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### Supplementary Information

## Investigation on the Active Sites for NO Oxidation Reaction over MnO<sub>x</sub>-CeO<sub>2</sub> catalysts

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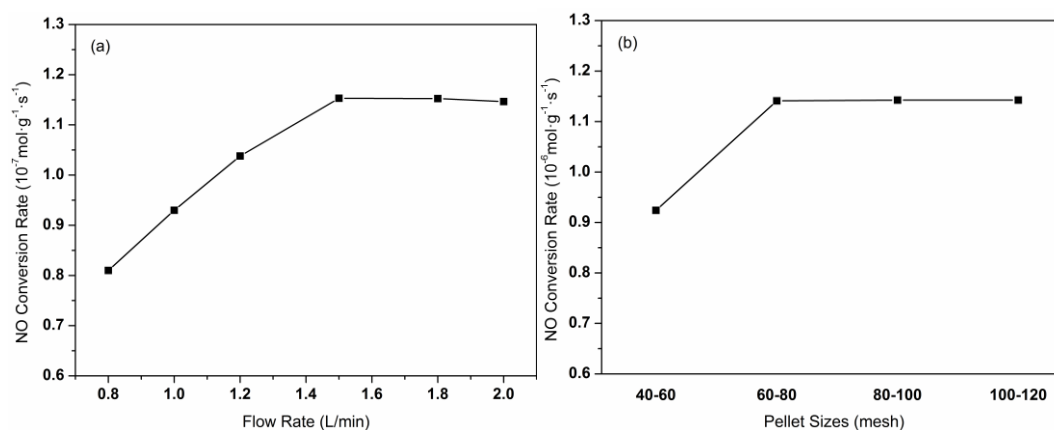
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### The kinetic condition tests

Effects of both the external and internal mass transfer limitations on the NO oxidation performance over MnO<sub>x</sub>-CeO<sub>2</sub> are investigated by comparing the reaction rates over MC-5.1 sample with varying the total flow rate (0.8 to 2.0 L/min) and pellet sizes (40-60, 60-80, 80-100 and 100-120 mesh) at 280 °C. As shown in Fig. S1(a), the NO conversion rates are similar when the flow rate is more than 1.5 L/min. In addition, the NO conversion rates are similar when the pellet size of the catalyst is less than 60-80 mesh (Fig. S1(b)). These results suggest that the external and internal diffusion limitations on NO oxidation reaction are ruled out under this condition (25 mg sample, 60-80 mesh, 1.5 L/min flow rate, GHSV: 432,000 h<sup>-1</sup>).

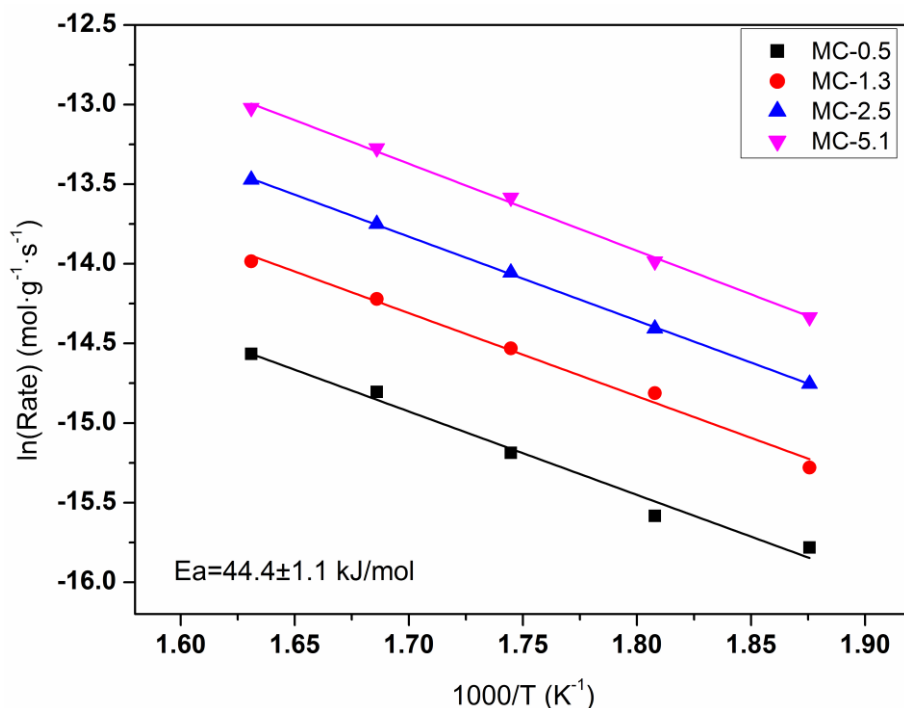


**Fig. S1** Effect of external mass transfer (a) and internal diffusion (b) on the NO oxidation activity over  $\text{MnO}_x\text{-CeO}_2$  catalyst at 280 °C. The inlets contained: 300 ppm NO, 150 ppm  $\text{NO}_2$ , 10%  $\text{O}_2$  balanced with  $\text{N}_2$ .

