

Ultrasmall and Stable Pd and Pt Nanoparticles Within Zeolite HY Through Impregnated Method with Enhanced Semihydrogenation Selectivity

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Abstract

In this study, with zeolite HY as support, ultrasmall Pd and Pt nanoparticles were successfully immobilized into zeolite HY crystals through an optimized impregnation approach. The success of this new approach mainly relied on the selecting appropriate metal precursor to make Pd and Pt element exists with the cation forms, which can facilitate their diffusion into inner channels of zeolite HY through electrostatic attraction and capillary force. Integration of confinement effect of zeolite HY, taking zeolite HY (Si/A1=3) encapsulation of ultrasmall Pd NPs (Pd@HY-3) as an instance, Pd@HY-3 catalyst exhibited enhanced catalytic selectivity in semihydrogenation of alkynes, in comparison with Pd/HY, Pd/C, Pd/Al₂O₃ and lindlar catalysts. This improved catalytic selectivity can be attributed to the constrained upright adsorption conformation of reactant alkyne and corresponding product alkene on encapsulated Pd surface to make alkyne adsorption on Pd surface with larger adsorption energy than that of alkene, thus achieving the high catalytic selectivity.

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Graphic Abstract



Keywords Impregnation \cdot Immobilization of ultrasmall nanoparticles \cdot Zeolite HY \cdot Semihydrogenation \cdot Confinement effect

1 Introduction

Zeolite supported ultrasmall noble metal nanoparticles (Z-UNMPs) have attracted much more attention as a significant class of nanocatalysts for their excellent catalytic activities and selectivities in heterogeneous catalytic reactions [1–4]. Ultrasmall nanoparticles possessing large surface-to-volume ratio and high exposed active sites marry zeolite support possessing shape-selective character, thus exhibiting such unique catalytic properties. It is reported that Z-UNMPs have shown great promise in various synthetic reactions, including hydrogenation, oxidation, isomerization, and so on [5-8]. However, due to the very high surface energy, these supported ultrasmall noble metal nanoparticles tend to aggregation and sintering during the practical applications, resulting in the decreased catalytic reactivity, especially under harsh reaction conditions [9–11]. Consequently, exploring appropriate strategy to control the size and dispersion of these zeolite supported ultrasmall nanoparticles to sustain their catalytic properties is highly desirable [12].

A great number of research efforts have been devoted to stabilizing ultrasmall nanoparticles onto zeolite support. Ion-exchange, followed by H₂ reduction, is a historical method to introduce noble metal nanoparticles into zeolite crystals to improve their stability. Although this method is favoured by its simplicity and economy, the distribution of these synthesized nanoparticles is relatively poor on zeolites, and some are unavoidably located at the outer surface, leading to the occurrence of aggregation and sintering at some severe occasions [13, 14]. Multistep postsynthesis route is another method to enhance the stability of zeolite supported ultrasmall nanoparticles [15–17]. For example, Xiao and co-workers developed an effective two-step seed-directing methodology to encapsulate noble metal nanoparticles into zeolite to prompt their stability [18]. In which, synthesized noble metal nanoparticles was initially impregnated onto the surface of zeolite seed, then this prepared sample was covered by crystalline zeolite shell through a further hydrothermal crystallization process. Such postsynthesis strategies can successfully confine nanoparticles within zeolite crystal to exhibit excellent stability, yet the complex synthesis procedures and relative strict experimental parameters limit their practical application in industry. The direct in situ hydrothermal synthesis method is a newly developed strategy to encapsulate noble metal nanoparticles within zeolite crystals to strengthen their thermal and chemical stability. The key for this method is to select appropriate noble metal precursor containing ammonia ligand or ethylenediamine ligand, since these precursors can facilitate the interaction with emerging incipient aluminosilicate moieties to favor them incorporation into zeolite crystals during the hydrothermal process, following by the calcination and H₂ reduction at high temperature to afford zeolite encapsulated ultrasmall nanoparticles [19-22]. This smart synthesis strategy is primarily developed by Prof. Iglesia group, and many ultrasmall noble metal nanoparticles (Pt, Pd, Au, Rh, Ag, etc.) have been successfully encapsulated into various zeolites with different framework structures to exhibit good to excellent thermal and chemical stability [23, 24]. Notably, in the synthesis system with very high basicity, noble metal precursors protected by ligands may also be precipitated. Therefore, it is still very interesting to develop facial and efficient alternatives to stabilize zeolite supported ultrasmall nanoparticles.

