

Effect of liquid property on adsorption and catalytic reduction of nitrate over hydrotalcite-supported Pd-Cu catalyst

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Abstract

This study focused on investigating the effect of liquid property on adsorption and catalytic reduction of nitrate over hydrotalcite-supported Pd-Cu catalyst. Batch experiments were conducted under specific operating conditions. It was found that nitrate ions were adsorbed apparently by hydrotalcite-supported Pd-Cu catalyst at different reaction temperature (10, 25 and 35 °C). Adsorption isotherms for NO_3^- were described by Langmuir's equation. Higher reaction temperature accelerated nitrate adsorption and reduction, and simultaneously decreased the accumulation of NO_2^- and NH_4^+ . Nitrate adsorption and reduction were independent of the initial pH because of the high buffering capacity of hydrotalcite when the initial pH of solution was from 5.25 to 7.4. However, the dissolve of hydrotalcite-supported Pd-Cu catalyst at low initial pH (3.77) and higher concentration of OH^- ions at high initial pH (10.74) decreased nitrate adsorption and reduction. When using various nitrate salts as a source of nitrate ions, nitrate adsorption and reduction removal efficiency decreased in the order: $\text{Fe}^{3+} > \text{Mn}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+$, which was attributed to different affinity toward OH^- . Co-existed cations in water with higher valence and lower crystal ionic radius and solubility constant of hydroxide showed stronger affinity toward OH^- and consequently increased the concentration of active sites accessible to NO_3^- and NO_2^- . The competitive adsorption of Cl^- , SO_4^{2-} and HCO_3^- with nitrate on the catalyst surface suppressed the adsorption and reduction of NO_3^- . Besides, few metals dissolved in neutral and alkaline solution. The activity of the hydrotalcite-supported Pd-Cu catalyst for nitrate reduction kept steady after repeated use. © 2007 Elsevier B.V. All rights reserved.

Keywords: Liquid property; Pd-Cu/hydrotalcite; Catalytic; Adsorption; Nitrate reduction

1. Introduction

The nitrate ions removal from groundwater is becoming an environmental problem of major concern due to its high toxicity (e.g. causing cancer and methemoglobinemia) [1,2]. Conventional physicochemical methods, including ion-exchange, reverse osmosis and electrodialysis [3,4], allow effective removal of nitrate ions from water by concentrating them in a secondary waste stream, but do not generally achieve their complete disposal. The most environmental friendly methods for nitrate removal, based on selective reduction of nitrate to nitrogen, are biological digestion [5,6] and catalytic reduction [7,8]. The biological denitrification process is currently the most widely used, however, possible bacterial contamination,

the presence of residual organics and the possible increase in chlorine demand in purified water [3] limit the application of this process.

The catalytic reduction of nitrate is attracting considerable interest due to many advantages, such as efficient chemical reaction, flexibility, simple configuration of reactor, etc. In this process, nitrate ions are reduced using hydrogen over bimetallic catalyst. The reaction obeys a consecutive reaction scheme in which nitrite appears as an intermediate, while nitrogen and ammonia are the final products. Recently, developing a catalyst possessed higher activity and selectivity for nitrate reduction [9–11] and studying the influence of liquid properties [12–14], such as temperature, pH, co-existed ions, etc., have received many researchers' attention.

In our previous study [15], hydrotalcite (HT)-supported Pd-Cu catalysts for nitrate reduction using hydrogen were investigated preliminarily. Hydrotalcite like compounds, as one of the most promising materials, were widely used as catalyst [16],

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catalyst support [17], adsorbent [18], etc. The general chemical formula is written as $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}]^{x-} \cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metal ions, A^{n-} is a n -valent anion and x can have values approximately between 0.25 and 0.33. This material presents a brucite-like structure, where metallic cations are located in the layer, while anions and water are found in the interlayer space. Therefore, Pd-Cu active metals could be introduced into the layers to obtain high dispersion, which may increase the stability and activity of the catalyst; toxic anions (such as nitrate) in contaminated water may be concentrated in the interlayer space to be removed.

Our preliminary experiments have shown that hydrotalcite-supported Pd-Cu catalyst possessed effective adsorptive and catalytic capacity for nitrate in water [15]. The reaction scheme for nitrate removal on HT3(Pd-Cu) catalyst, with H_2 provided, was a consecutive and dynamic adsorption and catalytic hydrogenation process. Then, it is a key to investigate the influence of liquid property, including temperature, pH and co-existed ions in water, on nitrate adsorption and reduction over hydrotalcite-supported Pd-Cu catalyst, which will be favorable for the determining the appropriate reaction conditions for nitrate reduction. From this aspect, systematical experiment was necessary to be conducted in this paper.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-supported Pd-Cu catalyst was prepared by coprecipitation at low supersaturation method [19]. In this method, two solutions, A and B, were added dropwise into a beaker containing 100 mL of deionized water while vigorous stirring. Solution A was $Mg(NO_3)_2$ (1.2 mol/L), $Al(NO_3)_3$ (0.4 mol/L), an appropriate amount of $Pd(NO_3)_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ mixed aqueous solution. The palladium and copper content are 1 and 0.25 wt.%, respectively. Solution B contained 1.65 mol/L NaOH and 0.5 mol/L Na_2CO_3 . During the process of synthesis, the pH of the suspensions was maintained at about 10. The resulting suspension was then maintained at 25 °C, with stirring, for 4 h. The product was filtered, washed thoroughly with deionized water until the pH of filtrate showed neutral and subsequently dried overnight at 105 °C and calcined at 550 °C for 8 h, finally reduced at 200 °C for 2 hr under flowing hydrogen/argon. The final product was mentioned as HT3(Pd/Cu).

