

Supporting Information

Additive-free CO₂ Hydrogenation to Pure Formic Acid Solution via Amine-modified Pd Catalyst at Room Temperature

Shuchao Jiang ^{a†}, Xiaokong Liu ^{b†}, Shengliang Zhai ^a, Xiuqin Ci ^a, Tie Yu ^a, Lei Sun ^a, Dong Zhai ^{a*}, Weiqiao Deng ^a, Guoqing Ren ^{a*}

^a Institute of Molecular Sciences and Engineering, Institute of Frontier and Interdisciplinary Science, Shandong University, Qingdao, Shandong, 266237, P. R. China.

^b School of Life Sciences, Shandong University, Qingdao, Shandong, 266237, P. R. China.

† These authors contribute equally to this work

* Corresponding author

Dong Zhai: zhaidong@sdu.edu.cn, Guoqing Ren: renguoqing@sdu.edu.cn

I Experimental Section

Chemicals

Na_2PdCl_4 , Active carbon (AC) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. The primary amine (PA) of (3-aminopropyl)triethoxysilane, secondary amine (SA) of (3-methylaminopropyl)trimethoxysilane and tertiary amine (TA) of (N,N-dimethylaminopropyl)trimethoxysilane were purchased from Shanghai Acme Biochemical Co., Ltd. All the reagents were of analytical purity and used as received without further purification.

Instrumentation and methods

The supported catalysts were characterized by N_2 -adsorption using Autosorb-IQ system (Quanta) at 77 K, and the samples were degassed in vacuum at 473 K for 10 h prior to analysis. X-ray diffraction (XRD) patterns were conducted by D8 Advance (Bruker), and the samples were scanned from 10° to 90° at a scanning rate of 5°min^{-1} . Transmission Electron Microscope (TEM) micrographs were obtained by using a JEM-2100F (JEOL). X-ray photoelectron spectroscopy (XPS) was detected on an Escalab 250Xi (Thermo Fisher), whose spectra were calibrated by the C1s peak (284.8 eV). The loading amounts of Pd in the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-ES) measurements. Thermogravimetric (TG) patterns were conducted by TG209F1 Libra. Prior to the TG test, dry the samples overnight at 353 K in a vacuum oven. Then weigh 5 mg of catalysts into the sample pool and heat it from 298 K to 873 K at a rate of 10 K/min in a N_2 atmosphere. After that, cool to room temperature to complete the test process. CO_2 adsorption was determined by Thermogravimetric-Differential Thermal Analysis (TG-DTA) (Netzsch STA449F3). Specifically, weigh 10 mg of catalyst into the sample pool and heat the temperature to 383 K at a rate of 10 K/min under N_2 flow (50 mL/min). After keeping 2 h, cool the sample to 298 K to absorb CO_2 under a CO_2 flow (50 mL/min) until the detected mass signal gets stable. Then the CO_2 capture capacity of the catalyst can be obtained by calculating the mass change of the catalyst before and after absorbing CO_2 gas.

DFT calculation details

All DFT calculations were performed using the Vienna ab initio simulation package (VASP version 6.1)¹. The exchange correlation energy was described within the generalized gradient approximation (GGA)², with the use of the Perdew-Burke-Ernzerhof (PBE) functional³. The projector-augmented-wave method (PAW) implemented in VASP was applied⁴. The vdW dispersion interaction was corrected using Grimme's DFT-D3 method with Becke–Johnson damping⁵. Spin polarization was considered in the calculations. The kinetic energy cut-off was set to 450 eV. The lattice parameters and ionic positions of the structures were fully relaxed until the Hellmann–Feynman forces were less than 0.02 eV Å⁻¹. The convergence criterion for the electronic self-consistent iteration was set to 1 × 10⁻⁵ eV. The (3 × 3 × 1) k-point mesh was used for the Brillouin-zone integration. The nudged elastic band (NEB) method was used to locate transition state (TS) in the reactions, and all the TSs were characterized as real first-order saddle points. To model the Pd (111) surface, we used a supercell slab that consisted of p(4 × 4) surface unit cells with 5 atomic layers. The bottom two layers of the slab were fixed at corresponding bulk positions, the upper three layers were fully relaxed. A vacuum space of 15 Å along the Z direction was set to avoid artificial interactions between adjacent images.

