Supporting information

Enhanced catalytic oxidation of toluene over amorphous cubic structured manganese oxide based catalysts promoted by functional designed Co-Fe nanowires

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1. Characterizations of catalysts

Morphology and surface elemental composition of the prepared catalyst were analyzed by a scanning electron microscopy (SEM) (Hitachi SU8010, Japan) equipped with an X-ray spectrometry (EDX) (Horiba EMAX). Crystalline structure was investigated by an XRD equipment (Rigaku Smartlab, Japan) with a Cu-Kα radiation (λ=0.15418 nm) in a range of 10°-90° with a scanning rate of 4° min^{-1}. Transmission electron microscopy (TEM) analysis was carried out on a JEM-2100F TEM JEOL instrument operating at 200 kV. An X-ray photoelectron spectroscopy (XPS, Thermo-Scientific ESCALab250i) equipped with an Al-Kα radiation (Kα=1486.6 eV) was applied to investigate the surface chemical composition and elemental valence states, in which the C 1s peak was fixed at the binding energy (BE) of 284.6 eV. Raman analysis was performed using a JASCO NRS-5100 Raman spectrometer at 532 nm. Hydrogen temperature-programmed reduction (H_2-TPR) and oxygen temperature-programmed desorption (O_2-TPD) were conducted on a BELCAT catalyst analyzer with a thermal conductivity detector (TCD). For each of test, 50 mg catalyst was loaded into a U-shape tube, which was pretreated firstly at 300 ºC for 30 min with a helium flow (50 cm^3/min) and cooled down to room temperature (RT). Thereafter, the temperature was raised from RT to 800 ºC with a heating rate of 10 ºC/min under a gas flow of 5 vol% H_2/Ar (50 cm^3/min). For the O_2-TPD analysis, 150 mg of sample was pre-treated in the helium flow (50 cm^3/min) for 1 h in order to remove surface water. After cooling down to RT, the sample was treated by a O_2 flow (50 cm^3/min) and purged by a helium flow (50 mL/min) for 1 h, successively. Finally, the sample was heated from RT to 900 ºC at a rate of 10 ºC/min for the analysis.

In-situ DRIFTS analysis was carried out for the investigation of the catalytic oxidation process, which was conducted on a Frontier FTIR spectrometer (PerkinElmer) equipped with a DRIFTS cell and a MCT detector, and the test range is from 4000 to 650 cm^{-1} with 32 scans. In details, the optimum sample, i.e., 5Mn/Co-Fe/NF sample, was firstly pre-treated by a pure nitrogen-flow (100 cm^3/min) with the increasing of reaction temperature and then maintained the temperature at 300 °C for 30 min to remove out of those adsorbed impurity. Subsequently, the background signals were collected in N_2 atmosphere when the temperature was cooled down to 250 °C. Under the constant temperature, the reactant

substance of toluene containing gas (1000 ppm) was introduced into the *in-situ* test chamber by a continuous N_2 gas flow with a flow rate of 100 cm^3/min, and meanwhile, the DRIFTS spectrum was recorded for 50 min. Soon after, N_2 purging was conducted for 60 min without toluene vapor accompanying. For the O_2/N_2 atmosphere, the test process was the same as that of the N_2 atmosphere, in which the DRIFTS spectrum was recorded in the range of 4000–650 cm^{-1} as the above described.

