



Titania supported Pd-Cu bimetallic catalyst for the reduction of nitrate in drinking water

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Abstract

Titania supported palladium-copper bimetallic catalysts (Pd-Cu/TiO₂) are prepared by the liquid phase chemical reduction method and then applied in the liquid phase catalytic reduction of nitrate ions (NO₃⁻). Compared with the conventional impregnation method that needs the post-thermal reduction to prepare the supported metallic catalysts, the liquid phase chemical reduction at room temperature can inhibit the aggregation of metal active components and have been proved to exhibit high catalytic activity in this work. The conversions of NO₃⁻ are 29.18% and 54.12% over the catalysts treated at 873 and 298 K, respectively. The conversion of NO₃⁻ and selectivity to N₂ influenced by the effect of the support, the loading of Pd + Cu, the molar ratio of Pd to Cu, the H₂ flow rate, the addition of CO₂ and the pH value of solution are also discussed in detail with the surface characterizations by X-ray photoelectron spectrum (XPS), X-ray diffraction (XRD), in situ FT-IR and transmission electron microscopy (TEM). A mechanism has been proposed that Cu₂O component involved the reaction course and acted as the active center for nitrate-to-nitrite conversion. The spilt-over hydrogen on Pd is suggested to reduce the adjacent Cu₂O into metal Cu, and on the latter the conversion of NO₃⁻ to NO₂⁻ occurs. However, in strongly acidic solution, copper is dissolved from the Pd-Cu/TiO₂ catalyst and released into the solution in the form of copper(II) ions, so the reduction of Cu₂O to Cu is inhibited and the nitrate reduction cannot be accomplished.

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1. Introduction

In recent years, nitrate (NO₃⁻) concentration in ground water, the main source of drinking water, has been increasing throughout the world because of the intensive agricultural activities, especially overusing of man-made fertilizers [1]. High concentra-

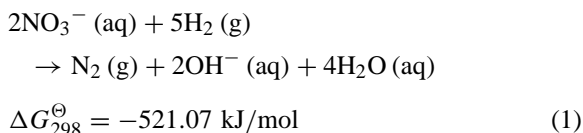
tion of nitrate in drinking water is fatal to infants under 6 months of age, in whose bodies, nitrate is reduced to nitrite (NO₂⁻), which can further combine with hemoglobin in the blood to form methaemoglobin, and as a result, leads to so-called “blue baby syndrome”. Furthermore, nitrate can be converted into nitrosamine, which can cause cancer and hypertension [2]. For these reasons, the US Environmental Protection Agency (EPA) established the maximum permitted level of nitrate to 10 mg NO₃⁻ (calculated by nitrogen, N/L) in drinking water, and

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the European Community set to 11.3 mg/l (N/L) and recommended to 5.65 mg/l (N/L). So, reducing the nitrate concentration in drinking water is imperative at the present time. Many methods like ion exchange, reverse osmosis, electrodialysis, chemical denitrification and biological denitrification have been used to removed nitrate from drinking water. However, these techniques usually need a post-treatment of the effluents, and cannot easily be performed practically [1]. More recently, liquid phase catalytic denitrification using a solid bimetallic catalyst has been proved to be a potential and promising method for the removal of nitrate from water [3–6]. In this process, nitrate is converted via intermediates into nitrogen in a three phase reactor system under mild reaction conditions (e.g. $T = 298\text{ K}$, $P = 1\text{ bar}$), which can be represented as below:



Many investigations have been published on the reduction of nitrate in aqueous solution by using the supported bimetallic catalysts, and the supported palladium catalysts with copper or tin acting as promoter have been discovered to show satisfied performance for the reduction of nitrate in aqueous solution [7–30]. Fig. 1 shows a simplified reaction scheme [10].

The reaction scheme shows that nitrate is reduced to the desired product nitrogen via several intermediate products involving NO_2^- , NO , N_2O . At the same time, the undesired by-product ammonium (NH_4^+) is formed by a side reaction due to the over-hydrogenation. Furthermore, it is proved that the catalytic nitrate reduction is only performed over the bimetallic catalysts system, preferably over palladium-copper catalysts, which suggests nitrate-to-

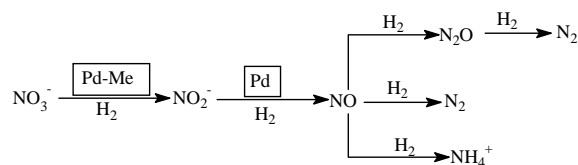
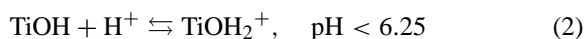


Fig. 1. Hypothetical reaction scheme of the catalytic hydrogenation of nitrate on Pd-Me catalysts. Reproduced from [10].

nitrite reduction step undergoes a structure-sensitive reaction and is catalyzed only by metal ensembles composed of Pd and Cu atoms [7,11,17], whereas nitrite and other following intermediates can be reduced with monometallic palladium catalyst. Moreover, many experimental results have also proved that the activity and selectivity of reaction are strongly influenced by the reaction conditions such as the preparation procedure, the nature of support, the pH value of solution, the hydrogen flow rate, the reaction temperature, the Pd:Cu ratio, and the salt effects etc. As for the support for Pd-Cu bimetallic catalysts, $\gamma\text{-Al}_2\text{O}_3$ [17–19,31], pumice [7], membrane [8,12,27], glass fiber [25], anion resin [30], active carbon [15] and SnO_2 [36] had been commonly investigated. It showed that different supports had greatly affected the catalytic activity and selectivity of reaction, which was partially ascribed to the surface state of the support. Therefore, selecting a suitable catalyst support is essential for the catalytic reduction of nitrate. Many excellent properties have been found on TiO_2 (P25 type) and are widely used in industrial fields. Major uses are as photocatalyst or catalyst support. Surface of TiO_2 exists a group named “titanol”(TiOH), which is amphoteric and occurs such an acid–base equilibrium [33], the absorption properties can be greatly changed under different pH value.



