

Supporting Informations

Identifying Fe₃Mn₃O₈ Phase as the Superior Catalyst for Low-Temperature Catalytic Oxidation of Formaldehyde in Air

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Experimental section

1. Preparation of catalysts

In detail, for the Fe-Mn oxide catalyst, stoichiometric quantities of 3.58 g $\text{Mn}(\text{NO}_3)_2$ and 8.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 20 ml distilled water under vigorous stirring at 30 °C to form a solution with the desired molar ratio of Fe/Mn (1:1). Then, an appropriate amount of citric acid was added to obtain a solution with a molar ratio of citric acid per metal ion of 1.2. After 15 min of constant stirring, the above solution was gradually heated to 80 °C and continuously stirred for 4 h at this temperature to form a gel. The resulting gel was dried at 100 °C for 12 h, and then calcined at 500 °C for 4 h. This preparation method is easy to be scaled up. Ca. 100 g catalyst could be prepared one time using a container with a volume of 2000 ml in the laboratory. Similarly, the samples with various M/Mn ratios were synthesized. In detail, for the Co-Mn oxide catalyst, stoichiometric quantities of 3.58 g $\text{Mn}(\text{NO}_3)_2$ and 5.82 g $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used with the desired molar ratio of Co/Mn (1:1). For the Ni-Mn oxide catalyst, stoichiometric quantities of 3.58 g $\text{Mn}(\text{NO}_3)_2$ and 5.82 g $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used with the desired molar ratio of Ni/Mn (1:1).

2. Characterization

H_2 -TPR was performed on an AutoChem II 2920 desorption apparatus. The catalyst (0.100 g) was pretreated in He (30 mL min⁻¹) at 250 °C for 1 h and then cooled to 80 °C in He. The sample was then exposed to 10 vol% H_2/Ar (30 mL min⁻¹), and the temperature was raised to 900 °C at a rate of 10 °C min⁻¹. The oxygen storage capacities of the catalysts were evaluated by the O_2 temperature-programmed desorption (O_2 -TPD) method on an AMI-300 desorption apparatus. In brief, 50 mg of catalyst was pretreated under an O_2 atmosphere (30 cm³/min) at 120 °C for 60 min and cooled down to 30 °C at the same condition. Then, the pretreated catalyst was heated from 30 to 900 °C in a He flow (30 cm³/min) at a heating rate of 10 °C/min.²⁸ Electron paramagnetic resonance (EPR) analyses were performed on an EMXplus spectrometer (Bruker, Germany). Before the test, 3 mg of sample was dispersed in 6

ml of methanol, and the dispersion was added into methanol with 60 mM of DMPO. The sample was tested after shaking up. The operating parameters were as follows: modulation frequency: 100.00 KHz; modulation amplitude: 2.00 G; sweep width: 100.00 G; conversion: 40.000 ms; time constant: 40.960 ms; microwave power: 20.00 mW; microwave frequency: 9.84 GHz; and sweep time: 60.70 s.

Co-Mn) in catalytic oxidation of formaldehyde at 25 °C. (Conditions: Catalyst: 0.100 g, HCHO: 115 ppm, GHSV: 300 L g⁻¹ h⁻¹).

Binary Oxides Catalysts	Specific activity (mg_{HCHO} g⁻¹_{cat} h⁻¹) at 25 °C
Fe-Mn(3:1)	8.90
Fe-Mn(1:1)	58.0
Fe-Mn(1:3)	37.0
Ni-Mn(3:1)	12.0
Ni-Mn(1:1)	23.0
Ni-Mn(1:3)	33.0
Co-Mn(3:1)	25.0
Co-Mn(1:1)	26.0
Co-Mn(1:3)	33.0

Table S2. Comparison of HCHO catalytic oxidation performance of Fe-Mn(1:1) with other catalysts reported in literature.

