

Titania-supported Pd–Cu bimetallic catalyst for the reduction of nitrite ions in drinking water

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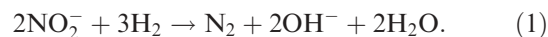
Titania-supported palladium–copper bimetallic catalysts (Pd–Cu/P25) are prepared by liquid-phase chemical reduction method and then applied in liquid-phase catalytic reduction of nitrite ions (NO_2^-). Compared with the conventional impregnation method, which usually needs a post-thermal reduction procedure to eliminate the introduced anions, liquid-phase chemical reduction at ambient temperature was proved to inhibit the aggregation of metal active components by means of TEM and DSC analysis in this work, and the catalyst exhibited superior catalytic activity. The conversion of nitrite reached a high level ($1 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{cat}}^{-1}$) and is about 14 times than that reported recently. The influences on the conversion of NO_2^- by support materials and the molar ratio of palladium to copper are also investigated, and further, the reaction mechanisms are discussed according to the characterization results of XPS and *in situ* FT-IR.

KEY WORDS: nitrite reduction; Pd–Cu/P25 bimetallic catalyst; liquid-phase chemical reduction; characterization.

1. Introduction

Nitrite is a common pollutant in urban atmosphere, where it is present at a concentration ranging from 1 to 10 ppb [1]. In recent years, the concentration of nitrite in drinking water is significantly being increased because of industrial effluents and incomplete abiotic and nitrification/denitrification process in the soil [2]. The role of nitrite on human body is to combine with hemoglobin in the blood to form methaemoglobin, and, as a result, this leads to the so-called “blue baby syndrome”. Furthermore, nitrite can be converted into carcinogenic nitrosamine, which can cause cancer and hypertension [3]. For these reasons, the European Drinking Water Directive established the maximum permitted level of nitrite to 0.02-mg NO_2^- (calculated by nitrogen, N/L) in drinking water to avoid these health risks. Conventional physicochemical methods (such as ion exchange, reverse osmosis, and electrodialysis) and biological denitrification methods are time consuming, complex, and sometimes require a costly posttreatment of effluents. More recently, liquid-phase catalytic reduction by using hydrogen as reductant over a solid catalyst has been proved to be a potential and promising method for the removal of nitrite ions 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:



Although relatively few results have been published on the reduction of nitrite ions in aqueous solution, it is well recognized that the Pd-based bimetallic catalyst is known as the potential catalyst for liquid-phase nitrite reduction till now [4,7,8]. As for the support for the Pd–Cu bimetallic catalyst, $\gamma\text{-Al}_2\text{O}_3$ [5,6], glass fiber [4], and pumice [9] had been commonly used. Results showed that different supports have great effects on the catalytic activity and selectivity to products, which was partially ascribed to the different surface state of the supports. Therefore, selecting a suitable catalyst support is necessary for the catalytic reduction of nitrite ions.

The conventional preparation procedures include the steps of impregnation, calcination, and final reduction of metal oxides by hydrogen at high temperature. These as-prepared catalysts have to suffer the high-temperature pretreatment; 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 by adding a reductant, e.g., potassium borohydride (KBH_4), which is recognized as a simple and fast method to prepare the supported metal catalyst [10]. 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 [10].

In this study, titania-supported palladium–copper bimetallic catalyst (described as Pd–Cu/P25) was prepared

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by liquid-phase chemical reduction method and then applied in liquid-phase catalytic reduction of nitrite ions. The properties of used catalysts are also discussed by means of characterizations with *in situ* FT-IR, DSC, XRD, TEM, and XPS.

2. Experimental

2.1. Catalyst preparation

The Pd–Cu/P25 bimetallic catalyst was prepared by liquid-phase chemical reduction method as following. First, P25 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 potassium borohydride (KBH₄, 1.0 M) under the nitrogen atmosphere. Excess KBH₄ was used to ensure complete reduction. The mixture was stirred 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 different loading amounts of palladium and copper on P25 were prepared by adjusting the amount of PdCl₂ and Cu(CH₃COO)₂ in the solution. The suspension was filtered and the obtained black solid was dried in nitrogen at 298 K. Then, the as-prepared Pd–Cu/P25 catalyst was crushed in agate mortar for further use. γ -Al₂O₃ was prepared by calcinating pseudoboehmite at 773 K; TiO₂ was prepared by sol–gel method and calcinated at 873 K; and the crystalline-phase component was identified by XRD analysis (Anatase 81%, Rutile 19%). The Pd–Cu/ γ -Al₂O₃ and Pd–Cu/TiO₂ catalysts were prepared as described above.