The impregnation method is a simple and useful technique to load noble metal into zeolite matrix, which can be easily scaled up for industrial applications. However, with this method, when noble metal precursors such as H₂PtCl₆ and H₂PdCl₆ diffuse into zeolite channel through capillary force, owing to co-existenced diffusion resistance between the internal and external surfaces, some noble metal precursors could absorb on the external surface of the zeolite, hence causing the surface aggregation of prepared noble metal nanoparticles [25]. How to make noble metal precursors diffuse into zeolite inner structure maximumly is still a challenging problem needed to be addressed. Recently, Prof. Wan group reported a Na⁺-pretreatment method to overcome this problem [26]. They disclosed that Na⁺-pretreatment of HY zeolite (Al/Si = 0.36) to form H(Na)Y can change the surface charge of pristine HY zeolite from negative to positive, thus facilitating to attract negative gold species such as $[AuCl_4]^-$ into positive zeolite internal pores effectively, minimizing the deposition of large Au nanoparticle onto the external surface of zeolite Y. However, the thermal stability of this synthesized Au nanoparticles in H(Na)Y zeolite support was not discussed. It also should be noted that the introduction of another ion, such as Na⁺, into zeolite structure could influence the intrinsic property of parent zeolite [27, 28].

Generally, aluminosilicate zeolites bear a negatively charged framework of micropores, into which cation species can be easily attracted and diffused into such micropores to balance the framework charges. In this study, based on this principle, choosing zeolite HY as support without the introduction of any other ions into it, the platinum-group ultrasmall nanoparticles such as Pd and Pt were successfully encapsulated into zeolite HY crystals through selecting $Pd(acac)_2$ and $Pt(acac)_2$ as precursors to ensure Pd and Pt elements existing with the cation forms, and the resulted encapsulated ultrasmall nanoparticles exhibited very high thermal stability, even when the calcination temperature was up to 700 °C. The effect of framework charge density in zeolite HY caused by different Si/Al ratio on the encapsulation has also been discussed by experimental results and DFT calculation. Combined with shape selectivity of zeolite HY, the afforded zeolite Y encapsulated ultrasmall noble metal nanoparticles showed enhanced catalytic selectivity in semihydrogenation reaction.

2 Experimental Section

2.1 Reagents and Materials

Zeolites HY with different ratios of Si/Al were supported by Sinopec in China. Palladium (II) acetylacetonate (Pd 34.7%), Platinum (II) acetylacetonate (Pt 48%), Didodecyldimethylammonium bromide (>98%), 1-Ethyl-4-ethynylbenzene (>98%), and 4-Vinylbiphenyl (97%) were purchased from Alfa Aesar. Sodium tetrachloropalladate, palladium acetate (>99%), 1-dodecanethiol (>98%), palladium on carbon (10 wt%), and palladium on alumina (5 wt%) were obtained from Sigma-Aldrich. 4-ethynyl-1-1'-biphenyl (>97%) were brought from Ark Pharm. Anhydrous ethanol (≥99.5%) was purchased from Sigma-Aldrich. Lindlar catalyst (5 wt%) were purchased from SPC scientific. And sodium borohydride (>99%) was obtained from Acros Organics.

