Catalytic Reduction of Nitrate by Pd/SnO₂ catalyst Using Formic Acid as Reducing Agent

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Abstract—In current study, the Pd/SnO₂ catalyst had been prepared successfully by using precipitation method and its characters were analyzed by XRD (X-ray diffraction), SEM (Transmission electron microscopy) and Specific surface area analyzer etc. The catalytic reduction of nitrate (100ppm) in deionized water was investigated in a batch reactor at room temperature and atmospheric pressure, with formic acid (FA) used as reducing agent. The results showed that nitrate could be removed completely by Pd/SnO₂ catalyst based on 3.2mmol of FA and optimal pH value of 3.

Key words-Formic acid; Catalytic reduction; Nitrate; Pd/SnO₂

I. INTRODUCTION

In theory, Chemical catalytic reduction can completely transfer nitrate into N₂ at rapid reaction rate, and is considered to be one of the most promising methods for nitrate removal [1]. Catalytic hydrogenation of nitrate with hydrogen as the reductant was first described in 1989 by Vorlop et al [2]. It is generally believed that bimetallic catalysts are more efficient in comparison to monometallic ones. Recently, it also found that TiO₂, CeO₂, SnO₂ carrier can promote the role of Pd and reduce nitrate. Therefore, improving the carrier can also obtain a good catalytic efficiency [3-5].

With hydrogen as reducing agent, a sharply increase of pH value to 10 cannot be avoided. It will induce a polarization of the support and has a repulsive effect on nitrate and nitrite, inducing a decrease in the activity and selectivity in the nitrogen [6]. Recently, different kinds of reducing agent such as formic acid, methanol, humic acid, sodium formate were tested to replace of hydrogen [7-9]. The FA can be easily decomposed into H₂ and CO₂, which were used either for its acidic properties or as a reducing agent [10-11].

In current study, nano-Pd/SnO₂ catalyst was successfully prepared by precipitation method and characterized by XRD, SEM and Specific surface area analyzer. The effect of formic acid on catalytic reduction of nitrate was studied by reduction of nitrate (100ppm) in wastewater in a batch reactor at room temperature and atmospheric pressure.

II. EXPERIMENTAL

A. Catalyst Preparation

An initial synthesis of nanometer-sized SnO₂ followed the procedure described by Zhang et al [12]. Once obtained,

nanometer-sized SnO₂ was mixed with an aqueous solution containing appropriate amount of PdCl₂. The mixture was stirred for 30 min in inert atmosphere and sequential drying at room temperature for 24h and at 120 °C for 2 h. then calcined at 350 °C in ceramic furnace for 3 h. After that, the materials were reduced by excess sodium borohydride solution at room temperature for 30 min and dried at 100 °C for 2 h in vacuum drying oven. The catalysts obtained from this procedure are called nano-Pd/SnO₂ catalysts.

B. Catalyst characterization

Powder X-ray diffraction (XRD) was carried out on a Bruker D8 X-ray diffraction meter with Ni-filtered Cu K α radiation ($\lambda=1.54056$ nm). The scanning rate was 10/min in the 2 θ diffraction angle between 10° and 80°. The SnO₂ particle size was calculated by or according to analyzing the SnO₂ (111) diffraction peak. The BET specific surface areas were measured by nitrogen adsorption and desorption at -196 °C on a Micromeritics ASAP 2000 instrument. Samples were pre-treated at 200 °C under vacuum (1.33 Pa). The morphology of the samples was determined by a SEM-3700N with an accelerating voltage of 200 kV. A certain amount of the samples was first suspended in 2-propanol, and then a small drop of each suspension was deposited on a thin amorphous carbon-coated copper grid.

C. Catalytic experiments

Catalytic experiments were performed according to the following procedure: powder catalysts (128mg) were placed in a three-mouth flask (500 ml). Several ports were installed in the batch reactor which convenient for the inpour of formic acid and N₂ and sample. The wastewater (200 ml) contained 100 mg/l of nitrate was prepared by dissolving NaNO₃ in deionized water. A certain amount of formic acid (0.8 mmol~6.4 mmol) was then added into the reactor for testing its reduction ability to nitrate. A magnetic stirrer was used to enhance the mix of the liquid. The reaction was maintained at atmospheric pressure and at a room temperature. Samples were taken from the reactor at desired sampling times and filtered through a 0.22 μ m membrane. NO₃⁻ and NO₂⁻ were determined by a Dionex-90 ion chromatograph, while the NH₄⁺-N was determined by using Nessler's method.

III. RESULTS AND DISCUSSION

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A. Catalyst characterization

The XRD pattern of SnO₂ power and Pd/SnO₂ catalysts are shown in Fig. 1. The XRD data of SnO₂ power is consistent with the literature, which report formation of tin oxide as a result of the fusion method from aqueous SnCl₂ and NaNO₃ solutions. The crystal size of SnO₂ is calculated from the full width at half maximum of the diffraction peak [110] using Scherrer equation. It is found that the crystal size of SnO₂ is 8.9 nm. The Pd/SnO₂ catalyst could be successfully synthesized by precipitation method according to the Pd (111) diffraction peak at 40.115° and Pd (200) diffraction peak at 46.848°. It is found that the Pd crystal size of Pd/SnO₂ is 24.4 nm. It is noticeable that addition of Pd metal slight increased the surface area of Pd/SnO₂ (SnO₂, surface area 21.6 m²/g, Pd/SnO₂, surface area 24.2 m²/g). Fig. 2 shows the SEM photograph of Pd/SnO₂ catalysts. As can be seen (Fig. 2) the morphology of Pd/SnO₂ catalysts almost are tetragonal phase.

