

Supporting Information

Mesoporous Mn-Ti amorphous oxides: a robust low-temperature NH₃-SCR catalyst

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In order to comprehensively evaluate the activity of Mn-Ti amorphous oxide catalysts in this study, the $\text{MnO}_x/\text{TiO}_2(\text{im})$ and $\text{MnO}_x\text{-}\text{TiO}_2(\text{co})$ catalysts with the same ratio of $n_{\text{Mn}}/(n_{\text{Ti}}+n_{\text{Mn}})$ in $\text{Mn}_{0.5}\text{Ti}_{0.5}$ were prepared as comparisons by conventional impregnation and co-precipitation methods, respectively.

For impregnation method, manganese nitrate and P25 were used as the precursor and support, respectively. After impregnation, the excess water was removed in a rotary evaporator. The sample was dried at 60 °C for 2 days and then calcined at 500 °C for 4 h to obtain $\text{MnO}_x/\text{TiO}_2(\text{im})$ catalyst.

For co-precipitation method, titanium sulphate and manganese nitrate were dissolved completely in 100 mL deionized water and stirred. Then ammonia water was gradually added until the pH value of mixed solution reached 10. The mixture was stirred at room temperature for 3 h and then aged for 1 h. The precipitation was filtered and washed with deionized water for five times. The sample was dried at 60 °C for 2 days and then calcined at 500 °C for 4 h to obtain $\text{MnO}_x\text{-}\text{TiO}_2(\text{co})$ catalyst.

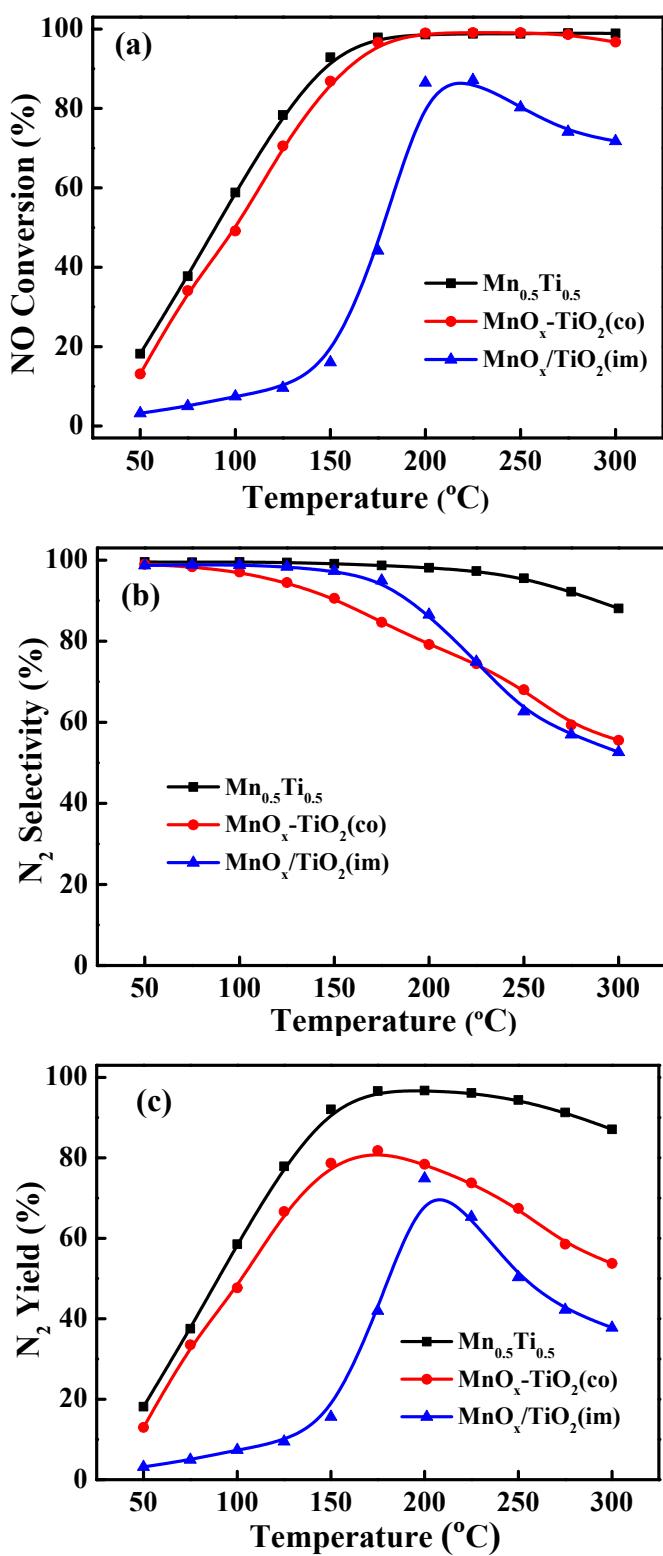


Fig. S1 NH₃-SCR performance of Mn_{0.5}Ti_{0.5}, MnO_x-TiO₂(co) and MnO_x/TiO₂(im)

catalysts: (a) NO conversion; (b) N₂ selectivity; (c) N₂ yield. Reaction conditions:

[NO] = [NH₃] = 1000 ppm, [O₂] = 3 vol.% and N₂ as balance gas.