2. Catalytic activity test

Catalytic performance of the prepared sample was evaluated on a fixed-bed system with a continuous flow at atmospheric pressure. In the test, the obtained catalyst coated NF was cut into small pieces with the size of 3×3 mm^2 , then 0.1 g of this catalyst was mixed with 0.3 g of silica sand (40~60 mesh) and transferred into a Pyrex reaction tube (i.d.=10 mm) with silicon wools packed at both ends of the catalyst bed. The packed catalysts were firstly pretreated in a nitrogen flow at 100 ºC for 1.5 h. The reaction temperature was set in the range of 150-300 ºC, and a mixture of a toluene (900 ppm), oxygen (O_2, 20 vol%), nitrogen (N_2, 80 vol% as balance) as the reaction gas with the total flow rate of 50 cm^3/min (at the standard temperature and pressure) was introduced into the reactor. For the optimum catalyst, its performances were also evaluated at different weight hourly space velocities (WHSVs) as well as different gaseous hourly space velocities (GHSVs) with the different catalyst amounts of 50 (WHSV=60,000 mL g^{-1} h^{-1}) and 150 mg (WHSV=20,000 mL g^{-1} h^{-1}), respectively. Simultaneously, the catalytic performances at different GHSVs by fixing the catalyst weight at 100 mg and increasing the total flow rate to 100 (GHSV=60,000 mL g^{-1} h^{-1}) and 140 mL (WGHSV=84,000 mL g^{-1} h^{-1}), respectively, were also conducted. The effect of water vapor on the catalytic performance was investigated by introducing 5.0 and 10 vol% of water vapors to the gas mixture through a saturated water bubbler. The inlet and outlet concentrations of toluene were analyzed by an on-line gas chromatograph (Shimadzu-2014) accompanied by a flame ionization detector (FID), and meanwhile, the produced CO_2 in the off-gas was detected online by a FTIR gas analyzer (Horiba, FG-120).

Herein, toluene conversion and CO_2 selectivity were calculated by the following formula:

$$X_{\text{Conversion}} = \frac{C_{\text{Inlet}} - C_{\text{Outlet}}}{C_{\text{Inlet}}} \times 100\% \quad (1)$$

$$CO_2 \text{ selectivity} = \frac{C_{CO_2}}{7(C_{\text{Inlet}} - C_{\text{Outlet}})} \times 100\% \quad (2)$$

where C_{Inlet} and C_{Outlet} are toluene concentrations of inlet and outlet of the reactor, respectively. In this work, the carbon balances of all experiments were closed with errors lower than 5%, as it stated in our previous work.[1]

