Supporting Information

Engineering 3D structure Mn/YTiO$_x$ nanotube catalyst with an efficient H_2O and SO_2 tolerance for low temperature selective catalytic reduction of NO with NH_3

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Experimental section

Catalysts characterization

The crystal structure of samples were analyzed by the powder X-ray diffraction (XRD) patterns in a 2θ range of 10-60° at a scanning speed of $0.02°\cdot s^{-1}$ using an X-ray diffractometer (Rigaku Smartlab-SE, Japan) employing Cu Kα radiation (λ =1.5404 Å). Raman spectra were collected by LabRAM HR Evolution Raman spectrometer (HORIBA Jobin Yvon SAS, France) with a 532 nm laser. The Brunauer-Emmett-Teller (BET) surface areas and pore structure characteristics were obtained through N_2 adsorption-desorption experiment using a physisorption analyzer (Micromeritics ASAP 2020, USA) at liquid nitrogen temperature (-196 °C) using N_2 as the probe molecule. H_2-temperature programmed reduction (H_2-TPR) and NH_3-temperature programmed desorption (NH_3-TPD) experiments were determined on a multifunctional automatic chemical adsorption apparatus (Xianquan TP-5080, China), equipped with thermal conductivity detector (TCD). For H_2-TPR experiment, 50 mg sample was firstly pretreated at 300 °C in a flow of Ar for 1 h, then cooled down to 30 ℃. Subsequently, the samples were heated from 30 ℃ to 700 ℃ at a rate of 10 °C min^{-1} in a mixture of 5% H_2/N_2 (100 mL min^{-1}) and the corresponding TPD curve was collected. For NH_3-TPD experiment, the samples were also preheated at 300 °C in a flow of Ar for 1 h prior to the measurement, then cooled down to 100 ℃. Subsequently, the samples were exposed to a mixture of 5% NH_3/N_2 for 30 min at 100 °C, then purged with N_2 to remove surface physisorbed NH_3. Finally, the samples were heated from 100 ℃ to 700 ℃ at a rate of 10 °C min^{-1}, and the corresponding TPD profile was recorded.The

morphology and structure of the samples was observed by transmission electron microscopy (TEM, JEOL JEM-2010). The X-ray photoelectron spectroscopy (XPS) measurement were recorded by a VG ESCALAB 210 Spectrometer using an Al Kα source (hv=1486.6 eV) radiation. The binding energy of C 1s at 284.6 eV was used as the standard for calibration of the spectrum of O, Mn, Ti and Y.

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to investigate the surface species involved in NO_x selectivity reduction over Mn/3%YTiO_x catalysts using a Fourier transform infrared spectrometer (VERTEX 70) equipped with a high temperature reaction chamber (HVC, harrick) and liquid nitrogen-cooled HgCdTe (MCT) detector. The spectra were measured by the parameter of 64 scans at a resolution of 4 cm^{-1}. The catalyst was firstly pretreated at 300 ℃ for 30 min using flowing 30 mL/min N_2. When the catalyst was cooled to 50 ℃, the background spectrum was recorded in the flow of N_2 and was automatically subtracted from spectrum collected in subsequent tests. The adsorption experiments of NH_3 or NO+O_2 were performed by exposing the catalyst to 1 vol% NH_3 or 1 vol% NO+O_2 at 50 ℃ for 30 min and followed by purging with N_2. Afterwards, the desorption spectra of catalyst was collected with ramping temperatures. In the case of the transient reactions, the catalyst was exposed to the reaction gases (1 vol% NH_3 or 1 vol% NO+O_2) at 180 ℃ for 30 min, another reaction gas (1 vol% NO+O_2 or 1 vol% NH_3) was then switched onto the catalyst surface accordingly, and meanwhile the spectra were recorded with different reaction times.

Catalytic performance evaluation

The catalytic performance of all catalysts for NH_3-SCR reaction was performed on a fix-bed reactor with a stainless steel tubular reactor of 1.2 cm inner diameter under atmospheric pressure. 0.4 g catalyst (40-60 mesh) was mixed with 0.6 g silica sand and placed in the reactor between two quartz wool plugs. The reactor temperature was controlled using an electric tubular furnace regulated by a temperature controller. The total flow of the simulated gas, which consisted of 500 ppm NO, 500 ppm NH_3, 5 vol% O_2, 5 vol% H_2O (when used), and 100 ppm SO_2 (when used) balanced with N_2, was kept as 200 mL·min^{-1}, and the corresponding gas hourly space velocity (GHSV) was calculated to be 30,000 h^{-1}. The flue gas analyzer (Kane, KM9106) was used to detect the inlet and outlet concentration of NO_x. All data were obtained when the SCR reaction reached a steady state at each temperature. The NO conversion and N_2 selectivity were calculated using Eqs. (1) and (2).

$$NO_x \text{ conversion } (\%)=\frac{[NO_x]_{in}-[NO_x]_{out}}{[NO_x]_{in}}\times 100\% \quad (1)$$

$$N_2 \text{ selectivity } (\%)=1-\frac{2[N_2O]_{out}+[NO_2]_{out}}{[NH_3]_{in}+[NO_x]_{in}-[NH_3]_{out}-[NO_x]_{out}}\times 100\% \quad (2)$$

Where NO_x represents the total concentration of NO and NO_2. $[NO_x]_{out}$, $[NO_x]_{out}$, $[NH_3]_{in}$, $[NH_3]_{out}$, $[N_2O]_{out}$ and $[NO_2]_{out}$ represent the corresponding concentrations of the inlet and outlet gases, respectively.