Synthesis of the catalysts

Typically, 0.2 g of active carbon was dispersed to 50 mL H₂O, then 0.1 mL of secondary amino (SA) was dropped to the resulting active carbon solution with magnetic stirring at room temperature. After 15 min, 2 mL aqueous solution containing 0.011 g Na₂PdCl₄ was added to above solution. One hour later, fresh NaBH₄ solution (50 mg NaBH₄ dissolved in 2 mL H₂O) was added to the mixture with continuous stirring for another 20 min. The resultant black product was separated by centrifugation and washed with pure water for three times. The final catalyst of Pd/AC-SA was dried in the vacuum oven at 333 K for 12 h. For comparison, Pd/AC-PA and Pd/AC-TA were prepared through above similar method except for using primary amine and tertiary amine, respectively.

CO₂ hydrogenation into FA without base additives

The hydrogenation of CO₂ to pure FA was performed in a 25 mL stainless steel autoclave. Initially, 10 mg of catalyst was transferred to the autoclave and followed by 10 mL of distilled water. Subsequently, reaction gas (CO₂/H₂ = 1:1) was injected to the autoclave. After 6 h, the liquid sample was separated from the reaction solution by filtration through 0.45 μm PTFE syringe filter. The liquid components were analyzed by HPLC analyzer (Agilent 1100) using a UV detector at 210 nm with 5 mmol/L sulfur acid aqueous solution as eluent.

After cyclic hydrogenation reaction, the catalyst was filtered out and thoroughly washed using 500 mL of deionized water. Then the catalyst is dried overnight in a vacuum oven at 333 K for the next cyclic reaction.

The turnover frequency (TOF) reported for CO₂ hydrogenation into FA is calculated as the following equation:

$$\text{TOF} = n_{FA} / (n_{pd} t)$$

Where n_{FA} is the molar of generated FA, n_{pd} is the total number of Pd metal atoms, and t is the reaction time in hours.