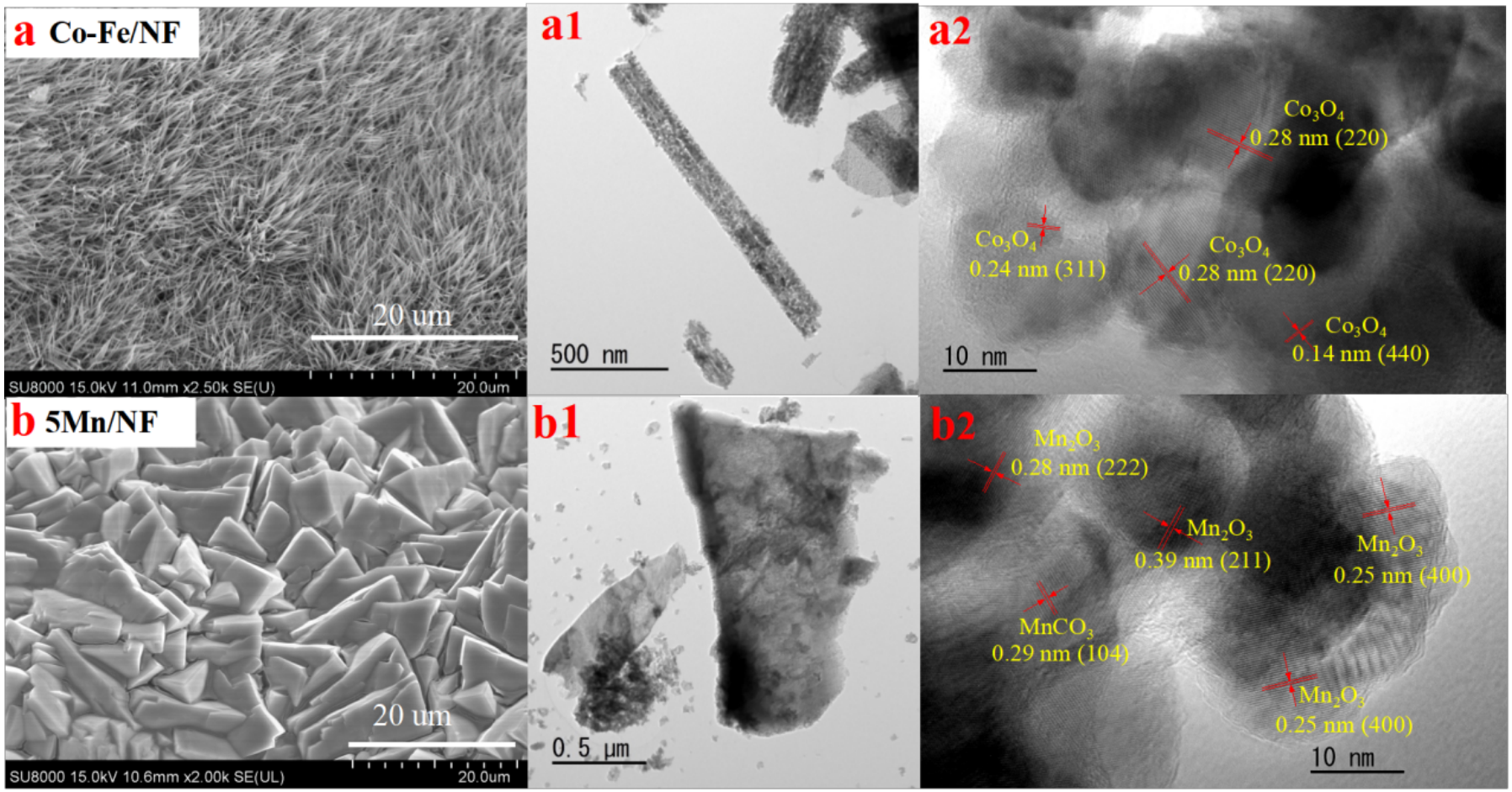


Figure S1. SEM and TEM images of the Co-Fe/NF and 5Mn/NF catalysts.

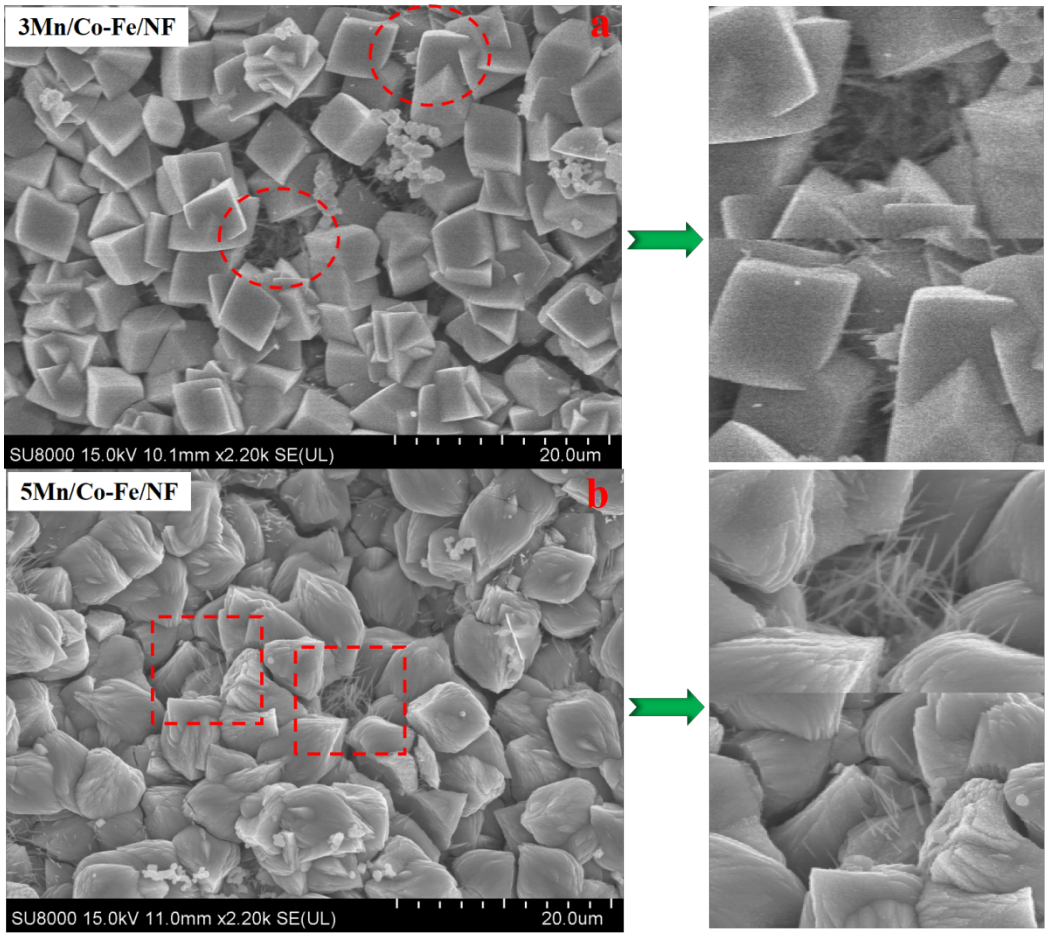


Figure S2. SEM images of the Mn/Co-Fe/NF catalysts.

