

Supporting Information

NaBH₄ reduced Mn-doped cobalt tetroxide R-Mn_xCo_{3-x}O₄ catalysts with abundant oxygen vacancies for formaldehyde oxidation at low temperature

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1. Experimental Section

1.1 Preparation of catalyst.

1.1.1 Preparation of Co_3O_4

Co_3O_4 catalyst was prepared using a simple co-precipitation method. First, 0.5 molL^{-1} Na_2CO_3 solution was added dropwise into a beaker containing 50 ml of 1 molL^{-1} CoSO_4 solution. During the dropping process, the stirring speed was controlled at 200-300 r/min and the temperature of the reaction solution was controlled at 60°C . The pH value was controlled in the range of 9.4-9.8. Then the suspension gradually turns purple, and it ages in a 60°C water bath for 1 hour before being vacuum filtered. The resulting sample was washed several times with distilled water until the pH reached about 7.0. The filter cake was then dried in an oven at 120°C for 12 h and calcines it in a muffle furnace at 300°C for 4 h to obtain powdered Co_3O_4 .

1.1.2 Preparation of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$

The preparation of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ was similar to that of Co_3O_4 . First, the CoSO_4 was added into 20ml distilled water under vigorous stirring to obtain CoSO_4 solution (0.5 M). Then MnSO_4 was added into 20ml distilled water under vigorous stirring to obtain MnSO_4 solution (0.05 M, 0.10 M, 0.15 M, 0.20 M, 0.25 M). During stirring, the MnSO_4 solution was slowly dripped into CoSO_4 solution. 0.5 molL^{-1} Na_2CO_3 solution was added dropwise into a mixed solution of CoSO_4 and MnSO_4 . During the dropping process, the stirring speed was controlled at 200-300 r/min and the temperature of the reaction solution was controlled at 60°C . The pH value was controlled in the range of 9.4-9.8. Then the suspension was aged in a water bath at 60°C for 1 h and then vacuum filtered. The resulting sample was washed several times with distilled water until the pH reached about 7.0. The filter cake was then dried in an oven at 120°C for 12 h and calcines it in a muffle furnace at 300°C for 4 h. The obtained composites were recorded as $\text{Mn}_{0.3}\text{Co}_{2.7}\text{O}_4$, $\text{Mn}_{0.7}\text{Co}_{2.3}\text{O}_4$, MnCo_2O_4 , $\text{Mn}_{1.3}\text{Co}_{1.7}\text{O}_4$ and $\text{Mn}_{1.7}\text{Co}_{1.3}\text{O}_4$.

1.1.3 Preparation of R- MnCo_2O_4

The prepared MnCo_2O_4 catalyst (0.5 g) was dissolved in 20 ml of deionized water, and then 5 ml of 0.5 molL^{-1} NaBH_4 solution was added dropwise into the MnCo_2O_4 solution. During the titration, the stirring speed was controlled at about 200-300r/min. After titration, the suspension was ultrasonicated for half an hour and then vacuum filtered. The filter cake was dried in an oven at $60 \text{ }^\circ\text{C}$ for 12 hours to obtain R- MnCo_2O_4 powder.

