

Impact of Catalyst Support on Water-Assisted CO Oxidation over PdO/MO₂ (M = Sn, Ti, Si) Catalysts: Experimental and Theoretical Investigation

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S1 Catalyst preparation and characterization

1. Preparation of Catalyst Supports:

(1) TiO₂ Preparation:

Commercially purchased rutile-type nano titanium dioxide was calcined at 550 °C for 4 h, ground after removal, and used as the support.

(2) SiO₂ Preparation:

A solution was prepared by dissolving 14.211 g of sodium silicate in 100 mL of water. Nitric acid was slowly added to the sodium silicate solution at room temperature until precipitation suddenly increased. After 1 h of stirring, the precipitate was filtered, washed until total dissolved solids (TDS) < 20 mg/L, and dried at 110 °C for 6 h. Finally, it was calcined at 800 °C for 4 h harvesting the resulted support.

(3) SnO₂ Preparation:

SnO₂ prepared by chemical vapor deposition (CVD) method was washed with deionized water, filtered until TDS < 20 mg/L, and dried at 110 °C for later use.

2. Preparation of PdO Catalyst:

PdO catalysts (PdO/SiO₂, PdO/TiO₂, and PdO/SnO₂) with a Pd loading of 2 wt% were prepared. 0.1143 g of Pd(NH₃)₄ (NO₃)₂ (Macklin, AR) was dissolved in 5 mL of deionized water, added to 1.9540 g of SiO₂ (TiO₂, SnO₂) support, and stirred for 6 hours at room temperature. The mixture was then evaporated at 60 °C, dried at 110 °C, and calcined at 400 °C with a heating rate of 2 °C min⁻¹ for 4 h. After cooling, the catalysts were ground and labeled accordingly.

3 Reaction rate calculation

Here are the formulas for calculating reaction rate (R_w) and turnover frequency (TOF) as presented in this study:

Reaction rate (R_w) formula:

$$R_w = \frac{RF \times V\% \times X_{CO}}{22.4 \times 60 \times m_{Cat.}} \quad (\text{mmol g}^{-1} \text{ s}^{-1}) \quad (1)$$

where: RF is the reaction gas flow rate (30 mL min⁻¹).

V% the volume fraction of CO in the reaction gas (1%).

X_{CO}: the CO conversion at 100 °C.

m_{Cat}: the catalyst mass (0.1 g).

Turnover frequency (TOF) formulas:

$$R_{CO,Pd} = \frac{RF \times V\% \times X_{CO}}{22.4 \times 60 \times m_{Cat.} \times w_{Pd}} \text{ (mmol g}_{Pd}^{-1} \text{ s}^{-1}) \quad (2)$$

$$TOF = \frac{R_{CO,Pd} \times M_{Pd}}{D_{Pd}} \text{ (s}^{-1}) \quad (3)$$

where: w_{Pd}: the loading of Pd.

M_{Pd}: the relative atomic mass of Pd.

D_{Pd}: the dispersion of surface Pd on the catalyst, typically determined using a 34.5% dispersed 0.5% Pt/Al₂O₃ sample as a standard.

S2 Characterization

Powder XRD patterns were recorded on a Bruker AXS D8 Focus diffractometer operating at 40 kV and 40 mA with Cu K α radiation. Scans were conducted over a 2 θ range from 10 to 90° with a step size of 2°/min. The mean crystallite sizes of the samples were calculated using the Scherrer equation based on the strongest peaks of PdO with the (111) hkl planes. The specific surface areas of the samples were determined by nitrogen adsorption-desorption at 77 K using an ST-08B instrument. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed using an ICP-715ES (Varian) to determine the bulk elemental compositions of the samples. H₂-TPR (Hydrogen Temperature-Programmed Reduction) experiments were performed on a FINESORB 3010C instrument in a 30 mL min⁻¹ flow of 10% H₂/Ar gas mixture. The temperature was ramped from room temperature to 850 °C at a rate of 10 °C/min. Typically, 50 mg of catalyst was used for each test. A thermal conductivity detector (TCD) monitored H₂ consumption, and CuO (99.99%) was used as a calibration standard for quantifying H₂ consumption. XPS (X-ray Photoelectron Spectroscopy) measurements were carried out on a PerkinElmer PHI 1600 system using a single Mg

