Supporting Information

Improved Activity and SO₂ Resistance by Sm modulated Redox of MnCeSmTiO_x Mesoporous Amorphous Oxides for Low-Temperature NH₃-SCR of NO

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S1. Experimental details

S1. 1 Chemicals and synthesis of catalysts

The Mn(NO₃)₂ (50 wt. %) solution and, and Ti(SO₄)₂ (99.7) powders with the analytical grade, Sm(NO₃)₃·6H₂O (99.99%), and Ce(NO₃)₂·6H₂O (99.95%) were purchased from Aladdin Inc. PEG solution with analytical grade and NH₄OH (25 wt. %) solution are purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used without further purification.

The catalysts were synthesized by a PEG assisted co-precipitation method already described ¹⁻². Adding PEG was proved that it could reduce the average crystallite and the size of nanoparticles during the co-precipitation process³³⁻³⁴. In a typical synthesis, 1.75 mL Mn(NO₃)₂ (50 wt. %) solution was diluted in 30 mL deionized water (DIW) at 30 °C under stirring for 30 min. Then, 1.63 g Ce(NO₃)₂·6H₂O, 1.67 g $Sm(NO_3)_3$ GH_2O_1 and 7.2 g Ti(SO_4)₂ powders, were added slowly into the solution mentioned above. The molar ratio of Mn: Ce: Sm: Ti was kept at 1: 0.5: 0.3: 4. In the next step, 1.98 g PEG was added dropwise into the above-mixed solution. The mixed solution was stirred for one more hour. The mixed solution was dropped into the diluted solution (40 mL, 12.5 wt. %) of NH₄OH dropwise under vigorous stirring (500 rpm) for 6 h. The pH was kept at ≈ 11 using an NH₄OH solution (2 mol·min⁻¹). The mixed solution was aged in a homogeneous reactor at 100 °C for 24 h to make the product homogeneous. The residual solid precipitate was washed by DIW for three times and dried in an oven at 110 °C for 12 h. The as-dried solid was calcined at 500 °C under air for 5 h. The as-synthesized catalyst was labeled as MnCeSmTiO_x. Other synthesized

catalysts by using different metal salts were labeled as $MnCeTiO_x$, $MnSmTiO_x$, and $CeSmTiO_x$, respectively. The $MnCeTiO_x$ and $MnCeSmTiO_x$ catalysts were used to study the SO₂ and H₂O resistance properties. These two catalysts in their already treated form with SO₂ and H₂O were labeled as $MnCeTiO_x$ -U and $MnCeSmTiO_x$ -U.

S1. 2 Catalytic testing

The evaluation of the catalytic activity was carried out on a temperature-programmed fixed bed reactor at a reaction gas hourly space velocity (GHSV) of 80000 h⁻¹. 0.15 mL catalysts were used to investigate the NH₃-SCR reaction, with the following reaction parameters: 500 ppm of NO, 500 ppm of NH₃, 5 vol% O₂, 50, 100, and 200 ppm of SO₂, 5 vol% H₂O. The balance gas was He with a total flow rate of 200 mL·min⁻¹. The reaction temperature was increased from 100 to 400 °C at a rate of 10 °C·min⁻¹. The conversion of NO was recorded from 100 to 400 °C with a temperature step rate of 20 °C. The concentrations of NO, NH₃, N₂O, and NO₂ were tested online by a NICOLET IS10 FTIR spectrometer. The NO conversion and the N₂ selectivity were calculated based on the following equations:

$$X_{\rm NO} = \frac{C_{\rm NO, \, in} - C_{\rm NO, \, out}}{C_{\rm NO, \, in}} \times 100\%$$
(1)

$$S_{\rm N_2} = \left(1 - \frac{2C_{\rm N_2O, out} + C_{\rm NO_2, out}}{C_{\rm NO, in} + C_{\rm NH_3, in} - C_{\rm NO, out} - C_{\rm NH_3, out}}\right) \times 100\%$$
(2)

Where X_{NO} is the NO conversion rate of the NH₃-SCR reaction. $C_{NO, in}$, $C_{NO, out}$, $C_{NH_3, in}$, and $C_{NH_3, out}$ are concentrations of NO and NH₃ in the inlet and outlet of the reactor. $C_{N_2O, out}$ and $C_{NO_2, out}$ are concentrations of N₂O and NO₂ in the outlet of the reactor, while S_{N_2} refers to the selectivity of N₂.

