Supporting Information

Fish-in-Hole: Rationally Positioning Palladium into Traps of Zeolite Crystals for Sinter-Resistant Catalysts

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Chemicals

All the chemicals were of analytical-reagent grade and directly used without further purification. The commercial toluene was treated by phosphorus pentoxide for obtaining anhydrous toluene. If it is not specially noted, the zeolite materials were all in H-form.

Catalyst preparation

Synthesis of Y and trap-rich Y zeolite. As a typical run, 3.17g of SiO₂ $3H_2O$ was mixed with 1.64g of NaAlO₂ under grinding for 15 min at room temperature, then the mixture was transferred to an autoclave and thermally treated at 100 °C for 24 h. After washing with water and ethanol, the Na-form Y zeolite was obtained. The Na-form Y zeolite was transferred into H-form by ion-exchange and calcination. Typically, 1 g of the Naform Y zeolite was stirred in 50 ml of ammonium nitrate solution (1 M) at 80 °C for 2 h, and the solid was filtered and calcined at 450 °C for 4 h. The above ion exchange and calcination steps were repeated to obtain the final H-form Y zeolite. After calcination at 700 °C for 4 h, the structure of Y zeolite framework was partially destroyed to form trap-rich Y zeolite.

Synthesis of soluble Pd nanoparticles from self-reduction of $Pd(OAc)_2$. As a typical run, 5.3 mg of $Pd(OAc)_2$ (OAc=acetate) was dissolved in 50 mL of dichloromethane. After stirring the liquor at room temperature for 24 h. The color of the solution changed from yellow to dark, indicating the formation of Pd nanoparticles. In this work, the stirring temperature and time were artificially adjusted for understanding the influence of reaction conditions to the Pd nanoparticle diameters.

Synthesis of FIH-Pd@trap-rich zeolite catalyst. As a typical run for the synthesis of FIH-Pd@Y, 0.495 g trap-rich Y zeolite was added to the solution containing 10.6 mg of Pd(OAc)₂ and 50 mL dichloromethane. After vigorous stirring for 24 h at room temperature, the precipitates were filtered, washed with dichloromethane, ethanol and deionized water for several times, and then dried at 100 $^{\circ}$ C for overnight. The FIH-

Pd@ZSM-5 and FIH-Pd@Beta samples were synthesized in the same procedures except for using trap-rich ZSM-5 and Beta as support instead of trap-rich Y zeolite.

Synthesis of ZSM-5 and trap-rich ZSM-5 zeolite. In a typical run for the synthesis of ZSM-5 zeolite, 8 mL of TAPOH (19.5 *wt%*) was added in to 10 mL of water containing 6.8 mL TEOS; After stirring for overnight, 0.08 g of NaAlO₂ and 10 mL of water were added and stirred for another 6 h. Then, the gel was transferred into an autoclave to crystallize at 180 °C for 2.5 days. After filtrating, drying, and calcining at 550 °C for 4 h, the ZSM-5 sample in Na-form was obtained. The ion-exchange treatment was performed by stirring 1 g of as-synthesized Na-form ZSM-5 in 50 mL of NH₄NO₃ aqueous solution (1 M) at 80 °C for 2 h, and then calcined at 450 °C for 4 h. The above ion-exchange and calcination steps were repeated to obtain the final H-form ZSM-5 zeolite. After calcination at 700 °C for 4 h, the structure of ZSM-5 zeolite framework was partially destroyed to form trap-rich ZSM-5 zeolite.

Synthesis of Beta and trap-rich Beta zeolite. As a typical run, 0.3 g of NaAlO₂ and 0.16 g of NaOH were dissolved in 12.64 g of water, followed by the addition of 19.36 g of TEAOH (20 *wt*% aqueous solution). After stirring at room temperature for 1 h, 4.8 g of SiO₂ was added and stirred for another 5 h. Then the mixture was transferred into an autoclave to crystallize at 140 °C for 4 days. After filtrating, drying, and calcining at 550 °C for 4 h, the Beta sample in Na-form was obtained. The ion-exchange treatment was performed by stirring 1 g of as-synthesized Na-form ZSM-5 in 50 mL of NH₄NO₃ aqueous solution (1 M) at 80 °C for 2 h, and then calcined at 450 °C for 4 h. The above ion-exchange and calcination steps were repeated to obtain the final H-form Beta zeolite. After calcination at 700 °C for 4 h, the structure of Beta zeolite framework was partially destroyed to form trap-rich Beta zeolite.