2.2 Synthesis of Zeolite HY Encapsulated Platinum-Group (Pd and Pt) Ultrasmall Nanoparticles

50 mg HY-3 support was suspended in 10 ml ethanol, and the ethanol solution (1.12 ml) of Pd(acac)₂ (2.74 mg) was added dropwise to the HY-3 gel very slowly under vigorous magnetic stirring. Then, the prepared mixture was stirred for 12 h at room temperature. Followed with centrifuging and washing with 10 ml ethanol for three times, the obtained samples were suspended again in 10 ml ethanol and treated at 60 °C under an H₂ atmosphere (1 atm) for 24 h. The solid was collected through centrifuged, washed with 5 ml deionized water and 5 ml ethanol for three times before drying in a vacuum dryer at room temperature overnight. ICP-MS analysis indicated that the loading amount of Pd in this encapsulated catalyst was 0.41%. Zeolite HY-3 encapsulated platinum ultrasmall nanoparticles catalyst was synthesized with the same procedure.

2.3 Synthesis of Pd/HY-3 Catalyst with Traditional Impregnation Method

For Pd/HY-3 catalyst with Pd nanoparticle supported on the surface (Pd/HY-3), according to the ultrasmall metal nanoparticles synthesized method supported by B. L. V. Prasad group [29], the 2 nm Pd nanoparticles (Pd NPs) has been synthesized and suspended in toluene. To load Pd NPs on HY-3 zeolite, 1 ml Pd NPs gel (0.02 M) was diluted with 2 ml ethanol, and 40 mg HY-3 zeolite powder was added. With 30 min ultrasonic dispersion, the sample was centrifuged (5000 rmp min⁻¹ for 5 min) and dried in a vacuum dryer at room temperature overnight to get the nominal 5.0% loading of Pd in this synthesized Pd/HY-3 catalyst.

2.4 Catalytic Hydrogenation of 4-Ethylphenylacetylene

In a typical hydrogenation reaction, Pd@HY-3 catalyst (50 mg), ethanol (2.5 ml), and 4-Ethylphenylacetylene (14 uL; 99%, Alfa Aesar) were held in an autoclave. After being flushed with H₂ three times, the reaction pressure in the autoclave was set to 1 MPa H₂ while the reaction temperature was 50 °C. The catalytic conversion and selectivity were determined by GC–MS (Agilent 5975C instrument with a thermal conductivity detector) and GC analysis.

2.5 DFT Calculations

All of the calculations based on density functional theory plus dispersion (DFT-D) were performed with the program package DMol3 in Materials Studio (version 8.0) of Accelrys Inc [30, 31]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerh (PBE) formulation of the exchange–correlation functional was employed [32, 33]. The valence electron wave functions were expanded into a set of atomic orbitals composed of the double numerical plus polarization (DNP) basis set, and the cutoff radius is 4 Å [34]. A cluster of 12 T model included a 12-memberring window was extracted from the crystal structure of Y zeolites to represent the HY zeolite [35]. H atoms were used to saturate the boundary of the zeolite cluster model, and thus Si-H dangling bonds were formed. Furthermore, all the dangling Si-H bonds are with the same direction of the faujasite framework, for keeping the intrinsic features of the zeolite. What is more, the Si-H bond lengths were fixed at 0.147 nm. The convergence tolerance of energy, maximum force, and maximum displacement for geometry optimization are 2×10^{-5} Ha, 0.004 Ha/Å, 0.005 Å, respectively. The adsorption energies, E_{ads} , are calculated by following:

$$E_{ads} = E_{adsorbate + HY} - (E_{adsorbate} + E_{HY})$$

Here, $E_{adsorbate + HY}$, $E_{adsorbate}$, and E_{HY} represent the total energy of HY cluster model covered with adsorbates, the energy of adsorbate, and the energy of HY cluster model, respectively. With this definition, a negative value of E_{ads} means a release of energy or a stable adsorption mode on the HY model.

2.6 Characterization

Powder XRD patterns were recorded by using a diffractometer (Xray diffractometer SmartLab (3), Rigaku) operated at 3 kW, equipped with CuKa radiation source from 6° to 90° with a scan rate of 5 deg min⁻¹. TEM images were recorded on a Hitachi HT-7700 microscope equipped with a tungsten filament, operating at 100 kV. HRTEM and HAADF-STEM images were recorded on a Philips Tecnai F20 FEG-TEM instrument with an accelerating voltage of 200 kV. Metal contents were determined by ICP-MS analysis with an Agilent 7500CE instrument.