On the basis of these considerations, it is interesting to support Pd-Cu on the TiO_2 for the reduction of nitrate in the aqueous solution in this work.

As to the preparation methods for bimetallic Pd-Cu catalyst, the conventional preparation procedure includes the steps of impregnation, calcination and the final reduction of metal oxides by hydrogen at high temperature. These as-prepared catalysts have to suffer from the high temperature treatment, so an aggregation of active metal component and a reasonable decrease of effective surface area are therefore unavoidable. Such disadvantages can be overcome by liquid phase chemical reduction of metal salts through adding a reductant, e.g. potassium borohydride (KBH_4), which is recognized as a simple and fast method to prepare supported metal catalyst [32]. It was also reported that the surface of the as-prepared catalysts was rich in

low-coordination sites and crystalline defects that may play an important role in catalysis [32].

In this study, combined with these two considerations, titania supported palladium-copper bimetallic catalysts (Pd-Cu/TiO₂) were prepared by the liquid phase chemical reduction method and then applied in the liquid phase catalytic reduction of nitrate ions. The catalytic activity and selectivity influenced by the effect of the support, the total metal content, the molar ratio of palladium to copper, the hydrogen flow rate, the addition of CO₂ and the pH value of solution are also discussed in detail with the surface characterizations by X-ray photoelectron spectrum (XPS), X-ray diffraction (XRD), in situ FT-IR and transmission electron microscopy (TEM).

2. Experimental

2.1. Preparation of catalyst

The Pd-Cu/TiO₂ bimetallic catalyst was prepared by liquid phase chemical reduction method as followings. TiO₂ powder (P25, Degussa, Japan, Anatase 79%, Rutile 21%) was impregnated with dilute PdCl₂ solution and Cu(II) acetate solution. After 20 min ultrasonic vibration and further 1 h stirring in order to get a well-dispersed sample, the obtained suspension was added dropwise by the aqueous solution of KBH₄ (1.0 M) under the nitrogen atmosphere. Excess KBH₄ (molar ratio of KBH₄ to Pd is 5:1) was used in order to ensure the complete reduction. The mixture was kept stirring until no bubbles were observed. The resulting suspension was washed free from Cl⁻ ions with distilled water and subsequently with 99.9% ethanol (EtOH). The as-prepared Pd-Cu/TiO₂ catalyst was stored in a certain amount of distilled water to protect it from oxidation. The different loading amounts of Pd and Cu on TiO₂ were prepared by adjusting the amount of PdCl₂ and Cu(CH₃COO)₂ in the solution. The thermal treated Pd-Cu/TiO₂ catalysts were obtained by heating the fresh Pd-Cu/TiO₂ catalyst at 673 and 873 K for 4 h in hydrogen gas flow. γ -Al₂O₃ was prepared by calcinating Pseudo-boehmite at 773 K; Another type of TiO₂ was prepared by sol-gel method and calcinated at 873 K, the crystalline phase component was identified by XRD analysis (Anatase 81%,

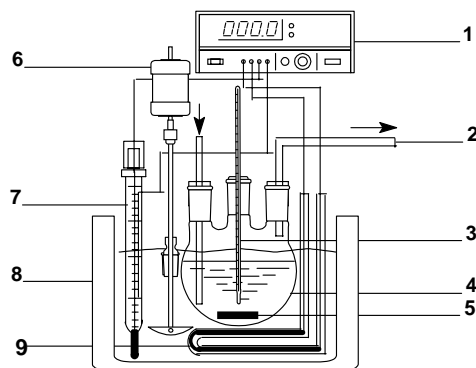


Fig. 2. Schematic diagram of reaction apparatus. (1) Temperature controller; (2) gas outlet; (3) thermometer; (4) reaction vessel; (5) magnetic stirrer; (6) motor stirrer; (7) contact thermometer; (8) bath; (9) heater.

Rutile 19%). The Pd-Cu/ γ -Al₂O₃ and Pd-Cu/TiO₂ (self-prepared TiO₂) catalysts were prepared as described above.

2.2. Catalytic reduction of nitrate

The catalytic reduction of nitrate was performed in a 100 ml all-glass batch reactor equipped with an electromagnetic stirrer and temperature control unit. The simplified schematic diagram of the experimental setting is shown in Fig. 2.

The operation conditions of catalytic nitrate reduction are listed in Table 1. Under the hydrogen flow, the mixture was continuously stirred. After 10 min, or a certain interval that will be particularly pointed out, samples were taken from the reaction system, from

Table 1
The operation conditions of catalytic nitrate reduction

Reaction temperature (K)	298
Operating pressure (bar)	1.0
Catalyst concentration (g/l) ^a	1.0
Initial nitrate concentration (mg/l) ^b	100
Total mixture volume (ml)	100
Hydrogen flow rate (ml/min)	60
Reaction time (min)	10

^a The 0.1 g Pd-Cu/TiO₂ was added by taking a certain volume of the well-dispersed suspension Pd-Cu/TiO₂ that was stored in the distilled water, as ascribed in Section 2.1.