Synthesis of Pd/zeolite catalyst. The Pd/zeolite samples were synthesized by the Pd colloid deposition method. As a typical run for the synthesis Pd nanoparticle colloid, 14 mg of PVA (polyvinyl alcohol, molecular weight at ~10000) and 1.35 mL PdCl₂

(80.8 mmol/L) were dissolved in 60 mL water. After stirring at 0 $\,^{\circ}$ C for 0.5 h, 5 mL of newly made NaBH₄ aqueous solution (0.1 mol/L) was quickly added under vigorous stirring. After stirring for another 2 h and dialyzing for 2 days to remove Na⁺, Cl⁻ and other unnecessary species, the Pd nanoparticle colloid was finally obtained.

As a typical run for the synthesis of Pd/Y, 1.15 g trap-rich Y zeolite was dispersed into the as-synthesized Pd nanoparticle colloid under ultrasonic treatment, followed by dropwise addition of 0.8 mL of H₂SO₄ (10 mol/L) under stirring for loading the Pd nanoparticles on the solid support. After stirring for 5 hours, the precipitates were filtered, washed with large amount of deionized water, dried at 100 °C for overnight, and calcined at 450 °C to remove the PVP species, the Pd/Y catalyst was finally obtained. The Pd/SiO₂, Pd/ZSM-5 and Pd/Beta samples were synthesized in the same procedures except for using amorphous SiO₂, trap-rich ZSM-5 and Beta as support instead of trap-rich Y zeolite.

Synthesis of Pd/Al_2O_3 . 1 g solid support Al_2O_3 was added into 50 mL of aqueous solution of urea and Na_2PdCl_4 (molar ratio of urea/Pd at 20). After stirring at 80 °C for 4 h, the liquor was cooled to room temperature, followed by separating the solid powder by filtration. After thermal treatment at 100 °C for 2 h, 400 °C for 2 h, and reduction with hydrogen at 400 °C for 2 h, the Pd/Al_2O_3 catalyst was obtained.

Grafting diethoxydimethylsilane on silanol groups

As a typical run, 0.5 g of the as-pretreated sample (trap-rich zeolite or SBA-15) was added into 20 mL of anhydrous toluene containing 0.5 g of diethoxydimethylsilane. After stirring and refluxed at 110 $^{\circ}$ C for 12 h, the solid was filtered, washed with a large amount of anhydrous toluene, ethanol, and water, and dried at 100 $^{\circ}$ C for overnight, the sample with reduced silanol groups was obtained, which was denoted as Del-SiOH-sample.

Pd(OAc)₂ adsorption tests

The adsorption tests were performed in a 100 mL glass reactor containing a solution of

Pd(OAc)₂ (5.3 mg) in dichloromethane (20 mL). Before the test, the solid samples were pretreated at 150 $^{\circ}$ C under vacuum. As a typical run, 0.25 g of the as-pretreated solid sample was added into 20 mL of the solution, and stirred at room temperature. In order to avoid the self-reduction of Pd(OAc)₂ during the adsorption test, the adsorption time was controlled at 1 h, then the solid was separated by centrifugation at 12000 rpm and dried at 100 $^{\circ}$ C for overnight. Pd contents in the samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. The procedure for the adsorption test and calculation of the adsorption capacity were given in Figure S22.

