

Supplementary information

1. The detailed experimental parameters of samples are listed in Table 1S. The samples' chemical formula is express as $Mn_aCa_bO_x(CO_3)_y-M$. 'a/b' represents the ratio of Mn and Ca, M represents the factors in preparation such as precursor, calcination temperature and etc.

Table S1. Experimental drug parameters of samples.

	$Mn(CH_3COO)_2 \cdot 4H_2O$	$Ca(NO_3)_2 \cdot 4H_2O$	$CaCO_3$	Na_2CO_3
$Mn_6Ca_1O_x(CO_3)_y-Ca(NO_3)_2$	0.0204 mol	0.0034 mol		0.0238mol
$Mn_{12}Ca_1O_x(CO_3)_y$	0.0204 mol	0.0017 mol		0.0221mol
$Mn_{10}Ca_1O_x(CO_3)_y$	0.0204 mol	0.00204 mol		0.0224mol
$Mn_8Ca_1O_x(CO_3)_y$	0.0204 mol	0.00255 mol		0.0229mol
$Mn_6Ca_1O_x(CO_3)_y$	0.0204 mol	0.0034 mol		0.0238mol
$Mn_4Ca_1O_x(CO_3)_y$	0.0204 mol	0.0051 mol		0.0255mol
$Mn_{10}Ca_1O_x(CO_3)_y-CaCO_3$	0.0204 mol		0.00204mol	
$Mn_6Ca_1O_x(CO_3)_y-CaCO_3$	0.0204 mol		0.0034 mol	

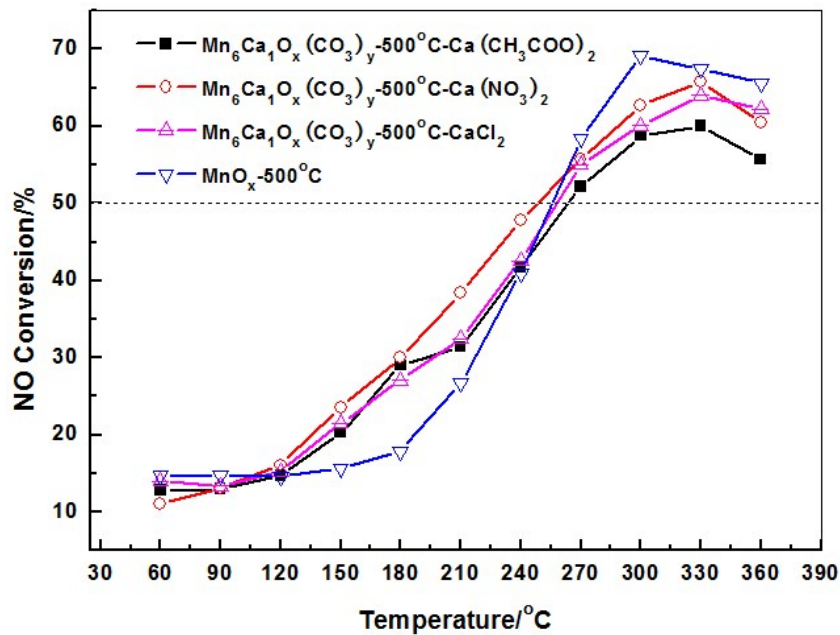
	$Mn(CH_3COO)_2 \cdot 4H_2O$	$CaCl_2$	$Ca(CH_3COO)_2 \cdot H_2O$	Na_2CO_3
$Mn_6Ca_1O_x(CO_3)_y-Ca(CH_3COO)_2$	0.0204 mol		0.0034 mol	0.0238mol
$Mn_6Ca_1O_x(CO_3)_y-CaCl_2$	0.0204 mol	0.0034 mol		0.0238mol
MnO_x	0.0204 mol			0.0204mol

2. The activity results for the $Mn-Ca-O_x-(CO_3)_y$ catalysts doped with different calcium precursors and the MnO_x catalyst are shown in Figure S1(a). The catalysts doped with

