Supporting Information

Mesostructured Pd/Mn₃O₄ Catalyst for Efficient Low-temperature CO Oxidation Especially Under Moisture Condition

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Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus powder diffractometer with graphite mono chromatized Cu K α radiation (λ =0.15405 nm) operated at 40 kV. Nitrogen adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 M analyzer at liquid nitrogen temperature (77 K). Prior to the measurements, the samples were degassed at 523K in vacuum for 6h. The specific surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Transmission electron microscopy (TEM) observations were performed on a field emission JEM-2100 (JEOL) electron microscope operated at 300kV equipped with a Gatan-666 electron energy loss spectrometer and energy dispersive X-ray spectrometer. XPS (X-ray photoelectron spectroscopy) signals were collected on a VG Micro MK II instrument using monochromatic Al Ka X-ray at 1486.6 eV operated at 200 W. All the elemental binding energies were referenced to the C (1s) line situated at 284.6 eV. H₂ temperature-programmed reduction (H₂-TPR) analysis was performed by using a Micromeritics ChemiSorb 2750 apparatus. For each analysis, accurate amounts of calcined sample (50 mg) were purged in a flow of pure argon at 200 °C for 30 min to remove traces water (heating rate 10 °C/min). After cooling to room temperature, H₂-TPR experiments were performed using a 10 vol% H₂ /Ar mixture at a flow rate of 25 ml/min. The sample was heated from ambient temperature to 700 °C at heating rate of 10 °C/min and H₂ consumption was detected by a thermal conductivity detector (TCD).



Figure S1. The HRTEM images of Pd/Mn₃O₄ catalysts with different Pd loading contents: 1.1 wt% (A), 2.7 wt% (B), 3.2 wt%

(C).

Sample	BET surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
Mn ₃ O ₄ support	73	4.3	0.34
1.1 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst	84	3.3	0.33
2.7 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst	130	2.6	0.33
3.2 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst	97	2.0	0.24

Table S1. Some physicochemical properties of supported Pd catalysts

Table S2. XPS binding energies Mn 2p, O1s and Pd 3d as well as the surface atomic ratios determined by quantitative XPS analysis for Pd/Mn_3O_4

Phase	Binding Energy (eV)	Mn ₃ O ₄ catalyst (%)	1.1 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst (%)	2.7 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst (%)	3.2 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst (%)
Mn ²⁺	640.2	0.3	1.5	0.2	0.6
Mn ³⁺	641.5	75.3	72.6	77.2	79.9
Mn ⁴⁺	643.5	24.4	25.9	22.6	19.5
O latt	530.4	76.9	68.0	57.5	57.2
O ads	531.5 532.3	23.1	32.0	42.5	42.8
Pd ⁰	335.8 341.1	-	93.5	90.1	85.4
Pd ²⁺	337.9 343.1	-	6.5	9.9	14.6

Table S3 The catalytic performance of Pd/Mn₃O₄ catalysts

Sample	T ₅₀ (°C)	T ₁₀₀ (°C)
Mn ₃ O ₄ support	-	-
1.1 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst	18	35
2.7 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst	5	25
3.2 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst	8	25
2.7 wt% Pd loaded Pd/Mn ₃ O ₄ catalyst reaction under moisture condition	0	22



Figure S2. The effect of space rate on the catalytic activity of 2.7 wt% loaded Pd catalyst. Feed gas: 1.0 vol% CO, 20.0 vol% O₂, 4.0 vol% H₂O balanced with N₂



Figure S3. The effect of oxygen concentration on the catalytic activity of 2.7 wt% loaded Pd catalyst.

Catalyst: 200 mg, space velocity: 15000 ml h⁻¹ g⁻¹.

Feed gas: 1.0 vol% CO, 4.0 vol% H₂O, desired O_2 banlance with N_2



Figure S4. The XRD patterns of 2.7 wt% Pd loaded catalyst (a), after CO oxidation under dry condition (b) and moisture condition (c).



Figure S5. The TEM images of 2.7 wt% Pd loaded catalyst after CO oxidation under dry condition (A) and moisture condition (B).



Figure S6. The N₂ adsorption-desorption isotherms of 2.7 wt% Pd loaded catalyst after reaction under dry condition (A) and moisture condition (B).

Table S4. The pore structural parameters of 2.7 wt% Pd loaded catalyst before and after reaction under different conditions

Parameters	Before Reaction	After reaction under dry condition	After reaction under moisture condition
Pd loadings (wt %)	2.7	2.7	2.7
BET surface area (m ² /g)	130	138	144
Average pore diameter (nm)	2.6	2.2	2.0
Pore volume (cm ³ /g)	0.33	0.31	0.31