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultimate IV diffractometer with Cu K α radiation (λ =1.5418 Å). Transmission electron microscopy (TEM) was performed on a JEM-2100F electron microscopy (JEOL, Japan) with an acceleration voltage of 200 kV. The samples are pretreated in 10% H₂/Ar at 300 °C for 1 h before the characterization. The powders were dispersed in ethanol by sonicating for 5 min. One drop was taken onto the holey carbon film supported on a copper grid, followed by 10 min heating on the heating stage at 90 °C. Metal contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Perkin-Elmer 3300DV). The samples were dried at 120 °C under vacuum for overnight. A certain amount of sample was dissolved in the mixture of aqua regia $(V_{HCl}:V_{HNO3}=3:1)$ and HF at 100 °C. After fully dissolving the samples, the solution was diluted to 100 mL. During this process, the pH was adjusted closely to the standard solution to minimize the background noise. Nitrogen sorption isotherms were measured at -196 °C using a Micromeritics ASAP 2020 M system. The samples were degassed for 10 h at 150 °C before the measurements. Scanning electron microscopy (SEM) experiments were performed with Hitachi SU-8010 electron microscopes. X-ray photoelectron spectra (XPS) of the samples were recorded using a Ktatos AXIS SUPRA with Al Ka X-ray radiation as the X-ray source. The binding energies were calibrated on the basis of the C1s (285.0 eV) peaks. IR spectra were recorded using a Nicolet is50 FT-IR spectrometer equipped with a MCT/A detector. For the FTIR and XPS characterization of the Pd nanoparticles solved in the CH₂Cl₂ liquor, the boron nitride was added into the liquor, followed by removing the CH₂Cl₂ at room temperature under vacuum. Then the powder of boron nitride supported Pd nanoparticles was used in the FTIR and XPS characterization.

Catalytic CO oxidation

CO oxidation was carried out in a temperature-controlled microreactor equipped with an on-line Shimadzu GC-2014 chromatograph equipped with TCD detector. The internal diameter of the reactor is 4 mm and length is 40 cm. As a typical run, 0.2 g of Pd catalyst (40~60 mesh) diluted with 0.4 g of quartz sand (40~60 mesh) were placed in the middle of the glass reactor. The catalysts were pretreated in 20% O₂/He at 350 °C for 0.5 h before the tests. A flow of the reaction gas (20 mL/min) with component of 1% CO, 18% O₂, and 81% He was introduced into the reactor to initiate the reaction, where the reaction temperature was programmed by a temperature-controlled instrument. The unconverted CO and produced CO₂ were quantified using an on-line gas chromatograph. During the reaction tests, the reaction temperature was periodically decreased to 170 °C for FIH-Pd@Y and 190 ° Cfor Pd/Y (rate at ~20 °C/min) with uncompleted conversion of CO to measure the average TOFs and re-increased to 350/450 °C (rate at 5 °C/min) to continue the reaction.

Sample	$S_{BET} (m^2/g)^a$	Pd loading	Pd nanoparticle
		$(wt\%)^b$	diameter (nm) ^c
Conventional Y	418		
Trap-rich Y	573		
FIH-Pd@Y	382	0.6	3.7
Pd/Y		0.6	3.7
FIH-Pd@ZSM-5	416	0.6	5.5
Pd/ZSM-5		0.5	3.2
FIH-Pd@Beta	378	0.7	4.1
Pd/Beta		0.9	3.3
Pd@SBA-15	670	0.8	3.9

Table S1. Structural parameters of various samples.

^{*a*} Measured from N₂ sorption isotherms; ^{*b*} Measured from ICP analysis; ^{*c*} Measured with more than 100 nanoparticles in the TEM images.

	Percentage adsorbed	Adsorption capacity
	on the sample	$(10^{-2} \text{ mmol/g})^a$
Sample	(%)	
Trap-rich Y	75	7.1
Conventional Y	18	1.7
Trap-rich ZSM-5	84	7.9
Trap-rich Beta	41	3.9
SBA-15	57	5.4
Al ₂ O ₃	15	1.4
SiO ₂	24	2.2

Table S2. Adsorption capacity of Pd(OAc)₂ on various samples.

^{*a*} molar of adsorbed Pd(OAc)₂ over per gram of solid sample.

Samples	Pd dispersion degree
	$(\%)^{a}$
FIH-Pd@Y	33.4
calcined FIH-Pd@Y at 600 °C	28.9
used FIH-Pd@Y in CO oxidation	30.8
Pd/Y	36.5
calcined Pd/Y at 600 °C	12.1
used Pd/Y in CO oxidation	14.8

 Table S3. Pd dispersion degree of various samples.