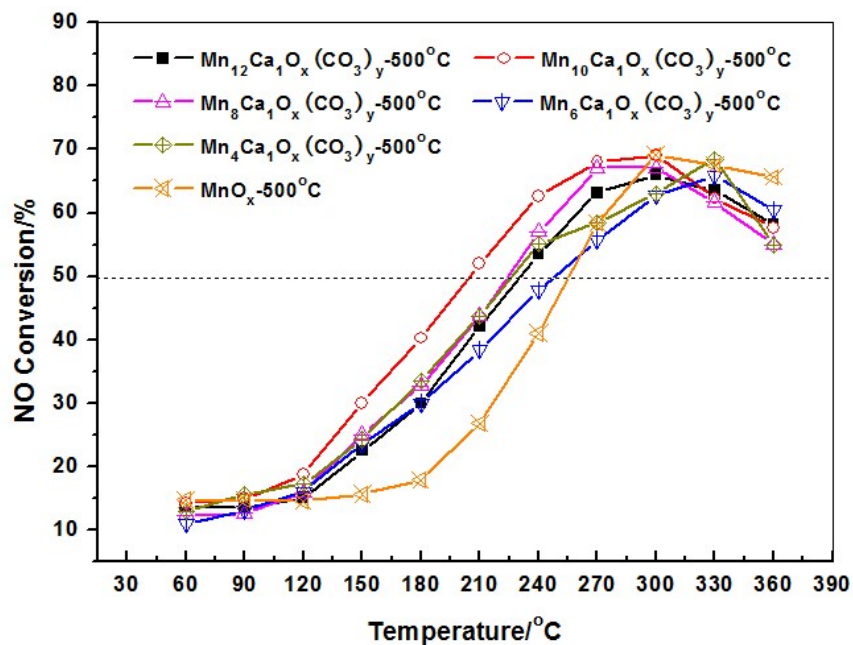
calcium improved the catalytic activity compared to that of MnO_x in a low reaction temperature range ($< 240\text{ }^\circ\text{C}$). In addition, different Ca precursors influenced the catalytic activity. When the reaction temperature was lower than $240\text{ }^\circ\text{C}$, the NO conversion trend was as follows: $\text{Mn}_6\text{Ca}_1\text{O}_x(\text{CO}_3)_y-500^\circ\text{C}-\text{Ca}(\text{NO}_3)_2 > \text{Mn}_6\text{Ca}_1\text{O}_x(\text{CO}_3)_y-500^\circ\text{C}-\text{CaCl}_2 > \text{Mn}_6\text{Ca}_1\text{O}_x(\text{CO}_3)_y-500^\circ\text{C}-\text{Ca}(\text{CH}_3\text{COO})_2$.

However, the maximum NO conversion was achieved over the $\text{MnO}_x-500\text{ }^\circ\text{C}$ catalyst at a high temperature (300°C).

Based on these results, doping with calcium can enhance the NO catalytic oxidation activity in a low temperature range. Therefore, the calcium content may be an important factor that can improve the maximum conversion performance of the $\text{Mn}-\text{Ca}-\text{O}_x-(\text{CO}_3)_y$ catalysts. As shown in Figure S1(b), the same maximum NO conversion was observed compared to $\text{MnO}_x-500\text{ }^\circ\text{C}$ when the ratio of Mn to Ca was 10:1. In addition, the conversion of $\text{Mn}_{10}\text{Ca}_1\text{O}_x(\text{CO}_3)_y-500\text{ }^\circ\text{C}$ reached more than 50% at $210\text{ }^\circ\text{C}$, which is considered excellent performance at low temperature. However, the conversion of $\text{MnO}_x-500\text{ }^\circ\text{C}$ only reached 30% at the same reaction temperature, and the approximately 20% promotion was remarkable. Figure S1(b) shows a tendency for samples doped with different calcium contents to enhance the catalytic activity compared to MnO_x in the low-temperature zone.



(a)



(b)

Figure.S1 Catalytic Oxidation activity of NO on catalysts doped with different calcium precursors (a) and calcium content (b).

