Thioether functionalized vinylene-linked Covalent Organic

Frameworks Boost the Semi-hydrogenation Selectivity of Alkynes

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1. Materials

All chemical reagents were purchased commercially and used directly in the reactions without further purification. 2,4,6-trimethyl-1,3,5-triazine (TMT) and 1,4-Benzenedicarboxaldehyde (TPA-SCH₃) were purchased from Shanghai Bide Pharmatech Co., Ltd, 1,4-Phthalaldehyde, Phenylacetylene, Styrene and Sodium tetrachloropalladate (II) were purchased from Tokyo Chemical Industry Co., Ltd. All organic solvents including o-dichlorobenzene, n-butanol, mesitylene, dioxane, acetonitrile, trifluoroacetic acid were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2. Characterization methods

The Fourier Transform Infrared (FT-IR) spectra were measured by the American Thermo Fischer, iN 10mx. Powder X-ray diffraction (PXRD) patterns were carried out by the Rigaku Corporation of MiniFlex 600. Thermogravimetric analysis (TGA) using TG 209F3 was measured to analyze the thermal stabilities of COFs with temperature ranging from 40 to 800°C in the air atmosphere. Scanning electron microscopies (SEM) were carried out using SU8010 microscope. Transmission electron microscopy (TEM) analysis and element energy dispersive spectroscopy (EDS) were performed on the Thermo Talos F200X. The porosities of COFs were measured by nitrogen adsorption and desorption at 77 K using ASAP2460 and before the analysis, all the materials were degassed for 12 h under vacuum. The contents of Pd in catalysts were analyzed by Inductively coupled plasma optical emission spectroscopy (ICP-OES) on Agilent 5110. Solid state nuclear magnetic resonance (¹³C CP/MAS sNMR) spectra of COFs were recorded on the Bruker AVANCE 400MHz. X-ray photoelectron spectroscopy (XPS) was performed by the Thermo Fischer, ESCALAB 250Xi. The catalytic reaction products

were measured by gas chromatography (GC, Scion 436C).

3. Experimental procedures

Synthesis of V-COF-1

Typically, a mixture of 2,4,6-trimethyl-1,3,5-triazine (TMT) (25 mg, 0.15 mmol), 1,4-Phthalaldehyde (TPA) (40 mg 0.3 mmol) and KOH (33.6 mg), o-dichlorobenzene 1.2 mL and n-butanol 2.8 mL were added to a 25 mL Schlenk tube and sonicated for 15 min¹. The Schlenk tube containing the mixture was frozen in liquid nitrogen, and after three cycles of freezing-extraction-thawing, the reaction was heated at 120 °C for 72 h. The solid was collected by centrifugation, washed three times with methanol and acetone, extracted by Soxhlet extraction in methanol for one day, and dried overnight under vacuum. Yellow powder was obtained in a yield of 84%.

Synthesis of V-COF-S

A mixture of 2,4,6-trimethyl-1,3,5-triazine (TMT) (25 mg, 0.15 mmol) and 1,4-Benzenedicarboxaldehyd (TPA-SCH₃) (67.9 mg 0.3 mmol), mesitylene (0.8 mL), dioxane (0.8 mL) and acetonitrile (0.1 mL) were added to a 25 mL Schlenk tube. After sonicated for 15 min, 0.8 mL of trifluoroacetic acid was quickly added as a catalyst. The Schlenk tube containing the mixture was frozen in liquid nitrogen, and after three cycles of freezing-extraction-thawing, it was placed in an oven of 150 °C for 72 h. After the reaction, the solid was collected by centrifugation, washed three times with methanol and acetone, and extracted by Soxhlet extraction in methanol for one day. Finally, the product was dried in a vacuum drying oven at 80 °C for 12 h to obtain an orange-red powder with 72% yield.