2.2. Catalytic reduction of nitrite ions

The initial concentration of nitrite solution is 50 mg L^{−1} (calculated by nitrogen weight, (N/L), and 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. Under the hydrogen flow, the mixture was continuously stirred. After 10 min, samples were taken from the 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). For detailed procedures, see reference [15].

2.3. Catalysts characterization

XRD analysis were carried out in a D/max-2500 powder diffractometer using Cu K α ($\lambda = 1.54178 \text{ \AA}$)

radiation from 5 to 90° (in 2θ) with the scanning rate of 2.4°/min^{−1}.

X-ray Photoelectron Spectroscopy (XPS) was 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 K α , 1253.6 eV). The C1s 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 a high-temperature and vacuum environment, was used for reduction studies.

Transmission electron microscopy (TEM) 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.

Differential scanning calorimeter (DSC, NETZSCH DSC 204) was performed to character the thermal properties of the used catalysts. Nitrogen was used as the protective gas and the heating-up rate was 10 K min^{−1}.

3. Results and discussion

3.1. Effect of support

Catalysts prepared from three different supports (γ -Al₂O₃, S_{BET} = 218 m² g^{−1}; P25, Degussa, S_{BET} = 50 m² g^{−1}; TiO₂, self-prepared, S_{BET} = 30 m² g^{−1}) were studied with the same total metal content (3 wt%). The results of catalytic nitrite reduction are displayed in figure 1. As we see, catalytic reduction activity was strongly influenced by the supports. The Pd–Cu/P25 catalyst showed much higher catalytic activity (1 × 10^{−4} mol min^{−1} g_{cat}^{−1}) than the Pd–Cu/ γ -Al₂O₃ catalyst (5 × 10^{−5} mol min^{−1} g_{cat}^{−1}). The catalytic activity of Pd–Cu/P25 elevated by approximately 14 times, compared to the recent report (Activity = 7 × 10^{−6} mol min^{−1} g_{cat}^{−1}) [6]. Furthermore, support of self-prepared TiO₂ (Activity = 5.2 × 10^{−5} mol min^{−1} g_{cat}^{−1}) exhibited much lower catalytic activity. This suggested that higher specific surface area of P25 might play a very important role in catalytic performance. Therefore, P25 was chosen to support Pd–Cu active components to reduce nitrite ions in this work.

3.2. Effect of Pd:Cu molar ratio

In general, the molar ratio of two metals in bimetallic catalyst is an important factor in catalytic activity. In this work, by fixing the total metal content (3 wt%), the molar ratios of palladium to copper varied from 1:0, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3 to 1:5, and the results are

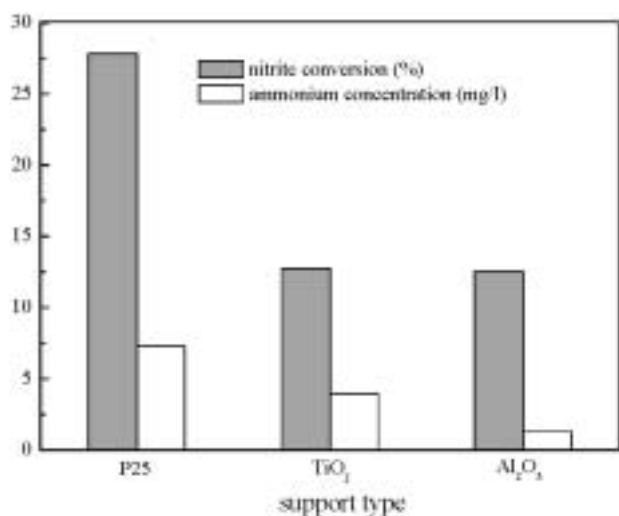


Figure 1. Nitrite conversion and the final concentration of ammonium ions on the Pd–Cu bimetallic catalyst loaded on different supports. (Pd:Cu molar ratio: 2:1, total metal content: 3 (wt%), nitrite initial concentration: 50 mg L⁻¹ (N/L), reaction volume: 100 mL, reaction temperature: 298 K, hydrogen flow rate: 60 mL min⁻¹, operating pressure: 1 bar, reaction time: 10 min).

