

Catalytic reduction of nitrite ions in drinking water over Pd–Cu/TiO₂ bimetallic catalyst

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Abstract

Titania supported palladium–copper bimetallic catalysts (Pd–Cu/TiO₂) are prepared by liquid-phase chemical reduction method and then applied in the catalytic reduction of nitrite ions in drinking water. The nitrite conversion and selectivity to N₂ influenced by metal molar ratio (Pd:Cu), H₂ flow rate, CO₂ flow rate, pH value of solution and reaction temperature are also discussed in detail with physical characterizations methods such as XPS, XRD, in situ FT-IR. It is discovered that bimetallic Pd–Cu/TiO₂ catalyst has higher activity than monometallic Pd/TiO₂ catalyst in the catalytic reduction of nitrite ions and a mechanism is proposed to explain this promoting effect of bimetallic catalyst in this paper.

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Keywords: Nitrite ions; Catalytic reduction; Pd–Cu/TiO₂ bimetallic catalyst; Characterization; Mechanism

1. Introduction

Nitrite is a common pollutant in urban atmosphere, where it is present at concentration ranging from 1 to 10 ppb [1]. In recent years, with the development of modern industry and agriculture, the concentration of nitrite ions in drinking water is significantly rising due to excessive industrial effluents, overusing nitrogenous fertilizer and incomplete abiotic denitrification process in the soil [2]. Excessive nitrite in the body can form methaemoglobin and as a result lead to “blue baby syndrome”; furthermore, nitrite can be converted into carcinogenic nitrosamine resulting in cancer and hypertension [3]. For these reasons, the European Drinking Water Directive established the maximum permitted level of nitrite to 0.02 mg/l (calculated by nitrogen, N/l) in drinking water to avoid these health risks. Conventional physicochemical methods (such as ion exchange, reverse osmosis, and electro dialysis) and biological denitrification methods are slow, complex and sometimes require a costly post-treatment of effluents. More recently, liquid-phase catalytic reduction by using hydrogen over a solid catalyst has been proved to be

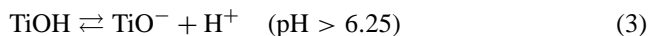
a potential and promising method for the removal of nitrite from drinking water [4,6]. In this process, nitrite is selectively converted into nitrogen in a three-phase reactor system under mild reaction conditions (e.g., $T = 298\text{ K}$, $P = 1\text{ bar}$), which can be represented as below



Relatively few investigations have been published on the reduction of nitrite in aqueous solution. Hörold et al. [7] had reported that among numerous noble metals (such as Pd, Pt, Ru, Ir, Rh) capable of promoting nitrite reduction, only Pd catalyst exhibited satisfactory catalytic performance. Vorlop and Tacke [8] found that the activity of nitrite removal and selectivity to ammonium ions strongly depended on the pH value of aqueous solution, and higher nitrite removal activity was obtained at low pH values. As far as the support for Pd–Cu bimetallic catalyst is concerned, $\gamma\text{-Al}_2\text{O}_3$ [5,6], glass fiber [4], pumice [9] had been commonly used. These results showed that different supports could greatly influence catalytic activity and selectivity, and this difference was partially ascribed to the different surface state of the supports. Therefore, selecting a suitable catalyst support is much essential for catalytic reduction of nitrite ions.

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Many excellent properties of TiO₂ (P25 type) have been found and it is widely used in industrial fields. Major uses are as photocatalyst or catalyst support. Surface of TiO₂ exists an amphoteric group named “titanol” (Ti–OH), so there can occur such an acid–base equilibrium [10] and change absorption properties in the catalyst surface under different pH values:



Upon the basis of these considerations, it is an interesting idea to load Pd–Cu bimetallic catalyst on the TiO₂ support for nitrite reduction in aqueous solution.

In this study, titania supported Pd–Cu bimetallic catalyst (described as Pd–Cu/TiO₂) was prepared by liquid-phase chemical reduction method and then applied in catalytic reduction of nitrite ions. The properties of used catalysts are also discussed by means of characterizations with XRD, in situ FT-IR and XPS, and catalytic nitrite mechanism was proposed according to these characteristic results.