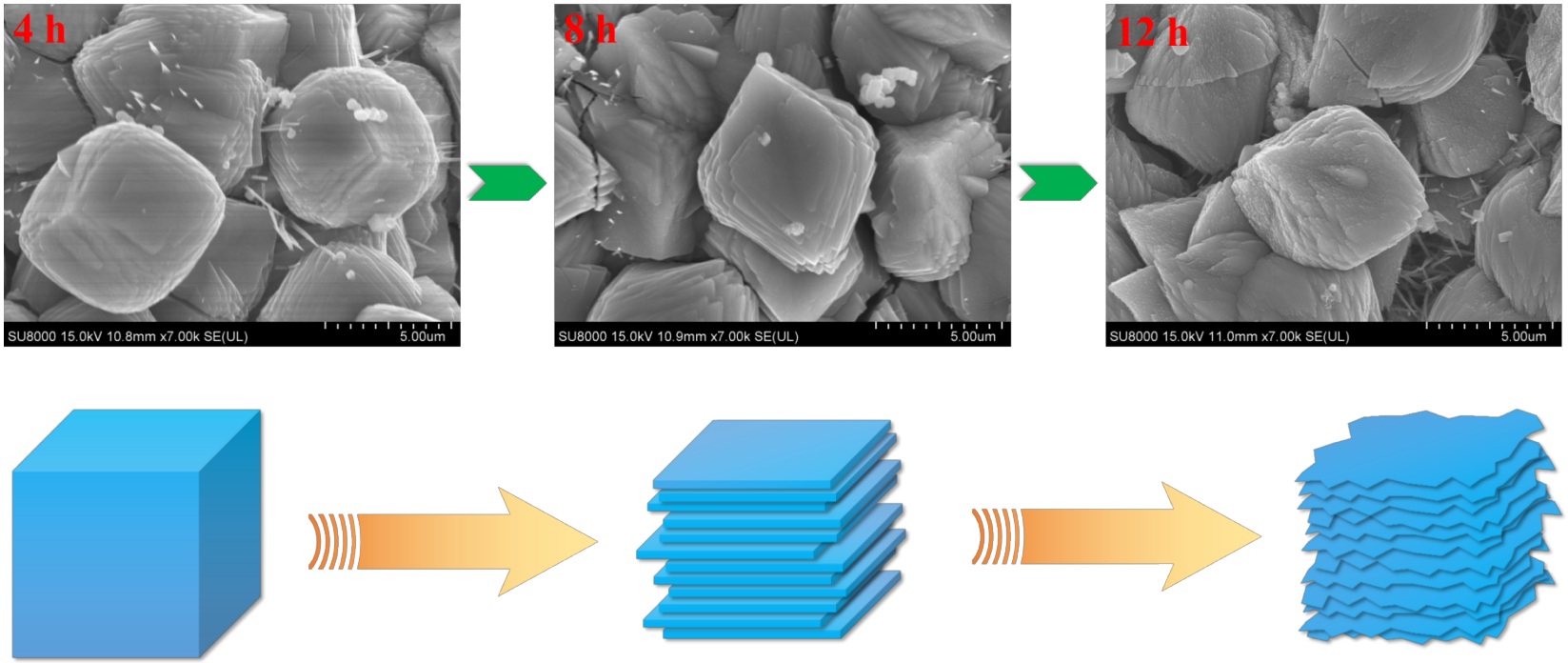


Figure S3. formation process of 5Mn/Co-Fe/NF catalyst displayed by SEM images.