Catalysts	HCHO concentrations	GHSV	Conversion	T (°C)	Ref.
K- δ -MnO ₂	10.0 ppm	130 L g ⁻¹ h ⁻¹	100%	25	1
Pd/TiO ₂	50.0 ppm	24.0 L g ⁻¹ h ⁻¹	100%	30	2
3D-MnO ₂	100 ppm	180 L g ⁻¹ h ⁻¹	100%	90	3
Fe-Mn(1:1)	115 ppm	300 L g ⁻¹ h ⁻¹	100%	25	This work
Pt/MnO ₂ -Ni(OH) ₂	200 ppm	Static state	90%	25	4

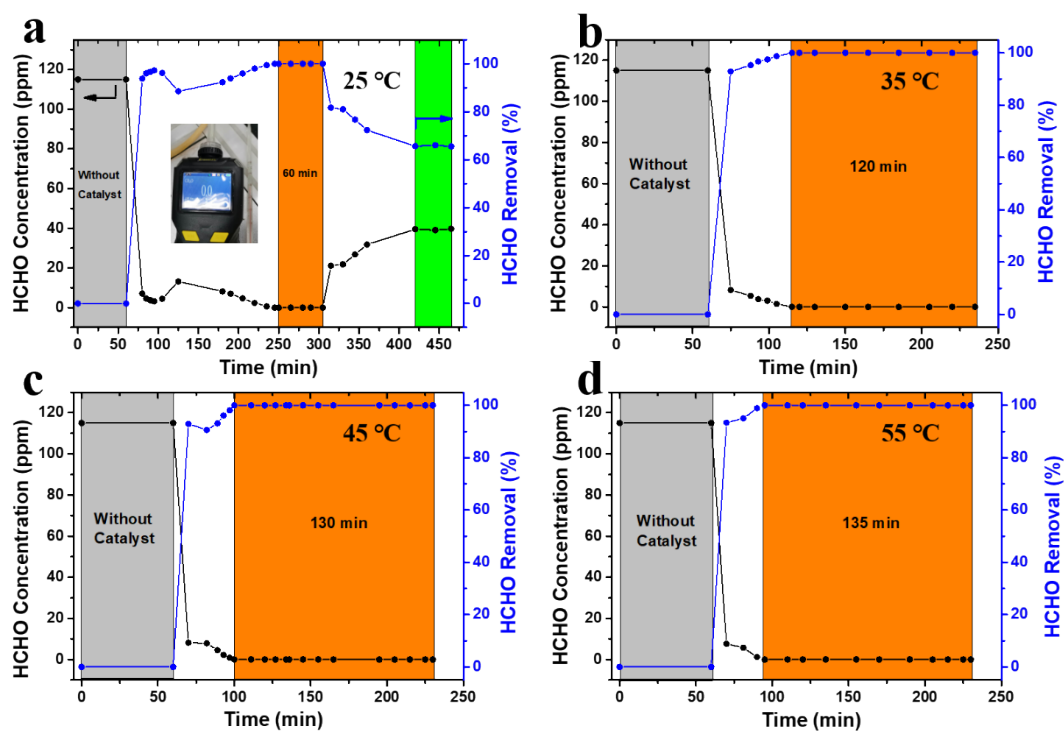


Fig. S1. Formaldehyde removal as a function of reaction time at different temperatures

over the Fe-Mn (1:1) mixed oxide catalyst at a GSHV of 300 L g⁻¹ h⁻¹, (a) 25 °C, (b) 35 °C, (c) 45 °C, and (d) 55 °C.

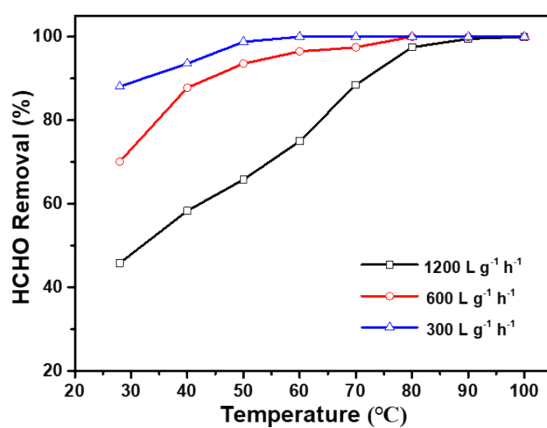


Fig. S2. Effect of GHSV on the catalytic performance of the Fe-Mn (1:1) oxide catalyst (catalyst: 25-100 mg, and HCHO concentration: 115 ppm, Temperature: 25 °C).

