

Supplementary Information

Structured Mesh-Type Pt/Mn/ γ -Al₂O₃/Al Catalyst Enhanced the CO Oxidation at Room Temperature by In Situ Generation of Hydroxyl: Behavior and Mechanism

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Supplementary Note S1. Preparation of flexible mesh-type γ -Al₂O₃/Al carrier

The aluminum mesh (1060-type, $\geq 99.6\%$, $240 \times 260 \text{ mm}^2$) was immersed in a 10 wt.% sodium hydroxide solution for 4 min, followed by 2 min immersion in a 10 wt.% nitric acid solution. Subsequently, the mesh was thoroughly rinsed with deionized water to remove any residual chemicals. After drying, the mesh was anodized in a 104 L 0.4 M oxalic acid solution for 12 h at 30 °C with a current density of $25 \text{ A}\cdot\text{m}^{-2}$, then rinsed with deionized water and air dried at room temperature. The obtained mesh (anodic aluminum oxide, AAO) was calcined at 350 °C for 1 h to remove residual oxalic acid on the surface. After the calcination, the AAO was immersed in deionized water at 80 °C for 1 h, and then dried to obtain anodic boehmite (denoted as AlOOH). The AlOOH was calcined in a muffle furnace at 500 °C for 4 h, ultimately yielding the monolithic γ -Al₂O₃/Al carrier.

Supplementary Note S2. Preparation of Mn_x/ γ -Al₂O₃/Al catalysts

The molar ratio of manganese acetate ($\text{Mn}(\text{Ac})_2\cdot 4\text{H}_2\text{O}$) to urea ($\text{CH}_4\text{N}_2\text{O}$) was 1:10. Deionized water was added to prepare the impregnation solution at various concentrations. Three pieces of γ -Al₂O₃/Al carriers ($60 \times 80 \text{ mm}^2$) were then immersed in the mixed solution, which was heated from room temperature to 90 °C under severe stirring and maintained at this temperature for 8 h. After the reaction, the residual solution on the carrier surfaces was rinsed off by using deionized water and drying naturally and calcined at 400 °C for 4 h. Different manganese contents were achieved by controlling the solution concentrations (0.01, 0.02, 0.03, 0.05, and 0.10 M). The as-prepared carriers were denoted as Mn_x/ γ -Al₂O₃/Al ($x = 1.2, 3.2, 4.7, 8.6, \text{ and } 10.1$), where x is the loading of Mn.

Supplementary Note S3. Preparation of Pt-based catalyst

First, 1 g of $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ was dissolved in deionized water and transferred to a 50 mL volumetric flask. 10 mL of the aqueous $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ solution and 1.25 mL $0.4 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution were mixed with 500 mL of ethylene glycol to form a $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ mixed solution. Three pieces of Mn_x/ γ -Al₂O₃/Al were loaded in the mixture for 4 h after the temperature of the heated water bath was raised to 80 °C. Subsequently, the catalysts were rinsed with deionized water and immediately placed into a prefabricated $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaBH₄ aqueous solution for an additional 4 h. Finally, the catalysts were rinsed with deionized water and dried to obtain the Pt/Mn_x/ γ -Al₂O₃/Al keeping the loading of Pt at 0.9 wt.%. For convenience, Pt/Mn_{4.7}/ γ -Al₂O₃/Al was simplified to Pt/Mn/ γ -Al₂O₃/Al.

Supplementary Note S4. Catalyst characterization

N₂ adsorption–desorption was determined through nitrogen adsorption on a Micromeritics ASAP 2020-M instrument, following degassing at 350 °C for 12 h. The

contents of Mn and Pt in the catalyst were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) on the Agilent 725. X-ray diffraction (XRD) analysis was conducted over a range of 10° to 80° on Bruker D8 Advance. Field emission scanning electron microscopy (FESEM) images were obtained with a JSM-6360LV operated at 200 kV, which is equipped with energy dispersive X-ray spectroscopy (EDS) at an acceleration voltage of 15 kV. Fourier-transform infrared spectroscopy (FTIR) was performed on a Thermo Scientific Nicolet iS20, covering a spectral range from 400 to 4000 cm⁻¹. Thermogravimetric (TG) analysis was performed by WRT-3 P-TGA; the temperature range was from 25 °C to 600 °C with a heating rate of 5 °C·min⁻¹. Electron paramagnetic resonance (EPR) spectra were measured on a spectrometer (Bruker E500, Germany) at room temperature. In situ FTIR with modulation excitation spectroscopy (MES) experiments were performed to identify the intermediate product using a Bruker Tensor 27 spectrometer equipped with an MCT detector and operated at a resolution of 4 cm⁻¹ for 64 scans. Prior to each in situ FTIR measurement, the sample was subjected to a 30-minute Ar purging process to eliminate air interference in the sample cell. A baseline spectrum was acquired following the Ar purging treatment. XPS was measured on Thermo Scientific K-Alpha using Al K α as an excitation X-ray source. To calibrate the effects of the charge, the C 1s peak from carbon contamination was set to 284.8 eV. This calibration facilitated the calculation of the average oxidation state (AOS) of Mn, which was evaluated according to the following equation:

$$\text{AOS} = 8.956 - 1.126 \cdot \Delta E_s \quad (\text{S1})$$

Where ΔE_s represents the difference in binding energy of different Mn3s peaks.

The gaseous product was analyzed by GC6600 gas chromatograph equipped with a flame ionization detector (FID). The calibration of gas chromatography (GC) was performed by pure gases of known concentrations.

Supplementary Note S5. Catalytic activity evaluation

To investigate the catalytic oxidation performance of CO, catalysts were selected for the catalytic activity evaluation in a fixed-bed reactor after being purged with different saturated water vapor volumes, as shown in Figure S1. The temperature range of the catalyst part in the quartz tube was 25 ± 2 °C, the total flow rate of the reaction gas was controlled at 100 mL·min⁻¹, and the inlet concentration of CO was controlled at 1,000 ppm. Ten samples were recorded by GC, with sample injections occurring every 7 min.

The CO removal efficiency was evaluated using the following equation:

$$\text{CO conversion (\%)} = \left(1 - \frac{[\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}}\right) \times 100\% \quad (\text{S2})$$

The reaction rate (r) and apparent activation energy (E_a) were calculated using the following equations:

$$r \text{ (mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}) = \frac{\text{GHSV (mL} \cdot \text{g}^{-1} \cdot \text{h}^{-1}) \times \text{CO vol. \%} \times X_{\text{CO}}}{1000 \text{ (L} \cdot \text{mL}^{-1}) \times 22.4 \text{ (mol} \cdot \text{L}^{-1})} \quad (\text{S3})$$

$$\ln r = - \frac{E_a}{R \times T} + \ln A \quad (S4)$$

Supplementary Note S6. DFT method

The DFT calculations for the catalytic system were performed using the Vienna Ab-initio Simulation Package (VASP) [1] with the Perdew–Burke–Ernzerhof (PBE) functional [2]. A plane-wave cutoff energy of 450 eV was applied. The Brillouin zone in the grid was sampled using a $(3 \times 3 \times 1)$ Monkhorst–Pack k-point mesh. To prevent interactions between adjacent slabs along the z-direction, a vacuum layer of 20 Å was set between any two consecutive slabs. The bottom two layers of all slabs were fixed, while the remaining layers were allowed to relax. Transition states were identified using the climbing image nudged elastic band (CI-NEB) method and were further validated through vibrational frequency analysis.

The adsorption (E_{ads}) and desorption energies of the molecules were defined by the following equations:

$$E_{ads} = E_{ads/sub} - E_{ads} \quad (S5)$$

$$E_{des} = E_{des/sub} - E_{des} - E_{sub} \quad (S6)$$

Where $E_{ad/sub}$, E_{ad} , and E_{sub} were the energy of the optimized adsorption system for adsorbates and substrates, gas-phase adsorbates, and substrates, respectively; and $E_{des/sub}$, E_{des} , and E_{sub} were the energy of the optimized adsorption system for desorbates, and substrates, gas-phase desorbates and substrates, respectively.

The activation energy barrier (E_b) during the reaction was defined by the following equation:

$$E_b = E_{TS} - E_{IS} \quad (S7)$$

where E_{TS} was the energy of the transition state, and E_{IS} was the energy of the initial.