^b Calculated by nitrogen weight (N/L), and the same to NO₂⁻ and NH₄⁺; the same hereinafter.

which, the solid catalyst was immediately separated from the aqueous phase by centrifugation and the remaining top solution was analyzed to determine the residual contents of nitrate, nitrite, and ammonium ions. The concentration of nitrate, nitrite and ammonium ions in the aqueous solution were determined by employing an UV-Vis spectrophotometer (Shimadzu, UV-240), the detailed procedures are described in [34].

2.3. Determination of catalytic activity and selectivity

The catalytic activity for the reduction of nitrate is defined as the reduced amount of nitrate ions per time and active metal weight ($\text{mol NO}_3^-/(\text{min g}_{\text{metal}})$).

The selectivity to nitrogen is defined as the ratio of formed nitrogen amount to the reduced nitrate amount, which is based on the assumption that no other side products are formed other than nitrite and ammonium.

2.4. Characterizations of catalyst

X-ray diffraction patterns were carried out in a D/max-2500 powder diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation from 5 to 90° (in 2θ) with the scanning rate of $2.4^\circ/\text{min}$.

Transmission electron microscopy was carried out in a Philips CM-120 model instrument operating at 100 keV . Before photographing, the samples were dropped onto the surface of carbon membrane and dried at ambient conditions.

X-ray photoelectron spectroscopy was performed using PHI 5300 ESCA commercial instrument (PHI Inc.). The analysis chamber was operated under ultra-high vacuum with a pressure close to 10^{-7} Pa . X-rays were produced by a monochromatized magnesium anode ($\text{Mg K}\alpha$, 1253.6 eV). The C1s photoelectron peak (binding energy of 284.6 eV) was used as the energy reference.

The IR spectra were obtained by using a Bruker VECTOR 22 FT-IR spectrometer equipped with an A-526 diffuse reflectance attachment and a DTCS detector. The in situ infrared cell, equipped with ZnSe windows and capable of operating in high temperature or vacuum, was used for reduction studies.

3. Results and discussion

3.1. Performance of Pd-Cu/TiO₂ catalyst

3.1.1. Effect of support

Pd-Cu bimetallic catalyst loaded on three different supports ($\gamma\text{-Al}_2\text{O}_3$, $S_{\text{BET}} = 218 \text{ m}^2/\text{g}$; TiO_2 , Degussa, P25, $S_{\text{BET}} = 50 \text{ m}^2/\text{g}$; TiO_2 , self-prepared, $S_{\text{BET}} = 30 \text{ m}^2/\text{g}$) were studied with the same total metal content of $3 \text{ wt.}\%$, and the results are displayed in Fig. 3. As can be seen, Pd-Cu/ TiO_2 (P25 type) catalyst showed much higher catalytic activity ($1.29 \times 10^{-2} \text{ mol}/(\text{min g}_{\text{metal}})$) than Pd-Cu/ $\gamma\text{-Al}_2\text{O}_3$ catalyst ($1.62 \times 10^{-4} \text{ mol}/(\text{min g}_{\text{metal}})$). Moreover, Pd-Cu supported over TiO_2 (self-prepared, activity = $5.14 \times 10^{-3} \text{ mol}/(\text{min g}_{\text{metal}})$) exhibited much lower catalytic activity than P25 type. This suggested that the higher specific surface area of P25 might play a very important role in catalytic performance. Therefore, TiO_2 (P25 type) was chosen to support Pd-Cu active components to reduce nitrate ions in this work.

3.1.2. Effect of Pd:Cu molar ratio

In general, the molar ratio of two metals in the bimetallic catalyst is an important factor for its catalytic activity, and many researchers [3,10,14,18,31] have investigated this effect. In this study, the molar

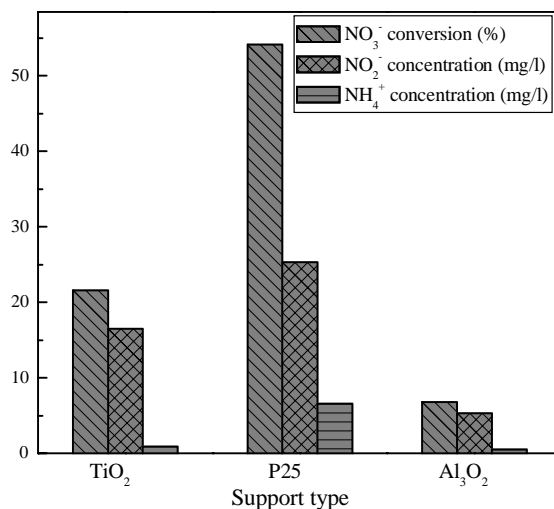


Fig. 3. Effect of support on the NO_3^- conversion, the concentrations of NO_2^- and NH_4^+ over the supported Pd-Cu bimetallic catalysts (Pd:Cu = 2:1 mol/mol, Pd + Cu = 3 wt.%).