2.2. Catalyst characterization

The specific surface area (BET method) was determined using an ASAP2000 Surface Analyser (Micromeritics Co., USA) using N_2 as the adsorbate.

X-ray powder diffraction (XRD) patterns of samples were obtained with a Bruker diffractometer using $Cu K\alpha$ radiation from 10° to 70° (in 2 θ).

Fourier transform infrared spectra were recorded with potassium bromide-pressed disks, by accumulating 32 scans at 4 cm^{-1} resolution between 400 and 4000 cm^{-1} using a Nicolet 5700 Fourier transform infrared spectrometer (FTIR).

Thermogravimetry (TG) and differential thermal analysis (DTA) of the sample was carried out using a Labsys™ TG-DSC Simultaneous Analyser referenced against recalcined alumina (SETRAM Co.), in flowing nitrogen (flow rate, 20 mL/min), at a heating rate of 10 °C/min.

2.3. Adsorptive and catalytic tests

For all adsorptive tests in this work, the studies were carried out in glass vessels with agitation provided by a shaker at 170 rpm and the temperature controlled by air bath. Nitrate solution (50 mL) was mixed with 0.1 g catalyst. Samples were taken at different time intervals. The initial nitrate concentration was equal to 100 mg/L. The adsorption equilibrium was obtained within 180 min, which was demonstrated in our previous study [15]. Consequently, the adsorption time was 180 min.

Catalytic capacity of different catalyst for nitrate reduction was tested in a thermostated batch reactor equipped with H_2 inlet and outlet and a sample port. The catalyst (1 g) was suspended in pure water (500 mL), which was saturated with the mixture of argon (400 mL/min) and hydrogen (200 mL/min) from the titanium plate situated in the bottom of the reactor for 60 min. Solution containing nitrate was introduced and the time was started. The initial nitrate concentration was equal to 100 mg/L. The reaction time was 180 min.

2.4. Analysis methods

Samples were taken from the reactor at desired sampling times and filtered through a 0.45 μm membrane. NO_3^- -N, NO_2^- -N and NH_4^+ -N were determined using a Hitachi-3010 model UV-spectrophotometer.

After the reaction, solution in the reactor was analyzed by ICP-AES (Perkin-Elmer Co.) to quantify any dissolving of the active metals (Mg^{2+} , Al^{3+} , Pd^{2+} , Cu^{2+}).

3. Results and discussion

3.1. Characterization of catalyst

The physical properties of the catalyst were very important and influenced the catalytic capacity of the catalyst remarkably. Before the calcination, the sample had a low specific surface area of 6.2 m^2/g . The X-ray diffraction (XRD) analysis showed that a well-crystallized hydrotalcite-like phase formed. After calcination, the specific surface area increased to 236.6 m^2/g . Meanwhile, hydrotalcite-like structure was changed while MgO phase was formed according to the peaks at 43.2° and 62.7°. After the sample contacted with the aqueous solution of nitrate, the specific surface area dropped to the value as low as 9.05 m^2/g . Simultaneously, MgO phase collapsed and turned into a hydrotalcite-like phase which was evidenced by the XRD analysis. This result sample was just the active catalyst during the denitrification process. In addition, due to the low active metals content, no peak related with Pd-Cu could be observed.

In order to clarify the decomposition process during the calcination, simultaneous thermogravimetry (TG) and differential

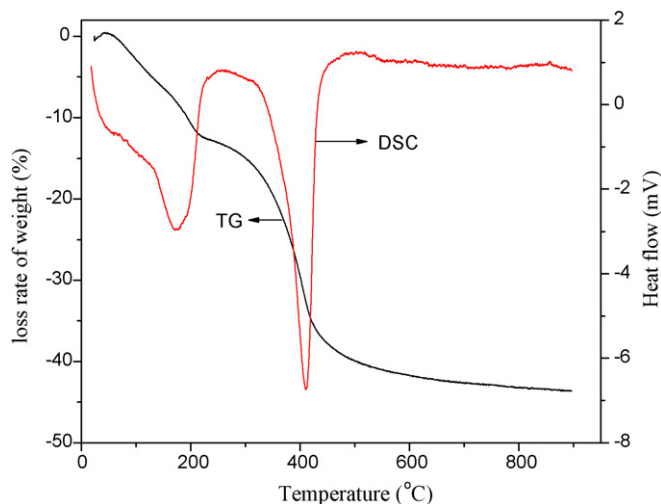


Fig. 1. Simultaneous TG/DSC thermogram of the HT3(Pd-Cu).

