

## Supporting Information

### Direct Synthesis of Pure Aqueous H<sub>2</sub>O<sub>2</sub> Solution within Aluminosilicate Zeolite Crystals

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## Materials and Methods

**Materials.** All reagents were commercially obtained without purification. Tetrapropylammonium hydroxide (TPAOH, *ca.* 40%) and boehmite (AlOOH) were supplied by Shanghai Cairui Chemical Technology Co. Ltd. Tetraethyl orthosilicate (TEOS), sodium borohydride, sodium chloride, ethanol, methanol, hydrofluoric acid, FeCl<sub>2</sub>, rhodamine B and polyvinyl pyrrolidone (PVP) were obtained from the Aladdin Chemical Reagent Company. Sodium hydroxide, ammonium acetate and sodium aluminate (NaAlO<sub>2</sub>) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ammonia solution (25-28 wt%) was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Chlorauric acid and palladium chloride (PdCl<sub>2</sub>) were obtained from Zhejiang Metallurgical Research Institute. Palladium chloride acid sodium (NaPdCl<sub>4</sub>) aqueous solution was made by dissolving 887 mg of PdCl<sub>2</sub> and 585 mg of NaCl in 100 mL of de-ionized water.

## Synthesis

**Synthesis of AuPd@SiO<sub>2</sub>.** Bimetallic Au-Pd nanoparticle colloid was firstly synthesized as a precursor for AuPd@SiO<sub>2</sub> preparation. As a typical run for the synthesis of AuPd nanoparticle colloid, 1.111 g of PVP was added to 100 mL of aqueous HAuCl<sub>4</sub> and Na<sub>2</sub>PdCl<sub>4</sub> solution (mass ratio of Au and Pd at 1, 25 mg of Au and 25 mg of Pd in the solution) in an ice bath and stirred for 0.5 h. Then, 10 mL of newly made NaBH<sub>4</sub> (0.1 M) aqueous solution was added to the solution. After stirring for another 2 h, the mixture was dialyzed by a membrane in de-ionized water for 2 days to remove the Na<sup>+</sup> and Cl<sup>-</sup> ions to finally obtain the Au-Pd nanoparticle colloid.

80 mL of ethanol and 6 mL of ammonia solution (25-28 wt%) were added into the aforementioned AuPd colloid under stirring. After stirring for 0.5 h, 3.47 g of TEOS was added into the mixture and stirred at room temperature for 12 h. Then the ethanol and water solvents were removed under vacuum at 60 °C, and the powder was dried at 100 °C for 12 h to obtain the amorphous silica fixed AuPd nanoparticle, which is denoted as AuPd@SiO<sub>2</sub>.

**Synthesis of AuPd@HZSM-5.** 1 g of AuPd@SiO<sub>2</sub>, 0.027 g of boehmite, and 0.833 g of TPAOH (40 wt%) was grinded in a mortar for 30 min, then the mixture was transferred into an autoclave and crystallized at 180 °C for 3 days. After washing the solid sample with distilled water for several times at room temperature, drying at 100 °C, and calcining at 550 °C for 4 h to remove the organic species, the AuPd@HZSM-5 sample with atomic Si/Al ratio at 36 was obtained. The other samples with different Si/Al ratio was synthesized following the similar precursors except changing the amount of boehmite in the precursors. If there is no special notification in this manuscript, the AuPd@HZSM-5 is the sample with atomic Si/Al ratio at 36.

**Synthesis of AuPd@S-1.** The AuPd@S-1 was synthesized from similar precursors of AuPd@HZSM-5 synthesis in the absence of boehmite in the starting gel.

*Synthesis of AuPd@NaZSM-5.* The AuPd@NaZSM-5 was synthesized from similar precursors of AuPd@HZSM-5 synthesis except for using 0.046 g of sodium aluminate instead of boehmite in the starting gel.

*Synthesis of Au@HZSM-5 and Pd@HZSM-5.* The Au@HZSM-5 and Pd@HZSM-5 were synthesized from similar precursors of AuPd@HZSM-5 synthesis except for using HAuCl<sub>4</sub> or Na<sub>2</sub>PdCl<sub>4</sub> as the metal precursor rather than their mixture.

*Synthesis of AuPd@HZSM-5-HF.* 1 g of AuPd@HZSM-5 was stirred in 20 mL of hydrofluoric acid aqueous solution (0.5 mol/L) for 5 min. Then the solid was filtered and washed with a large amount of water, and dried at 100 °C for 8 h to obtain the AuPd@HZSM-5-HF sample.

*Synthesis of ZSM-5 zeolite.* 0.052 g of sodium aluminate, 3 mL of TPAOH (40 wt%), and 3.5 mL of TEOS were dissolved in 11.28 g of water and stirred for 30 min at room temperature. Then the mixture was transferred into an autoclave and hydrothermally treated at 180 °C for 3 days. After filtrating, washing with water, and calcining to remove the template at 550 °C for 4 h in air, the Na-form ZSM-5 zeolite was obtained. An ion-exchange process was performed to obtain the H-form ZSM-5. Typically, 1 g of Na-form ZSM-5 zeolite was dispersed in 50 mL of ammonium acetate (0.1 M), followed by stirring at 80 °C for 4 h. Then the solid powder was collected by filtrating, washing with water, drying at 100 °C, and calcining at 400 °C for 2 h. The aforementioned procedures were repeated to obtain the H-form ZSM-5 zeolite, which is denoted as HZSM-5.

*Synthesis of AuPd/HZSM-5.* 1 g of HZSM-5 zeolite was added into 5.6 g of aqueous HAuCl<sub>4</sub> (4.46 g/L of Au) and Na<sub>2</sub>PdCl<sub>4</sub> (4.46 g/L of Pd) solution. The mixture was treated under ultrasonic at room temperature for 1 h, and localized quietly for 12 h. Then, the mixture was grinded at 70-80 °C to remove the water, heated at 100 °C for 6 h, and calcined at 400 °C for 3 h in air to obtain the AuPd/HZSM-5 sample. The AuPd/TiO<sub>2</sub> and AuPd/SiO<sub>2</sub> samples were synthesized from similar procedures except for using titania and silica as the supports.

## **Characterizations**

X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu K $\alpha$  ( $\lambda=1.5418$  Å). The step size was 0.02°, and the scanning speed was 20° min<sup>-1</sup>. Si/Al ratios and the amount of Au and Pd elements were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Nitrogen sorption isotherms were measured using a Micromeritics ASAP2020 system. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy dispersivespectrometer (EDS) were performed on a JEM-2100F electron microscopy (JEOL, Japan) with an acceleration voltage of 200 kV. In the STEM and EDS characterizations, the sample was loaded on a Cu mesh with carbon film. The end

point of titration was judged by an automatic potentiometric titrator LeiCi ZDJ-4B with a burette of 10 mL and coefficient of 0.9979. UV-Vis spectra were collected on a UV-2600 spectrophotometer made in Shimadzu with wavelength accuracy of  $\pm 0.3$  nm. The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was performed on a Micromeritics ChemiSorb 2720 Pulse Chemisorption System. MS test was performed using a Tilon mass spectrometer (SRD200M) connected to the autoclave. Thermogravimetric analysis (TG) was performed on a SDT Q600 Simultaneous DSC-TGA in flowing air with a heating rate of 10 K/min. FT-IR spectra were recorded using a Bruker Vector22 FT-IR spectrometer equipped with a MCT/A detector.

### Catalyst evaluation

*H<sub>2</sub>O<sub>2</sub> synthesis.* The direct synthesis of H<sub>2</sub>O<sub>2</sub> with H<sub>2</sub> and O<sub>2</sub> was carried out in a stainless-steel autoclave containing a Teflon liner vessel with a total volume of 30 mL. The catalysts were reduced in hydrogen at 300 °C for 2 h before the catalysis. As a typical run, 8.6 g of methanol, 3.2 g of water, and 30 mg of solid catalyst were mixed in the autoclave, which was localized in an ice bath at  $0 \pm 2$  °C (the temperature was measured *via* a thermometer). After removing the air in the autoclave with 10% H<sub>2</sub>/90% Ar (2 MPa) for three times, the feed gas containing 5% H<sub>2</sub>, 10% O<sub>2</sub>, 45% Ar, and 40% He was induced with the desired pressure (e.g. 4.0 MPa, the pressure was measured at reaction temperature). The stirring speed was controlled at 1200 rpm. After reaction for 30 min, the autoclave was directly connected into a gaseous chromatograph (GC) containing a thermal conductivity detector (TCD) with a TDX-1 column for analyzing the gas composition using Ar as an internal standard. The GC lines were swept for 20 s before analysis. The reactions were repeated for multiple times to obtain the error bounds.

The conversion of H<sub>2</sub> was calculated according to the following equations:

$$mol_{H_2} = \frac{mol_{Ar}}{Area_{peak\ of\ Ar\ in\ TCD}} * f(correction\ factor) * Area_{peak\ of\ H_2\ in\ TCD}$$

$$H_2\ Conversion = \frac{mol_{initial\ H_2} - mol_{H_2\ after\ reaction}}{mol_{initial\ H_2}} \times 100\%$$

After analyzing the gaseous phase, the solid catalyst was separated from the liquor *via* centrifugation and the liquor was analyzed by potentiometric titration using a standard aqueous solution of acidified Ce(SO<sub>4</sub>)<sub>2</sub> (0.01 M). The end of titration was judged by the potential jump of the solution as identified by a potentiometric titrator (Leici). The Ferroin indicator was also used to judge the end of titration for data conformation.

$$Yield = \frac{mol_{produced\ H_2O_2}}{mol_{initial\ H_2}} \times 100\%$$

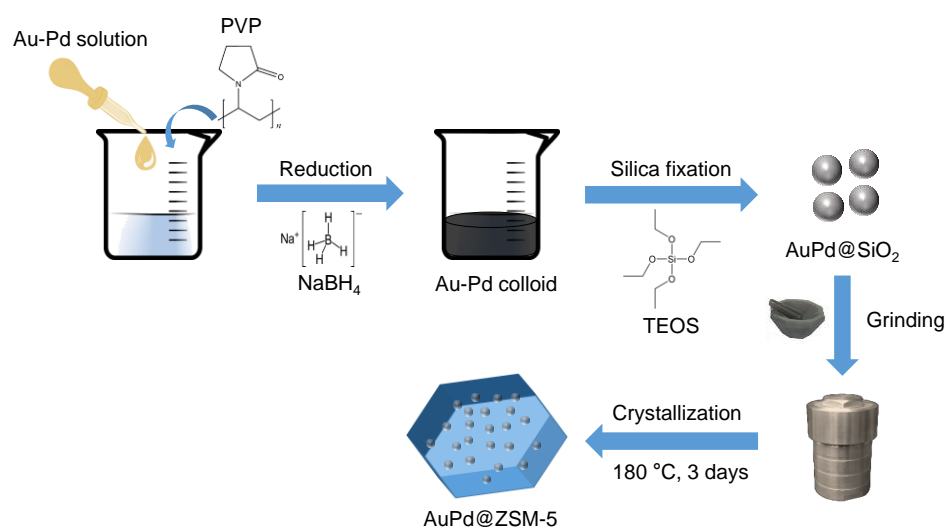
$$Selectivity = \frac{Yield}{Conversion} \times 100\%$$

The productivity of H<sub>2</sub>O<sub>2</sub> was calculated *via* the equation in the following:

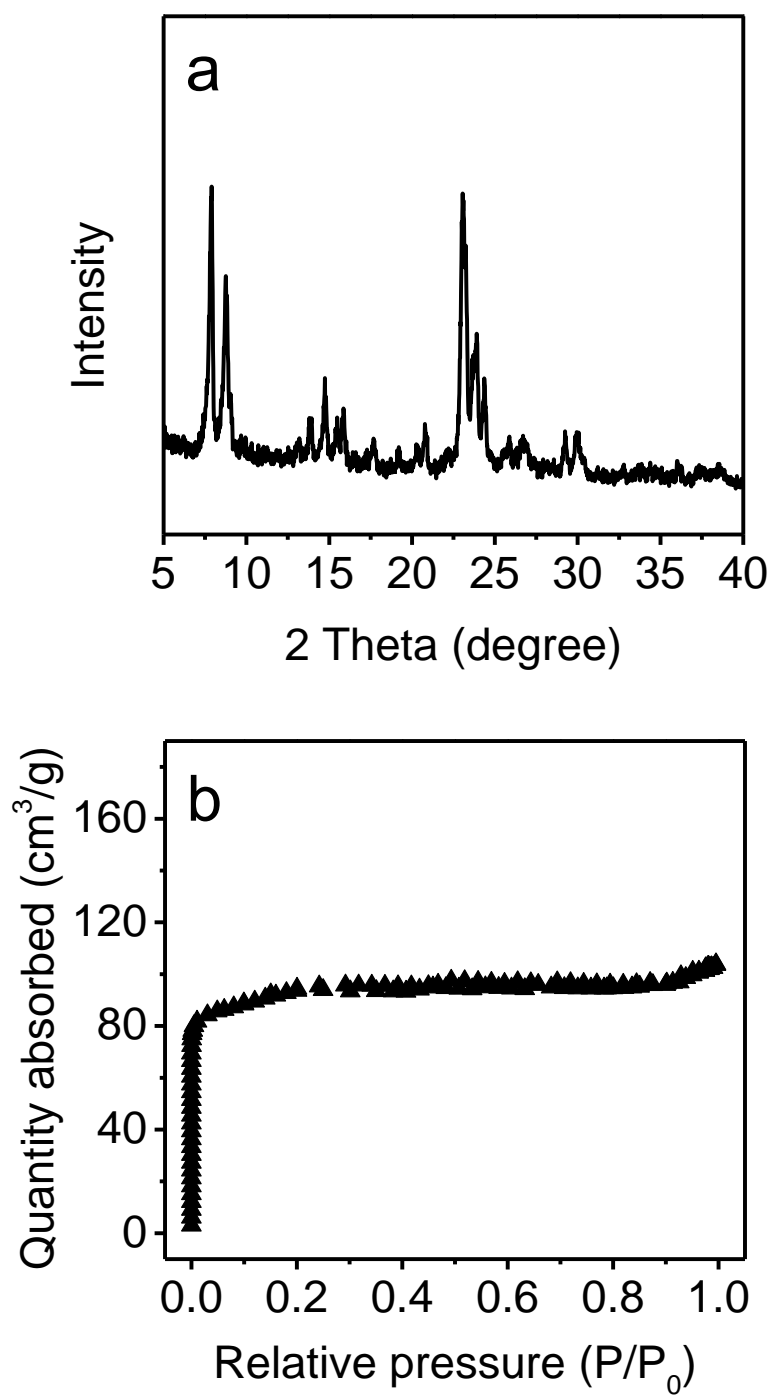
$$Productivity [mol/(g_{AuPd} * h)] = \frac{produced\ H_2O_2\ (mol)}{weight\ of\ AuPd\ (g) * reaction\ time\ (h)}$$

*H<sub>2</sub>O<sub>2</sub> degradation.* The degradation of H<sub>2</sub>O<sub>2</sub> was carried out in an autoclave with a total volume of 30 mL. As a typical run, the water (10 g), H<sub>2</sub>O<sub>2</sub> (~50 mmol/L), and solid catalyst (30 mg) were mixed in the autoclave, which was localized in an ice bath (the temperature was measured *via* a thermometer in the autoclave). Then, 2 MPa of 20% O<sub>2</sub> with 80% He were fed into the autoclave and kept as 2 MPa. After reaction, the solid catalyst was separated and the H<sub>2</sub>O<sub>2</sub> amount in the liquor was analyzed.

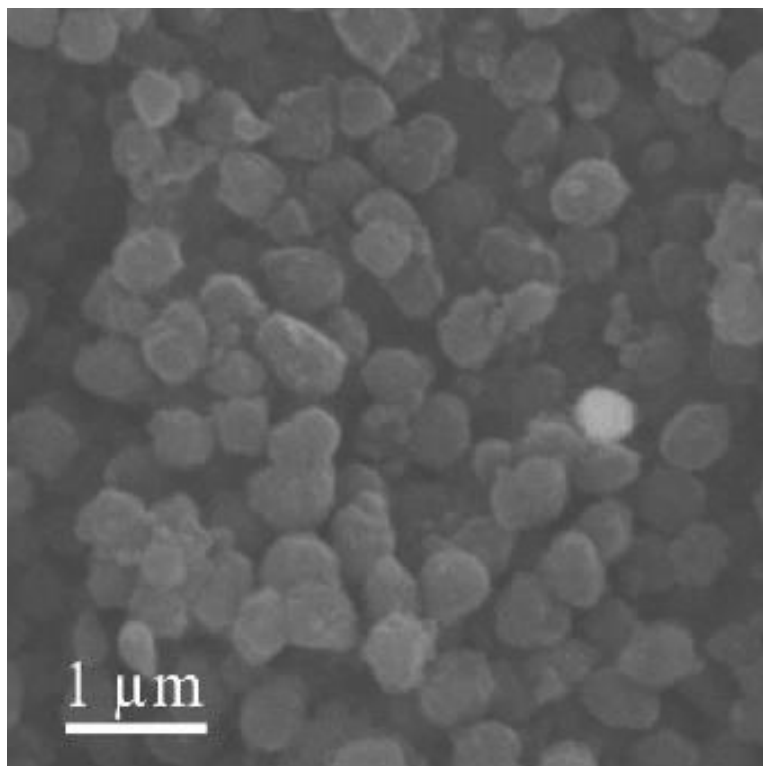
*Catalyst recycle test.* After each reaction, the solid catalyst was separated by centrifugation and dried at 100 °C for 12 h. Then, the catalyst was reduced with hydrogen at 300 °C for 2 h and used in the next run.



**Figure S1.** Synthesis procedures of the AuPd@HZSM-5.

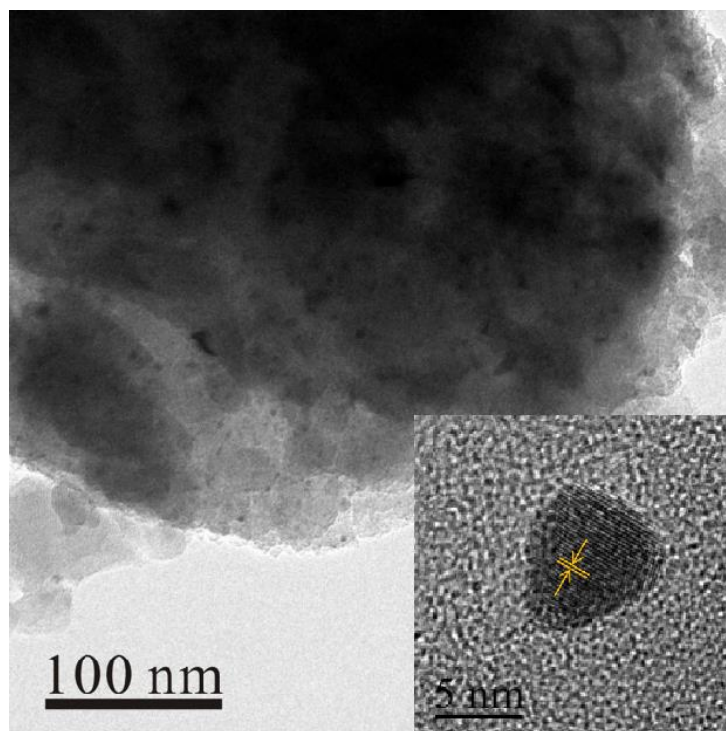


**Figure S2.** (a) XRD pattern and (b) N<sub>2</sub> sorption isotherms of the AuPd@HZSM-5.

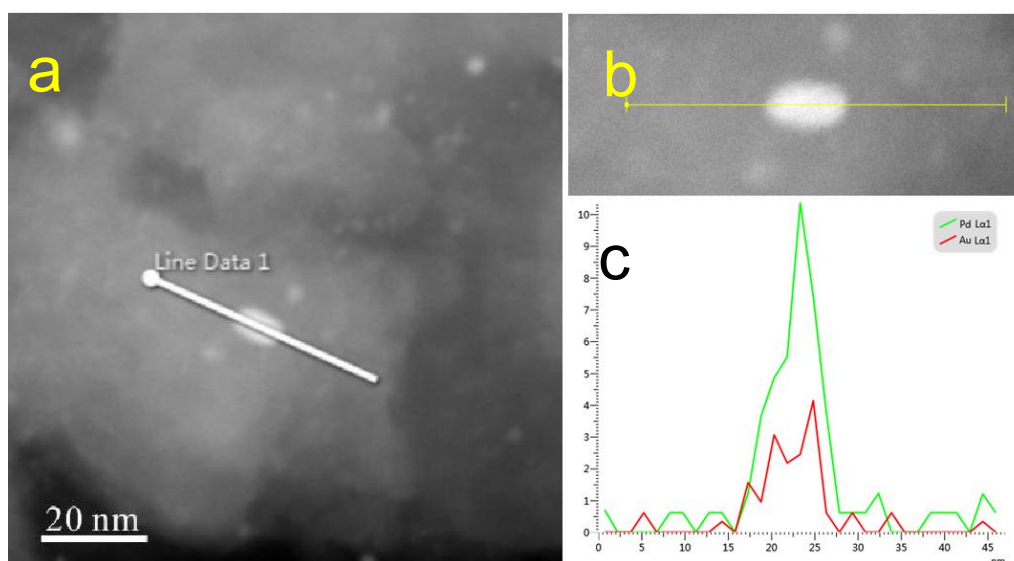


**Figure S3.** SEM image of the AuPd@HZSM-5.

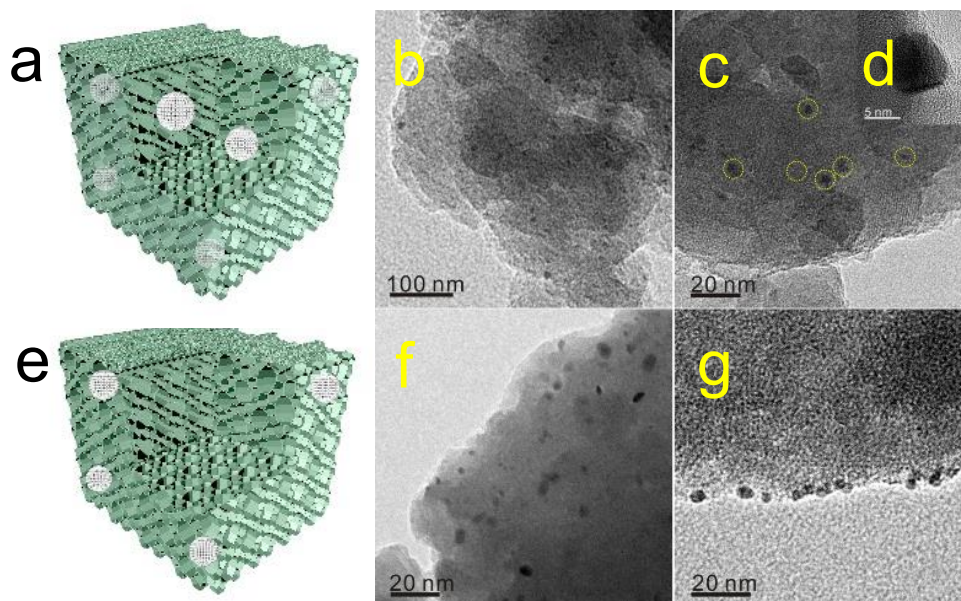




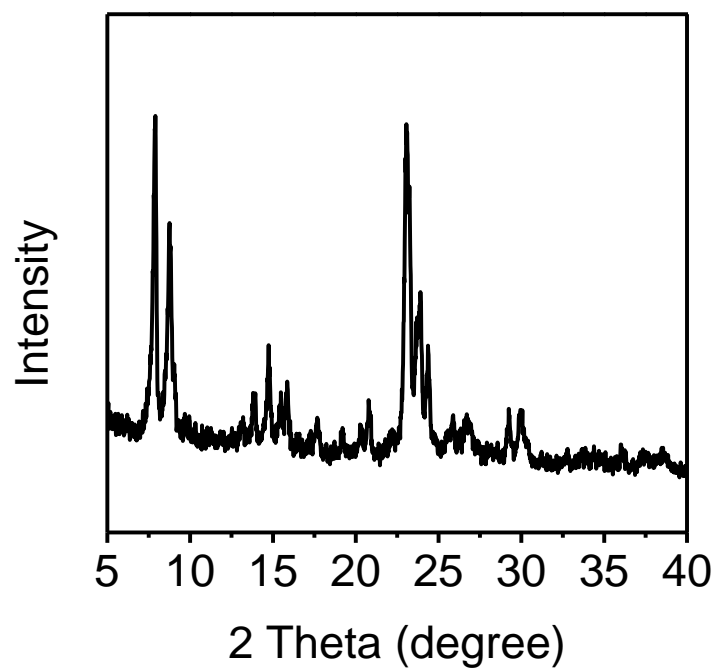
**Figure S4.** TEM images of AuPd@HZSM-5 and AuPd nanoparticle.