B. Decomposition mechanics of FA

Effect of the nitrate on FA decomposition was shown in Fig. 3. The Fig. 3 confirmed that no FA conversion was observed in the presence of nitrate. This result also showed that nitrate promotes the catalytic conversion of FA. Ruthven and Upadhye [13] have demonstrated that the FA can be decomposed on palladium black in liquid phase between 30 and 60 °C. According to Eq (1), Eq(2) and Eq(3), the FA decomposition requires two adjacent sites allowing the dissociative adsorption

Logically, the promoting effect of nitrate could be explained by the reduction of these species indirectly (reduction of the promoter oxidized during nitrates reduction) allowing the uptake of the hydrogen species generated during Eq (2) that is the kinetically determining step, thus increasing the rate of the FA decomposition.

C. Effect of the reaction time on nitrate reduction

Fig. 4 presented the experimental curves for nitrate reduction with a monometallic palladium supported on tin oxide and 3.2mmol of FA under nitrogen.

As is shown in Fig. 4, the reduction rate of nitrate was very fast in initial few minutes. We speculated that high activity was attributed to the low pH value of the reaction liquid and adsorption performance of Pd/SnO₂. The FA decomposition could limit the reduction rate of the nitrate.

It is noticeable that little intermediates were formed during the nitrate reduction in presence of FA. Centi and Perathoner [14] have demonstrated that the amount of intermediate nitrite in solution decreases with the pH.

D. Effect of the initial concentration of formic acid on nitrate reduction

According to Eq (1), Eq (2) and Eq (3), the FA can be decomposed to form hydrogen and carbon dioxide during nitrate reduction reaction. Then nitrate is reduced to nitrogen or NH₄⁺ under hydrogen according reaction scheme of the catalytic nitrate reduction. Therefore, nitrate reduction with formic acid as reducing agent can be described correctly by following chemical equation.

In theory, about 0.8 mmol of FA was needed for the complete conversion of nitrate (20 mg) into nitrogen according to Eq (7). In order to determine the optimum ratio between initial amounts of FA introduced in the reaction media and nitrate, effect of the initial concentration of formic acid on nitrate reduction and the variation of pH before and after reaction are investigated. As shown in Fig. 5, nitrate can be removed completely only when the initial concentration of FA up to 3.2 mmol. With 0.8 mmol of FA, the conversion of nitrate was only 36.15%. Table1 showed that with FA initial amount of 0.8 mmol and 1.6 mmol, the final pH of reaction solution reach to 9.3 and 8.6. This pH gradient is unacceptable

Table.1 Effect of initial concentration on catalytic performances of different catalysts for nitrate reduction

Initial amount of formic acid (mmol)	pH _a	pH _b	Nitrate conversion (%)
0.8	3.6	9.3	36.15
1.6	3.3	8.6	63.01
3.2	3.1	6.8	100
6.4	2.8	6.1	100

Reaction conditions: catalyst 0.128 g, nitrate 100 mg/l (200mL), temperature 25°C, without pH control. pH_a the pH value of adding formic acid, pH_b the final pH value of reaction.

for drinking water. Moreover, Vorlop and Prüsse have demonstrated that basic pH would induce a polarization of the support and has a repulsive effect on nitrates, inducing a decrease of the activity and the selectivity in nitrogen. It is no question that the FA serves as an 'in situ' buffer for the inhibitor OH⁻, but sufficient amount of FA should be needed to prevent sharply increase of pH. The best molar ratio between FA and nitrate could be settled in 4 for nitrate reduction.

E. Effect of the pH on nitrate reduction

According to Eq. (2) and Eq. (3), a certain amount of hydroxide ions would be formed in this reaction. Using formic acid as reductant, formed carbon dioxide can be served as an 'in situ' buffer for the inhibitor OH⁻. However, above results show that if the initial concentration of formic acid is too low, the pH value also would increase to 8 or 9.

The activity and selectivity of the nitrate reduction strongly depends on the pH value [15]. For the catalytic reduction of nitrate by the Pd-Cu catalysts, the activity considerably decreases whereas the ammonium formation rises with increasing pH value. The optimum pH for nitrate reduction with Pd-Cu/γ-Al₂O₃ catalysts was 4, with Pd-Cu/TiO₂ catalysts was 10 and Pd-Sn/SiO₂ catalysts was 3 [16-17]. These results suggested that the optimum pH value of nitrate reduction mostly depended on the catalyst and support.

Effect of the pH value on conversion of nitrate and NH₄⁺ formation was displayed in Fig. 6, different activity and selectivity could be noticed when the pH increased from 2 to 9. These results show that the maximum activity of nitrate

reduction was achieved at pH 3 accompanied with increased NH_4^+ formation. Obviously, sharply increase or decrease of pH would inhibit nitrate reduction. Almost no nitrates reduction was observed when the pH up to 8 or 9. These figures also explained the reason why the nitrate decomposition rate was so fast in initial few minutes and the activity decrease with prolong of time.

IV. CONCLUSIONS

This study suggests that

- Monometallic nano-Pd/SnO₂ catalysts could be successfully synthesized by the precipitation method.
- The nitrates could promote the catalytic conversion of FA.
- Nitrate in deionized water can be reduced by Pd/SnO₂ catalyst with FA as reducing agent.
- In this work, the best molar ratio between FA and nitrate is 4, it leads to a complete conversion of nitrate.
- For nitrate reduction by Pd/SnO₂ catalyst with FA as reducing agent, the best pH value is at 3.

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