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# Nitrate hydrogenation on Pd–Cu/TiO<sub>2</sub> catalyst prepared by photo-deposition

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## ABSTRACT

Bimetallic Pd–Cu/TiO<sub>2</sub> is prepared by successive photo-deposition process and characterized by means of TEM, H<sub>2</sub>-TPR and FTIR spectra of CO adsorption. The as-prepared Pd–Cu/TiO<sub>2</sub> is studied as promising catalyst for nitrate hydrogenation and a step-wise reaction process, divided into nitrate hydrogenation to nitrite and nitrite hydrogenation to nitrogen, is observed. The active sites for nitrate and nitrite hydrogenation over Pd–Cu/TiO<sub>2</sub> are discussed individually. It is observed that basic conditions of reaction solution favor the hydrogenation of nitrate to nitrite, while acidic conditions favor the hydrogenation of nitrite to nitrogen. For nitrite hydrogenation, acetic acid is more efficient acidic buffer than hydrochloric acid due to an in situ buffering effect. Based on these results, a two-step process, by changing the reaction solution from basic conditions to acidic conditions at midterm, is developed to realize the hydrogenation of nitrate to nitrogen over bimetallic Pd–Cu/TiO<sub>2</sub>.

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## 1. Introduction

Groundwater pollution by nitrate, originated from intensive agricultural activities and especial excessive fertilization, is a widespread problem all over the world. Nitrate in drinking water is a great threat to human health. It may cause diseases, such as methaemoglobin, when it is consumed with drinking water and converted into nitrite in human body [1,2]. Catalytic denitrification was developed by Vorlop and Tacke [3] in the late 1980s. In this process, nitrate ions are converted into nitrogen on certain catalysts using hydrogen as reductant. Besides economical advantages, this process allows operating at room temperature and atmospheric pressure [4–8].

Generally, bimetallic catalysts are employed for nitrate hydrogenation, because although nitrite can be easily reduced on monometallic noble metal sites, nitrate has to be reduced on bimetallic sites with the addition of a second metal [9,10]. A step-wise reaction mechanism is widely accepted for nitrate hydrogenation, where nitrate is reduced to intermediate nitrite and then to nitrogen with ammonium as the final products [11–13]. Nitrite accumulation during nitrate degradation has been found in many studies when bimetallic catalysts are used [12,14–17]. Recently, great efforts have been made to improve the catalytic activity and selectivity for nitrate hydrogenation. Besides the choice of the supported metals and the nature of the supports, the preparation methods for bimetallic catalysts are important issues influencing the catalytic performances [8,18–24]. Wet impregna-

tion is frequently used to prepare supported catalysts for nitrate hydrogenation. Other methods, such as chemical reduction [16], ion exchange [25] and catalytic reduction [26], have also been employed. Thereinto, catalytic reduction is proposed to be a promising method for the preparation of bimetallic catalysts, because it catalytically reduces the promoter ions on the surface of noble metal particles and is said to bring the noble metal and the promoter in close contact. Alternatively, successive photo-deposition method has been applied to prepare Pd–Cu/TiO<sub>2</sub> catalyst with close contact between Pd–Cu and good nitrate hydrogenation activity over as-prepared Pd–Cu/TiO<sub>2</sub> has been achieved [14].

In the present study, bimetallic Pd–Cu/TiO<sub>2</sub> prepared by successive photo-deposition is studied as promising catalyst for nitrate and nitrite hydrogenation. The structure of bimetallic catalyst is investigated and the active sites for nitrate and nitrite hydrogenation are discussed. Moreover, the influence of solution pH values on the catalytic performances is investigated and a two-step process is proposed for nitrate hydrogenation to final product nitrogen.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Monometallic catalyst

Commercial TiO<sub>2</sub> (P25, Degussa, Anatase 79%, Rutile 21%), with an average particle size of ca. 20 nm and a BET surface area of ca. 50 m<sup>2</sup>/g, was used as catalyst support. Supported monometallic catalyst was prepared by a photo-deposition method, as described in our previous work [27]. In a typical process, 100 mL PdCl<sub>2</sub> solution, 500 mg of TiO<sub>2</sub> and 8 mL of ethanol were added into a round-bottom quartz flask under vigorous stirring to form slurry. The slurry was

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adjusted to pH 11 using either 1 M HCl or 1 M NaOH aqueous solutions and irradiated by a high-pressure mercury light with the main wavelength of 365 nm for 6 h under N<sub>2</sub> protection. After 6 h of irradiation, the particles were filtered, washed, and dried at ambient conditions.

