

Supporting Information:

Improved Low Temperature NH₃-SCR Performance of FeMnTiO_x Mixed Oxide with CTAB-assisted Synthesis

Shiguo Wu^{a,c}, Xiaojiang Yao^d, Lei Zhang^a, Yuan Cao^a, Weixin Zou^a, Lulu Li^a, Kaili Ma^a, Changjin Tang^a, Fei Gao^{b,*}, Lin Dong^{a,b,*}

^a Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

^b Jiangsu Key Laboratory of Vehicle Emissions Control, Center of Modern Analysis, Nanjing University, Nanjing 210093, PR China

^c Changzhou Institute of Engineering Technology, Changzhou 213164, PR China

^d Research Center of Atmospheric Environment, Key Laboratory of Reservoir Aquatic Environment, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, PR China

Catalysts preparation

FMT: FMT mixed oxide was prepared by inverse co-precipitation method. Fe(NO₃)₃·9H₂O, Mn(AC)₂·4H₂O, Ti(SO₄)₂ (mole ratio = 0.1:0.1:1.0) with suitable amount were dissolved in distilled water with subsequent mixing for 10 min. Then the mixture was added dropwise to an ammonia solution (25 wt. %) and the pH value of the final solution is maintained at 11. During the reaction, the system was continuously stirred at 300 rpm. 3 h later, the particles were then separated by filtrate and washed with distilled water for 3 times at least. Then the particles were collected and dried in an oven at 110 °C for 12 h. Then the samples were calcined in muffle furnace in air condition at 500 °C for 6 h and the heating rate was kept at 2 °C·min⁻¹. The calcined samples were crushed and sieved to 40-60 mesh for activity test.

FMT(S): FMT(S) mixed oxide catalyst was prepared by inverse co-precipitation method. Suitable CTAB (30 mmol/L) were added to distilled water, and then the solution was heated to 30 °C to ensure that the CTAB dissolved. Fe(NO₃)₃·9H₂O, Mn(AC)₂·4H₂O, Ti(SO₄)₂ with suitable amount (mole ratio = 0.1:0.1:1.0) were dissolved in CTAB solution with subsequent mixing for 30 min. Then the mixture was added dropwise to an ammonia solution (25 wt.%) and the pH value of the final solution is maintained at 11, and other steps just the same as FMT mixed oxide catalyst.

Characterization

XRD: X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu K α radiation ($\lambda = 0.15418\text{nm}$). The X-ray tube was operated at 40 kV and 40 mA. The intensity data were collected over a 2θ range

of 10-80°. The scan speed was set at 10° min⁻¹ with a step size of 0.02°.

TPR: H₂-temperature programmed reduction (H₂-TPR) experiments were performed in a quartz U-type reactor connected to a thermal conductivity detector (TCD) with Ar-H₂ mixture (7.0% of H₂ by volume, 70 mL·min⁻¹) as a reductant. Prior to the reduction, the sample (50 mg) was pretreated in a high purified N₂ stream at 300 °C for 40 min and then cooled to room temperature. After that, the TPR started from 50 °C to target temperature at a rate of 10 °C·min⁻¹.

BET and BJH: Textural characteristics of these catalysts were measured by N₂-physisorption at -196 °C on a Micromeritics ASAP-2020 analyzer, using the Brunauer-Emmet-Teller (BET) method to determine their specific surface area. The pore size distributions were calculated from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. The sample was degassed under vacuum at 90 °C for 1 h and 300 °C for 4 h before each analysis.

XPS: X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versa Probe system, using monochromatic Al K α radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the sample was outgassed at room temperature in a UHV chamber (<5×10⁻⁷ Pa). The sample charging effects were compensated by calibrating all binding energies (BE) with the adventitious C1s peak at 284.6 eV. This reference gave BE values with accuracy at ±0.1 eV.