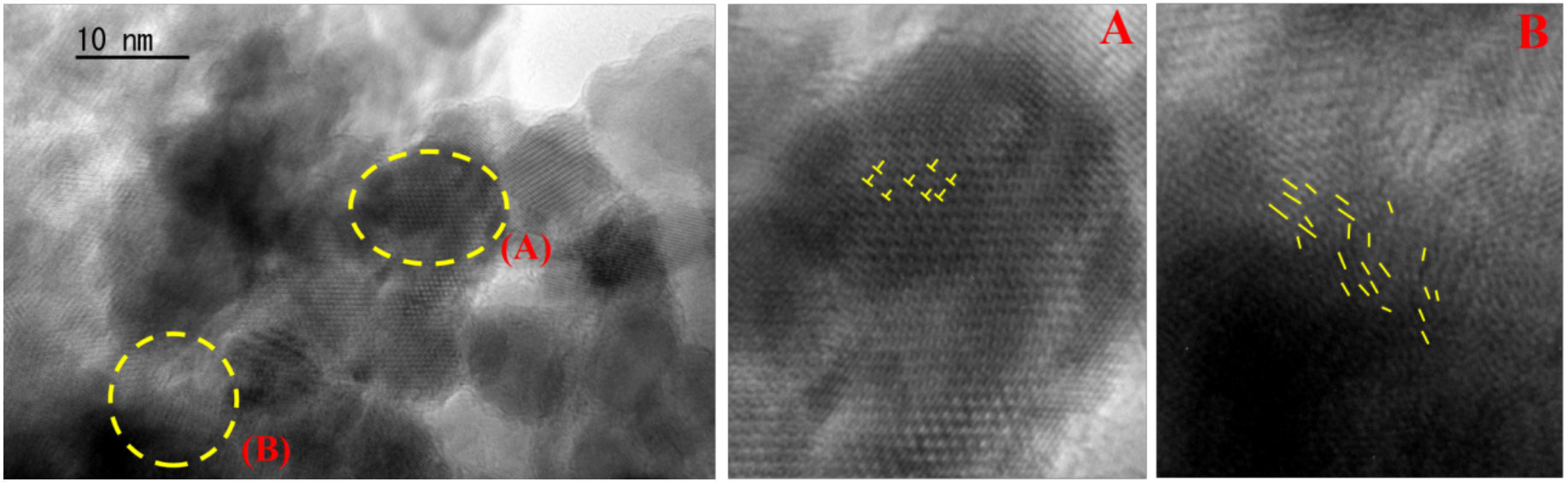


Figure S4. TEM images of the 5Mn/Co-Fe/NF catalyst (A and B are the enlarged TEM images).