listed in figure 2. The optimum Pd:Cu molar ratio with the highest catalytic activity was found to be 2:1. It was well recognized that catalytic nitrate reduction is only performed over bimetallic catalyst system, preferably over palladium–copper catalysts, whereas nitrite and other following intermediates can be reduced with monometallic palladium catalyst system [11,12]. As indicated in figure 2, although the monometallic palladium catalyst can reduce nitrite ions into other low-oxidation nitric compounds, its catalytic activity is much lower than the bimetallic Pd–Cu catalyst (especially because Pd:Cu = 2:1). By means of physical

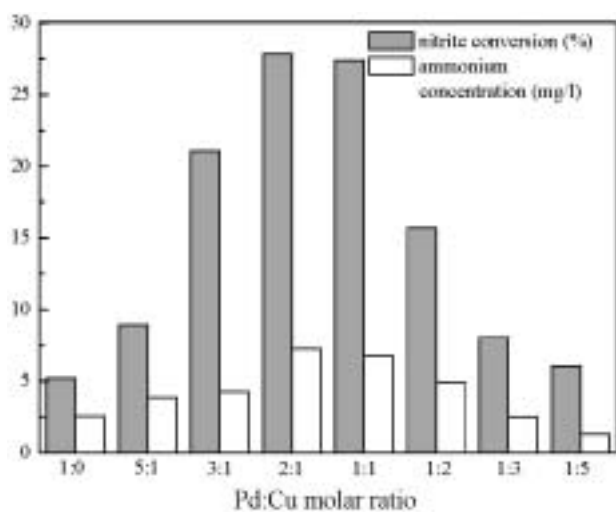


Figure 2. Nitrite conversion as a function of the Pd:Cu molar ratio (total metal content: 3 (wt%), nitrite initial concentration: 50 mg L⁻¹ (N/L), reaction volume: 100 mL, reaction temperature: 298 K, hydrogen flow rate: 60 mL min⁻¹, operating pressure: 1 bar, reaction time: 10 min).

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 lately investigated [6,13,14]. A. Edelmann *et al.* [13] applied X-ray absorption spectroscopy to study the oxidation state of Al₂O₃-supported bimetallic Pd–Cu catalysts and concluded that the noble metal component (palladium) was in a reduced state, while the less noble metal (copper) was in a partially oxidized state. F. Epron *et al.* [6] found that nitrite ions could be reduced either on metal copper or on the precious metal platinum's surface. In our study, XRD patterns (figure 3) of the Pd–Cu/P25 catalyst showed all the main characteristic peaks of TiO₂ support; however, no characteristic reflections for Pd- or Cu-containing phases are recorded, which indicates that metal particles are well dispersed and their size may be too small to be detected. XPS analysis (figure 4) was applied to confirm the oxidation state of palladium (a) and copper (b) species. In figure 4(a), the peak of 335.1 eV is assigned to Pd3d_{5/2} and shows that palladium was present on the catalyst surface in metallic form. Meanwhile, copper was found to be in the forms Cu⁰ and Cu²⁺ (figure 4(b)). 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 [13]. Furthermore, *in situ* FT-IR spectrum (figure 5) was used to study the catalytic mechanism of nitrite reduction. At room temperature (298 K), the sample cell was vacuumized and hydrogen was introduced to reduce the Pd–Cu/P25 catalyst to simulate the reaction course. Compared to the process without hydrogen treatment (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 activated on metal palladium

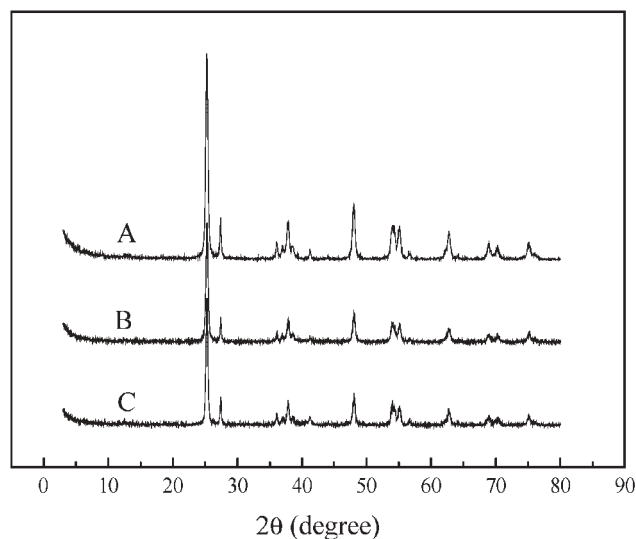


Figure 3. XRD patterns of P25 (A), Pd–Cu/P25 (B, NaBH₄ reduced sample) and Pd–Cu/P25 (C, thermally reduced sample at 673 K).

