# Highly Dispersed Pd-Based Pseudo-Single Atoms in Zeolites for Hydrogen Generation and Pollutant Disposal

Kai Zhang,<sup>a</sup> Ning Wang,<sup>d</sup>\* Yali Meng,<sup>a</sup> Tianjun Zhang,<sup>e</sup> Pu Zhao,<sup>a</sup> Qiming Sun<sup>a, b</sup>\*, Jihong Yu<sup>c</sup>\*

a. Innovation Center for Chemical Sciences, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123 (P. R. China). E-mail: sunqiming@suda.edu.cn

b. Jiangsu Key Laboratory of Advanced Negative Carbon Technologies, Soochow University, Suzhou, 215123, Jiangsu (P. R. China)

c. State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Center of Future Science, College of Chemistry, Jilin University, Changchun 130012 (P. R. China). E-mail: jihong@jlu.edu.cn

d. Institute of Sustainable Energy and Resources, College of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071 (P. R. China). E-mail: wangning2021@qdu.edu.cn

e. College of Chemistry and Materials Science, Hebei University, Baoding 071002 (P.R. China)

#### **Experimental section**

**1.** Materials. Tetrapropylammonium hydroxide solution (TPAOH, 25 wt% in water, Accela ChemBio Co., Ltd.), tetraethylorthosilicate (TEOS,  $C_8H_{20}O_4Si$ ), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), palladium chloride (PdCl<sub>2</sub>), formic acid (HCOOH) were purchased from Macklin, ethylenediamine (abbreviation: en, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 0.5 M, Aladdin).

#### 2. Synthesis of zeolite-encapsulated metal catalysts.

**2.1 Preparation of [Pd(en)\_2]Cl\_2 and [Ni(en)\_3](NO\_3)\_2 precursors.** The  $[Pd(en)_2]Cl_2$  solution (0.18 M) was prepared by mixing 0.320 g of PdCl<sub>2</sub> into 10 mL of aqueous solution containing 2 mL of ethylenediamine under stirring at room temperature until complete dissolution. The  $[Ni(en)_3](NO_3)_2$  solution (0.18 M) was prepared by mixing 0.524 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O into 10 mL of aqueous solution containing 2 mL of ethylenediamine under stirring at room temperature until complete dissolution.

**2.2 Preparation of Pd@S-1-C and Pd@S-1-H catalysts.** The Pd@S-1-C and Pd@S-1-H catalysts were synthesized with a molar composition of 1.0 SiO<sub>2</sub>: 0.4 TPAOH: 35 H<sub>2</sub>O: 0.0045 [Pd(en)<sub>2</sub>]Cl<sub>2</sub> under the hydrothermal condition at 170 °C for 3 days by taking different reduction methods. Typically, the mixture was first prepared by mixing 15 g of deionized water with 13.5 g of TPAOH solution (25 wt%). Following, the 8.32g of TEOS was added into the above mixture with continuous stirring for 6 h until the solution was clear. Finally, 1 mL of [Pd(en)<sub>2</sub>]Cl<sub>2</sub> solution (0.18 M) was added to the above mixture. After stirring for 1 min, the reaction mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and the crystallization was conducted in a conventional oven at 170 °C for 3 days. The obtained Pd(en)<sub>2</sub>@S-1 sample was reduced via two methods: (a) Pd(en)<sub>2</sub>@S-1 sample was first calcinated in air at 550 °C for 6 h and then reduced in H<sub>2</sub> at 500 °C for 2 h (named as Pd@S-1-C); (b) Pd(en)<sub>2</sub>@S-1 sample was directly reduced in pure H<sub>2</sub> flow with linear heating to 500 °C for 2 h and then holding for 2 h (named as Pd@S-1-H).