thermal analysis techniques were carried out. The result was shown in Fig. 1. As TG analysis revealed, gradual weight loss was observed from about 50 °C to approximately 600 °C, with two main endothermic effects at about 173 and 410 °C. The first large endothermic effect at about 173 °C involved inter-layer water loss [20]; the second endothermic effect at 410 °C accounted for hydrotalcite decomposition which was accompanied by dehydroxylation and the decomposition of CO_3^{2-} in the brucite-like layers [20]. Carbon dioxide evolution induced the formation of pores, which was the reason for the drastic increase in the specific surface area. The total weight loss (*ca.* 40% of the starting mass) is similar to that calculated from weights taken before and after calcination.

3.2. Effect of liquid property on adsorption and catalytic reduction of nitrate on HT3(Pd-Cu)

For the natural water, the property of the liquid phase was obviously various in different area. Therefore, the effect of the liquid property on the adsorption and catalytic hydrogenation for nitrate over hydrotalcite-supported Pd-Cu catalyst should be discussed in detail.

3.2.1. The effect of temperature

The influence of temperature on nitrate uptake and catalytic hydrogenation over HT3(Pd/Cu) was discussed, respectively. Fig. 2(a) showed adsorption isotherm for NO_3^- at temperature of 10, 25 and 35 °C. The result showed that HT3(Pd/Cu) catalyst possessed apparent adsorption capacity for NO_3^- , especially at 25 and 35 °C, which could be explained by considering the capacity of hydrotalcite to concentrate anions in the inter-layer space. Although the specific surface area of the regenerated hydrotalcite was very low, nitrate ions could be concentrated by ionic forces between the layers. Therefore, effective adsorption for nitrate was obtained.

Additionally, adsorption data were tested using Langmuir model. It was discovered that, at different temperature, adsorption isotherm for NO_3^- fit well with Langmuir's equation