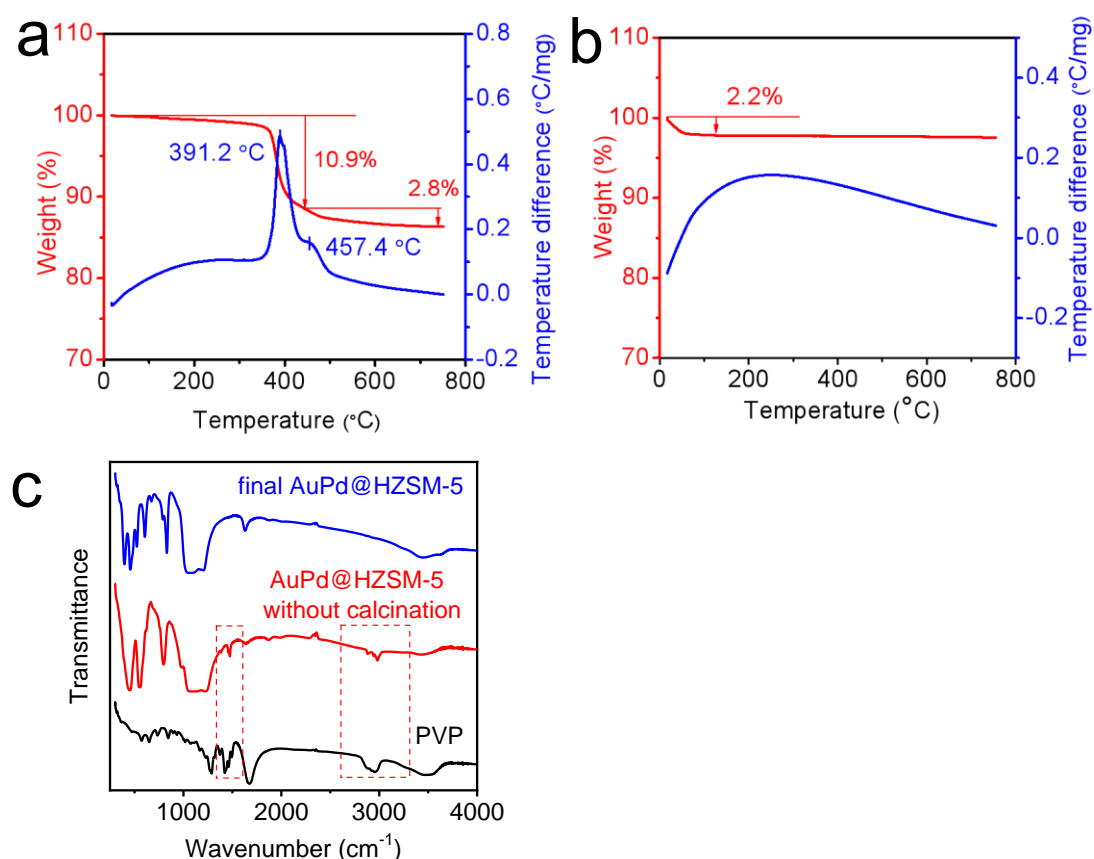
**Figure S5.** (a,b) STEM images and (c) linear scan analysis of AuPd of in the AuPd@HZSM-5. The Au and Pd element distributions are highly constant with each other, which is a typical feature of alloyed structure.



**Figure S6.** Structure and TEM images of the (a-d) AuPd@HZSM-5 and (e-g) AuPd/HZSM-5 samples.

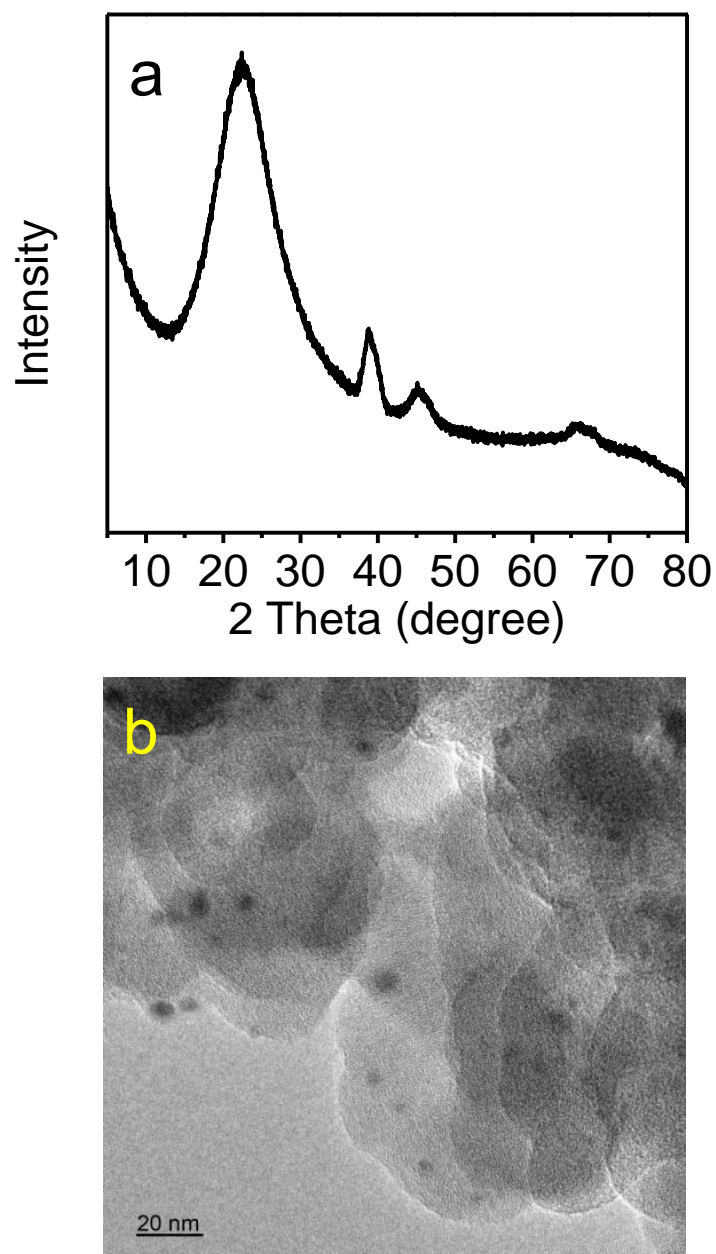


**Figure S7.** XRD pattern of the AuPd/HZSM-5.

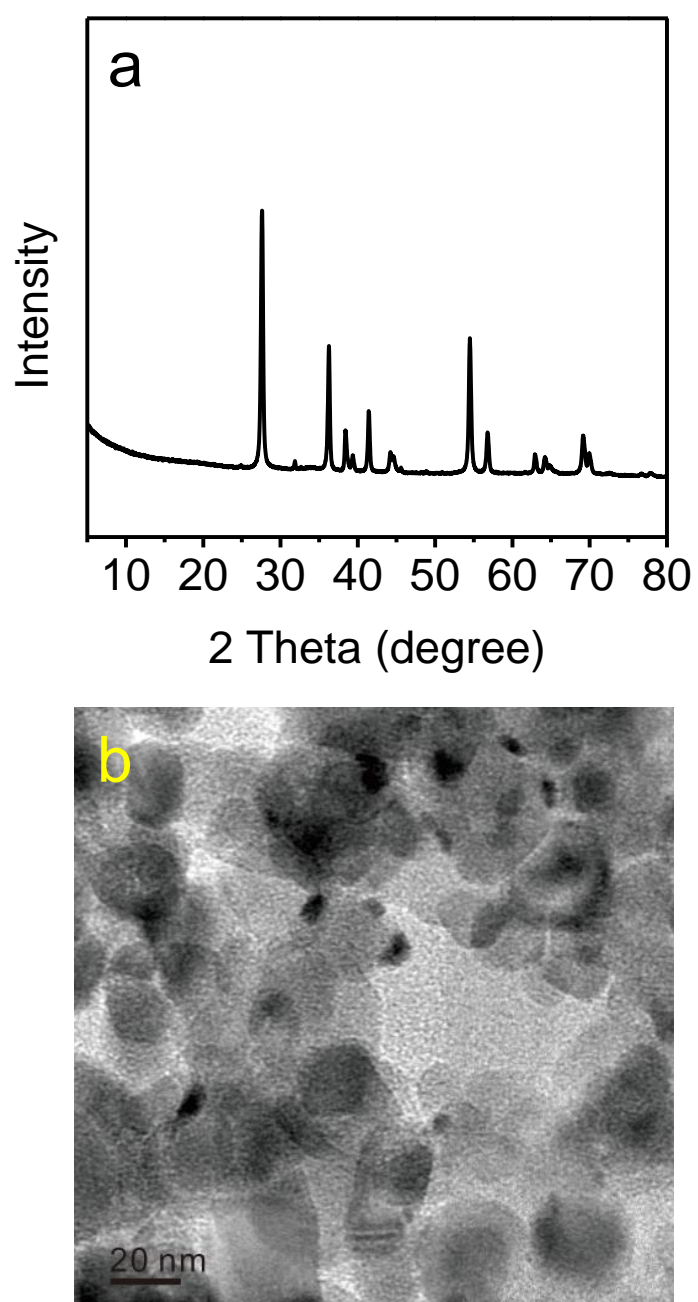


**Figure S8.** TG analysis of (a) as-synthesized AuPd@HZSM-5 sample without calcination and (b) the final AuPd@HZSM-5 catalyst after calcination treatment. (c) FT-IR spectra of various samples.