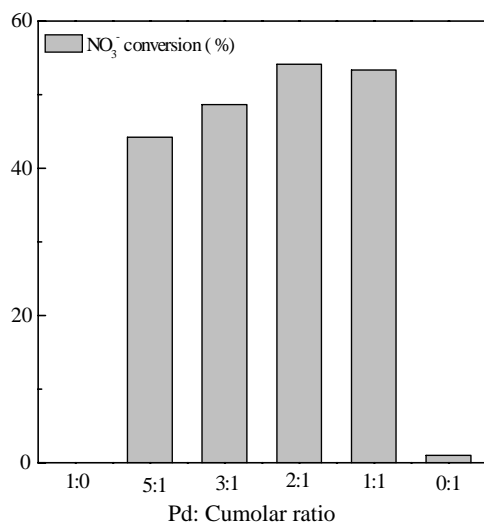


Fig. 4. Effect of Pd:Cu loading ratio on the NO₃⁻ conversion over the Pd-Cu/TiO₂ catalysts (P25, Pd + Cu = 3 wt.%).

ratio of Pd:Cu was varied by fixing the total metal content of 3 wt.% (Fig. 4), and has been found to be the optimum at a definite ratio of 2:1. Furthermore, although Pd-Cu bimetallic catalyst exhibits excellent catalytic activity, the pure Pd or pure Cu monometallic catalysts hardly have any catalytic activity in this work, which are in accordance with the recent results [7,11,17].

3.1.3. Effect of total metal content

By fixing molar ratio Pd:Cu = 2:1, the effect of total metal content has been investigated. As shown in Fig. 5, low metal content (1.5 wt.%) or high metal content (6 and 9 wt.%) is not beneficial to the reduction of nitrate and the optimum content is obtained at metal content 3 wt.%. This suggests that active atomic arrangement and active particles size on the surface of catalyst may have a great influence on the removal of nitrate, rather than the metal loading amount. In order to further observe the morphology of bimetallic Pd-Cu catalyst, TEM of the catalyst (3.0 wt.%) was taken and one representative photograph is shown in Fig. 6. TEM images shows that the supported active metals clusters are clearly visible and are homogeneously dispersed on the TiO₂ particles. The size of most of the metal clusters is below 10 nm.

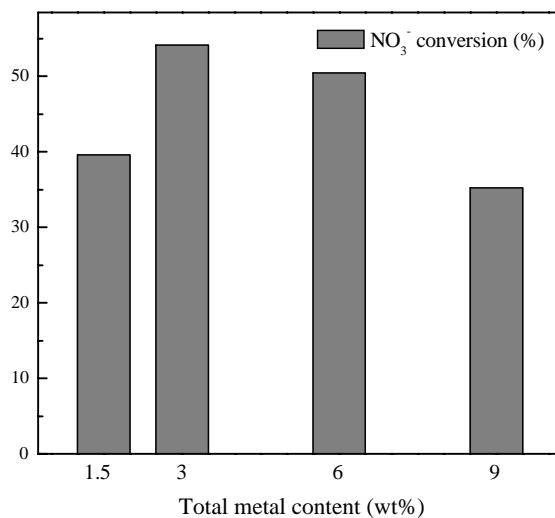


Fig. 5. Effect of Pd+Cu loading content on the NO₃⁻ conversion over the Pd-Cu/TiO₂ catalysts (P25, Pd:Cu = 2:1 mol/mol).

3.1.4. Influence of the thermal treatment

In order to understand the effect of thermal treatment, i.e. the main difference between the liquid phase chemical reduction method and the conventional impregnation method for the preparation of a metal-loaded catalyst, the Pd-Cu/TiO₂ catalysts with different post-treatments were studied, and the summary of results is listed in Table 2. As can be seen, the effect of the thermal treatment is much evident for the nitrate reduction. Under the same given reaction conditions, catalysts 1 and 4, which were not

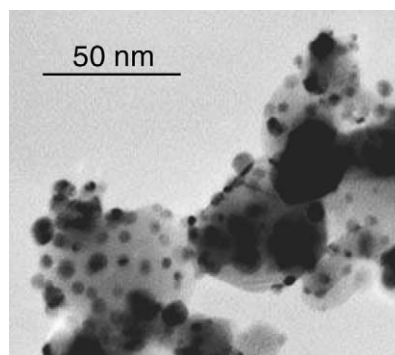


Fig. 6. TEM photograph of Pd-Cu/TiO₂ catalyst (P25, Pd:Cu = 2:1 mol/mol, Pd + Cu = 3 wt.%). Small particles represent clusters of the active metals; large particle represent TiO₂ particle.

Table 2

The catalytic reduction performance of some catalysts after different thermal treatment

Catalyst ^a	Conversion of NO ₃ ⁻ (%)	Concentrations of (mg/l)		Selectivity to N ₂ (%)
		NO ₂ ⁻	NH ₄ ⁺	
1	54.12	25.28	6.58	41.13
2	29.18	27.32	1.87	0
3	46.07	34.77	2.20	19.75
4	55.32	38.26	2.85	25.69
5	35.11	28.41	2.30	12.53

^a Catalyst 1: fresh Pd-Cu/TiO₂; catalyst 2: catalyst 1 reduced in H₂ at 873 K for 4 h; catalyst 3: catalyst 1 reduced in H₂ at 673 K for 4 h; catalyst 4: catalyst 1 dried in air; catalyst 5: catalyst 1 calcined in Ar at 873 K for 4 h.

thermally treated at high temperature, had the highest catalytic activities than the catalysts 2, 3, and 5, which were either reduced (in H₂) or calcined (in Ar) at high temperature. Although the NO₃⁻ conversions on catalysts 1 and 4 are almost equivalent; much higher amounts of intermediate NO₂⁻ were produced on catalyst 4, and the selectivity to N₂ of catalyst 1 is better than catalyst 4. The catalysts treated at high temperature exhibit lower catalytic activity. Moreover, the catalytic nitrate reduction activity largely decreased with the rising of treatment temperature from 673 to 873 K. This decrease of catalytic activity is probably due to the aggregation of active metal caused by the high temperature treatment.