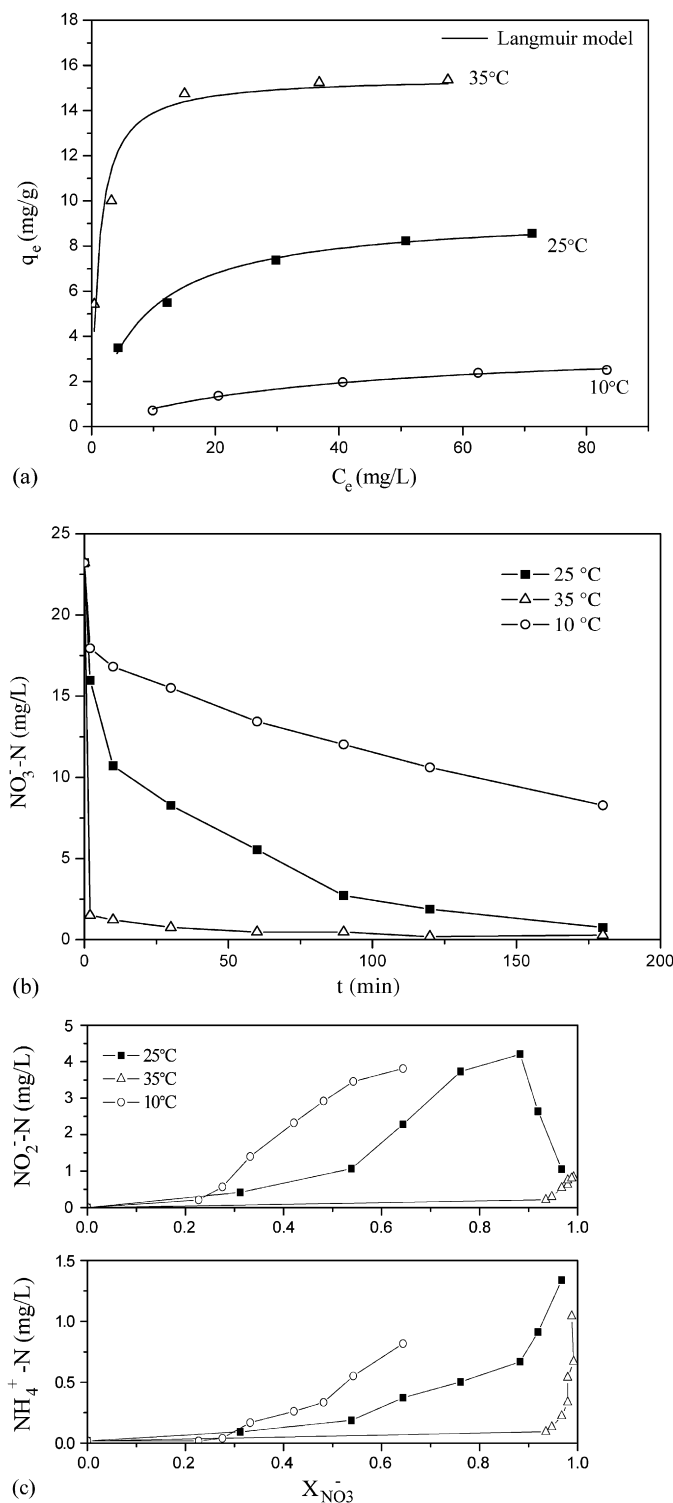


Fig. 2. The effect of temperature on the adsorption and reduction of nitrate over HT3(Pd-Cu), without pH control: (a) adsorption isotherms of NO_3^- -N; (b) NO_3^- -N concentration with time during the catalytic hydrogenation of aqueous nitrate solution; (c) NO_2^- and NH_4^+ concentration with NO_3^- conversion during the catalytic hydrogenation of aqueous nitrate solution ($X_{\text{NO}_3^-} = ([\text{NO}_3^-]_{t=0} - [\text{NO}_3^-]_t) / ([\text{NO}_3^-]_{t=0})$).

($q_e = q_m bc_e / (1 + bc_e)$), where q_e (mg/g) was the amount of NO_3^- -N adsorbed at equilibrium, q_m (mg/g) the maximum sorption capacity corresponding to complete monolayer coverage, c_e (mg/L) the equilibrium solute concentration and b was the equilibrium constant (L/mg). The maximum adsorption capacity (q_m) obtained by the linear regression was 3.685 mg- NO_3^- -N/g at 10 °C, 9.441 mg- NO_3^- -N/g at 25 °C, 15.491 mg- NO_3^- -N/g at 35 °C, respectively, which suggested that the nitrate uptake obviously increased with an increase in the adsorption temperature. Usually, the uptake decreases with temperature due to the exothermic nature of the simple physical adsorption reaction. The present result indicated that a chemical interaction involved the adsorption of nitrate on HT3(Pd/Cu).

Fig. 2(b) showed the catalytic reduction of nitrate at different temperature (10, 25 and 35 °C). It was found that nitrate concentration decreased rapidly at the initial 2 min, especially at 35 °C nitrate removal efficiency reaching as high as 93.5%. Then, NO_3^- removal efficiency became slowly gradually. After 180 min, the total removal efficiency for nitrate was 64.37, 96.76 and 98.78% at 10, 25 and 35 °C, respectively. Thus, it was concluded that higher reaction temperature may increase nitrate removal.

Simultaneously, nitrite and ammonium ions were formed during the catalytic hydrogenation for nitrate. The results were shown in Fig. 2(c). With the decrease of the reaction temperature, the concentration of NO_2^- and NH_4^+ increased, that is, the selectivity for N_2 decreased. At 35 °C, the concentration of NO_2^- and NH_4^+ formed at the same NO_3^- conversion were the lowest. At 25 °C, nitrite concentration increased first, going through a maximum at 88% of nitrate conversion and then decreased, which indicated that nitrite was an intermediate product of the reduction of nitrate. Ammonium increased steadily because it was a final product. At 10 °C, more NO_3^- was reduced to NH_4^+ , and an increased accumulation occurred in NO_2^- change. Consequently, the results obtained indicated that higher temperatures favor the increase of nitrate reduction efficiency and selectivity for N_2 .

3.2.2. The effect of pH

The effect of the initial pH on nitrate adsorption and reduction over HT3(Pd/Cu) was shown in Fig. 3. Diluted HNO_3 and NaOH solutions were used for pH adjustments. Buffer solutions were not used in order to avoid contamination of foreign anions. The results indicated that, in the process of nitrate adsorption, the nitrate removal remained practically constant from 5.25 to 7.4, reaching over 47%. However, a significant decline occurred when the initial pH was 3.77 and 10.74. In the process of nitrate catalytic reduction, at the initial pH of from 5.25 to 10.74, nitrate removal decreased slightly with the increasing of pH. There was no obviously different in the final NH_4^+ concentration. However, the final NO_2^- concentration increased with the increasing of pH, especially for pH of 10.74, NO_2^- -N concentration reached as high as 4.85 mg/L, which was about three times higher than that at pH of 7.4. During the process of nitrate reduction to N_2 , the electroneutrality of the system was maintained by the OH^- anions produced, which was supported by the observed incre-

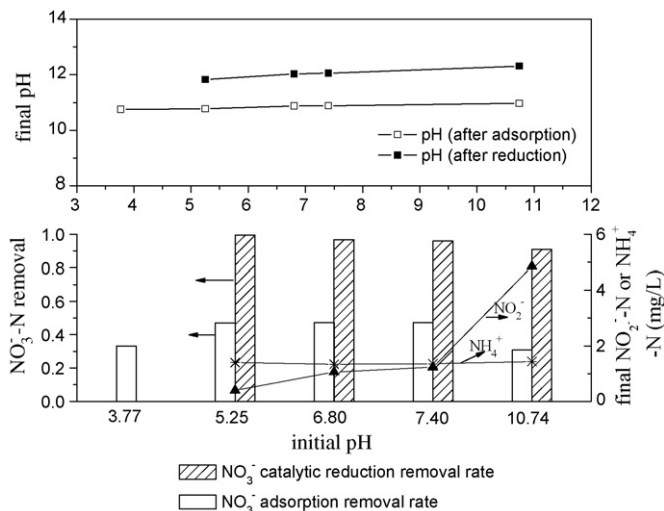


Fig. 3. The effect of the initial pH on the adsorption and reduction of nitrate over HT3(Pd/Cu), $T = 25$ °C.

ment of the final pH from adsorption process (about 10.8) to reduction process (about 12).