^{*a*} By CO titration, $\pm 4\%$.



Figure S1. TEM images of different regions on trap-rich Y zeolite. The red arrows highlighted the traps on the zeolite.



Figure S2. (A) Photographs of the trap-rich Y zeolite in Pd(OAc)₂ solution before and after stirring for 24 h. (B) Photographs of the (a) trap-rich Y zeolite and (b) FIH-Pd@Y.

Note: The brown color of liquor CH_2Cl_2 containing $Pd(OAc)_2$ mixed with trap-rich Y zeolite disappeared after stirring for 24 h at room temperature, suggesting that the Pd species are loaded on the Y zeolite.



Figure S3. XRD patterns of (a) trap-rich Y zeolite, (b) FIH-Pd@Y, (c) calcined FIH-Pd@Y, (d) Pd/Y, (e) trap-rich Beta, (f) FIH-Pd@Beta, (g) trap-rich ZSM-5, (h) FIH-Pd@ZSM-5.



Figure S4. N₂ sorption isotherms of (a) trap-rich Y zeolite, (b) FIH-Pd@Y, (c) FIH-Pd@ZSM-5, and (d) FIH-Pd@Beta.



Figure S5. Mesopore size distribution of (a) trap-rich Y, (b) FIH-Pd@Y, and (c) conventional Y zeolite.



Figure S6. SEM images of various trap-rich zeolites of (A) Y, (B) Beta, and (C) ZSM-5.



Figure S7. Particle size distribution of (A) as-synthesized FIH-Pd@Y, (B) calcined FIH-Pd@Y at 600 $\,^{\circ}$ C for 2h, and (C) used FIH-Pd@Y in CO oxidation test at 350 $\,^{\circ}$ C for 10 h and 450 $\,^{\circ}$ C for 30 h. d_{av} is the average nanoparticle diameter. The data were

obtained by measuring more than 100 nanoparticles in the TEM images. Less than 2% of the nanoparticles are larger than 8 nm, which were not included in the data.



Figure S8. STEM image and EDX analysis of different regions on FIH-Pd@Y.

Note: EDX analysis of Region 2 gives an obvious signal assigned to Pd due to the presence of Pd nanoparticles in this region. To avoid the presence of ultra-small Pd nanoclusters, we also performed the EDX analysis of the region 1, where no Pd nanoparticles could be observed. The EDX analysis shows that it is undetectable Pd signal in the Region 1, indicating the absence of ultra-small Pd clusters in the FIH-Pd@Y.





Figure S9. (A) TEM image and (B) Pd nanoparticle size distribution of Pd/Y. The Pd nanoparticles are randomly dispersed on the zeolite.



Figure S10. TEM images and Pd nanoparticle size distribution of (A and B) Pd/ZSM-5 and (C and D) Pd/Beta. The Pd nanoparticles are randomly dispersed on the zeolites.



Figure S11. (A) Photographs of the liquor before and after the Pd(OAc)₂ self-reduction.(B) TEM image of Pd nanoparticles synthesized from Pd(OAc)₂ self-reduction.



Figure S12. Pd3d XPS spectra of (A) $Pd(OAc)_2$ and (B) Pd nanoparticles synthesized from self-reduction of $Pd(OAc)_2$.

Note: The Pd3d XPS spectrum of Pd(OAc)₂ gives the Pd3d_{5/2} and 3d_{3/2} binding energies at 338.2 and 343.5 eV, respectively, which are assigned to typical Pd species in Pd(OAc)₂ [The Pd3d binding energies of Pd(OAc)₂ are known to be higher than the conventional Pd²⁺ due to the interaction with acetic group].^{1,2} In contrast, the Pd nanoparticles synthesized from self-reduction of Pd(OAc)₂ gives two additional binding energies at 340.5 and 335.2 eV, related to the typical metallic Pd⁰ species.³ These data confirm that the self-reduction of Pd(OAc)₂ in CH₂Cl₂ indeed occurs to form metallic Pd⁰.



