Electronic Supplementary Information

Potassium-incorporated manganese oxide enhances the activity and durability of platinum catalyst for low-temperature CO oxidation

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Experimental details

1. *Reagents*

The chemical reagents $KMnO_4$, $Mn(CH_3COO)_2 \cdot 4H_2O$, HNO_3 solution and $H_2PtCl_6 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. $(NH_4)_2S_2O_8$, $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$ were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). These chemicals were analytical grade and used directly in the catalyst preparation without further purification.

2. *Catalyst preparation*

Synthesis of α-MnO$_2$, α-MnO$_2$(K), β-MnO$_2$, γ-MnO$_2$, δ-MnO$_2$(K). α-MnO$_2$, α-MnO$_2$(K), γ-MnO$_2$ and δ-MnO$_2$(K) were prepared through hydrothermal synthesis method.[1] β-MnO$_2$ were purchased from Commercial manganese dioxide.

For α-MnO$_2$, $MnSO_4 \cdot H_2O$ (1.35 g, 8.0 mmol), $(NH_4)_2S_2O_8$ (1.83 g, 8.0 mmol) and $(NH_4)_2SO_4$ (1.98 g, 15.0 mmol) were dissolved in 40 mL distilled water with vigorous stirring, then sealed in stainless steel autoclave at 120 °C for 20 h. After cooling to room temperature, the products was filtered, washed with deionized water thoroughly, and then dried at 100 °C for 24 h.

For α-MnO$_2$(K), typically, $Mn(CH_3COO)_2 \cdot 4H_2O$ (4.73 g, 19.3 mmol), $KMnO_4$ (4.4 g, 27.8 mmol) and concentrated HNO_3 were added to 100 mL of distilled water under stirring. The resulting solution was transferred to a Teflon-lined autoclave (100 mL in capacity) and maintained at 100 °C for 24 h. The resulting black precipitate was filtered, washed with deionized water. The black powder was then dried at 80 °C for 6 h. As-prepared samples were calcined in muffle furnace at 400 °C for 4 h.

For γ-MnO$_2$, $MnSO_4 \cdot H_2O$ (3.38 g, 20.0 mmol) and $(NH_4)_2S_2O_8$ (4.564 g, 20.0

mmol) were dissolved in 70 mL of deionized water, stirred for 30 min. The resulting solution was transferred to a Teflon-lined autoclave (100 mL in capacity) and maintained at 90 °C for 24 h. After cooling, the products was filtered, washed with deionized water thoroughly. The sample was then dried at 80 °C for 6 h. As-prepared samples were calcined in muffle furnace at 350 °C for 4 h.

For δ-MnO$_2$(K), KMnO$_4$ (1.896 g, 12.0 mmol) and MnSO$_4\cdot$ H$_2$O (0.338 g, 2.0 mmol) were dissolved in 70 mL of deionized water and stirred for 60 min, The resulting solution was transferred to a Teflon-lined autoclave (100 mL in capacity), then maintained at 240 °C for 24 h. After cooling, the products was filtered, washed with deionized water thoroughly. The sample was then dried at 80 °C for 6 h. As-prepared samples were calcined in muffle furnace at 350 °C for 4 h.

β-MnO$_2$ was commercial manganese dioxide. Before use, it was calcined in muffle furnace at 350 °C for 4 h.

Preparation of Pt colloid nanoparticles. Platinum colloids nanoparticles were prepared by a polyol reduction method which was reported in our previous work.[2] Typically, 27 mL glycol solution of sodium hydroxide (0.68 mol L^{-1}) and 60 mL glycol solution of H$_2$PtCl$_6\cdot$6H$_2$O (1.7 × 10^{-3} mol L^{-1}) were mixed under vigorous stirring for 20 min, and then heated at 140 °C for 30 min in N$_2$ flow.

Preparation of Pt/MnO$_2$ Catalysts. Pt/ MnO$_2$ catalysts were prepared by a colloid deposition method. All as-prepared catalysts support was added to the above Pt colloids. The mixture was heated at 80 °C for 12 h. After filtered from the above mixture, the obtained solid was completely washed with deionized water to eliminate

chloride ions (detected by $AgNO_3$ reagent). The resulting solid were dried at 100 °C overnight and calcinated at 200 °C for 2 h in the stream of O_2 (20 vol%) and Ar (80 vol%). The Pt weight content of the final catalysts is controlled at 1.0%.