2. Experimental

2.1. Preparation of catalysts

Pd–Cu/TiO₂ bimetallic catalyst was prepared by liquid-phase chemical reduction method as follows. First, TiO₂ powder (P25, Degussa, Japan; anatase 79%, rutile 21%) was impregnated with dilute PdCl₂ solution and Cu(II) acetate solution. After well dispersed by 20 min ultrasonic dispersion and further 1 h stirring, 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 99.9% ethanol (EtOH) and subsequently with distilled water, then the obtained black solid was dried in nitrogen atmosphere at 298 K. 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. In the end, these as-prepared Pd–Cu/TiO₂ catalysts were crushed in agate mortar for use.

2.2. Catalytic reduction of nitrite ions

The initial concentration of nitrite solution is 50 mg/l (calculated by nitrogen weight (N/l), the same to NH₄⁺ and hereinafter). The catalytic reduction of nitrite was performed in a 100 ml all-glass batch reactor equipped with an electromagnetic stirrer and temperature control unit. The operation conditions of catalytic nitrite reduction were listed in Table 1. Under the hydrogen flow, the mixture was continuously stirred. After 10 min, samples were taken from the

Table 1

The operation conditions of catalytic nitrite reduction

Reaction temperature (K)	298
Operating pressure (bar)	1.0
Catalyst weight (g)	0.1
Initial nitrite concentration (mg/l)	50
Reaction volume (ml)	100
Hydrogen flow rate (ml/min)	90
Reaction time (min)	10

reaction system, from which, the solid catalyst was immediately separated from the aqueous phase by centrifugation and the upper solution was analyzed to determine the residual contents of nitrite and ammonium ions by employing an UV-VIS Spectrophotometer (Shimadzu, UV-240). The detailed procedures are referred to [11].

2.3. Characterizations of catalyst

X-ray diffraction (XRD) patterns were measured in a D/max-2500 powder diffractometer using Cu Kα (λ = 1.54178 Å) radiation from 5 to 90° (in 2θ) with the scanning rate of 2.4° min^{−1}.

X-ray photoelectron spectroscopy (XPS) measurements were performed using PHI 5300 ESCA commercial instrument (PHI Inc.). The analysis chamber was operated under ultrahigh vacuum with a pressure close to 10^{−7} Pa. X-rays were produced by a monochromatized magnesium anode (Mg Kα, 1253.6 eV). The C 1s photoelectron peak (binding energy of 284.6 eV) was used as the binding energy reference.

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

3. Results and discussion

3.1. Effect of Pd:Cu molar ratio

In general, molar ratio of two metals in the bimetallic catalyst is an important factor for its catalytic performance. In this study, Pd:Cu molar ratio was varied from 1:0, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3 to 1:5 with constant total metal content (3 wt.%) and nitrite conversion was shown in Fig. 1. It has been found that the optimum Pd:Cu molar ratio for the optimal catalytic activity is reached about at the metal ratio of 2:1 (nitrite conversion: 27.83%) and 1:1 (nitrite conversion: 27.39%). In the present study, the metal ratio (Pd:Cu = 2:1) has been chosen for further investigation. It has been well recognized that catalytic nitrate reduction is only performed over the bimetallic catalysts system, preferably over palladium–copper catalysts, whereas nitrite and other fol-

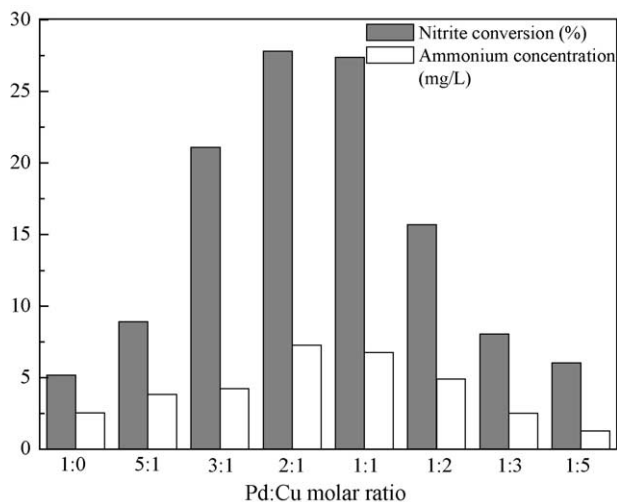


Fig. 1. Nitrite conversion as a function of the Pd:Cu molar ratio over Pd-Cu/TiO₂ (3 wt.%) catalyst.

lowing intermediates can be reduced over monometallic palladium catalyst [12,13]. Our present results were well consistent with this conclusion. However, we also found that although monometallic Pd catalyst could reduce nitrite ions into other low oxidation nitric compounds, its catalytic activity was much lower than bimetallic Pd-Cu catalyst. This promoting effect of bimetal catalyst will be discussed in detail in Section 3.6.