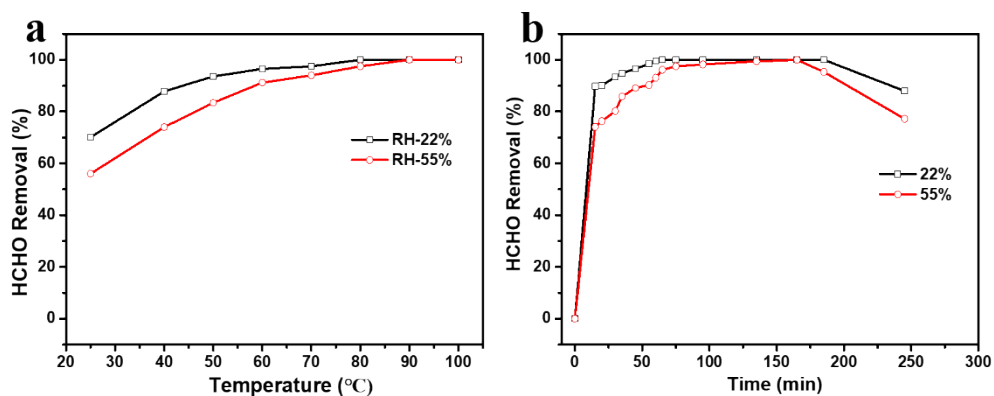


Fig. S3. (a) Effect of relative humidity (RH) on the activity of the Fe-Mn (1:1) oxide catalyst (catalyst: 50 mg, and HCHO concentration: 115 ppm, GHSV = 600 L g⁻¹ h⁻¹, Temperature: 25-100 °C). (b) Effect of relative humidity (RH) on the stability of the Fe-Mn (1:1) oxide catalyst (catalyst: 100 mg, Temperature: 25 °C, GHSV = 300 L g⁻¹ h⁻¹, and HCHO concentration: 115 ppm).

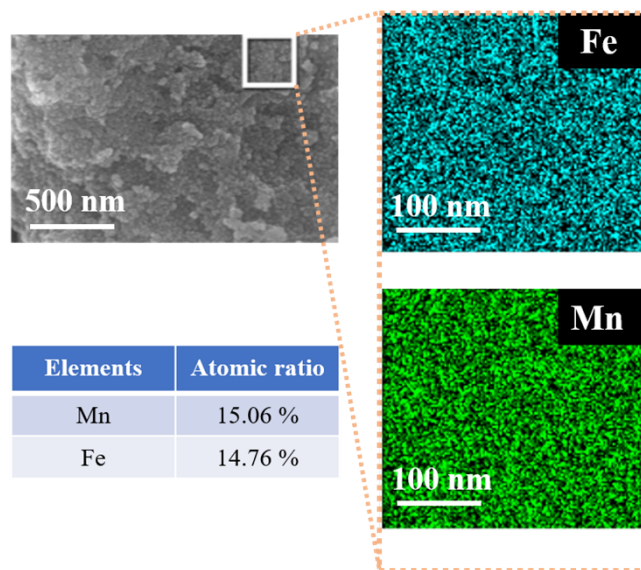


Fig. S4. The EDS-mapping of the Fe-Mn (1:1) oxide catalyst.

