Role of the Mg/Al atomic ratio in hydrotalcite-supported Pd/Sn catalysts for nitrate adsorption and hydrogenation reduction

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ABSTRACT

Hydrotalcite-supported Pd/Sn catalysts with different Mg/Al atomic ratios (2, 3, 4, and 5) for nitrate adsorption and hydrogenation reduction were successfully synthesized by a coprecipitation method. The results showed that different atomic ratios of Mg/Al resulted in different interlayer spacings and zeta-potentials of the catalysts, which thus influenced its adsorption capacity. With the increase of Mg/Al atomic ratio, the interlayer spacing rose and zeta-potential decreased. The adsorption properties of the catalysts were mainly affected by interlayer spacing when Mg/Al atomic ratios increased from 2 to 4. However, when Mg/Al atomic ratios further increased from 4 to 5, there was a negative impact on the adsorption properties of zeta-potential. Also, the adsorption capacity of the catalysts for nitrate followed the order: Mg/Al = 2 < Mg/Al = 3 < Mg/Al = 5 < Mg/Al = 4. In the catalytic reduction process, the adsorbed nitrates were further reduced to nitrites that remained in the same position in catalysts, but some of superabundant nitrites were released into water as primary and unstable products. The concentration of released nitrites was in the reverse order of the adsorption capacity. The catalytic selectivity and activity of the catalysts for nitrate reduction had the same sequence as its adsorption capacity.

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1. Introduction

In recent years, extensive use of chemical fertilizers and improper treatment of waste water from the industrial sites has led to several environmental problems, such as an increase in the concentration of nitrate in ground and surface water [1]. Nitrate is a potential human health hazardous substance [2,3] and legislators all over the world set strict levels for nitrate in drinking water, e.g., 10 mg/L NO₃⁻-N for China (2007). As the water demand is still increasing throughout the world, processes for nitrate removal from drinking water have regained interest in recent years.

There is a wide range of technologies to remove nitrate from water including physical–chemical [4–6], biological [7–9], and catalytic processes [10–18]. Conventional physical–chemical techniques such as ion-exchange, reverse osmosis, and sorption processes cannot convert nitrate into harmless compounds but only remove nitrate from water to brine which afterward needs treatment. Biological denitrification is the most widely used way to remove nitrate but it is complex and difficult to handle. A new

technology based on the catalytic hydrogenation of nitrate to nitrogen was first described in 1989 by Vorlop and co-workers [10]. Nitrate can be reduced to nitrogen using H₂ as the reductant over bimetallic catalysts. The catalysts combining a noble metal, such as Pd or Pt, and another metal, usually Cu, Sn, and Ni supported on γ-Al₂O₃, HZSM, etc., have been studied for this reaction [10–18]. Generally, the favorable adsorptive capability of the support is beneficial for the catalytic performance. Thus, preparing a suitable catalyst support which has excellent nitrate adsorptive capacity is required.

Hydrotalcite is a kind of favorable catalysts support with large anion adsorption capacity. Their chemical composition can be described by the general formula: [M_(1-x)²⁺N_x³⁺(OH)₂]^{x+}[Aⁿ⁻]_{x/n}·mH₂O, where M²⁺ is a divalent cation (Mg²⁺, Zn²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cd²⁺), N³⁺ is a trivalent cation (Al³⁺, Fe³⁺, Cr³⁺, Ga³⁺), Aⁿ⁻ is an anion, and x is defined as the M³⁺/(M²⁺ + N³⁺) ratio, whose value varies between 0.17 and 0.33. Accordingly, the atomic ratio of M²⁺/M³⁺ varies from 5 to 2. Its structure can be derived from the layered mineral brucite Mg(OH)₂, where Mg²⁺ is located in the center of an edge-sharing octahedral surrounded with hydroxyls. Isomorphous substitution of divalent cations by trivalent ones (e.g., Al³⁺) generates positive charges on the layers, which are compensated by anions located in the interlayer region. Water molecules are also found in the interlayer space. Therefore, hydrotalcite (HT)

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compounds can be viewed as a stacking of positive (brucite-like sheets) and negative (anions) layers [19–22]. Moreover, the structure size of HT compounds is affected by the M^{2+}/M^{3+} atomic ratio and their species [22].