3. The changing of NO₂ concentration in tail gas with temperature and reaction time are showed in Figure S1 and S2. It indicates that NO was effective oxidized to NO₂. The stability of the catalyst in high temperature is better. However, the ratio of NO conversion to NO₂ formation is not 1:1, there are three possible reasons. First, a small amount of NO can react with NO₂ to generate N₂O₃, but we cannot detect the N₂O₃ by the KM9106 gas analyser; second, a small amount of NO₂ can be adsorbed on the catalyst surface, and from DRIFTS results, we can see that NO₂ (1625 cm⁻¹) and N₂O₄ (1710 cm⁻¹) were observed on the catalyst surface during the catalysis reaction, reference 35 had the similar results; third, sometimes, the accuracy of equipment is not so ideal, the minor deviation may be existed. In the further research, we will further research the N balance and the mechanism of deactivation.

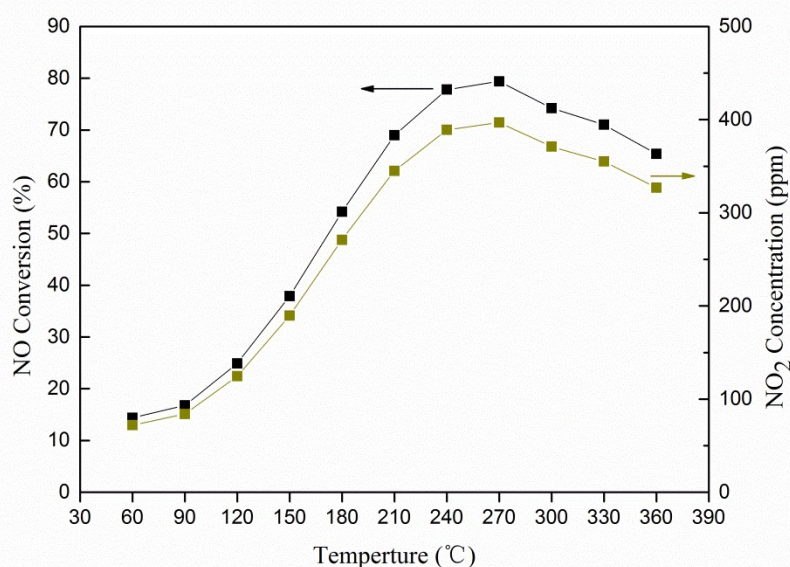


Figure S2. Catalytic Oxidation activity of NO on Mn₁₀Ca₁O_x(CO₃)_y (500 ppm NO, 3% O₂, 30000h⁻¹ GHSV).

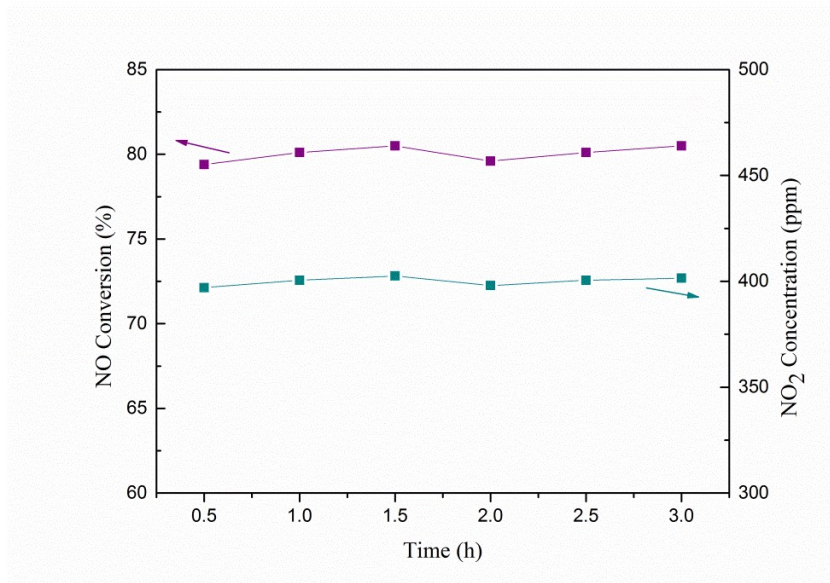


Figure S3. Catalytic Oxidation activity of NO on $Mn_{10}Ca_1O_x(CO_3)_y$ for a long-playing (500 ppm NO, 3% O_2 , 30000h⁻¹ GHSV).