In situ DRIFTS: *In situ* diffuse reflectance infrared Fourier transform spectra (*in situ* DRIFTS) were collected from 650 to 4000 cm⁻¹ at a spectral resolution of 4 cm⁻¹ (number of scans, 32) on a Nicolet 5700 FT-IR spectrometer equipped with a high-sensitive MCT detector cooled by liquid N₂. The DRIFTS cell (Harrick) was fitted with a ZnSe window and a heating cartridge that allowed sample be heated to 300 °C. The same amount of fine catalyst powder was placed in a sample holder every time, and flattened to enhance IR reflection. The sample was pretreated with a high purified N₂ stream at 300 °C for 60 min to eliminate the physical adsorbed water and other impurities. The sample background of each target temperature was collected during the cooling process. At ambient temperature, the sample was exposed to a controlled stream of 1% NH₃ (by volume, N₂ balance, hereinafter the same) or 1% NH₃ +1% NO +5% O₂ at a rate of 50 mL·min⁻¹ for 1 h to be saturated. And then, the gaseous and weakly adsorbed NH₃ molecules were purged by a high purified N₂ stream (50 mL·min⁻¹) for 1 h. Desorption/reaction studies were performed by heating the adsorbed species and the spectra were recorded at various target temperatures at a rate of 10 °C·min⁻¹ from room temperature to 300 °C by subtraction of the corresponding background reference.

TPD: NH₃-temperature programmed desorption (NH₃-TPD) experiments were carried out on a multifunction chemisorption analyzer with a quartz U-tube reactor, detected by a thermal conductivity detector (TCD). About 100 mg of the sample was pretreated by passage of high purified N₂ (40 mL·min⁻¹) at 400 °C for 1 h. After pretreatment, the sample was saturated with NH₃-N₂ (1% of NH₃, 10 mL·min⁻¹) at room temperature for 1 h, and then flushed with the flowing high purified N₂ (40 mL·min⁻¹) at 100 °C for 1 h to remove gaseous and weakly adsorbed NH₃. Subsequently the sample was heated to 600 °C at a rate of 10 °C·min⁻¹ with the flowing high purified

N₂ (40 mL·min⁻¹).

Catalytic performance measurements

The catalytic performances of FMT(S) and FMT for NH₃-SCR in the presence of excess oxygen were measured under the following conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, 3.5% H₂O (when used), and N₂ balance. firstly, the sample (200 mg) was fitted in a quartz tube and pretreated in a high purified N₂ stream at 300 °C for 1 h; secondly, the sample was cooled down to room temperature; the third, feed gas (O₂, NO and NH₃) were introduced, and the catalyst adsorbed feed gases until the sample got saturated; next, increasing to the aimed temperature at the rate of 10 °C·min⁻¹ and holding the temperature for 15 minutes to get the steady state; then, collecting data at aimed temperature, and so on. Sampling and recording a data point per 25 °C until 375 °C. The whole process is stepwise. The reactions were carried out with a space velocity of 30,000 mL·g⁻¹·h⁻¹. The concentrations of NO, NH₃, NO₂, and N₂O were measured at 150 °C by a Thermofisher IS10 FTIR spectrometer equipped with 250 mL volume gas cell. The gas path from the reactor to FTIR spectrometer was kept a fixed temperature of 150 °C to avoid the deposition of nitrite/nitrate and the dissolution of NH₃ in liquid H₂O. The NO conversion and N₂ selectivity were calculated from the following equations:

$$NO \text{ conversion } (\%) = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100.$$

$$N_2 \text{ selectivity } (\%) = \frac{[NO]_{in} - [NO]_{out} + [NH_3]_{in} - [NH_3]_{out} - [NO_2]_{out} - 2[N_2O]_{out}}{[NO]_{in} - [NO]_{out} + [NH_3]_{in} - [NH_3]_{out}} \times 100$$

