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Effect of chlorine on performance of Pd catalysts prepared via colloidal immobilization

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ABSTRACT

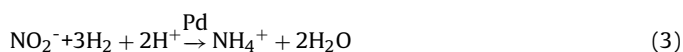
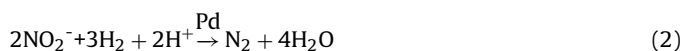
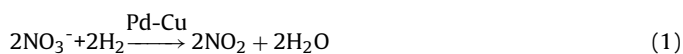
This contribution shows the effect of residual chlorine on the catalytic performance of a Pd-based catalyst in the hydrogenation of nitrite for cleaning of drinking water. The catalyst was prepared via immobilization a colloidal Pd nanoparticles using activated carbon as support. Different amount of hydrochloric acid (HCl) was added to immobilize the Pd colloid on the carbon support, facilitating the removal of the residual stabilizer, polyvinyl alcohol (PVA), from the surface of the Pd nanoparticles (NPs). The catalysts were characterized by TEM, CO-chemisorption, XRF, N₂ physisorption, UV–vis spectroscopy, and XPS. The activity and selectivity of the catalysts were measured for nitrite hydrogenation in semi-batch operation. The results show that PVA can be removed completely at pH below 2. The residual chlorine on the catalysts can be removed by reduction in H₂/N₂ at a mild temperature, i.e. 200 °C, regardless the amount of HCl used. Nevertheless, high concentration of HCl during immobilization (pH 1) causes partial Pd re-dissolution according to UV–vis spectroscopy, resulting in formation of highly dispersed Pd clusters that could not be detected with TEM. Reduction of this catalyst with high chlorine content in H₂ at 200 °C is resulting in formation of relatively large Pd particles via sintering. Without pre-reduction at 200 °C, residual chlorine can also be removed almost completely during the hydrogenation reaction at room temperature. The activity of the Pd catalyst is insensitive to the chlorine concentration below 30 μmol L⁻¹ in the aqueous reaction mixture. Interestingly, the selectivity to N₂ is improved by adding chlorine to the reaction mixture, independent of the way chlorine is added, i.e. via the catalyst or added directly to the reaction solution.

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1. Introduction

Nitrate and nitrite contamination in groundwater has become a rising risk for supplying of drinking water, especially in agricultural areas where synthetic nitrogen fertilizers are extensively used [1–3]. Catalytic hydrogenation of nitrate/nitrite (Eqs. (1)–(3)) using Pd-based catalysts has been developed since the late 1980s, as a highly efficient method operated under mild conditions (typically around 25 °C and ambient pressure) [4,5]. This method prevents formation of any contaminating brines as in ion-exchange proce-

dures, and is able to convert nitrate and nitrite in water lacking any organic contamination, as is required for biological treatment [6,7].



Colloidal method has been developed extensively for preparation of metal nanoparticles (NPs) for catalytic application in the last few decades [8,9]. The advantage of the method is well-known: the sizes of the NPs can be well controlled and manipulated, facilitating studies on structure–performance relationships. Advanced methods allow formation of NPs with well-defined shapes, offering interesting opportunities on even more detailed studies on the influence of surface structure on catalysis [10,11].

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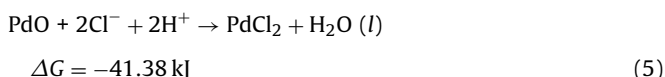
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Pd based catalysts for nitrate/nitrite hydrogenation have been studied using colloid preparation methods [11–16], reporting that the rate of nitrite hydrogenation is independent on Pd particle size [14,17,18]. Nevertheless, it is also well reported that residual stabilizers, such as polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP), can block part of the active sites by covering the majority of the metal surface [14,19–22]. Stabilizers and capping agents can also manipulate adsorbed reactive species on metal surface, influencing the activity as well as the selectivity of Pd catalysts [14,22–25]. As a result, it is generally preferred to remove the residual stabilizers on metal surface.

Removal of the residual stabilizers is challenging, normally including oxidation and thermal treatment, making it difficult to maintain particle size and crystal structure of the NPs, and still, the removal can be incomplete [26–30]. In our previous work [13], the Pd colloid was immobilized on activated-carbon (AC) in aqueous HCl solution at pH 2. It was observed that PVA could be completely removed from the Pd surface, according to TEM and CO chemisorption results. It was proposed that extensive chemisorption of Cl on the Pd surface, promoted by the presence of O₂ according to reactions in Eqs. (4) and (5), is weakening the interaction between PVA and the NPs [13].



After the PVA removal, the catalysts were reduced mildly in H₂/N₂ atmosphere at 200 °C, in order to reduce PdCl₂ to Pd⁰, removing chlorine from the Pd surface. On the other hand, chlorine removal is not complete and a small but significant amount of chlorine remains on catalyst support i.e. activated carbon.