3. *Catalytic performance test*

The catalytic CO oxidation activity was measured using a continuous-flow fixed-bed reactor system. The Pt/MnO_2 catalysts samples were directly used without further reduction treatment. 100 mg of the solid catalyst sample (40–60 mesh) was loaded between two glass wool beds in a quartz tube reactor. The gas mixture consisted of 1 vol% CO, 4 vol% H_2O and 5 vol% O_2/Ar, balanced with Ar. The total flow rate was 100 mL min^{-1} . GHSV=60000 $mL·g^{-1}·h^{-1}$. Kinetic data were taken after 10 min on stream at each reaction temperature. Product analysis was carried out using a Shimadzu GC-8A gas chromatograph equipped with a TCD. The CO conversion rates (X_{CO}) were calculated according to the below equation:

$$X_{CO} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

4. *Characterizations*

X-ray diffraction (XRD) patterns were collected at room temperature on an automated Rigaku diffractometer using a Cu Kα ($\lambda = 1.54056$ Å) radiation.

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250 system with a Mg Kα source (1254.6 eV). The XPS spectra were calibrated by adjusting the position of the C 1s peak to 284.6 eV.

The field-emission high resolution transmission electron microscopy Talos F200X

with operating voltage of 200 kV was employed to obtain the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images.

N_2-adsorption/desorption isotherms were recorded by Micromeritics analyzer (ASAP 2010N) and the surface areas were calculated by the Brunauer-Emmett-Teller (BET) model.

The *in-situ* DRIFT data were obtained by Thermo Nicolet 6700 spectrometer equipped with a reaction cell. Firstly, the catalyst was treated at room temperature under Ar atmosphere for 20 min. Then different reaction gases were introduced into the *in-situ* reaction cell according to predefined reaction process. The water vapor was introduced by bubble method. Each spectra data was recorded about 1 min.