Figure S13. (A, C, E) TEM images and (B, D, F) particle size distributions of Pd nanoparticles synthesized from $Pd(OAc)_2$ self-reduction at room temperature for different time of (A, B) 16 h, (C, D) 24 h, and (E, F) 36 h. (G) Dependences of average diameters of Pd nanoparticles on synthesis time.

Note: The Pd nanoparticles from $Pd(OAc)_2$ self-reduction at room temperature for different time are always highly dispersed with the diameters less than 2 nm, indicating that the self-reduction benefits the synthesis of relatively small Pd nanoparticles even in the absence of N- or S-containing ligands. Notably, stirring time of the $Pd(OAc)_2$ self-reduction cannot change the sizes of the nanoparticles.



Figure S14. TEM images and particle diameter distribution of Pd nanoparticles synthesized from self-reduction of Pd(OAc)₂ at (A and B) 0 $^{\circ}$ C for 3 days, (C and D) room temperature for 16 h, (E-G) 50 $^{\circ}$ C for 16 h, (H-J) 50 $^{\circ}$ C for 24 h (four times of initial Pd(OAc)₂ concentration), and (K-M) 100 $^{\circ}$ C for 16 h (the scale bar is 200 nm for

H and 100 nm for K).

Note: The synthesis temperature remarkably influences the Pd nanoparticle diameters. The sample synthesized at 0 $^{\circ}$ C exhibits very small Pd nanoparticles with average diameter at 1.02 nm. Increasing the synthesis temperature to room temperature (~27 $^{\circ}$ C) leads to relatively larger average diameter at 1.62 nm. When the self-reduction was carried out at 50 and 100 $^{\circ}$ C, the bulky particles at 15-20 nm are formed with co-existence of small Pd nanoparticles (< 3 nm).



Figure S15. IR spectra of (a) Pd(OAc)₂ and (b) Pd nanoparticles synthesized from self-reduction of Pd(OAc)₂.

Note: The Pd nanoparticles synthesized from self-reduction of $Pd(OAc)_2$ were loaded on the boron nitride support for IR characterization.

The Pd(OAc)₂ gives the bands at 1400 and 1580-1596 cm⁻¹, which are assigned tov_s(OCO) and v_{as}(OCO) of the acetic group (CH₃COO⁻), respectively. Compared with Pd(OAc)₂, the bands associated with CH₃COO⁻ disappear on Pd nanoparticles, confirming to the transformation of CH₃COO⁻ group during the formation of Pd nanoparticles. Notably, the Pd nanoparticles give the bands at 1550 and 1720 cm⁻¹, assigned to the C-O and C=O bonds, and two bands at 1460 and 1375 cm⁻¹ assigned to the C-H bonds in ethyl group. These data suggest that the presence of C₂-oxygen group (CH₃CH_xO^{δ -}) on the surface of Pd nanoparticles, which could stabilize the small Pd nanoparticles. Combining the fact that CO and CO₂ are detected in the emission gas of the synthesis reactor, we proposed that the CH₃COO⁻ could react with Pd²⁺ species to form CO, CO₂, and CH₃CH_xO^{δ -} species.



Figure S16. C1s XPS spectra of (A) Pd(OAc)₂ and (B) Pd nanoparticles synthesized from self-reduction of Pd(OAc)₂.

Note: The Pd nanoparticles synthesized from self-reduction of $Pd(OAc)_2$ were loaded on the boron nitride support for XPS characterization.

The Pd(OAc)₂ exhibits the peaks at 288.8 eV assigned to the O-C=O species. In the sample after self-reduction, it is appeared the C1s peak at 286.2 eV, which is shifted from the peak at 288.8 eV of Pd(OAc)₂. The 2.6 eV shift is reasonably assigned to the transformation of carbon bonded with two oxygen atoms (O-C=O) in CH₃COO⁻ to relatively electron-rich carbon bonded with one oxygen atom (C-C-O or C-C=O) in CH₃CH_xO^{δ -,⁴} which are well consistent with those of their FTIR spectra.



Figure S17. Pd3d XPS spectra of the (A) trap-rich Y and (B) conventional Y zeolite after stirring in CH₂Cl₂ liquor containing Pd(OAc)₂.

