

Supporting Information

CO oxidation over MO_x (M = Mn, Fe, Co, Ni, Cu) supported on SmMn₂O₅ composite catalysts

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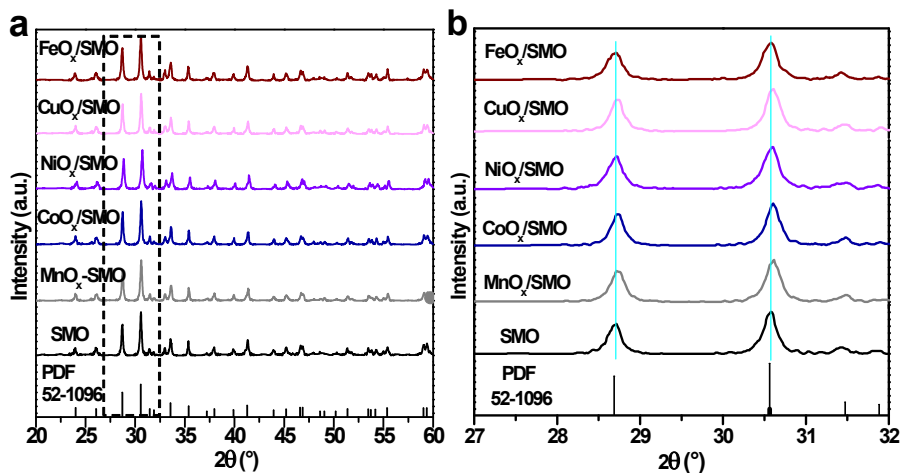


Fig. S1 (a) XRD patterns of all MO_x/SMO samples; (b) corresponding enlarged figures.

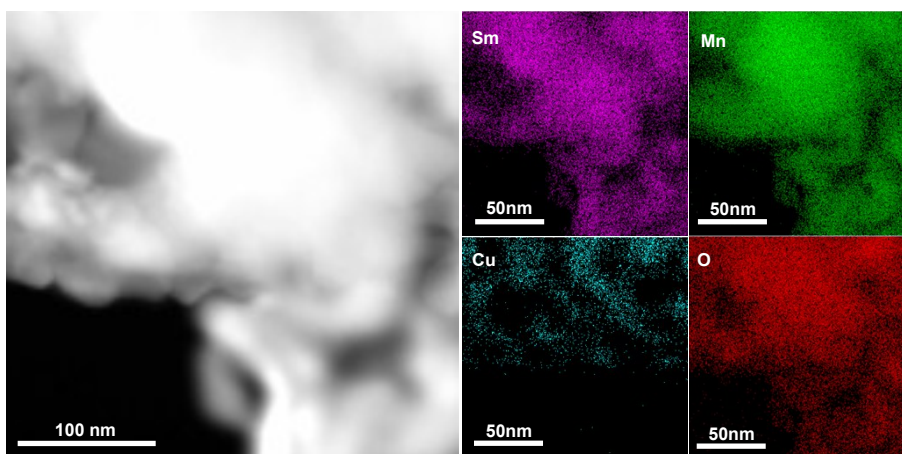


Fig. S2 Dark field STEM and EDX-mapping images of CuO_x/SMO sample.