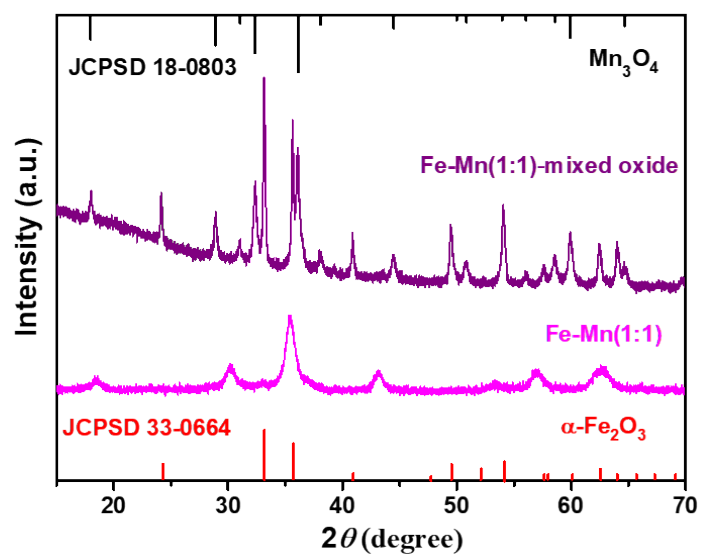


Fig. S5. XRD patterns of the Fe-Mn (1:1) ($\text{Fe}_3\text{Mn}_3\text{O}_8$) and the mechanically mixed Fe-Mn (1:1) oxide catalysts.

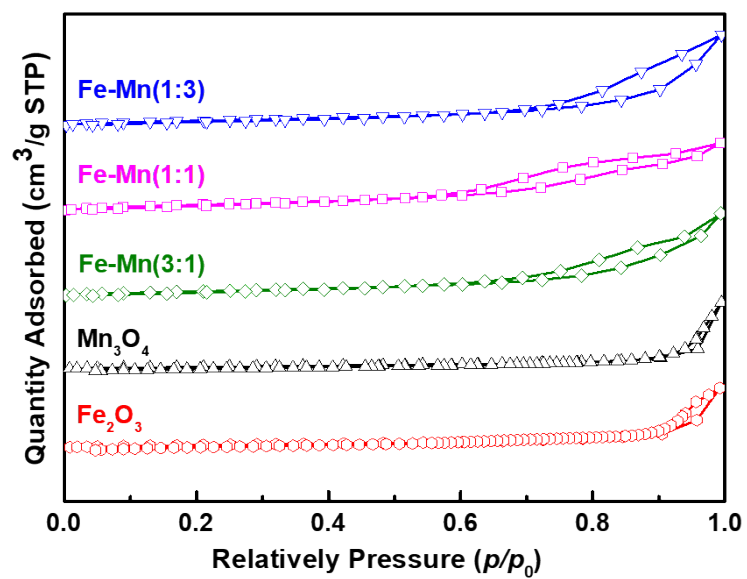
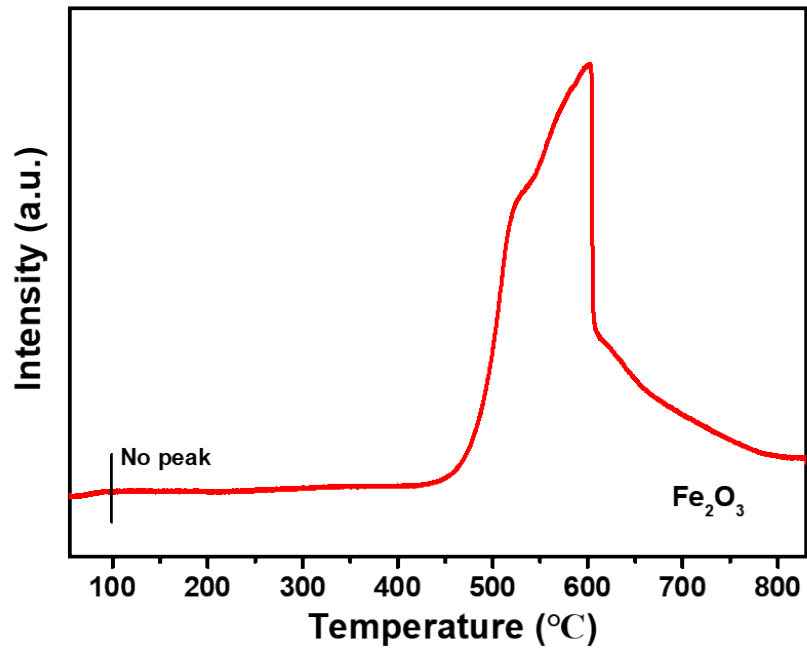


Fig. S6. Nitrogen adsorption-desorption isotherms of the Fe-Mn oxide catalysts with different Mn/Fe ratios.



g. S7. O₂-TPD profile of Fe₂O₃.