II Results and discussion

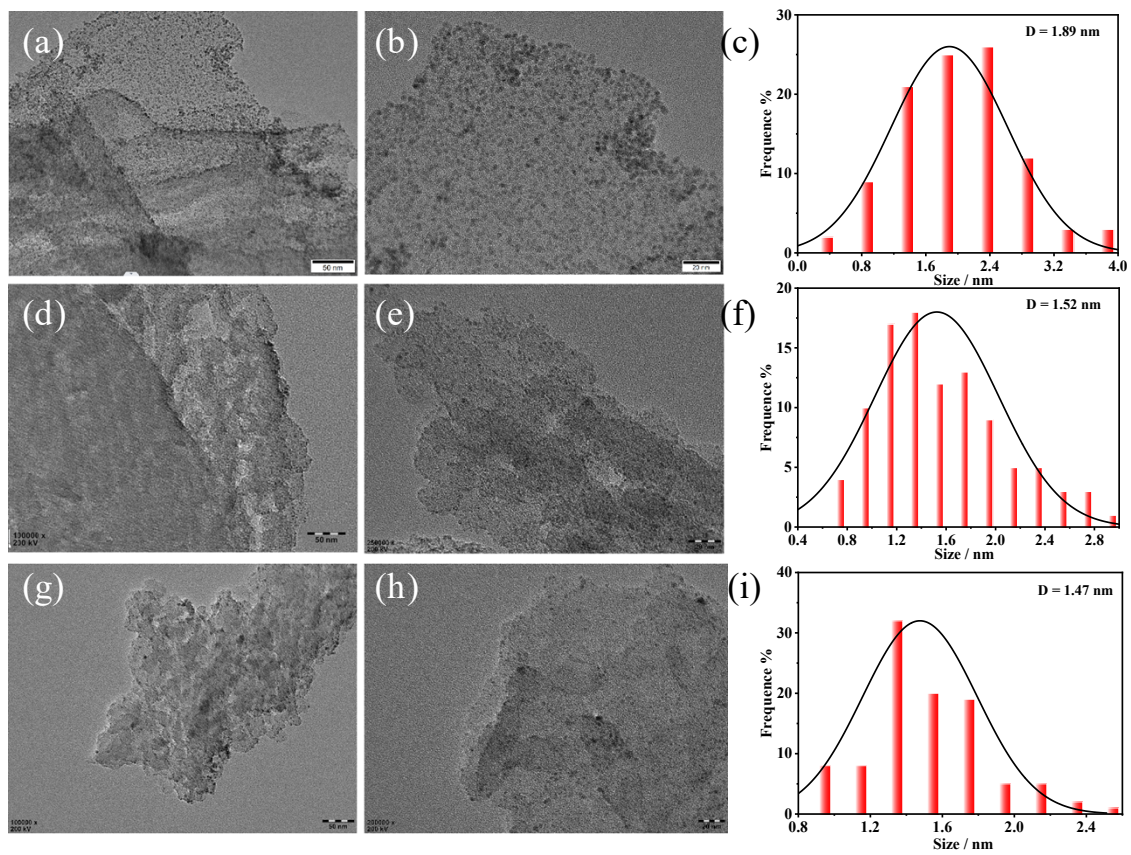


Fig. S1 TEM images and corresponding particle size distribution for the catalyst of Pd/AC-PA (a-c), Pd/AC-SA (d-f) and Pd/AC-TA (g-i).

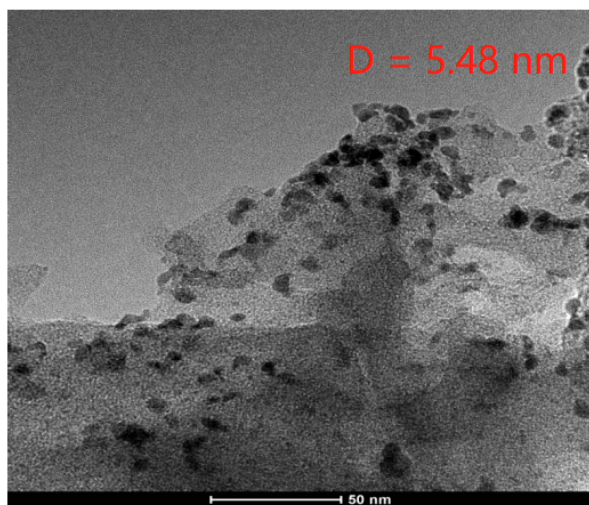


Fig. S2 TEM image of Pd/AC with no modification of amine groups.

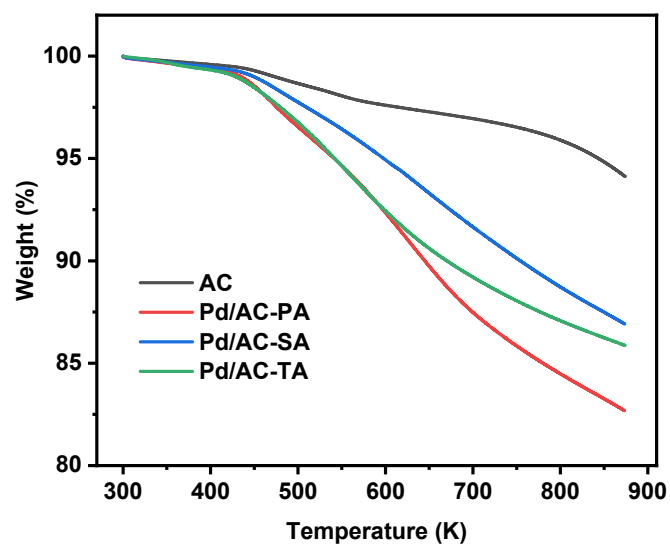


Fig. S3 TGA testing of Pd/AC-PA, Pd/AC-SA, Pd/AC-TA and AC.

