Supporting Information

A Schiff base-modified silver catalyst for efficient fixation of CO2 as carboxylic acid at ambient pressure

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Experimental

1. Catalyst Synthesis

1.1 Schiff base modified SiO_2 support was synthesized according to our previous report with slightly modification.¹

The SiO₂ powders were prepared by the aldimine condensation of (3-aminopropyl) triethoxysilane (APTES) with formaldehyde (HCHO). Typically, 2.5 mL HCHO solution (37%) was added into 0.010 mol L⁻¹ APTES aqueous solutions while stirring at 30 °C (HCHO/APTES, mol/mol = 2.5). The resulting white precipitation generated by aldimine condensation was then filtered and washed with deionized water and dried under reduced pressure to obtain Schiff base-functionalized SiO₂ support, named as Schiff-SiO₂.

1.2 Preparation of Ag/Schiff-SiO₂ catalyst by *in situ* reduction method.

Silver NPs were prepared by *in situ* reduction method. Briefly, 0.2 g Schiff-SiO₂ powder was immersed in methanol (40 mL) and then treated by ultrasonic wave for 10 min at room temperature. 2 mL water containing various amounts of silver nitrate (5 mg, 10 mg, 20 mg and 40 mg) was quickly added into the above mixture, and the mixture was then treated by ultrasonic wave for 5 min at room temperature, the precipitate was filtered and washed with an excess amount of deionized water until no Silver ions were detected in the filtrate. Following drying in vacuum at 120 °C for 12 h, Ag/Schiff–SiO₂ catalysts were obtained, and the catalysts were respectively named as **1a**, **1b**, **1c**, **1d**.

1.3 Preparation of Ag/SiO₂ Catalyst by NaBH₄ reduction method.

Silver NPs supported on the surface of SiO₂ were prepared by NaBH₄ reduction method. Briefly, 0.2 g SiO₂ powder was immersed in methanol (40 mL) and then treated by ultrasonic wave for 10 min at room temperature. 2 mL water containing various amounts of silver nitrate (20 mg) was added into the above mixture. Then, 2 mL water containing NaBH₄ (50 mg) was quickly added into the above mixture with ultrasonic wave for 5 min at room temperature, the precipitate was filtered and washed with an excess amount of deionized water until no Silver ions were detected in the filtrate. Following drying in vacuum at 120 °C for 12 h, Ag/SiO₂ catalysts was obtained, and the catalyst was named as **2a**.

1.4 Preparation of Ag/SiO₂-Schiff Catalyst by NaBH₄ reduction along with stirring method.

Silver NPs supported on the surface of Schiff base-functionalized SiO₂ were prepared by NaBH₄ reduction method. First, 0.2 g Schiff-SiO₂ powder was immersed in methanol (40 mL) and then treated by ultrasonic wave for 10 min at room temperature. 2 mL water containing silver nitrate (20 mg) was added into the above mixture with vigorous stirring for 1 min. Then, 2 mL water containing NaBH₄ (50 mg) was added into the above mixture with vigorous stirring for 30 min. The precipitate was filtered and washed with an excess amount of deionized water until no Silver ions were detected in the filtrate. Following drying in vacuum at 120 °C for 12 h, Ag/Schiff-SiO₂ catalyst was obtained, and the catalyst was named as **3a**.