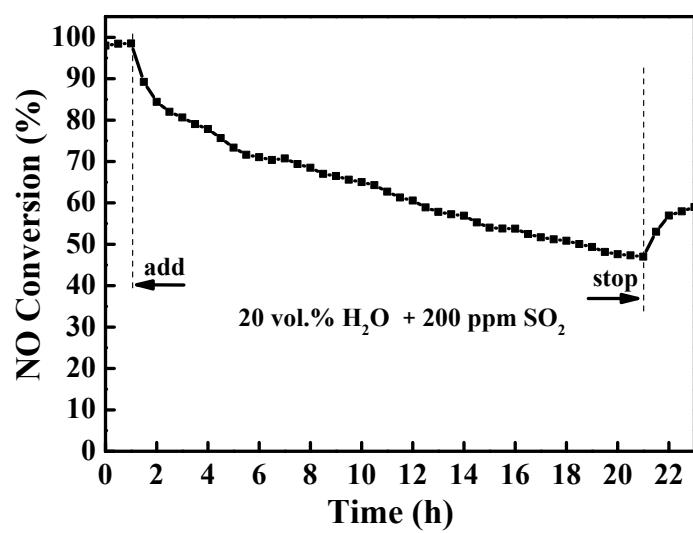


Fig. S2 $\text{H}_2\text{O} + \text{SO}_2$ durability tests of $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst at 200 °C. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 1000 \text{ ppm}$, $[\text{SO}_2] = 200 \text{ ppm}$, $[\text{H}_2\text{O}] = 20 \text{ vol.\%}$, $[\text{O}_2] = 3 \text{ vol.\%}$, balance N_2 .

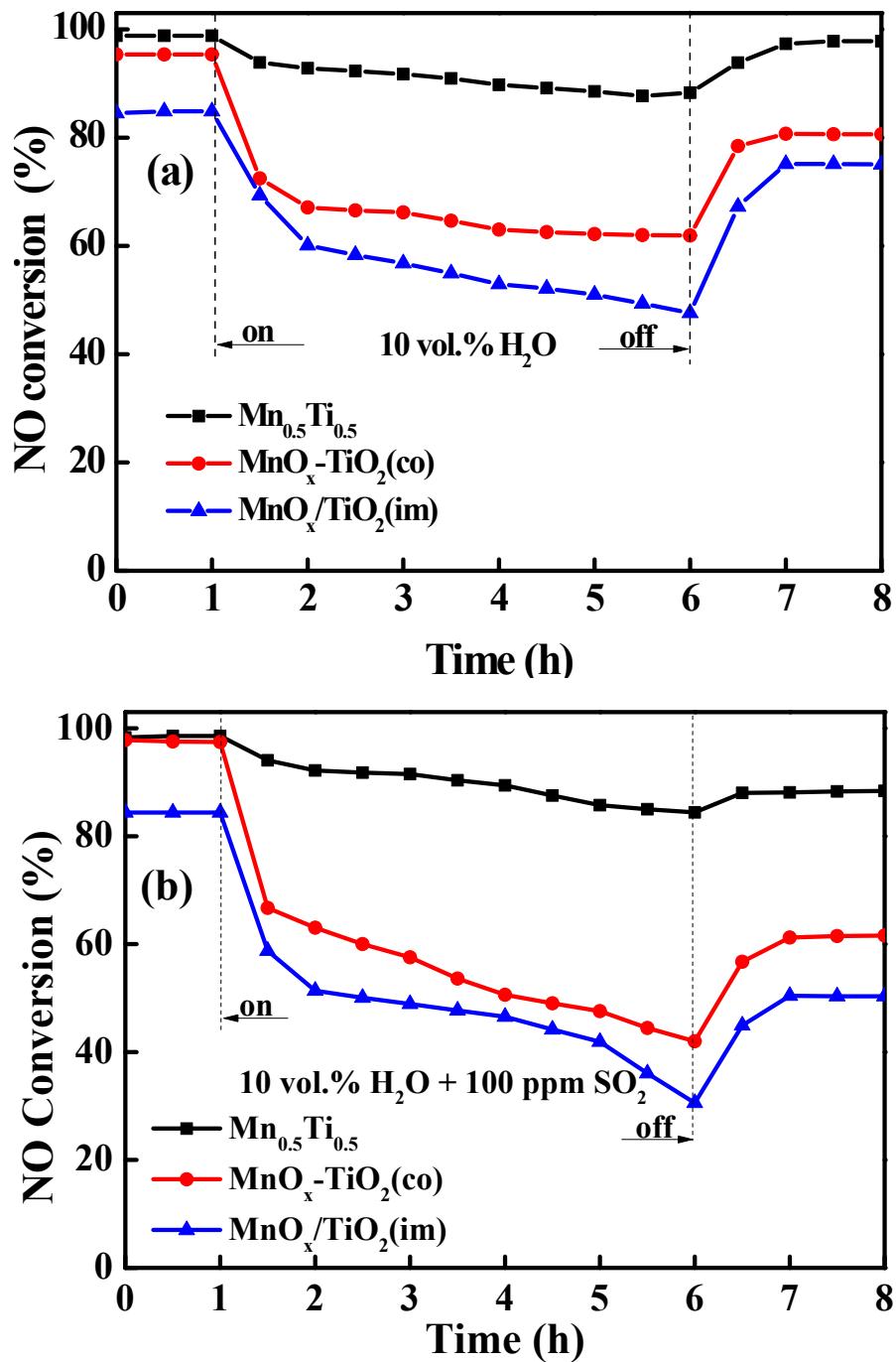


Fig. S3 (a) H₂O and (b) H₂O + SO₂ durability tests of Mn_{0.5}Ti_{0.5}, MnO_x-TiO₂(co) and MnO_x/TiO₂(im) catalysts at 200 °C. Reaction conditions: [NO] = [NH₃] = 1000 ppm, [SO₂] = 100 ppm, [H₂O] = 10 vol.%, [O₂] = 3 vol.%, balance N₂.