The interesting property of hydrotalcites arises when they are calcined (CHT); during this process, the interlayer water, interlayer anions, and the hydroxyls are removed. The resulting material is a mixture of metal oxides which can take up anions from aqueous solution with concomitant reconstruction of the original layered structure, as expressed by the following equations:

Many studies have been done on the adsorptive behaviors of anions by HT and CHT; for example, some toxic anion such as $\text{Cr}_2\text{O}_7^{2-}$, Cl^- , PO_4^{3-} , AsO_3^{3-} , and $\text{B}_4\text{O}_7^{2-}$, can be adsorbed by CHT [23–27]. As a catalyst support, CHT can be used for nitrous oxide decomposition [28], MIBK synthesis [29], etc.

For hydrogenation reduction of nitrate, hydrotalcites as catalyst supports were first investigated by Palomares et al. in 2004 [30]. The nitrates were first forced to be adsorbed between the positively charged layers of the catalysts and then reduced to nitrites that remained in the same position, and nitrites were finally reduced to nitrogen or ammonium. Since the catalysts had excellent adsorptive ability toward anions, the nitrites concentration was to a much lower extent. In the previous study of our group, it was demonstrated that hydrotalcite-supported Pd/Cu catalysts had both excellent adsorption and catalytic properties for nitrate reduction [31,32]. Also, the catalyst synthesized via a coprecipitation method exhibited higher adsorption and catalytic activity than that prepared by coimpregnation method [31]. It was proposed that the interlayer spacing [22] and electrical properties [33] of HT compounds are affected by the M^{2+}/M^{3+} atomic ratio. From this aspect, systematic experimentation of the impact of the M^{2+}/M^{3+} atomic ratio was necessary. In this study, CHT-supported Pd/Sn catalysts of different Mg/Al atomic ratios were synthesized using a coprecipitation method and the Mg/Al atomic ratio impact on nitrate adsorption and hydrogenation reduction was systematically investigated.

2. Materials and methods

In this study, all reagents used including PdCl_2 , SnCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH , Na_2CO_3 , and NaNO_3 were A-R grade. The solutions were all prepared with deionized water. A synthetic nitrate wastewater was prepared from NaNO_3 (A-R).

2.1. Synthesis of hydrotalcite-based catalysts

HT-supported 1.0 wt% Pd and 0.25 wt% Sn catalysts (Pd/Sn = 4/1) were obtained by a conventional coprecipitation method. The two solutions, A and B, were simultaneously added dropwise into 100 ml deionized water with vigorous stirring. Solution A (200 ml) contained an appropriate ratio of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2 mol/L), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1.2/X mol/L), and catalysts PdCl_2 and SnCl_2 . The Mg/Al atomic ratio (X) in the solution was selected as 2, 3, 4, and 5. Solution B (200 ml) contained NaOH and Na_2CO_3 , which was stoichiometric enough to precipitate the salt in the first solution. The temperature was fixed at 40°C , and the pH was maintained at 10–11. The resulting precipitate was then aged at 65°C for 18 h, separated by centrifugation, and washed thoroughly with deionized water till the precipitate was free from Cl^- .

The precipitate was dried at 100°C for 8 h, and the product was noted as HTX(Pd–Sn). The HTX(Pd–Sn) powder was calcined in a muffle furnace at 500°C for 4 h, sieved at 100 meshes, and re-dried at 200°C for 2 h under flowing H_2 and N_2 (flow rate: 100/200 ml^3/min). The final product was noted as CHTX(Pd–Sn).

For calculation of chemical reagent amount, the formula of HT can be expressed as $[\text{Mg}_{(1-x)}\text{Al}_x(\text{OH})_2]^{x+}[\text{CO}_3^{2-}]_{x/2}$, and the formula of CHT can be expressed as $\text{Mg}_{(1-x)}\text{Al}_x\text{O}_{1+x/2}$. The Mg/Al atomic ratio (X) in the solution was selected as 2, 3, 4, and 5; therefore, the value of x was 1/3, 1/4, 1/5, and 1/6. The amount of NaOH and Na_2CO_3 could be calculated by the formula of HTX and its amount. Since solution A contained 0.24 mol Mg, the amount of NaOH and Na_2CO_3 in solution B could be calculated as $\frac{0.24}{1-x} \times 2$ mol and $\frac{0.24}{1-x} \times \frac{x}{2}$ mol, respectively.

