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2012.04.020>.

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