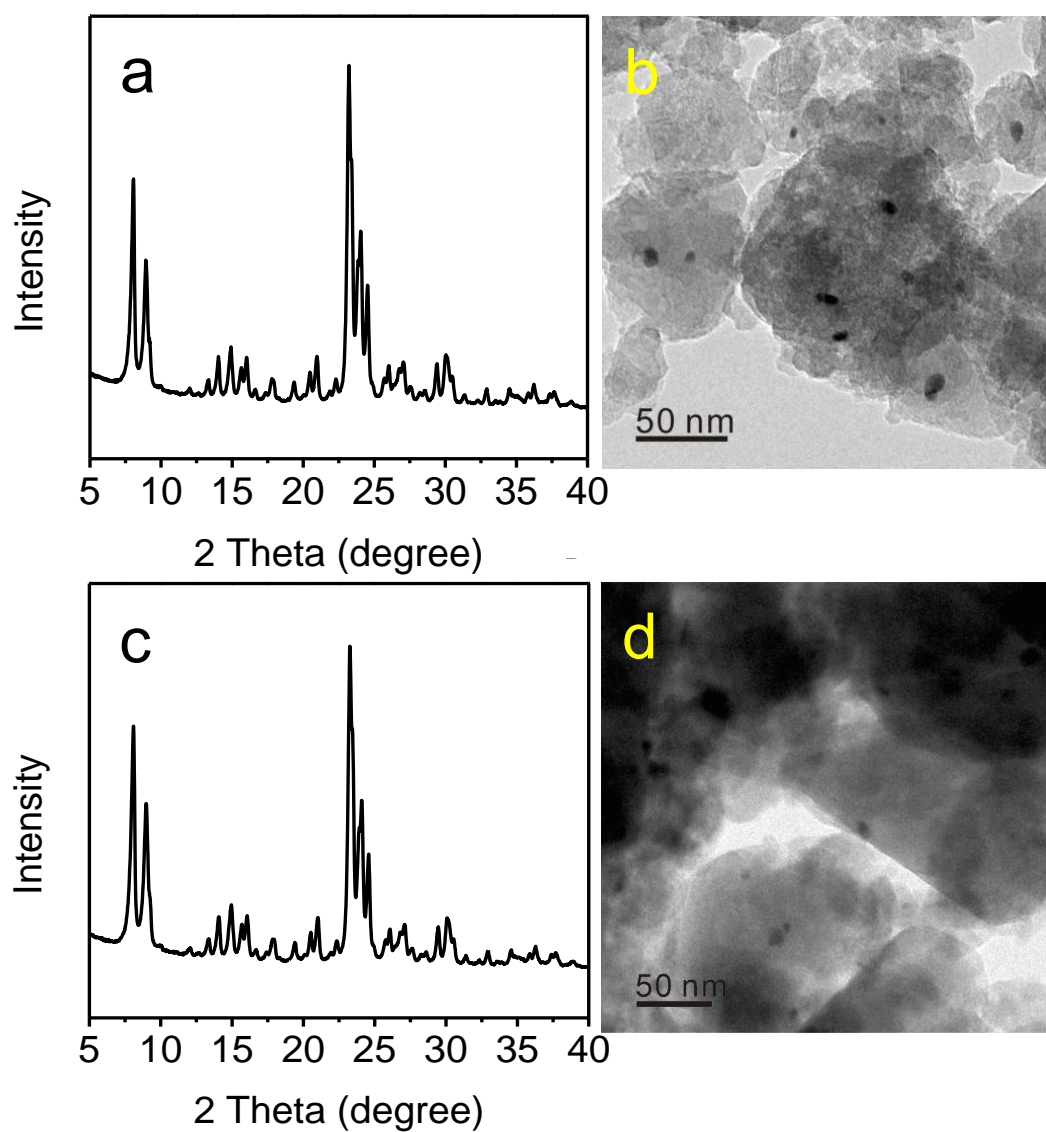
**Note:** As shown in Figures S8a and b, the as-synthesized AuPd@HZSM-5 sample without calcination treatment exhibited an obvious weight loss at about 360-500 °C, which is assigned to the combustion of organic template and PVP species. For the final AuPd@HZSM-5 catalyst (the sample after calcination treatment at 550 °C and reduction with H<sub>2</sub> at 300 °C), the weight loss was undetectable, suggesting the negligible organic species. Figure S8c shows FT-IR spectra of these samples, where the as-synthesized AuPd@HZSM-5 sample without calcination shows the bands at about 2860-2980 and 1423 cm<sup>-1</sup>, confirming the existence of PVP species. In contrast, these signals are undetectable on the final AuPd@HZSM-5 catalyst, suggesting the successful removal of PVP species by calcination, which is in good agreement with the TG result.