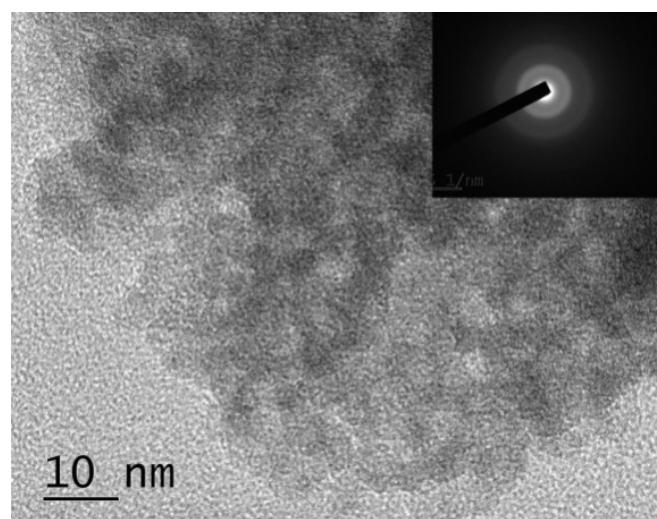


Fig. S4 HRTEM image and SAED pattern (inset) of the Mn_{0.3}Ti_{0.7} catalyst.

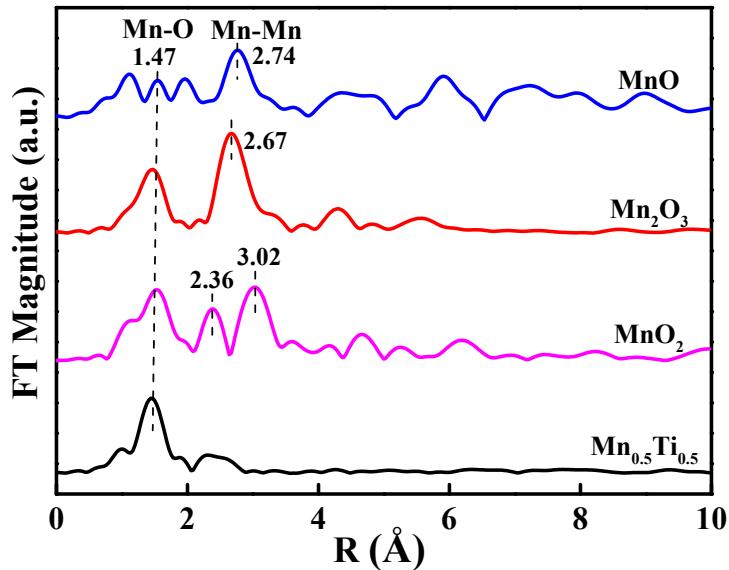


Fig. S5 Mn K-edge radial structure functions of reference compounds and $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst.

Fig. S5 presents the radial structure functions of Mn K-edge of the reference oxides (MnO , Mn_2O_3 , and MnO_2) and the $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst. As shown in **Fig. S5**, All spectra of the samples showed the coordination peaks with different intensities at 1.47 \AA , which could be ascribed to Mn-O band, while the peaks at 2-4 \AA were attributed to Mn-Mn bonds.^{1,2} Furthermore, the EXAFS spectrum for $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst was different from that of the reference oxide, indicating that the unique chemical states of manganese species in $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst caused by the strong interaction between Mn and Ti.

- [1] Q. Tang, X. Huang, C. Wu, P. Zhao, Y. Chen and Y. Yang, *J. Mol. Catal. A: Chem.*, 2009, 306, 48-53.
- [2] Q. Li, M. Meng, H. Xian, N. Tsubaki, X. Li, Y. Xie, T. Hu and J. Zhang, *Environ. Sci. Technol.*, 2010, 44, 4747-4752.

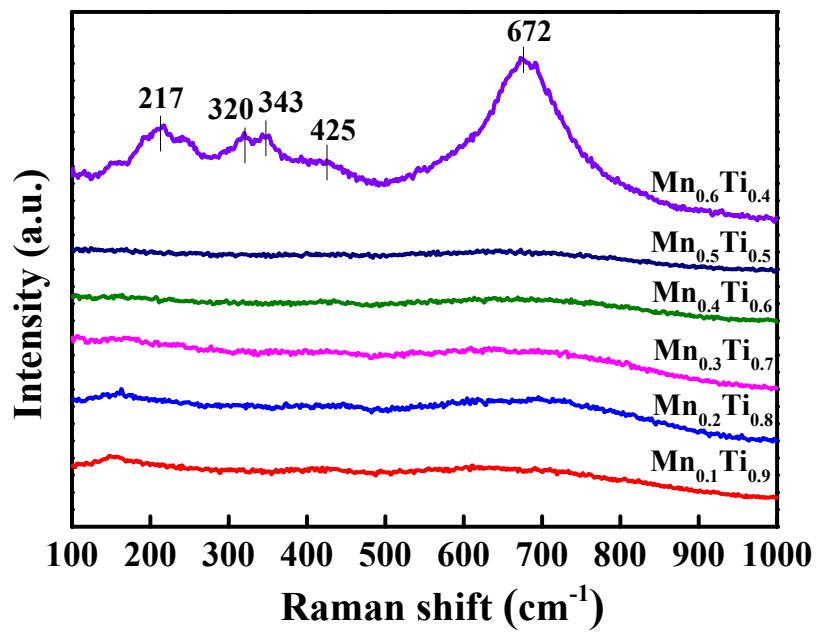


Fig. S6 Raman spectra of Mn_aTi_{1-a} catalysts.