## 2.2. Bimetallic catalyst

Pd–Cu/TiO<sub>2</sub> was prepared by a successive photo-deposition process. Typically, 100 mL CuAc<sub>2</sub> solution, the as-prepared Pd/TiO<sub>2</sub> and 8 mL ethanol were added into a round-bottom quartz flask under vigorous stirring to form slurry. The slurry was adjusted to pH 12 and irradiated by a high-pressure mercury light for 6 h under N<sub>2</sub> protection. After 3 h of irradiation, the particles were filtered, washed, and dried at ambient conditions. The palladium loading was 1.20% and copper loading was 0.30% in final Pd–Cu/TiO<sub>2</sub> sample prepared by photo-deposition, as determined by ICP analysis.

For reference, Pd–Cu/TiO<sub>2</sub> bimetallic catalyst with similar Pd and Cu loadings was prepared by chemical reduction method. Typically, TiO<sub>2</sub> and certain amount of PdCl<sub>2</sub> and CuAc<sub>2</sub> solution were added into distilled water and dispersed by ultrasonic vibration for 30 min. Palladium and copper ions were reduced by the addition of sufficient 1 mol/L KBH<sub>4</sub> under the protection of nitrogen. The resulting suspension was filtered, washed by distilled water and dried at ambient conditions.

## 2.3. Catalyst characterization

Transmission electron microscopy image of Pd–Cu/TiO<sub>2</sub> was acquired on a JEOL 2010 transmission electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature. The particle-size distribution was obtained from TEM image and the average particle diameter was calculated from  $d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$ .

FTIR spectra of CO adsorption on samples were collected on the Bruker Tensor 27 spectrometer with 128 scans at a resolution of 4 cm<sup>-1</sup>. A self-supporting pellet made of the catalyst sample was placed in the IR flow cell and the background spectrum was taken at room temperature. After the He stream was switched to a gas mixture containing 1% CO in He at a total flow rate of 30 ml/min, a series of time-dependent FTIR spectra of CO adsorption on the samples were sequentially recorded.

The temperature-programmed reduction experiments of samples were carried out on a chemisorption analyzer (Quantachrome ChemBET 3000) with 8 vol.% H<sub>2</sub>/Ar at a heating rate of 10 °C/min from room temperature to 700 °C. Prior to reduction, the sample was pretreated in flowing He at 200 °C for 1 h.

## 2.4. Catalyst test

Nitrate and nitrite hydrogenation was performed in a semibatch reactor at atmospheric pressure and 25 °C. In a typical experiment, 100 mg catalyst powder and 100 mL nitrate or nitrite aqueous solution were introduced in the reactor to start the reaction under stirring. The pH value of the reaction solution was measured with a digital pH meter and was adjusted by adding acid (HCl or HAC) or base (NaOH) solution. In order to monitor the progress of the reaction, reactant solution of 4 mL was periodically withdrawn from the reactor. The concentrations of nitrate, nitrite and ammonium ions were analyzed by colorimetric method [28] on an UV-vis spectrophotometer (Shimadzu, UV-240) and were calculated by nitrogen weight as mg<sub>N</sub>/L. The general operating conditions were summarized in Table 1.

**Table 1**

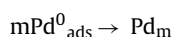
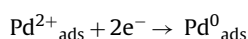
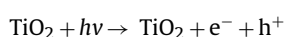
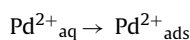
Operating conditions for nitrate and nitrite hydrogenation.

Reaction time	60 min
Reaction temperature	25 °C
Reaction volume	100 mL
Catalyst weight	100 mg
Initial nitrate/nitrite concentration	100 mg <sub>N</sub> /L
Nitrate source	KNO <sub>3</sub>
Nitrite source	NaNO <sub>2</sub>
Hydrogen flow-rate	120 mL/min

## 3. Results and discussion

### 3.1. Catalyst characterization

The scheme for the preparation of Pd–Cu/TiO<sub>2</sub> catalysts by two successive photo-deposition processes is described in Fig. 1. In the first photo-deposition step, Pd/TiO<sub>2</sub> is obtained according to the following equations.