**Figure S9.** (a) XRD pattern and (b) TEM image of AuPd/SiO<sub>2</sub>.

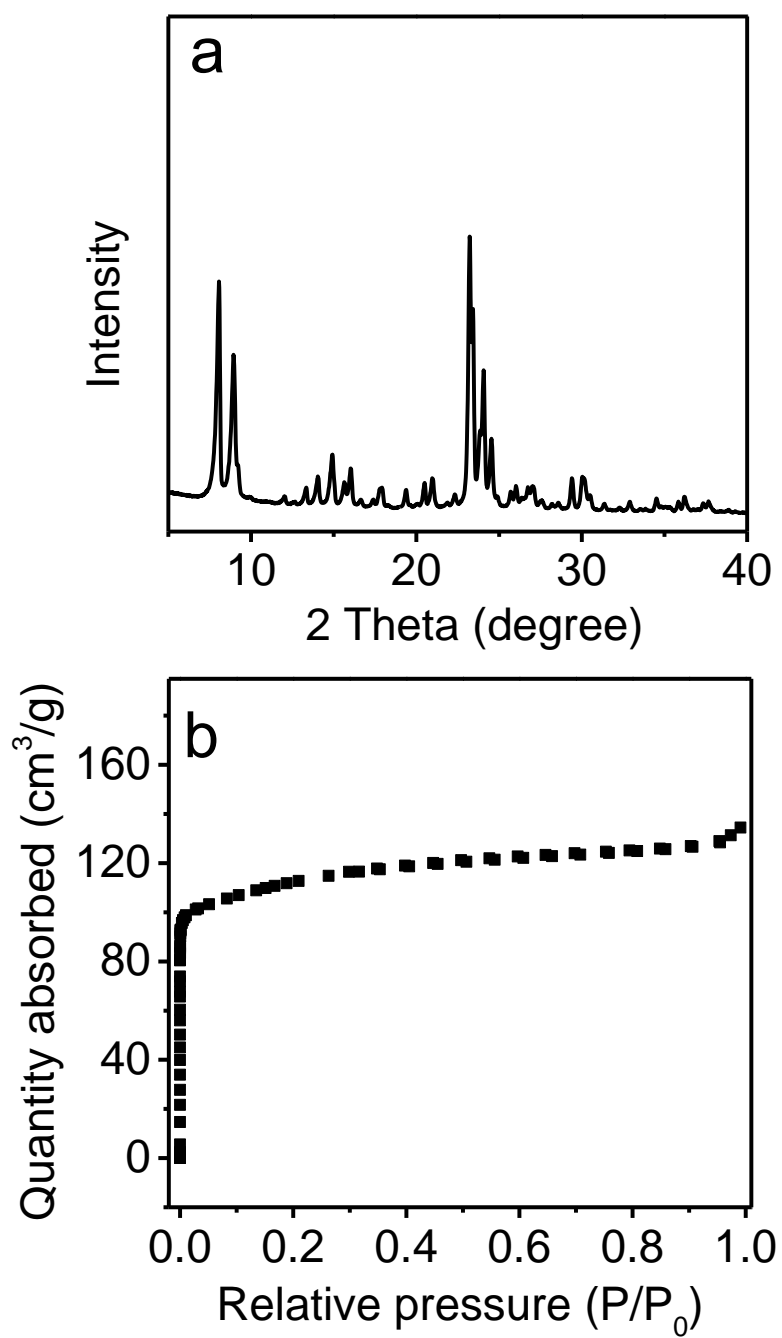


**Figure S10.** (a) XRD pattern and (b) TEM image of AuPd/TiO<sub>2</sub>.

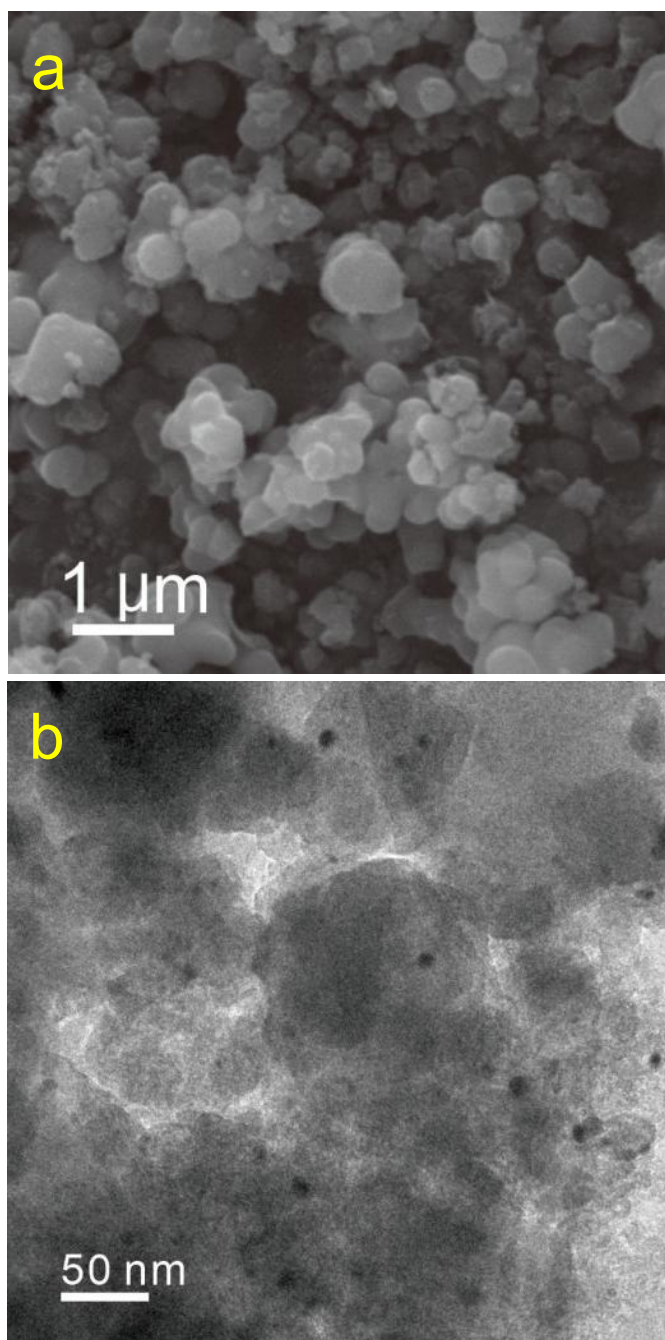


**Figure S11.** (a,c) XRD patterns and (b,d) TEM images of the Pd@HZSM-5 and Au@HZSM-5.

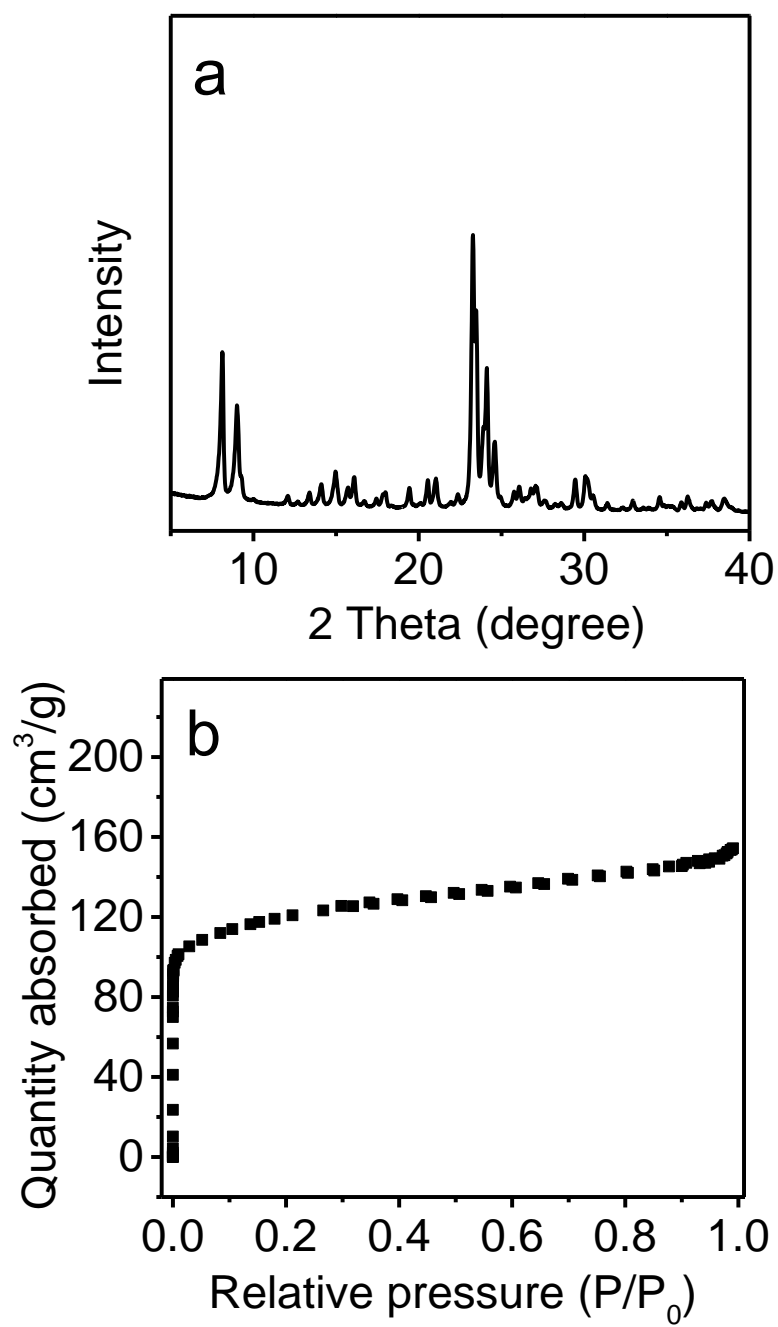




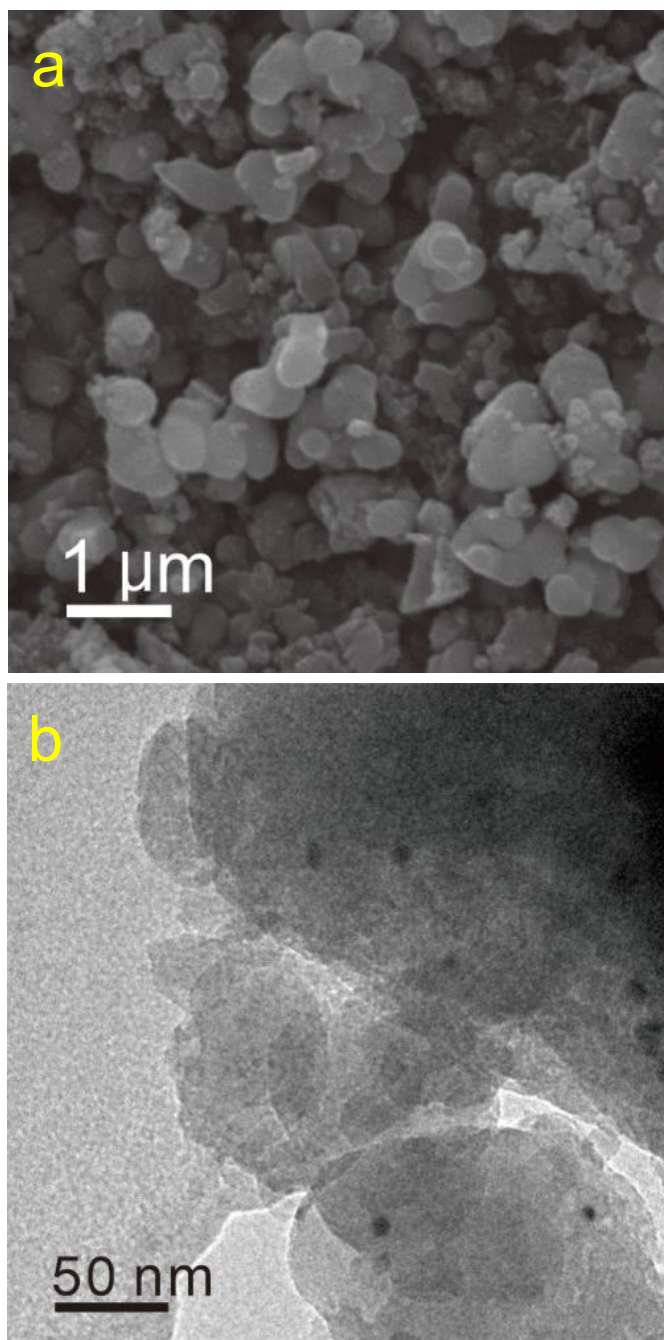
**Figure S12.** (a) XRD pattern and (b) N<sub>2</sub> sorption isotherms of the AuPd@NaZSM-5.



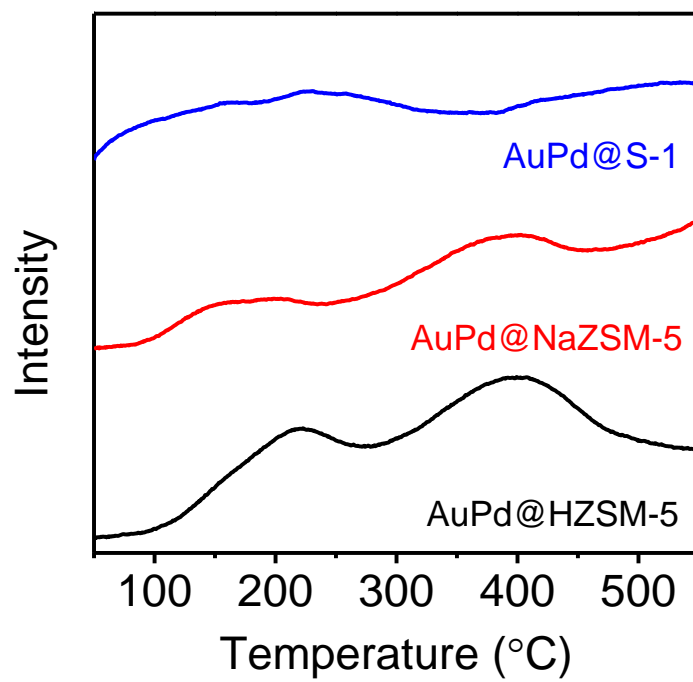
**Figure S13.** (a) SEM and (b) TEM images of the AuPd@NaZSM-5.



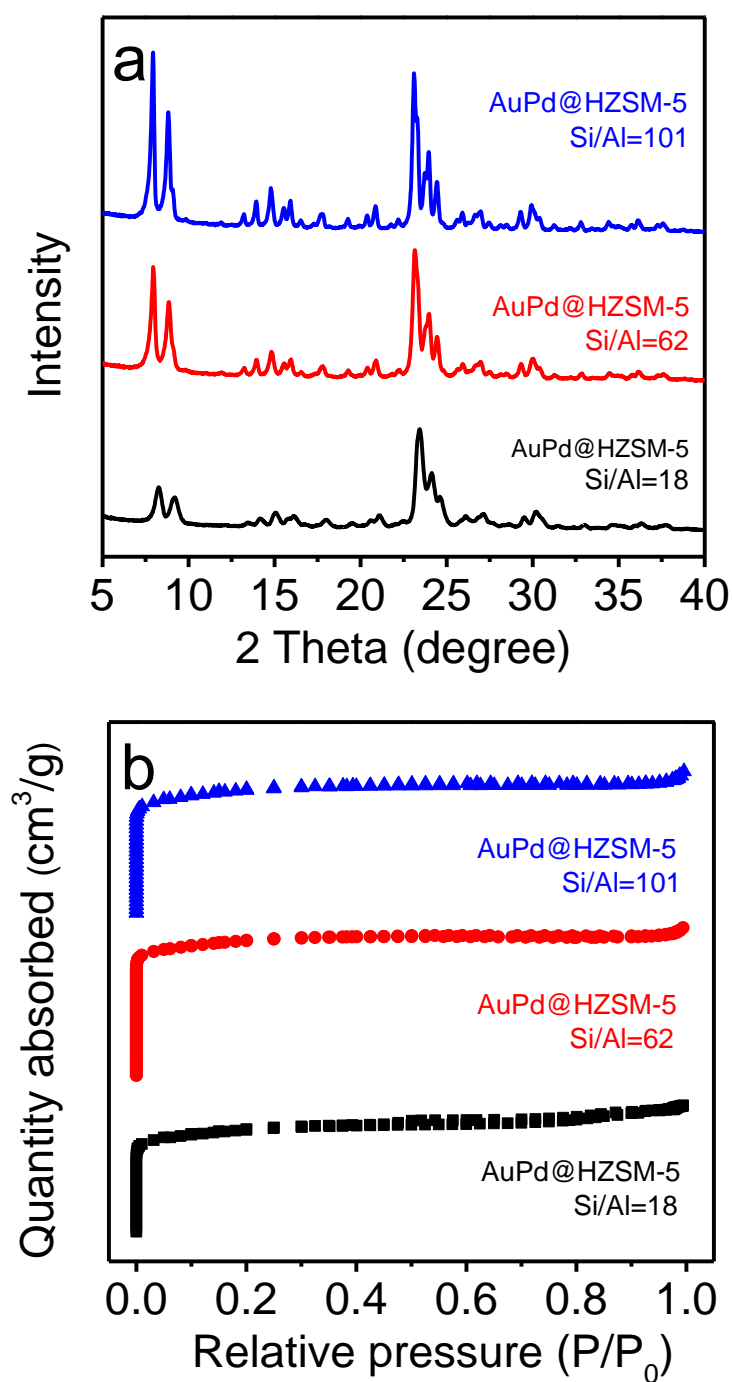
**Figure S14.** (a) XRD pattern and (b) N<sub>2</sub> sorption isotherms of the AuPd@S-1.



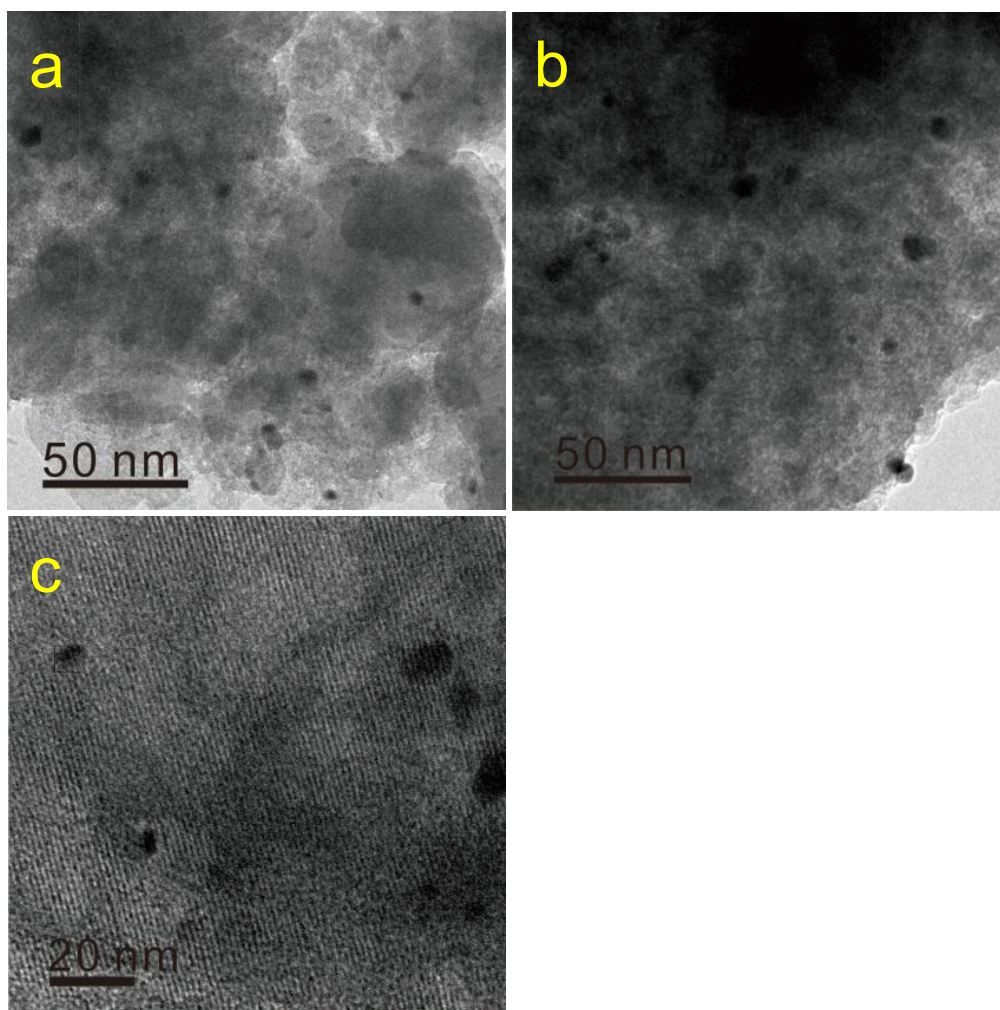
**Figure S15.** (a) SEM and (b) TEM images of the AuPd@S-1.