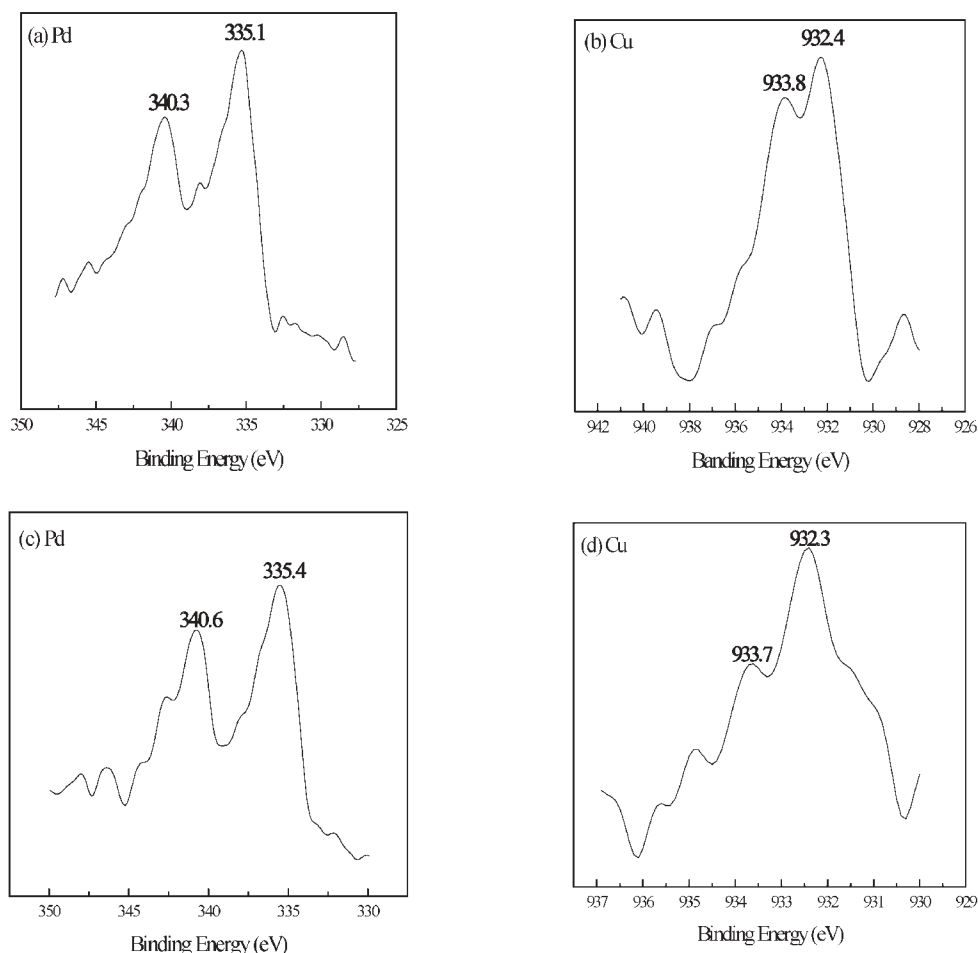


Figure 4. XPS spectra of NaBH_4 reduced sample ((a), (b)) and thermally reduced sample ((c), (d)) for Pd-Cu/P25 catalysts.

and then reduced part of CuO to copper, so that water was produced. Epron *et al.* [6] reported that metal copper could easily reduce nitrite ion to other low nitric compounds according to their redox potential. Derived