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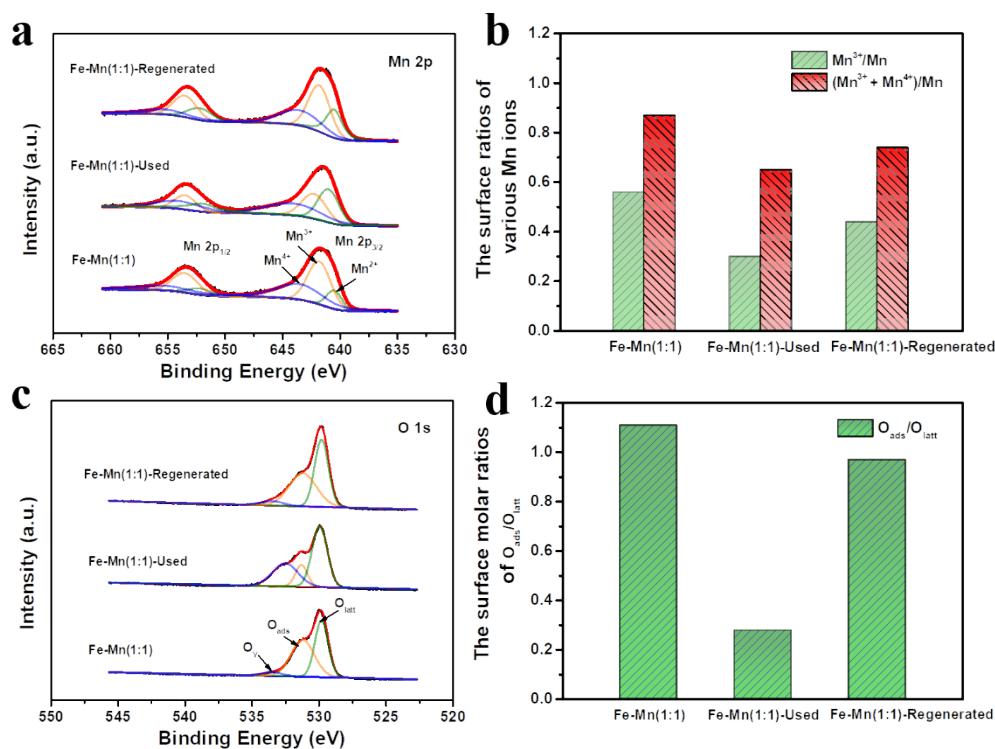


Fig. S8. (a) XPS spectra of Mn 2p for the fresh, used the regenerated Fe-Mn(1:1)-regenerated oxide catalysts. (b) Comparison of the surface molar ratios of Mn^{3+}/Mn , $(Mn^{3+} + Mn^{4+})/Mn$ on the surface of the respective catalysts. (c) XPS spectra of O 1s for the Fe-Mn(1:1) oxide, the Fe-Mn(1:1)-Used oxide and the Fe-Mn(1:1)-regenerated oxide catalysts. (d) Comparison of the surface molar ratios of O_{ads}/O_{latt} on the surface of the respective catalysts.