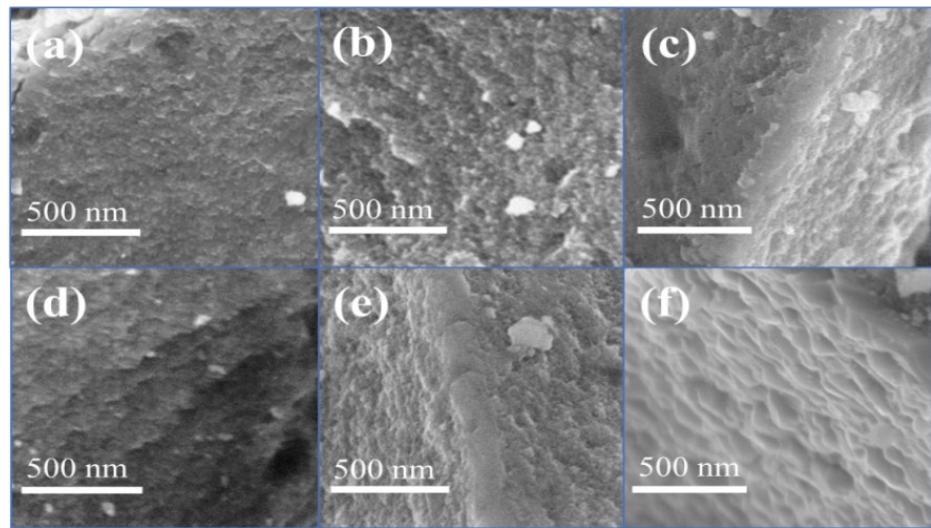


Fig. S7 SEM images of (a) $\text{Mn}_{0.1}\text{Ti}_{0.9}$, (b) $\text{Mn}_{0.2}\text{Ti}_{0.8}$, (c) $\text{Mn}_{0.3}\text{Ti}_{0.7}$, (d) $\text{Mn}_{0.4}\text{Ti}_{0.6}$, (e) $\text{Mn}_{0.5}\text{Ti}_{0.5}$ and (f) $\text{Mn}_{0.6}\text{Ti}_{0.4}$.

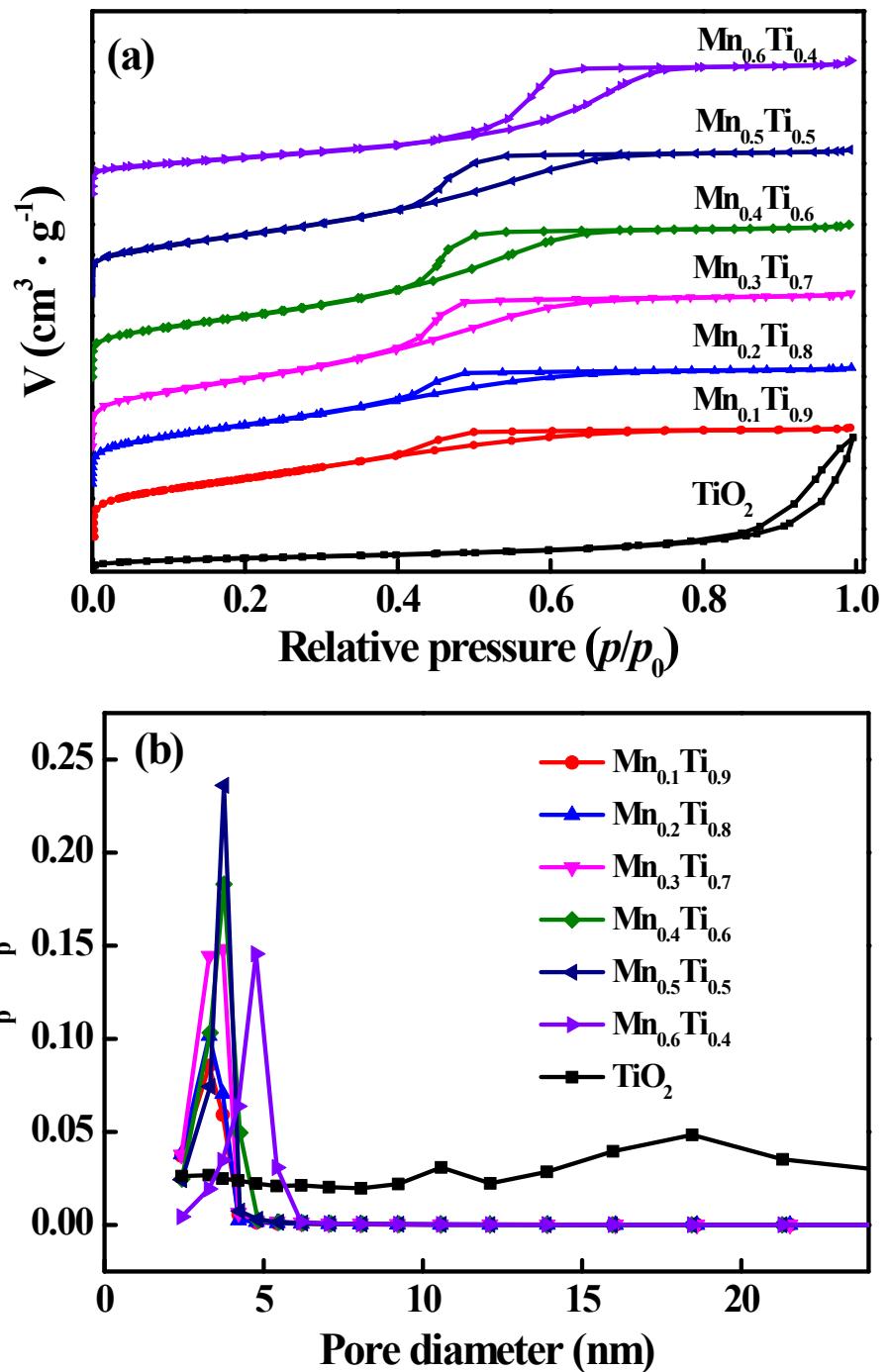


Fig. S8 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of the Mn_xTi_{1-x} and TiO₂ catalysts.