## The kinetic study results

The kinetic tests were conducted in a thin quartz tube using 25 mg of catalyst (60-80 mesh) and 125 mg of quartz sand (60-80 mesh). Prior to the kinetic experiments, the samples were pre-treated in 10%  $\text{O}_2/\text{N}_2$  at 500 °C for 30 min. The inlets were controlled at 1.5 L/min ( $\text{GHSV}=432,000 \text{ h}^{-1}$ ) and contained 300 ppm NO, 150 ppm  $\text{NO}_2$  and 10%  $\text{O}_2$  with  $\text{N}_2$  as balance. In the differential reactor, kinetic tests were conducted in the range of 260-340 °C in order to ensure the NO conversions were controlled less than 15%.

The NO conversion rate is defined as NO moles converted per unit mass of catalyst per second. As shown in Fig. S2, the Arrhenius plots of NO oxidation over the four samples perform as parallels, indicating the same reaction path. According to the slope of  $\ln(\text{Rate})-1000/T$ , the apparent activation energy is 44.4 (1.1) kJ/mol.



**Fig. S2** Arrhenius plots of NO oxidation over  $\text{MnO}_x\text{-CeO}_2$  samples at 260-340 °C. The inlets contained: 300 ppm NO, 150 ppm  $\text{NO}_2$ , 10%  $\text{O}_2$ , balanced with  $\text{N}_2$ . GHSV: 432,000  $\text{h}^{-1}$ .

## The calculations on average Mn valences of $\text{MnO}_x\text{-CeO}_2$ samples

In this study, the average Mn valences of all the samples are calculated according to quantification of  $\text{H}_2\text{-TPR}$ . We would like to take MC-0.5 as an example and the detailed calculations are as follows:

- 1) Standardization of peak area: We choose CuO as the basic reference, because CuO can be reduced to Cu by  $\text{H}_2$  below 800°C completely. In our experiment, the  $\text{H}_2$  consumption peak area of 10 mg standard CuO is integrated to be  $2.1 \times 10^4$ . Since 10 mg CuO reduced to Cu need  $\frac{0.010\text{g}}{80\text{g}\cdot\text{mol}^{-1}} \times 2 = 5.0 \times 10^{-4}$  mol electrons, the unit peak area stands for  $\frac{5 \times 10^{-4}}{2.1 \times 10^4} = 2.38 \times 10^{-8}$  mol H consumption.
- 2) Extra value of Mn according to  $\text{H}_2$  consumption: The first  $\text{H}_2$  consumption peak area of MC-0.5 is 119.5, which indicates that  $\text{MnO}_x$  reduction to  $\text{Mn}_3\text{O}_4$  consumes  $119.5 \times 2.38 \times 10^{-8} = 2.84 \times 10^{-6}$  mol H. Since 0.1g MC-0.5 sample contains  $\frac{0.1\text{g}}{172\text{g}\cdot\text{mol}^{-1}} \times 0.50\% = 2.91 \times 10^{-6}$  mol Mn atoms according to ICP result, each

Mn may receive  $\frac{2.84 \times 10^{-6}}{2.91 \times 10^{-6}} = 0.98$  electron on an average in the first reduction step.

- 3) Since the average Mn valence of  $\text{Mn}_3\text{O}_4$  is 2.67, the average Mn valence of  $\text{MnO}_x$  is 3.65 (2.67+0.98).

The results of other samples are listed in Table R1.

**Table S1.** The relative computation results of  $\text{MnO}_x\text{-CeO}_2$  and  $\text{MnO}_x$  samples

Samples (0.1 g)	Mn amount ( $\mu\text{mol}$ )	The first peak area	H consumption ( $\mu\text{mol}$ )	H/Mn	Average Mn valence
MC-0.5	2.91	119.5	2.84	0.98	3.65
MC-1.3	7.44	221.4	5.28	0.71	3.38
MC-2.5	14.7	369.8	8.82	0.60	3.27
MC-5.1	29.8	624.7	14.9	0.50	3.17
$\text{MnO}_x$	35.0	587.0	14.0	0.40	3.07