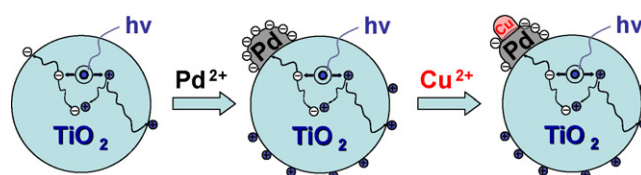


Under ultraviolet irradiation ( $h\nu \geq E_g = 3.02 \text{ eV}$ ), electron-hole pairs are created on the surface of TiO<sub>2</sub>. The palladium ions with positive charge adsorb to the electrons through electrostatic interaction, and subsequently reduced by electrons to palladium atoms. The palladium atoms agglomerate to some extent to form palladium nano-clusters on TiO<sub>2</sub>, while the holes are eliminated by the scavenger ethanol. The palladium nano-clusters on TiO<sub>2</sub> can effectively trap photo-induced electrons and thus promote the electron-hole separation under ultraviolet irradiation. Since electrons are accumulated on the surface of palladium, the copper ions with positive charge selectively adsorb to palladium due to electrostatic interaction, and subsequently reduced by electrons to copper atoms in the second photo-deposition step. Based on the processes proposed above, the exact structure of Pd–Cu/TiO<sub>2</sub> prepared by photo-deposition should be Cu@Pd@TiO<sub>2</sub>.

The TEM image of Pd–Cu/TiO<sub>2</sub> prepared by photo-deposition is shown in Fig. 2. It is seen that homogeneous clusters, probably Pd–Cu, are well dispersed on the TiO<sub>2</sub> support. The average size of the supported clusters is calculated to be ca. 3 nm based on the TEM observation.

In order to reveal the exact existence states of copper and palladium in Pd–Cu/TiO<sub>2</sub> (before and after reaction), TPR and FTIR spectra of CO adsorption are employed and results are analyzed with cross-reference.

The TPR profiles of different samples are shown in Fig. 3. A negative peak centered at 90 °C is observed in Pd/TiO<sub>2</sub>, due to the decomposition of β-PdH formed at room temperature [29]. This peak disappears in Pd–Cu/TiO<sub>2</sub> before and after reaction (nitrate hydrogenation without pH control), indicating that copper addi-



**Fig. 1.** Scheme for the preparation of Pd–Cu/TiO<sub>2</sub> by photo-deposition.

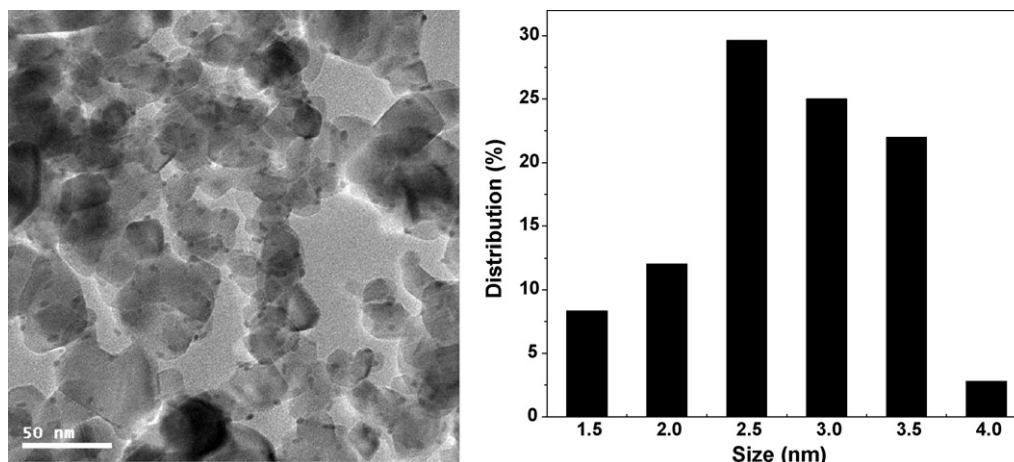


Fig. 2. TEM image of Pd-Cu/TiO<sub>2</sub> and Pd-Cu particle size distribution.