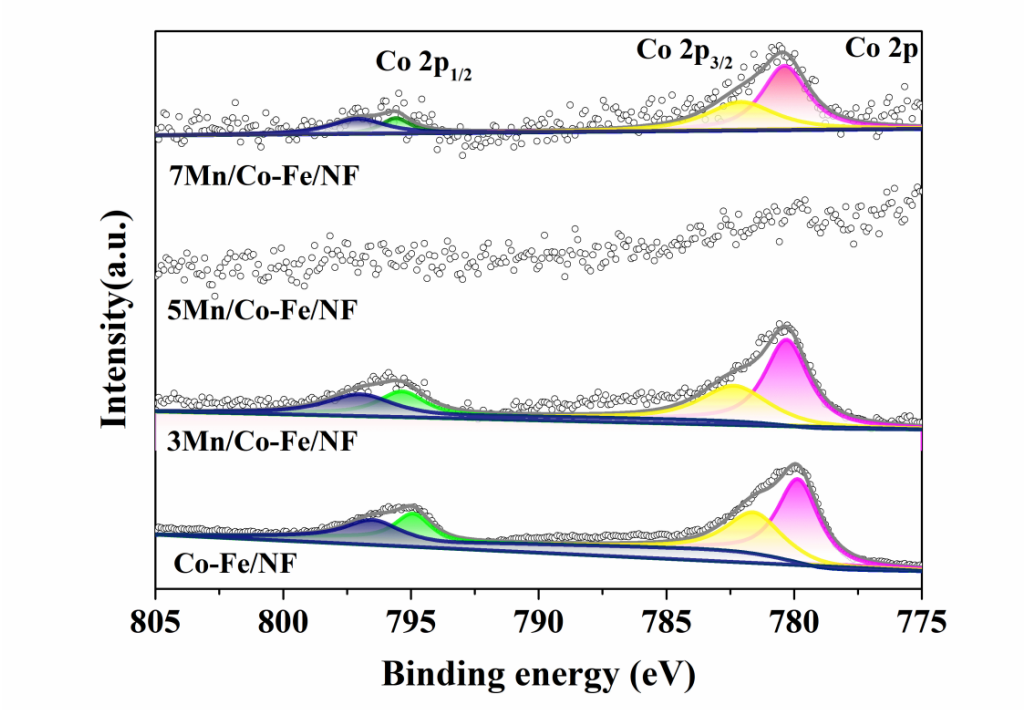
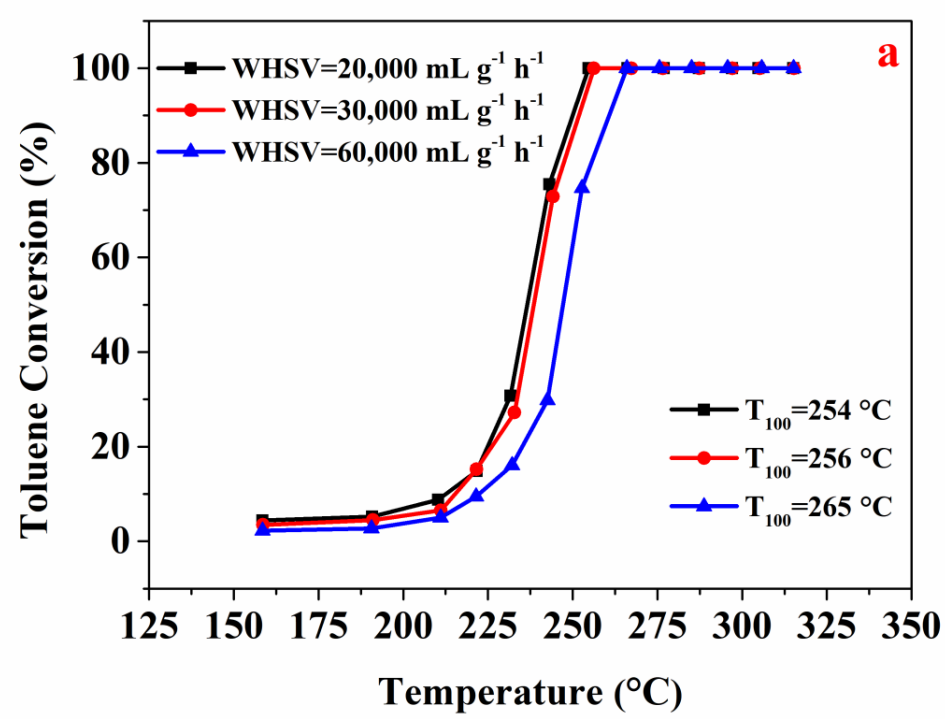


Figure S5. Co 2p XPS spectra of the prepared catalysts.