3.2. Effects of the variation of reaction conditions

3.2.1. Hydrogen flow rate

The influence of hydrogen flow rate is depicted in Fig. 7. With the increase of the flow rate, an increase of the nitrate reduction activity is observed. However, the selectivity to nitrogen does not follow this trend simply. The optimum hydrogen flow rate is shown to 60 ml/min; the lower (30 ml/min) or the higher (90 ml/min) had the much lower selectivity to N₂. So, the hydrogen flow rate of 60 ml/min is chosen in this work.

3.2.2. pH value

According to Eq. (1), when nitrate is reduced to nitrogen, hydroxide ions are formed in stoichiometric amounts, so pH value of the reaction solution shall be

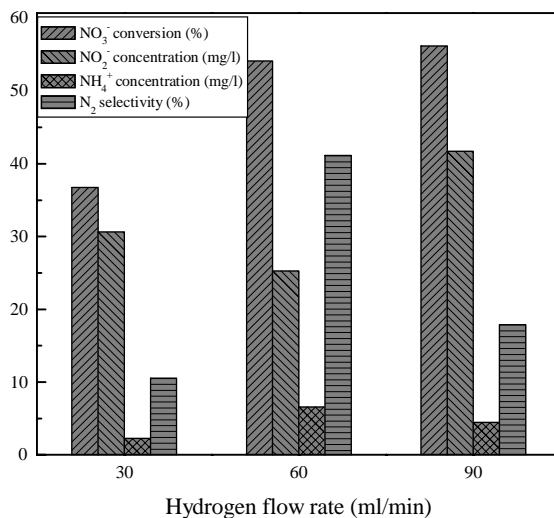


Fig. 7. Effect of H₂ flow rate on the NO₃⁻ conversion, the product selectivity to N₂, the concentrations of NO₂⁻ and NH₄⁺ on Pd-Cu/TiO₂ catalysts (P25, Pd:Cu = 2:1 mol/mol, Pd + Cu = 3 wt.%).

increasing with the proceeding of reaction. Therefore, it was certainly recognized that increasing pH value of the solution was unfavorable to the nitrate removal and nitrogen formation, and this phenomenon have be confirmed by many researchers [7,17,35]. However, it is surprised that an opposite effect has been observed in this study (Fig. 8). In our experiments, the catalytic reduction of nitrate was performed by keeping the pH values at 2, 4, 6, 8, 10, and 12, respectively. As is shown, under strongly acidic condition (pH = 2), no nitrate ions had been reduced. With the increase of pH value of the reaction solution, the catalytic activity increased dramatically and reached the maximum value until pH = 10. After this point, the conversion of nitrate began to decrease. In addition, the amount change of produced nitrite and ammonium also accord with this tendency. This difference in pH dependence was probably ascribed to the different nature of supports. The nature of supports such as surface hydroxyl group, the specific surface area, the hydrophilic or hydrophobic properties and the adsorption capability for reactants can greatly influence the degree and path of reaction. There are reports, in which the optimal pH value was 4 on γ -Al₂O₃ support by Prüsse et al. [10], and 5 on glass fibers by Meytal et al. [25]. Our data show that the mostly suitable pH value was

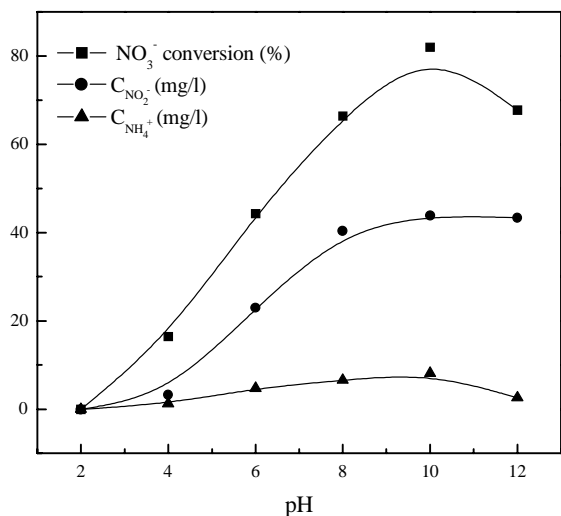
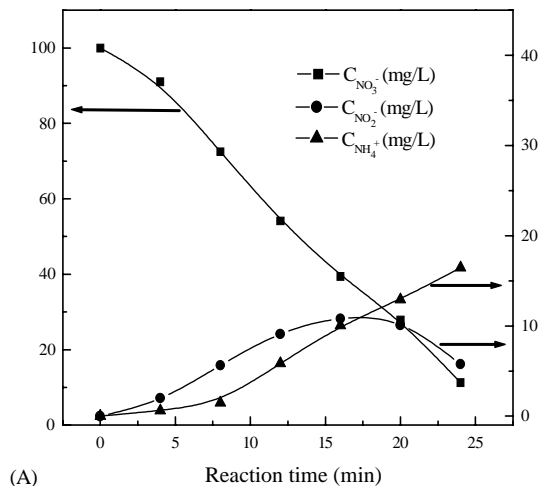


Fig. 8. Effect of solution pH value on the NO_3^- conversion, the concentrations of NO_2^- and NH_4^+ over Pd-Cu/TiO₂ catalysts (P25, Pd:Cu = 2:1 mol/mol, Pd + Cu = 3 wt.%).