Synthesis of Pd@V-COF-1

The activated V-COF-1 (20 mg) was dispersed into methanol (10 mL) and sonicated for 30 min. The aqueous Na_2PdCl_4 (0.5 mL, 0.00376 mol/L) was added to the solution and stirred at room temperature for 6 h. The impregnated samples were washed twice with methanol and dried at 50 °C. The dried solid was dispersed into ethanol (3 mL) and NaBH₄ solution (1 mL, 1 mg/mL) was added quickly under an ice-water bath, and the reaction was carried out for 0.5 h. At the end of the reaction, grey-green powder

was obtained, and the solid was washed thoroughly with ethanol and dried in a vacuum drying oven at 60 °C overnight.

Synthesis of Pd@V-COF-S

Pd@V-COF-S was prepared by a similar method described above. V-COF-S (20 mg) was dispersed into 10 mL of methanol and sonicated for 30 min. The aqueous Na₂PdCl₄ (0.5 mL, 0.00376 mol/l) was added and stirred at room temperature for 6 h. After centrifugation and drying, 2 mL of NaBH₄ (1 mL, 1 mg/mL) was added to the reaction under an ice water bath and carried out for 0.5 h. The powder was collected by filtration and washed with ethanol to give an orange-red solid.

Selective hydrogenation of phenylacetylene

2 mg of Pd@V-COF-1 or Pd@V-COF-S was added to a 25 mL cigar-shaped flask with a hydrogen balloon, 22 μ L (0.2 mmol) of phenylacetylene was added, and 3 mL of methanol was used as a solvent. The vial was purged five times with a hydrogen balloon to remove air from the vial, ensuring that the reaction was always carried out under a hydrogen atmosphere. The reaction was carried out at 30 °C at 400 r.p.m. At the end of the reaction, the products were analyzed by gas chromatography (GC) using decans as an internal standard.

The stability test of Pd@V-COF-S

After the reaction, the catalyst was collected by centrifugation, washed with methanol three times, and reused for the next cycle. The products were analyzed by gas chromatography (GC) using decans as an internal standard.

4. Calculation methods

All calculations were performed using the Vienna ab initio simulation package (VASP) of first-principles calculations based on density functional theory². The core separation and valence electron interactions are described by projected added waves (PAW)³, and the local density is described using the generalized gradient approximation (GGA) based on exchange correlation energy PBE^{4, 5}. Brillouin zone divisions were sampled using Monkhorst-Pack method. ENCUT=400 eV was selected as the cutoff energy value for the calculation. The K points of dimensions 1*1*1-3*3*1

were generated by optimizing the convergence sampling in the calculation of the diffusion barrier and the mechanical strength, respectively. The precision values for electron and ion relaxation convergence are 1.0×10^{-4} eV and 1.0×10^{-3} eV, and the force convergence criterion is 0.02 eV/Å.



5. Supplementary Figures

Figure S1. (a) FT-IR spectra of TMT, TPA-SCH₃, V-COF-S, (b) FT-IR spectra of TMT, TPA, V-COF-1.



Figure S2. PXRD patterns of V-COF-1 and Pd@V-COF-1.



Figure S3. TGA curves of Pd@V-COF-1 and V-COF-1 under an air atmosphere.



Figure S4. PXRD patterns of V-COF-S after exposure to different solvents.



Figure S5. (a) N_2 adsorption and desorption isotherms of Pd@V-COF-1 and V-COF-1 at 77 K; (b) Pore size distributions of Pd@V-COF-1 and V-COF-1.



Figure S6. Pore size distributions of Pd@V-COF-S and V-COF-S.



Figure S7. (a) SEM image of V-COF-1; (b) SEM image of Pd@V-COF-1; (c) TEM image of Pd@V-COF-1; (d) The corresponding particle size distribution of Pd NPs in Pd@V-COF-1.



Figure S8. Catalytic performance for phenylacetylene semihydrogenation over Pd@V-COF-S.



Figure S9. Recycling catalytic performance of Pd@V-COF-1 with adding 10 eq. thioanisole in the semihydrogenation reaction of phenylacetylene.



Figure S10. Recycling catalytic performance of Pd@V-COF-S in the semihydrogenation reaction of phenylacetylene.