2.3 Preparation of xPd(1-x)Ni(OH)<sub>2</sub>@S-1-H (x=0.9, 0.8, and 0.7), 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-C, and Ni(OH)<sub>2</sub>@S-1-H. xPd(1-x)Ni(OH)<sub>2</sub>@S-1-H (x=0.9, 0.8, and 0.7) catalysts were synthesized with the same procedure as Pd@S-1-H catalyst, except that suitable amounts of both [Pd(en)<sub>2</sub>]Cl<sub>2</sub> and  $[Ni(en)_3](NO_3)_2$  solutions (0.9 mL and 0.1 mL, 0.8 mL and 0.2 mL, 0.7 mL and 0.3 mL) were added to the reaction mixtures, resulting in molar ratios  $n_{Pd}/(n_{Pd}+n_{Ni})$  equal to 0.9, 0.8, and 0.7, respectively, The total molar ratios of metal species to SiO<sub>2</sub> were kept at a constant 0.0045. The obtained catalysts were directly reduced in flowing H<sub>2</sub> with linear heating to 500 °C for 2 h and then held for 2 h. The 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-C was synthesized with the same molar composition as 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H, and was subjected to calcination in air at 550 °C for 6 h and reduction in H<sub>2</sub> at 500 °C for 2 h. The Ni(OH)<sub>2</sub>@S-1-H catalyst was synthesized with a similar synthesis procedure to the Pd@S-1 catalyst, except adding 1 mL of [Ni(en)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> solution instead of [Pd(en)<sub>2</sub>]Cl<sub>2</sub> solution.

**2.4 Preparation of Pd/S-1-im and 0.8Pd0.2Ni(OH)**<sub>2</sub>/S-1-im catalysts. The Pd/S-1-im catalyst was prepared using the incipient wetness impregnation method. Typically, 1 g of calcined silicalite-1 zeolite that synthesized with a molar composition of 1.0 SiO<sub>2</sub>: 0.4 TPAOH: 35 H<sub>2</sub>O was impregnated with 0.20 mL of (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub> solution (0.3 M), followed by reduced in H<sub>2</sub> flow for 2 h at 500 °C. The 0.8Pd0.2Ni(OH)<sub>2</sub>/S-1-im catalyst was prepared by impregnating 0.2 mL of mixed solution containing (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub> (0.24 M) and Ni(NO<sub>3</sub>)<sub>2</sub> (0.06 M) into 1 g of calcined silicalite-1 zeolite, followed by reduced in H<sub>2</sub> flow for 2 h at 500 °C.

**3.** Characterizations. The powder X-ray diffraction (PXRD) of samples was recorded on the Rigaku D/Max 2550 diffractometer using Cu K $\alpha$  radiation ( $\lambda$ =1.5418 Å). The transmission electron microscopy (TEM) images were measured with a Tecnai F20 electron microscope. C<sub>s</sub>-corrected HAADF-STEM images were taken at 300 kV on an JEM-ARM200F scanning transmission electron microscope (STEM). The inductively coupled plasma (ICP) analyses were performed on a Perkin-Elmer Optima 3300 DV ICP instrument. N<sub>2</sub> adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 77.35 K after the samples were degassed at 350 °C under vacuum. The X-ray absorption spectroscopy data at Ni K-edge and Pd K-edge were collected at the Sector 20-BM beamline of the Advanced Photon Source at Argonne National Laboratory. The energy was calibrated accordingly to the absorption edge of a pure Ni or Pd foil. Athena and Artemis software were used to extract and fit the data. The generated gas from formic acid decomposition was analyzed using Agilent GC 6890N, equipped with thermal conductivity detector (TCD) and the detailed CO analysis in the generated gas was performed on GC9790Plus (FULI INSTRUMENTS)

using a flame ionization detector (FID)-methanator (detection limit: ~10 ppm). The X-ray total scattering data were collected at the I15-1 beamline of Diamond Light Source (UK). The incident energy was 76.69 keV with a wavelength of 0.161669 Å. GudrunX software was used for the Fourier transform to pair distribution functions. The hydrogenolysis experiment of organic species in the sample was measured on an Altamira AMI-300 instrument equipped with a thermal conductivity detector (TCD). Typically, 70 mg of Pd(en)<sub>2</sub>@S-1 without any thermal treatment was heated from 50 °C to 650 °C with a rate of 10 °C/min flowing 10% H<sub>2</sub>/N<sub>2</sub> (30 mL/min). The H<sub>2</sub>-TPR profile was recorded by the TCD detector and the released NH<sub>3</sub> with the signal of m/z = 17 was monitored by mass spectrometry (HIDEN DECRA/EXQ RM).