tion may cover parts of the available palladium sites and inhibit the formation of  $\beta$ -hydride phase [6]. The peak centered around 360 °C in Pd/TiO<sub>2</sub> is associated with the reduction of surface capped oxygen of TiO<sub>2</sub> [30]. The presence of palladium promotes the reduction of oxygen species through hydrogen spillover [31]. For Cu/TiO<sub>2</sub>, two reduction peaks centered at 200 and 350 °C can be observed, corresponding to the reduction of copper oxides on TiO<sub>2</sub> [32]. For Pd-Cu/TiO<sub>2</sub>, two peaks at 430 and 590 °C are observed, which can be assigned to the reduction of capped oxygen of TiO<sub>2</sub>. The temperature is obviously higher than that in Pd/TiO<sub>2</sub> (360 °C), probably due to the inhibition of hydrogen spillover by the addition of copper. Besides, no reduction peaks corresponding to the reduction of copper oxides can be observed, indicating that copper species exist in the metallic form. As for Pd-Cu/TiO<sub>2</sub> after reaction of nitrate hydrogenation, the reduction peak at 340 °C assignable to reduction of copper oxides is observed, indicating the appearance of copper oxides appear in Pd-Cu/TiO<sub>2</sub> after nitrate hydrogenation.

FTIR of CO adsorption is performed to probe the existence states of Pd-Cu and the results are shown in Fig. 4. Three obvious bands of CO adsorbed on Pd can be seen in Pd/TiO<sub>2</sub>. The band at 2095 cm<sup>-1</sup> is attributed to linearly adsorbed CO and the band at 1975 cm<sup>-1</sup> is attributed to bridged CO on metallic palladium [26]. The band at 2130 cm<sup>-1</sup> is assigned to CO adsorbed at Pd<sup>2+</sup> sites [33]. Besides these bands, the band centered at 2170 cm<sup>-1</sup> corresponds to CO

adsorption on exposed Ti species [34]. It should be mentioned that the reduction of Pd<sup>2+</sup> cannot be observed from TPR profile because the reduction process may proceed in hydrogen even at room temperature.

The band at 2115 cm<sup>-1</sup> in Cu/TiO<sub>2</sub> is assigned to CO linearly bonded to Cu<sup>+</sup>. No band associated with Cu<sup>2+</sup>-CO is observed, because the CO adsorption is carried out at room temperature and Cu<sup>2+</sup>, even if existed, can be reduced to Cu<sup>+</sup> after the contact with CO [35]. The band at 2115 cm<sup>-1</sup> is not observed in Pd-Cu/TiO<sub>2</sub>, indicating that copper species exist in the form of metal, in consistent with TPR results. After nitrate hydrogenation, the band at 2115 cm<sup>-1</sup> appears again, indicating the oxidation of copper metal to copper oxides during reaction. The palladium species exist in the form of both metal form (Pd<sup>0</sup>, corresponding bands at 1975 and 2095 cm<sup>-1</sup>) and oxides form (Pd<sup>2+</sup>, corresponding band at 2130 cm<sup>-1</sup>) in Pd-Cu/TiO<sub>2</sub>. While after nitrate hydrogenation, palladium oxides cannot be observed by FTIR analysis (disappearance of IR band at 2130 cm<sup>-1</sup>), suggesting that palladium oxides are reduced to metal palladium during reaction.

### 3.2. Nitrate reduction

A comparison of the catalyst activity between bimetallic catalyst Pd-Cu/TiO<sub>2</sub> prepared by photo-deposition and by chemical reduction is made, and the results are shown in Fig. 5. Although

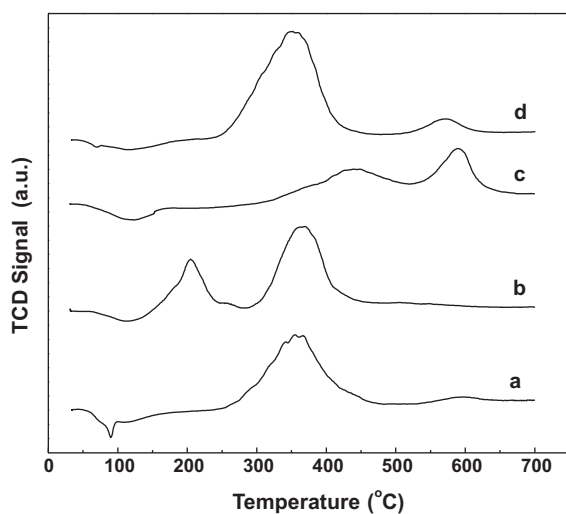


Fig. 3. TPR profiles of (a) Pd/TiO<sub>2</sub>, (b) Cu/TiO<sub>2</sub>, (c) Pd-Cu/TiO<sub>2</sub> and (d) Pd-Cu/TiO<sub>2</sub> after reaction.