3 Results and Discussion

Drawing lessons from Prof wan group's interesting result, encapsulation of ultrasmall platinum-group (Pd and Pt) nanoparticles into zeolite HY were successfully prepared through a modified impregnation method. Taking zeolite HY (Si/Al = 3) encapsulation of ultrasmall Pd nanoparticles (denoted as Pd@HY-3) as an example, for this zeolite HY possessing negative zeta potential, choosing Pd(acac)₂ as metal precursor, ethanol as solvent, the positive charge Pd²⁺ species in Pd(acac)₂ precursor can smoothly diffuse into the inner micropores of zeolite HY through electrostatic attraction and capillary force, then obtained zeolite HY encapsulated Pd species was reduced with H₂ balloon at 60 °C to get desired Pd@HY-3 catalyst. Noteworthily, the reduction of $Pd(acac)_2$ to Pd nanoparticles by H_2 at very mild condition has also been reported by another authors, such as the disclosed reaction temperature at 75 °C with 5 min to afford Pd nanoparticles from $Pd(acac)_2$ [36, 37].

XRD characterization in Fig. 1a showed that the synthesized Pd@HY-3 catalysts exhibited the identical XRD peaks as the zeolite HY catalyst, which implied that inclusion of palladium species into zeolite HY did not interfere with parent zeolite HY structure. Besides, no observation of lines corresponding to palladium metals indicated the absence of large palladium NPs in zeolite HY support. HAADF-STEM



Fig. 1 a Powder XRD patterns of synthesized Pd@HY-3 catalysts and zeolite HY catalysts. b HAADF-STEM image of Pd@HY-3 catalysts. c High-resolution (HR) TEM images of the Pd@HY-3 catalyst.

And **d** size distribution of palladium NPs in Pd@HY-3 catalysts. Typical encapsulated palladium NPs are highlighted by red circles

image in Fig. 1b suggested that the brighter Pd nanoparticles for the heavier atomic weight than the elements of parent zeolite HY were distributed uniformly throughout the zeolite HY crystal. The statistical average size of formed Pd NPs is 1.57 nm, which was belonging to the ultrasmall nanoparticle size (Fig. 1d). Notably, the larger size of synthesize Pd NPs than the diameter size of supercage (1.3 nm) in zeolite Y could reflect the local disruption of zeolite Y crystal structures around the position of the formed Pd NPs, yet this disruption was not detectable in diffractograms based on the XRD characterization. This local disruption phenomenon has also been observed in the MFI structure encapsulation of Pt NPs [21]. Presumably, the formed Pd NPs should reside in the supercage instead of SOD cage in zeolite Y crystal, due to the molecular size of metal precursor Pd(acac)₂ much larger than the diameter size of SOD cage (0.22 nm) in zeolite Y, thus preventing such diffusion. In addition, as shown in Fig. 1c, the reduced palladium NPs can be directly observed to be within zeolite HY micropore instead of on the surface, demonstrating that these Pd NPs are true to be encapsulated into zeolite structure with a manner similar to the formation of a core–shell structure.

X-ray photoelectron spectroscopy (XPS) of the synthesized Pd@HY-3 catalyst in Fig. 2a showed that there was no obvious XPS signals appeared, indicating the ultrasmall Pd NPs indeed confined into zeolite HY structure (Fig. 2b). Contrastly, when the structure of Pd@HY-3 was destroyed with a high concentrated NaOH solution (Fig. 2c), the typical peaks at 337.1 and 342.3 eV could be observed clearly, corresponding to the Pd^{II} species (Fig. 2d). This XPS result



Fig. 2 Pd@HY-3 catalyst for the XPS characterization (a) and TEM image (b). Concentrated NaOH solution treated Pd@HY-3 catalyst for the XPS characterization (c) and TEM image (d)

clearly indicated that the synthesized Pd nanoparticles were confined into the zeolite Y crystals.