K α X-ray source operating at 300 W and 15 kV. Spectra were acquired at ambient temperature under ultrahigh vacuum conditions. Binding energies were calibrated using the C 1s peak of graphite at 284.5 eV as a reference. Carbon monoxide temperature-programmed desorption (CO-TPD) was conducted with a Micromeritics AutoChem 2920 apparatus to determine Pd dispersion and active Pd surface area on the reduced catalysts. Typically, 50 mg of catalyst was used for this test. The sample was reduced in pure hydrogen at 200 °C for 1 h, then cooled to 50 °C and maintained at this temperature for 1 h under a flowing 10% CO/Ar mixture. The sample was then purged with ultra-high purity Ar flow for 30 minutes. Subsequently, H₂ temperature-programmed desorption was performed from 50 °C to 500 °C in a 30 mL min⁻¹ ultra-high purity Ar flow to measure CO desorption. A 0.5% Pt/Al₂O₃ standard with a metal dispersion of 34.5%, provided by Micromeritics, was used for calibration. Metallic Pd dispersion and surface area calculations were based on the stoichiometry of one hydrogen atom per palladium surface atom. Additional CO-TPD experiments were conducted using a Micromeritics ASAP2920 instrument to evaluate the CO adsorption properties of the catalysts. The experimental procedure was similar to the previous CO-TPD, except the catalysts were not reduced before CO adsorption. H₂O temperature-programmed desorption (H₂O-TPD) was performed on a DAS-7000 instrument to assess the effect of supports on the H₂O adsorption behavior of the catalysts. Typically, 50 mg of catalyst was placed in a quartz reactor and pretreated in a 99.99% He flow at 300 °C for 2 hours, then cooled to 50 °C under He protection. The pretreated catalyst was saturated in a 30 mL min⁻¹ He flow passing through a water bubbler controlled at 30 °C for 1 hour. The sample was then purged with a 30 mL min⁻¹ He flow for 60 minutes to remove any physically adsorbed H₂O at 50 °C. H₂O-TPD was conducted from 50 °C to 300 °C with a heating rate of 10 °C min⁻¹ in a 30 mL min⁻¹ 99.99% He flow.

Activity evaluation

The catalysts were evaluated for CO oxidation using a U-shaped quartz tube reactor with an inner diameter of 6 mm. The feed gas consisted of 1% CO, 22% O₂, and

high-purity N₂ as the balance, with a total flow rate of 30 mL min⁻¹. Typically, 25 mg of catalyst was used for activity evaluation, with a weight hourly space velocity (WHSV) of 72,000 mL·g⁻¹·h⁻¹. A K-type thermocouple was positioned at the top of the catalyst bed, with the thermocouple tip in direct contact with the catalyst to ensure accurate temperature measurement. To determine the light-off behavior of the catalysts, data were collected while incrementally increasing the temperature. The reactants and products were analyzed online using a GC9310 gas chromatograph equipped with a TDX-01 column and a thermal conductivity detector (TCD). Prior to analysis, the reaction at each temperature was stabilized for at least 30 minutes to obtain steady-state reaction data.

CO conversion (*X*_{CO}) is calculated by the formula:

$$XCO = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\%$$

where [CO]_{in} and [CO]_{out} are the concentrations of CO (vol %) at the reactor inlet and outlet, respectively.

S3. Supplementary Table

Table S1 Calculations and experimental values of lattice parameters for PdO, TiO₂, and SnO₂, along with corresponding crystal plane parameters.

	Space group	lattice parameters	
		Calculated value (Å)	Experimental Value (Å)
PdO	P4 ₂ /mmc	a = b = 3.058, c = 5.420	a = b = 3.030, c = 5.330
TiO ₂	P4 ₂ /mnm	a = b = 4.570, c = 2.990	a = b = 4.594, c = 2.959
SnO ₂	P4 ₂ /mnm	a = b = 4.724, c = 3.205	a = b = 4.737, c = 3.186
PdO (101) R90	—	a = 3.058, b = 6.223	—
TiO ₂ (110)	—	a = 2.990, b = 6.462	—
SiO ₂ (110)	—	a = 3.220, b = 6.740	—

Table S2 Surface area and grain size of catalysts

Samples	Surface area (m ² /g) ^[a]	Mean crystallite size of PdO (nm) ^[b]
PdO/SnO ₂	30	17
PdO/TiO ₂	25	13
PdO/SiO ₂	25	24
SnO ₂	34	-
TiO ₂	27	-
SiO ₂	26	-