The H_2-TPR profiles were obtained by Quantachrome ChemBET Pulsar TPR apparatus with 25 mg sample in each test. Firstly, the catalyst was treated at the temperature of 150 °C under inert atmosphere (99.99% Ar) for 30 min. Secondly, 5 vol% H_2/Ar was introduced at room temperature, then the heating procedure was performed with 10 °C·min^{-1} .
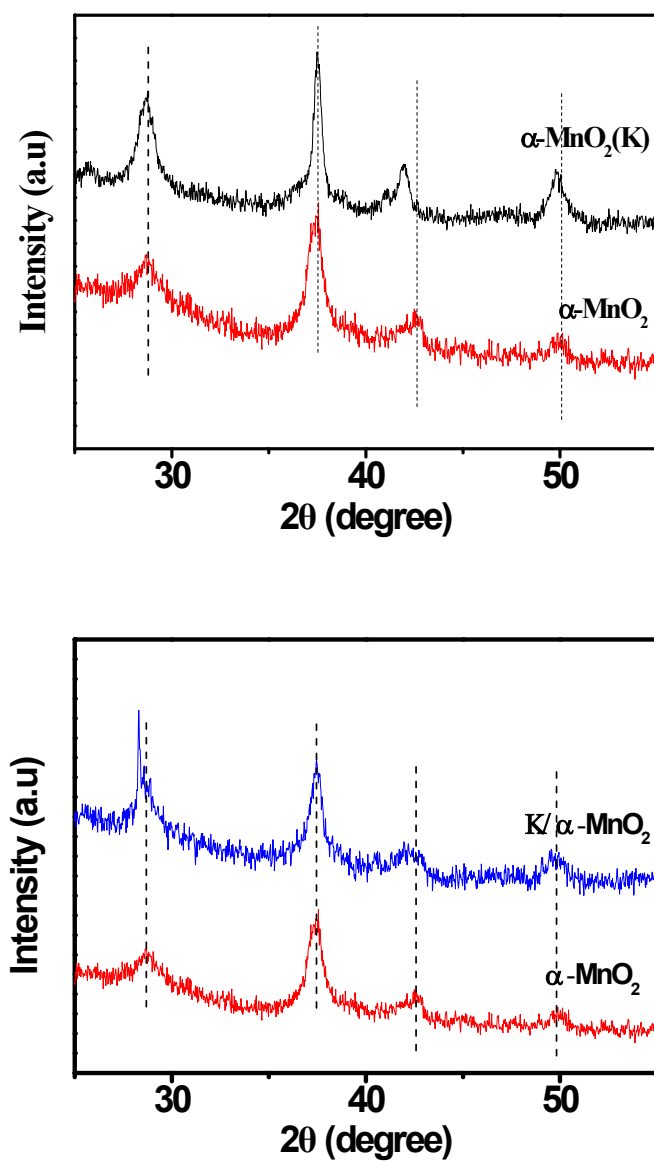
Fig. S1 Magnified XRD peaks of α-MnO$_2$ (K), K/α-MnO$_2$ and α-MnO$_2$ in the 2θ range of 25° to 55°.
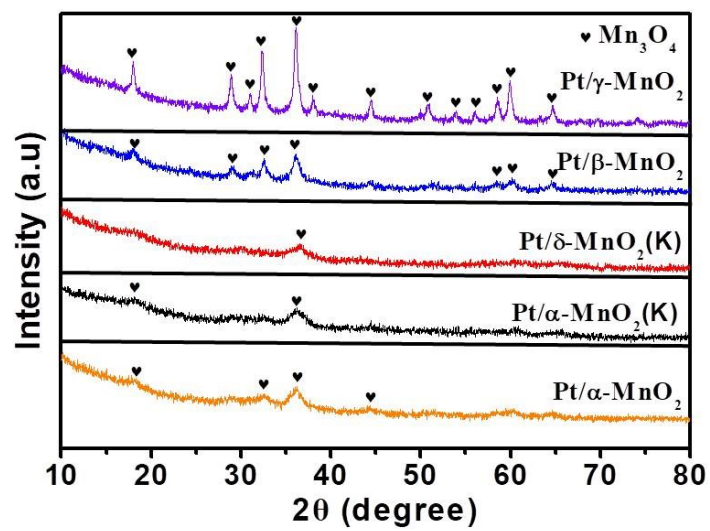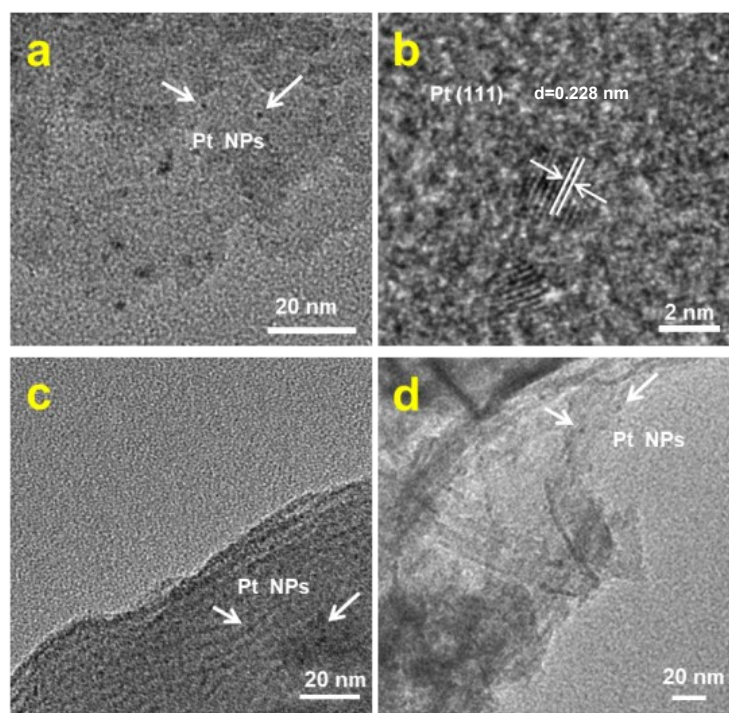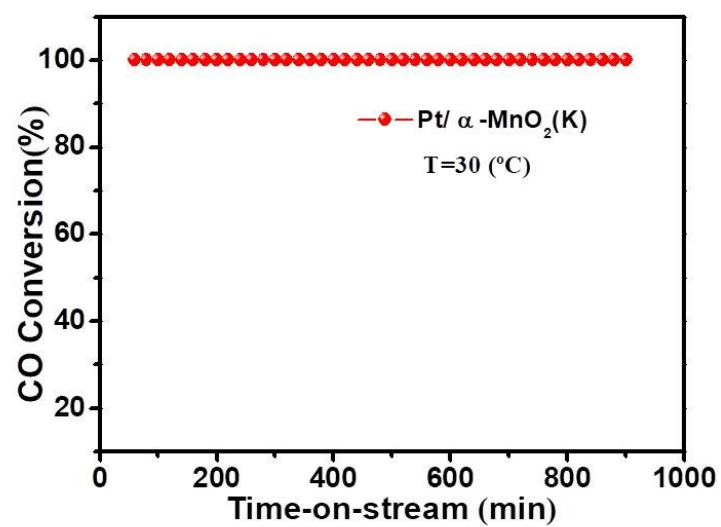
Fig. S2 XRD patterns of various Pt/MnO₂ catalysts.