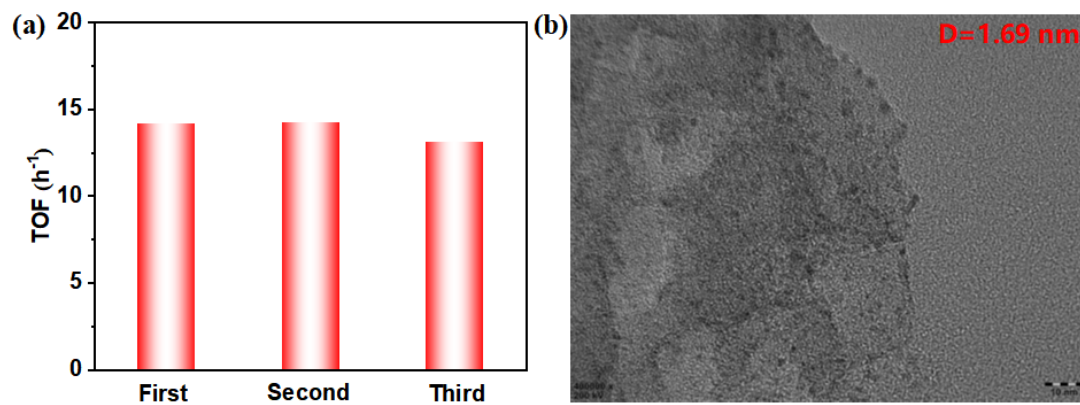


Fig. S4 (a) Cyclic stability evaluation of Pd/AC-SA catalyst for the synthesis of pure formic acid at room temperature. (b) TEM picture of the recycled Pd/AC-SA catalyst after three cycles.