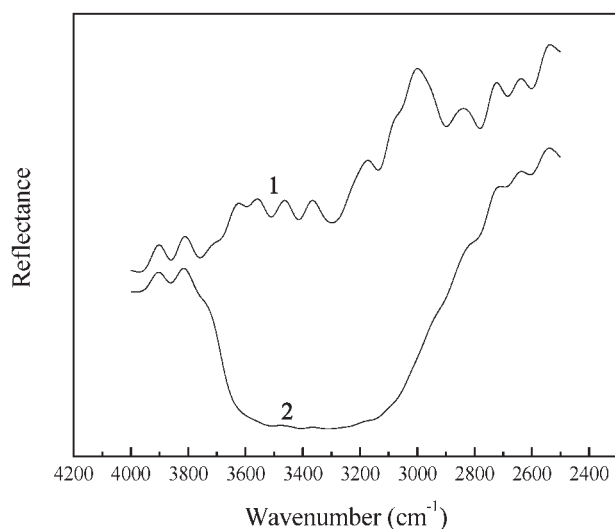


Figure 5. The *in situ* FT-IR spectra of Pd-Cu/P25; operating condition: vacuum and no hydrogen induction at 298 K (curve 1); vacuumized and then induced hydrogen gas at 298 K (curve 2).

from these results, we suggest that this enhancement of activity over Pd-Cu/P25 bimetallic catalyst is due to the extra formation of the copper active center. A reaction scheme is presented in figure 6. From this point of view, on monometallic and bimetallic Pd-based catalyst, the role of palladium was to split H_2 into absorbed Pd-H atoms. Dissociated hydrogen atoms can reduce the adjacent copper oxides into metal copper. It is valuable that these active metal copper atoms are also likely to act as the active center to reduce nitrite ions. So, the Pd-Cu bimetallic catalyst can provide more active centers for nitrite reduction than the monometallic catalyst. The

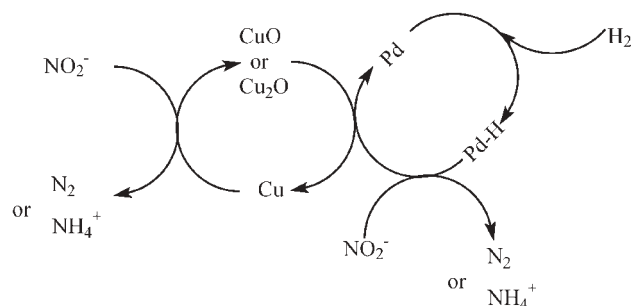


Figure 6. The hypothetical reaction mechanism of catalytic reduction of nitrite ions.

Table 1

The catalytic nitrite reduction performances of some catalysts prepared by different methods. (Pd : Cu molar ratio: 2 : 1, total metal content: 3 wt%, nitrite initial concentration: 50 mg L⁻¹ (N/L), reaction volume: 100 mL, reaction temperature: 298 K, hydrogen flow rate: 60 mL min⁻¹, operating pressure: 1 bar, reaction time: 10 min)

Catalyst ^a	Nitrite conversion (%)
Cat 1	20.47
Cat 2	15.34
Cat 3	12.14

^aCat 1: Pd–Cu/P25; Cat 2: reduce Cat 1 in hydrogen gas for 4 h at 673 K; Cat 3: reduce Cat 1 in hydrogen gas for 4 h at 873 K.

coexistence of two activity centers greatly promoted the nitrite conversion.

3.3. Influence of the thermal treatment

With or without the prethermal treatment, i.e., the main difference between liquid-phase chemical reduction method and the conventional impregnation method in preparation of metal-loaded catalyst, Pd–Cu/P25 catalysts with different treatment conditions were studied, and the results of catalytic nitrite reduction are listed in table 1. As indicated, the effect of the thermal treatment on the nitrite reduction is obvious. Under the given reaction conditions, Cat 1, which was not thermally treated, exhibited higher catalytic activities than Cat 2 and Cat 3, both were reduced in H₂ gas at high temperature. Moreover, the catalytic activity of nitrite reduction decreased dramatically while the treatment temperature was increased from 673 K to 873 K. The decrease of catalytic activity might be due to the aggregation of active metal at high temperature and the difference between two catalysts are discussed by XRD (figure 3), XPS (figure 4(c) and (d) and table 2), TEM image (figure 7), and DSC analysis (figure 8). In XRD patterns, there is no difference between the thermally reduced sample and the thermal treatment sample, and no characteristic reflections for Pd- or Cu-containing phases are also detected. XPS data indicated that the position of Pd3d_{5/2} peak shifted from 351.1 eV to 351.4 eV after thermal reduction; moreover, the peak intensity of Cu²⁺ weakened after thermal treatment, and

Table 2

Measured binding energy (eV) of Pd 3d_{5/2} and Cu 2p_{3/2} and Pd : Cu atomic molar ratio for NaBH₄-reduced sample and thermally reduced sample

Sample	Pd 3d _{5/2}	Cu 2p _{3/2}		Atomic molar ratio (Pd : Cu)
		Cu ⁰	Cu ²⁺	
Cat A	335.1	932.4	933.8	1.07 : 2.16
Cat B	335.4	932.3	933.7	0.43 : 1.67

Note: Cat A: NaBH₄ reduced sample; Cat B: thermally reduced sample.