^[a] Baesd on BET method

^[b] Baesd on Scherrer Equation

Table S3 Catalyst surface reactivity in CO oxidation

Samples	E_a^a (kJ mol ⁻¹)	R_{w100}^b (10 ⁻⁴ mmol s ⁻¹ g ⁻¹ cat)	LnA	TOF ^c (10 ⁻² s ⁻¹)
PdO/SnO ₂	61.3	5.41	9.42	9.82
PdO/SnO ₂ -H ₂ O	52.5	9.66	12.83	17.53
PdO/TiO ₂	21.9	28.87	3.91	15.57
PdO/TiO ₂ -H ₂ O	30.2	10.49	0.22	5.66
PdO/SiO ₂	145.9	~ 0	31.32	~ 0
PdO/SiO ₂ -H ₂ O	198.5	~ 0	44.27	~ 0

^a E_a : apparent activation energy.

^b R_{w100} , R_{w80} : the differential reaction rates normalized by weight of catalysts at 100 °C and listed as formula in **S1 section**

^c TOF : listed as formula in **S1 section**.

Table S4 Quantitative results of XPS, ICP, and dispersion testing.

Catalyst	O _{1s} Binding [^a]		$\frac{O_{ads}}{O_{ads} + O_{latt}}$ [^a]	Pd contents by ICP (wt%) [^b]	Surface Pd contents by XPS (wt%) [^a]	Pd dispersion (%)
	Energy(eV)					
	O _{ads}	O _{latt}				
PdO/SnO ₂	531.8	530.5	31.96%	1.69	2.31	3.47
PdO/TiO ₂	531.5	529.3	47.70%	1.64	4.76	12.03
PdO/SiO ₂	532.8	531.9	31.96%	1.75	1.08	2.00

[^a] Baesd on XPS results

[^b] Baesd on ICP results

Table S5 Surface H₂O-TPD and CO-TPD Quantitative Analysis

	H ₂ O desorption amount (a.u.)		CO desorption amount (a.u.)
	50 ~ 170 °C	171 ~ 360 °C	
PdO/SnO ₂	1308	1759	1937
PdO/TiO ₂	2060	3676	2013
PdO/SiO ₂	1121	—	785

Table S6 Adsorption of OH and H₂O on catalyst and carrier surfaces, and dissociation of H₂O

Samples	OH Adsorption capacity (eV)	H ₂ O Adsorption capacity (eV)	H ₂ O Activation energy (eV)	H ₂ O Dissociation activation barrier (eV)
PdO	3.33	1.01	0.26	—
PdO/TiO ₂	3.34	1.16	0.35	0.48
PdO/SnO ₂	2.89	1.12	0.31	0.40

Table S7 Surface CO adsorption structure parameters and Bader charge variation on catalysts.

Catalysts surface	Adsorption site	Adsorption energy (eV)	d (Å)				Δq (e)		
			C–O	C–Pd _{cus}	C–O _{cus}	CO	H ₂ O	Pd _{cus}	O _{cus}
PdO	Pd-top	1.66	1.150	1.885	—	-0.04	—	-0.06	—
PdO-H ₂ O	Pd-top	1.59	1.154 (2.854)	1.879	—	0	-0.12	-0.08	—
PdO-H-OH	Pd-top	1.63	1.149	1.894	—	-0.06	-0.19	-0.09	—
PdO/TiO ₂	Pd-O bridging	2.08	1.227	1.927	1.308	-0.48	—	+0.18	+0.29
PdO/TiO ₂ -H ₂ O	Pd-O bridging	2.34	1.241 (1.795)	1.929	1.303	-0.45	-0.13	+0.20	+0.34
PdO/TiO ₂ -H-OH	Pd-O bridging	2.05	1.224	1.930	1.313	-0.50	-0.22	+0.19	+0.31
PdO/SnO ₂	Pd-O bridging	2.13	1.228	1.917	1.312	-0.50	—	+0.19	+0.31
PdO/SnO ₂ -H ₂ O	Pd-O bridging	2.39	1.246 (1.807)	1.916	1.301	-0.44	-0.15	+0.20	+0.35
PdO/SnO ₂ -H-OH	Pd-O bridging	2.09	1.226	1.920	1.317	-0.47	-0.20	+0.18	+0.30

Note: The bond length in the parentheses is the distance from O in the adsorption structure of CO to the closer H in the H₂O molecule.