2. Catalytic Activity Characterization

2.1 General experimental procedure for carboxylation of terminal alkynes

In a 10 mL Schlenk reaction tube, terminal alkyne (1.0 mmol), Cs_2CO_3 (0.489 g, 1.5 mmol), indicated amount of catalyst (Ag: 1-ethynylbenzene = 1:719 mol mol⁻¹), and anhydrous DMSO (5 mL) were added. The flask was capped with a stopper and sealed. Then the "freeze-pump-thaw" method was employed for gas exchanging process. The reaction mixture was stirred at 60 °C for desired time under the atmosphere of CO_2 (99.99%, balloon), then the reaction mixture was cooled to room temperature. For the reaction under pressure using the heterogeneous catalyst, the pre dried autoclave was consecutively loaded with the catalyst (Ag: 1-ethynylbenzene = 1:719 mol mol⁻¹), Cs_2CO_3 (0.489 g, 1.5 mmol), phenylacetylene (1.0 mmol), and anhydrous DMSO (5 mL). The autoclave was closed and purged with CO_2 three times, and carbon dioxide was fed at operating pressure. The reaction mixture was stirred for 6 h at 60 °C and 2 MPa. After the end of the reaction, the autoclave was cooled to room temperature. The yield of propiolic acid product can be analyzed by Agilent High performance liquid chromatography (HPLC).

2.2 Durability testing of Ag/Schiff-SiO₂

The Ag/Schiff-SiO₂ catalyst (**1c**) was recovered in the solid residue after filtration and separation from the reaction mixture. The solid residue was washed thoroughly with water and ethanol, following drying in vacuum at 120 °C for 12 h, then directly used as recycled catalyst in the subsequent runs without the addition of more catalyst.

3. Catalyst characterization

3.1 Elemental analysis

Elemental analysis was performed on Vario EL III (Elementar, Hanau, Germany). Elemental analysis result of Schiff-SiO₂ was shown that C (36.2 wt%), H (6.5 wt%) and N (10.6 wt%).

3.2 ICP-AES

The Ag loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The results of Ag loading were shown in Table S1.

3.3 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra were acquired with a spectrometer (Bruker tensor 27) equipped with a DLATGS detector and operated at a resolution of 4 cm^{-1} .

3.4 Solid state NMR spectroscopy

All the solid state NMR experiments were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet. The resonance frequencies were 156.4 and 119.2 MHz for ¹³C, and ²⁹Si, respectively. ¹H \rightarrow ¹³C and ¹H \rightarrow ²⁹Si CP/MAS NMR experiments were performed on a 4 mm MAS probe with a spinning rate of 12 and 8 kHz, respectively. ¹H \rightarrow ¹³C CP/MAS NMR experiments were carried out with a contact time of 5 ms and a recycle delay of 2 s. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm. 1H \rightarrow ²⁹Si CP/MAS NMR experiments were carried out with a contact time of 3 ms and a recycle delay of 2 s. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS).

3.5 XRD

X-ray diffraction (XRD) experiments were carried out on a PANalytical X'Pert-Pro powder X-ray

diffractometer, using Cu K α monochromatized radiation ($\lambda = 0.1541$ nm) with a scanning angle (2 θ) of 10°–80°, operated at 40 kV and 40 mA.

3.6 EDS and HR-TEM

The EDS and HR-TEM images were obtained using a JEOL JEM-2100F at 200 kV. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

3.7 X-ray photoelectron spectroscopy (XPS)

XPS was performed on a Kratos AXIS ULTRA DLA X-ray photoelectron spectrometer equipped with an Al K α radiation source (1486.6 eV, 15 kV). All binding energies were calibrated with the C1s peak at 284.8 eV for the adventitious carbon.

4. Computational methods

All calculations were performed with Beck's three-parameter B3LYP hybrid exchange-correlation function²⁻⁴ using the Gaussian 09 software package⁵ based on the DFT method. For the geometry optimizations, frequency calculations, and IRC calculations, the CEP-121G basis sets⁶⁻⁸ with effective core potentials (ECPs) were employed for Ag, and the 6-311++G(d,p) basis set⁹ was used for H, C, O, S and N. The single-point energy is directly obtained from the optimized results. The solvent effects have been considered in every calculation by using the SMD model¹⁰ with the DMF and DMSO solvents. The corresponding step of the reaction mechanism was investigated by locating the transition state (TS) and the associated reactants and products. To confirm first-order saddle points, local minima on the potential energy surfaces, and the zero-point energy, we have calculated the harmonic frequency at the equilibrium geometries. The corresponding imaginary frequency model and intrinsic reaction coordinate (IRC) calculation correlation were performed to confirm the transition states and the stable structures (Figure S13). Here, Ag_n (n=8) cluster with the global minimum configuration^{11, 12} was employed for the simulation of silver NPs.