Kinetics studies were performed to investigate the intrinsic catalytic activity, we calculated the reaction rate and apparent activation energy of Mn/TiO_2-NT, Mn/1%YTiO_x, Mn/3%YTiO_x and Mn/5%YTiO_x, where the NO conversion was kept

below 40% (in order to ensure that all of the catalytic active sites were at operational states). The specific reaction rates based on the catalyst's mass (R_m) and specific surface area (R_s) can be calculated according to the following equations, as shown in Eqs.(3-4):

$$R_m(\mathrm{mol\cdot g^{-1}\cdot s^{-1}}) = \mathrm{GHSV(mL\cdot h^{-1}\cdot g^{-1})}\times\frac{1}{3600}(\mathrm{h\cdot s^{-1}})\times\frac{1}{1000}(\mathrm{L\cdot mL^{-1}})\times C_{NO}\times X_{NO}\times\frac{1}{22.4}(\mathrm{mol\cdot L^{-1}}) \quad (3)$$

$$R_s(\mathrm{mol\cdot m^{-2}\cdot s^{-1}}) = R_m(\mathrm{mol\cdot g^{-1}\cdot s^{-1}})\times\frac{1}{S_{BET}}(\mathrm{g\cdot m^{-2}}) \quad (4)$$

Where, GHSV is the air velocity, C_{NO} is the concentration of NO and X_{NO} is the conversion of NO.

Results and discussion

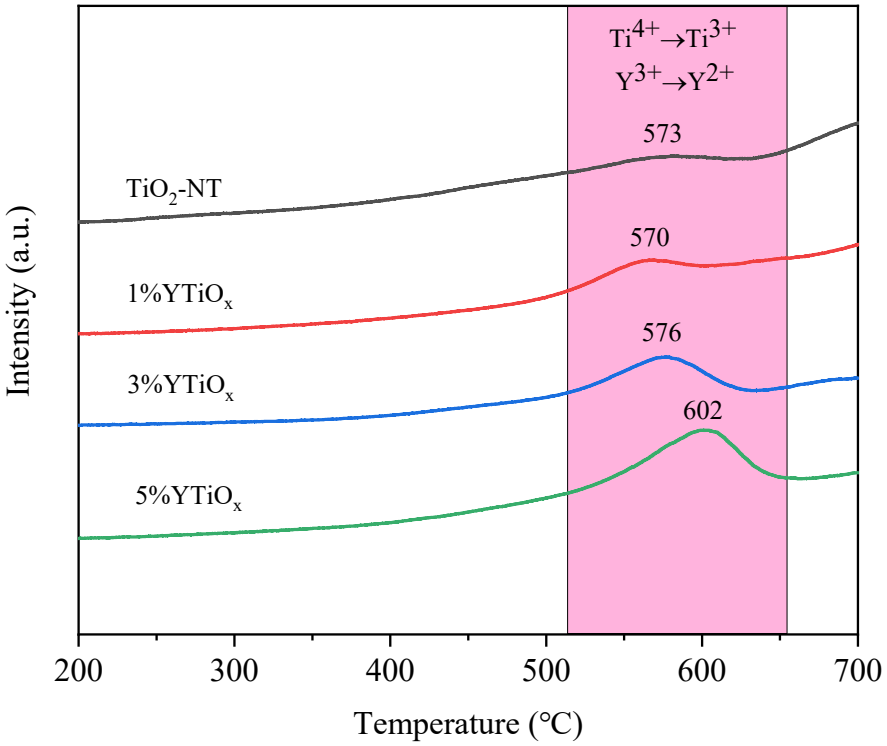


Fig. S1. H_2-TPR profiles of TiO_2-NT and Y-doped TiO_2.

