

Metal nanocatalysts confined within hydrophobic zeolite for selective hydrogenation of nitroaromatics

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Abstract: This study focuses on the encapsulation of palladium-based nanocatalysts within Silicalite-1 zeolite through in-situ synthesis, with an aim to enhance the selective hydrogenation of nitroaromatic compounds. By controlling the size of palladium metal nanoclusters to approximately 1nm and incorporating hydrophobic organic groups into the zeolite framework, we significantly improved the hydrogenation efficiency. The modification with hydrophobic groups, specifically methyl groups, not only augmented the hydrophobicity of the zeolite but also its catalytic performance, especially for Pd@S-1-CH₃, in the hydrogenation of nitrobenzene, surpassing that of Pd@S-1. This modification was instrumental in achieving enhanced performance due to the improved mass transfer of reactants within the zeolite pores. The catalytic activity and stability of the modified catalysts were thoroughly investigated, with Pd@S-1-CH₃ demonstrating considerable activity and selectivity across various nitrobenzene derivatives. Notably, after 10 reaction cycles, the catalyst maintained high conversion rates and selectivity for 4-fluoronitrobenzene, underlining its robustness. This research provides valuable insights into the design of highly efficient and stable nanocatalysts for the selective hydrogenation of nitroaromatic compounds, offering a promising approach for the synthesis of aromatic amines, crucial intermediates in the chemical industry.

1. Introduction

Aromatic amines are extremely important and fundamental raw materials in the chemical manufacturing process, acting as pivotal intermediates in the fabrication of pharmaceuticals, dyes, pesticides, plastics, rubber, and various chemical products. The principal method for synthesizing aromatic amines involves the catalytic hydrogenation of nitroaromatic compounds, a process reliant on noble metal catalysts, including palladium and platinum [1]. The quest for efficient reduction of nitroaromatic compounds under benign conditions, with a concurrent reduction in by-product formation, represents a significant area of ongoing research. While palladium-based nanocatalysts facilitate the gentle catalysis of nitroaromatic compounds, the inadvertent production of by-products during practical application can compromise both product purity and yield. Furthermore, the high cost and the long-term stability associated with palladium-based nanocatalysts merit further investigation

Optimization of the catalytic activity of palladium-based nanocatalysts can be accomplished through meticulous control of the metal clusters' size and dispersity, alongside the judicious selection of suitable catalyst carriers. Such strategic manipulation facilitates precise control at the nanoscale. An illustrative example of this approach is provided by Fengshou Xiao et al.[2], who employed BEA-type zeolites for the encapsulation of palladium metal nanoclusters. The considerable surface area and distinctive pore architecture of the zeolite significantly enhance the selective adsorption of nitroaromatic compounds, thereby substantially improving product selectivity[3]. Additionally, the modification of the zeolite framework with organic functional groups—such as the incorporation of alkyl groups to augment its hydrophobicity—has been shown to positively influence the catalytic efficiency in oil-phase reactions.

Taking into account these considerations, the present study utilized the all-silica MFI-type zeolite, Silicalite-1 [4, 5]. Palladium metal nanoclusters were encapsulated within this structure through in-situ synthesis and subsequently reduced by hydrogen, with the cluster size meticulously controlled to approximately 1 nm[6]. Furthermore, the synthesis incorporated organosilanes bearing methyl groups, introducing hydrophobic entities into the zeolite framework. This modification resulted in the enhanced efficacy of the hydrophobic catalyst, Pd@S-1-CH₃, for hydrogenation reactions, surpassing that of Pd@S-1. The study further examined the hydrogenation reactions of various nitrobenzene derivatives and assessed the long-term stability of the catalyst. Notably, after 10 reaction cycles, the conversion rate and selectivity for 4-fluoronitrobenzene remained elevated, underscoring the catalyst's robust performance.

2. Method

2.1. Reagents and Materials

Tetrapropylammonium hydroxide solution (TPAOH, Shanghai Shaoyuan Co. Ltd.), tetraethyl orthosilicate (TEOS, Shanghai Hushi Chemical Co. Ltd.), Palladium chloride (Pd \geq 59%, Macklin), ethylenediamine (99.7%, Shanghai Hushi Chemical Co. Ltd.), triethoxymethylsilane (C₇H₁₈O₃Si, 98%, Macklin reagents), and trimethoxy(propyl)silane (C₆H₁₆O₃Si, 98%, Aladdin reagents).