To further certify that the ultrasmall Pd NPs are encapsulated into zeolite HY crystal rather than on the external surface, shape-selective reduction of nitrobenzene and 2,4,6-tri-tetra-butylnitrobenzene were conducted over the Pd@HY-3 catalysts and Pd/C catalyst. As shown in Fig. 3, for the reduction of small molecule nitrobenzene, the Pd@ HY-3 and Pd/C catalysts both exhibited very high catalytic activity, and the conversion was up to 100%. Conversely, for the reduction of large molecule 2,4,6-tri-tetra-butylnitrobenzene, Pd/C catalyst showed modest catalytic activity to give the hydrogenation product 2,4,6-tri-tetra-butylaniline, but not any catalytic activity was observed over Pd@HY-3 catalyst even at extended reaction time, which was attributed to the confining effect of the zeolite to block this large reactant to enter into zeolite micropore. These results demonstrated that prepared ultrasmall Pd NPs were encapsulated into zeolite HY crystal successfully instead of locating on the surface.

Significantly, the synthesized Pd@HY-3 catalyst exhibited excellent thermal stability, which would be very valuable in view of industrial utilization. As shown in Fig. 4, the calcination at 500 °C for 2 h under air atmosphere, palladium NPs were still distributed uniformly throughout the zeolite crystal without observed aggregation and sintering. The calculated average size of Pd NPs after treatment at 500 °C became 1.68 nm, compared to that of fresh Pd@HY-3 catalyst (1.57 nm). Furthermore, increasing the treatment temperature to 600 °C and 700 °C, as shown by HAADF-STEM,



Fig. 3 Catalytic properties of Pd@HY-3 and Pd/C catalysts in hydrogenation of nitrobenzene and 2,4,6-tri-tert-butylnitrobenzene respectively. Reaction condition in hydrogenation of nitrobenzene Reaction condition: (T=120 °C, 1 MPa H₂); Reaction condition in hydrogenation of 2,4,6-tri-tert-butylnitrobenzene: Reaction condition: (T=120 °C, 1 MPa H₂)

palladium NPs were also dispersed evenly over the zeolite crystal, and the average size of encapsulated Pd NPs was 1.43 nm and 1.61 nm, respectively, indicating the extremely good thermal stability of immobilized Pd NPs in zeolite HY during such harsh treatment, thus possessing great ability

to resist sintering and aggregation. Notably, compared with calcination at 500 °C, the decreased average size of Pd NPs calcination at 600 °C and 700 °C could be due to the dissolution of Pd atoms from the ultrasmall nanoparticles, which is consistent with the reported literature [38].

On the basis of above results, it could be sure that positive charge Pd species from Pd(acac)₂ precursor diffused into the micropores of zeolite HY-3 successfully through eletrostatistic attraction and capillary force, and formation of ultrasmall Pd NPs within zeolite HY-3 crystal via the reduction of balloon H₂ atmosphere at mild temperature without high-temperature treatment. To further study the effect of negative charge property of zeolites HY framework on the preparation of ultrasmall Pd NPs within zeolite crystals, zeolites HY with different ratios of Si/Al (zeolite HY-4, zeolite HY-5, zeolite HY-10) have been employed. Clearly, Pd NPs with large size located on the surface of zeolite HY were formed when the zeolite HY-5, zeolite HY-10 was chosen as parent supports (Fig. 5a, b). As the ratio of Si/Al decreased to 3 and 4 respectively, the formation of ultrasmall Pd NPs within zeolites was observed distinctly, and their dispersions on corresponding supports were very uniformly (Fig. 5c and d). Hence, zeolite HY with a smaller ratio of Si/Al to give



Fig. 4 HAADF-STEM images of Pd@HY-3 catalyst after treatment at 500 °C (**a**), 600 °C (**b**) and 700 °C (**c**). Corresponding size distribution of Pd NPs after treatment at 500 °C (**d**), 600 °C (**e**) and 700 °C (**f**). Typical encapsulated palladium NPs are highlighted by red circles



Fig.5 TEM image of synthesized Pd/HY-5 (a) and Pd/HY-10 (b) samples. HAADF-STEM images of synthesized Pd@HY-3 (c) and Pd@HY-4 (d) samples. Typical palladium atoms are highlighted by red circle

higher negative charge value on zeolite framework was very necessary to afford ultrasmall Pd NPs within zeolite crystal. As proposed, NaPdCl₄ as a precursor would cause the formation of large nanoparticles at the surface of zeolite HY-3 (Figure S1).