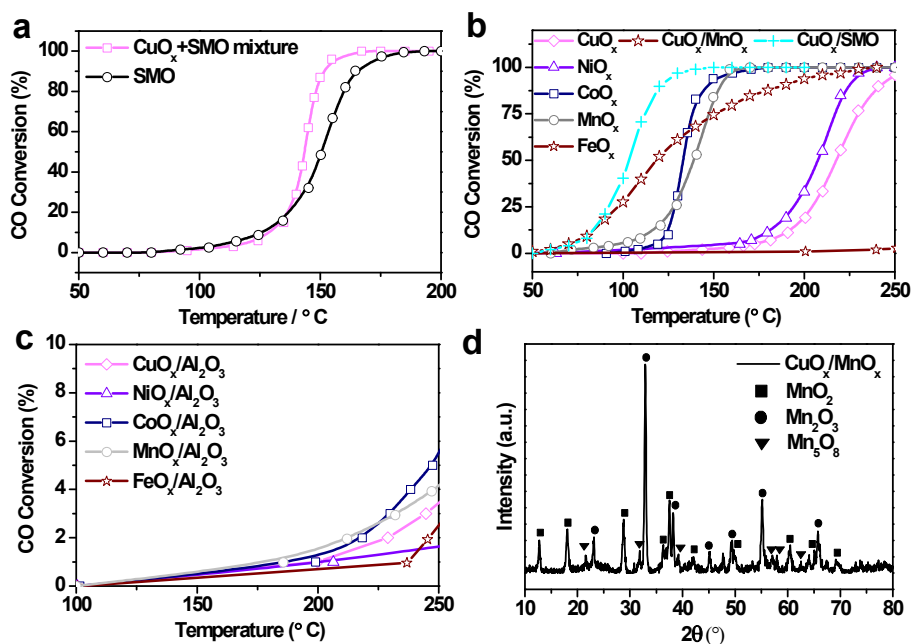


Fig. S3 Light off CO oxidation curves of (a) 1 wt.% CuO_x + SMO mechanical mixture and pure SMO; (b) pure MO_x, 1 wt.% CuO_x/MnO_x and 1 wt.% CuO_x/SMO; (c) 1 wt.% MO_x/Al₂O₃ samples, below 200 °C, CO conversion of MO_x/Al₂O₃ samples is negligible (<2%), which suggests that MO_x surface is not the active center for CO oxidation over MO_x/SMO composites; (d) XRD pattern of 1 wt.% CuO_x/MnO_x sample, the peaks of Cu or Cu₂O can't be detected in the pattern, as the same as the MO_x/SMO samples.

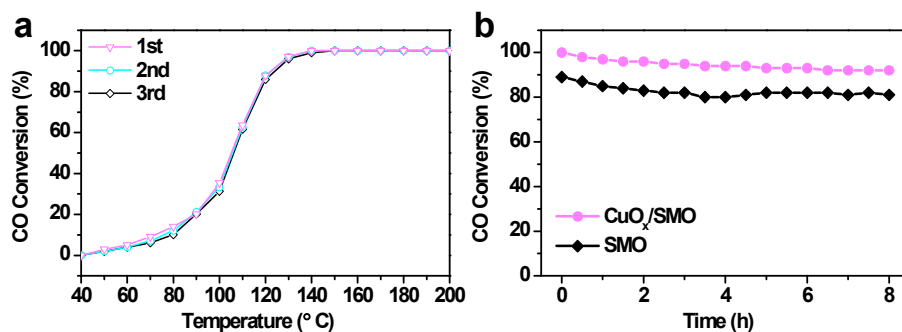


Fig. S4 (a) Reusability test for CO oxidation over CuO_x/SMO, the sample had been repeatedly tested for three times; (b) catalytic performance at 160 °C for CO oxidation versus time on line over the CuO_x/SMO and bare SMO, the feed gas was the same with that in the activity tests (1.3 %CO/10 %O₂/N₂ at 100 ml min⁻¹, with a space velocity of 120000 ml g⁻¹ h⁻¹).

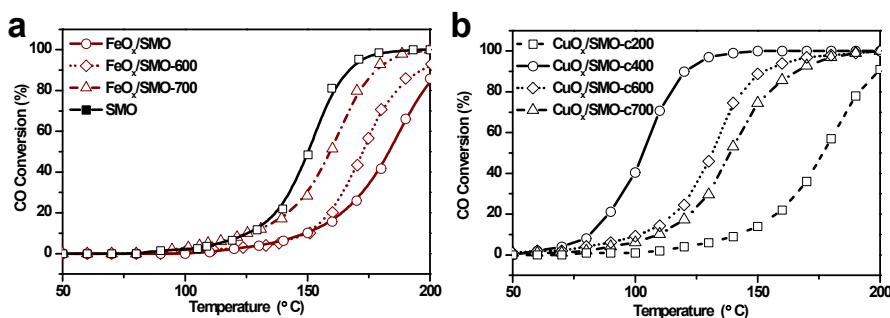


Fig. S5 Light off CO oxidation curves of (a) FeO_x/SMO, FeO_x/SMO-600, FeO_x/SMO-700 and bare SMO, where FeO_x/SMO-600 and FeO_x/SMO-700 are ascribed to FeO_x/SMO samples annealed at 600 and 700 °C in static air for 2h; (b) CuO_x/SMO samples which were calcined at 400, 600 and 700 °C for 4h after the precipitation process (in the catalysts preparation).