2.2. Synthesis of Catalysts

In the synthesis process, 6.5 g of TPAOH was dissolved in 7.5 g of water. Subsequently, 4.16 g of TEOS was introduced and stirred until completely dissolved, establishing a molar ratio of 0.4:36:1 in the mother liquor with silicon at 20 mmol. Following this, 1 mL of a 0.18 mol/L Pd(en)₂Cl₂ solution was incorporated, which was prepared by dissolving 0.32 g of PdCl₂ in 2 mL of water and adding 2 mL of ethylenediamine, then diluting the mixture to 10 mL. The quantity of organosilane introduced constituted 0.5% of the molar quantity of Si, thus 0.1 mmol of triethoxymethylsilane was added to the synthesis mother liquor for the Pd@S-1-CH₃ catalyst. In a similar manner, for the Pd@S-1-C₃H₇ catalyst synthesis, 0.1 mmol of trimethoxy(propyl)silane was also included. The prepared mixture was then transferred to an autoclave lined with polytetrafluoroethylene and subjected to crystallization at 443 K for a duration of 4 days. Following crystallization, the resultant solid was thoroughly washed with water until it reached a neutral pH and subsequently freeze-dried. Finally, the catalyst powder underwent reduction under pure hydrogen at 673 K for 2 hours, culminating in the acquisition of the finalized catalyst.

2.3. Characterization of Catalysts

The phase composition of the catalyst was determined by X-ray diffraction (XRD) using a Cu

target ($\lambda = 1.5418 \text{ \AA}$). The composition and content of the metal loaded on the catalyst were ascertained through Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis. The morphological features were characterized using Scanning Electron Microscopy (SEM). The size and distribution of the metal nanoparticles were determined by Scanning Transmission Electron Microscope (STEM).

2.4. Hydrogenation Reduction of Nitroaromatic Compounds

In this study, 0.5 mmol of nitroaromatic compounds were dissolved in 5 mL of isopropanol. This solution was then subjected to ultrasonic dispersion with the addition of 10 mg of Pd@S-1-R catalyst. The catalytic reaction proceeded in a high-pressure autoclave, maintaining a hydrogen pressure of 1 MPa and a temperature of 353 K. The nitroaromatic compounds used in this paper include nitrobenzene, 4-fluoronitrobenzene, 4-chloronitrobenzene, 4-nitroaniline, 4-nitrotoluene, 4-nitroethylbenzene, and 2, 4-dimethylnitrobenzene, all from Macklin reagents.

Upon completion of the catalytic hydrogenation of nitroaromatic compounds, the reaction products were diluted and subjected to analysis via gas chromatography (GC-9790, Fuli Instruments), utilizing a flame ionization detector (FID).

2.5. Preparation and characterization of catalysts

The X-ray diffraction patterns for the Pd@S-1-R catalyst and Silicalite-1 support, depicted in Figure 1, show congruence, both characteristic of MFI-type zeolites. Notably, there were no detectable peaks for metallic palladium or its oxides, suggesting the palladium nanoclusters are encapsulated within the zeolite rather than being located on its surface.

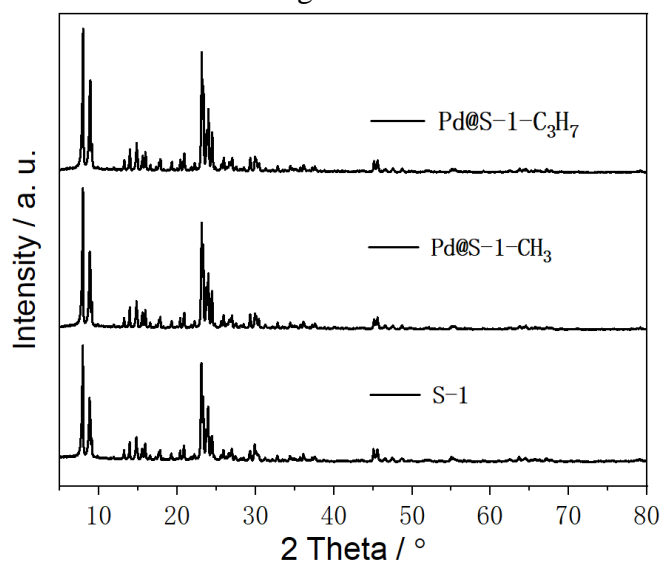


Figure 1: XRD patterns of S-1 and Pd@S-1-R samples.