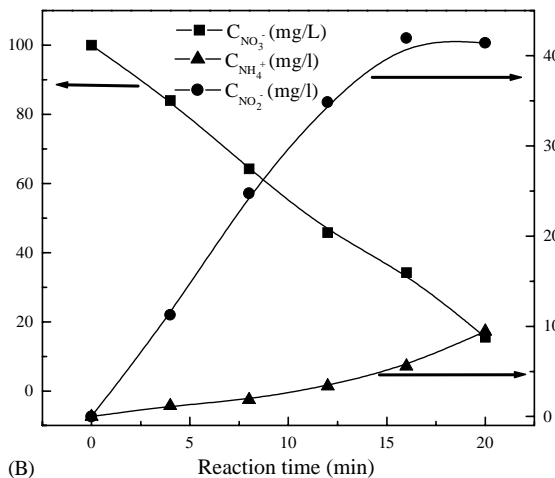
10 by using TiO₂ supports. Since different supports can affect the optimal operating conditions, selecting a suitable support is important to reduce nitrate ions in aqueous solution according to the practical conditions.

3.2.3. CO₂

As stated above, pH value of solution shall be increasing in the course of catalytic nitrate reduction; thereby, catalytic activity and selectivity will be changed correspondingly during the reduction process. In order to minimize the amount of undesired product such as nitrite and ammonium, controlling pH value of solution is essential. Bubbling CO₂ into the reaction solution to buffering produced hydroxyl ions is a simple and feasible approach to keeping the pH value constant. This factor was measured as displayed in Fig. 9. Compared to no CO₂ buffering (Fig. 9B), the application of CO₂ to control the pH of solution (Fig. 9A) appears to be beneficial for the reaction, because the later significantly suppressed the formation of intermediate nitrite and increased the selectivity to nitrogen. This result is probably arising from a more efficient pH buffering effect and had already been reported [9,10]. Although the addition of CO₂ can better the selectivity to nitrogen, the catalytic activity for nitrate has not been improved. So, it may be inferred that the addition of CO₂ is probably change the re-



(A)



(B)

Fig. 9. The concentrations of NO_3^- , NO_2^- and NH_4^+ ions as a function of reaction time during the catalytic reduction of NO_3^- on Pd-Cu/TiO₂ catalyst (P25, Pd:Cu = 2:1 mol/mol, Pd + Cu = 3 wt.%). (A) with CO₂ flow and (B) without CO₂ flow.

duction path of the intermediate nitrite, but no effects take place to the course of nitrate-to-nitrite reduction.

3.3. Mechanism of the reduction of nitrate

As we know, monometallic Pd catalyst is inactive to catalytic reduction of nitrate, but the bimetallic Pd-Cu catalyst can easily reduce nitrate into other nitric compounds. In order to investigate the existing states of the Pd-Cu and the reaction mechanism, many characterizations had been employed [16–19,24,31]. Edelman

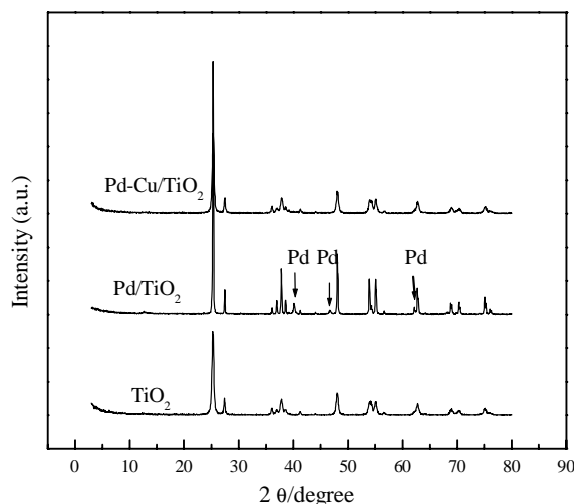


Fig. 10. XRD patterns of TiO₂, Pd/TiO₂ (Pd = 3 wt.%) and Pd-Cu/TiO₂ (Pd:Cu = 2:1 mol/mol, Pd + Cu = 3 wt.%).

et al. [21] applied X-ray absorption spectroscopy to study the oxidation state of Al₂O₃ supported bimetallic Pd-Cu catalysts and concluded that noble metal component (Pd) was in a reduced state, while the less noble metal (Cu) was in a partially oxidized state. Epron et al. [16] found that nitrate ions could be reduced on metal copper surface. Although these characterizations offered some information about the surface state of the catalyst, the detailed mechanism was still vague. In our study, by means of physical characterizations such as XRD, XPS and in situ FT-IR, the reaction mechanism as well as the role of the Pd-Cu bimetallic catalyst has further been investigated. XRD patterns (Fig. 10) showed no distinguished characteristic peaks of palladium, or copper, or their Pd-Cu combination (alloy) on the bimetallic Pd-Cu/TiO₂ catalyst. However, there appears three sharp metal Pd peaks in the XRD spectra of the monometallic Pd/TiO₂ catalyst. This gives a hint that the addition of the second metal copper may improve the dispersion state of metal Pd or change the crystallinity of metal palladium. In order to simulate the actual reaction condition, the Pd-Cu/TiO₂ catalyst was treated in hydrogen at room temperature (298 K) and XPS and in situ FT-IR were used to observe the difference between the treated catalyst and the untreated catalyst. IR spectra (Fig. 11) showed that a tense hydroxyl group peak between 3100 and 3600 cm⁻¹ appeared for the catalyst (curve 2) treated