Note: After stirring in CH_2Cl_2 liquor containing $Pd(OAc)_2$ and conventional Y zeolite, it is observed the Pd3d binding energies at 343.5 and 338.3 eV, which are typically assigned to $Pd(OAc)_2$ species. In contrast, the same treatment with trap-rich Y zeolite results in the formation of Pd⁰ nanoparticles with Pd²⁺ citations.



Figure S18. C1s XPS spectrum of trap-rich Y after stirring in CH₂Cl₂ liquor containing Pd(OAc)₂.

Note: After stirring in CH₂Cl₂ liquor containing Pd(OAc)₂ and trap-rich Y zeolite, it is observed the C1s binding energies at 289.1 and 286.2 eV. The band at 289.1 eV is assigned to the carbon species in physically adsorbed Pd(OAc)₂. The band at 286.2 eV is assigned to carbon species in CH₃CH_xO^{δ -} groups, confirming the reactions between acetic group and Pd cations in the self-reduction process, which is in good agreement with the results in IR characterization.



Figure S19. (A) XRD, (B) N₂ sorption isotherms, and (C) TEM image of conventional Y zeolite.

Note: The XRD pattern gives typical peaks of FAU zeolite structure. The N_2 sorption isotherms exhibits a small uptake at relatively high pressure region, suggesting the lack of mesoporosity/traps in the sample, as confirmed by its TEM image.

complex		Ti	me		aammlaa	Time			
samples	0h	6h	12h	24h	samples	0h	6h	12h	24h
(A) blank					(E) trap-rich Y				
(B) SBA-15					(F) conventional Y				
(C) trap-rich Beta					(G) SiO ₂				
(D) trap-rich ZSM-5					(H) Al ₂ O ₃				

Figure S20. The color change of the liquor in the $Pd(OAc)_2$ self-reduction over various supports.



Figure S21. (A) TEM image of conventional Y zeolite stirring in the $Pd(OAc)_2$ solution in CH_2Cl_2 for 6 h. (B) TEM image of the reduced sample (A) with H_2 at 400 °C for 2 h.

Note: It is difficult to observe the Pd nanoparticles in the TEM images of the conventional Y zeolite treated in CH_2Cl_2 solution with $Pd(OAc)_2$ for 6 h owing to the lack of Pd nanoparticles, which is in good agreement with the color change observed in Figure S20F. After further reduction by hydrogen, it is also difficult to observed the Pd nanoparticles. The red cycle highlights a bulky Pd particle, which might be from the reduction of physically adsorbed Pd(OAc)₂ precursors on the zeolite surface.



Figure S22. The absorption tests on various samples. In the equations, m_1 is the mass amount of the solid sample (the unit: g), n_1 is the molar amount of the Pd(OAc)₂ before adsorption (the unit: mmol), n_2 is the molar amount after adsorption (the unit: mmol) analyzed by ICP. The adsorption measurement was performed at ~5 °C.



Figure S23. (A) TEM image and (B) Pd particle size distributions of FIH-Pd@SBA-15.



Figure S24. TEM image of FIH-Pd@Y-CA sample synthesized from the citric acid (CA) pretreated Y zeolite.

Note: Apart from hydrothermal treatment for constructing mesopores in the zeolite crystals, the liquid-phase acid (*e.g.* nitric acid and hydrochloric acid) treatment has been widely regarded to be another route for the construction of mesoporous channels.⁵⁻⁷ In order to construct traps on the surface of zeolite crystals rather than mesoporous channels, we employed citric acid for dealumination because the citric acid has weak acidity than the generally used nitric acid and hydrochloric acid. In addition, the citric acid has large molecule diameters, which diffuses slowly in the zeolite micropores, thus leading to the delamination on the surface of zeolite crystals to obtain Y-CA with rich traps.

After the Pd(OAc)₂ self-reduction, the FIH-Pd@Y-CA also gives ideal *fish-in-hole* distribution of Pd nanoparticle localized in the traps. These results confirm the importance of the traps of zeolites for the formation of *fish-in-hole* structure.



Figure S25. Proposed adsorption of the Pd precursor on conventional and trap-rich zeolites.