The amount of Pd and Sn could also be calculated by the formula of CHT and its amount. The formula of CHT can be expressed as $\text{Mg}_{(1-x)}\text{Al}_x\text{O}_{1+x/2}$. Its nominal amount (M) can be calculated as

$$M = \frac{0.24}{24 \times (1-x)} \times [24 \times (1-x) + 27 \times x + 16 \times (1+x/2)] \text{ g}.$$

The amount of PdCl_2 (M1) could be calculated as

$$M1 = M \times 1\% \times \frac{177.31}{106.42} \text{ g}.$$

The amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (M2) could be calculated as

$$M2 = M \times 0.25\% \times \frac{225.63}{118.69} \text{ g}.$$

2.2. Adsorptive test

Kinetics experiments of adsorption were carried out in 500-ml flasks at a controlled temperature (25°C) with vigorous stirring. The sorbent dose was 5 g/L, and the initial nitrate concentration was fixed at 22.58 mg N/L. Nitrate adsorbed by the CHTX(Pd–Sn) was calculated by

$$q_t = (C_0 - C_t)V/m, \quad (3)$$

where q_t is the adsorption loading of adsorbent at time t (mg N/g), V is the volume of solution (L), C_0 (mg N/L) and C_t (mg N/L) are the initial concentration of nitrate and that at time t , and m is the mass of adsorbent (g).

The equilibrium isotherms were obtained by contacting a constant mass of CHTX (0.15 g) with a range of different nitrate concentration solutions. The CHTX(Pd–Sn) and nitrate solutions were agitated in a series of 150-ml conical flasks placed in a temperature-controlled orbital shaker (25°C , stirring speed of 130 rpm) with equal volumes of solutions of 100 ml to achieve adsorption equilibrium (18 h). The reaction mixture pH was not controlled in order to avoid other anion affecting nitrate uptake. After being shaken for 18 h, the solution sample was taken for analysis of nitrate. The nitrate loading on CHTX(Pd–Sn) was calculated from the following equation,

$$q_e = (C_0 - C_e)V/m, \quad (4)$$

where q_e is the adsorption loading of CHTX(Pd–Sn) at equilibrium (mg N/g), V is the volume of solution (L), C_e (mg N/L) is the equilibrium concentrations of nitrate, and m is the mass of adsorbent (g).

In this study, all the adsorption experiments were carried out in closed flasks with deionized water which is free of atmosphere. Before adsorption, the water was saturated with N_2 for 30 min to avoid atmosphere CO_2 interference.

2.3. Catalytic test

The hydrogenation of nitrate in water was performed using a 1:2 mixture of H₂ and N₂ (flow rate: 100:200 ml³/min) in a thermostated (25 °C) batch reactor. The pressure in the reactor was equal to the atmospheric pressure. The catalyst (1 g) was suspended in pure water (450 ml) and saturated with H₂ and N₂ for 1 h under vigorous stirring. Then solution containing nitrate was added. The initial nitrate concentration was equal to 22.58 mg N/L. The reaction time was 240 min. Samples were periodically taken from the suspension for analysis of NO₃[−], NO₂[−], and NH₄⁺.

Activity and selectivity of catalysts were calculated from the equations

$$\text{activity} = (-N \text{ mg/catal g h}) = (C[\text{NO}_3^-]_0 - C[\text{NO}_3^-]_t) / (t \cdot m), \quad (5)$$

$$\text{selectivity} = \left\{ 1 - \frac{(C[\text{NO}_2^-]_t + C[\text{NH}_4^+]_t)}{(C[\text{NO}_3^-]_0 - C[\text{NO}_3^-]_t)} \right\} \times 100\%, \quad (6)$$

where C[NO₃[−]]₀ and C[NO₃[−]]_t (mg N/L) are the initial concentration of nitrate and that at time *t*; C[NO₂[−]]_t and C[NH₄⁺]_t (mg N/L) are the concentration of nitrite and ammonium at time *t*; *t* is the reaction time, 240 min; *m* is the catalysts dose, 2 g/L.