It was concluded that, from 5.25 to 7.4, both nitrate adsorption and catalytic reduction processes were almost pH independent. Simultaneously, the relationship between the initial and equilibrium pH showed that, the final pH remained constant at about 10.8 for nitrate adsorption process and at 12 for nitrate reduction process, respectively, in spite of obvious changes of the initial pH. These results demonstrated that hydrotalcite-like compound possessed pH buffering capacities at the initial pH of from 5.25 to 7.4, which was due to the release of hydroxyl during the regeneration of hydrotalcite structure. Therefore, at initial pH of from 5.25 to 7.4, nitrate adsorption (or nitrate reduction) was carried out at only one pH and, as a consequence, the nitrate removal remained constant irrespective to the initial pH of the solution due to the buffering effect of the HT3(Pd/Cu). Other authors have also observed the buffering effect of hydrotalcite-like compounds. You et al. [21] observed that the amount of SeO_3^{2-} adsorption in Mg-Al and Mg-Fe hydrotalcites was almost constant in a wide range of pH.

At too low initial pH of 3.77, a significant decline in nitrate adsorption removal efficiency may be due to the dissolution of HT3(Pd/Cu), which was confirmed by the examination of dissolution ions by ICP-AES. At too high initial pH (10.74), buffering effect of HT3(Pd/Cu) disappeared. High concentration of OH^- ions cause the competitive effect with NO_3^- , which decreased nitrate removal efficiency for adsorption or reduction and selectivity to N_2 .

3.2.3. The effect of co-cations in water

To study the influence of familiar anions in the aqueous solution on the adsorption and reduction of nitrate over HT3(Pd/Cu), the following reagent-grade compounds were employed as a source of nitrate ions: NaNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$. As shown in Fig. 4, nitrate adsorption removal efficiency decreased in the order: $\text{Fe}^{3+} > \text{Mn}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+$, which was on the contrary

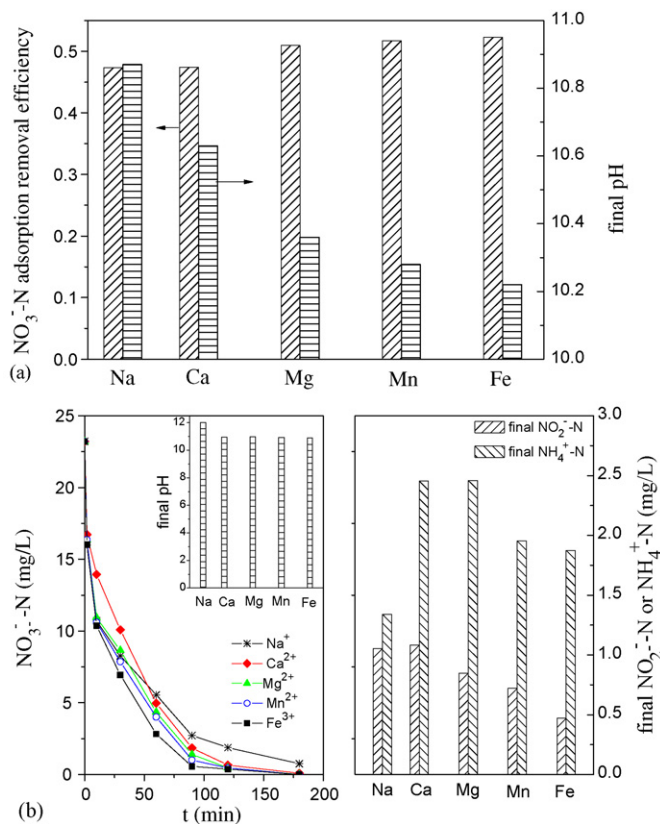


Fig. 4. The effect of the co-cations on the (a) adsorption and (b) reduction of nitrate over HT3(Pd-Cu), $T = 25^\circ\text{C}$, without pH control.

to the order of final pH decrease. Similarly, in the process of nitrate catalytic reduction, the order of nitrate catalytic reduction removal efficiency was consistent with the order of nitrate adsorption removal efficiency. The final pH in the presence of Na^+ was apparently higher than others, which was the same as the result during the process of adsorption. Simultaneity, the final NO_2^- and NH_4^+ concentrations were obviously different for various nitrate salts. The final NO_2^- concentration decreased with the increase of nitrate catalytic reduction removal efficiency, which meant favorable effect on nitrate catalytic reduction advanced nitrite reduction alike. Additionally, the NH_4^+ accumulation was the lowest in the presence of Na^+ .