Supplementary Figures

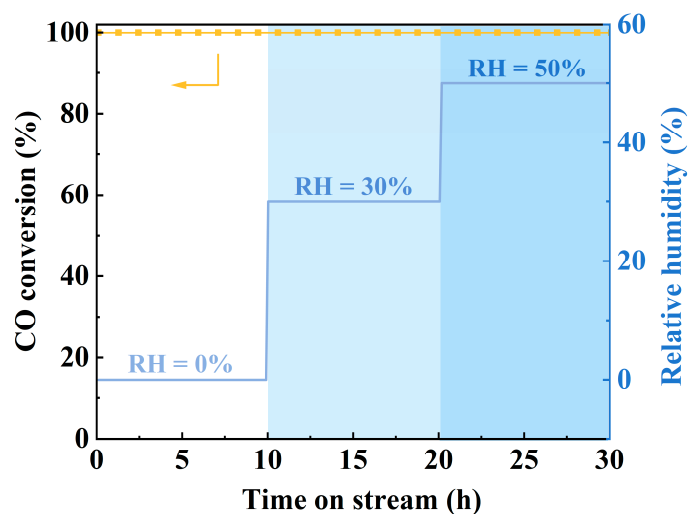


Figure S1. Activity performance of Pt/Mn/ γ -Al₂O₃/Al-WVT-2 under different relative humidity (RH). (Condition: $T = 25 \pm 2$ °C, $m = 0.58$ g, CO=1,000 ppm, WHSV = 26,000 mL·g_{cat}⁻¹·h⁻¹)

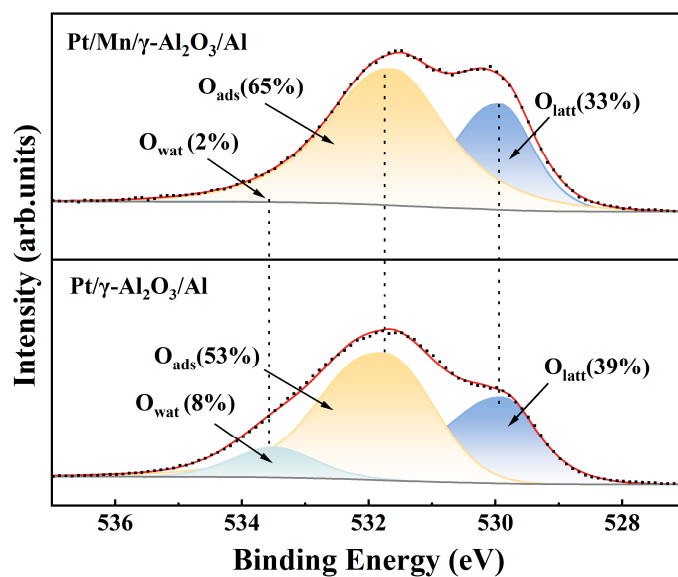


Figure S2. XPS O 1s results of Pt/Mn/ γ -Al₂O₃/Al and Pt/ γ -Al₂O₃/Al.

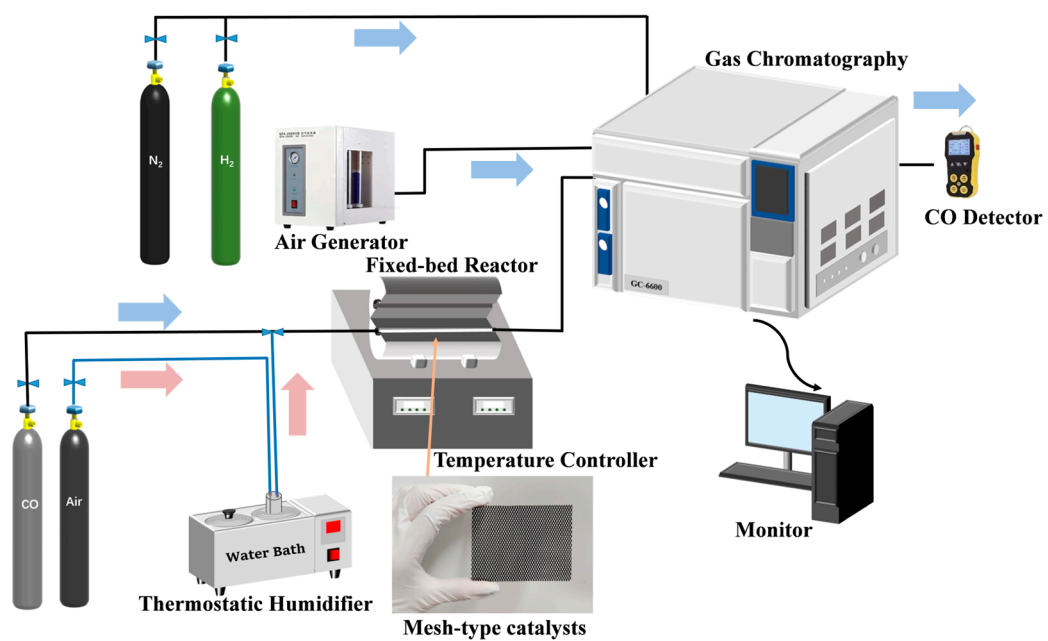


Figure S3. Flowchart of experiment device for CO catalytic oxidation reaction.

References

1. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science*. **1996**, 6, 15–50.
2. P.P. John, B. Kieron, Generalized Gradient Approximation Made Simple, **1996**.