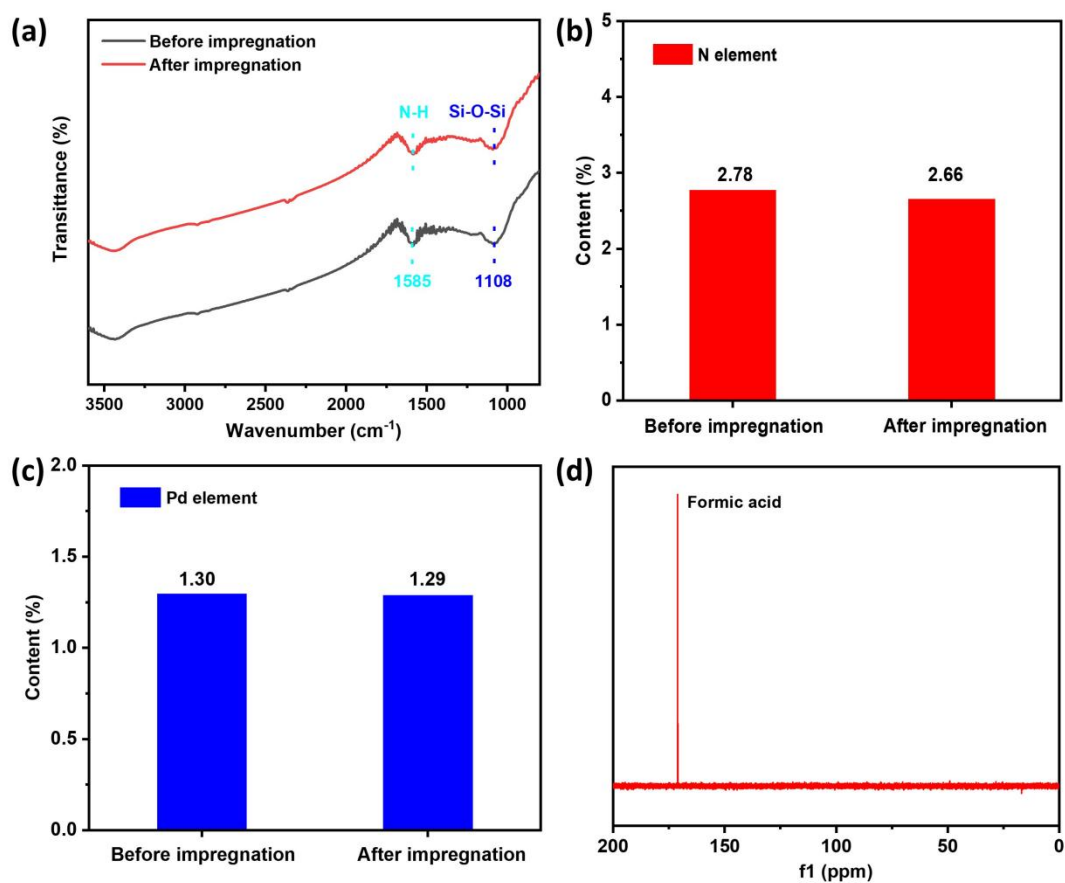


Fig. S5 (a) FTIR, (b) N content and (c) Pd content of Pd/AC-SA catalyst before and after impregnation in formic acid aqueous solution. (d) ^{13}C NMR of formic acid aqueous solution after impregnating Pd/AC-SA catalyst. (Pd/AC-SA catalyst was impregnated in formic acid solution for 24 h (the formic acid concentration corresponds to the yield of CO_2 hydrogenation over Pd/AC-SA catalyst for reacting 6 h), followed by filtration, washing and vacuum overnight drying at 333 K)

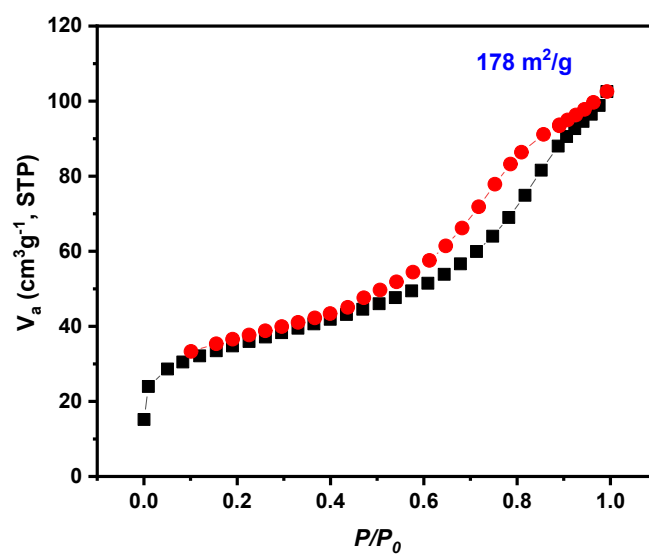


Fig. S6 N₂ adsorption and desorption isotherms (77 K) for the catalyst of Pd/AC-AE.