Table S8 The reaction enthalpy (ΔH) and activation energy barriers for the surface oxygen extraction process on PdO/TiO₂ and PdO/SnO₂ catalysts during CO oxidation.

Small molecules	PdO/TiO ₂		PdO/SnO ₂	
	Energy barrier (eV)	ΔH (eV)	Energy barrier (eV)	ΔH (eV)
CO	0.83	0.30	1.33	1.15
H ₂ O-CO	1.25	1.18	1.48	1.28
H-OH-CO	1.37	0.97	1.25	0.91

Table S9 A literature summary of non-noble and noble metal catalysts in CO oxidation

Entry	Cat.	S _{BET} (m ² /g)	Reaction condition		Temp. for conversion. (°C)			Ref
			P	GHSV	T10	T50	T90	
			(bar)	(mL/g _{cat} h)				
Non-noble metal catalysts								
1	Mn5Co1O _x -800	10	1	-	300	-	-	1
2	Mn5Co1O _x -600	21	1	-	175	250	315	1
3	Mn5Co1O _x -400	60	1	-	140	190	215	1
4	Co ₃ O ₄ /SiO ₂ (particle)	11	1	120 000	100	140	170	2
5	Co ₃ O ₄ /SiO ₂ (cuber)	-	1	120 000	180	225	-	2
6	Co ₃ O ₄ /SiO ₂ (sheets)	14	1	120 000	115	165	-	2
7	Mn-SBA-15	403	1	6000	92	135	158	3
8	1Co2Mn-SBA-15	349	1	6000	170	220	250	3
9	Co ₃ O ₄	-	1	6000	80	130	150	4
10	CeO ₂	-	1	6000	190	250	300	4
11	MnO	18	1	-	245	325	345	5
12	4%Co-MnO	-	1	-	125	135	145	5
Noble metal catalysts								
13	Ir/Al ₂ O ₃	-	1	40000	180	-	-	6
14	Ir/Fe ₂ O ₃	-	1	40000	90	-	-	6
15	Pt/CeO ₂	-	1	39960	275	325	375	7
16	Pd/CeO ₂	-	1	39960	100	275	325	7
17	Rh/CeO ₂	-	1	39960	75	120	140	7
18	0.6% Pt/Fe-C4	66.1	1	18750	-	-	30	8
19	3PdCe-600	-	1	240000	45	90	130	9
20	3PdCe-700	-	1	240000	25	75	110	9
21	Pd/TiO ₂	25	1	72000	60	100	110	This work

S4. References

1. O. A. Bulavchenko, T. N. Afonassenko, S. S. Sigaeva, A. V. Ivanchikova, A. A. Saraev, E. Y. Gerasimov, V. V. Kaichev, S. V. Tsybulya, *Top. Catal.*, 2020, **63**, 75-85.
2. M. Khasu, T. Nyathi, D. J. Morgan, G. J. Hutchings, M. Claeys, N. Fischer, *Catal. Sci. Technol.*, 2017, **7**, 4806-4817.
3. S. Todorova, J. L. Blin, A. Naydenov, B. Lebeau, H. Kolev, P. Gaudin, A. Dotzeva, R. Velinova, D. Filkova, I. Ivanova, L. Vidal, L. Michelin, L. Josien, K. Tenchev, *Catal., Today*, 2020, **357**, 602-612.
4. W. Huan, J. Li, J. Ji, M. Xing, *Chin. J. Catal.*, 2019, **40**, 656-663.
5. H. Yu, L. Yi, F. Jiang, X. Wang, K. Xie, *Catal. Sci. & Technol.*, 2023, **13**, 750-757.
6. W. Zhang, A. Wang, L. Li, X. Wang, T. Zhang, *Catal. Today.*, 2008, **131**, 457-463.
7. B. Han, T. Li, J. Zhang, C. Zeng, H. Matsumoto, Y. Su, B. Qiao, T. Zhang, *Chem. Commun.*, 2020, **56**, 4870-4873.
8. B. Qiao, A. Wang, L. Li, Q. Lin, H. Wei, J. Liu, T. Zhang, *ACS Catal.*, 2014, **4**, 2113-2117.
9. R. V. Gulyaev, E. M. Slavinskaya, S. A. Novopashin, D. V. Smovzh, A. V. Zaikovskii, D. Y. Osadchii, O. A. Bulavchenko, S. V. Korenev, A. I. Boronin, *Appl. Catal. B: Environ.*, 2014, **147**, 132-143.