3.2. Effect of catalyst amount

In three-phase reactor system, catalyst amount is an important experimental parameter to influence the catalyst activity because of the reactant diffusion limitation. By varying the catalyst amount, it was demonstrated that the kinetics of the overall process is not influenced by diffusion limitation in this study. Fig. 2 exhibited the relationship between

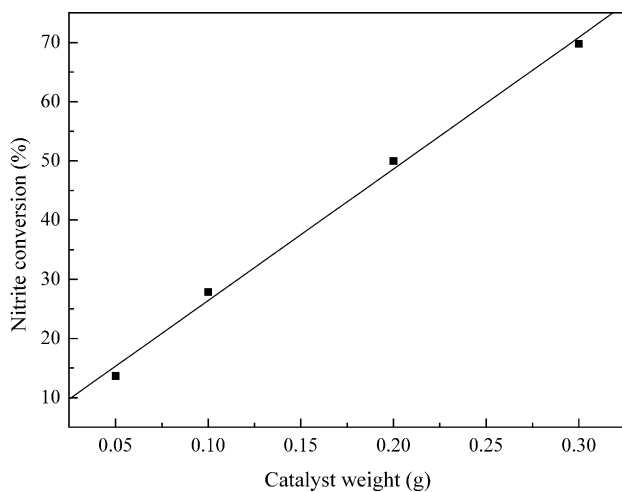


Fig. 2. Nitrite conversion as a function of the catalyst weight over Pd-Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst.

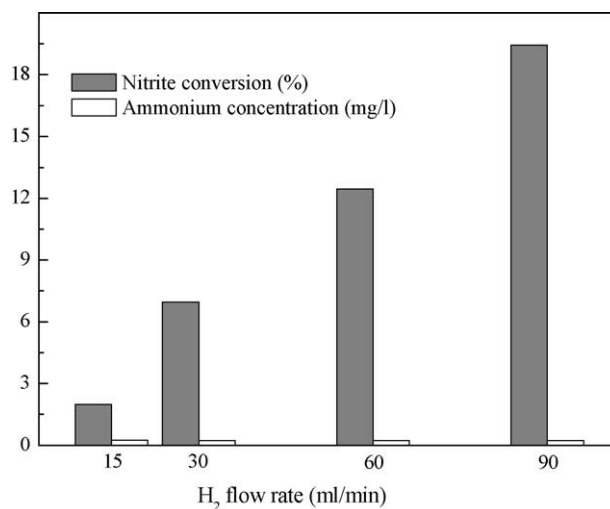


Fig. 3. Nitrite conversion and the final concentration of ammonium ions as a function of hydrogen flow rate over Pd-Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst (CO₂ flow rate: 60 ml/min).

nitrite conversion and catalyst amount. It is shown that nitrite conversion is proportional to the catalyst amount up to 0.3 g/100 ml catalyst. This confirms that nitrite disappearance rate was not influenced by diffusion limitation with the catalyst amount of 0.1 g/100 ml applied in the present study.

3.3. Effect of H₂ flow rate and CO₂ flow rate

The influence of hydrogen flow rate on nitrite conversion is depicted in Fig. 3. By varying the hydrogen flow rate from 15 to 90 ml/min and fixing the flow rate of CO₂ at 60 ml/min, it is observed that nitrite conversion is proportional to hydrogen flow rate. Furthermore, it can be seen that the amount of produced ammonium ions is very low, which suggested that the selectivity to nitrogen is much higher. However, our further study indicates the influence of CO₂ flow rate on nitrite conversion does not follow this trend (Fig. 4). By varying the CO₂ flow rate from 15 to 90 ml/min and fixing the hydrogen flow rate at 90 ml/min, it shows that the optimum CO₂ flow rate is 30 ml/min, the lower (15 ml/min) or the higher (60 or 90 ml/min) had a lower nitrite conversion. So the hydrogen flow rate of 90 ml/min and CO₂ flow rate of 30 ml/min are chosen in this paper.

