Product Selectivity Controlled by Steric Adsorption in Zeolite Micropores over a Pd@Zeolite Catalyzed Hydrogenation of Nitroarene

Jian Zhang,[a] Liang Wang,[a] Feng-Shou Xiao[a,]*
[a] *Department of Chemistry, Hangzhou, 310028, China*
**Corresponding author: 086-057188273334, fsxiao@zju.edu.cn*

Abstract: This work delineates the persuasive example for controlling the steric adsorption of molecules on metal nanoparticles by zeolite crystals, thus enhancing the product selectivity in hydrogenation of reactants with more than one reducible group. Key to this success is by fixing Pd nanoparticle inside of Beta zeolite crystals to form a fixed structure (Pd@Beta). In the hydrogenation of substituted nitroarenes with multiple reducible groups as model reaction, the Pd@Beta exhibits superior selectivity for the hydrogenation of the nitro group. The extraordinary selectivity of Pd@Beta is reasonably attributed to the steric adsorption of nitroarenes on Pd nanoparticle controlled by zeolite micropores.

Keywords: zeolite, Pd nanoparticle, selective hydrogenation.

1. Introduction

Numerous supported transition metals catalyze the hydrogenation of compounds such as olefins, aromatic hydrocarbons, carboxylic acids, aldehydes, and ketones, but when more than one reducible group is present in the reactant (such as in a nitroaromatic compound), most hydrogenation catalysts are non-selective. To overcome this limitation, various strategies such as introducing inorganic additives (e.g., Pb and V) or organic additives such as soluble compounds with N- or S-containing groups into these metal catalysts have been developed. Changing the mode of adsorption of the reactant molecules on the metal sites in ways that improve the selectivities. However, it is a challenge to tune the adsorption mode and to minimize the leaching of the organic groups from the metal surface.

In this work, we report a methodology for selective hydrogenation by sterically controlling the adsorption on metal@zeolite core-shell catalysts, whereby the advantages of metal nanoparticles with high catalytic activities and zeolite micropores facilitating selective adsorption of reactants are synergistically combined. Pd nanoparticles fixed inside the regular porous structure of crystalline zeolite Beta (Pd@Beta) give both high activities and excellent selectivities combined with long catalyst lifetimes.

2. Experimental

Synthesis of Pd@Beta. The metal nanoparticles fixed inside of zeolite crystals were synthesized by a two-step method. As a typical run for synthesis of the Pd@Beta, the Zeolite Beta seeds were impregnated with $PdCl_2$, followed by drying at 80 ℃ for 4 h, calcination at 400 ℃ for 4 h in air, and reduction at 300 ℃ in 10% H_2/Ar for 2 h to obtain Pd/seed Beta. Meanwhile, the synthesis gel was obtained from mixture of 0.64 g of $NaAlO_2$, 1.12 g of NaOH, 13.6 mL of H_2O, and 4 g of fumed silica. After stirring, a desired amount of Pd/Beta seeds was introduced into the synthetic gel. After hydrothermal treatment at 120 ℃ for 4 days, the samples were collected by filtrating, washing with water, and drying at room temperature.

3. Results and discussion

Figure 1A shows a scanning electron microscopy (SEM) image of Pd@Beta, demonstrating the uniform morphology. The scanning transmission electron microscopy (STEM) image gives direct evidence of the Pd nanoparticles within Pd@Beta (Figure 1B). The data show clearly that the synthesis technique completely prevents the formation of metal nanoparticles on the external surfaces of the catalyst particles—they are all encapsulated and subject to the steric control of the zeolite pores that provide the only access to the metal surface. Tomographic images of Pd@Beta (Figures 1C-E) confirms the encapsulation; the Pd nanoparticles can be observed directly, fully encapsulated inside of the zeolite Beta crystals. The images further show that the Pd nanoparticles with significantly brighter contrast than the zeolite crystals, are highly dispersed inside of the zeolite crystals, with a distribution of diameters of 0.9-3.1 nm (Figure 1F), which is very similar to the sizes of Pd nanoparticles on the seed, suggesting the Pd nanoparticles are stable during the zeolite crystallization.

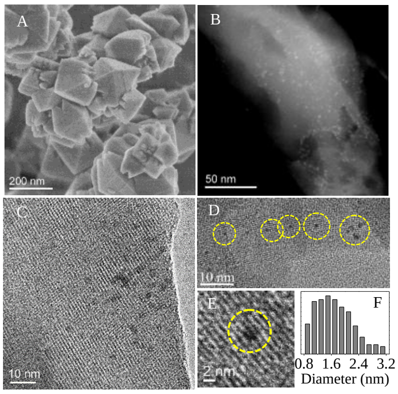

Figure 1. (A) SEM, (B) STEM, (C-E) HR-TEM images of Pd@Beta. The yellow cycles highlighted the Pd nanoparticle. (F) The size distribution of Pd nanoparticles on Pd@Beta.