2. Materials characterization

The specific surface area of the catalysts was determined by an automated physical adsorption meter (Autosorb-iQ-1MP) from Quantachrome, Inc. (Quantachrome), USA. The chemical composition analysis was performed on a PerkinElmer Optima 8300DV inductively coupled plasma-atomic emission spectrometer (ICP-AES). Scanning electron microscopy (SEM): the catalyst was characterized using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan) to observe the catalyst morphology. X-ray photoelectron spectroscopy (XPS): was determined using an axial supersystem with an x-ray anode at 225 W and 15 K_v of Al K_α radiation ($h\nu = 1486.6 \text{ eV}$). The binding energy (BE value) was calibrated with the C 1s peak (284.8 eV). Surface relative compositions were estimated using integrated intensities corrected for atomic sensitivity factors. Hydrogen Temperature Programmed Reduction (H_2 -TPR): used to characterize catalyst redox capacity tests. Instrumentation Autochem 2920 chemisorbentimeter, also from Micromeritics, USA, equipped with a TCD detector. The experimental procedure was as follows: 100 mg catalyst was placed in a U-shaped quartz tube. The catalyst was purged in-situ with 30 mLmin^{-1} of high purity Ar at $150 \text{ }^\circ\text{C}$ for 1 h, then cooled down to $30 \text{ }^\circ\text{C}$. The carrier gas was switched to 50 mLmin^{-1} of 10 Vol.% H_2/Ar mixture, and after the baseline was stabilized, the H_2 -TPR test was carried out by ramping up to $800 \text{ }^\circ\text{C}$ at a heating rate of 10°Cmin^{-1} , and the change in signal value was recorded by TCD. O_2 temperature programmed oxidation (O_2 -TPD): O_2 -TPD was used to characterize the oxygen activation capacity of the catalyst. The

experimental instrument was an Autochem 2920 chemisorbent analyzer from Micromeritics, USA, equipped with a TCD detector. The experimental procedure was as follows: 100 mg catalyst was placed in a U-shaped quartz tube and purged with 30 mLmin⁻¹ Ar at 150 °C for 1h to remove the surface impurities, then switched to high-purity He and purged to 30 °C, and then pre-treated the sample with a mixture of 50 mLmin⁻¹ 5 vol.% CO and He for 1h. Then the atmosphere was switched to high-purity Ar and purged for 30 min to remove the surface impurities. The sample was then purged with 50 mLmin⁻¹ of a 5 vol.% O₂ and He mixture for 1h. Afterwards, the atmosphere was switched to high-purity Ar for 30 min to remove residual physically adsorbed oxygen on the surface, and then the sample was purged with high-purity He for 20 min. After the baseline was stabilized, the temperature was increased to 800 °C at a rate of 10 °Cmin⁻¹ and the change in signal value was recorded. O₂-temperature programming oxidation (O₂-TPO) experiments were performed on an analyzing instrument (PCA-140 TPD/TPR) with a thermal conductivity detector (TCD). The sample was treated in a flow of 8% O₂/N₂ (50 ml/min) at 30 °C for 30 min, and then heated from 30 to 800 °C in a flow of N₂ at a heating rate of 10 °C/min.

3. Evaluation of HCHO catalytic oxidation performance

As shown in Fig. S1, a 50 mL stainless-steel batch reactor was employed as the reactor (CEL-GPR100, AULTT, China). The photocatalyst (20 mg) were dispersed in 5 ml ethanol and ultrasonicated for 10 minutes. Then, the mixed liquid is loaded on the quartz plate, and the catalyst are loaded on the dishes after heated at 60°C in a oven to completely remove the ethanol. Then, the quartz plate with catalyst was placed into the closed reactor. 37% formalin solution was used as the gas source of HCHO. 1 mL formalin solution is directly dropped into the glass reagent bottle in the reactor (20 ppm), then the upper quartz window is sealed, and then the formalin solution was heated by infrared light to accelerate evaporation. The water vapor or N₂ were injected into the reactor through a gas distribution system (CEL-GPPCN, AULTT, China). The reactor temperature can be control by external circulation

heating and cooling device. The relative humidity (RH) was 80%. The gas circulation pump was used to promote the diffusion of HCHO gas. Before thermal catalysis, the HCHO gas was diffused in the dark for 1 h to achieve the uniform distribution of HCHO gas and to ensure the adsorption-desorption equilibrium between HCHO and catalyst powder. When the balance of gas desorption is reached, the temperature of reactor was set to 50 °C and the reaction was begin.