2.4. Analysis methods

The solution sample was filtered by passing through 0.45-μm membrane. NO₃[−], NO₂[−], and NH₄⁺ concentrations were determined by using a Hitachi-3010 UV-spectrophotometer.

The actual quantity of active metals (Pd and Sn) of the catalyst was analyzed as follows. First, the catalyst was dissolved in royal water (HNO₃:HCl = 1:3). Then the solution was diluted for measuring the quantity of Pd and Sn in solution by ICP-OES, which is the actual amount of active metals on the support. The XRD-ray diffraction pattern of the samples was obtained using a Philips X'pert-MPD diffractometer with CuKα radiation (40 kV and 40 mA). The surface area of the samples was obtained in an ASAP 2000 apparatus, using the BET method. Zeta-potential at various pH was measured by a Malvern Zetasizer 2000.

3. Results and discussion

3.1. Characterization

In this study, the main chemical composition and physical characteristics of the four HT-supported Pd/Sn catalysts are summarized in Table 1. Chemical composition analysis revealed that the Mg/Al atomic ratios were 1.96, 2.94, 4.01, and 5.03 for CHT2(Pd-Sn), CHT3(Pd-Sn), CHT4(Pd-Sn), and CHT5(Pd-Sn), respectively. The atomic ratios and the contents of active metals (Pd/Sn) observed for the calcined solids were very close to the nominal ratios used for preparing the starting solutions, thus showing that the precipitation process was efficient. Generally, the capacity of the catalysts was evidently influenced by their characteristics such as

the specific surface area, the volume, and the average diameter of the pores, etc. As shown in Table 1, the CHTX(Pd-Sn) is a kind of porous catalysts with high BET-surface area (134–180 m²/g), mesopore volume (0.46–0.78 ml/g), and large average pore diameter (136–189 Å).

X-ray diffraction patterns of the synthetic HTX(Pd-Sn) and CHTX(Pd-Sn) are shown in Fig. 1. Before calcination, the HTX(Pd-Sn) (Fig. 1a) exhibited a typical HT-CO₃^{2−} structure with sharp and symmetric reflections for (003), (006), (110), and (113) planes and wide and asymmetric reflexions for (012), (015), and (018) planes which are characteristic peaks of hydrotalcite-like compounds [21]. After heat treatment of HTX(Pd-Sn) at 500 °C the layered compound was destroyed and a mixed oxide (Mg(Al)O) was formed according to the peaks at 43 and 62° (Fig. 1b). In addition, no peak related to Pd-Sn was observed because of their low content and good dispersion. The layered structure reconstruction was observed when the sample was put in nitrate aqueous solution (Fig. 1c), indicating that the layered structure of HTX(Pd-Sn) was reformed after adsorption. Nitrate in water was adsorbed on the positive layer and formed the negative layer.

Table 1 lists the cell parameter *a* (calculated by the equation: *a* = 2 · *d*₁₁₀) and *c* (calculated by the equation: *c* = 3 · *d*₀₀₃) [22,34]. The parameter *a* was not changed which means there was no obvious change to the average cation–cation distance in the brucite sheets. Assuming that the width of brucite-like layer was 0.480 nm [34], the interlayer spacing could be obtained by subtracting the width of the brucite-like layer from the basal spacing (*d*₀₀₃). The results are also given in Table 1. It should be noted that higher Mg/Al atomic ratios led to larger interlayer spacings: 0.280 nm (HT2(Pd-Sn)) < 0.296 nm (HT3(Pd-Sn)) < 0.308 nm (HT4(Pd-Sn)) < 0.326 nm (HT5(Pd-Sn)). And the same order was observed for CHTX(Pd-Sn)-A catalysts: 0.286 nm (CHT2(Pd-Sn)-A) < 0.305 nm (CHT3(Pd-Sn)-A) < 0.318 nm (CHT4(Pd-Sn)-A) < 0.328 nm (CHT5(Pd-Sn)-A).