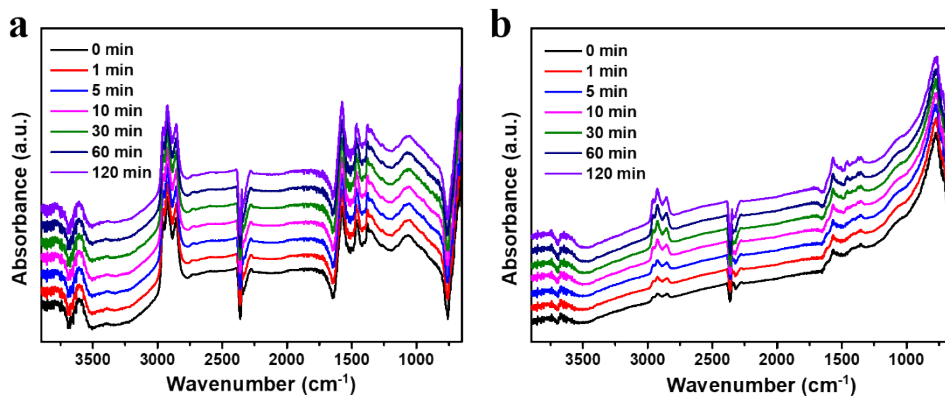


Fig. S9. (a) In situ DRIFT spectra of formaldehyde oxidation as a function of reaction time in N₂ atmosphere at 25 °C over the Fe-Mn(1:1) oxide catalyst. (Experimental conditions: 5 mg catalyst; HCHO concentration: 12 ppm, balanced by N₂, RH=22%, GHSV = 300 L g⁻¹ h⁻¹). (b) In situ DRIFT spectra of formaldehyde oxidation as a function of reaction time without water at 25 °C over the Fe-Mn(1:1) oxide catalysts. (Experimental conditions: 5 mg catalyst; HCHO concentration: 12 ppm, released by paraformaldehyde and balanced by air, RH=0%, GHSV = 300 L g⁻¹ h⁻¹).

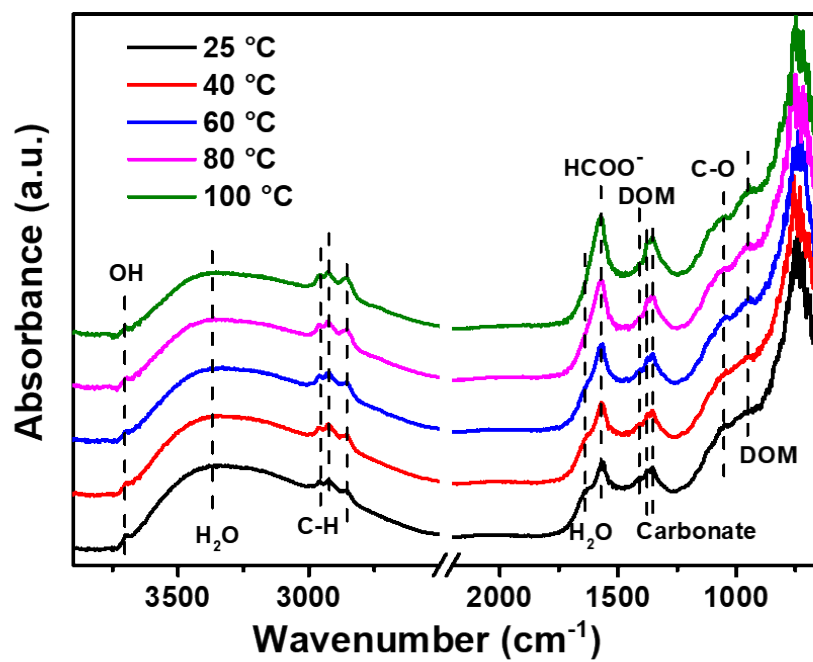


Fig. S10. In situ DRIFT spectra of formaldehyde oxidation as a function of the reaction temperature over the Fe-Mn(1:1) oxide catalyst.

Table S3 IR bands of the adsorption of HCHO on the Fe-Mn(1:1) mixed oxide catalyst.

IR band wavenumber (cm ⁻¹)								
-OH	C-H			HCOO ⁻		DOM		Carbonates
$\nu(\text{OH})$	ν_{as} (CH)	ν_{s} (CH)	$\delta(\text{CH})$	ν_{as} (OCO)	ν_{s} (OCO)	$\delta(\text{CH}_2)$	$\nu(\text{CO})$	$\nu(\text{CO}_3)$
~3700	~2856	~2925	~2958	~1564	~1519	~1456	~1047	~1386
~3369								~1348
Refer. 5-7	Refer. 5-7			Refer. 5-7		Refer. 5-7		Refer. 5-7

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