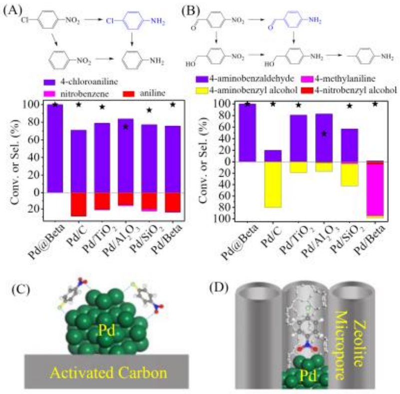

Figure 2. Data of substrate conversion (the black stars) and product selectivities (the colorized columns) characterizing the hydrogenation of (A) 4-nitrochlorobenzene and (B) 4-nitrobenzaldehyde with various catalysts. Reaction conditions: 1 mmol of substrate, 0.2 mol% Pd catalyst, 10 mL of toluene, 1 MPa H_2, 110 ℃ for 45 min in hydrogenation of 4-nitrochlorobenzene, 80 ℃ for 2 h in the hydrogenation of 4-nitrobenzaldehyde. Proposed model of 4-nitrochlorobenzene adsorbed on (C) Pd/C and (D) Pd@Beta. The blue, red, light green, dark green, gray, white circles represent N, O, Cl, Pd, C, and H atoms, respectively.

The zeolite pore diameters are small enough (~6.7 Å) that at the zeolite-metal interface they can constrain molecules interacting with the metal. Thus, the performance of the catalyst is expected to depend on how the reactants adsorb on the metal. Figure 2A shows catalytic conversion of 4-nitrochlorobenzene to 4-chloroaniline in the presence of various Pd-containing catalysts, whereby the selective hydrogenation of the nitro group (to give 4-chloroaniline) is a highly desirable practical goal. Normally, dechlorination occurs on the conventional supported Pd catalysts (Pd/C, Pd/TiO_2, Pd/Al_2O_3, and Pd/SiO_2), giving aniline as a by-product. As a result, the conventional catalysts exhibit 4-chloroaniline selectivities ranging from 70.9% to 89.6%. Significantly, Pd@Beta displays selectivity greater than 99.0%, and 4-chloroaniline is the sole product. These results suggest that Pd@Beta favors the reduction of nitro groups over chloro groups in our reactants. Similar results were also observed in the hydrogenation of nitroarenes incorporating carbonyl groups, with 4-nitrobenzaldehyde used as a model reactant (Figure 2B). Again, Pd@Beta exhibits excellent selectivity, with that to 4-aminobenzaldehyde being greater than 99.0%. If the Pd nanoparticles are not encapsulated with the zeolite crystals, the Pd/zeolite Beta gives very low selectivity for the aniline (1.6%). When 4-nitrochlorobenzene was adsorbed on Pd/C, both chloro- and nitro-groups might interacted with the Pd sites. The parallel adsorption of 4-nitrochlorobenzene on the surface of Pd nanoparticles, with both the nitro- and chloro- groups interacting with Pd sites (Figure 2C), could give hydrogenation of both groups. In contrast, when 4-nitrochlorobenzene is adsorbed on Pd@Beta, we infer that the molecule is parallel to the microporous channels due to the structure confinement (Figure 2D). Thus, the zeolite micropores change the sterics of the molecular adsorption on Pd sites in contact with these micropores, leading to the bonding of 4-nitrochlorobenzene to the Pd sites *via* the nitro group rather than aldehyde group or chloro group because of the stronger interaction of the nitro group than of chloro group with the metal surface.

4. Conclusions

In summary, we report a novel strategy to improve the selectivity of Pd nanoparticles in the hydrogenation of substituted nitroarenes by using a core-shell Pd@Beta catalyst obtained from a Pd-containing seed-directed synthesis of zeolite crystals. Because the zeolite micropores control the steric adsorption of substrate molecules on the Pd sites, the Pd@Beta exhibits outstanding selectivity and extraordinary stability for the hydrogenation of substituted nitroarenes to the corresponding anilines. The metals@zeolites catalysts reported here appear to open the way to developing a class of highly selective metal catalysts.

References

1. J. Zhang, L. Wang, Y. Shao, Y. Wang, B. C. Gates, F.-S. Xiao, Angew. Chem. Int. Ed 56 (2017) 9747.