3.4. Effect of pH value

In the previous studies [4,5], it has been proved that pH value of reaction solution played an important role in the catalytic nitrite reduction. According to Eq. (1), when nitrite is reduced to nitrogen, hydroxide ions in stoichiometric amounts are formed; therefore, pH value of reaction solution should be increasing with the proceeding of reaction. In this experiment, nitrite ions were reduced with hydrogen by keeping pH value of the solution at 3, 4, 5, 6, 8, 10 and 12, respectively, and experimental results are shown in

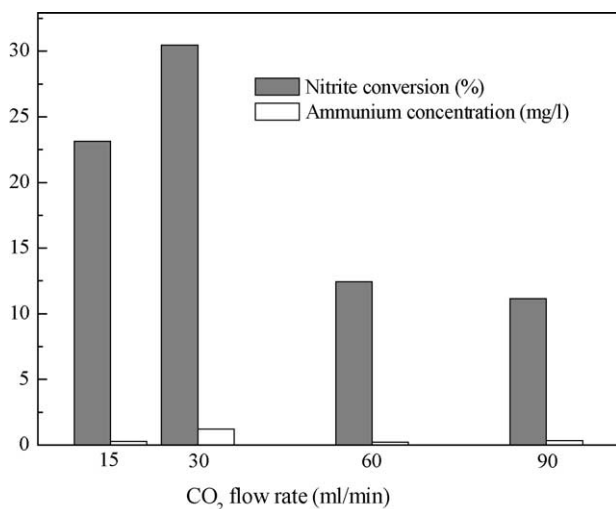


Fig. 4. Nitrite conversion and the final concentration of ammonium ions as a function of CO₂ flow rate over Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst (hydrogen flow: 90 ml/min).

Fig. 5. As is shown, catalytic nitrite activity and selectivity are strongly dependent on the pH value of the reaction solution. Under strongly acidic condition (pH = 3, 4), low nitrite conversion is obtained and no ammonium ions are produced. With the increase of pH value, catalytic nitrite activity increased dramatically and reached the maximum value until pH = 8. Then, nitrite conversion began to decrease by further increasing pH value. In addition, the amount of produced ammonium ions also accord with this tendency. This pH dependence was more likely to arise from amphoteric property of TiO₂ support. In the surface of TiO₂ [12], there can occur such an acid–base equilibrium ($\text{Ti-OH} + \text{H}^+ \rightleftharpoons \text{Ti-OH}_2^+$, $\text{Ti-OH} \rightleftharpoons \text{Ti-O}^- + \text{H}^+$). In acidic solution, TiO₂ surface accumulates a net positive charge due to the increasing fraction of total surface sites present as TiOH_2^+ , anion nitrite can be absorbed sufficiently in the surface of catalyst

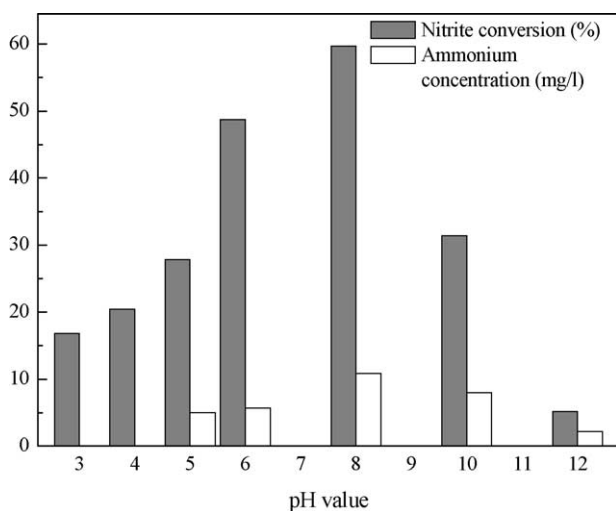


Fig. 5. Nitrite conversion and the final concentration of ammonium ions as a function of pH value over Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst.