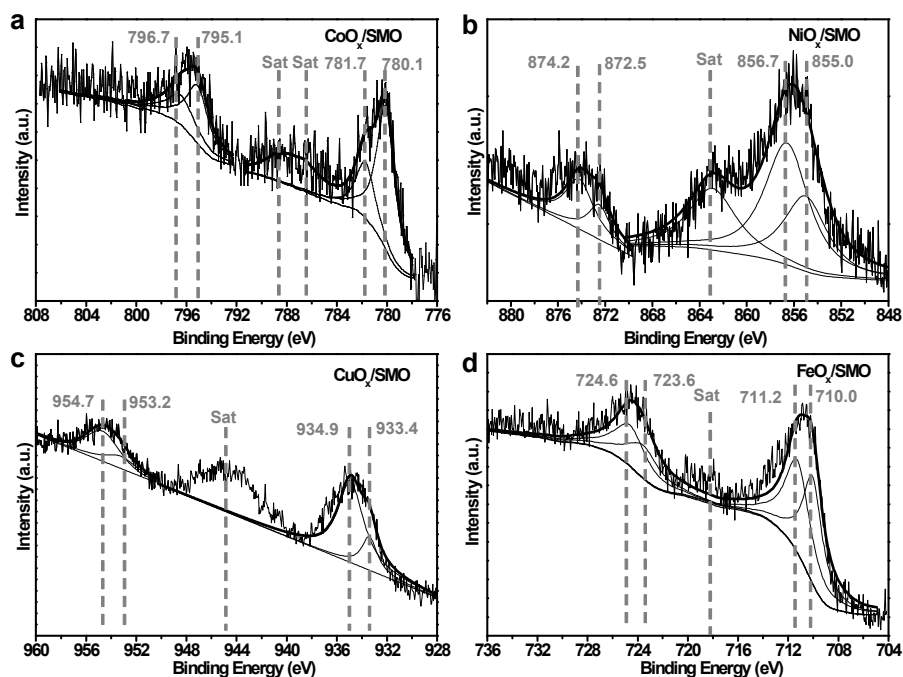


Fig. S6 XPS patterns of (a) Co 2p (b) Ni 2p (c) Cu 2p (d) Fe 2p over MO_x/SMO samples. Sat stand for the satellite peak.

The XPS pattern of Co, Ni and Cu in MO_x/SMO is given in Fig. S4. For Co 2p core levels, peak at 780.1 and 795.1 eV is assigned to Co^{3+} , the 781.7 and 796.7 eV is assigned to Co^{2+} .¹ For Ni 2p core levels, peak at 855.0 and 872.5 eV is assigned to Ni^{2+} , the 856.7 and 874.2 eV is assigned to Ni^{3+} .^{2,3} For Cu 2p core levels, peak at 933.4 and 953.2 eV is assigned to Cu^+ , the 934.9 and 954.7 eV is assigned to Cu^{2+} .^{4,5} For Fe 2p core levels, peak at 710.0 and 723.6 eV is assigned to Fe^{2+} , the 711.2 and 724.6 eV and is assigned to Fe^{3+} .^{6,7}

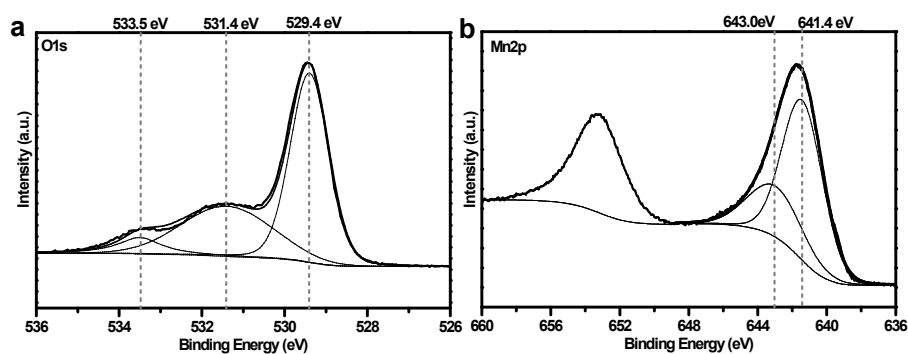


Fig. S7 XPS patterns of pure MnO_x .

The XPS pattern of Mn 2p and O 1s over pure MnO_x is shown in Fig. S5. Peak at 641.4 eV is identified as Mn^{3+} and the 643.0 eV is referred to Mn^{4+} . The atomic ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ in MnO_x is 0.43, the molar ratio of $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ is 0.59. For either MnO_x or bare SMO, their $\text{Mn}^{4+}/\text{Mn}^{3+}$ atomic ratio is much lower than that of MnO_x/SMO catalyst.