**4.** Thermal stability tests of catalysts. To investigate the thermal stability of the metal-containing zeolite catalysts, the 0.1 g of  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalyst was calcined in flowing N<sub>2</sub> (40 mL/min) with linear heating to 700 °C for 2 h and holding for 2 h. For comparison, the  $0.8Pd0.2Ni(OH)_2/S-1-im$  synthesized using the impregnation method were also treated with N<sub>2</sub> under the same condition. Following, the  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalysts were also calcined in flowing H<sub>2</sub> and O<sub>2</sub> at 600 °C with the same thermal treatment of N<sub>2</sub>. The aging treatments in presence of water were also investigated. 0.1 g of  $0.8Pd0.2Ni(OH)_2@S-1$  were heated in a tube furnace at 600 °C for 5 h with the water vapor flow of 18 mL/min, respectively.

#### 5. Methane combustion

The combustion experiments were carried out on PLR-PTSR III catalytic reaction instrument (Beijing Perfectlight Technology Co., Ltd.). Typically, 50 mg of catalyst (40-60 mesh) sample mixed with 250 mg of quartz sand was loaded into a 6 mm quartz column. The activity was test from 200-550 °C and atmospheric pressure under 2% CH<sub>4</sub>-20% O<sub>2</sub>-78% N<sub>2</sub>. The total gas flow was fixed as 30 mL min<sup>-1</sup>, which corresponds to a gas hourly space velocity (GHSV) was fixed at 36000 mL g<sup>-1</sup> h<sup>-1</sup>. For water resistance ability, 4.5 vol% water vapor were introduced by a water pump. The exhaust gas was analyzed by using an online gas chromatograph (FULI Instruments GC9790 plus). For long-term stability evaluation, the methane combustion experiments were carried out at 470 °C over Pd@S-1-H and Pd/S-1-im catalysts.

#### 6. Catalytic test of FA dehydrogenation

**6.1. FA dehydrogenation over different catalysts.** The dehydrogenation reaction of formic acid was carried out using an apparatus containing a reaction unit and a gas collecting device. Typically, a suitable amount of catalyst (i.e., 0.6 g Pd@S-1-H) and 1.0 mL deionized water were first placed in a 10 mL two-necked round-bottomed flask, which was placed in a water bath with magnetic stirring (600 rpm) at a preset temperature (298~333 K) under ambient atmosphere. The reaction started when 0.5 mL of FA (6.0 M) aqueous solution was injected into the flask using a syringe. The volume of released gases was measured via a gas burette as well as an electronic balance recording the weight of excurrent water continuously. The molar ratios of  $n_{(Pd+Ni)}/n_{FA}$  were fixed at 0.012.

**6.2. Recycling test of catalysts for FA decomposition.** To test the recycling stability of catalysts, the catalysts were isolated from the reaction solution by centrifugation and washed with water after the completion of a previous run and dried in the atmosphere. The dried catalysts were then reused in the FA dehydrogenation under the same condition as the previous run. The isolated spent catalysts of each recycling test were characterized using PXRD and TEM.

6.3 The calculation of turnover frequency (TOF) and H<sub>2</sub> generation rate  $\binom{R_{H_2}}{}$ . The initial TOF is calculated based on the quantity of Pd atoms in the catalysts when the FA conversion reaches up to 20% as the following equations:

$$TOF_{Initial} = \frac{P_{atm}V_{Initial gas}/RT}{2 n_{Pd}t}$$

Wherein  $P_{atm}$  is the atmospheric pressure (101.325 kPa),  $V_{Initial gas}$  are the initially generated volume of H<sub>2</sub> and CO<sub>2</sub>, corresponding to the conversions of 20% of the FA conversion. *R* is the universal gas constant (8.3145 m<sup>3</sup> Pa mol<sup>-1</sup> K<sup>-1</sup>), *T* is the room temperature (298 K),  $n_{Pd}$  is the total mole number of Pd atoms in the catalyst and *t* is the completion time of the reaction in hours.

### 7. Catalytic reduction of hexavalent chromium (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) coupled with FA decomposition

7.1. Catalytic reduction of  $Cr_2O_7^{2-}$  over different catalysts. 28 mg of catalyst, 0.2 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), and 5.8 mL deionized water were placed in a 25 mL round-bottomed flask followed by an ultrasonic dispersion for 10 min. Next, the flask was placed in a water bath with magnetic stirring (600 rpm) at 323 K under ambient atmosphere until the physical adsorption of the catalyst to the

 $Cr_2O_7^{2-}$  is saturated that was determined by the UV-Vis spectrometer. The reaction started when 4.0 mL of FA (6.0 M) aqueous solution was added into the flask with a molar ratios of n(HCOOH)/n(K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) of 1200/1. The transformation efficiency of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> to Cr<sup>3+</sup> was determined by using a UV-Vis spectrometer (SHIMADZU, UV-1900i).

