Supporting information for

Remarkable difference in CO₂ hydrogenation to methanol on Pd nanoparticles supported inside and outside of carbon nanotubes

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Catalyst preparation

The CNTs (inner diameter, 5-10 nm; outer diameter, 10-20 nm) were purchased from Chengdu Organic Chemicals. 10 g raw CNTs were refluxed in 500 mL HNO₃ (68 wt%) for 12 h at 140 °C in an oil bath to remove amorphous carbon and the residual catalyst. The suspension was then washed and filtered with deionized water and dried at 110 °C for 12 h. (Some influencing factors were explored; see the supporting information.)

For the preparation of the Pd/CNTs-in catalyst, 1 g CNTs were immersed in 25 mL of acetone solution of stoichiometric PdCl₂. The acetone solution was drawn into the channels of the CNTs by capillary forces aided by ultrasonic treatment for 3 h. The mixture was stirred at room temperature for several days until the acetone had completely volatilized and was then dried at 60 °C for 24 h.

Although metal selectively deposited inside of the CNTs has been reported in many cases, there are still a lot of unclear factors affecting filling efficiency of metal inside of CNTs. The optimal conditions we have explored are as follow, CNTs: Purity 99.9%, Outer Diameter 10-20 nm, Inner Diameter 5-10 nm, Length 10-30 μ m; Pretreatment: HNO₃(68 wt%) at 140 °C for 12 h, 50 mL/g_{-CNTs}; The amount of Pd loading is <5 wt%, the precursor of Pd salt is PdCl₂; The amount of solvent is 30 mL/g_{-CNTs}, the solvent is acetone; The conditions of ultrasonic are 100 W, 45 kHz, 3 h; The conditions of drying are first making solvent evaporated at room temperature till

the mixture changes to slurry, then drying at 40-60 °C for 24-36 h. Owing to the large number of samples prepared, and to the fact that conventional 2D-TEM with sample tilting are time-consuming methods, we measured the filling efficiency from conventional 2D-TEM micrographs. We consider that the filling efficiency(FE) was calculated as follows:

$FE = \frac{number of particles inside}{total number of particles}$

The filling efficiency was calculated for more than 100 particles deposited in 10 different CNTs. Although this method is not very accurate, it is convenient for comparison purposes.

Some conditions we have explored are as follow:

1. Pretreatment of CNTs

The pretreatment of CNTs is essential to open the end of CNTs and improve the CNTs surface properties such as surface wettability, surface energy and surface charge. Figure S1a is TEM of the pristine CNTs; Figure S1c is TEM of the CNTs treated by HNO₃(68 wt%) at 140 °C for 12 h; Figure S1h is TEM of the Pd-CNTs-in with CNTs treated by HNO₃(68 wt%) at 140 °C for 6 h; Without pretreatment, FE of Pd nanoparticles inside of CNTs is 10%(see Figure S1b).

2. The amount of Pd loading

FE of Pd nanoparticles inside of CNTs is 90% when the amount of Pd loading is 2.5%(see Figure S1d); FE of Pd nanoparticles inside of CNTs is 80% when the amount of Pd loading is 5%(see Figure S1e). More Pd loading, less Pd filling efficiency.

3. CNTs inner diameter

FE of Pd nanoparticles inside of CNTs is 71% when the inner diameter of CNTs is 3-5 nm(see Figure S1f); FE of Pd nanoparticles inside of CNTs is 80% when the inner diameter of CNTs is 20-50 nm (see Figure S1g).

4. The proportion of solvent to CNTs

FE of Pd nanoparticles inside of CNTs is 36% when the proportion of solvent to CNTs is $10 \text{ mL/g}_{-\text{CNTs}}$ (see Figure S1i); FE of Pd nanoparticles inside of CNTs is 70%

when the proportion of solvent to CNTs is 100 mL/g_{-CNTs} (see Figure S1j).