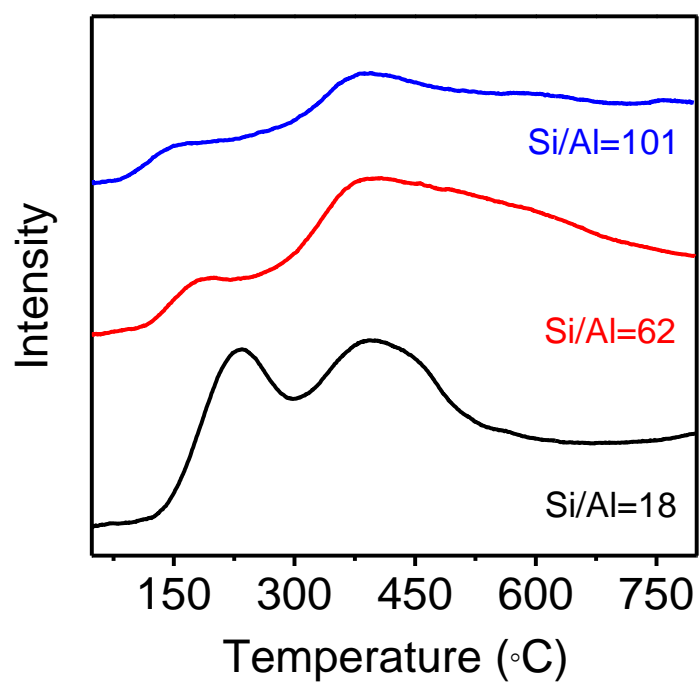
**Figure S16.** NH<sub>3</sub>-TPD of the AuPd@HZSM-5, AuPd@NaZSM-5, and AuPd@S-1 samples.



**Figure S17.** (a) XRD patterns and (b) N<sub>2</sub> sorption isotherms of the AuPd@HZSM-5 with atomic Si/Al ratios at 18, 62, and 101, respectively.

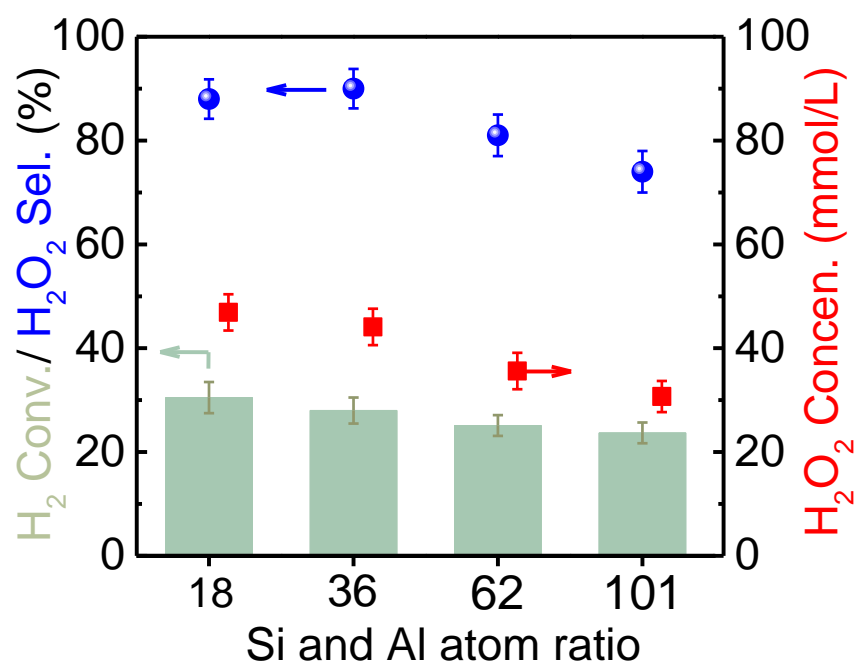


**Figure S18.** TEM images of the AuPd@HZSM-5 with atomic Si/Al ratio at (a) 18, (b) 62, and (c) 101, respectively.

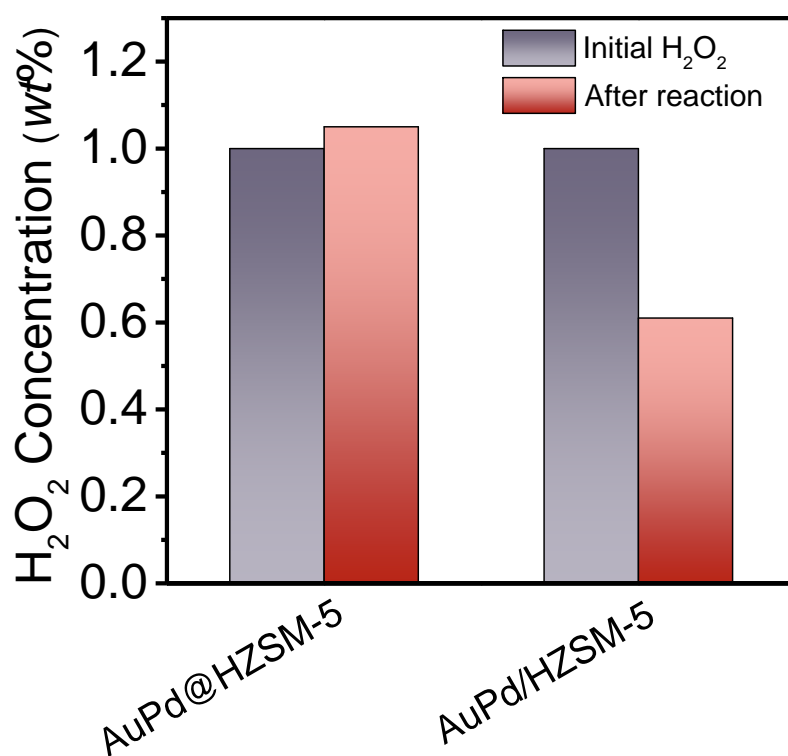


**Figure S19.** NH<sub>3</sub>-TPD curves of the AuPd@HZSM-5 samples with different atomic Si/Al ratios.

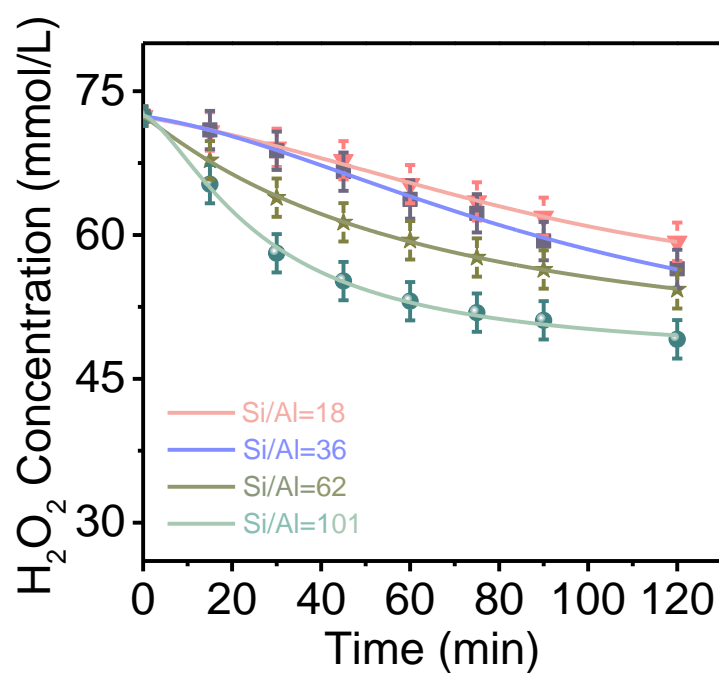




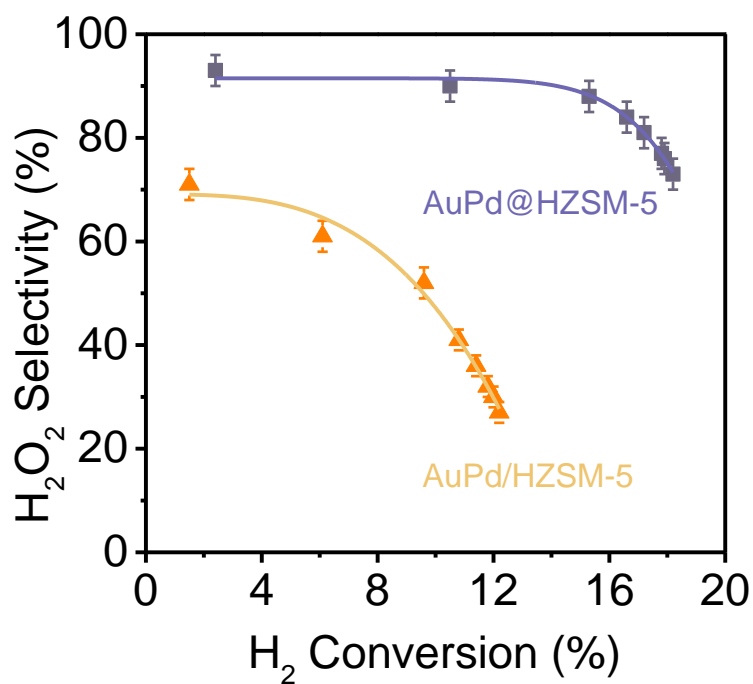
**Figure S20.** Data characterizing the performances of the AuPd@HZSM-5 catalysts with different atomic Si/Al ratios. Reaction conditions: 5% H<sub>2</sub>/10% O<sub>2</sub>/40% He/45% Ar, total pressure at 4 MPa, 10 g of H<sub>2</sub>O, 30 mg of catalyst, 1200 rpm, 2 ± 2 °C. The columns, H<sub>2</sub> conversions; blue dots, H<sub>2</sub>O<sub>2</sub> selectivities; red dots, H<sub>2</sub>O<sub>2</sub> concentrations.



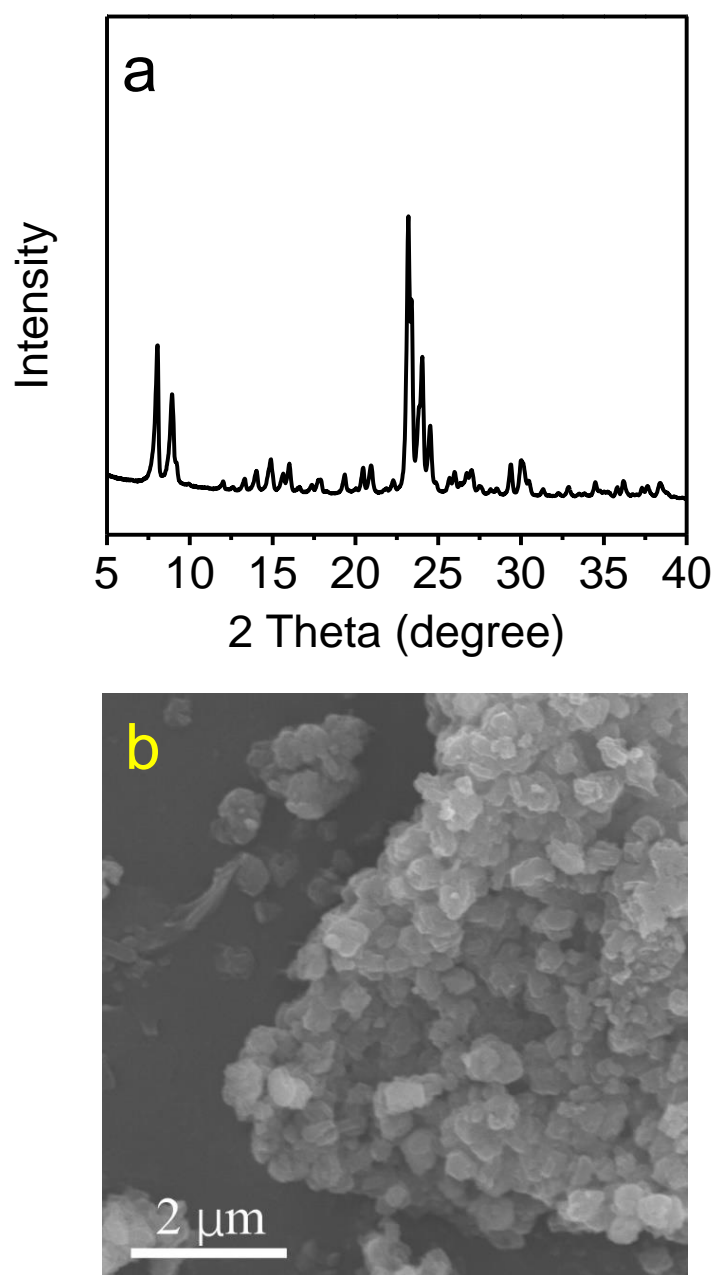
**Figure S21.** Data characterizing the performance of the AuPd@HZSM-5 and AuPd/HZSM-5 in the direct synthesis of H<sub>2</sub>O<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> in the starting solution. Reaction conditions: 5% H<sub>2</sub>/10% O<sub>2</sub>/40% He/45% Ar, total pressure at 4 MPa, 10 mL of 1 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution, 30 mg of catalyst, 1200 rpm, 2 ± 2 °C, 30 min.