7.2 Catalytic reactions of  $Cr_2O_7^{2-}$  reduction with different molar ratios of  $n(HCOOH)/n(K_2Cr_2O_7)$ . 28 mg of 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H, 0.05~0.4 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), and 5.95~5.6 mL deionized water were placed in a 25 mL round-bottomed flask followed by an ultrasonic dispersion for 10 min. Next, the flask was placed in a water bath with magnetic stirring (600 rpm) at 323 K under ambient atmosphere. The reaction started when 4.0 mL of FA (6.0 M) aqueous solution was added into the flask with molar ratios of  $n(HCOOH)/n(K_2Cr_2O_7)$  in range of 4800/1 to 600/1.

7.3 Catalytic reactions of  $Cr_2O_7^{2-}$  reduction at different temperatures. 28 mg of  $0.8Pd0.2Ni(OH)_2@S-1-H$ ,  $0.05 \text{ mL } K_2Cr_2O_7$  (0.1 M), and 5.95 mL deionized water were placed in a 25 mL round-bottomed flask followed by an ultrasonic dispersion for 10 min. Next, the flask was placed in a water bath with magnetic stirring (600 rpm) at 303~333 K under ambient atmosphere. The reaction started when 4.0 mL of FA (6.0 M) aqueous solution was added into the flask.

7.4. Recycling test of catalysts for  $Cr_2O_7^{2-}$  reduction. To test the recycling stability of  $0.8Pd0.2Ni(OH)_2@S-1-H$ , the catalyst was isolated from the reaction solution by centrifugation and washed with water after the completion of a previous run and dried in the atmosphere. The dried catalysts were then reused in  $Cr_2O_7^{2-}$  reduction under the same condition as the previous run.

7.5. Durability test of catalysts for  $Cr_2O_7^{2-}$  reduction. To test the durability of  $0.8Pd0.2Ni(OH)_2@S-1-H$ , the  $Cr_2O_7^{2-}$  reduction was performed with a large amount of  $K_2Cr_2O_7$ : 28 mg of  $0.8Pd0.2Ni(OH)_2@S-1-H$ , 40 mL  $K_2Cr_2O_7$  (0.1 M), and 260 mL deionized water were placed in a 1L round-bottomed flask followed by an ultrasonic dispersion for 10 min. Next, the flask was placed in a water bath with magnetic stirring (600 rpm) at 323 K under ambient atmosphere. The reaction started when 200 mL of FA (6.0 M) aqueous solution was added to the flask.

**7.6. The calculation of catalytic activity and turnover number (TON).** The catalytic activity of each catalyst is calculated according to the quantity of Pd in the catalyst when the conversion of

 $K_2Cr_2O_7$  reaches up to 100% as the following equations:

Catalytic activity 
$$= \frac{n(Cr_2O_7^{-})}{n(Pd) t}$$
$$TON = \frac{n(Cr_2O_7^{-})}{n(Pd)}$$

The  $n(Cr_2O_7^{2-})$  and n(Pd) are the mole number of  $K_2Cr_2O_7$  in catalytic system and Pd atoms in the catalyst and t is the completion time of the reaction in min.



**Figure S1**. Powder X-ray diffraction patterns of various zeolite-encaged Pd-based metal samples as compared with the simulated MFI zeolite.



Figure S2. SEM images of A1-A3) Pd/S-1-im, B1-B3) Pd@S-1-C, C1-C3) Pd@S-1-H, D1-D3) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-C, and E1-E3) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H.



Figure S3. TEM images of A-C) Pd@S-1-H, D-F) Pd@S-1-C, and G-I) Pd/S-1-im.



Figure S4. TEM images of A-C) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H and D-F) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-C.



**Figure S5**. (A) H<sub>2</sub>-temperature-programmed reduction/mass spectrometry profiles of Pd(en)<sub>2</sub>@S-1 without any thermal treatment. (B) Thermogravimetry curves of Pd@S-1-uncalcination, Pd@S-1-C, and Pd@S-1-H samples.



Figure S6. The  $N_2$  adsorption/desorption curves of pure S-1, Pd@S-1-C, Pd@S-1-H, and  $0.8Pd0.2Ni(OH)_2@S-1-H$  samples.