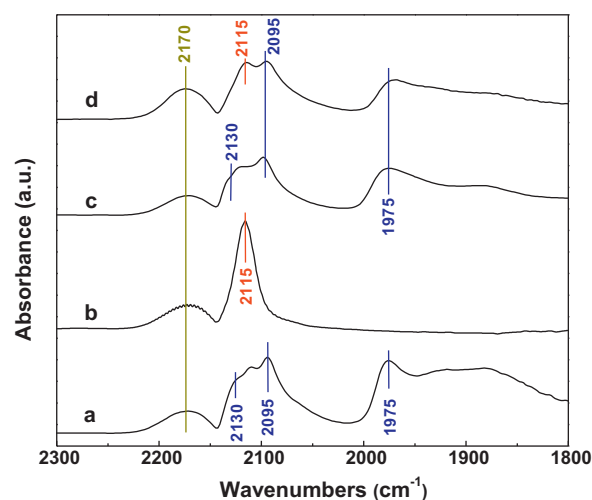


Fig. 4. FTIR spectra of CO adsorbed on (a) Pd/TiO<sub>2</sub>, (b) Cu/TiO<sub>2</sub>, (c) Pd-Cu/TiO<sub>2</sub> and (d) Pd-Cu/TiO<sub>2</sub> after reaction.

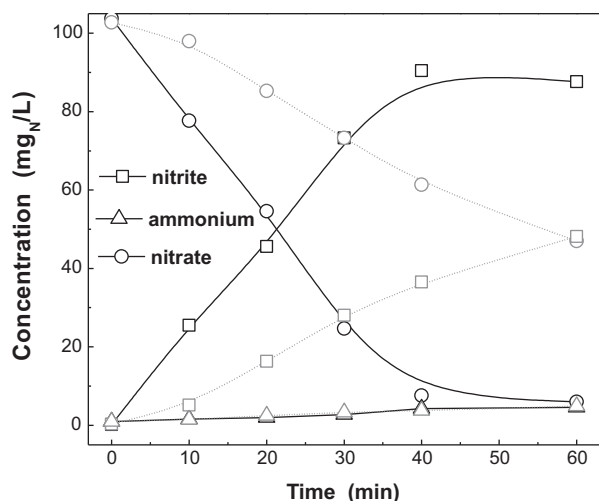


Fig. 5. Nitrate hydrogenation on Pd–Cu/TiO<sub>2</sub> prepared by photo-deposition (solid line) and chemical reduction (dash line) without pH control.

nitrite is the main product in both cases, the catalyst prepared by photo-deposition exhibits much higher activity in nitrate hydrogenation than that prepared by chemical reduction. The advantage of Pd–Cu/TiO<sub>2</sub> prepared by photo-deposition should be ascribed to the special Cu@Pd@TiO<sub>2</sub> structure, which provides a close contact between palladium and copper species.

During nitrate hydrogenation over Pd–Cu/TiO<sub>2</sub>, we observe that the pH value of reaction system increases gradually. This implies that the pH value may influence nitrate hydrogenation. For this consideration, we conduct the experiments of nitrate hydrogenation over Pd–Cu/TiO<sub>2</sub> at different pH values, and the results are summarized in Table 2. Both the nitrate hydrogenation activity and the selectivity to nitrite increase with increasing pH values. Obviously, high nitrate to nitrite activity can be achieved in basic environment. The results are somewhat different from those reported. Yoshinaga et al. [37] and Prusse et al. [13] set the pH value in basic region for nitrate hydrogenation and a decrease in nitrate removal activity with increasing pH value was observed. Besides, most studies have chosen moderate pH values or even in the acidity region with the aim to improve the hydrogenation selectivity [17,23,36] and the formation of ammonium was favored at high pH values [13,15]. The difference between our results and the literature results should be ascribed to the different preparation method employed.