S1. 3 Kinetics experiments

Here, we calculate the reaction rate, apparent activation energy, and turnover frequency (TOF) of the catalysts by performing macroscopic kinetics experiments. The NO conversion was kept below 15% (in order to ensure that all of the catalytic active sites were at operational states) by tuning the mass of catalysts and gas flow rate. The catalysts were ground for about 10 min in an agate mortar in order to eliminate the effect of internal diffusion. The NH₃ molecules were used as a probe to measure the amounts of active oxidization catalytic sites of the catalysts by the NH₃-TPD-FTIR process. The TOF is defined by the eigenvalue equation according to the references 3,4 :

$$TOF = \frac{r}{[C_t]}$$
(3)

Where *r* is the reaction rate of the NH₃-SCR reaction, $[C_t]$ is the total concentration of the catalyst's active sites of the rate-determining step. The reaction rate *r* can be calculated assuming the ideal gas behavior according to references⁵:

$$r (mol g^{-1} s^{-1}) = GHSV (mL h^{-1} g^{-1}) \times \frac{1}{3600} (h s^{-1}) \times \frac{1}{1000} (L mL^{-1}) \times NO \text{ vol. }\%$$
$$\times X_{NO} \times \frac{1}{22.4} (mol L^{-1})$$
(4)

Where, GHSV is the air velocity, X_{NO} is the conversion of NO (%).

We can calculate the *r* and apparent activation energy (E_a) of the reaction by performing NH₃-SCR reactions at different temperatures to obtain the NO conversion. Reaction conditions are 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, balance Ar, and GHSV 600,000 h⁻¹. The outlet gases were analyzed with IR (Nicolet 6700) equipped with a gas cell (Harrick DRIFT) and an MCT detector. The *r*, *Ea*, and the reaction order of the catalysts were determined by adjusting the contents of catalysts and the flow rate to keep NO conversion below 15%. To eliminate the effects of internal diffusion, the catalysts were ground in to particles with size below 300 mesh. The results are shown

different temperatures.								
<i>T</i> (°C)	MnCeTiO _x		MnCeSmTiO _x					
	X _{NO} (%)	r (10 ⁻⁶ mol g ⁻¹ s ⁻¹)	X _{NO} (%)	<i>r</i> (10 ⁻⁶ mol g ⁻¹ s ⁻¹)				
90	6.80	0.253	7.20	0.268				
100	8.00	0.298	8.40	0.312				
110	8.90	0.331	9.60	0.357				
120	9.70	0.361	10.60	0.394				
130	10.80	0.402	11.80	0.439				
140	11.90	0.443	13.40	0.498				
150	13.20	0.491	14.50	0.539				

Table S1 The measured X_{NO} and calculated r of MnCeTiO_x and MnCeSmTiO_x catalysts at
different temperatures.

The *r* could also be expressed by the Arrhenius equation:

$$r = A e^{(-E_a/RT)}$$
(5)

Where, *A* is the pre-exponential factor (S⁻¹), E_a is the apparent activation energy (kJ mol⁻¹). Taking the natural log of both sides of the equation (2), we get:

$$\ln r = -\frac{E_a}{RT} + \ln A \tag{6}$$

By plotting ln *r* versus 1000/T, the apparent activation energy E_a can be calculated from the slope.

The *r* could be expressed as a function of the reactant concentrations⁶:

$$r = k \left[\text{NO} \right]^{\alpha} \left[\text{NH}_3 \right]^{\beta} \left[\text{O}_2 \right]^{\chi} \tag{7}$$

Where [NO], [NH₃], and [O₂] are the concentrations of the reactants. α , β , χ are the reaction orders, respectively. We carried out the NH₃-SCR reaction under the condition of the various concentrations of NO, NH₃ to determine each reaction order. Typically, the content of O₂ is excessive, and thus the reaction order of O₂ can be considered to be 0. The logarithms of r were approximated by a straight line as follows:

 $\ln[r] = \alpha \ln[\text{NO}] + ([\text{NH}_3]^{\beta}) \ln k \tag{8}$

$$\ln[r] = \beta \ln[\mathrm{NH}_3] + ([\mathrm{NO}]^{\alpha}) \ln k \tag{9}$$

The experimental results of logarithms of r versus the concentration of NO and NH₃

are shown in Table S2.

different 100 C.								
NH ₃ (ppm)	$ln(Cat_1)$	ln(Cat ₂)	NO (ppm)	$ln(Cat_1)$	$ln(Cat_2)$			
300	-15.38	-15.32	300	-15.19	-15.13			
400	-15.21	-15.14	400	-15.09	-15.05			
500	-15.03	-14.98	500	-15.03	-14.98			
600	-14.91	-14.84	600	-14.98	-14.93			
700	-14.79	-14.74	700	-14.90	-14.84			

Table S2. The calculated logarithmic value of r of MnCeTiO_x and MnCeSmTiO_x catalysts at different 100 °C.

 $\overline{*Cat_1 \text{ is } MnCeTiO_x}$, Cat₂ is MnCeSmTiO_x.

The calculated reaction order is 0.30 (NH₃) and 0.75 (NO). The [C_1] can be determined by the NH₃-TPD measurement. The outlet gases were analyzed with IR (Nicolet 6700) equipped with a gas cell (Harrick DRIFT) and an MCT detector. The catalysts were pretreated at 300 °C for 1 h in the Ar atmosphere before adsorbing NH₃. When the catalyst was cooled down to room temperature (below 50 °C), the gas was switched to 500 ppm NH₃/Ar for 1 h. Then the gas is switched to Ar and heated to 150 °C by 10 °C/min. the system was kept at 150 °C to desorb the physical adsorbed NH₃. When there is no NH₃ detected by the FT-IR at the outlet, the system was heated to 750 °C by 5 °C/min, and the outlet gas was detected online by the FT-IR.

S2 Supplemental data



Figure S1. XRD patterns of $MnCe(0.1)TiO_x$, $MnCe(0.3)TiO_x$, $MnCe(0.5)TiO_x$ and $MnCe(0.7)TiO_x$ catalysts.



Figure S2. Low resolution TEM images of $MnCeTiO_x$ (a), $MnSmTiO_x$ (b), $CeSmTiO_x$ (c), and $MnCeSmTiO_x$ (d) catalysts. Scale bars are 50 nm.



Figure S3. In situ DRIFTS spectra of NH_3 adsorption-desorption over the (a) $MnSmTiO_x$, (b) CeSmTiO_x catalysts.



Figure S4. In situ DRIFTS spectra of NO + O_2 adsorption-desorption over the (a) MnSmTiO_x, (b) CeSmTiO_x catalysts.

References

1. Yixuan, R.; Li, G.; Junguo, R., Effect of PEG addition on the properties of YAG: Ce phosphor synthesized via a homogeneous precipitation method. *Rare Metal Mater. Eng.*

2015, 44, 2100-2104.

2. Anbarasu, M.; Anandan, M.; Chinnasamy, E.; Gopinath, V.; Balamurugan, K., Synthesis and characterization of polyethylene glycol (PEG) coated Fe_3O_4 nanoparticles by chemical co-precipitation method for biomedical applications. *Spectrochim. Acta A* **2015**, 135, 536-539.

3. Kozuch Sebastian, Shaik Sason, A combined kinetic-quantum mechanical model for assessment of catalytic cycles: application to cross-coupling and heck reactions. *J. Am. Chem. Soc.* **2006**, *128*: 3355-3365.

4. Kozuch Sebastian, Martin Jan M. L., "Turning over" definitions in catalytic cycles. *ACS Catal.* **2012**, *2*: 2787-2794.

5. Confined transformation of organometal-encapsulated MOFs into spinel $CoFe_2O_4/C$ nanocubes for low temperature catalytic oxidation. *Adv. Funct. Mater.* **2020**, *30*: 1910257.

Teramura Kentaro, Tanaka Tsunehiro, Yamazoe Seiji, Arakaki Kyoko, Funabiki Takuzo. Kinetic study of photo-SCR with NH₃ over TiO₂. *Appl. Catal. B: Environ.* 2004, 53: 29-36.