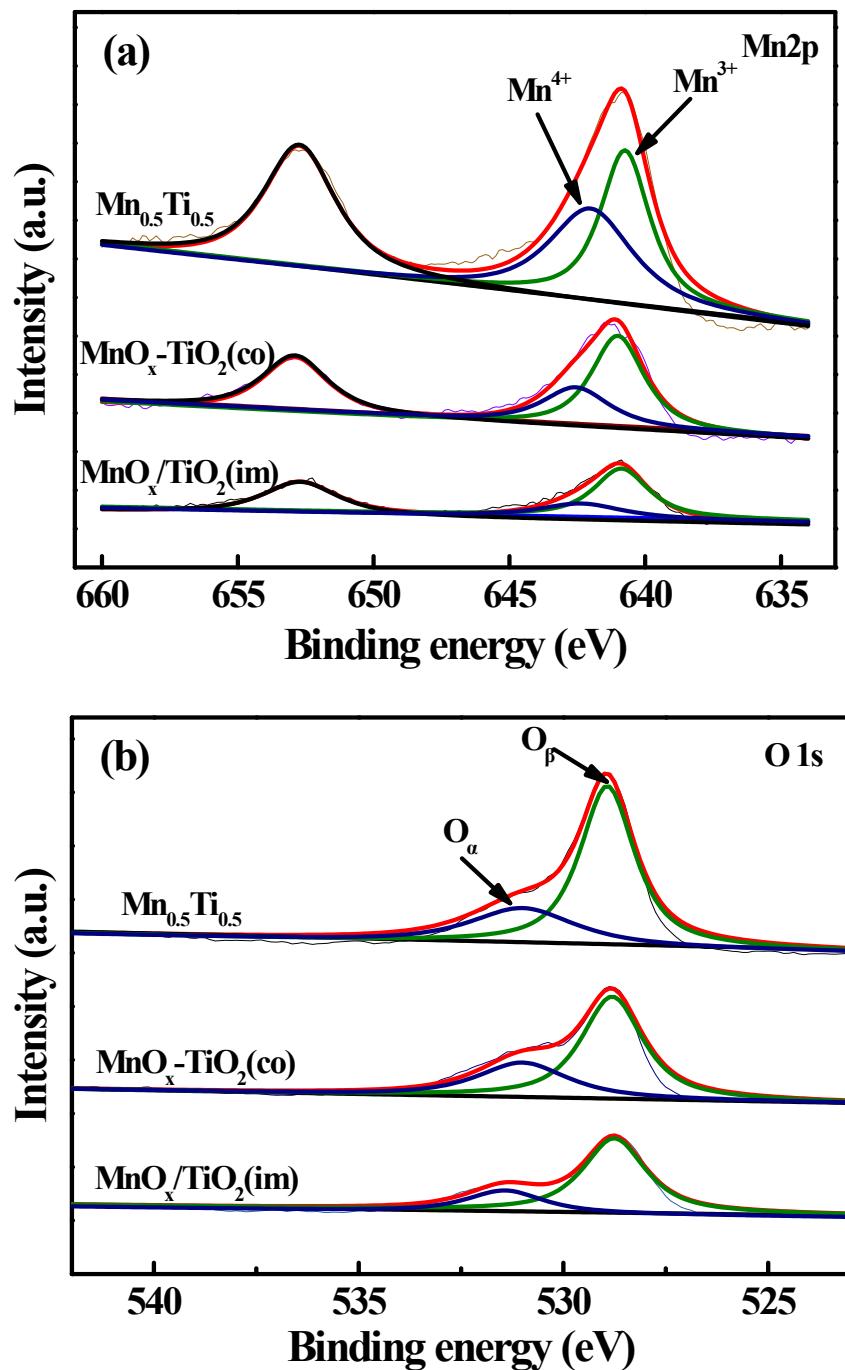


Fig. S9 (a) Mn 2p and (b) O 1s XPS spectra of $\text{Mn}_{0.5}\text{Ti}_{0.5}$, $\text{MnO}_x\text{-TiO}_2(\text{co})$ and $\text{MnO}_x/\text{TiO}_2(\text{im})$ catalysts.