Entry	Catalyst	Ag loading (wt%)
1	1a	1.17
2	1b	1.36
3	1c	1.45
4	1d	2.52
5	2a	1.20
6	3a	0.71

Table S1. The Ag loading of the catalysts was measured by ICP-AES.

Entry	Catalyst	т (°С)	t (h)	Yields	TON ^[b]	Reference
				(%)		
1	Ag@P-NHC ^[c]	25	20	98	327	Ref.13
2	Ag@MIL-101 ^[c]	50	15	97	36	Ref.14
3	$Ag/F-Al_2O_3^{[d]}$	50	18	62	12	Ref.15
4	Nd complex	40	24	90	23	Ref.16
5	Pd _{0.2} -Cu _{0.8} /MIL-101 ^[c]	25	24	96	691	Ref.17
6	Ag/Schiff-SiO ₂	60	24	98	705	This work

Table S2: Synthesis of 3-phenylpropiolic acid from CO₂ and 1-ethynylbenzene with catalysts. ^[a]

[a] Reaction conditions: 1-ethynylbenzene (1.0 mmol), Cs_2CO_3 (1.5 mmol), solvent (DMSO, 5 mL), CO_2 (1.0 atm). [b] TON = (moles of product)/(moles of metal in the catalyst). [c] Solvent (DMF, 5 mL). [d] CO_2 (60 atm).



Figure S1 FT-IR spectra of the support Schiff-SiO₂.



Figure S2 (a) ²⁹Si CP-MAS NMR and (b) ¹³C CP-MAS NMR spectra of the support Schiff-SiO₂.



Figure S3 Powder XRD patterns of Ag/Schiff-SiO₂ (**1a-d**, **1c-recycled**, **3a**) and **2a** Ag/Schiff-SiO₂, which show the characteristic peaks of Ag (111), Ag (200), Ag (220) and Ag (311) and confirm the successful deposition of Ag NPs in the surface of Schiff-SiO₂ as well as confirm the maintenance of the NPs size during the whole reaction circles.



Figure S4 Recycling tests of catalysts 1.45wt% Ag/Schiff-SiO₂ (**1c**) for the carboxylation of terminal alkynes with CO₂, reaction conditions: 1-ethynylbenzene (1.0 mmol), catalyst (**1c**, 10 mg), Cs_2CO_3 (1.5 mmol), CO_2 (1.0 atm), 60 °C, DMSO (5 mL), 24 h.



Figure S5 HR-TEM image of the Ag/SiO₂-Schiff sample (**1c**-recycled; left) and size distribution of the Ag NPs in a sample of **1c** (Ag NPs size: 6.4 ± 2.6 nm) (right).



Figure S6 HR-TEM image of the Ag/SiO₂-Schiff sample (**1a**; left) and size distribution of the Ag NPs in a sample of **1a** (Ag NPs size: 8.3 ± 2.3) (right).



Figure S7 HR-TEM image of the Ag/SiO_2 -Schiff sample (**1b**; left) and size distribution of the Ag NPs in a sample of **1b** (Ag NPs size: 8.5±2.3) (right).



Figure S8 HR-TEM image of the Ag/SiO_2 -Schiff sample (**1d**; left) and size distribution of the Ag NPs in a sample of **1d** (Ag NPs size: 7.9±2.2) (right).



Figure S9 XPS spectra for catalyst Ag/SiO₂-Schiff (**1c**) at the Ag 3d levels exhibiting metallic Ag (0) peaks Ag $3d_{3/2}$ and $3d_{5/2}$.



Figure S10 Core level XPS spectra in N 1s region of Ag/SiO₂-Schiff (1c).



Figure S11 XPS spectra for catalyst Ag/SiO₂-Schiff (**1c**-recycled) at the Ag 3d levels exhibiting metallic Ag (0) peaks Ag $3d_{3/2}$ and $3d_{5/2}$.