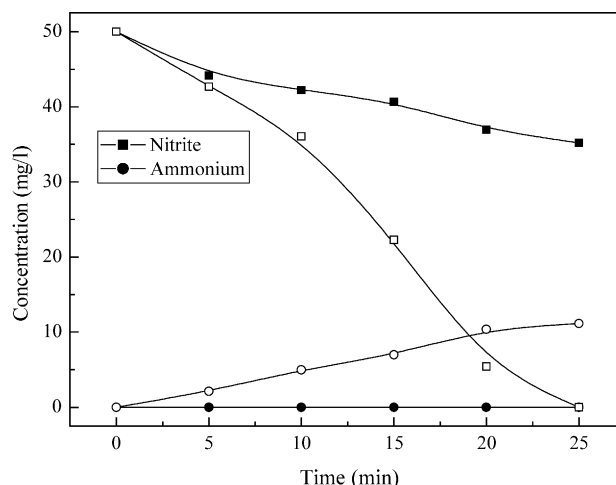


Fig. 6. The concentration of nitrite and ammonium as a function of reaction time over Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst at different pH values: pH = 4 (filled symbols) and pH = 5 (open symbols).

because of attraction between positive charge and negative charge. It is well recognized that pre-adsorption of reactants in catalyst surface is an essential step for a catalytic reaction, so we can certainly believe that acidic solution is favorable for nitrite reduction. However, because tiny metal Cu particles can be dissolved from surface of catalyst in strong acidic solution and result into the loss of active component, pH value of reaction solution must be control within a suitable range in order to get the highest catalytic activity.

As indicated in Fig. 5, we can observe that no ammonium are produced when pH value of reaction solution is controlled below 4, which suggests that pH value can well control the reaction direction and improve the reaction selectivity. So if we can control pH value below 4, the selectivity to desired product (N₂) will be 100%. This result is more advantageous for water cleaning in industrial application and provides a convenient and feasible method to avoid producing undesired by-products, and the influence curve of pH value on nitrite removal activity and selectivity was shown in Fig. 6. From this time dependence curve, we can obviously discover although lower pH value (●4) is unbeneficial to reaction activity, it can highly improve the selectivity to N₂; pH value at 4 is a turning point for reaction selectivity, beyond which by-product ammonium ions can be produced in this reduction reaction.

3.5. Effect of reaction temperature

The influence of reaction temperature on nitrite reduction over Pd–Cu/TiO₂ catalyst was investigated from 298 to 338 K (Fig. 7). Under the given reaction conditions, it was shown that nitrite conversion was basically proportional to reaction temperature, higher nitrite conversion was achieved at high reaction temperature, and this conclusion was also accordant with other researchers' results [5].

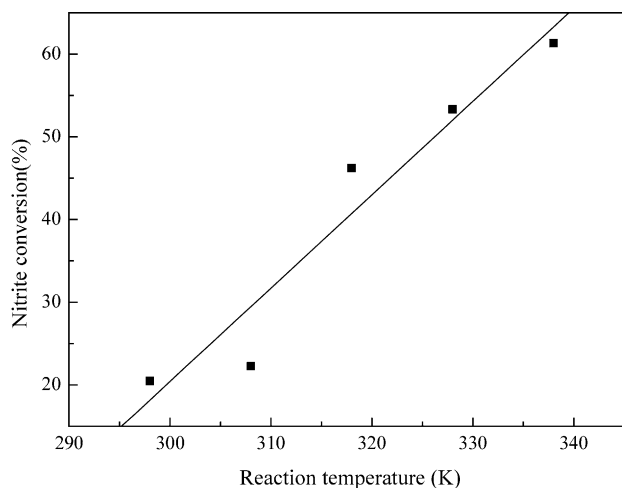


Fig. 7. Nitrite conversion as a function of reaction temperature over Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst.

3.6. Reaction mechanism investigation

As discussed above, bimetallic Pd–Cu/TiO₂ catalyst has higher activity than monometallic Pd/TiO₂ catalyst in the catalytic reduction of nitrite ions and the time reaction curve of these two catalysts is shown in Fig. 8. It clearly exhibits that nitrite conversion over Pd–Cu/TiO₂ catalyst is two times of that of Pd/TiO₂ catalyst. 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 been investigated. XRD patterns (Fig. 9) showed no distinguished characteristic peaks of palladium, or copper, or their Pd–Cu combination (alloy) for the bimetallic Pd–Cu/TiO₂ catalyst. However, there appeared three sharp metal Pd peaks in the XRD spectra of the monometallic Pd/TiO₂ catalyst. This gives a hint