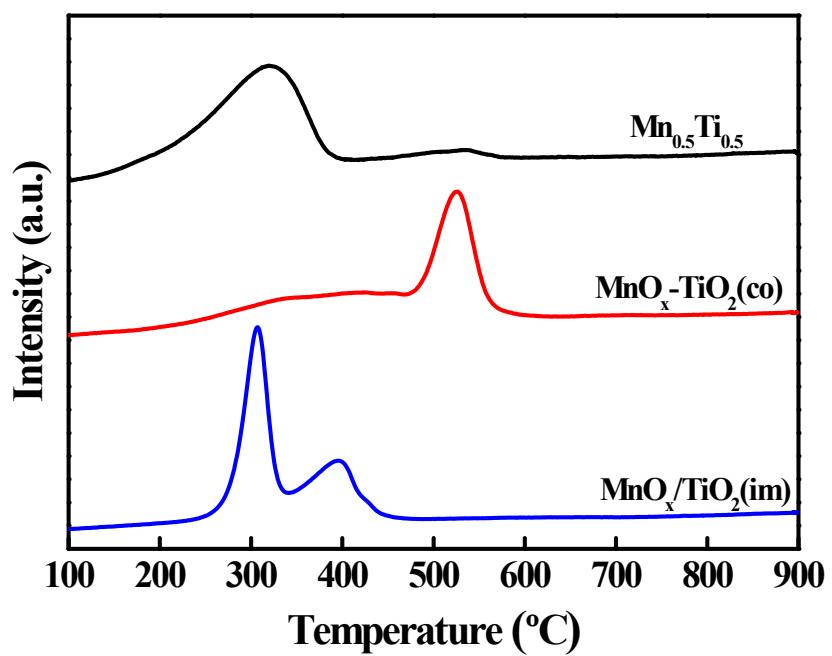


Fig. S10 H₂-TPR profiles of $\text{Mn}_{0.5}\text{Ti}_{0.5}$, $\text{MnO}_x\text{-TiO}_2(\text{co})$ and $\text{MnO}_x/\text{TiO}_2(\text{im})$ catalysts.

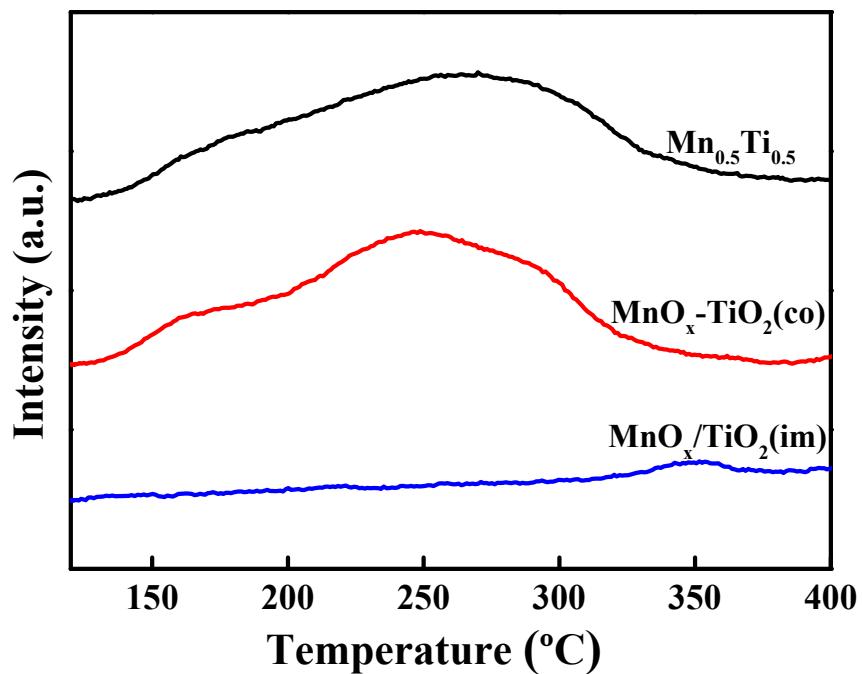


Fig. S11 NH₃-TPD profiles of $\text{Mn}_{0.5}\text{Ti}_{0.5}$, $\text{MnO}_x\text{-TiO}_2(\text{co})$ and $\text{MnO}_x/\text{TiO}_2(\text{im})$ catalysts.

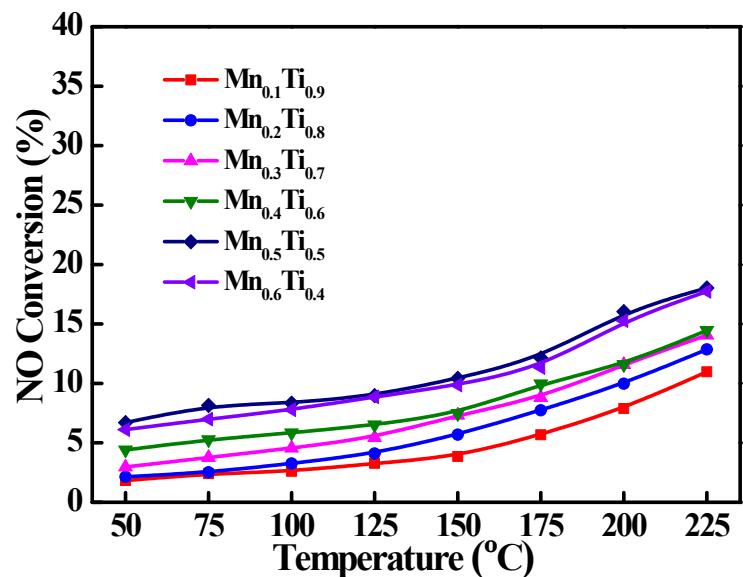


Fig. S12 NO oxidation activities to NO_2 over the $\text{Mn}_a\text{Ti}_{1-a}$ catalysts. Conditions: $[\text{NO}] = 1000 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol.\%}$ and N_2 as balance gas.