These results could be related to the electric charge density between the positive layers of hydrotalcites. The atomic ratio of Mg/Al was related to the Al³⁺ content, which had a direct influence on the electric charge density between the positive layers. With the Mg/Al atomic ratio increased, Al³⁺ content decreased and thus weakened the electric charge density between the positive layers, which resulted in an increase of interlayer spacing. As reported [30], nitrate in solution may enter the interlayer of hydrotalcites or be adsorbed on the positive layer; large interlayer spacing was favorable for both adsorption and catalytic reduction processes.

Zeta-potential is an important index for electrostatic adsorption processes. Fig. 2 gives the results of zeta-potential at various pH for CHTX(Pd-Sn) in suspension. It can be concluded that the isoelectric points (IEPs) of the CHTX(Pd-Sn) are all around pH 11. Therefore, all the CHTX(Pd-Sn) had a surface residual positive charge in suspension in a wide pH range (pH < 11.4), and could take anions onto its positive surface in acidic, neutral, and alkaline media.

Obviously, the zeta-potentials of these samples under the same experimental condition follow the trend CHT2(Pd-Sn) > CHT3(Pd-Sn) > CHT4(Pd-Sn) > CHT5(Pd-Sn), which could also be explained

Table 1
Chemical composition and physical characterization of catalysts.

Sample	Mg/Al	Pd/Sn (wt%/wt%)	BET (m ² /g)	Mesopore volume (ml/g)	Average pore diameter (Å)	<i>a</i> (nm)	<i>c</i> (nm)	Interlayer spacing (nm)
CHT2(Pd-Sn)	1.96	1.06/0.24	134.57	0.46	136.77	0.304	2.280	0.280
CHT3(Pd-Sn)	2.94	1.10/0.26	145.81	0.55	151.40	0.306	2.328	0.296
CHT4(Pd-Sn)	4.01	1.03/0.23	152.16	0.62	163.38	0.306	2.364	0.308
CHT5(Pd-Sn)	5.03	1.12/0.26	180.82	0.78	189.32	0.307	2.418	0.326

(a)

(b)

(c)

Fig. 2. Zeta potential of CHTX(Pd-Sn) at various pH.

by the electric charge density between the layers of hydrotalcites. That is, lower zeta-potential which resulted from weak electric charge density between the layers of hydrotalcites was observed for the sample with lower Al^{3+} content. This phenomena was in accordance with Sideris et al.'s report [33], in which they found that higher Al^{3+} content was consistent with stronger hydrogen bonding to the interlayer anions and water with increasing charge on the hydroxide layers. When nitrate in solution was adsorbed on the positive layers by electric force, the lower Al^{3+} content or zeta-potential was unfavorable for both adsorption and reduction process.

3.2. The effect of Mg/Al atomic ratio on adsorption

3.2.1. Kinetics study

The time course of nitrate uptake by CHTX(Pd-Sn) from synthetic water is shown in Fig. 3.

Kinetics for nitrate sorption by CHTX(Pd-Sn) was modeled by two commonly used kinetics equations: first-order kinetics model and pseudo-second-order kinetics model.

First-order kinetics model. The first-order kinetics adsorption model was suggested by Lagergren (1898) for the sorption of solid/liquid systems. It can be expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (7)$$

where k_1 (min^{-1}) is the rate constant of adsorption and q_e and q_t (mg/g) are the adsorption loadings of nitrate at equilibrium and that at time t (min), respectively. The equilibrium loading q_e (mg/g) is calculated from the Langmuir adsorption isotherm. After integration, with the initial conditions $q_t = 0$ at $t = 0$, this equation becomes

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t. \quad (8)$$

By plotting $\ln(q_e - q_t)$ against t , a straight line is obtained and the value of the rate constant k_1 can be calculated. And the initial sorption rate can be expressed as

$$V_0 = k_1 q_e. \quad (9)$$

Pseudo-second-order kinetics model. Ho [35] first developed the pseudo-second-order kinetic expression for sorption systems, in which chemical sorption was the rate-limiting step; development

Fig. 1. X-ray diffraction patterns of (a) HTX(Pd-Sn), (b) CHTX(Pd-Sn), (c) CHTX(Pd-Sn)-A after nitrate adsorption (CHTX(Pd-Sn)-A).