It has been widely known that the nitrate reduction efficiency and the selectivity to N_2 are severely limited by diffusion [22]. During the process of nitrate catalytic reduction, OH^- ions were produced continuously and baffled the access of nitrate and nitrite to the surface of the catalyst. With this respect, one can conclude that faster removal of OH^- ions from the surface of catalyst would lead to faster regeneration of active sites. In other words, a large number of Pd-Cu sites can be accessed by nitrate and nitrite in the subsequent reaction cycles. Accordingly, different effect of cations on nitrate and nitrite hydrogenation might be ascribed to various affinities toward OH^- , which was related with physical properties of cations, such as valence, crystal ionic radius and solubility constant of hydroxide. With the increase of valence and the decrease of ionic radius, attraction forces towards OH^- improved. Thus, OH^- on the surface

of the catalyst can be quickly withdrawn. Moreover, the lower the solubility constant of hydroxide precipitation was, the easier the combination of OH^- ions with cations to form the precipitation was. For the cations employed in this experiment, the solubility constant of hydroxide precipitation according to the order: $\text{Fe}(\text{OH})_3 < \text{Mn}(\text{OH})_2 < \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{NaOH}$ ($\text{Fe}(\text{OH})_3$: $K_{\text{sp}} = 4 \times 10^{-38}$; $\text{Mn}(\text{OH})_2$: $K_{\text{sp}} = 1.9 \times 10^{-13}$; $\text{Mg}(\text{OH})_2$: $K_{\text{sp}} = 1.8 \times 10^{-11}$; $\text{Ca}(\text{OH})_2$: $K_{\text{sp}} = 5.5 \times 10^{-6}$ at 298 K), which was just contrary to the order of the nitrate and nitrite removal efficiency. That is, more hydroxide precipitation made more OH^- in the solution reduced, and thus improved nitrate removal efficiency and decreased the nitrite accumulation. Additionally, the lower final pH in the presence of bivalent and trivalent cations also demonstrated that more OH^- ions in the solution were removed.

3.2.4. The effect of co-anions in water

Cl^- , SO_4^{2-} and HCO_3^- are common co-existing anions together with NO_3^- in water. The effect of these anions in water on the adsorption and catalytic reduction of nitrate by HT3(Pd/Cu) was studied in Fig. 5. Obviously, the presence of Cl^- , SO_4^{2-} and HCO_3^- anions suppressed the adsorption and reduction of NO_3^- . The inhibitory effect was in the order of $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. It was observed that there was only a little decrease on the adsorption and reduction of NO_3^- at the concentration range of 0–0.01 mol/L Cl^- ions. When the concentration of Cl^- ions was higher than 0.01 mol/L, the inhibitory effect increased apparently. Generally, the concentration of Cl^- ions in the groundwater or surface water was lower than 0.01 mol/L. So Cl^- ions in natural water exhibited little effect on nitrate adsorption and reduction over HT3(Pd/Cu) catalyst. However, the effect of HCO_3^- and SO_4^{2-} on the removal of NO_3^- by adsorption and reduction was significant at the concentration range of 0–0.1 mol/L. With the increasing concentration of HCO_3^- and SO_4^{2-} , the amounts of NO_3^- removal by adsorption and reduction decreased quickly. For example, in the presence of HCO_3^- or SO_4^{2-} at 0.001 mol/L, the nitrate removal by HT3(Pd/Cu) during the catalytic hydrogenation process dropped from 97 to about 86%; at a concentration of 0.05 mol/L HCO_3^- or SO_4^{2-} , the nitrate removal declined to about 70%; while at a concentration of 0.01 mol/L, the removal of nitrate decreased to 46%. Additionally, during the catalytic hydrogenation process, the presence of Cl^- , SO_4^{2-} or HCO_3^- increased the nitrite and ammonia accumulation. That is, Cl^- , SO_4^{2-} or HCO_3^- as co-existed anions inhibited the reduction of nitrite and decreased the selectivity to N_2 . The inhibitory order of $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ was similar to that for nitrate adsorption and reduction. It was found that the inhibitive effect of HCO_3^- ions on the adsorption and reduction of nitrate was higher than that of SO_4^{2-} and Cl^- , which might be due to the identical structures of NO_3^- and HCO_3^- ions. They are both planar, and the angles between the N–O and C–O bonds are equal to 120° .

To clarify the inhibitory effect of Cl^- , SO_4^{2-} or HCO_3^- on nitrate adsorption and reduction, we took the influence of SO_4^{2-} ions, for example. During nitrate reduction process, infrared spectra of the catalyst at different reaction time was