Figure S12 Core level XPS spectra in N 1s region of as-prepared Ag/SiO₂-Schiff (1c-recycled).



Figure S13. IRC plots for selected transition states in DMF (a) and DMSO (b) solvents.

5. NMR data and spectra of products

NMR spectra were recorded with a Bruker Avance 500 spectrometer at 500z (¹H NMR), 126 (¹³C NMR). Data for ¹H and ¹³C NMR of acids were all conducted in DMSO-d₆.

5.1 Phenylpropiolic acid

¹H NMR (500 MHz, DMSO-d₆): δ=13.59 (br, s, 1H, -COOH), 7.62 (d, J = 7.7 Hz, 2H, Ar-H), 7.55 (t, J = 7.5 Hz, 1H, Ar-H), 7.47 (t, J = 7.5 Hz, 2H, Ar-H) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ=154.26, 132.54, 130.85, 129.0, 118.98, 84.31, 81.78 ppm.







5.2 4-Methoxylphenylpropiolic acid

¹H NMR (500 MHz, DMSO-d₆): δ = 13.67 (br, s, 1H, -COOH), 7.57 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H, CH₃) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 161.17, 154.61, 134.61, 114.74, 110.72, 84.97, 81.33, 55.46 ppm.





5.3 4-Fluorophenylpropiolic acid

¹H NMR (500 MHz, DMSO-d₆): δ=13.63 (br, s, 1H, -COOH), 7.75–7.66 (m, 2H), 7.32 (t, J = 8.5 Hz, 2H) ppm. ¹³C NMR (126 MHz, DMSO): δ=162.31, 154.23, 135.35, 116.53, 116.35, 83.34, 81.66 ppm.







5.4 4-Nitrophenylpropiolic acid

¹H NMR (500 MHz, DMSO-d₆): δ=13.67 (br, s, 1H, -COOH), 8.28 (d, J=7.4 Hz, 2H, Ar-H); 7.92 (m, J=8.8 Hz, 2H, Ar-H) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ=153.8, 148.21, 133.82, 125.63, 123.98, 85.12, 81.65 ppm.







5.5 3-(Thiophen-3-yl) propiolic acid

¹H NMR (500 MHz, DMSO-d₆): δ=13.10 (br, s, 1H, -COOH), 8.17 (s, 1H, Ar-H); 7.70 (s, 1H, Ar-H); 7.32 (d, J = 4.8 Hz, 1H, Ar-H) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ=154.44, 134.68, 129.92, 127.73, 118.03, 81.08, 80.00 ppm.







5.6 Hept-2-ynoic acid

¹H NMR (500 MHz, DMSO-d₆): δ=13.10 (s, 1H, -COOH), 2.37 (t, J = 6.9 Hz, 2H, CH₂); 1.48 (p, J = 7.2 Hz, 2H, CH₂); 1.37 (h, J = 7.3 Hz, CH₂); 0.89 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ=154.26, 88.36, 74.2, 29.17, 21.35, 17.34, 13.33 ppm.





5.7 Hept-6-en-2-ynoic acid

¹H NMR (500 MHz, DMSO-d₆): δ=13.10 (s, 1H, -COOH), 5.83 (ddt, J = 16.8, 11.7, 6.7 Hz, 1H, CH); 5.09 (dd, J = 29.0, 13.7 Hz, 2H, CH₂); 2.47 (t, J = 7.1 Hz, 2H, CH₂); 2.26 (q, J = 7.0 Hz, 2H, CH₂) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ=154.20, 136.32, 116.30, 87.69, 74.40, 31.10, 17.35 ppm.