A bi-functional mechanism for nitrate hydrogenation has been reported by Epron et al. [10]. It is proposed that nitrate hydrogenation occurs firstly on copper sites through a direct redox mechanism and copper is maintained in metallic state by chemisorbed hydrogen from palladium. Alternatively, Gao et al. [16,38] has proposed that Cu<sub>2</sub>O may involve in nitrate-to-nitrite conversion on Pd–Cu/TiO<sub>2</sub> catalyst, considering that negatively charged nitrate ions are more easily adsorbed on the positively charged surface of Cu<sub>2</sub>O instead of Cu. In our experiments, mono-metallic Pd/TiO<sub>2</sub> and Cu/TiO<sub>2</sub> are completely inactive for nitrate hydrogenation, indicating that nitrate hydrogenation proceeds on Pd–Cu bi-functional

Table 2  
Nitrate hydrogenation on Pd–Cu/TiO<sub>2</sub> at different pH values.

pH	Nitrate conversion (%)	Nitrite selectivity (%)	Ammonium selectivity (%)	Nitrogen selectivity (%)
6	57.4	27.2	9.0	63.8
8	93.3	39.3	9.7	51
10	96.2	81.8	4	14.2
11	99.9	96.9	3.1	0
12	99.9	98.9	1.1	0

sites. Before reaction, palladium species exist in both the metallic and oxides form, while copper species exist in the metallic form. After reaction, palladium species are completely reduced to metallic form, while copper species are partially oxidized to oxides form. So, we propose that hydrogen is activated on metallic palladium species and nitrate species adsorb on copper oxides, probably Cu<sub>2</sub>O. The hydrogenation of nitrate is realized by hydrogen spillover from palladium sites to copper sites. It has been proposed that the metal crystallites in nitrate hydrogenation catalysts can be, to some extent, compared with electrodes in water. The catalyst is in a more reduced state under acidic or neutral conditions, whereas it is more oxidized under basic conditions [13]. From this point of view, basic reaction conditions, *i.e.*, high pH values, favor the adsorption of nitrate species and thus favor the hydrogenation of nitrate to nitrite on Pd–Cu/TiO<sub>2</sub> prepared by photo-deposition.

### 3.3. Nitrite reduction

As the intermediate of nitrate hydrogenation, nitrite accumulation has been found in most studies. As a common strategy, many studies have been focused on how to eliminate nitrite and improve the nitrogen selectivity. Here, we conduct nitrite hydrogenation on Pd–Cu/TiO<sub>2</sub> prepared by photo-deposition at different pH values.

As seen in Table 3, nitrite hydrogenation activity decreases with increasing pH value and acidic condition favors nitrite hydrogenation on Pd–Cu/TiO<sub>2</sub>. The highest selectivity to target product nitrogen is obtained under acidic condition at pH value of 4. When the pH value is set to below 4, leaching of supported metal from the catalyst can be observed, which should be absolutely avoided to prevent the secondary pollution. It is also seen from Table 3 that higher nitrite hydrogenation activity as well as nitrogen selectivity can be obtained using HAc as buffer than that using HCl as buffer, indicating that HAc is a more suitable buffer. Time-on-stream curves in Fig. 6 show that nitrite hydrogenation over Pd–Cu/TiO<sub>2</sub> at pH 4 is a typical zero-order reaction. The rate constant is calculated to be 9.3 mg<sub>N</sub>/(L min g<sub>cat</sub>) with HCl as buffer and 22.3 mg<sub>N</sub>/(L min g<sub>cat</sub>) with HAc as buffer. The ammonium concentration–time curve with HAc and HCl are quite similar, indicating the good capability of both acids in controlling the hydrogenation selectivity. The much better activity with HAc as buffer may come from the in situ buffering effect. HAc could neutralize hydroxyl ions at the very proximity of the active sites where it is formed, while hydroxyl neutralization by HCl could only happen after its diffusion into the bulk of the reaction solution [39].

The results in Table 3 show that nitrite hydrogenation activity decreases with increasing pH value, indicating that hydroxyl ions in the solution may have negative effects on nitrite hydrogenation. The prohibiting effect of hydroxyl ions on nitrite reduction were observed by Sakamoto et al. [2] and they proposed that the decreasing in the catalytic activity was due to hydroxyl retarded nitrite adsorption onto the palladium sites [40].