Figure S11. (a) SEM image of Pd@V-COF-S after ten catalytic cycles; (b) TEM image of Pd@V-COF-S after ten catalytic cycles (c) and the corresponding particle size distribution.



Figure S12. PXRD patterns of Pd@V-COF-S before catalytic reaction and after ten catalytic cycles.

Entry	Catalysts	Pd content (wt%)		
1	Pd@V-COF-S	1.01		
2	Pd@V-COF-1	1.18		

Table S1. The contents of Pd were determined by the ICP-AES.

Entr Т $P(H_2)$ Time Conv. Sele. Catalysts Ref. (h) (%) (%) (bar) у (°C) 1 Pd@V-COF-S 30 1 3 >99 96 This work Angew. Chem. Int. Ed. 2 PdCu₂@MF-CH₃ 4 30 1 >99 96 2023, 62, 05212 J.Am.Chem.Soc. 2015, 3 Au@CeO₂ 30 30 12 98 98 137, 13452 Adv. Mater. 4 Pd₁/Ni@G 30 2 1.1 >99 93 2022, 34, 2110455. 5 Pd-PEI-HAS 1 6 88 ACS Catal. 2013, 3, 1700 25 98 Catal. Today. 2016, 264, 6 $PdCu_6/Al_2O_3$ 40 1 1.7 92 89 37–43. J. Am. Chem. Soc. 2024, 7 6 95 h-Pd-Mn/NC 60 15 99 146, 32132-2140 ACS Catal. 8 Pd-Pb NSs 40 4 100 95.8 0.5 2021, 11, 9, 5231-5239 Nano Res. 9 MS Pd-Ru@ZIF-8 100 1 2 98 96 2022, 15(3): 1983-1992 Angew. Chem. Int. Ed. 10 Ru₃@ZIF-8 80 40 5 47 97 2019, 131, 4315 J. Am. Chem. Soc. $Pd_1 - Fe/Fe_2O_3(012)$ 80 15 99 11 1.4 >99 2022, 144, 573 Adv. Mater. 12 Pd@Ag@CeO₂ 40 15 12 97 99 2017, 29, 1605332 J. Am. Chem. Soc. 13 20 20 99 99 Au₂₅(SR)18/TiO₂ 100 2014, 136, 11347 5 14 Pd NCs@NCMs 25 1 99 95 ACS Catal. 2019, 9, 4632

Table S2. Catalytic performance comparison of Pd@V-COF-S with recently reported catalysts for the semihydrogenation of phenylacetylene.

Table S2 (continued)

Entr	Catalysts	т	P(H₂)	Time	Conv.	Sele.	Ref.
у		(°C)	(bar)	(h)	(%)	(%)	
15	Fe ₃ O ₄ @ZIF-8/Pd	40	1	4.5	99	90.5	Chem. Res.
							2017, 56, 14182
10	Dd Db (27%) allow NCc	25	1	7 5	00	91	Angew. Chem. Int. Ed.
10		25	T	7.5	55		2015, 128, 8389
17	meso-PdP alloy	60	1	1	100	97	Angew. Chem. Int. Ed.
17	nanobundles	00	T	Ţ	100		2022 <i>, 61,</i> e202114539
19	Pd₃Pb CNCs	50	2	5	99	94.6	Chem. Mater. 2018, 30,
10		50					18, 6338–6345
19	PdCx@S-1	25	2	4	99	99	Angew. Chem. Int.Ed.
							2023, 62, e202313101
20	Pd /Cu (111)	30	1	15	100	96	Nature. Nano.
20		50	T	1.5	100		2020, 15, 848–853.
21		50	10	0.83	9/1 Q	94.0	ACS Catal.
21	146/1102	50	10	0.05	54.5		2024, 14, 4, 2463–2472
22	Pd/Nb ₂ C	25	1	0.67	99	96	Nat Commun.
							2023,14,6611
23	Pd _{0.5} /Ni _{0.5} @γ-Al ₂ O ₃	25	1	0.33	98	94	ACS Catal.
							2022, 24, 14846–14855
24	Pd@PPy-600	35	1	0.67	99	96	Adv. Mater.
24							2023,2209635

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