6. Computational Geometries (in ${\rm \AA}$)

6.1 Reactant in DMSO: PhC≡C−Ag₈

Ag	-2.94271400	-0.00938000	0.00859000
Ag	-2.06196800	-1.92714900	-1.85482700
Ag	-2.05237700	-0.67312300	2.59599500
Ag	-0.39991000	-1.57505100	0.44631000
Ag	-2.08224900	2.56493000	-0.74166100
Ag	-0.44227200	1.18382800	1.13952700
Ag	-0.42408700	0.40169500	-1.59649500
Ag	1.97419100	0.03719100	0.00403700
С	5.36528200	0.02331200	0.00301200
С	4.13462700	0.03786100	0.00669500
С	6.79688200	0.00586500	0.00017400
С	7.53648700	1.20394600	0.07297800
С	7.50643300	-1.21009000	-0.07587200
С	8.92852000	1.18308700	0.07014200
Н	7.00654300	2.15191000	0.13300400
С	8.89855600	-1.22343000	-0.07918500
н	6.95309300	-2.14473600	-0.13358100
С	9.61740500	-0.02883700	-0.00608100
н	9.47917000	2.12026900	0.12817000
н	9.42588200	-2.17378500	-0.13962900
Н	10.70532800	-0.04221600	-0.00849500
6.2 Transition State i	n DMSO: PhC≡C–	Ag ₈ + CO ₂	
Ag	3.03532200	-0.46531100	0.00402100
Ag	1.91229000	-1.60905000	-2.31943100
Ag	2.71715600	2.33774300	0.00081500
Ag	0.75491700	0.84724400	-1.43557000
Ag	1.89190300	-1.60456900	2.32146400
Ag	0.74427500	0.85059800	1.42614100
Ag	0.24570200	-1.57812300 S19	-0.00506300

Ag	-1.73860200	0.51890600	-0.01532200
С	-5.02103000	0.27978500	-0.01012400
С	-3.93415300	0.86605100	-0.00386200
С	-6.27736900	-0.39644800	-0.01289800
С	-6.98023200	-0.60938400	-1.21677700
С	-6.84293200	-0.86946900	1.18925600
С	-8.20554400	-1.26854400	-1.21334600
н	-6.55415600	-0.25118700	-2.15116500
С	-8.06777100	-1.52943300	1.18366700
н	-6.30968800	-0.71337300	2.12420200
С	-8.75421800	-1.73127500	-0.01551000
н	-8.73575300	-1.42348300	-2.15106800
н	-8.48954000	-1.88891200	2.12031900
н	-9.71200800	-2.24749200	-0.01680400
С	-3.87031200	3.02535200	0.07225300
0	-3.87516400	3.34979300	-1.06821500
0	-3.86692900	3.26833600	1.23283900
6.3 Product in DMSO:	PhC≡C-COO-Ag	8	
Ag	3.38505000	0.02806500	-0.00799000
Ag	2.53713300	-0.71246700	2.58603100
Ag	2.51946700	-1.85842100	-1.92423700
Ag	0.91064400	-1.58109300	0.41508600
Ag	2.53009300	2.63325100	-0.69000600
Ag	0.90621900	0.47328300	-1.60029900
Ag	0.94480000	1.19228300	1.18967300
Ag	-1.40617900	0.04881800	0.02661000
С	-7.16207200	-0.28039000	0.00922700
С	-5.97214400	-0.50694200	0.01530600
С	-8.56003700	0.00479300	0.00057500
С	-9.50349000	-1.03475300 S20	-0.09878100

С	-9.01213600	1.33489400	0.08977900
С	-10.86460700	-0.74609100	-0.10803200
Н	-9.15908400	-2.06421000	-0.16797100
С	-10.37503500	1.61355300	0.08060800
н	-8.28654000	2.14162000	0.16568300
С	-11.30387700	0.57599800	-0.01828600
н	-11.58652900	-1.55664400	-0.18515800
н	-10.71417700	2.64516000	0.15051700
н	-12.36928100	0.79765800	-0.02543700
С	-4.52925300	-0.77026500	0.02065200
0	-3.78987200	0.26148600	0.03390200
0	-4.15615100	-1.96438200	0.01075400
6.1 Reactant i	n DMF: PhC≡C−Ag ₈		
Ag	-2.94442100	-0.01263400	0.00703800
Ag	-2.05877700	-1.91389100	-1.87024700
Ag	-2.05337400	-0.69360400	2.58961400
Ag	-0.39880000	-1.57815400	0.43436900
Ag	-2.08689500	2.56977000	-0.72101400
Ag	-0.44470900	1.17462700	1.14907800
Ag	-0.42468700	0.41583600	-1.59237400
Ag	1.97370200	0.04036900	0.00494500
С	5.36679900	0.02597200	0.00375800
С	4.12919300	0.04120300	0.00772600
С	6.80134500	0.00724100	0.00037500
С	7.54379300	1.20827500	0.06949800
С	7.51117600	-1.21315800	-0.07252400
С	8.93962900	1.18583000	0.06640800
н	7.01345100	2.15847400	0.12686800
С	8.90709900	-1.22784800	-0.07610300
н	6.95541300	-2.14886800	-0.12732000