DFT calculation was also conducted to investigate the influence of the Si/Al ratio on the formation of ultrasmall Pd NPs within zeolite HY crystals. In consideration of the Pd^{2+} species in Pd(acac)₂ diffusing into micropores of zeolite HY through their twelve-membered ring, the change of Si/Al ratio in the zeolite HY was reflected in their twelve-membered ring structure to simplify the DFT calculation process [39, 40]. As shown in Figure S2, after the introduction of one aluminum atom into a twelve-membered ring structure, the calculated energy based on the electrostatic interactions between this twelve-membered ring structure and Pd(acac)₂ precursor was 72.1 kJ/mol. When further introducing two and six aluminum atoms into a twelve-membered ring structure, the calculated energy was increased to 95.8 and 109.2 kJ/mol respectively, indicating that smaller Si/Al ratio in zeolite HY could enhance the electrostatic interactions between the Pd(acac)₂ and micropores of zeolite HY to facilitate their diffusion into zeolite inner structure. Reasonably, compared with zeolites HY-5 and HY-10 (Si/Al = 5 and Si/ Al = 10 respectively), zeolites HY-3 and HY-4 with smaller Si/Al ratio (Si/Al=3 and Si/Al=4 respectively) possessed stronger negatively charged frameworks, which can make Pd^{2+} in $Pd(acac)_2$ more easily to be diffused into zeolite micropores through electrostatic interactions to overcome the diffusion resistance to afford desired ultrasmall nanoparticles lastly. Instead, relatively weaker electrostatic interactions between Pd(acac)₂ precursor and zeolites HY-5 and HY-10 could cause some Pd(acac)₂ species located at outer surface of zeolite due to the existed internal diffusion resistance. Clearly, these DFT calculations were consistent with the above experimental results in Fig. 5 very well.

Combined with the shape selectivity of zeolite, catalytic selectivity of zeolite encapsulated ultrasmall Pd NPs should be improved [41, 42]. Herein, with prepared Pd@ HY-3 catalyst as an instance, the catalytic property of this encapsulated catalyst was evaluated and compared with Pd/ HY-3 catalyst (Pd NPs supported on the external surface of zeolite HY, Figure S3), classical lindlar catalysts, Pd/C and Pd/Al₂O₃ catalysts using semihydrogenation of 4-ethylphenylacetylene as a probe reaction. Time dependent catalytic property of Pd@HY-3 catalyst in this hydrogenation reaction was summarized in Fig. 6a. Clearly, Pd@HY-3 catalyst showed good catalytic selectivity throughout the reaction and could give desired 4-ethylphenylene product in more than 95% yield, indicating that the undesired over-hydrogenation byproduct 1,4-diethylbenzene could be circumvented well. As shown, Pd@HY-3 catalyst exhibited 100% catalytic selectivity at the initial of the reaction and slightly decreased to 95% selectivity at the end of the reaction. The performed catalytic selectivity of Pd@HY-3 catalyst was much better than other compared catalysts. As can be seen in Fig. 6b, for supported Pd/HY-3 catalyst with similar Pd size (1.8 nm in Figure S3) to Pd@HY-3, at 100% conversion of the reactant, the selectivity was around 30%, indicating Pd NPs located at the surface of zeolite HY unfavourable for this reaction. Commercial Pd/C and Pd/Al₂O₃ catalysts were also exhibited much lower catalytic selectivity than the encapsulated Pd@HY-3 catalyst at the end of this reaction. Even for the industrially used Lindlar catalyst, it can only give 80% selectivity to desired alkene products, which was inferior to the prepared encapsulated Pd catalyst. The reaction was further conducted at high stirring speed (700 rpm) to exclude external diffusion effect, and the selectivity to 4-ethylphenylene was evaluated at the $10\% \pm 3\%$ conversion of 4-ethylphenylacetylene to minimize the further conversion of the alkene intermediate. As shown in Figure S4, for Pd/HY-3 catalyst, the selectivity to product was only 55%, yet for the encapsulated Pd@HY-3 catalyst, the selectivity was nearly 100%, indicating that encapsulation played a key role in the enhancement of catalytic selectivity. In addition, Pd@HY-3 also showed a higher catalytic selectivity than that of Pd/C and Pd/Al₂O₃ catalysts. Although Lindlar catalyst exhibited comparable catalytic selectivity (96%) to Pd@HY-3, the main problem for the Lindlar catalyst is its toxicity in practical usage. Therefore, Pd@HY-3catalyst is the optimal choice in this semihydrogenation reaction. The