Table 2Kinetic parameters and correlation coefficients (R^2) for the two kinetics models.

Adsorbent	q_e , exp (mg/g)	First order				Pseudo-second order			
		q_e , cal (mg/g)	$k_1 \times 10^{-2}$ (min $^{-1}$)	$V_0 \times 10^{-2}$ (mg/g min)	R^2	q_e , cal (mg/g)	$k_2 \times 10^{-4}$ (g/mg min)	$V_0 \times 10^{-2}$ (mg/g min)	R^2
CHT2(Pd–Sn)	3.13	7.29	0.16	1.17	0.8806	4.61	14.74	3.13	0.9727
CHT3(Pd–Sn)	4.21	10.69	0.13	1.39	0.8426	5.05	28.30	7.22	0.9931
CHT4(Pd–Sn)	4.29	17.84	0.06	1.07	0.7645	4.68	55.31	12.11	0.9945
CHT5(Pd–Sn)	4.26	11.77	0.11	1.29	0.8257	4.87	49.99	11.86	0.9972

Fig. 3. Kinetics of nitrate adsorbed onto CHTX(Pd–Sn) at 25 °C (sorbent dose: 5 g/L; initial NO_3^- -N concentration: 22.58 mg/L).

of this model had been applied in a number of studies [36–38]. It can be expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (10)$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption. To simplify the equation, by applying the boundary conditions $q_t = 0$ at $t = 0$, this equation becomes

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e}. \quad (11)$$

Plotting t/q_t against t , a line is obtained and the rate constant k_2 as well as q_e can be calculated. And the initial sorption rate can also be expressed as

$$V_0 = k_2 q_e^2. \quad (12)$$

In the above two kinetics models, Eqs. (8) and (11) offer methods to calculate rate constant k . These constants can give information concerning rate-limiting steps. Equations (9) and (12) provide methods to calculate adsorption rate, which is a very important parameter for describing the adsorption process. Table 2 lists the results of experimental data fitted to the two kinetics models. It can be seen that the experimental data of CHTX(Pd–Sn) are in better agreement with the pseudo-second-order kinetics model than the first-order kinetics model. The correlation coefficient R^2 shows higher correlation, suggesting that the nitrate adsorption process appears to be controlled by chemical sorption processes [24]. After being calcined, the CHTX(Pd–Sn) generated positive charges which were the reason for the adsorption of anions from aqueous solution. Therefore the adsorption kinetics type was attributed to chemical sorption.

As shown in Table 2, it should be noted that the initial sorption rate of nitrate on the four CHTX adsorbents have the tendency

Fig. 4. Adsorption isotherm of nitrate on CHTX(Pd–Sn) at 25 °C.

$\text{CHT2(Pd–Sn)} < \text{CHT3(Pd–Sn)} < \text{CHT5(Pd–Sn)} < \text{CHT4(Pd–Sn)}$ and the rate constant k_2 is in the same order. This implies that the integrative adsorptive affinity between nitrate and CHTX(Pd–Sn) becomes stronger as the Mg/Al atomic ratio increases from 2 to 4, and then become weaker as the ratio increases from 4 to 5.

3.2.2. Equilibrium study

The equilibrium isotherms of nitrate uptake by CHTX(Pd–Sn) from synthetic water are shown in Fig. 4. Isotherms for nitrate sorption by CHTX(Pd–Sn) were modeled by two commonly used isotherm equations: Langmuir and Freundlich. The adsorption constants of isotherms are listed in Table 3.