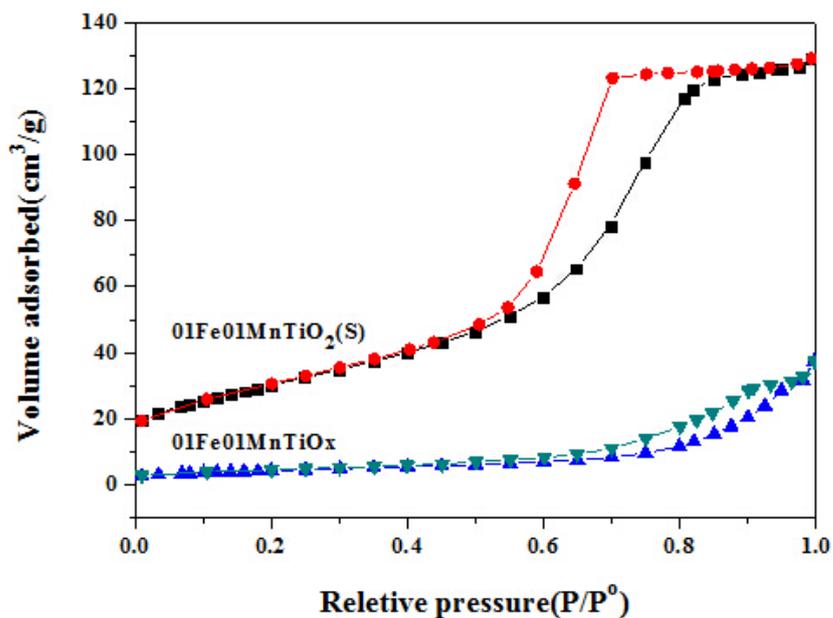


Fig. S1. The N₂ adsorption-desorption isotherms curves of FMT(S) and FMT.

Table S1 Textural properties of FMT(S) and FMT.

Samples	BET surface area	
	(m ² ·g ⁻¹)	Average pore diameter (nm)
FMT(S)	109	6
FMT	15	16

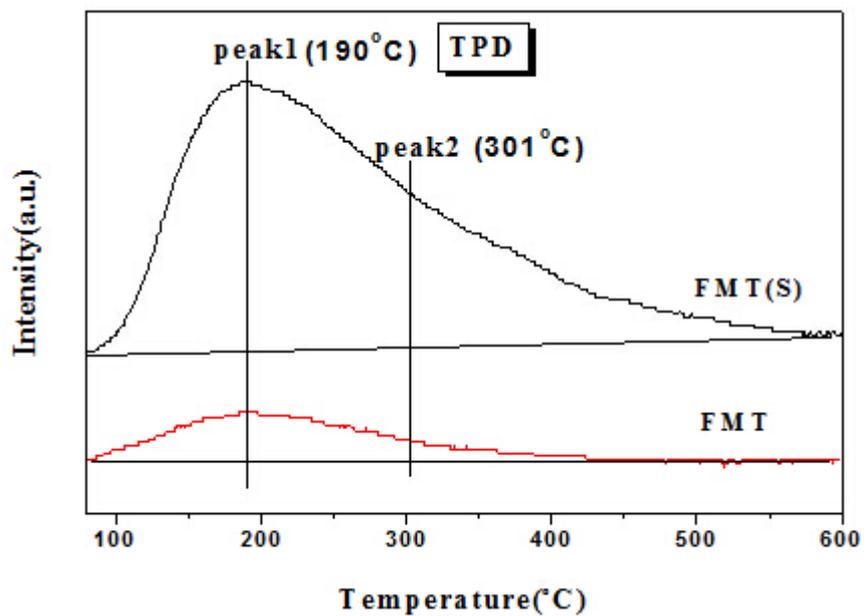


Fig. S2. NH₃-TPD profiles over FMT(S) and FMT.

Table S2 The quantitative analysis data of NH₃-TPD over the obtained samples.

catalysts	Information of peaks				Area 2/(Area 1 + Area 2)
	Peak 1		Peak 2		
	Area 1	Center (°C)	Area 2	Center (°C)	
FMT(S)	3943	190	6735	301	0.63
FMT	1062	190	368	302	0.26