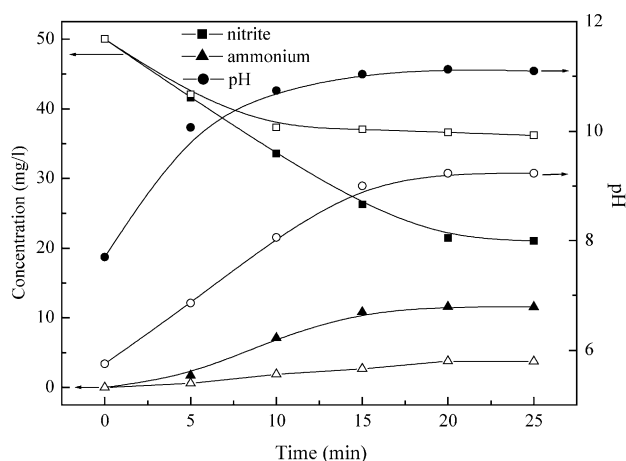


Fig. 8. The concentration of nitrite, ammonium and pH value as a function of reaction time over different catalysts without pH control: Pd/TiO₂ (3 wt.%) (open symbols) and Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) (filled symbols).

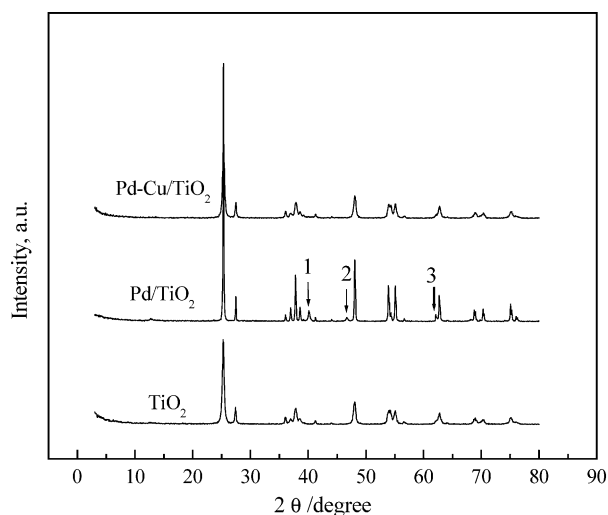


Fig. 9. X-ray diffraction patterns of TiO₂, Pd/TiO₂ (3 wt.%) and Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalysts. Numbers 1–3 denote the peak position of the metal Pd.

that the addition of the second metal copper may improve the dispersion state of metal Pd or an interaction exists between active metal and support. XPS analysis (Fig. 10) was applied to confirm the oxidation state of Pd and Cu species. In Fig. 10a, the peak of 335.1 eV is assigned to Pd 3d_{5/2}, showed palladium was present on the catalyst surface in metallic form. Meanwhile, Copper was found to be in the form of Cu⁰ and Cu²⁺ (Fig. 10b). The peak located at 932.4 eV is attributed to metallic copper, while the peak of 933.8 eV is assigned to CuO, which is consistent with the reference [14]. Furthermore, in situ FT-IR spectrum (Fig. 11) was used to study the catalytic mechanism of nitrite reduction. At room temperature (298 K), sample cell was vacuumized and hydrogen was introduced to simulate the reaction course. Compared to the process without hydrogen introduction (curve 1), a tense hydroxyl group peak between 3100 and 3600 cm⁻¹ appeared for the catalyst (curve 2) treated with hydrogen. It could be deduced that hydrogen was activated on metal palladium and then reduced part of CuO to Cu, so that water produced. This phenomenon provides an evident that active atomic hydrogen can be produced in the surface of catalyst and then can reduce higher reduction potential compounds. Epron et al. [6] found that metallic copper could reduce the nitrate according to a redox process but deactivate rapidly since copper was passivated to form CuO or Cu₂O in the water. From these results, we can suppose that this enhancement effect of activity over Pd–Cu/TiO₂ bimetallic catalyst is due to the formation of copper active centers besides Pd. The simplified reaction mechanism scheme is presented in Fig. 12. On monometallic and bimetallic Pd-based catalyst, the role of Pd was to split H₂ into absorbed Pd–H atoms. These dissociated hydrogen atoms not only can reduce nitrite to other nitric species, but also reduce the adjacent copper oxides into metal copper. It is important that these