It can be seen from Table 3 that the Langmuir isotherm is a better fit to the experimental data than the Freundlich isotherm on the basis of the correlation coefficients (R^2). Over the entire concentration range studied, the uptake of nitrate by CHTX(Pd–Sn) is in the order of $\text{CHT2(Pd–Sn)} < \text{CHT3(Pd–Sn)} < \text{CHT5(Pd–Sn)} < \text{CHT4(Pd–Sn)}$. This sequence was the same as the result of previous kinetics study. From the adsorption isotherm, the maximum NO_3^- -N adsorption capacity Q_0 was obtained for CHT2(Pd–Sn) of 11.23 mg/g, CHT3(Pd–Sn) of 26.88 mg/g, CHT4(Pd–Sn) of 33.70 mg/g, and CHT5(Pd–Sn) of 33.20 mg/g. The removal of nitrate by different adsorbents has been studied in recent years and some of this research has provided adsorption capacities of nitrates [4–6]. The CHT4(Pd–Sn) shows much more efficiency and larger adsorption capacity for nitrate removal compared with other adsorbents (Table 4). The ideal stoichiometric uptake calculated by Eq. (2) was 66 mg/g for CHT4. However, Eq. (2) was based only on the assumption of 100% electrical compensation for positive layers in the adsorption process, in which the interlayer spacing was not considered as an influential factor. Therefore, it was understandable that the experimental adsorption capacity (33.70 mg/g) was lower than ideal stoichiometric uptake value (66 mg/g).

In this study, the results of XRD analyses demonstrated that as the Mg/Al atomic ratio increased from 2 to 5, the interlayer spac-

Table 3

Sorption isotherm parameters for different adsorbents (C_e , the concentration of nitrate solution at equilibrium; Q_0 , the maximum sorption capacity; K_L , K_F , and n , sorption isotherm constants).

Adsorbent	Langmuir: $q_e = \frac{Q_0 C_e K_L}{1 + C_e K_L}$			Freundlich: $q_e = K_F C_e^n$		
	Q_0 (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg) ⁿ	n	R^2
CHT2(Pd–Sn)	11.23	0.266	0.9976	3.42	0.3233	0.9504
CHT3(Pd–Sn)	26.88	0.434	0.9893	10.74	0.2552	0.9646
CHT4(Pd–Sn)	33.70	0.992	0.9983	17.37	0.2017	0.9265
CHT5(Pd–Sn)	33.20	0.421	0.9930	16.11	0.1786	0.9638

Table 4

Maximum nitrate adsorption capacities of some adsorbents.

Adsorbent	Max adsorption capacity NO_3^- -N (mg/g)	Ref.
Activated sepiolite	8.62	[4]
Bamboo powder charcoal	1.25	[5]
Purolite A 520E	18.51	[6]
CHT4(Pd–Sn)	33.70	This study

ing of CHTX(Pd–Sn) rose, which benefited the adsorption of nitrate. However, in view of the trend of zeta-potential to decline with the increase of Mg/Al atomic ratio (Fig. 2), higher Mg/Al atomic ratios would debased the adsorption capacity of CHTX(Pd–Sn). So it was speculated that the adsorption capacity of CHTX(Pd–Sn) for nitrate was determined by interlayer spacings and zeta-potentials. When the Mg/Al atomic ratio increased from 2 to 4, the influence of interlayer spacing is dominant. That is, higher Mg/Al atomic ratios enhanced the adsorption capacity. When the Mg/Al atomic ratio further increased from 4 to 5, there was a negative impact on the adsorption capacity of the zeta-potential, resulting in that the adsorption capacity of CHT4(Pd–Sn) is higher than that of CHT5(Pd–Sn). So the maximum adsorption capacity was obtained at a Mg/Al atomic ratio of 4.

3.3. The effect of Mg/Al atomic ratio on catalytic process

Fig. 5 is the typical catalytic behavior of the CHT4(Pd–Sn), in which the concentration of ammonium and nitrite formed during the catalytic nitrate reduction as by-products is plotted. As described in our previous publication [31], nitrite appeared as a primary and unstable product; it increased slowly with reaction time, presented a maximum concentration at 85.1% of nitrate conversion, and then decreased. Ammonium as a kind of final product increased during the whole reaction time.