The SEM images of the Pd@S-1-R catalyst, shown in Figure 2, confirm that the inclusion of organic functional groups does not alter the intrinsic hexagonal prism shape of the Silicalite-1 zeolite. Furthermore, the STEM images of the Pd@S-1-R catalyst, as shown in Figure 3, demonstrate that the metals are uniformly dispersed within the zeolite with an average particle size of around 1 nm. This demonstrates the effective encapsulation of metal clusters by ligand-protect method.

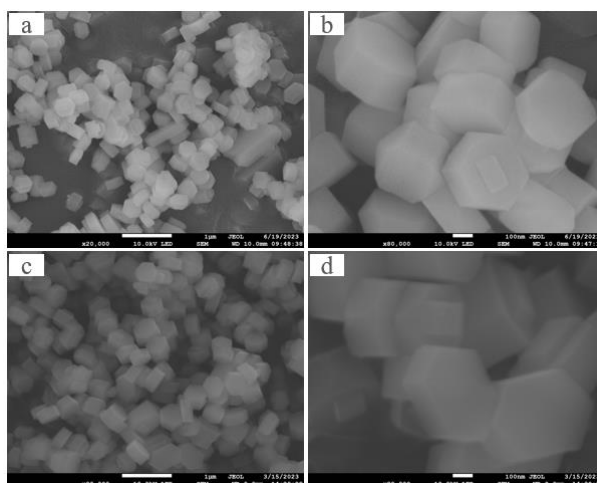


Figure 2: SEM images of (a-b) Pd@S-1-CH₃ ,(c-d) Pd@S-1-C₃H₇ .

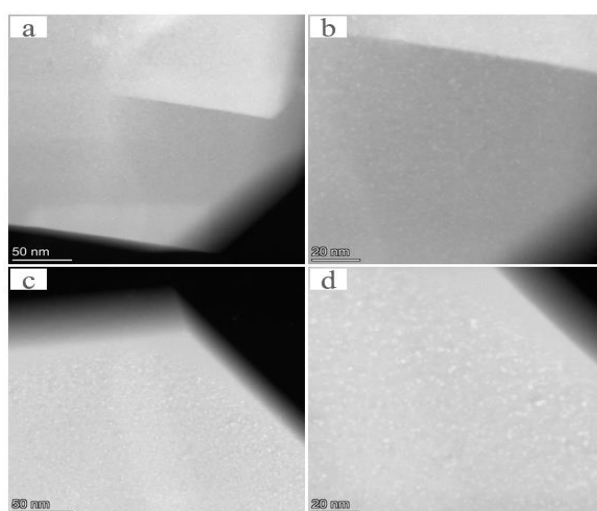


Figure 3: STEM images of (a-b) Pd@S-1-CH₃,(c-d) Pd@S-1-C₃H₇ .

Figure 4 illustrates the significant enhancement in hydrophobicity upon the incorporation of methyl groups into the zeolite framework, confirming the successful functionalization with organic moieties.

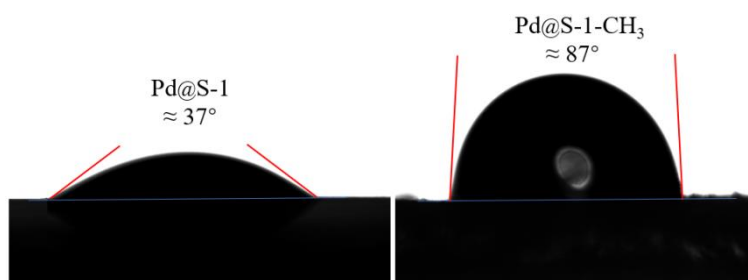


Figure 4: Contact angles of water droplets on the surface of samples.

2.6. Catalytic Performance of Hydrophobic Modification for Nitroaromatic Compounds

Table 1 reveals that the integration of hydrophobic groups led to an improved hydrogenation efficacy of Pd@S-1-CH₃ towards nitrobenzene. Conversely, the incorporation of bulkier propyl groups in Pd@S-1-C₃H₇, coupled with an increase in zeolite dimensions, impeded the mass transport

of reactants within the zeolite pores, adversely affecting the catalytic performance. The Pd@S-1-CH₃ exhibited the highest catalytic activity for the nitrobenzene hydrogenation, affording a notable turnover frequency (TOF) of 354.7 h⁻¹ at 353 K.