Fig. S1 50 mL stainless-steel batch reactor was employed as the reactor (CEL-GPR100, AULTT, China)

The change of HCHO concentration was detected by spectrophotometry. Every 10 minutes, 5 ml of gas was extracted by syringe and quickly injected into the brown glass reagent bottle with rubber stopper. The bottle was filled with phenol reagent (MBTH) chromogenic solution in advance. The brown bottle was shaken sufficiently to make the HCHO completely dissolved in the solution, then it was placed in a 40 °C water bath for 10 minutes, then $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ was added, and then it was shaken sufficiently and placed in a 40 °C water bath for 10 minutes, and the color of solution gradually turned blue-green. The formed blue-green solution has characteristic absorption peak at 630 nm. The change trend of HCHO relative content was determined according to the intensity of the absorption peak at 630 nm. The removal rate of HCHO was calculated as $\text{HCHO} (\%) = (1 - C/C_0) \times 100\%$, where C and C_0 were the concentrations of HCHO at a certain time and at the beginning of the reaction respectively.

Table. S1. Combined results of elemental analysis determined by ICP-AES of $Mn_xCo_{3-x}O_4$ catalysts.

Catalyst	Mn%(mass)	Co%(mass)	Mn/Co (molar)
$Mn_{0.3}Co_{2.7}O_4$	7.407	69.84	0.113
$Mn_{0.7}Co_{2.3}O_4$	18.91	60.03	0.341
$MnCo_2O_4$	25.14	53.19	0.492
$Mn_{1.3}Co_{1.7}O_4$	33.57	48.14	0.759
$Mn_{1.7}Co_{1.3}O_4$	47.37	39.51	1.315

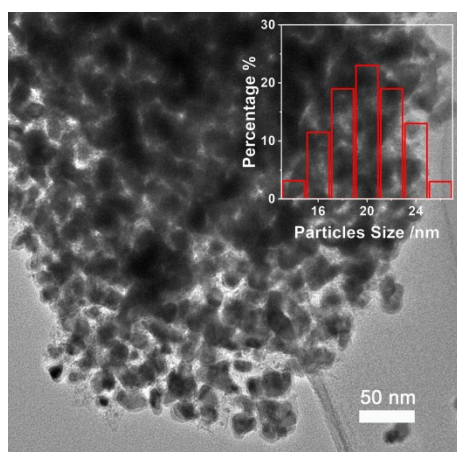


Fig. S2 TEM image of MnCo₂O₄

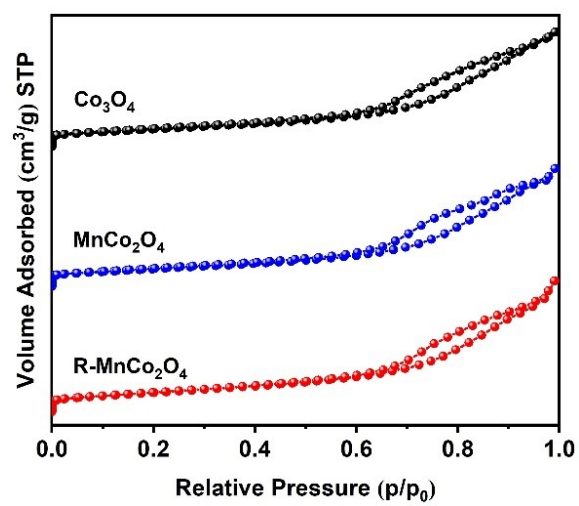


Fig. S3 N₂ adsorption-desorption isotherms of catalysts

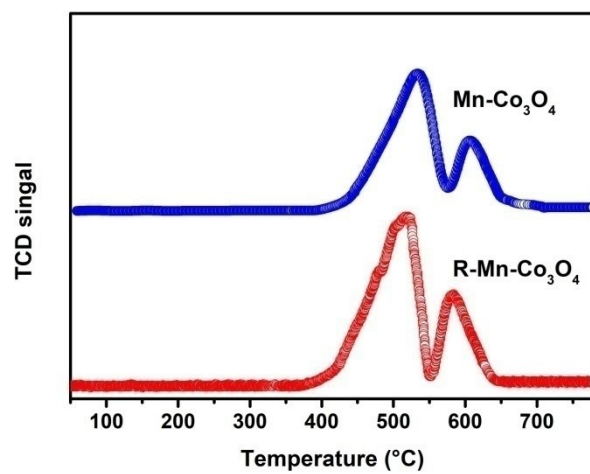


Fig. S4 O₂-TPO profiles of MnCo₂O₄ and R- MnCo₂O₄

Table.S2 Comparison of catalytic oxidation efficiency of HCHO gas by different catalysts.