S21

С	9.62927200	-0.03041400	-0.00652600	
Н	9.49208700	2.12441100	0.12156100	
н	9.43422400	-2.18073100	-0.13387200	
Н	10.71919100	-0.04493000	-0.00911600	
6.2 Transi	tion State in DMF: PhC≡C–A	g ₈ + CO ₂		
Ag	3.05375200	-0.44728800	-0.00000200	
Ag	1.92950400	-1.59270800	-2.32237800	
Ag	2.70749600	2.35130500	-0.00036200	
Ag	0.74667800	0.84801800	-1.42799400	
Ag	1.92966700	-1.59205200	2.32278700	
Ag	0.74676900	0.84840800	1.42778500	
Ag	0.27672600	-1.58450700	0.00025300	
Ag	-1.74149100	0.48045200	0.00001800	
С	-5.04340200	0.21745100	0.00000100	
С	-3.92975000	0.76613600	-0.00001900	
С	-6.32852800	-0.41017300	0.00004600	
С	-6.97772200	-0.72787600	-1.21522500	
С	-6.97827200	-0.72655700	1.21536900	
С	-8.23202300	-1.33887400	-1.21078400	
н	-6.48672900	-0.49012000	-2.15842000	
С	-8.23257700	-1.33754600	1.21102300	
н	-6.48771100	-0.48776500	2.15852600	
С	-8.86439200	-1.64654100	0.00014400	
н	-8.71870800	-1.57734900	-2.15682600	
н	-8.71970100	-1.57497200	2.15710300	
н	-9.84397400	-2.12467500	0.00018300	
С	-3.89479200	2.97637300	-0.00037400	
0	-3.89765200	3.24818800	-1.16073900	
0	-3.89762200	3.24855800	1.15990600	

6.3 Product in DMF: PhC≡C-COO-Ag₈

S22

Ag	3.38505000	0.02806500	-0.00799000
Ag	2.53713300	-0.71246700	2.58603100
Ag	2.51946700	-1.85842100	-1.92423700
Ag	0.91064400	-1.58109300	0.41508600
Ag	2.53009300	2.63325100	-0.69000600
Ag	0.90621900	0.47328300	-1.60029900
Ag	0.94480000	1.19228300	1.18967300
Ag	-1.40617900	0.04881800	0.02661000
С	-7.16207200	-0.28039000	0.00922700
С	-5.97214400	-0.50694200	0.01530600
С	-8.56003700	0.00479300	0.00057500
С	-9.50349000	-1.03475300	-0.09878100
С	-9.01213600	1.33489400	0.08977900
С	-10.86460700	-0.74609100	-0.10803200
н	-9.15908400	-2.06421000	-0.16797100
С	-10.37503500	1.61355300	0.08060800
н	-8.28654000	2.14162000	0.16568300
С	-11.30387700	0.57599800	-0.01828600
Н	-11.58652900	-1.55664400	-0.18515800
Н	-10.71417700	2.64516000	0.15051700
Н	-12.36928100	0.79765800	-0.02543700
С	-4.52925300	-0.77026500	0.02065200
0	-3.78987200	0.26148600	0.03390200
0	-4.15615100	-1.96438200	0.01075400

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