Table 1: Hydrogenation performance of nitrobenzene

Sample	Time/h	Con/%	Sel/%	TOF/h ⁻¹
Pd@S-1-C ₃ H ₇	1	9.92	100	87.9
	3	11.23	100	
Pd@S-1	1	26.33	100	233.5
	3	88.54	100	
Pd@S-1-CH ₃	1	40.31	100	357.4
	3	100	100	

As shown in Figure 5a, Pd@S-1-CH₃ exhibits substantial catalytic activity and selectivity (> 97%) selectivity for hydrogenation of various nitroaromatics (4-fluoronitrobenzene, 4-chloronitrobenzene, 4-bromonitrobenzene, 4-nitrophenol, and 4-nitrotoluene), making it an excellent catalyst for the hydrogenation reduction of nitroaromatic compounds. Pd@S-1-CH₃ catalyst showed no conversion for hydrogenation of 2,4-dimethylnitrobenzene, whose molecular size was larger than the pore size of silicalite-1. This result further proved that metal nanoclusters did not appear on the zeolite surface. Moreover, the activity of the Pd@S-1-CH₃ catalyst in reducing 4-fluoronitrobenzene to 4-fluoroaniline did not decrease over ten cycles, as shown in Figure 5b. Moreover, STEM analyses confirmed that the zeolite structure and metal size of Pd@S-1-CH₃ catalyst kept unchanged after ten cycles for 4-fluoronitrobenzene hydrogenation, with no aggregation could be observed as shown in Figure 6.

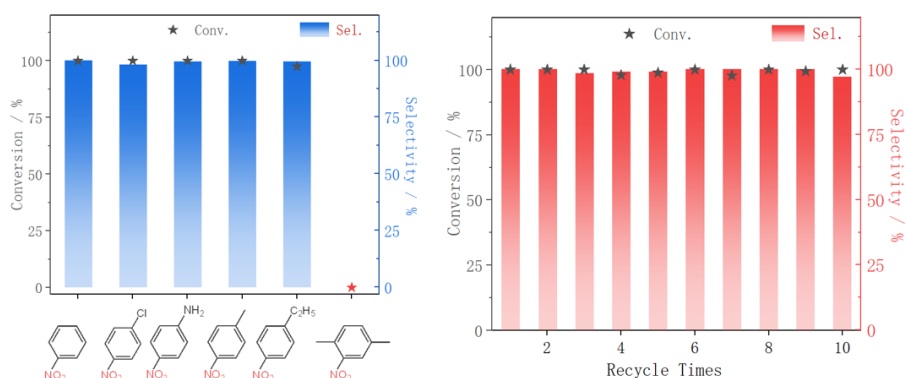


Figure 5: Catalytic performance of Pd@S-1-CH₃ for (a) for hydrogenation of various nitroaromatics and (b) durability test for 4-fluoronitrobenzene hydrogenation.

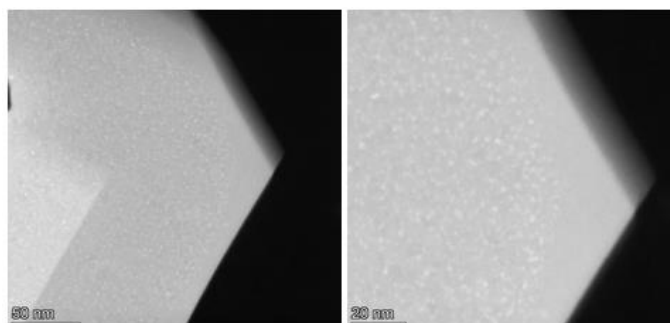


Figure 6: STEM images of recycled Pd@S-1-CH₃

3. Conclusions

In conclusion, we successfully applied in-situ synthesis to confine palladium-based nanocatalysts within the Silicalite-1 zeolite, and the particle size of palladium metal nanoclusters was controlled at around 1 nm. The introduction of hydrophobic organic functionalities into the zeolite structure significantly bolstered the selective hydrogenation capability of Pd@S-1-CH₃ against nitroaromatic compounds at a low operational temperature of 353 K. In hydrogenation of nitrobenzene, a notable turnover frequency (TOF) of 354.7 h⁻¹ was achieved at 353 K. Furthermore, the Pd@S-1-CH₃ catalyst demonstrated exceptional stability, providing a viable strategy for the selective hydrogenation of nitroaromatic compounds.

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