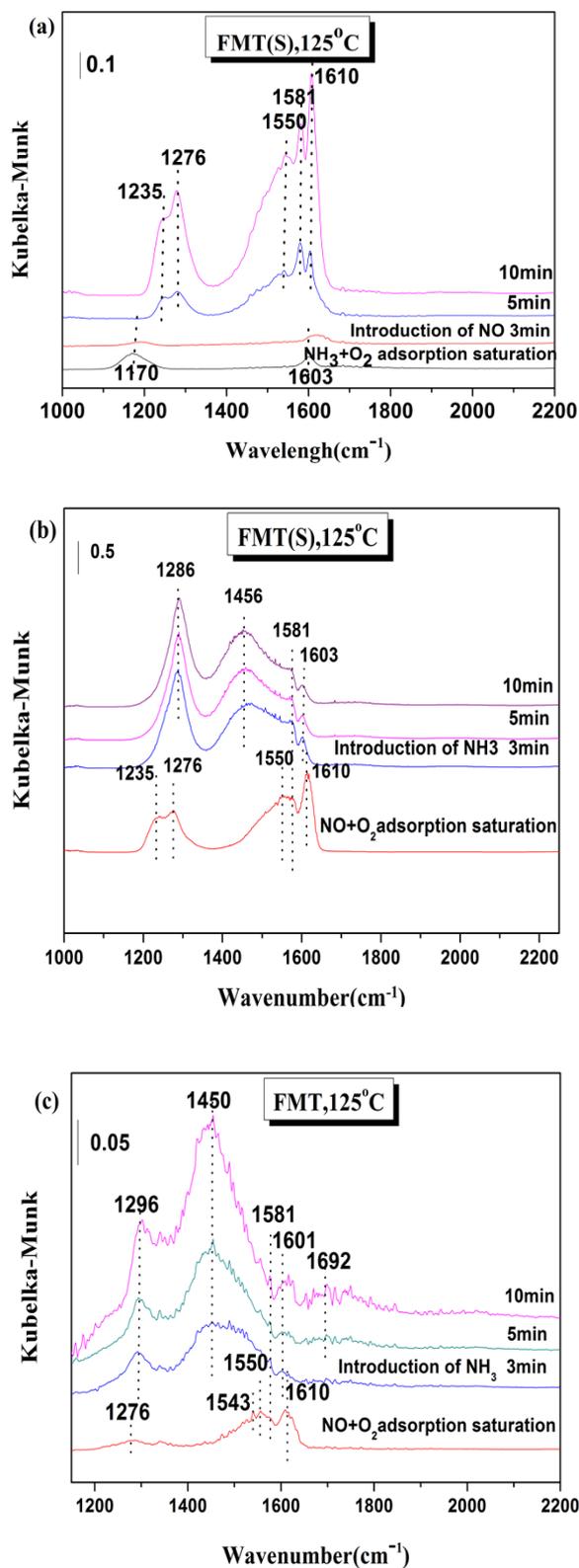


Fig. S3. *In situ* DRIFTS of (a) NO was introduced into IR sample cell after the NH₃+O₂ adsorption saturation on FMT(S) sample at 125 °C, (b) NH₃ was introduced into IR sample cell after the NO+O₂ adsorption saturation at 125 °C on FMT(S) and NH₃ was introduced into IR sample cell after the NO+O₂ adsorption saturation at 125 °C on FMT sample.