4. In this research, the catalytic oxidation activity of used catalysts was studied. As shown in the Figure S4, the activities of used catalysts (one time and two times) were decreased slightly, but they also had good ability to catalytic oxidation of NO. Thus, this kind of catalyst has a good stability and reproducibility.

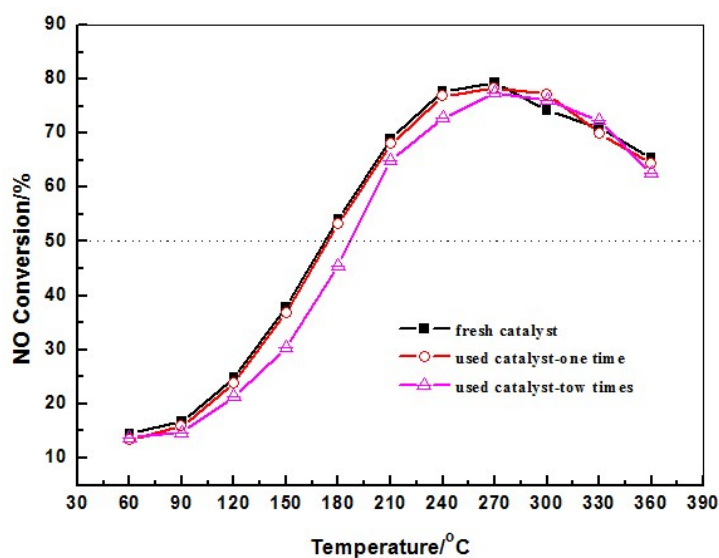


Figure S4. Catalytic oxidation activity of NO on used catalysts (500 ppm NO, 3% O_2 , 30000h⁻¹ GHSV).

5. $\text{Mn-Ca-O}_x\text{-(CO}_3)_y$ prepared by mixing method was tested, the results are shown in Figure S5. From Figure S5, it could be seen that adding CaCO_3 directly also could improve catalytic activity, but it had a certain difference with the co-precipitation method. Firstly, $\text{Mn}_6\text{Ca}_1\text{O}_x\text{(CO}_3)_y\text{-CaCO}_3\text{-350 }^\circ\text{C}$ showed higher activity in high-temperature range (>210 $^\circ\text{C}$) which got the maximum conversion at 270°C . $\text{Mn}_{10}\text{Ca}_1\text{O}_x\text{(CO}_3)_y\text{-CaCO}_3\text{-350 }^\circ\text{C}$ did not have the same activity curve with $\text{Mn}_{10}\text{Ca}_1\text{O}_x\text{(CO}_3)_y\text{-350 }^\circ\text{C}$ which was prepared before. The activity curves of $\text{Mn}_{10}\text{Ca}_1\text{O}_x\text{(CO}_3)_y\text{-CaCO}_3\text{-350 }^\circ\text{C}$ and $\text{MnO}_x\text{-350 }^\circ\text{C}$ were similar, which indicate that small addition of CaCO_3 in preparation by mixing method had low effect of activity. But $\text{Mn}_6\text{Ca}_1\text{O}_x\text{(CO}_3)_y\text{-CaCO}_3\text{-350 }^\circ\text{C}$ showed high activity. This result can prove that the CaCO_3 can play a stimulative role on catalytic oxidation of NO.