Note: The acetic acid palladium(II) salt [denoted as $Pd(OAc)_2$ in this work] is generally present as a complex containing three Pd atoms and six acetic acid groups $[Pd_3(OAc)_6]$.^{8,9} The complex have larger diameters (9 Å) than the zeolite micropore diameter (~7.4 Å for Y and Beta zeolite, ~5.1 Å for ZSM-5 zeolite), which hindered the diffusion of Pd precursor complexes into the zeolite micropores. When this Pd complexe is loaded on the conventional Y zeolite, the Pd precursor is randomly dispersed on the external surface of zeolite crystals. On the contrary, the traps (mesopores) in the zeolites can efficiently adsorb and enrich the Pd complexes.



Figure S26. (A) Proposed partial elimination of silanol groups *via* organosilane modification. IR spectra of (B) trap-rich Y zeolite and (C) SBA-15 before (a) and after (b) the organosilane modification.

Note: Both Del-SiOH-Y (B-b) and Del-SiOH-SBA-15 (C-b) samples give the band at 1265 cm⁻¹ and 2965 cm⁻¹, which are assigned to the vibration of δ (CH₃) and v(CH₃), respectively, indicating the successfully grafting organosilane on the Y zeolite and SBA-15.

	Time				Time		
samples	0h	12h	24h	samples	0h	12h	24h
(A) Trap-rich Y				(C) SBA-15			
(B) Del-SiOH-Y				(D) Del-SiOH- SBA-15			

Figure S27. Color change of the liquors in the $Pd(OAc)_2$ self-reduction on various supports.

time	0 h	8h	16 h	24 h
toluene				
toluene +water				

Figure S28. Photographs of the mixture during the $Pd(OAc)_2$ self-reduction process in toluene and mixture of water and toluene.

time	0 h	12h	24 h	36 h	48 h
CH ₂ Cl ₂					
CH ₂ Cl ₂ +phenol					

Figure S29. Photographs of the mixture during the $Pd(OAc)_2$ self-reduction process in CH_2Cl_2 and mixture of CH_2Cl_2 and phenol.

Note: we studied the influence of hydroxyl groups for the self-reduction of $Pd(OAc)_2$. When the reaction was performed in toluene solvent, the self-reduction never occurred under stirring at room temperature for 24 h, as confirmed by the unchanged color of the liquor (Figure S28). In comparison, when a slight amount of water as added into the liquor, the reduction immediately occurred within 8 h (Figure S28). Another experiment was performed in CH₂Cl₂ solvent, which gives slow self-reduction process in pure CH₂Cl₂, when a light amount of phenol was added into the liquor, the self-reduction process is remarkable promoted (Figure S29). All these results demonstrate the important role of polar environment in promoting the self-reduction process, which is constant with the knowledge reported in literature. On the basis of these knowledge, it is reasonable to conclude that the silanols provided polar environment in the traps, which promoted the reduction of Pd(OAc)₂ in the traps.

Time	0 h	12 h	24 h
a			
b			
c			
d			

Figure S30. Photographs showing the color change observed in the synthesis processes with different amount of sodium acetate additive. Synthesis conditions: 0.245 g of traprich Y zeolite, 5.3 mg of Pd(OAc)₂, 20 mL of CH₂Cl₂, (a) 0, (b) 10, (c) 20, and (d) 50 mg of sodium acetate, 20 °C.



Figure S31. TEM images and particle size distributions of FIH-Pd@Y samples synthesized with different amount of sodium acetate additive. Synthesis conditions: 0.245 g of trap-rich Y zeolite, 5.3 mg of Pd(OAc)₂, 20 mL of CH₂Cl₂, (A and B) 0, (C and D) 10, (E and F) 20, and (G and H) 50 mg of sodium acetate, 20 °C, 12 h.

Note: We performed the self-reduction of $Pd(OAc)_2$ with different concentration of sodium acetate additive. As shown in Figure S30, the liquors with different amount of

sodium acetate additive gives very similar color change during the synthesis process. Figure S31 shows the TEM images of various samples after self-reduction for 12 h, where most Pd nanoparticles are localized in the traps of trap-rich Y zeolite. Notably, the Pd nanoparticle diameters are slightly increased with more sodium acetate additive. These results indicate that the concentration of acetate group in the liquor can slightly influence the diameters of Pd nanoparticles in the FIH-Pd@Y samples.