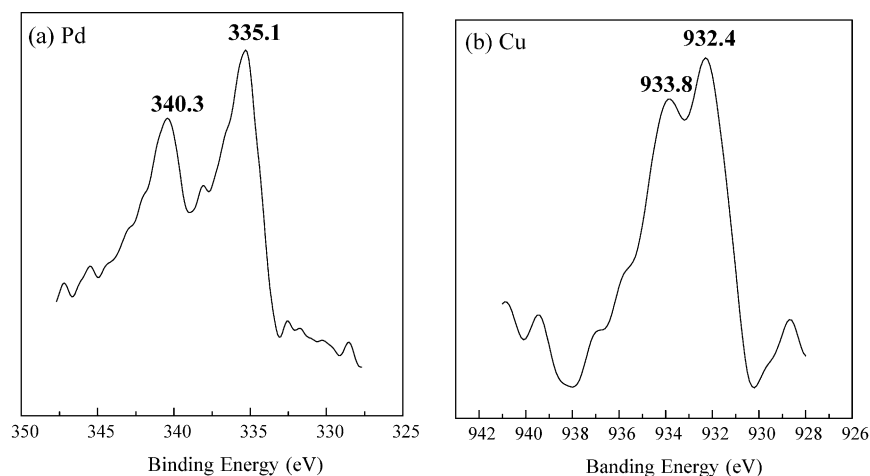


Fig. 10. Pd 3d and Cu 2p XPS spectrum of Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst.

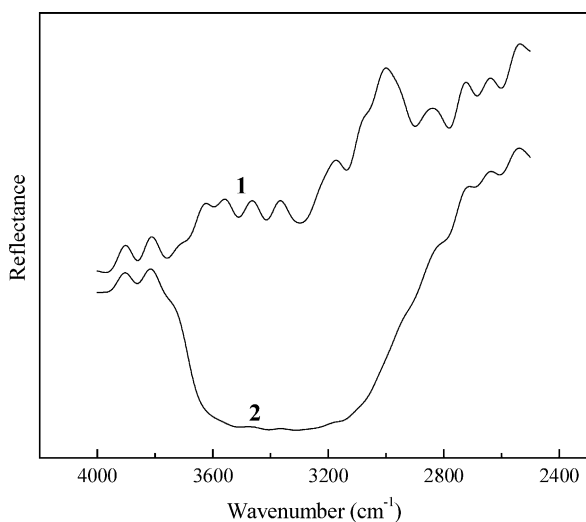


Fig. 11. The in situ FT-IR spectra of Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%); operating conditions: vacuum and no hydrogen introduction at 298 K (curve 1); vacuumized and then induced hydrogen gas at 298 K (curve 2).

active metal copper atoms are also likely to act as the active center to reduce nitrite ions. Compared to the monometallic catalyst, Pd–Cu bimetallic catalyst can provide more active centers for nitrite reduction. The coexistence of two activity centers promoted the conversion of nitrite.

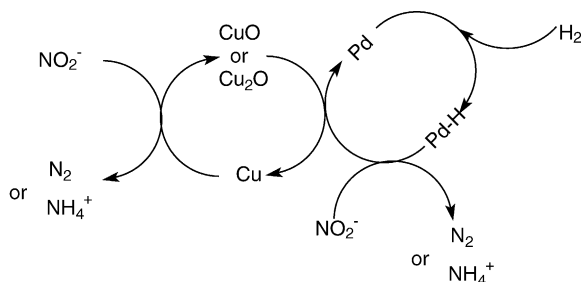


Fig. 12. The hypothetical reaction mechanism of catalytic reduction of nitrite ions.

4. Conclusions

Studies on the catalytic reduction of nitrite over Pd–Cu/TiO₂ bimetallic catalyst have led to the following conclusions:

1. Compared with monometallic catalyst Pd/TiO₂, bimetallic catalyst Pd–Cu/TiO₂ has shown more excellent activity in the catalytic reduction of nitrite under the given conditions. The highest activity is achieved by using Pd–Cu/TiO₂ (Pd:Cu = 2:1, 3 wt.%) catalyst.
2. pH value of the reaction medium plays an important role in the catalytic reduction of nitrite ions, and the selectivity to N₂ can be improved to 100% when pH value was controlled below 4.
3. XPS spectrum indicates that noble metal component (Pd) is in a reduced state, while the metal (Cu) is in a partially oxidized state. Derived from these characterization results, a mechanism has been proposed that the promoting effect of activity over Pd–Cu/TiO₂ bimetallic catalyst is due to the extra formation of copper active centers besides the Pd–H active centers.

Acknowledgements

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