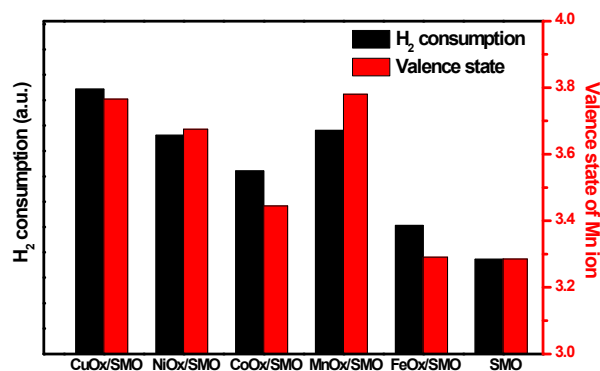


Fig. S8 H₂ consumptions in the reduction process of “Mn⁴⁺ to Mn³⁺” and the average valence states of Mn ion over the MO_x/SMO composites and pure SMO sample.

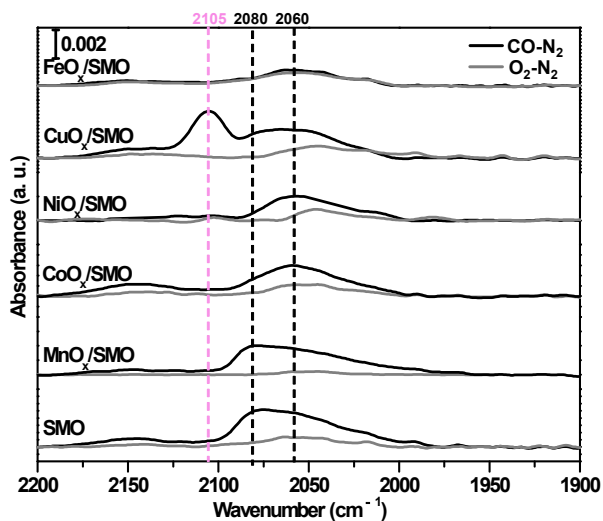


Fig. S9 linear CO adsorption spectra of MO_x/SMO and SMO.

Linear CO adsorption spectrum of MO_x/SMO series catalysts is shown in Fig. S6. The CO adsorption band on Mn can be observed over all SMO samples, which is located around 2080¹ and 2060¹ cm⁻¹^{8,9}. Among loaded MO_x/SMO, additional linear CO adsorption only appears over CuO_x-SMO catalyst at 2105¹ cm⁻¹, it's indicated by CO adsorption on Cu⁺^{10,11}.

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- 1 L. Fu, Z. Liu, Y. Liu, B. Han, P. Hu, L. Cao, D. Zhu, *Adv. Mater.*, 2005, 17, 217-221.
 - 2 A. R. Gonzalez-Elipe, J. P. Holgado, R. Alvarez, C. Munuera, *J. Phys. Chem.*, 1992, 96, 3080-3086.
 - 3 A. F. Carley, S. D. Jackson, J. N. O'Shea, M. W. Roberts, *Surf. Sci.*, 1999, 440, 868-874.
 - 4 H. Einaga, A. Kiya, S. Yoshioka, Y. Teraoka., *Catal. Sci. Technol.*, 2014, 4, 3713-3722.
 - 5 S. Sun, D. Mao, J. Yu, Z. Yang, G. Lu, Z. Ma, *Catal. Sci. Technol.*, 2015, 5, 3166-3181
 - 6 H. Einaga, A. Kiya, S. Yoshioka, Y. Teraoka., *Catal. Sci. Technol.*, 2014, 4, 3713-3722.
 - 7 S. Sun, D. Mao, J. Yu, Z. Yang, G. Lu, Z. Ma, *Catal. Sci. Technol.*, 2015, 5, 3166-3181
 - 8 L. Cai, Z. H. Hu, P. Branton, W. Li, *Chinese J. Catal.*, 2014, 35, 159-167.
 - 9 B. D. Adams, R. M. Asmussen, A. Chen, R. C. Mawhinney, *Can. J. Chem.*, 2011, 89, 1445-1456.
 - 10 W.W. Wang, W.Z. Yu, P.P. Du, H. Xu, Z. Jin, R. Si, C. Ma, S. Shi, C.J. Jia, C.H. Yan, *ACS Catal.*, 2017, 7, 1313-1329.
 - 11 Y. Tang, L. Dong, C. Deng, M. Huang, B. Li, H. Zhang, *Catal. Commun.*, 2016, 78, 33-36.