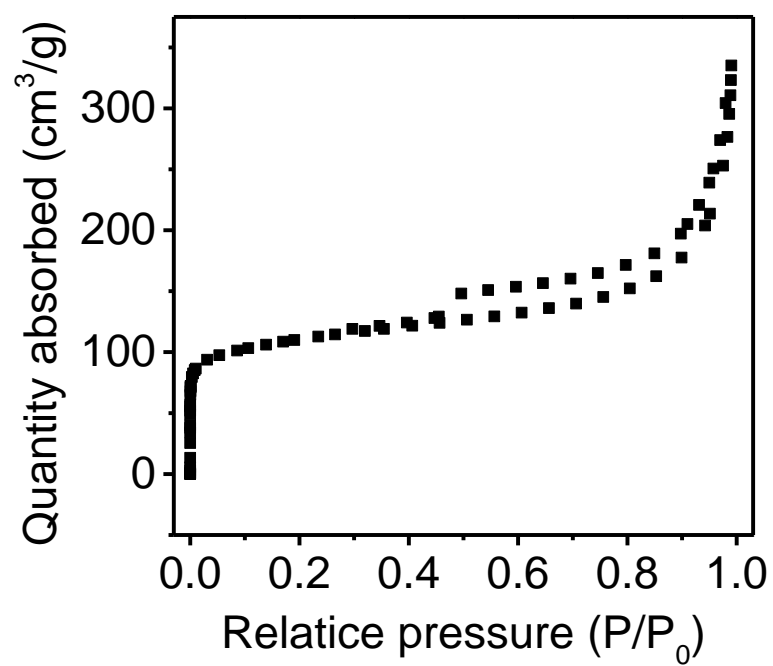
**Figure S22.** Dependences of H<sub>2</sub>O<sub>2</sub> concentration on time in the degradation test over the AuPd@HZSM-5 catalysts with different Si/Al ratios. Reaction conditions: 20% O<sub>2</sub>/80% Ar, total pressure at 2 MPa, 30 mg of catalyst, 8.6 g methanol and 3.2 g of H<sub>2</sub>O, 75 mmol/L of H<sub>2</sub>O<sub>2</sub>, 1200 rpm, 2 ± 2 °C.



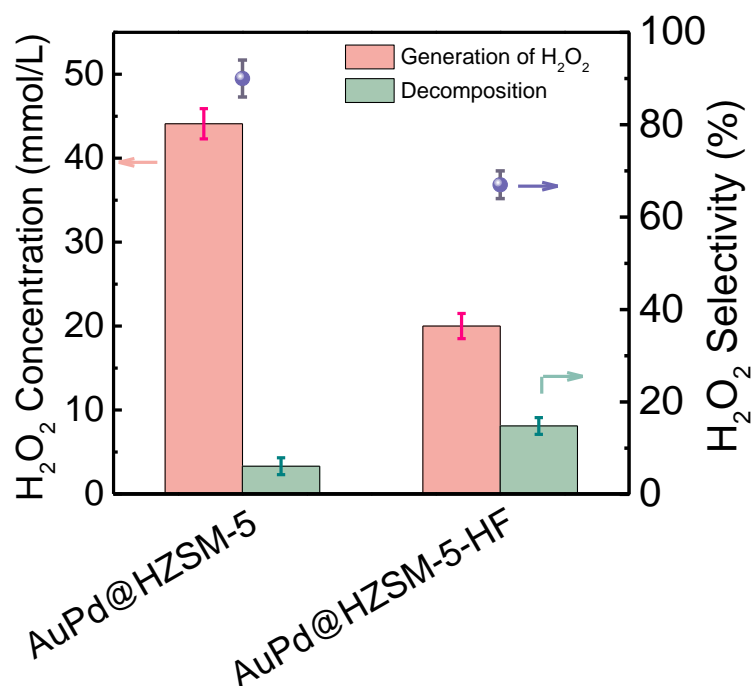
**Figure S23.** Dependence of H<sub>2</sub>O<sub>2</sub> selectivity on H<sub>2</sub> conversion in H<sub>2</sub>O<sub>2</sub> synthesis reaction over the AuPd@HZSM-5 and AuPd/HZSM-5 catalysts. Reaction conditions: 5% H<sub>2</sub>/10% O<sub>2</sub>/40% He/45% Ar, total pressure at 4 MPa, 8.6 g methanol and 3.2 g of H<sub>2</sub>O, 30 mg of catalyst, 1200 rpm, 2 ± 2 °C, 30 min.



**Figure S24.** (a) XRD pattern and (b) SEM image of the AuPd@HZSM-5-HF.

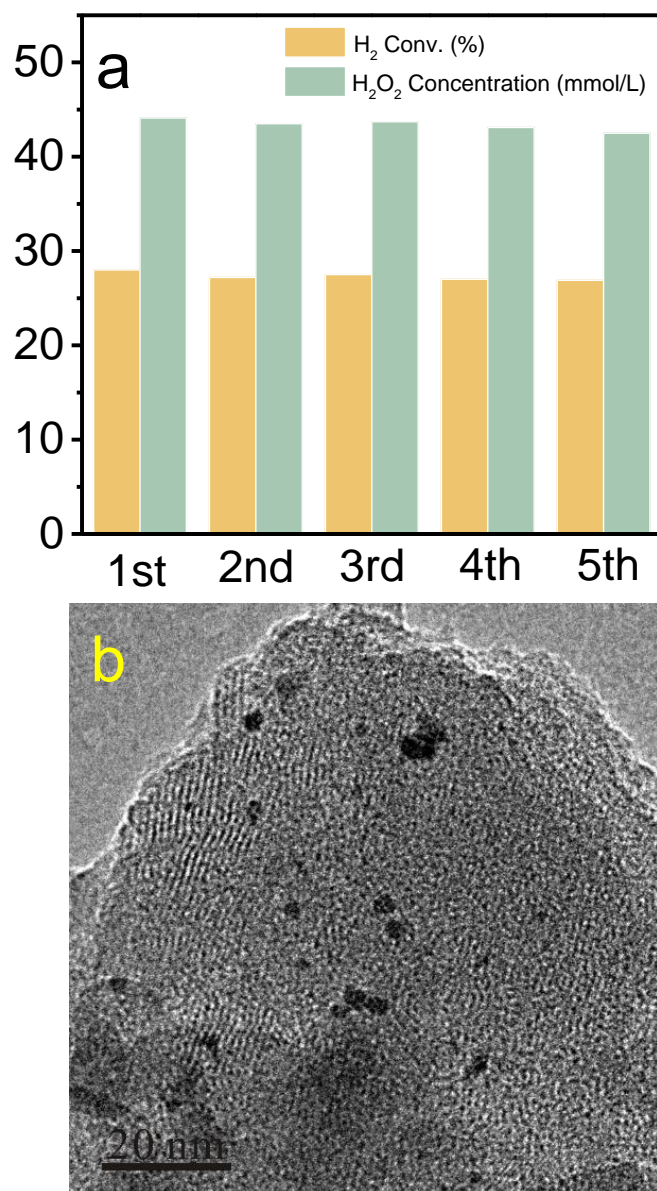


**Figure S25.** N<sub>2</sub> sorption isotherms of the AuPd@HZSM-5-HF. The isotherms show a loop at  $0.5 < P/P_0 < 0.9$ , assigning to the mesoporous structure after HF treatment.



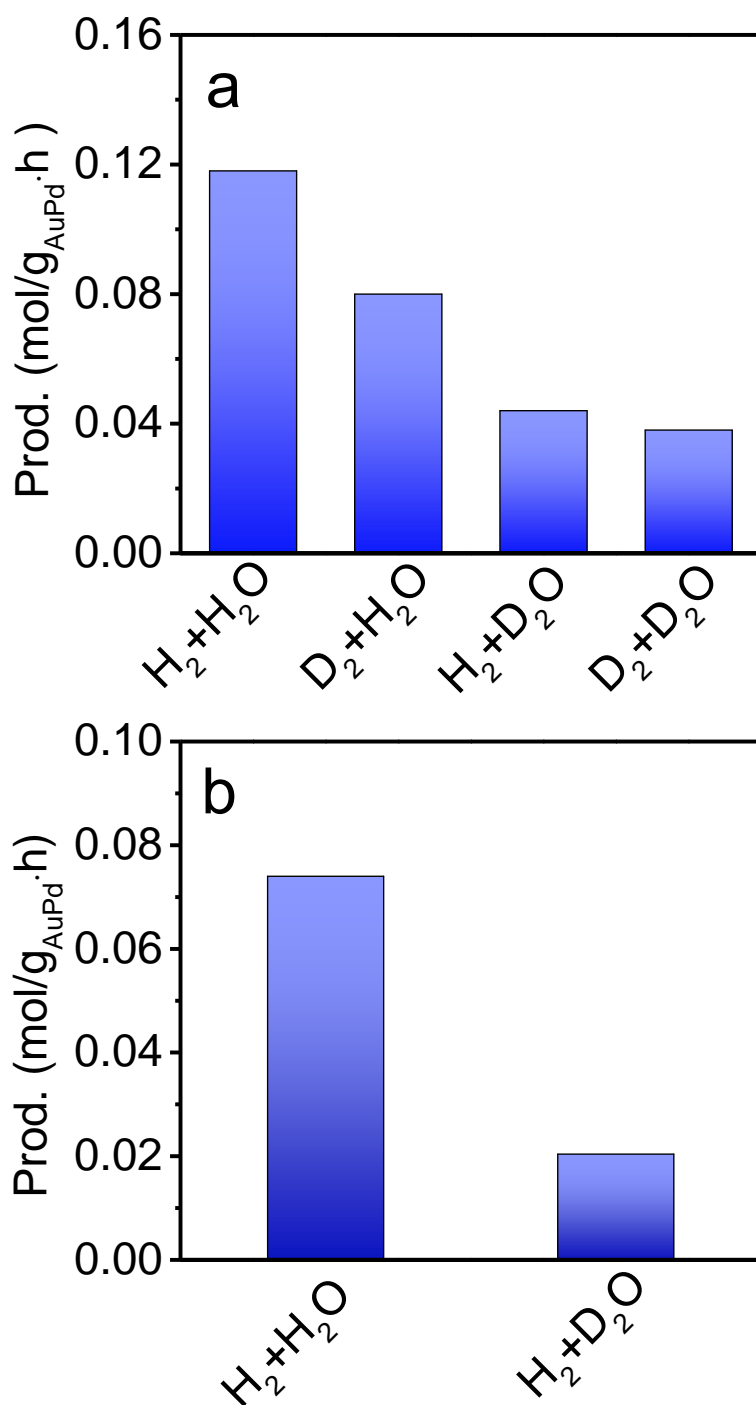
**Figure S26.** Data of  $\text{H}_2\text{O}_2$  synthesis over the AuPd@HZSM-5 and HF corrosion AuPd@HZSM-5-HF under standard conditions. The reaction conditions are the same to those in Table 1 of the main text.

**Note:** In the previous studies using supported metal nanoparticle catalysts, the halide species were normally used as efficient promoter for improving the  $\text{H}_2$  conversion and  $\text{H}_2\text{O}_2$  selectivity (*U.S. Patent 1992, 5169618; Appl. Catal. A 2007, 317, 234-243; ChemSusChem 2009, 2, 575-580; J. Catal. 2006, 238, 28-38*). However, in this work, after the HF treatment, the catalytic activity and selectivity of AuPd@HZSM-5 was obviously reduced, which is different from the previous phenomena on halide-promoted metal catalysts, suggesting the importance of zeolite sheath for this reaction.