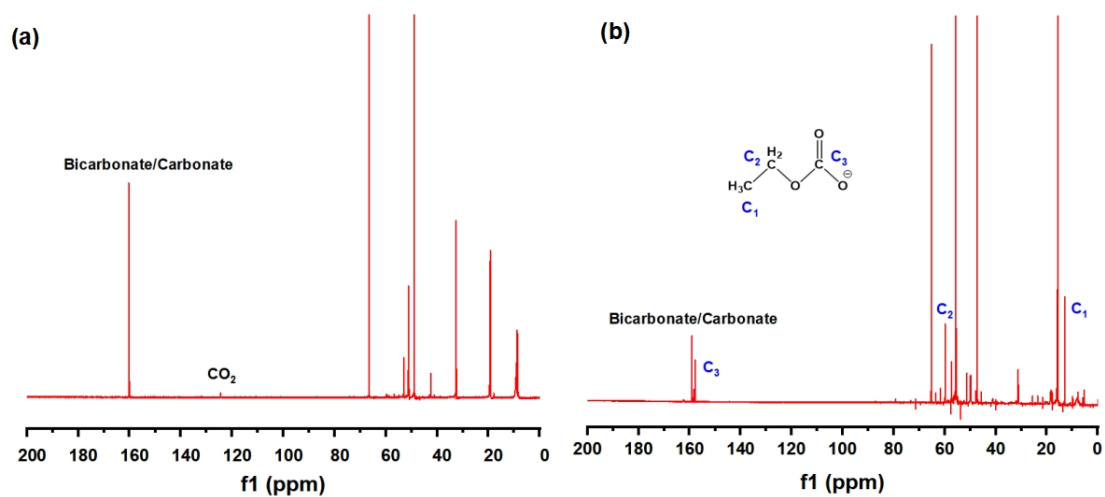


Fig. S7 ^{13}C NMR spectra of CO_2 derived species after CO_2 was captured by (3-methylaminopropyl)trimethoxysilane (SA) in (a) water and (b) ethanol. CO_2 capture conditions: 10 mL ethanol/water solvent, 0.3 mL SA, 2.0 MPa CO_2 , 25 $^\circ\text{C}$, 60 min.

1,4-dioxane was used as an internal standard.

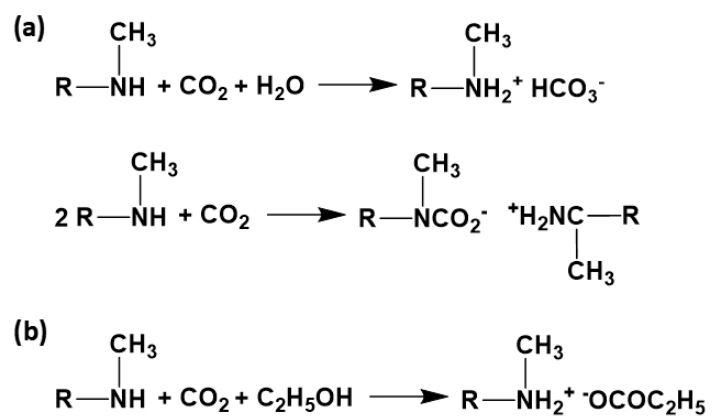


Fig. S8 CO₂ conversion species in (a) water and (b) ethanol.

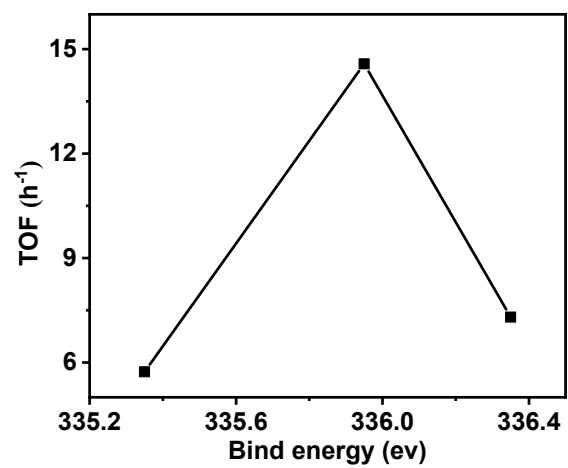


Fig. S9 The relationship between the TOF value and Pd binding energy.

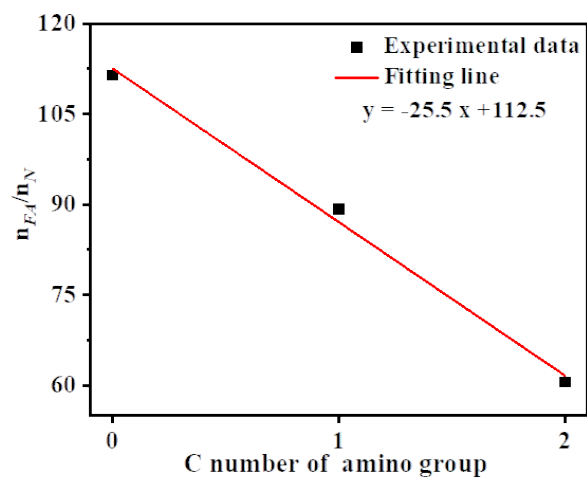


Fig. S10 Formic acid adsorption as a function of the number of methyl groups on the amino group (PA is 0, SA is 1, and TA is 2).