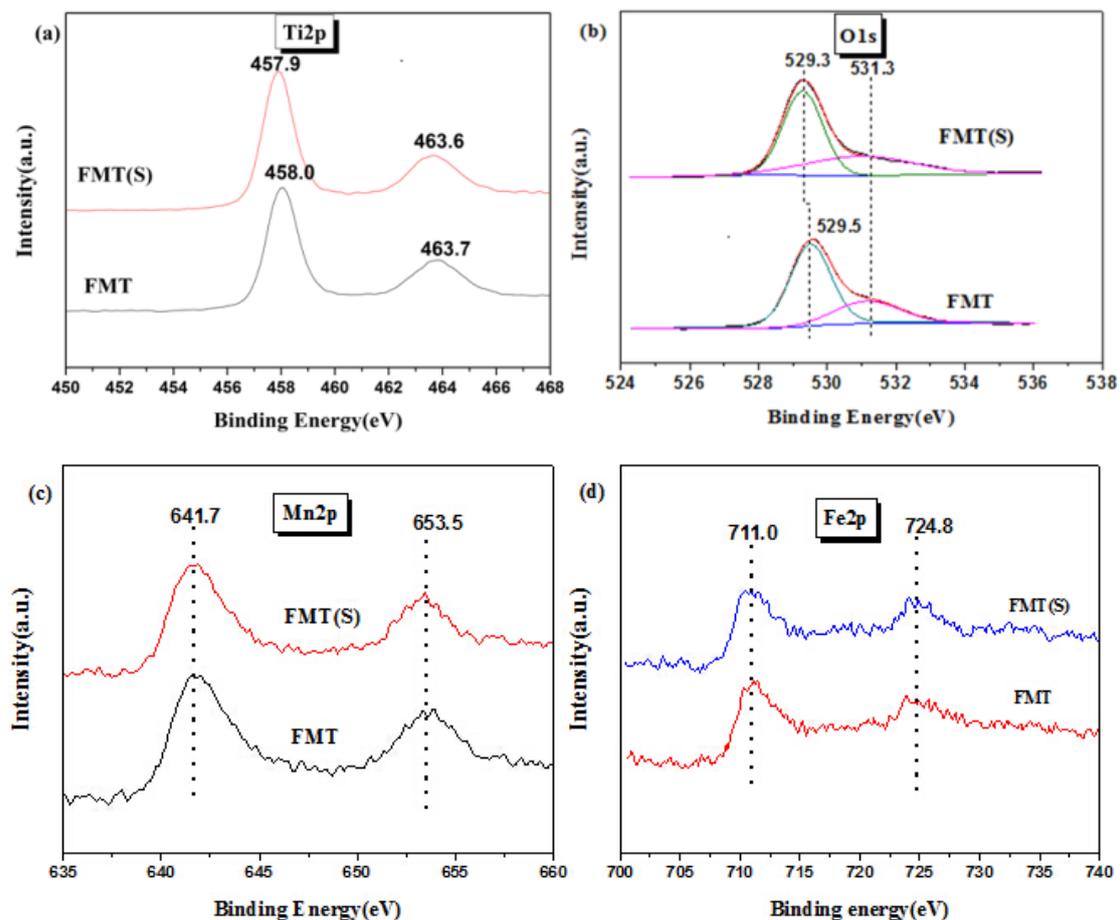


Fig. S4. XPS spectra of (a) Ti 2p, (b) O 1s, (c) Mn 2p and (d) Fe 2p for obtained samples.

Table S4 XPS elementary surface concentration of these catalysts.

catalysts	Amount of oxygen species				
	Lattice oxygen (O_{α})		Adsorbed oxygen (O_{β})		
	BE (eV)	AO_{α} (a.u.)	BE (eV)	AO_{β} (a.u.)	$AO_{\beta}/(AO_{\alpha} + AO_{\beta})$ (%)
FMT(S)	529.3	14630	531.0	9127	38.4
FMT	529.5	15707	531.0	6341	28.8

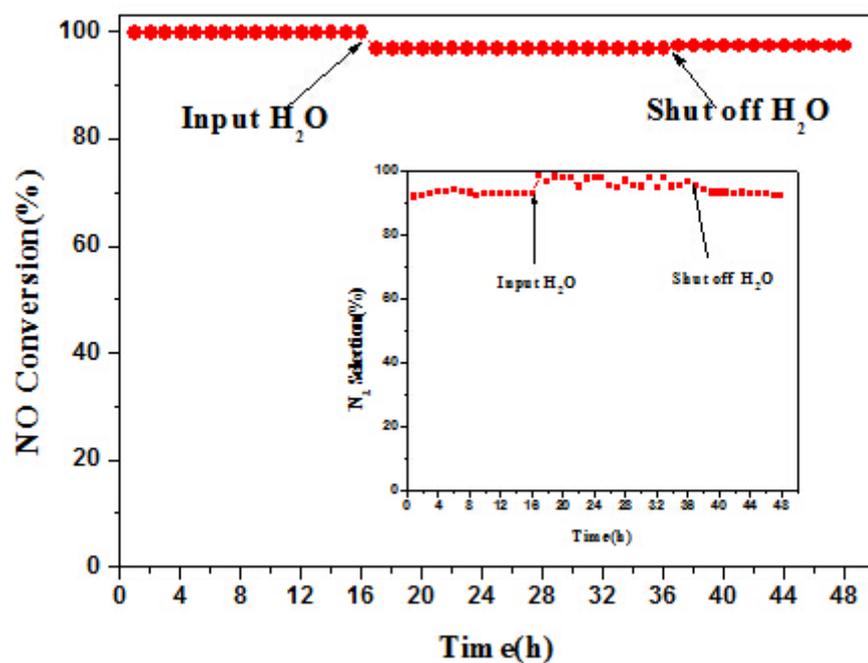


Fig. S5. NO conversion and N₂ selectivity (inserted) in NH₃-SCR reaction over FMT(S). Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, N₂ balance, catalyst mass = 200 mg, total flow rate = 100 mL·min⁻¹, [H₂O] = 3.5%, GHSV = 30000 mL·min⁻¹·h⁻¹ and T = 150 °C.