Catalyst	Co ₃ O ₄	Mn _{0.3} Co _{2.7} O ₄	Mn _{0.7} Co _{2.3} O ₄	MnCo ₂ O ₄	Mn _{1.3} Co _{1.7} O ₄	Mn _{1.7} Co _{1.3} O ₄	R-MnCo ₂ O ₄
HCHO degradation (%)	24	50	59	62	54	45	79

Table.S3 Catalytic activities for the oxidation of HCHO of various samples reported in the literature.

Catalyst	HCHO concentration	Temperature (°C)	HCHO degradation (%)	TOF	Ref.
R-MnCo ₂ O ₄	20 ppm	50	79	$3.1 \times 10^{-2} \text{ s}^{-1}$	This work
Pd/TiO ₂ -300R	140ppm	125	85	$1.8 \times 10^{-3} \text{ s}^{-1}$	[1]
F-Pt-P25	260ppm	25	58	1.64min ⁻¹	[2]
1% Pt/TiO ₂	36ppm	25	47	$2.7 \times 10^{-3} \text{ s}^{-1}$	[3]
3.4% K-1% Pd/TiO ₂	550ppm	25	60	$4.1 \times 10^{-2} \text{ s}^{-1}$	[4]
K-Ag/Co ₃ O ₄	100ppm	60	55	0.22 s^{-1}	[5]
PEG-MnO ₂	200ppm	25	94	$6.41 \times 10^{-6} \text{ h}^{-1}$	[6]

References

- [1]. Li Y, Zhang C, Ma J, et al. High temperature reduction dramatically promotes Pd/TiO₂ catalyst for ambient formaldehyde oxidation. *Appl. Catal. B-Environ*, 217(2017),560-569, <https://doi.org/10.1016/j.apcatb.2017.06.023>.
- [2]. Zhu X, Cheng B, Yu J, et al. Halogen poisoning effect of Pt-TiO₂ for formaldehyde catalytic oxidation performance at room temperature. *Appl. Surf. Sci*, 364(2016), 808-814, <https://doi.org/10.1016/j.apsusc.2015.12.115>.
- [3]. S.S. Kim, K.H. Park, S.C. Hong, A study on HCHO oxidation characteristics at room temperature using a Pt/TiO₂ catalyst, *Appl. Catal. A-Gen*. 398 (2011) 96–103, <https://doi.org/10.1016/j.apcata.2011.03.018>.
- [4]. Y.B. Li, C.B. Zhang, H. He, J.H. Zhang, M. Chen, Influence of alkali metals on Pd/TiO₂ catalysts for catalytic oxidation of formaldehyde at room temperature, *Catal. Sci. Technol*. 6 (2016) 2289–2295, <https://doi.org/10.1039/C5CY01521A>.
- [5]. Bai B, Li J. Positive effects of K⁺ ions on three-dimensional mesoporous Ag/Co₃O₄ catalyst for HCHO oxidation. *Acs Catalysis*, 4.8 (2014): 2753-2762, <https://doi.org/10.1021/cs5006663>.
- [6]. Do S B, Lee S E, Kim T O. Oxidative decomposition with PEG-MnO₂ catalyst for removal of formaldehyde: Chemical aspects on HCHO oxidation mechanism[J]. *Appl. Surf. Sci*, 598 (2022): 153773, <https://doi.org/10.1016/j.apsusc.2022.153773>.