**Figure S7**. The Fourier transform of k<sup>3</sup>-weighted EXAFS spectra of A) Pd@S-1-C, B) Pd@S-1-H, and C) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H samples at Pd K-edge as well as D) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H sample at Ni K-edge.



**Figure S8.** The average valence states of palladium in different samples according to the edge position of XANES spectra.



**Figure S9.** TEM images of A, B) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H sample and C) corresponding size distributions of metal particles as well as (D, E) 0.8Pd0.2Ni(OH)<sub>2</sub>/S-1-im and F) corresponding size distributions of metal particles after treatment at 700 °C for 2 h under N<sub>2</sub> atmosphere. Surface weighted mean cluster diameter  $d_{TEM} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$ , where  $n_i$  is the number of metallic clusters having diameter  $d_i$ .



**Figure S10**. TEM images of A, B) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H sample and C) corresponding size distributions of metal particles after treatment at 600 °C for 2 h under H<sub>2</sub> atmosphere; D, E) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H sample and F) corresponding size distributions of metal particles after treatment at 600 °C for 2 h under O<sub>2</sub> atmosphere; G, H) 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H sample and I) corresponding size distributions of metal particles after ageing treatments at 600 °C for 5 h in the presence of water vapor with water vapor flow of 18 mL/min. Surface weighted mean cluster diameter  $d_{\text{TEM}} = \sum n_i d_i^3 / \sum n_i d_i^2$ , where n<sub>i</sub> is the number of metallic clusters having diameter d<sub>i</sub>.



**Figure S11**. Catalytic performance of methane combustions over Pd@S-1-H under dry and humidity condition (4.5 vol% water vapor was introduced by a water pump) with a gas hourly space velocity (GHSV) of 36,000 mL $\cdot$ g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>.



Figure 12. GC spectra for the evolved gaseous products from the FA dehydrogenation over  $0.8Pd0.2Ni(OH)_2@S-1-H$  at 333 K as compared with pure CO<sub>2</sub>, H<sub>2</sub>, and CO. (A) equipped with TCD detector and (B) equipped with FID-Methanator.



Figure S13. The volume of the generated gas versus time over physical mixture of Pd@S-1-H and Ni(OH)<sub>2</sub>@S-1-H as well as  $0.8Pd0.2Ni(OH)_2@S-1-H$ , Pd@S-1-H, and Ni(OH)<sub>2</sub>@S-1-H counterparts (2 M FA, 3 mmol,  $n_{metal}/n_{FA} = 0.012$ ).



Figure S14. A) Volume of the generated gas versus time and B) corresponding TOF values of  $H_2$  generation for the FA dehydrogenation at different temperatures over Pd@S-1-H catalyst (2 M FA, 3 mmol,  $n_{metal}/n_{FA} = 0.012$ ). Inset of A: Arrhenius plot (ln TOF vs. 1/T).



Figure S15. TOF values of H<sub>2</sub> generation for the FA dehydrogenation at different temperatures over  $0.8Pd0.2Ni(OH)_2@S-1-H \text{ catalyst} (2 \text{ M FA}, 3 \text{ mmol}, n_{metal}/n_{FA} = 0.012).$ 



Figure S16. A) Recycling tests for the FA dehydrogenation over Pd@S-1-H catalyst at 333 K and B) corresponding TOF values of every recycle ( $n_{metal}/n_{FA} = 0.012$ ).



Figure S17. The TOF values of every recycle over  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalyst at 333 K ( $n_{metal}/n_{FA} = 0.012$ ).



Figure S18. TEM images of Pd@S-1-H catalysts after A, B) 3<sup>rd</sup> and C, D) 5<sup>th</sup> recycling experiments at 333 K.



Figure S19. TEM images of  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalysts after A, B)  $3^{rd}$  and C, D)  $5^{th}$  recycling experiments at 333 K.



Figure S20. XRD patterns of 0.8Pd0.2Ni(OH)<sub>2</sub>@S-1-H after 5<sup>th</sup> recycling experiment at 333 K and the corresponding fresh one.



**Figure S21**. UV-vis absorption spectra before and after Cr(VI) reduction over  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalysts as well as Cr(III) standard. Catalytic condition: 28 mg catalyst, 0.2 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), 4 mL HCOOH (6 M) (n(HCOOH)/n(K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) = 1200/1), 5.8 mL H<sub>2</sub>O, T = 323 K. reaction time = 10 min.