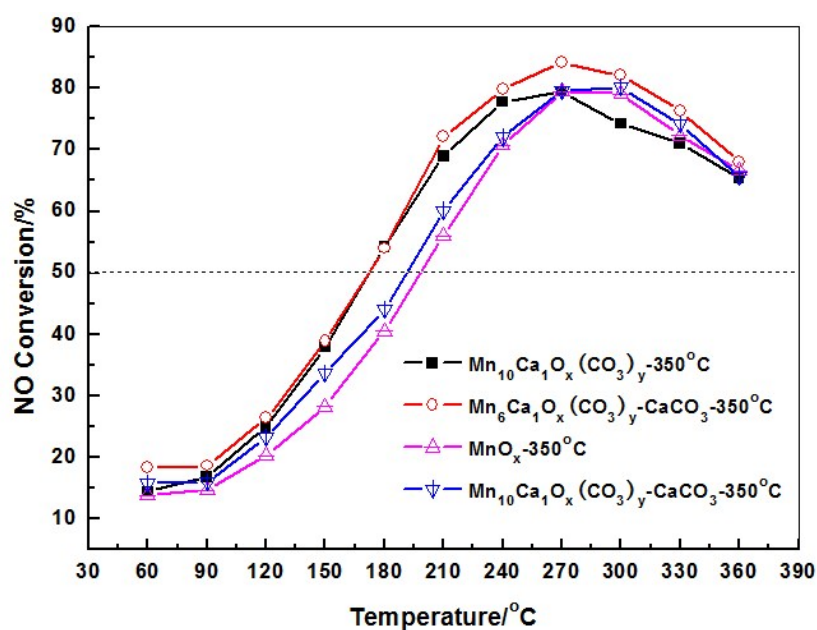


Figure S5. Catalytic oxidation activity of NO on $\text{Mn-Ca-O}_x\text{-(CO}_3)_y$ catalysts with two methods (500 ppm NO, 3% O_2 , 30000h^{-1} GHSV).

6. The effect of Ca doping can be clarified during the mechanism research about NO catalytic oxidation process over $\text{MnO}_x\text{-350 }^\circ\text{C}$ and $\text{Mn}_{10}\text{Ca}_1\text{O}_x\text{(CO}_3)_y\text{-350 }^\circ\text{C}$ catalysts

at low temperature zone (<240 °C) respectively. Thus, in this section, the DRIFT method was used to analyze the NO catalytic oxidation reaction process over MnO_x-350 °C and Mn₁₀Ca₁O_x(CO₃)_y-350 °C catalysts at different reaction temperature of 130 °C, 200 °C, and 270 °C. The whole process was divided into two part: NO adsorption (Only NO/N₂ was injected) and NO oxidation (Both O₂ and NO/N₂ were injected). The compounds produced on the two catalysts were summarized in Table S2 and S3.

Table S2 Compounds produced on catalysts in the progress of NO adsorption

	Reaction at 130 °C		Reaction at 200 °C		Reaction at 270 °C	
	MnO _x	Mn ₁₀ Ca ₁ O _x (CO ₃) _y	MnO _x	Mn ₁₀ Ca ₁ O _x (CO ₃) _y	MnO _x	Mn ₁₀ Ca ₁ O _x (CO ₃) _y
NO ₂ ⁻ (bridging bidentate)	√					√
NO ₃ ⁻ (monodentate)		√	√	√	√	√
NO					√	
NO ₂ ⁻ (uncertain form)					√	

Table S3 Compounds produced on catalysts in the progress of NO oxidation

	Reaction at 130 °C		Reaction at 200 °C		Reaction at 270 °C	
	MnO _x	Mn ₁₀ Ca ₁ O _x (CO ₃) _y	MnO _x	Mn ₁₀ Ca ₁ O _x (CO ₃) _y	MnO _x	Mn ₁₀ Ca ₁ O _x (CO ₃) _y
NO ₂ ⁻ (bridging bidentate)	√					
NO ₃ ⁻ (bridging bidentate)	√				√	√
NO ₃ ⁻ (monodentate)		√	√		√	√
NO ₃ ⁻ (chelating bidentate)				√		
NO ₂				√	√	√

N ₂ O ₄	√	√	√
NO		√	
NO ₂ (nitro)		√	
N-OH		√	