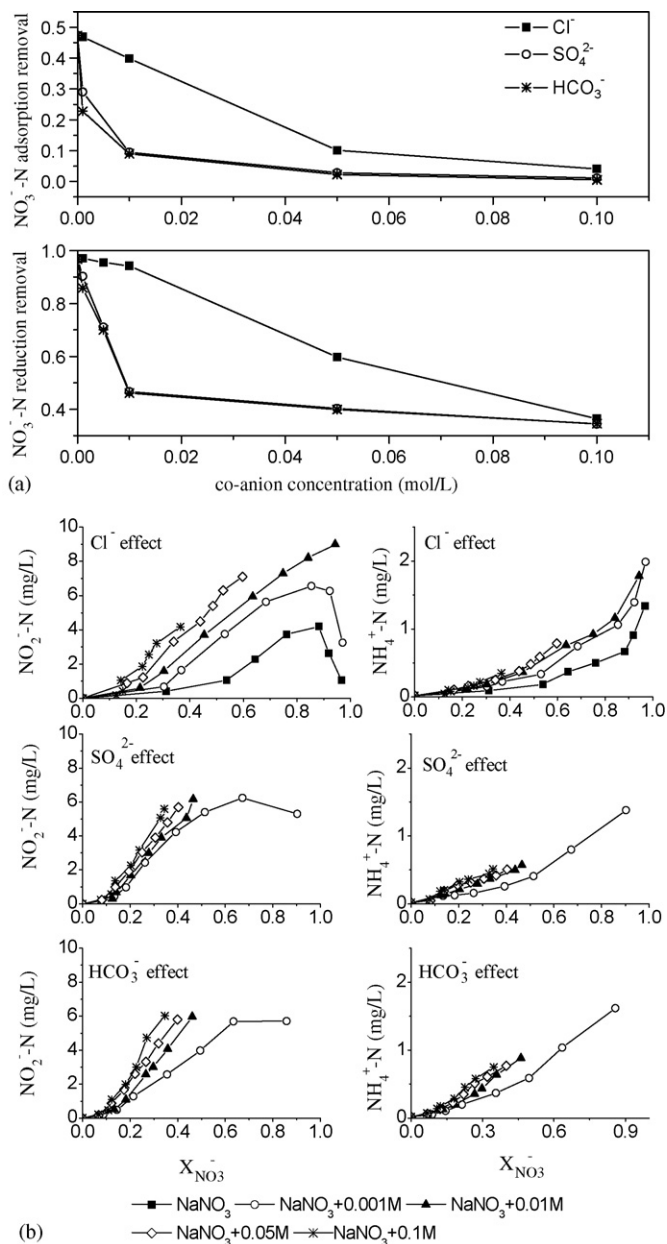


Fig. 5. The effect of the co-anions (Cl^- , SO_4^{2-} and HCO_3^-) on the adsorption and reduction of nitrate over HT3(Pd-Cu), $T=25^\circ\text{C}$, without pH control: (a) nitrate removal efficiency with different co-anions concentration during adsorption and reduction process; (b) NO_2^- and NH_4^+ concentration with NO_3^- conversion at different co-anions concentration during nitrate reduction process ($X_{\text{NO}_3^-} = ([\text{NO}_3^-]_{t=0} - [\text{NO}_3^-]_t) / ([\text{NO}_3^-]_{t=0})$).

studied in Fig. 6. We can see that, when SO_4^{2-} ions occurred in nitrate solution or not, it presented two infrared bands at 1647 and 1385 cm^{-1} assigned to the bending O–H vibration of the water molecules and to the asymmetric stretching N–O vibration of the nitrate ions, respectively. However, in nitrate solution with SO_4^{2-} ions, the existence of an apparent infrared band at 1109 cm^{-1} can be found, but not be observed in the solution without SO_4^{2-} ions. Therefore, it was concluded that the band at 1109 cm^{-1} was assigned to SO_4^{2-} . Moreover, during the course of the reaction, this band (1109 cm^{-1}) increased grad-

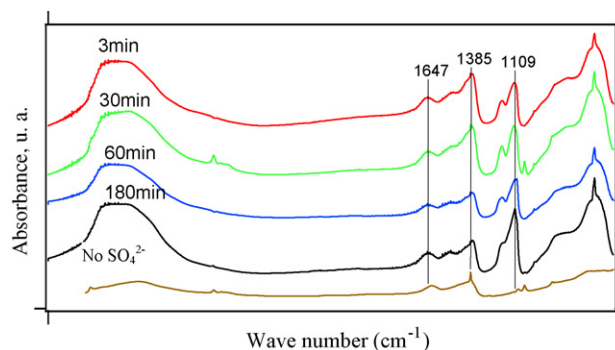


Fig. 6. Infrared spectra of HT3(Pd-Cu) catalyst withdrawn at different reaction times, $T=25^\circ\text{C}$, without pH control, the concentration of SO_4^{2-} is 0.01 mol/L .

ually. Therefore, by IR study, the effect of SO_4^{2-} on nitrate reduction over HT3(Pd/Cu) catalyst could be attributed to competitive adsorption with nitrate on the catalyst surface, which leads to the active sites decreased apparently, and consequently nitrate adsorption and reduction decreased and nitrite was accumulated.