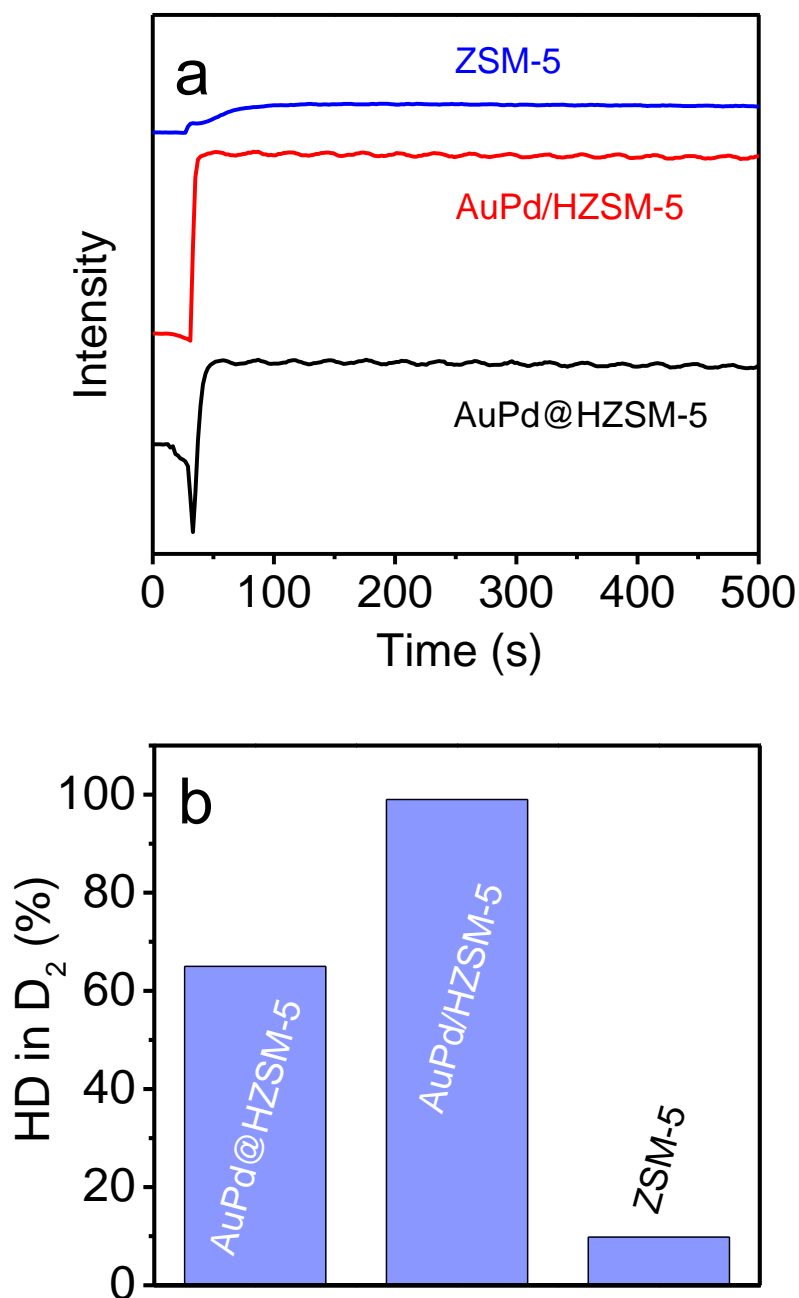


**Figure S27.** (a) Catalytic recycle test (under standard conditions) of AuPd@HZSM-5 and (b) TEM image of the catalyst after reaction.

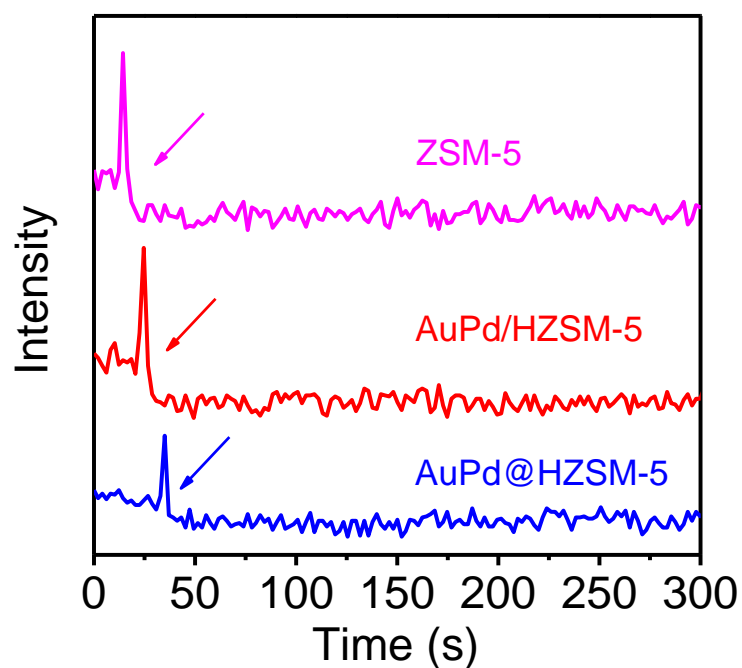




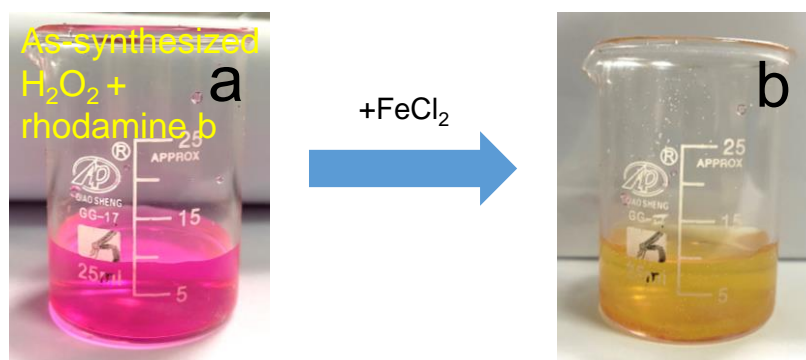
**Figure S28.**  $\text{H}_2\text{O}_2$  productivities in D-labeled experiments over the (a) AuPd/HZSM-5 and (b) AuPd@NaZSM-5 catalysts. Reaction conditions: 5%  $\text{H}_2$  (or  $\text{D}_2$ )/10%  $\text{O}_2$ /40% He/45% Ar, total pressure at 4 MPa, 10 g of  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ), 30 mg of catalyst, 1200 rpm,  $2 \pm 2$  °C, 30 min.



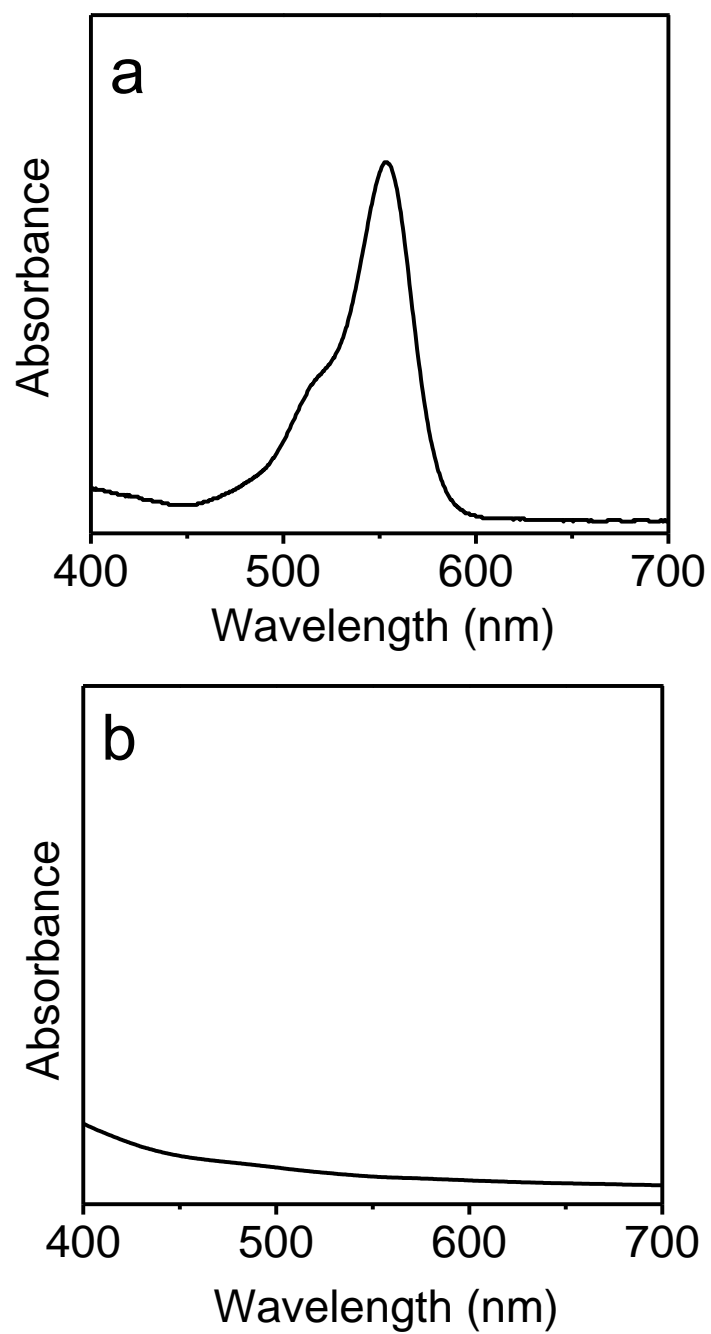
**Figure S29.** (a) HD signal of mass spectrum over H-D gas phase exchange. (b) The ratio of HD in D<sub>2</sub> over the AuPd@HZSM-5, AuPd/HZSM-5, and ZSM-5. Reaction conditions: 10% H<sub>2</sub>/10% D<sub>2</sub>/80% inert gas, total pressure of 3.3 MPa, 30 mg of catalyst, 1200 rpm, 30 min.



**Figure S30.** MS spectra characterizing the  $^{16}\text{O}$ - $^{18}\text{O}$  exchange over the AuPd@HZSM-5, AuPd/HZSM-5 and ZSM-5 catalysts. Reaction conditions: 1 bar of  $^{18}\text{O}_2$ , 5.8 bar of  $^{16}\text{O}_2$ , 23.2 bar of He, room temperature, 30 mg of catalyst, 30 min. The  $^{16}\text{O}^{18}\text{O}$  are undetectable over all the catalysts. The peaks (highlighted by the arrows) are from gas shaking when changing the feed gases.



**Figure S31.** The photographs of (a) rhodamine b (10 ppm) in the as-synthesized H<sub>2</sub>O<sub>2</sub> solution and (b) the liquor after Fenton reaction using FeCl<sub>2</sub>.



**Figure S32.** UV-Vis spectra of (a) rhodamine b (10 ppm) in the as-synthesized  $\text{H}_2\text{O}_2$  solution and (b) the liquor after Fenton reaction using  $\text{FeCl}_2$ .

**Table S1.** Structural parameters of various catalysts.

Catalyst	$S_{BET}$ (m <sup>2</sup> /g)	$V_{pore}$ (cm <sup>3</sup> /g)	Si/Al atomic ratio	Metal content (wt %)	
				Au	Pd
AuPd@HZSM-5 (Si/Al=18)	319	0.16	18	2.3	2.6
AuPd@HZSM-5 (Si/Al=36)	332	0.15	36	2.3	2.4
AuPd@HZSM-5 (Si/Al=62)	336	0.16	62	2.2	2.5
AuPd@HZSM-5 (Si/Al=101)	365	0.15	101	2.4	2.5
AuPd@NaZSM-5	327	0.15	34	2.4	2.5
AuPd@S-1	419	0.17	>500	2.1	2.4
AuPd/HZSM-5	359	0.15	33	2.6	2.5

**Table S2.** Data of  $k_{H_2}/k_{D_2}$ ,  $k_{H_2O}/k_{D_2O}$  and  $k_{H_2+H_2O}/k_{D_2+D_2O}$  of various catalyst.

Entry	Catalyst	$k_{H_2}/k_{D_2}$	$k_{H_2O}/k_{D_2O}$	$k_{H_2+H_2O}/k_{D_2+D_2O}$
1	AuPd@HZSM-5	1.3	2.2	2.6
2	AuPd/HZSM-5	1.5	2.7	3.1
3	AuPd@NaZSM-5	-	3.6	-

**Table S3.** Na/Al and Si/Al ratios of AuPd@NaZSM-5 and AuPd@HZSM-5 catalysts by ICP analysis.

Catalyst	Si/Al	Na/Al
AuPd@NaZSM-5	36	0.27
AuPd@HZSM-5	36	<0.01