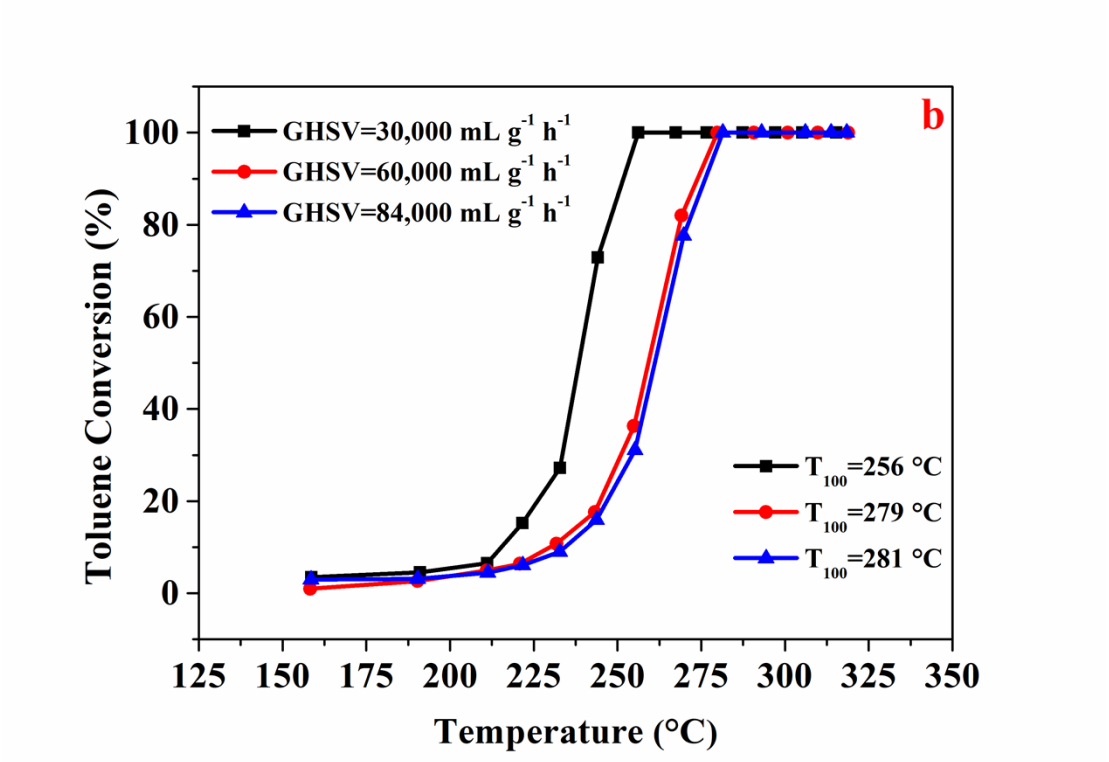
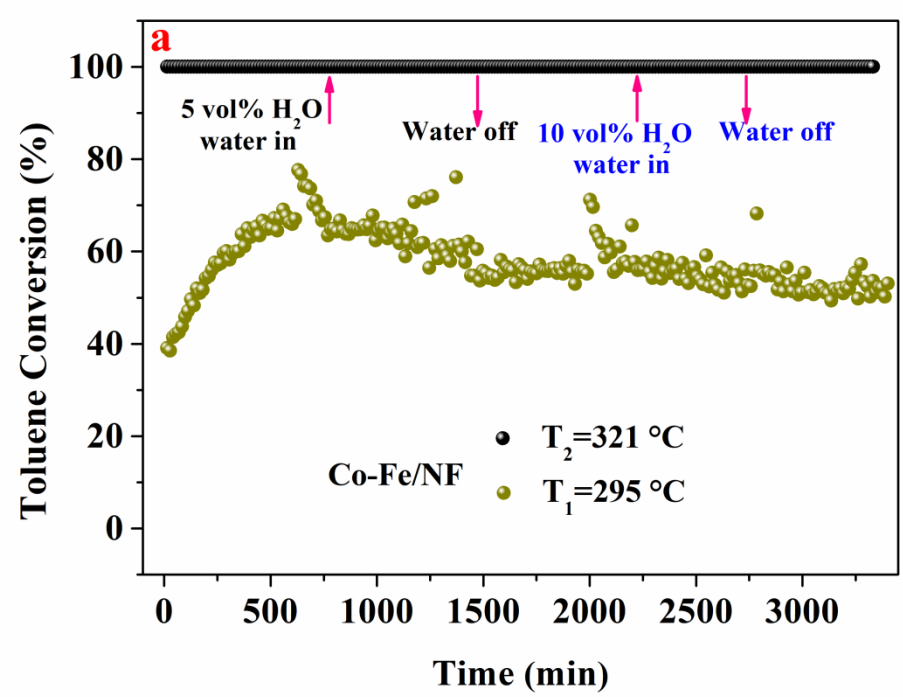


Figure S6. Catalytic toluene oxidation over 5Mn/Co-Fe/NF catalyst at different values of WHSV (a) and GHSV (b).