Fig. 6 Time dependent catalytic property of Pd@HY-3 catalyst during the semihydrogenation of 4-ethylphenylacetylene (a). Reaction condition: (T=65 °C, 1 MPa H₂). Compared with different Pd-based

leaching test was further conducted to elucidate the chemical stability of Pd@HY-3 catalyst (Scheme S1). Meanwhile, ICP-MS analysis of the supernatant of reaction mixture was introduced. Both results suggested that no Pd species was leached from encapsulated Pd NPs to the reaction solution, demonstrated good chemical stability of Pd@HY-3 catalyst during this semihydrogenation reaction.

The origin of the high catalytic selectivity of Pd@HY-3 catalyst in the semihydrogenation reaction was studied with FT-IR analysis to illustrate the adsorption behavior of alkyne substrates on the encapsulated catalyst surface. Because it has been proven that the adsorption step would be very critical to determine the catalytic selectivity in semihydrogenation process. Due to the undetectable FT-IR signal of 4-ethylphenylacetylene on Pd@HY-3 catalyst surface (Figure S5), conjugated ethynyl-1,1'-biphenyl (EB-H) was chosen as a model molecule. As shown in Fig. 7a, EB-H adsorbed on encapsulated PdNPs surface exhibited aromatic C-H vibrational stretch from 3100 to 2900 cm⁻¹ and characteristic aromatic C-H deformation vibration from 840 to 700 cm^{-1} , which was similar to the corresponding stretching band of pure EB-H, indicating the adsorption of the substrate on the encapsulated Pd NPs surface definitely [43, 44]. Notably, the C \equiv C vibrational stretch at 2120 cm⁻¹ was disappeared after the adsorption of EB-H on encapsulated Pd surface, which could be due to the interparticle charge delocalization, further certifying the interaction between the alkynyl group and the Pd@HY-3 catalyst [45]. Notably, compared with pure EB-H, the disappearance of an intense characteristic band at 3200 cm⁻¹ assigned to a vibrational stretch of terminal \equiv C–H moiety was observed, indicating the adsorption of this substrate molecule on encapsulated Pd NPs surface through the process of dissociation of the alkynyl C-H bond, thus leading to the upright adsorption conformation rather than common flat-lying adsorption



catalysts during the semihydrogenation of 4-ethylphenylacetylene at approaching 100% conversion (b)



Fig. 7 FT-IR spectras of pure 4-ethynyl-1-1'-biphenyl (EB-H) and Pd@HY-3 catalyst treated with EB-H molecule (**a**). FT-IR spectras of pure 4-ethynyl-1-1'-biphenyl (EB-H), 4-vinylbiphenyl molecule, and Pd@HY-3 catalyst treated with mixture EB-H and 4-vinylbiphenyl molecules (**b**)