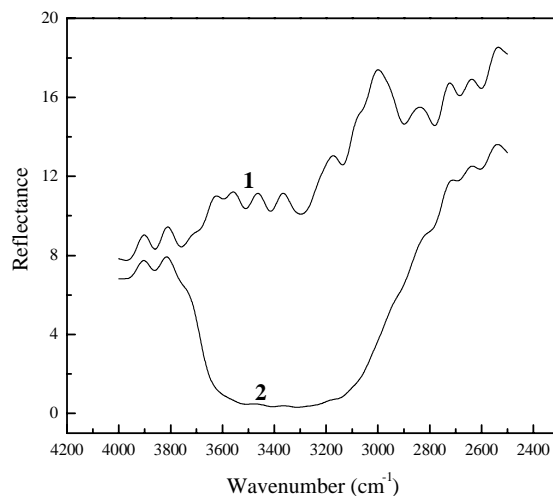


Fig. 11. The in situ FT-IR spectra of Pd-Cu/TiO₂. Operating condition: vacuum and no hydrogen induction at 298 K (curve 1); vacuumized and then induced hydrogen gas at 298 K (curve 2).

with hydrogen. It could be deduced that hydrogen activated on metal palladium and then reduced part of copper oxide to metal Cu, so the water produced. XPS analysis also proved that copper oxides on the surface has been reduced into metal copper in hydrogen at room temperature, and the detailed figures were shown in Fig. 12. As to oxidation state of Pd ((a) and (b)), it showed that Pd existed in form of metal whatever catalysts were treated with hydrogen or not. The peak of 335.7 (335.8) eV is assigned to metal Pd 3d_{5/2} and the peak of 340.9 (341.0) eV is attributed to metal Pd 3d_{3/2}. Meanwhile, copper was found to be in form of Cu⁰ and Cu²⁺ (Cu (a)) for the untreated catalyst in hydrogen at 298 K. The peak located at 932.3 eV is attributed to metallic copper, while the peak of 933.8 eV is assigned to CuO, which is consistent with the reference [21]. But for the treated catalyst in hydrogen at 298 K, the peak for CuO disappeared, which suggested that copper oxides on the catalyst surface have been reduced into metal Cu at room temperature.

Some authors [7,11,17] reported that catalytic nitrate-to-nitrite reduction step underwent a structure-sensitive reaction and was catalyzed only by metal ensembles composed of Pd and Cu atoms. We mixed the Pd/TiO₂ with CuO or Cu₂O powder by grinding them thoroughly, and then put it as a catalyst into use. From Table 3, we can see that the catalytic nitrate reduction proceeded successfully after the addition of Cu₂O

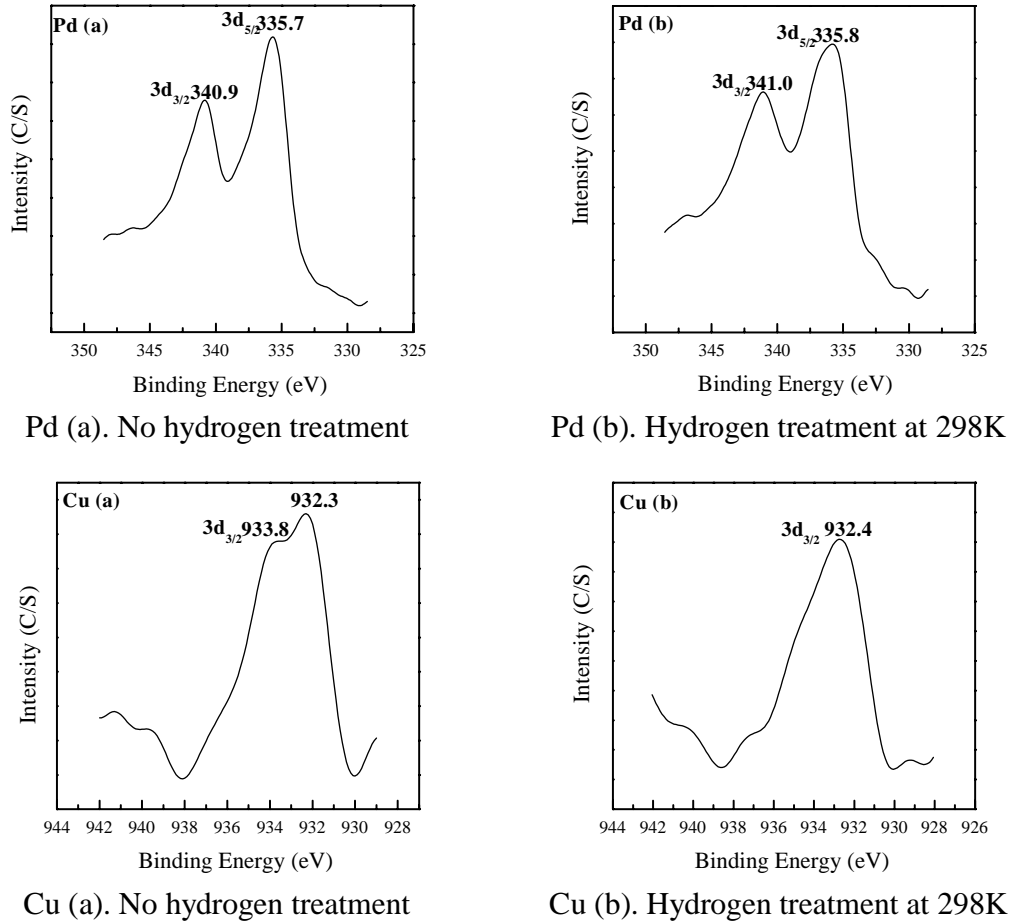


Fig. 12. Under hydrogen treatment or no hydrogen treatment, Pd 3d and Cu 2p XPS spectrum of Pd-Cu/TiO₂ catalyst.

or CuO on Pd/TiO₂. Because the above-mentioned grinding is a simple physical process, there is little interaction between the active components copper and palladium. But, the catalytic reduction of nitrate is still well accomplished. That means the nitrate-to-nitrite conversion is a less structure-sensitive reaction. In this process, the active component palladium or copper

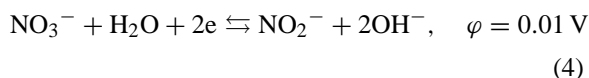
acts as the active centers separately and consecutively to convert nitrate into nitrite, not in a collective manner. Moreover, we found nitrate conversion was largely increased by adding Cu₂O compound. This result could also be illustrated according to the redox potential of Cu/CuO and Cu/Cu₂O [37]. In alkaline solution, such a redox reaction should occur.