3.3. The stability and reusability of HT3(Pd-Cu)

From a practical viewpoint, to evaluate the stability and reusability of HT3(Pd-Cu) must be required. After the reduction of nitrate, the dissolution of metals in solution at different initial pH was analyzed by ICP-AES (Table 1). In the neutral (pH 7.4) and alkaline (pH 10.74) solution, no palladium ions were detected in the solution. The concentrations of copper, magnesium and aluminium ions were lower than 0.0025, 0.477 and 0.58 mg/L, which were all lower than the standard for drinking water in China. However, in acid (pH 3.77) solution, the dissolution of metals increased apparently. The concentrations of palladium and copper reached as high as 5.8 and 1.24 mg/L, which accounted for 29 and 24.8% of the amount loaded on the catalyst, respectively. The concentrations of magnesium and aluminium ions were higher than 200 mg/L. These results demonstrated that HT3(Pd-Cu) catalyst dissolved in acid solution, but keep stable in neutral and alkaline solution. Generally, most waters were about neutral or alkaline. Therefore, the reduction of nitrate on HT3(Pd-Cu) catalyst may be used in most case.

Fig. 7 showed average activity of HT3(Pd-Cu) for nitrate reduction during five cycles. The experiment was conducted as follows. After the reaction, the catalyst was taken out by the centrifugation, and then washed to remove excess ions on the surface of the catalyst. Whereafter, the recycled catalyst was

Table 1
The dissolution of HT3(Pd-Cu) at different initial pH ($C_0(\text{NO}_3^-) = 100\text{ mg/L}$, 2 g/L catalyst, at 25°C)

pH	Pd (mg/L)	Cu (mg/L)	Mg (mg/L)	Al (mg/L)
3.77	5.8	1.24	>200	>200
7.40	–	0.0025	0.477	0.39
10.74	–	–	0.0051	0.58

–: lower than detective level by ICP-AES.

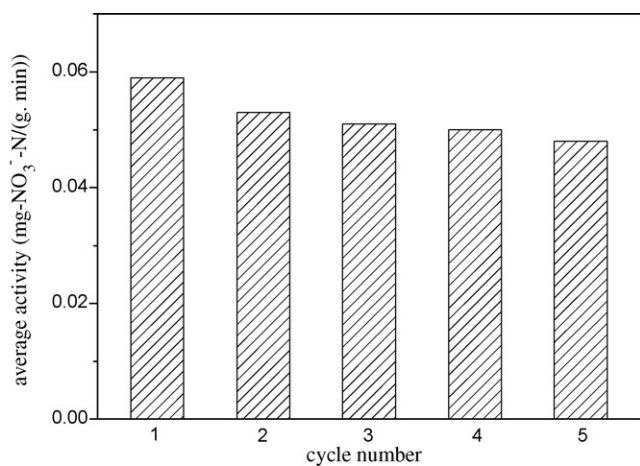


Fig. 7. Reusability of HT3(Pd-Cu) for nitrate reduction for an initial NO₃⁻ concentration of 100 mg/L, 2 g/L catalyst, at 25 °C, without pH control.

dried at 60 °C and weighed. Finally, the capacity of the recycled catalyst for nitrate reduction was examined again. It was observed that the average activity decreased obviously in the first cycle and then decreased slowly with the increase of cycles, which indicated that HT3(Pd-Cu) catalyst exhibited excellent stability and may be used for a long term.

3.4. Conclusions

In this paper, the effect of liquid property on adsorption and catalytic reduction of nitrate over hydrotalcite-supported Pd-Cu catalyst were investigated systematically. The results demonstrated that temperature, pH and co-existed ions in water showed apparent influence on nitrate removal. At different reaction temperature (10, 25 and 35 °C), HT3(Pd/Cu) catalyst possessed apparent adsorption capacity for NO₃⁻, which could be explained by considering the capacity of hydrotalcite to concentrate anions in the interlayer space. Adsorption isotherms for NO₃⁻ were good agreement with Langmuir's equation. Moreover, Higher reaction temperature advanced nitrate adsorption and reduction, and simultaneously decreased the accumulation of NO₂⁻ and NH₄⁺. When the initial pH of solution was from 5.25 to 7.4, the initial pH exhibited little influence on the nitrate adsorption and catalytic reduction, which was due to high pH buffering capacities of HT3(Pd-Cu) catalyst. However, at too low initial pH of 3.77, the dissolution of HT3(Pd/Cu) resulted in a significant decline in nitrate adsorption removal. At too high initial pH of 10.74, buffering effect of HT3(Pd/Cu) disappeared. High concentration of OH⁻ ions decreased nitrate adsorption and reduction. Co-existed cations in water with higher valence

and lower crystal ionic radius and solubility constant of hydroxide showed stronger affinity toward OH⁻ and consequently increased the concentration of active sites accessible to NO₃⁻ and NO₂⁻. Thus, when using various nitrate salts as a source of nitrate ions, nitrate adsorption and reduction removal efficiency decreased in the order: Fe³⁺ > Mn²⁺ > Mg²⁺ > Ca²⁺ > Na⁺. The presence of Cl⁻, SO₄²⁻ and HCO₃⁻ anions suppressed the adsorption and reduction of NO₃⁻ on HT3(Pd-Cu), which could be attributed to competitive adsorption with nitrate on the catalyst surface. Additionally, few metals dissolved in neutral and alkaline solution. The activity of HT3(Pd-Cu) for nitrate reduction kept steady after repeated use, which favored the long-term use.

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