Table S1 Specific chemical structures of different amine modified catalysts.

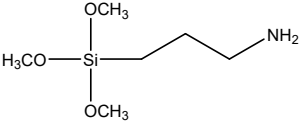
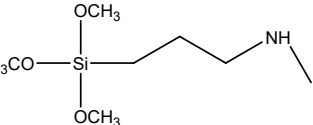
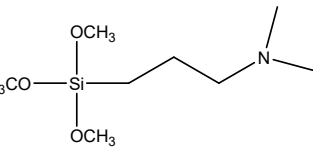
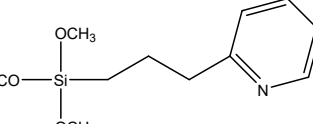
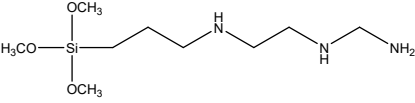
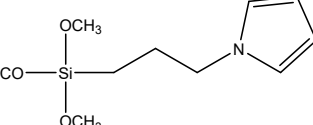
Entry	Catalysts	Modified compounds	Structures
1	Pd/AC-PA	(3-aminopropyl) triethoxysilane	
2	Pd/AC-SA	(3-methylaminopropyl) trimethoxysilane	
3	Pd/AC-TA	(n,n-dimethylaminopropyl) trimethoxysilane	
4	Pd/AC-PD	2-(2-pyridyl) ethyltrimethoxysilane	
5	Pd/AC-AE	3-[2-(2-aminoethylamino) ethylamino]propyl-trimethoxysilane	
6	Pd/AC-PR	1-[3-(Trimethoxysilyl) propyl]-1H-pyrrole	

Table S2 ICP results of the as prepared catalysts.

Catalyst	Pd / wt. %
Pd/AC-PA	1.28
Pd/AC-SA	1.30
Pd/AC-TA	1.32
Pd/AC-SA ^a	1.27

^a The spent catalyst element content measured after three cycles.

Table S3 Elemental content analysis of various catalysts.

Samples	C / wt. %	H / wt. %	N / wt. %
Pd/AC-PA	62.00	2.65	2.91
Pd/AC-SA	63.24	2.52	2.78
Pd/AC-TA	64.35	3.11	3.20
Pd/AC-SA ^a	64.74	2.65	2.70

^a The spent catalyst element content measured after three cycles.

Table S4 The textural properties of various samples measured by N₂ adsorption/desorption isotherms.

Different stages	SBET/ m ² g ⁻¹	Pore volume / cm ⁻³ g ⁻¹
Pd/AC	951	0.73
Pd/AC-PA	447	0.62
Pd/AC-SA	300	0.49
Pd/AC-TA	273	0.47

Table S5 CO₂ capture ¹³C NMR species in (3-methylaminopropyl)trimethoxysilane (SA) using different solvents.

Solvent	Captured CO ₂ species (mM)			
	HCO ₃ ⁻	CO ₃ ²⁻	Ethyl-CO ₃ ²⁻	CO ₂
Water	25.96	2.64	—	0.88
Ethanol	4.10	0.71	2.2	—

CO₂ capture conditions: 10 mL ethanol/water solvent, 0.3 mL SA, 2.0 MPa CO₂, 25 °C, 60 min. 1,4-dioxane was used as an internal standard.

Table S6 Adsorption of HCOOH in water using the prepared catalysts.

Catalyst	FA adsorption mmol/g
Pd/AC	0
Pd/AC-PA	232
Pd/AC-SA	177
Pd/AC-TA	138

Adsorption conditions: 10 mg of catalyst and 10 ml of HCOOH (0.25 M) with string for 1 h at 298 K. The amine steric hindrance is defined as the reduced moles of HCOOH absorbed by per mole of amine.

References

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