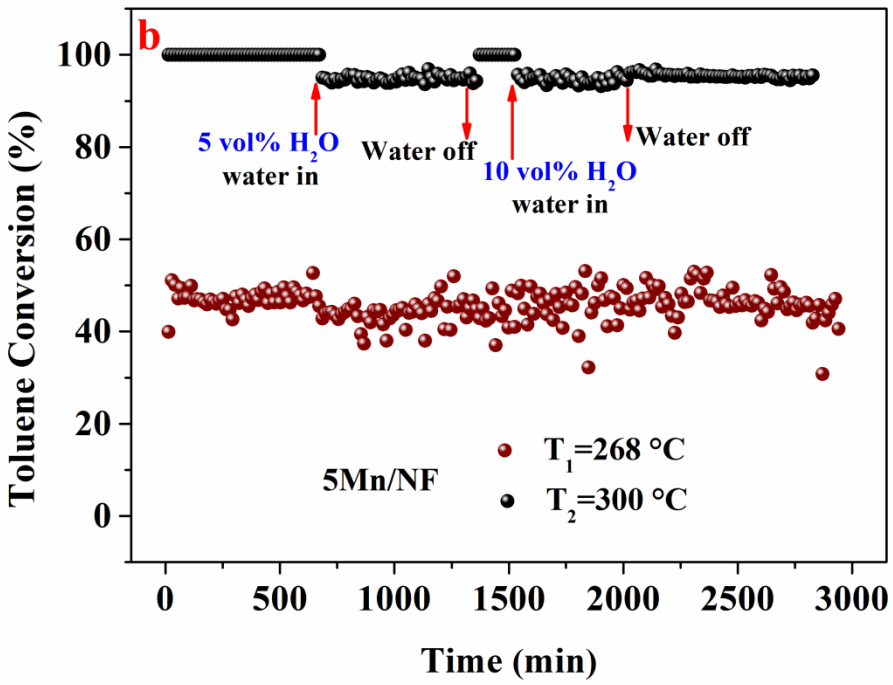


Figure S7. Long-term evaluation at different reaction temperatures and the effect of water vapor in the catalytic toluene oxidation over Co-Ce/NF (a) and 5Mn/NF (b) catalysts.

Table S1 Reported works related to the catalytic oxidation of toluene for comparison.

Sample	VOCs concentration (ppm)	WHSV ($mL.g^{-1}.h^{-1}$)	Toluene conversion (%)	Temperature (°C)	References
Mn-MOF	1000	60,000	90	267	[2]
Layered δ-MnO_2	1000	60,000	90	199	[3]
Mn-Cu hollow microsphere	1000	30,000	100	252	[4]
Mesoporous hollow structured Mn-Co oxide	1000	60,000	90	247	[5]
Manganese oxide	1000	90,000	100	240	[6]
Coral-like hierarchical structured La_yMnO_x nanosphere	1000	20,000	95	218	[7]
MnO_2 with different crystal	1000	30,000	90	228	[8]
Cubic structured Mn/Co-Fe/NF	1000	30,000	100	256	This work

Reference

1 J. Wang, A. Yoshida, P. Wang, T. Yu, Z. Wang, X. Hao, A. Abudula, G. Guan, Appl. Catal. B-Environ. 2020, **271**, 118941.

2 J. Wang, D. Zhang, G. Zhao, H. Yuan, D. Liu, A T. Kuvarega, B B. Mamba, H. Li, J. Gui, Colloids. Surfaces. A. 2024, **686**, 133357.

3 R. Li, L. Zhang, S Zhu, S. Zhu, S. Fu, X. Dong, S. Idac, L. Zhang, L. Guo, Appl. Catal. A-Gen. 2020, **602**, 117715.

4 Z. Xiao, J. Yang, R. Ren, J. Li, N. Wang, W. Chu, Chemosphere. 2020, **247**, 125812.

5 P. Liu, Y. Liao, J. Li, L. Chen, M. Fu, P. Wu, R. Zhu, X. Liang, T. Wu, D. Ye, J. Colloid. Interf. Sci. 2021, **594**, 713-726.

6 Y Lyu, C Li, X Du, Y. Zhu, Y. Zhang, S. Li, Fuel, 2020, **262**, 116610.

7 M. Li, C. Zhang, L. Fan, Y. Lian, X. Niu, Y. Zhu, ACS. Appl. Mater. Interfaces. 2021, **13**, 10089-10100

8 X. Zhai, L. Li, S. Song, J. Zhang, J. Ma, C. Xie, W. Chu, Fuel. 2023, **334**, 126780.