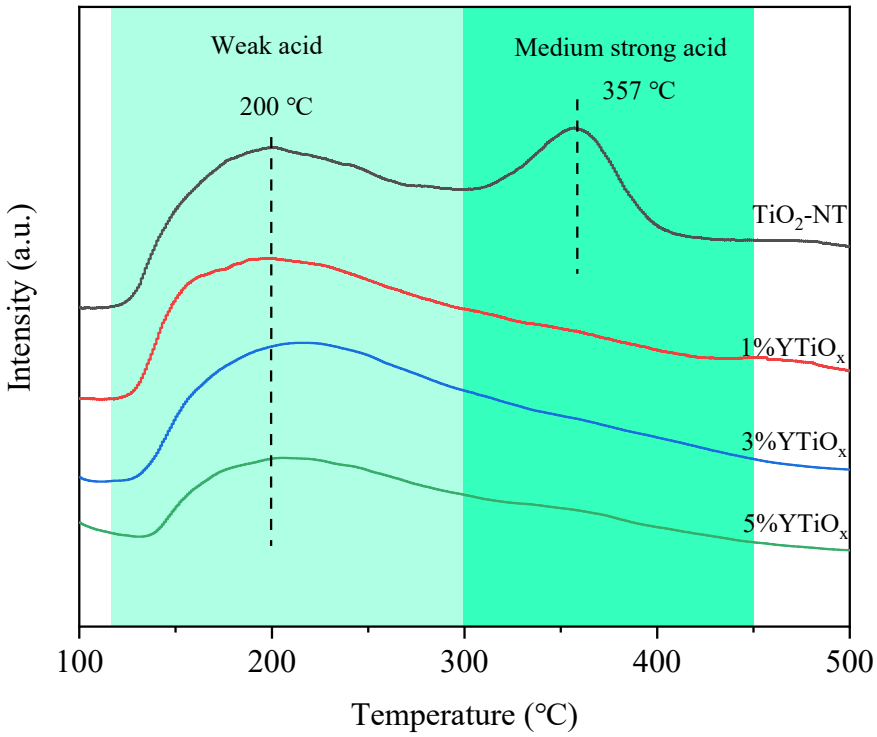
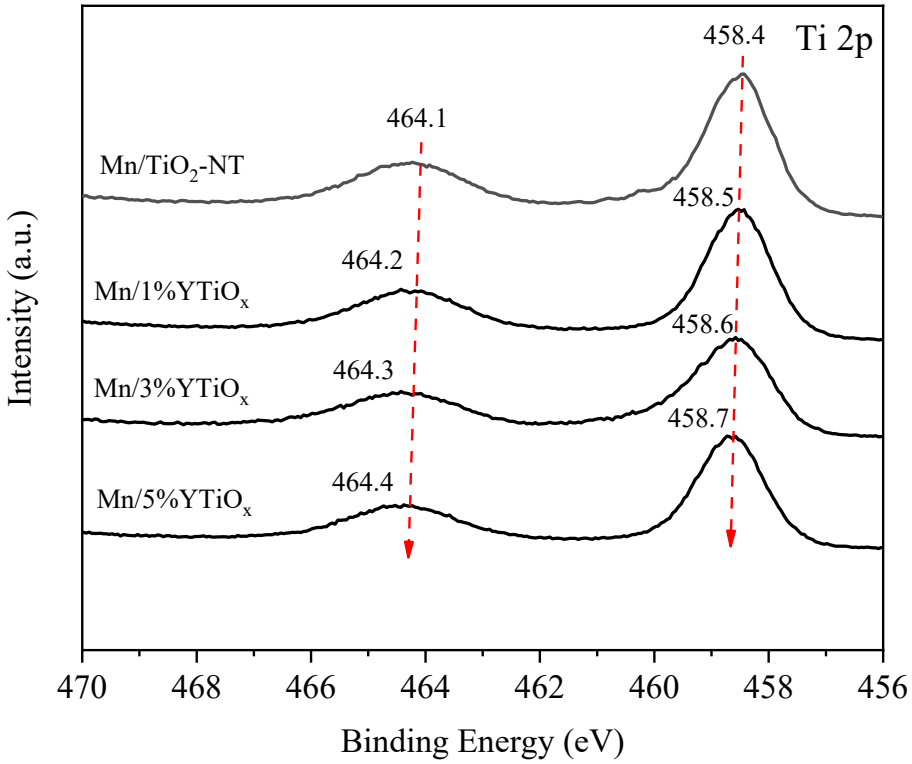


Fig. S2. NH_3-TPD profiles of TiO_2-NT and Y-doped TiO_2.



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138 Fig. S3. Ti 2p XPS spectra of Mn/TiO_2-NT and Y-doped TiO_2 supported MnO_x

139 catalysts.

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Table S1 Composition and proportion of surface elements of Mn/TiO_2-NT and Y-doped TiO_2 supported MnO_x catalysts.

Catalysts	Atom concentration (%)				Atom ratio		Mn 2p (eV)			Y 3d (eV)		O 1s (eV)	
	Mn	Y	Ti	O	Mn/Ti	Y/Ti	Mn^{4+}	Mn^{3+}	Mn^{2+}	Y^{3+}	Y^{2+}	O_α	O_β
Mn/TiO_2-NT	3.5	-	27.5	69.0	0.13	-	643.0	641.6	640.7	157.7	156.9	531.0	529.9
$Mn/1\%YTiO_x$	3.7	0.3	28.0	68.0	0.13	0.01	643.0	641.6	640.7	157.7	156.9	531.0	529.9
$Mn/3\%YTiO_x$	3.5	0.9	26.4	69.0	0.13	0.03	643.0	641.6	640.7	157.7	156.9	531.0	529.9
$Mn/5\%YTiO_x$	3.9	1.5	26.9	67.6	0.14	0.05	643.0	641.6	640.7	157.7	156.9	531.0	530.0