5. The conditions of ultrasonic

FE of Pd nanoparticles inside of CNTs is 77% when the conditions of ultrasonic are 100 W, 100 kHz, 3 h(see Figure S1k); FE of Pd nanoparticles inside of CNTs is 77% when the conditions of ultrasonic are 100 W, 28 kHz, 3 h(see Figure S1l).

Other important factors, such as the choise of solvent and precursor Pd salt, have been researched[1-3], we accept the results.







Figure S1. TEM of CNTs(a, c) and Pd/CNTs-in(b, d-l). (a) pristine CNTs; (b) CNTs without pretreatment; (c) CNTs treated with HNO₃(68 wt%) at 140 °C for 12 h; (d) 2.5% Pd loading; (e) 5% Pd loading; (f) inner diameter of CNTs is 3-5 nm; (g) inner diameter of CNTs is 20-50 nm; (i) the proportion of solvent to CNTs is 10 mL/g_{-CNTs}; (j) the proportion of solvent to CNTs is 100 mL/g_{-CNTs}; (k) the frequency of ultrasonic is 100 kHz; (l) the frequency of ultrasonic is 28 kHz.

For the preparation of the Pd/CNTs-out catalyst, a mixture of 1 g CNTs and 25 mL of dimethylbenzene was subjected to ultrasonic treatment for 3 h to ensure that the channels of the CNTs had been filled with dimethybenzene. A solution of stoichiometric PdCl₂ and 3 g (NH₄)₂CO₃ dissolved in 35 mL NH₃·H₂O was added into

the CNTs and dimethybenzene mixture. The mixture was evaporated within 0.5 h by heating to 110 °C for 24 h.

The Pd/SiO₂ and Pd/AC catalysts were prepared by impregnation. These two catalysts had the same metal composition as the Pd/CNTs. SiO₂ with a surface area of 225 m²/g was obtained from Alfa Aesar Company. AC was purchased from Sinopharm Chemical Reagant Co., Ltd.

The Pd loading of the four Pd catalysts was 5 wt%. All samples of catalyst precursor were calcined at 300 °C for 4 h and then pressed, crushed, and sieved to the size of 40-80 mesh for the activity evaluation.

Catalyst evaluation

The activity tests of the catalysts for CO₂ hydrogenation to methanol were carried out in a fixed-bed continuous-flow reactor-gas chromatography (GC) combination system. Before the reaction, the catalyst (0.5 g; 40-80 mesh) was prereduced in situ in a H_2 stream at 0.2 MPa and 1800 mL h⁻¹ g⁻¹. The reduction temperature was programmed to increase from room temperature to 250 °C and remain there for 6 h, and then decline to the temperature desired for the catalyst test. The reaction was conducted at a stationary state under reaction conditions of 2.0 MPa, 180 °C to 260 °C, $V(H_2)/V(CO_2)/V(Ar) = 72/24/4$, and GHSV = 1200 mL h⁻¹ g⁻¹. The exit gas from the reactor was maintained at 130 °C and immediately transported to the sampling valve of the GC (Agilent GC-6890), which was equipped with dual thermal conductivity and flame ionization detectors and dual columns filled with carbon molecular sieve (TDX-01) and capillary column (PEG-20M). The former column (3.0 m long) was used for the analysis of Ar (as an internal standard), CO, and CO₂, and the latter column (30 m \times 0.32 mm \times 10 μ m) for hydrocarbons, alcohols, and other Ccontaining hydrogenation products. CO₂ conversion (denoted as X(CO₂)) and the carbon-based selectivity for the carbon-containing products, including methane, methanol, and dimethyl ether, were calculated with an internal normalization method. All data were collected 12 h after the reaction started (unless otherwise specified).