It has been proposed that nitrite reduction does not occur on bimetallic Pd–Cu sites where it is formed through nitrate reduction. Nitrite desorbs or spillovers from these sites and adsorbs

Table 3  
Nitrite hydrogenation on Pd–Cu/TiO<sub>2</sub> at different pH values.

pH	Nitrite conversion (%)		Ammonium selectivity (%)		Nitrogen selectivity (%)	
	HCl	HAc	HCl	HAc	HCl	HAc
Buffer						
4	52	99.6	0.9	0.6	99.1	99.4
5	43	73.7	5.1	0.3	94.9	99.7
6	41.2	73.1	10.1	6.1	89.9	93.9
7	33.7	63.2	15.3	6.7	84.7	93.3
8	25.4	42.9	12.6	9.5	87.4	90.5

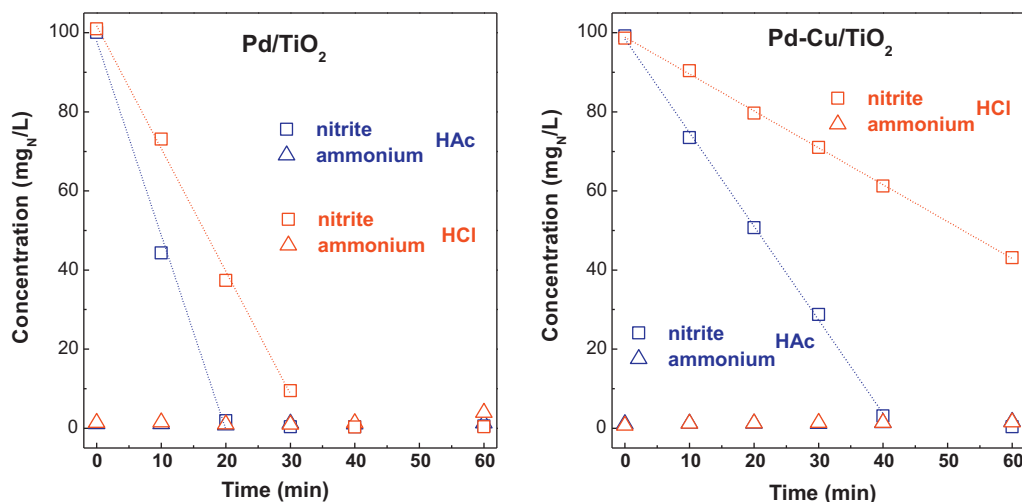


Fig. 6. Nitrite hydrogenation on Pd/TiO<sub>2</sub> and Pd-Cu/TiO<sub>2</sub> at pH 4.

at monometallic palladium sites for further reduction [13]. Alternatively, Epron et al. has proposed that nitrite could be reduced either on copper sites or on the precious metal sites [10]. In our experiments, monometallic Pd/TiO<sub>2</sub> catalyst (prepared by photo-deposition) shows much higher activity for nitrite hydrogenation than bimetallic Pd-Cu/TiO<sub>2</sub> with similar palladium loading. HAC appears to be more effective a buffer for nitrite hydrogenation on Pt/TiO<sub>2</sub>, similar to the circumstances on Pd-Cu/TiO<sub>2</sub>. Besides, high nitrogen selectivity can be obtained on both Pd/TiO<sub>2</sub> and Pd-Cu/TiO<sub>2</sub> prepared by photo-deposition. Based on these observations, we propose that exposed palladium species are the active sites for nitrite hydrogenation under acidic conditions while copper species do not contribute to the nitrite hydrogenation activity. For Pd-Cu/TiO<sub>2</sub> prepared by photo-deposition, the structure is Cu@Pd@TiO<sub>2</sub> and the addition of copper may block some palladium sites for nitrite hydrogenation. Consequently, Pd-Cu/TiO<sub>2</sub> exhibits lower nitrite hydrogenation activity than Pd/TiO<sub>2</sub> under identical reaction conditions.

### 3.4. A two-stage process for nitrate reduction

As discussed above, the highest activity for nitrate reduction is obtained under basic condition of pH 12, while the highest activ-

ity and nitrogen selectivity for nitrite reduction are obtained under acidic condition of pH 4. To achieve a high nitrate conversion to target production nitrogen, we propose here a two-step process with pH control for nitrate elimination from drinking water. This strategy has once been proposed by Lemaigen et al. [12] and Sakamoto et al. [2], however, they met with a sharp decrease in catalyst activity at high pH values.