Table 3

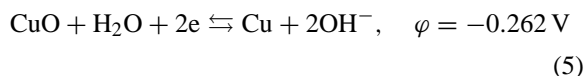
The catalytic performance of Pd/TiO₂ catalyst after the addition of different copper compounds

Compound	pH	NO ₃ ⁻ conversion (%)	Concentrations of product (mg/l)	
			NO ₂ ⁻	NH ₄ ⁺
Cu ₂ O	7.70–10.21	56.04	41.93	2.63
CuO	6.60–9.75	38.50	28.70	0.51

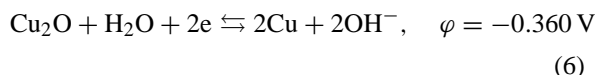
In cathode



In anode



or



From these data, we can estimate when nitrate is reduced into nitrite, metal copper might more easily be oxidized into Cu_2O and such a redox cycle will much likely happen:



That means that Cu_2O is probably to act as the active centers and participate in the catalytic nitrate reduction process, and this conclusion is also consistent with the present results [16]. Epron et al. [16] had found that metallic copper could reduce nitrate and nitrite according to a redox process but deactivate rapidly since copper was passivated to form CuO or Cu_2O in the water. Based on these results, the following mechanism is proposed to this work:

1. $\text{H}_2 + 2\text{Pd}[*] \rightarrow 2\text{Pd}[\text{H}]$
2. $\text{NO}_3^- + 2\text{Pd}[\text{H}] - x \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2\text{Pd}[*]$
3. $\text{NO}_3^- + 2\text{Cu}[*] \rightarrow [\text{Cu}_2\text{O}]_{\text{surf.}} + \text{NO}_2^-$
4. $[\text{Cu}_2\text{O}]_{\text{surf.}} + 2\text{Pd}[\text{H}]_{\text{spill}} \rightarrow 2\text{Pd}[*] + 2\text{Cu}[*] + \text{H}_2\text{O}$
5. $[\text{Cu}_2\text{O}]_{\text{surf.}} + 2\text{Pd}[\text{H}]_{\text{spill}} - x \rightarrow 2\text{Pd}[*] + 2\text{Cu}[*] + \text{H}_2\text{O}$ (in strongly acidic solution)
6. $\text{NO}_2^- + \text{Pd}[\text{H}] \rightarrow \dots \rightarrow \text{Pd}[*] + \text{N}_2$.

According to this mechanism, hydrogen molecules are activated on the $\text{Pd}[*]$ active sites and can further be split into two absorbed hydrogen atoms $\text{Pd}[\text{H}]$. These absorbed hydrogen atoms can cause the hydrogen spill-over and Cu_2O adjacent to these palladium atoms can therefore be reduced into metallic copper species $\text{Cu}[*]$, which are likely to act as active center to reduce nitrate into nitrite, but rapidly deactivate after the formation of Cu_2O . The reduction of nitrite ions may also occur on the surface of metallic copper

species. As is shown in Fig. 1, nitrite can be reduced on monometallic Pd catalyst, whereas nitrate ions cannot. Moreover, as mentioned above, nitrate ions cannot be reduced in strongly acidic solution on Pd-Cu/ TiO_2 bimetallic catalyst. Under strongly acidic solution environment, copper oxides are unstable and can be dissolve into the solution, so Cu_2O cannot be reduced into active metallic state copper, as a result, the active copper centers for nitrate reduction shall not be formed.

4. Conclusion

For the Pd-Cu/ TiO_2 bimetallic catalysts prepared by the liquid phase chemical reduction at normal temperature, it showed much higher NO_3^- reduction activity (54.1%) than the thermal treated one at 873 K (29.2%), since the former preparation method can inhibit the aggregation of metal active components. The optimal conversion of NO_3^- and selectivity to N_2 were obtained over the TiO_2 support (P25 type), with the Pd + Cu loading of 3 wt.%, the atomic ratio of Pd:Cu = 2:1, H_2 = 60 ml/min and pH = 10. Bubbling CO_2 greatly improved the selectivity to N_2 , although the conversion of NO_3^- changed little.

On monometallic Pd catalyst, the role of Pd was reported to split H_2 into absorbed H atoms. Although these dissociated hydrogen atoms can reduce nitrite to other nitric species, but they are inactive to nitrate reduction. Based on our experimental results, we proposed a mechanism that over the bimetallic Pd-Cu catalyst, Cu_2O component involved the reaction course and acted as the active center for nitrate-to-nitrite conversion. The spilt-over hydrogen on Pd was deduced to reduce the adjacent Cu_2O into metal Cu, and on the latter, the conversion of NO_3^- to NO_2^- occurred. However, in strongly acidic solution, the reduction of Cu_2O to Cu was inhibited, and so the nitrate reduction cannot be accomplished.

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