Figure S32. (A) STEM image, (B-D) Pd, Al, and Si elemental maps of FIH-Pd@meso-Y. The red arrows highlight the Pd nanoparticles positioned in the mesoporous channels. The regions 1, 2 and 3 in the STEM images are corresponded to the regions 1, 2 and 3 in the Pd elemental map, respectively.



Figure S33. TEM images of FIH-Pd@Y with Pd loading amount at (a) 0.1, (b) 0.2, (c) 0.5, and (d) 10%.

Note: The samples with Pd loading amount at 0.1, 0.2 and 0.5% still exhibit Pd nanoparticles dispersed within the traps, but the sample with Pd loading amount at 10% have bulky particles and the fish-in-hole distribution was unobservable.



Figure S34. TEM image and particle size distribution of (A and B) Pd/Y after calcination at 600 $^{\circ}$ C for 2 h and (C and D) used Pd/Y in CO oxidation test.



Figure S35. TEM image and particle size distribution of (A and B) Pd-FIH@Beta, (C and D) Pd-FIH@ZSM-5 after calcination at 600 $\,^{\circ}$ C for 2 h.



Figure S36. TEM image and particle size distribution of (A and B) Pd/Beta and (C and D) Pd/ZSM-5 after calcination at 600 $\,^{\circ}$ C for 2 h.



Figure S37. TEM images of (A and B) FIH-Pd@Y, (C and D) Pd/Al₂O₃, (E and F) Pd/SiO₂ before and after calcination at 800 °C. (A, C, E) as-synthesized and (B, D, F) calcined samples.



Figure S38. Recycle test of FIH-Pd@Y in the hydrogenation of styrene to ethylbenzene. Reaction conditions: 2 mmol styrene, 1 atm H₂, 20 mg catalyst, 5 mL toluene, 50 °C, 0.5 h. The ethylbenzene selectivity is over 99.9% in each run.

Note: We performed the hydrogenation of styrene in liquid phase to investigate the reusability of FIH-Pd@Y catalyst. As shown in the figure, the styrene conversions were unchanged within error in the continuous recycle tests (8 runs), suggesting the good recyclability.



Figure S39. Data of various catalysts in CO oxidation. (a) As-synthesized FIH-Pd@Y, (b) calcined FIH-Pd@Y, (c) Pd/Al₂O₃, (d) Pd/SiO₂, (e) calcined Pd/Al₂O₃, and (f) calcined Pd/SiO₂. The reaction conditions are the same to those in Table 1 in the main text.

Note: Figure S38 shows the dependences of CO conversion on reaction temperature over various catalysts before and after calcination at 800 °C. After thermal treatment of the catalyst at 800 °C, the obtained FIH-Pd@Y still gave the temperature for full conversion of CO at 180 °C. In contrast, the temperatures for full conversion of CO were remarkably increased over the Pd/SiO₂ and Pd/Al₂O₃ (Figure S39), which is reasonably attributed to the aggregated Pd nanoparticles, as confirmed by the TEM characterization (Figure S37). These results demonstrate that the *fish-in-hole* structure in the catalysts is sinter-resistant, which offers a good opportunity for design and preparation of highly efficient and stable metal nanoparticles for catalytic applications in the future.

The strong metal-support interactions have been widely used for stabilizing metal nanoparticles (*e.g.* Au) in CO oxidation. For example, the hydroxyapatite-titanium dioxide support Au nanoparticles with strong metal-support interactions, which have been reported to be one of the most stable catalysts, gives the full conversion of CO at 0 \mathbb{C} .¹⁰ After calcination treatment at 800 \mathbb{C} , the resulted catalyst was slightly deactivated, reaching full conversion of CO at 100 \mathbb{C} . Interestingly, the FIH-Pd@Y zeolite gives comparable catalytic performances before and after the calcination

treatment, where the fresh and calcined catalysts both gives full conversion of CO at 180 $^{\circ}$ C, demonstrating the high efficacy of *fish-in-hole* strategy for sinter-resistant catalysts.

Supporting References

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