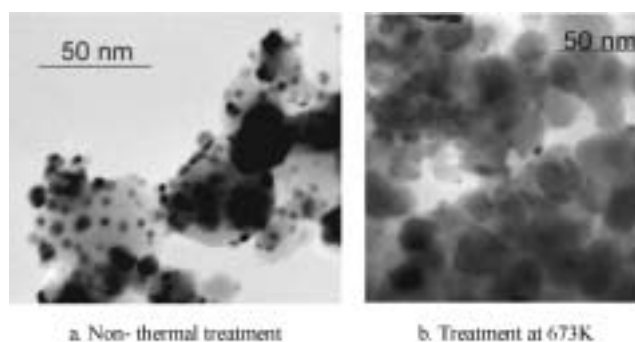


Figure 7. (a) TEM images of nonthermal treatment catalyst and (b) thermal treatment catalyst.

the ratio of palladium and copper (Pd : Cu) was also decreased after thermal reduction. TEM images show that the active metal particles of the nonthermal treatment catalyst (figure 7(a)) are dispersed very well on the TiO₂ surface, and the sizes are mostly below 10 nm. In contrast to this, the active metals on the surface of catalysts treated at high temperature (figure 7(b)) have apparently appeared aggregated and agglomerated. The DSC analysis (figure 8) also shows that there is a huge exothermal peak in curve 2, curve 3, and curve 5, respectively, of the catalysts that are not treated at high temperature, while such distinct exothermal peaks do not appear for the catalysts (curve 4 and 6) treated at high temperature. On the untreated catalysts, the active metals exist in the form of tiny metal clusters; these tiny metal clusters can provide more effective specific surface area, more low-coordination sites and more defects, which play an important role in catalysis [10]. However, active metal clusters may become larger through aggregation at high temperature and thereby the exothermal peaks resulting from this process is formed. The decrease of effective surface area may result in a decline of the catalytic activity.

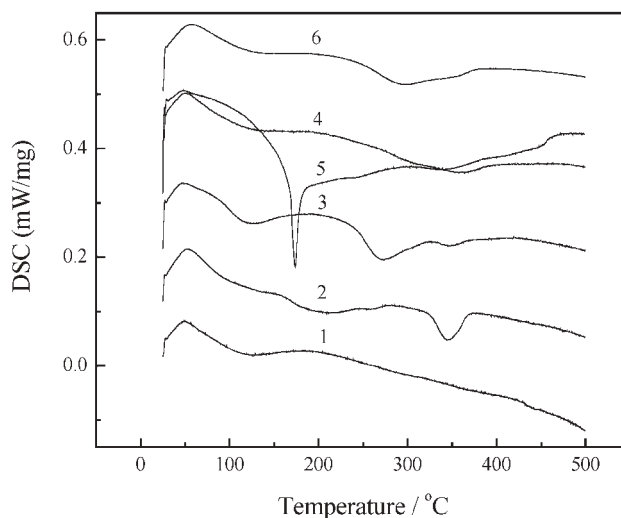


Figure 8. DSC analysis of some catalysts. 1: P25, 2: Cu/P25, 3: Pd/P25 (reduced in H₂ at 673 K), 4: Pd/P25 (reduced in H₂ at 673 K), 5: Pd–Cu/P25, 6: Pd–Cu/P25 (reduced in H₂ at 673 K).

4. Conclusions

Titania supported palladium–copper bimetallic catalysts (Pd–Cu/P25) prepared by liquid-phase chemical reduction method showed a superior activity in conversion of NO_2^- in drinking water ($1 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{cat}}^{-1}$) and was about 14 times than that of reported in the recent references. TEM and DSC proved that liquid-phase chemical reduction at ambient temperature could inhibit the aggregation of metal active components. Compared with monometallic palladium catalyst, there are more active centers (Cu and Pd–H) in the bimetallic Pd–Cu catalyst; it is the coexistence of these two active centers that greatly promoted the nitrite conversion. The reaction mechanism is discussed according to the characterization results of XPS and *in situ* FT-IR.

Acknowledgments

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