As is shown in Fig. 7, the whole process of nitrate reduction is divided into two steps, the selective hydrogenation of nitrate to nitrite and the selective hydrogenation of nitrite to nitrogen. During the first 28 min the pH value is adjusted to be 12 by adding sufficient NaOH solution, nitrate hydrogenation to nitrite proceeds at a reaction rate of 40.1 mg<sub>N</sub>/(L min g<sub>cat</sub>) with ca. 99% selectivity to nitrite. At 28 min, when 85.1% of nitrate conversion is obtained, the pH value is adjusted to 4 by adding HAC solution. Then nitrite hydrogenation starts at a rate of 25.8 mg<sub>N</sub>/(L min g<sub>cat</sub>). After total reaction for 60 min, 91.6% of nitrate is hydrogenated to nitrogen and 3.1% of nitrate to ammonium, while no nitrite can be detected in the hydrogenation product.

We have proved that Pd/TiO<sub>2</sub> prepared by photo-deposition is more active for nitrite hydrogenation than Pd-Cu/TiO<sub>2</sub>. So we can also propose another type of two-step process for nitrate hydrogenation to nitrogen using the combination of

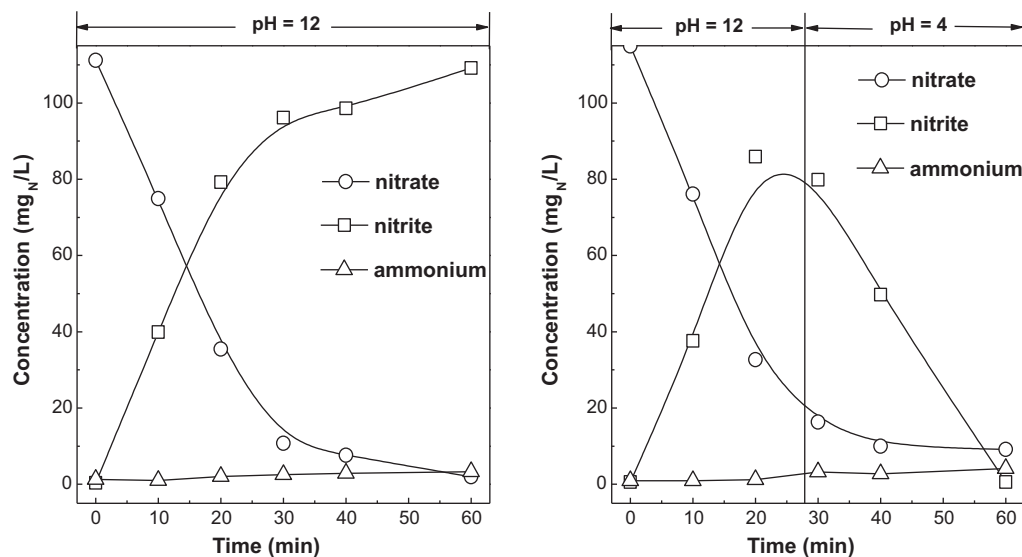


Fig. 7. A two-stage process for nitrate hydrogenation on Pd-Cu/TiO<sub>2</sub>.

Pd–Cu/TiO<sub>2</sub> (for nitrate to nitrite) and Pd/TiO<sub>2</sub> (nitrite to nitrogen) catalysts.

#### 4. Conclusion

Bimetallic Pd–Cu/TiO<sub>2</sub>, with typical structure of Cu@Pd@TiO<sub>2</sub>, is prepared by successive photo-deposition and studied as promising catalyst for nitrate dehydrogenation in drinking water. The high dispersion of the supported metals and the closely contact between copper and palladium, which are essential factors for nitrate hydrogenation, are ensured by the photo-deposition preparation process.

A step-wise reaction process, divided into nitrate hydrogenation to nitrite and nitrite hydrogenation to nitrogen, is observed for nitrate hydrogenation over Pd–Cu/TiO<sub>2</sub>. For nitrate hydrogenation to nitrite, hydrogen is activated on metallic palladium sites and spillover to reduce nitrate species adsorb on Cu<sub>2</sub>O sites. Basic conditions favor this process and high hydrogenation activity as well as high nitrite selectivity can be achieved at pH 12. For nitrite hydrogenation to nitrogen, hydrogen is activated on palladium sites and reduces nitrite on the same sites. Acidic conditions favor this process and acetic acid is more efficient acidic buffer than hydrochloric acid due to an in situ buffering effect.

Based on the characteristics of nitrate hydrogenation on Pd–Cu/TiO<sub>2</sub>, a two-step process is developed by changing the reaction solution from basic conditions to acidic conditions at midterm and satisfying denitrification results are achieved.

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