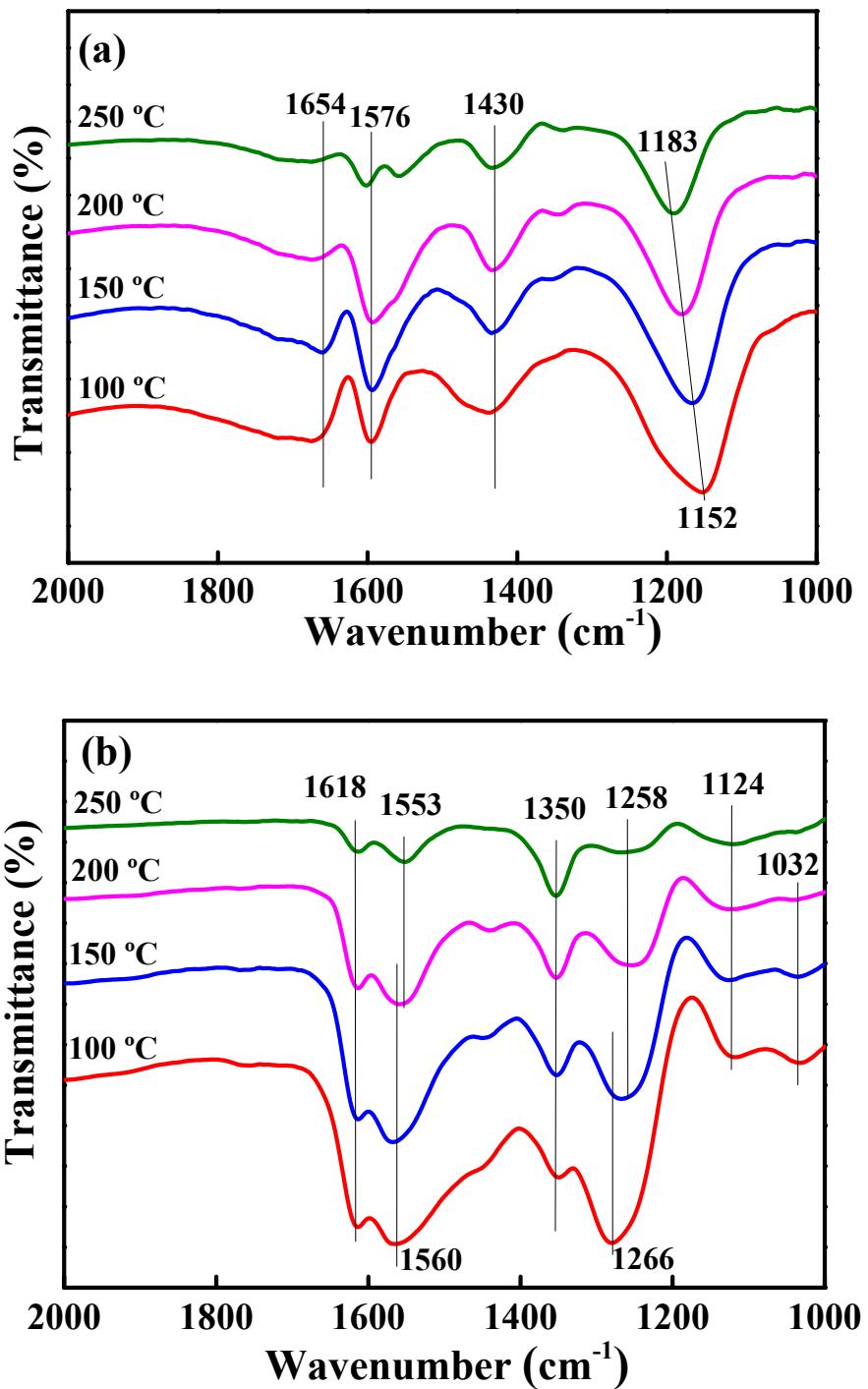


Fig. S13 *In-situ* FTIR spectra of (a) NH_3 and (b) $\text{NO} + \text{O}_2$ adsorption over the $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst at different temperatures. Conditions: $[\text{NH}_3] = 1000$ ppm (when used), $[\text{NO}] = 1000$ ppm (when used), $[\text{O}_2] = 3$ vol.% (when used), balance N_2 .