Calculation of X(CO₂), S(CO), S(MeOH), STY(MeOH), and TOF:

$$X(CO_2) = \frac{f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{MeOH}A_{MeOH} + 2f_{DME}A_{DME})}{f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{MeOH}A_{MeOH} + 2f_{DME}A_{DME}) + f_{CO_2}A_{CO_2}}$$

$$S(CO) = \frac{f_{CO}A_{CO}}{f_{CO}A_{CO} + i(f_{CH_4}A_{CH_4} + f_{MeOH}A_{MeOH} + 2f_{DME}A_{DME})}$$

 $i = \frac{f_{CH_4-TCD}A_{CH_4-TCD}}{f_{CH_4-FID}A_{CH_4-FID}}$

$$S(MeOH) = \frac{f_{MeOH} A_{MeOH}}{f_{CH_4} A_{CH_4} + f_{MeOH} A_{MeOH} + 2f_{DME} A_{DME}}$$

$$STY(MeOH) = \frac{\frac{GHSV}{22.4} \times V\%(CO_2) \times X(CO_2) \times (1 - S_{CO}) \times S_{MeOH}}{\frac{Wt_{Pd}\%}{M_{Pd}}}$$

$$TOF = \frac{\underline{STY(MeOH)}}{D}$$

Catalyst characterization

1. Transmission Electron Microscopy (TEM)

The TEM images were obtained using a JEOL 2010 microscope with a highresolution pole piece. The samples were prepared by placing a drop of nanoparticle ethanol suspension onto a carbon-coated copper grid and allowing the solvent to evaporate.

2. Brunauer-Emmett-Teller (BET)

The specific surface area was determined by N_2 adsorption using a Micromeritics ASAP 2020 system.

3. CO Chemiadsorption Test

The CO chemiadsorption tests were carried on quantachrome autosorb automated gas sorption system. The samples were prereduced in H_2 at 250 °C for 2 h with a gas flow rate of 30 mL/min.

4. X-ray Photoelectron Spectroscopy (XPS)

XPS was performed using a Kratos Ltd XSAM800 with Al Kα radiation (15 kV; 25 W; hv = 1486.6 eV) under ultrahigh vacuum (5 × 10⁻⁷ Pa), calibrated internally by the carbon deposit C(1s) (E_b = 284.7 eV). The samples were first pressed to disk for XPS test, then reduced in H₂ at 250 °C for 2 h with gas flow rate of 30 mL/min before XPS test and then reacted in V(H₂)/V(CO₂) = 3/1 at 250 °C for 2 h then continual to be tested.

5. Powder X-Ray Diffraction (XRD)

The XRD studies were performed on a Philips PW1050/81 diffractometer operating in Bragg-Brentano focusing geometry and using CuK α radiation ($\lambda = 1.5418$ Å) from a generator operating at 40 kV and 30 mA.

6. High-Resolution Transmission Electron Microscopy (HRTEM)

HRTEM images were obtained with an F30 microscope. The samples were prepared by placing a drop of nanoparticle ethanol suspension onto a lacey support film and allowing the solvent to evaporate.

7. Temperature Programmed Desorption (TPD)

The tests of H₂-TPD of the catalysts were conducted with an adsorption/desorption system. A 200 mg sample of the prereduced catalyst was treated in situ in a H₂ stream of 99.999% purity (1800 mL h⁻¹) at 250 °C for 2 h, flushed by an Ar stream of 99.999% purity (1800 mL h⁻¹) at 250 °C for 60 min to clean its surface, and then cooled to 50 °C; it was then returned to the H₂ stream of 99.999% purity for hydrogen adsorption for 60 min and then to at room temperature for 2 h. The sample was then flushed by the Ar stream at room temperature until a stable baseline in the GC appeared. TPD measurements were then conducted from 25 °C to 600 °C. The temperature increase was 10 °C/min. Changes in the hydrogen signal were monitored by an online GC (Agilent 6890A) with a TCD detector.

The evaluation results of catalyst

Catalyst	S _{BET} (m ² /g)	Pore volume	Pore size	Pd dispersion	X(CO ₂) (%)	S(MeOH) (%)	STY(MeOH) (mmol/(mol	TOF(h ⁻¹)
		(m²/g)	(nm)	(%)			h))	
Pd/CNTs-in	264	0.92	13.9	10.7	0.77	48.8	34.8	0.33
Pd/CNTs-out	316	0.86	10.8	9.9	0.61	13.4	9.3	0.09
Pd/SiO ₂	269	0.59	8.9	11.2	0.33	31.6	7.2	0.06
Pd/AC	663	0.71	4.3	16.8	0.60	34.6	18.4	0.11

Table S1. The physical properties and Pd dispersion of supported Pd catalysts, and reactivity of CO_2 hydrogenation to methanol on the supported Pd catalysts.