geometry [46]. Such interesting upright adsorption mode was consistent with the confinement effect of zeolite HY. Because of the molecule size of EB-H larger than the diameter of twelve membered ring (7.4 Å), micropores of zeolite HY would constrain EB-H adsorbed on encapsulated Pd surface with end-on adsorption mode instead of thermodynamically favorable flat-lying mode. Fortunately, such imposed upright adsorption geometry of substrate on encapsulated Pd surface discriminated the adsorption energy between EB-H molecule and semihydrogenation product 4-vinylbiphenyl molecule. As indicated in Fig. 7B, when Pd@HY-3 catalyst was exposed to the mixture of EB-H and 4-vinylbiphenyl molecules, the FT-IR curve of Pd@ HY-3-mixture was similar to that of pure EB-H molecular rather than 4-vinylbiphenyl in view of the lack of aromatic C-H vibration band at 3000 cm⁻¹ and 690 cm⁻¹ assigned to pure 4-vinylbiphenyl, suggesting that EB-H preferring to adsorb on the encapsulated Pd surface for a larger adsorption energy in the presence of EB-H and 4-vinylbiphenyl. Reasonably, attributed to the stronger adsorption energy of EB-H on encapsulated Pd surface through the deprotonation process with upright geometry than that of constrained endon adsorbed 4-vinylbiphenyl, Pd@HY-3 catalyst achieved a high and enhanced catalytic selectivity in semihydrogenation. In contrast, for the supported catalyst such as Pd/C, when it was treated with the mixture of EB-H and 4-vinylbiphenyl molecules, the similar FT-IR signal of 4-vinylbiphenyl was appeared on the Pd/C-mixture sample, in view of the observance of C-H stretching vibration band of -C=C-H moiety at 3100-2800 cm⁻¹ and aromatic C-H vibration band at 800–750 cm⁻¹ both assigned to pure 4-vinylbiphenyl (Figure S6), indicating that 4-vinylbiphenyl can adsorb on the supported Pd surface for the comparable adsorption energy in the presence of EB-H and 4-vinylbiphenyl, thus resulting the decreased catalytic selectivity.

Significantly, this optimized impregnation approach can be extended to stabilize other ultrasmall platinum-group nanoparticles, such as Pt. Selecting $Pt(acac)_2$ as a metal precursor, ethanol as solvent, the positive charge Pt species in $Pt(acac)_2$ can enter into the inner structure of zeolite HY -3 through electrostatic attraction and capillary force, following by the reduction process with H₂ balloon at mild temperature to obtain Pt@HY-3 catalyst. Figure 8 showed ultrasmall PtNPs distributed uniformly throughout the zeolite crystal, and the calculated average size was 1.9 nm.

4 Conclusion

In conclusion, a facial and versatile approach to stabilize ultrasmall Pd and Pt nanoparticles within zeolite HY was developed through an optimized impregnation process. Due to the essence on the negative charge of zeolite framework,



Fig. 8 HAADF-STEM image of Pt@HY-3 catalysts (left), and size distribution of Pt NPs inPt@HY-3 catalysts (right)

cationic rather than anionic Pd and Pt precursors were selected to successfully achieve easy diffusion into the micropores of zeolite HY (Si/Al=3) with higher negative charge density via electrostatic attraction and capillary force, then following the reduction with H₂ balloon at mild temperature to obtain desired metal@zeolite HY samples to achieve the objective of stabilization of ultrasmall nanoparticles, without any high temperature treatment step. Combined with shape selectivity of zeolite HY, taking Pd@zeolite catalyst as an example, this catalyst exhibited enhanced catalytic selectivity in semihydrogenation of alkynes, in comparison with Pd/HY catalyst and other most widely used commercial catalysts such as Pd/C, Pd/Al₂O₃ and lindlar catalysts. The improvement in catalytic selectivity can be well attributed to the confinement effect of zeolite HY, which discriminated the adsorption energy through constrained upright adsorption conformation to facilitate alkyne preferred to adsorption on encapsulated Pd surface than corresponding alkene substrate, thus exhibiting the enhanced catalytic selectivity. The modified impregnation approach proposed in this work not only develops a new method to stabilize ultrasmall nanoparticles for practical chemical industries, but also improves our understanding of the confinement catalysis.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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