This contribution aims at optimization of the HCl concentration during immobilization of Pd-PVA colloid on activated carbon. The effect of residual chlorine influencing the activity and the selectivity in nitrite hydrogenation will also be shown.

2. Experimental

2.1. Chemicals

Sodium tetrachloropalladate(II) (Na₂PdCl₄ ≥ 99.995% (metal basis)), polyvinyl alcohol (PVA, average MW = 13000–23000, 87%–89% hydrolyzed), sodium borohydride (NaBH₄, ≥ 96% (gas-volumetric)), and formic acid (98%–100%) were purchased from Sigma-Aldrich. Sodium nitrite (>99%) was purchased from Merck. Activated carbon (AC, S_{BET} = 1000 m² g⁻¹) was supplied by Norit. AC was sieved in the range of 38–45 μm in diameter before used as catalyst support. All the aqueous solutions were prepared using ultra purified water obtained (Millipore, Synergy).

2.2. Pd colloid preparation

The preparation of palladium nanoparticles via colloidal method has been described previously, which can be summarized as follows [13]. PVA was dissolved in water at 70 °C with stirring for at least 2 h. The solution (2 wt%) was then cooled down to room temperature. Aqueous solution of Na₂PdCl₄ (20 mL, containing 0.086 mmol Pd) and 1.76 mL of freshly prepared PVA solution were added to 240 mL water, obtaining a yellow-brown solution. After 3 min, NaBH₄ solution (1.72 mL, 0.172 mmol) was added under vigorous stirring. The

brown Pd colloid solution was immediately formed. The final pH was typically 8–8.5.

2.3. Colloid immobilization

Typically, 0.75 g AC or graphite was added to the Pd colloid solution (260 mL, 3.3 × 10⁻⁴ mol L⁻¹) immediately after preparation. Hydrochloric acid (HCl) was added to adjust pH to either 1, 2 or 3. The slurry was stirred in air with a mechanical 6-blade-stirrer (ϕ 44 mm, 1000 rpm) with the propeller positioned at the centre of liquid for 2 h at room temperature, filtered and thoroughly washed with water. After that, the catalysts were dried in vacuum at 40 °C overnight.

2.4. Catalyst reduction

Catalysts prepared as described above were carefully treated in a tube furnace. In a typical procedure, the temperature was raised to 200 °C at a rate of 5 °C min⁻¹, then kept for 1 h at 200 °C, in 10 vol% H₂/90 vol% N₂. Then the sample was flushed in N₂ for 30 min at 200 °C, and cooled down at a rate of 20 °C min⁻¹ to room temperature in the same atmosphere. The catalysts were flushed in N₂ for 24 h before exposure to air. In the following, the sample notation will be used as shown in Table 1.

2.5. Characterization

Pd particle size distribution was determined using TEM (Philips CM300ST-FEG) allowing reliable detection of metal nanoparticles of 1 nm and larger on AC. The AC supported catalysts were firstly ground into sub-micron fragments and dispersed in ethanol. Then the suspension was dropped on a copper grid covered with hollow carbon for TEM image taking. At least five of these fragments were randomly selected for determination of Pd particle sizes, and typically 300 Pd particles were measured. Note that information on the spatial distribution of nanoparticles through the support cannot be obtained as the samples were ground. The metal loading on the supports were analyzed by XRF. The total surface area of samples were calculated based on N₂ physisorption data, using the BET method for *p/p*₀ values between 0.03 and 0.13 for catalysts prepared with AC following the recommendations of Rouquerol et al. [31], with a typical error margin of 5%.

Re-dissolution of Pd by HCl was measured with UV–vis spectroscopy of the colloidal suspension in a UV-spectrometer (Perkin Elmer Lambda 850, wavelength from 200 to 800 nm, scanning speed 266.75 nm min⁻¹) at room temperature. The pH of freshly prepared unsupported Pd-PVA colloid suspension was adjusted to 1, 2 and 3 by adding HCl solution, followed by stirring the suspension in air atmosphere for 2 h. Then 500 μL of the treated suspension was introduced in a quartz cell (QS1000) for performing the measurement.

CO chemisorption at room temperature was used to determine the metal surface area that is accessible in gas phase. Typically, the sample was pre-reduced at room temperature in hydrogen and then flushed in He at the same temperature. Then CO was

Table 1
Sample notations and details of corresponding preparation procedure.

Sample	Preparation Procedure
Pd.AC.1.A	Pd-PVA colloid immobilized on AC using HCl to adjust pH to 1
Pd.AC.2.A	Pd-PVA colloid immobilized on AC using HCl to adjust pH to 2
Pd.AC.3.A	Pd-PVA colloid immobilized on AC using HCl to adjust pH to 3
Pd.AC.1.R	Pd.AC.1.A reduced in H ₂ /N ₂ at 200 °C
Pd.AC.2.R	Pd.AC.2.A reduced in H ₂ /N ₂ at 200 °C
Pd.AC.3.R	Pd.AC.3.A reduced in H ₂ /N ₂ at 200 °C

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