Reaction conditions: 2.0 MPa, 1200 h^{-1} , 250 °C.

Table	S2.	The	catalytic	performance	of	Pd/CNTs-in	and	Pd/CNTs-out	catalysts	for	CO ₂
hydro	gena	tion	to methan	iol.							

Catalyst	Т	X(CO ₂)	S(CO)	S(Hydr.)	S(CH ₄)*	S(DME)	S(MeOH) *	STY(MeOH)
	(°C)	(%)	(%)	(%)	(%)	*	(%)	(mmol/(mol h))
						(%)		
	180	0.11	75	25	18.4	0	81.6	6.0
	200	0.15	82	18	25.7	0	74.3	5.6
Pd/CNTs-out	220	0.23	79	21	61.5	0	38.5	5.3
	240	0.46	64	36	81.3	0.8	17.9	8.1
	260	0.84	54	56	89.0	0.3	10.7	11.2
	180	0.20	54	46	13.0	1.4	85.6	21.5
	200	0.31	55	45	20.3	1.9	77.8	29.4
Pd/CNTs-in	220	0.45	60	40	32.9	1.5	65.6	32.1
	240	0.63	65	35	42.8	2.4	54.8	33.0
	260	0.97	67	33	57.7	2.9	39.4	34.9

 $p = 2.0 \text{ MPa}, \text{ GHSV} = 1200 \text{ h}^{-1}.$

*The S of hydrogenation products (CH₄, DME, MeOH) is calculated free of CO.

The XRD of reduced Pd/CNTs catalysts



Figure S2. XRD patterns of reduced Pd/CNTs catalysts.

XRD of the reduced Pd/CNTs-in and Pd/CNTs-out catalysts shows that the two reduced catalysts are alike in their XRD features related with the Pd components. The Pd components existed mainly in the forms of metal Pd particle with the corresponding XRD features appearing at $2\theta = 40.1^{\circ}/46.7^{\circ}/68.1^{\circ}$, which represents the diffraction of the (111)/(200)/(220) plane of metal Pd.

The HRTEM of reduced Pd/CNTs catalysts

A high-resolution image of the two catalysts shows that the lattice fringes are clearly aligned in parallel. The lattice space averaged 0.22 nm, which matches the value of the d-spacing of metal Pd (111) estimated from the XRD results.



Figure S3. HRTEM images of catalysts: (a), (b) Reduced Pd/CNTs-in catalyst. (c), (d) Reduced Pd/CNTs-out catalyst.



Proposed mechanism

Scheme S1. Proposed mechanism for the methanol synthesis from CO₂ hydrogenation on

Pd/CNTs catalysts

 Pd^0 activates H_2 and $Pd^{\delta+}$ activates CO_2 . CO_2 and H_2 first form HCOO*, and HCOO*

is further hydrogenated to HCOOH* and then to H_2COOH^* , which itself forms H_2CO^* by splitting off a OH group. H_3CO^* is the final intermediate for the formation of CH₃OH* and subsequently CH₃OH.

The TPD of reduced Pd/CNTs catalysts



Figure S4. TPD profiles of H₂ adsorption on the Pd/CNTs catalysts.

The lower temperature peaks were a result of the desorption of molecularly adsorbed hydrogen, and the higher temperature peaks (i.e., the peak at 390-400 °C) were attributed to the desorption of dissociatively chemisorbed hydrogen, which is closely associated with the reaction activity of CO_2 hydrogenation. Much greater intensity of the higher temperature desorption peak was observed for the Pd/CNTs-in catalyst than that for the Pd/CNTs-out catalyst.

Reference

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