Fig. S3 TEM and HRTEM images of different catalysts. (a,b) TEM and HRTEM images

of Pt/α-MnO$_2$(K). (c) TEM image of Pt/α-MnO$_2$. (d) TEM image of Pt/δ-MnO$_2$.

Fig. S4. CO conversion as a function of the time-on-stream over Pt/α-MnO$_2$(K) at 30 °C. Reaction condition: 1 vol% CO, 4 vol% H$_2$O, 5 vol% O$_2$/Ar and Ar balance；GHSV=60000 mL·g^{-1}·h^{-1}.
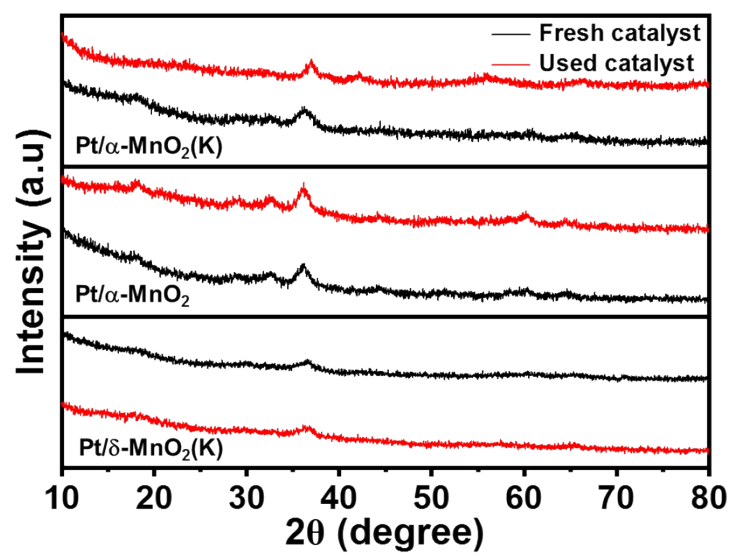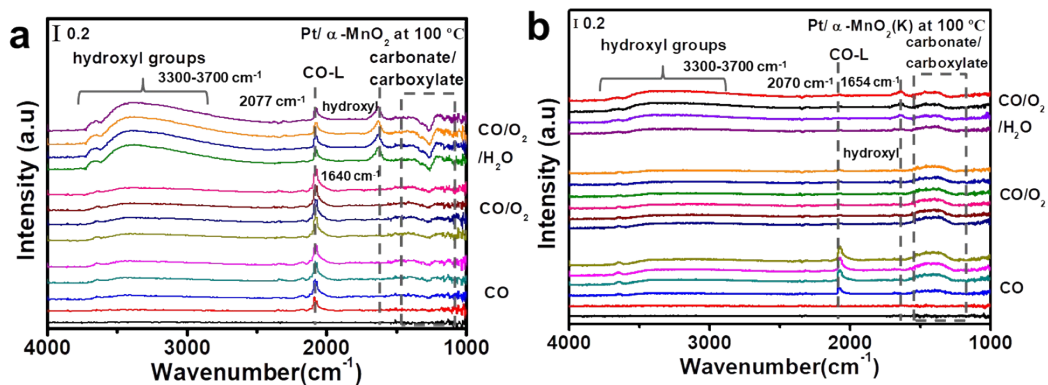
Fig. S5 XRD patterns of fresh and used Pt/MnO$_2$ samples.

Fig. S6. In-situ DRIFT spectra of CO oxidation over Pt/α-MnO$_2$(K) and Pt/α-MnO$_2$ catalysts at 100 °C: (a) Pt/α-MnO$_2$; (b) Pt/α-MnO$_2$(K).

Table S1. Summary of textural parameters of the samples.

Catalysts	$S_{BET}(m^2 \cdot g^{-1})$	Pore Volume$(m^3 \cdot g^{-1})$	Pore Size[a](nm)
Pt/δ-MnO$_2$(K)	118	0.44	11.3
Pt/α-MnO$_2$(K)	90	0.44	16.6
Pt/α-MnO$_2$	83.3	0.38	14.8
Pt/β-MnO$_2$	55	0.19	10.4
Pt/γ-MnO$_2$	41.5	0.21	17.9

[a] Average pore diameters calculated from adsorption branches using BJH model.

Notes and references

[1] B. Chen, B. Wu, L. Yu, M. Crocker and C. Shi, *ACS Catal.*, 2020, **10**, 6176-6187.

[2] B. Zheng, G. Liu, L. Geng, J. Cui, S. Wu, P. Wu, M. Jia, W. Yan and W. Zhang, *Catalysis Science & Technology*, 2016, **6**, 1546-1554.