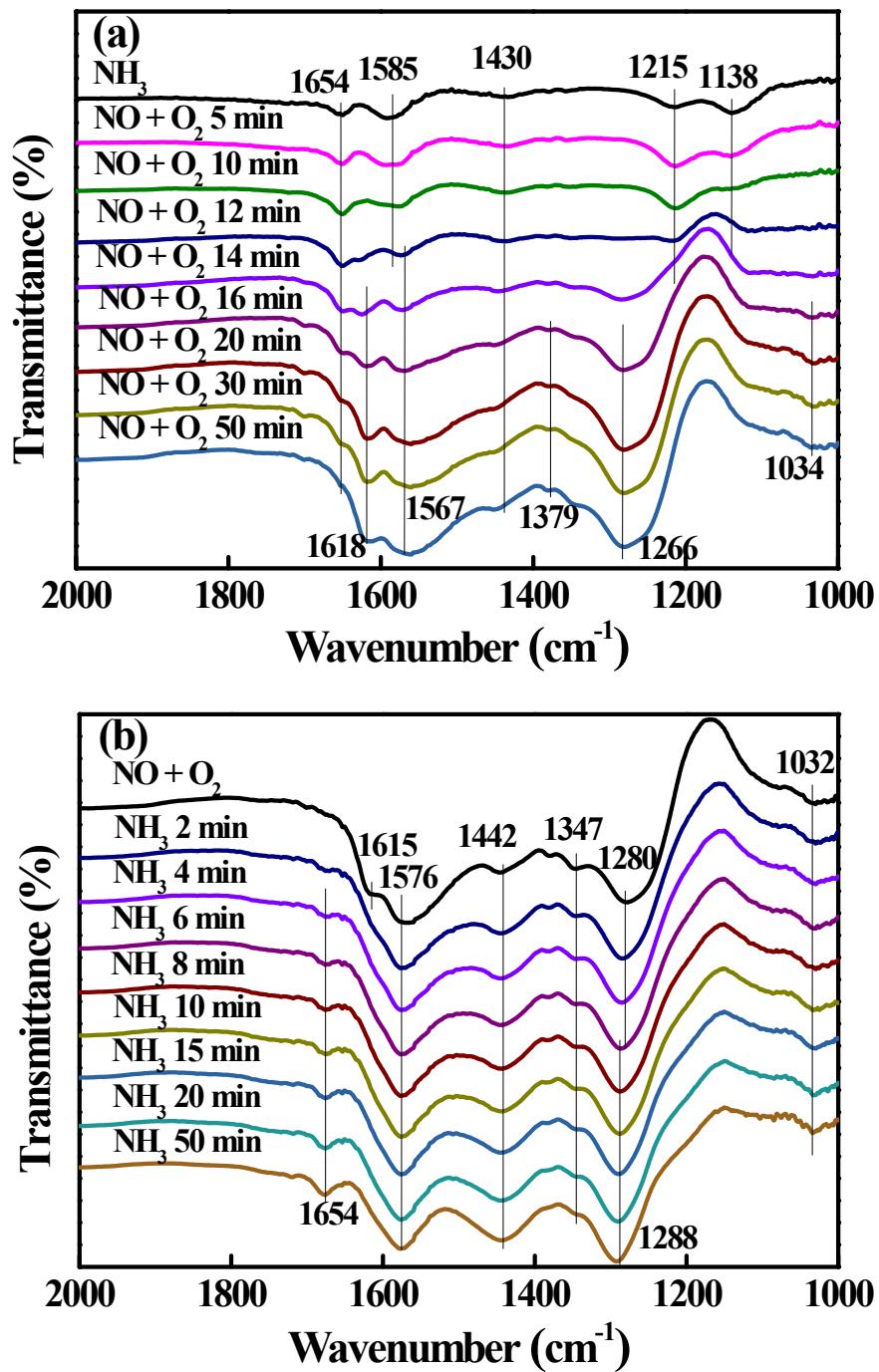


Fig. S14 *In-situ* FTIR spectra of (a) $\text{NO} + \text{O}_2$ reacted with pre-adsorbed NH_3 species and (b) NH_3 reacted with pre-adsorbed NO_x species over the $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst at 100 $^{\circ}\text{C}$.

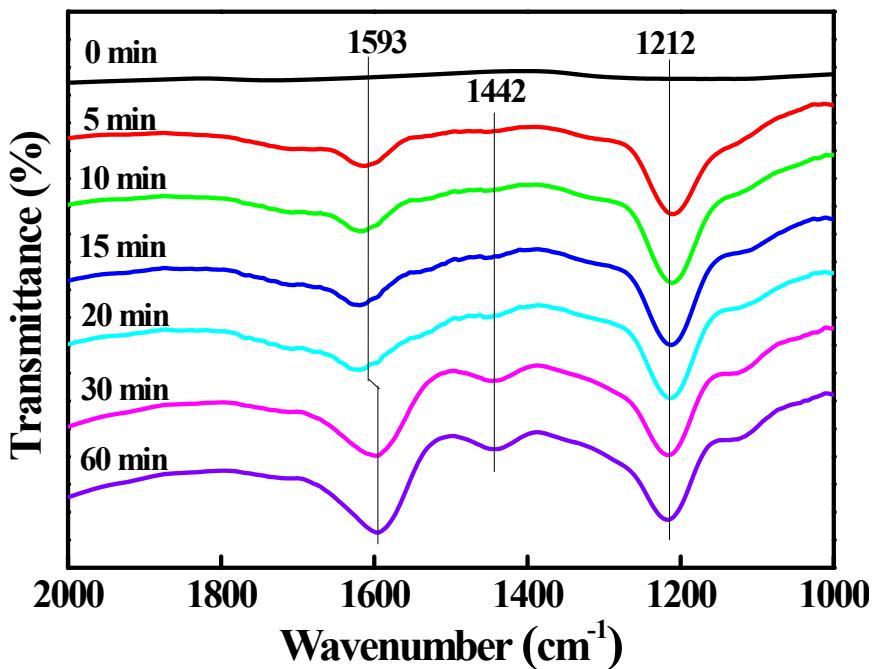


Fig. S15 *In-situ* FTIR spectra of $\text{NH}_3 + \text{NO} + \text{O}_2$ absorption over the $\text{Mn}_{0.5}\text{Ti}_{0.5}$ catalyst with different times at $150\text{ }^\circ\text{C}$. Conditions: $[\text{NH}_3] = [\text{NO}] = 1000\text{ ppm}$, $[\text{O}_2] = 3\text{ vol.\%}$, balance N_2 at $150\text{ }^\circ\text{C}$.

Table S1 H₂ consumption and atomic ratio of Mn_{*a*}Ti_{*l-a*} catalysts

Catalysts	H ₂ consumption (cm ³ ·g _{cat} ⁻¹)	Acid amount (mmol·g _{cat} ⁻¹)	Surface atomic concentration (%)			Atomic ratio (%)	
			Mn	O	Ti	Mn ⁴⁺ /(Mn ⁴⁺ +Mn ³⁺)	O _{<i>a</i>} /(O _{<i>a</i>} +O _{<i>B</i>})
Mn _{0.5} Ti _{0.5}	69.46	0.37	13.34	71.48	15.18	46.30	23.87
MnO _x -TiO ₂ (co)	68.03	0.32	10.05	75.35	14.60	33.71	32.06
MnO _x /TiO ₂ (im)	59.03	0.01	11.53	71.91	16.56	30.48	26.92