

Unsupported PVA and PVP stabilized Pd nanoparticles as catalyst for nitrite hydrogenation

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Introduction

Catalytic hydrogenation has emerged as a promising method to reduce nitrate and nitrite contaminations in drinking water since study starting from 1980s. [1] It has been demonstrated that a bimetallic system typically containing a noble metal (Pd or Pt) as well as a promoter (Cu, Ni, Sn, In, etc.) is necessary for nitrate hydrogenation with nitrite as a intermediate; whereas nitrite itself only require a monometallic catalyst for hydrogenation, and Pd was found to be a most active candidate. [2] Nitrogen is the aim product of the hydrogenation whereas ammonium can also form as a harmful by-product, and understanding on reaction mechanism as well as optimization on catalyst preparation are necessary for a best selectivity of catalyst.

Colloidal methods have been widely used to prepare nanoparticles (NPs) as model catalysts in both academic studies and industrial applications. Generally, stabilizing agents used for colloid preparation are regarded as surface poison and thus need to be removed. In previous work, polymer stabilizer polyvinyl alcohol (PVA) was completely removed from the surface of Pd NPs supported on activated carbon [3]. Interestingly, the polymer stabilizer on Pd NPs can also influence catalytic performance of the Pd NPs otherwise then just blocking sites. Somorjai et al. reported charge transfer interaction of polyvinyl pyrrolidone (PVP) with NPs of noble metal like Pt and Rh [4]. The choice of polymer used for stabilization of Pd colloids was found important to achieve both high activity and good selectivity [5].

In this contribution, colloidal Pd catalysts were prepared with PVA or PVP as polymer stabilizer. Different amount of polymer was used during catalyst preparation to vary the Pd particle size in range of 2 – 4 nm. This report shows the size-dependence of Pd catalysts on activity and selectivity, as well as the importance of the type of polymer for a high selectivity to nitrogen.

Materials and Methods

Colloidal Pd catalysts were prepared via a variation of method reported elsewhere. [6] Typically aqueous solution of Na₂PdCl₄ (20 mL, containing 0.086 mmol Pd) and 1.76 mL of freshly prepared polymer 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 with a syringe pump under vigorous stirring. Brown Pd colloid solution was immediately formed.

The as-prepared catalysts were tested in a home-build slurry reactor without any further separation or washing, and ion chromatographs were used to determine the concentrations of nitrite and ammonium during the reaction. Pd particle sizes were observed by TEM and the numbers of active sites in aqueous phase were determined by CO chemisorption

in aqueous phase. ATR-IR was used to reveal the interaction between polymer and Pd nanoparticles.

Results and Discussion

TEM images show Pd particle sizes increased with decreasing amount of polymer used during colloid preparation, varying from 2 to 4 nm in diameter, with sphere shaped. No significant increase was observed by CO chemisorption, indicating polymer blocking Pd surface. On the other hand, the initial activity of Pd colloid increased with increasing of number of active site determined by CO chemisorption as shown in **Figure 1**, indicating nitrite hydrogenation on Pd catalyst is size independent in this study.

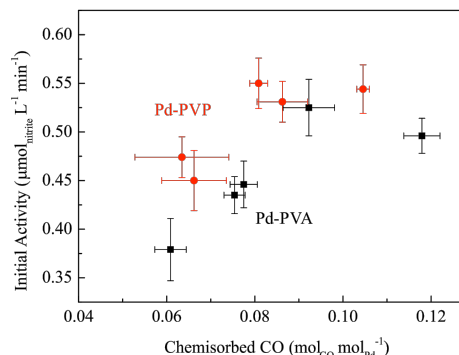


Figure 1 Initial activity of Pd colloids as function of the amount of CO chemisorbed on Pd colloid per mole of Pd.

The results also show that the selectivity of the reaction, *i.e.* formation of N₂ versus NH₄⁺, is influenced by both the metal particles size (2-4 nm) as well as the choice of stabilizer; PVP suppresses the formation of NH₄⁺. The molecular interaction between Pd surface active sites and neighborhood polymer was investigated with ATR-IR in both gas phase and aqueous phase. The ability of Pd sites to dissociate H₂ is suppressed in the presence of PVP, resulting in decreasing formation of NH₄⁺ as compared to PVA stabilized Pd.

Significance

Nitrite hydrogenation on Pd catalyst performs size independent, and selectivity of Pd colloidal catalyst to ammonium increase with increasing Pd particle size in range of 2 – 4 nm. The present of PVP instead of PVA as stabilizer could also suppress ammonium formation via polymer-Pd interaction.

References

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