**Figure S22**. The photographs of Cr(VI) reduction by using FA ads reducing agent over  $0.8Pd0.2Ni(OH)_2@S-1-H$  at different reaction times. As the reaction progresses, the reaction solution becomes lighter until it finally becomes colorless, proving that all the Cr(VI) has been transformed to  $Cr^{3+}$ .



Figure S23. Catalytic performance on the Cr(VI) reduction over pure S-1 catalyst by using FA as a reducing agent. Catalytic condition: 28mg catalysts, 0.2 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), 4mL HCOOH (6 M) (n(HCOOH)/n(K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) = 1200/1), 5.8mL H<sub>2</sub>O, T = 323 K.



Figure S24. Catalytic performance on the Cr(VI) reduction over  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalyst by using H<sub>2</sub> as a reducing agent. Catalytic condition: 28mg catalysts, 0.2 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), 9.8mL H<sub>2</sub>O, 1 bar H<sub>2</sub>, T = 323 K.



Figure S25. UV-vis absorption spectra for the Cr(VI) reduction by FA over  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalysts at different temperatures. Catalytic condition: 28 mg catalyst, 0.05 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), 4 mL HCOOH (6 M), 5.95 mL H<sub>2</sub>O, T = 303~323 K.



Figure S26. UV-vis absorption spectra for the Cr(VI) reduction by FA over fresh and reused  $0.8Pd0.2Ni(OH)_2@S-1-H$  catalyst. Catalytic condition: 28 mg catalyst, 0.05 mL K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 M), 4 mL HCOOH (6 M), 5.95 mL H<sub>2</sub>O, T = 323 K.



Figure S27. TEM images of the spent  $0.8Pd0.2Ni(OH)_2@S-1-H$  after five consecutive cycles during Cr(VI) reduction reactions.

Sample	Metal loading <sup>a</sup> (wt %)	Molar ratio of Pd/Ni <sup>a</sup>	S <sub>total</sub> <sup>b</sup> (m <sup>2</sup> /g)	S <sub>micro</sub> <sup>c</sup> (m <sup>2</sup> /g)	S <sub>ext</sub> <sup>c</sup> (m <sup>2</sup> /g)	V <sub>micro</sub> <sup>c</sup> (cm <sup>3</sup> /g)
Pure S-1	0	-	432	236	196	0.115
Pd@S-1-C	0.64	-	415	214	201	0.105
Pd@S-1-H	0.64	-	411	212	199	0.103
0.9Pd0.1Ni(OH)2@S-1-H	0.61	0.89/0.11	-	-	-	-
0.8Pd0.2Ni(OH)2@S-1-H	0.52	0.81/0.19	399	217	181	0.105
0.7Pd0.3Ni(OH)2@S-1-H	0.48	0.72/0.28	-	-	-	-

**Table S1.** Metal loading and porosity of various samples.

<sup>a</sup> Analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). <sup>b</sup> S<sub>total</sub> (total surface area) calculated by applying the BET equation using the linear part ( $0.05 < P/P_0 < 0.30$ ) of the adsorption isotherm. <sup>c</sup> S<sub>micro</sub> (micropore area), S<sub>ext</sub> (external surface area) and V<sub>micro</sub> (micropore volume) were calculated using the *t*-plot method.

Sample	Shell	C.N.	R (Å)	σ (Å-2)	$\Delta E_0$ (eV)	R- factor
Pd foil	Pd-Pd	12	2.74(1)	0.005(1)	-9(1)	0.01
Pd@S-1-C	Pd-O	1.9(1)	2.02(1)	0.001(1)	-4(1)	0.001
	Pd-Pd	3.5(2)	2.72(1)	0.007(1)	-9(1)	0.001
Pd@S-1-H	Pd-O	2.9(2)	2.01(1)	0.002(2)	-3(1)	0.002
	Pd-Pd	1.9(4)	2.72(1)	0.008(2)	-4(1)	0.002
0.8Pd0.2Ni(OH) <sub>2</sub> @S- 1-H	Pd-O	2.4(2)	2.02(1)			
	Pd-Ni	0.13(11)	2.45(6)	0.003(1)	-4(1)	0.017
	Pd-Pd	0.8(2)	2.73(1)			
	Ni-O	5.0(11)	2.03(2)			
	Ni-Pd	0.13(11)	2.45(6)	2.45(6) 0.004(3) -5		0.017
	Ni-Ni	3.0(12)	3.06(1)			

**Table S2.** EXAFS parameters of Pd@S-1-C, Pd@S-1-H, and 0.8Pd0.2Ni(OH)2@S-1-H samplesas compared with Pd foil.

C.N., coordination number; R, distance between absorber and backscatter atoms;  $\sigma^2$ , Debye-Waller factor to account for both thermal and structural disorders;  $\Delta E_0$ , inner potential correction; R-factor indicates the goodness of the fit.