It could be noted that the concentration of released NO_2^- -N had the tendency $\text{CHT2(Pd–Sn)} > \text{CHT3(Pd–Sn)} > \text{CHT5(Pd–Sn)} > \text{CHT4(Pd–Sn)}$, in reverse order of its adsorption capacity (Fig. 6a). However, there was no significant tendency of ammonium generation by these catalysts. After a 240-min reaction, the final concentration of NH_4^+ -N was 1.24, 1.26, 1.16, and 1.12 mg/L for CHT2(Pd–Sn), CHT3(Pd–Sn), CHT4(Pd–Sn), and CHT5(Pd–Sn), respectively. The result of a different tendency here could be explained by the different adsorption capacity of CHTX(Pd–Sn) with various Mg/Al atomic ratios. According to previous studies [30,31], hydrogenation reduction of the nitrate process contains several steps: nitrates were first adsorbed by ionic forces between the layers; then the nitrates were reduced by the Pd/Sn active sites to nitrites; finally the nitrites were further reduced to nitrogen or ammonium. Since the first reduction step did not change the charge of the anions adsorbed between the positively charged layers, the generated nitrites should remain in the interlayer space to compensate the positive charges on the layers. And some of superabundant nitrites were released into water as a primary and unstable product. In this study, released nitrite concentration of the catalysts had the re-

Fig. 5. Typical catalytic behavior of CHT4(Pd–Sn) at 25 °C (initial NO_3^- -N concentration: 22.58 mg/L; catalysts dose: 2 g/L; H_2 : N_2 = 100:200 ml³/min).

verse tendency with its adsorption capacity. CHT4(Pd–Sn) had the highest adsorption capacity and released the lowest NO_2^- , whose maximum concentration of released NO_2^- -N was only 0.178 mg/L during the whole process (Fig. 6a).

Fig. 6b lists the activity, selectivity, and final NH_4^+ -N and maximum NO_2^- -N concentration of the four catalysts. The nitrate removal rate reached 75.6%, 84.1%, 89.3%, and 86.8% after 240 min hydrogenation for CHT2(Pd–Sn), CHT3(Pd–Sn), CHT4(Pd–Sn), and CHT5(Pd–Sn), respectively. Thus the activity of the four catalysts had the following order: $\text{CHT2(Pd–Sn)} < \text{CHT3(Pd–Sn)} < \text{CHT5(Pd–Sn)} < \text{CHT4(Pd–Sn)}$. The selectivity of catalysts mainly related to concentrations of the by-products generated during the catalysis process. Since the concentration of nitrite generated during the whole hydrogenation reduction had the tendency of $\text{CHT2(Pd–Sn)} < \text{CHT3(Pd–Sn)} < \text{CHT5(Pd–Sn)} < \text{CHT4(Pd–Sn)}$, and the ammonium concentrations did not show much difference, the selectivity of catalysts had the same sequence: $\text{CHT2(Pd–Sn)} (87.3\%) < \text{CHT3(Pd–Sn)} (91.6\%) < \text{CHT5(Pd–Sn)} (92.8\%) < \text{CHT4(Pd–Sn)} (94.0\%)$.

It can be concluded that the slight differences of activity, selectivity, and maximum NO_2^- -N concentration between the four catalysts were mainly due to the adsorption capacity difference. CHT4(Pd–Sn) with the highest adsorption capacity had the highest nitrate removal rate and released the lowest NO_2^- -N, hence exhibiting the highest catalytic activity and selectivity.

4. Summary

Catalysts with higher Mg/Al atomic ratios had larger interlayer spacings and lower electrical affinities. The effects of interlayer spacing and electrical affinity on sample adsorption properties were adverse. The maximum adsorption and reduction capacity of

Fig. 6. (a) Maximum concentration of released NO_2^- -N compared with its maximum adsorption capacity of nitrate. (b) Activity, selectivity, final NH_4^+ -N and maximum NO_2^- -N concentration of each catalyst at 25°C (initial NO_3^- -N concentration: 22.58 mg N/L; catalysts dose: 2 g/L; H_2 : N_2 = 100:200 ml³/min).

nitrate by CHTX(Pd-Sn) was obtained at $\text{Mg}/\text{Al} = 4$. The adsorption kinetics and isotherm of nitrate could be satisfactorily described with the pseudo-second-order model and the Langmuir model, respectively.

During hydrogen reduction of nitrate, the nitrates were first forced to be adsorbed between the positively charged layers of the catalysts and then reduced to nitrites that remain in the same position. The difference of adsorption capacity led to the different concentrations of released NO_2^- -N. Furthermore, the activity and selectivity of the catalysts had the same sequence as its adsorption capacity.

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