	T/K	TOF/h <sup>-1</sup>	Ref.	
Without additives				
	333	9308		
0.8Pd0.2Ni(OH) <sub>2</sub> @S-1-H	323	4500	This work	
	298	1002		
Pd/C	323	1500	[1]	
Pd/C	333	650	[2]	
Pd/NMC-400	298	913	[3]	
Pd/NHPC-NH <sub>2</sub>	298	1265	[4]	
AP-SiO2@PDA-NGO@Pd	323	8274	[5]	
Pd@UIO-66/NH <sub>2</sub> -SEP	323	2020	[6]	
Pd-ZrO <sub>2</sub> /SBA-15-NH <sub>2</sub>	318	3571	[7]	
PdAcet. <sub>Acet.</sub> /C <sub>darco</sub>	323	135	[8]	
Au@Schiff-SiO <sub>2</sub>	323	2968	[9]	
Pd/PDA-rGO	323	3505	[10]	
AuPd-MnOx /ZIF-8-rGO	298	409	[11]	
Cr0.4Pd0.6/MIL-101-NH <sub>2</sub>	323	2009	[12]	
Pd <sub>1</sub> Au <sub>1</sub> /30-LA	333	8355	[13]	
AuPd/NH <sub>2</sub> -N-rGO	298	4445	[14]	

**Table S3.** Comparisons of catalytic activities for the FA dehydrogenation catalyzed by previously

 reported heterogeneous catalysts with that synthesized in this work.

Pd <sub>5</sub> Ag <sub>5</sub> NWs@g-C <sub>3</sub> N <sub>4</sub>	298	260	[15]	
Cr <sub>0.4</sub> Pd <sub>0.6</sub> /M-β-CD-A	323	5771	[16]	
Au <sub>0.3</sub> Pd <sub>0.7</sub> /A-M-β-CD	323	7352	[17]	
PdMn <sub>0.6</sub> @S-1	333	6860	[18]	
Pd <sub>90</sub> Rh <sub>10</sub> /HHT	303	1793	[19]	
Pd <sub>0.8</sub> Au <sub>0.2</sub> /UiO-66-D	333	3122	[20]	
With additives				
Pd/MSC-30	323	3511	[21]	
Arg-Pd/MSC-30	333	5723	[22]	
Pd@SS-CNR	333	7200	[23]	
Au <sub>2</sub> Pd <sub>3</sub> @(P)N-C	303	5400	[24]	
Pd/OB-C1	323	5354	[25]	
Pd@Bi/C	323	6940	[26]	
g-CN/Ag/Ag <sub>3</sub> PO <sub>4</sub> -AgPd	323	1595	[27]	

Catalysts	T / K	n(FA)/ n(Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> )	TON	Ref
0.8Pd0.2Ni(OH)2@S-1-H	323	300	2980	This work
CoA-Pd (1:45)	323	325	1701	[28]
CC/Pd NPs	323	270	1005	[29]
Pd@MIL-101	323	78	36	[30]
Pd-NICaR	323	680	22	[31]
Pd@PEI/PVA	323	765	16	[32]
Pd@LPR	323	852	16	[33]
PVP-Pd <sub>10</sub>	318	1.4	177	[34]
Fe <sub>3</sub> O <sub>4</sub> /Pd@ N-C	318	222	9	[35]
Pd NPs/fTiO <sub>2</sub>	308	225	26	[36]
Pd-NWWs	298	563	1133	[37]
Pd <sub>2</sub> /GO	298	225	43	[38]
Pd@SiO <sub>2</sub> -NH <sub>2</sub>	298	225	15	[39]
Pd@GAC	298	56	13	[40]
PdCu/NCG	298	500	12	[41]
Pd <sub>6</sub> Cu <sub>4</sub> /NG	298	500	10	[42]
Pd@ZIF-67	298	225	5	[43]

**Table S4.** Comparisons of catalytic activities for the Cr(VI) reduction catalyzed by previously

 reported heterogeneous catalysts with that synthesized in this work.

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