Efficient Sm modified Mn/TiO_2 catalysts for selective catalytic reduction of NO with NH_3 at low temperature

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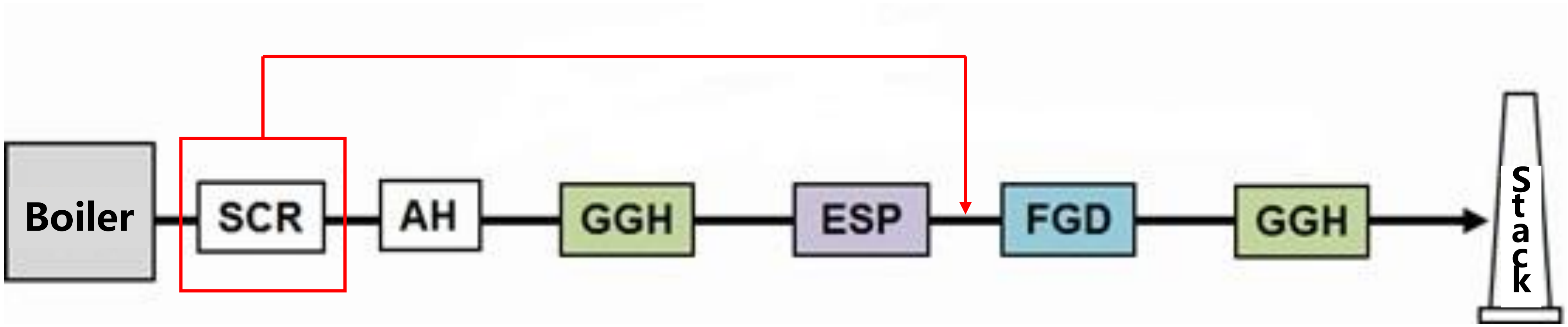
Research background



300-420℃

current position

present problem

- abrasion caused by fly ash
- deactivation caused by alkali metal
- high conversion of SO_2 to SO_3

solution →

100-150℃

new location

new problem

- excellent low-temperature SCR activity
- good resistance to H_2O and SO_2

← **meet** — novel SCR catalyst

Experimental

Catalyst design

Propose

$Mn^{[1]}$-$Sm/TiO_2^{[2]}$

MnO_x has excellent low temperature SCR activity

TiO_2-supported MnO_2 catalysts showed more promising SCR activity

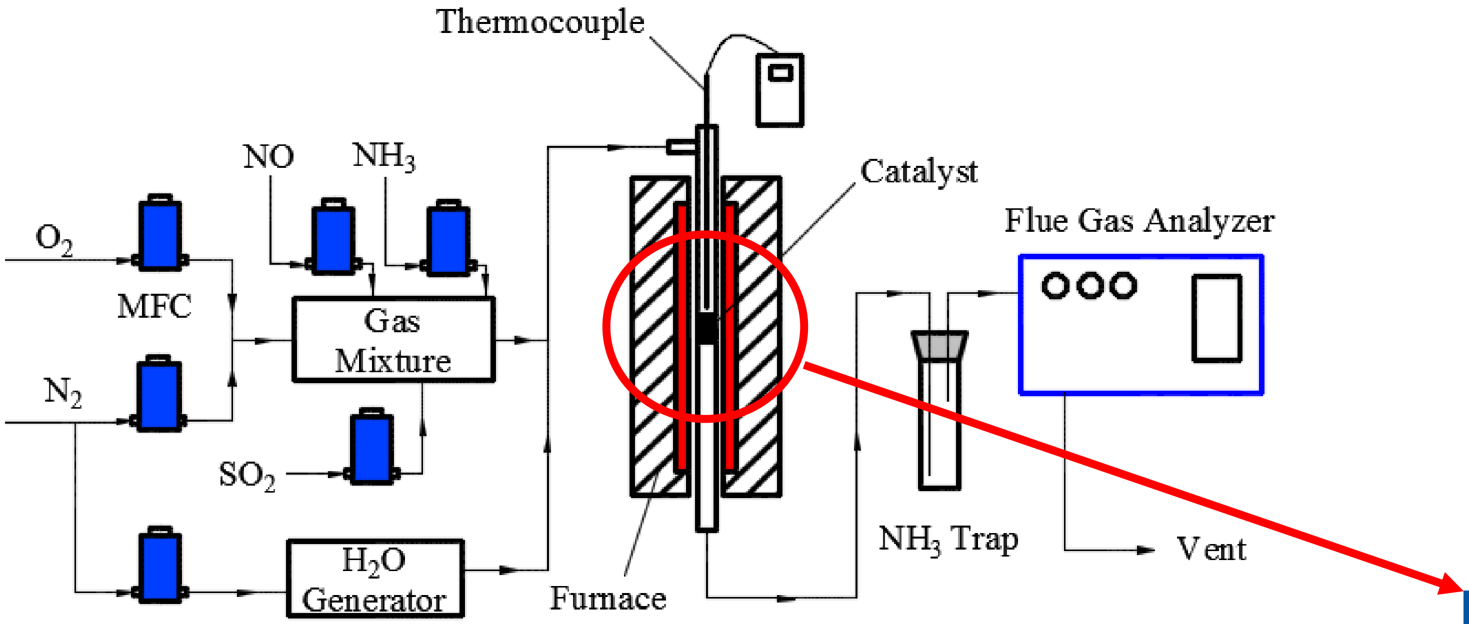
Sm can prevent transition from Mn^{4+} to Mn^{3+}

[1] D.A. Peña, B.S. Uphade, P.G. Smirniotis, J. Catal. 221 (2004) 421-431.

[2] P.G. Smirniotis, P.M. Sreekanth, D.A. Peña, R.G. Jenkins, Ind. Eng. Chem. Res. 45 (2006) 6436-6443.

Experimental

Catalytic activity test



Schematic diagram of the experimental system.

$$NO_x \text{ conversion} = \frac{[NOx]_{in} - [NOx]_{out}}{[NOx]_{in}} \times 100\%$$

$$N_2 \text{ selectivity} = \frac{[NOx]_{in} + [NH_3]_{in} - [NOx]_{out} - [NH_3]_{out} - 2[N_2O]_{out}}{[NOx]_{in} + [NH_3]_{in} - [NOx]_{out} - [NH_3]_{out}} \times 100\%$$

Test condition

Simulated flue gas:

500 ppm NO, 500 ppm NH_3, 5% O_2, 5% H_2O(when used), 100 ppm SO_2(when used) and N_2 as balance

Total flow rate: 1L/min

Particle size: 40-60 mesh

Gas hourly space velocity: 60000 h^{-1}

Characterization

Physicochemical properties

XRD BET XPS NH_3-TPD H_2-TPR

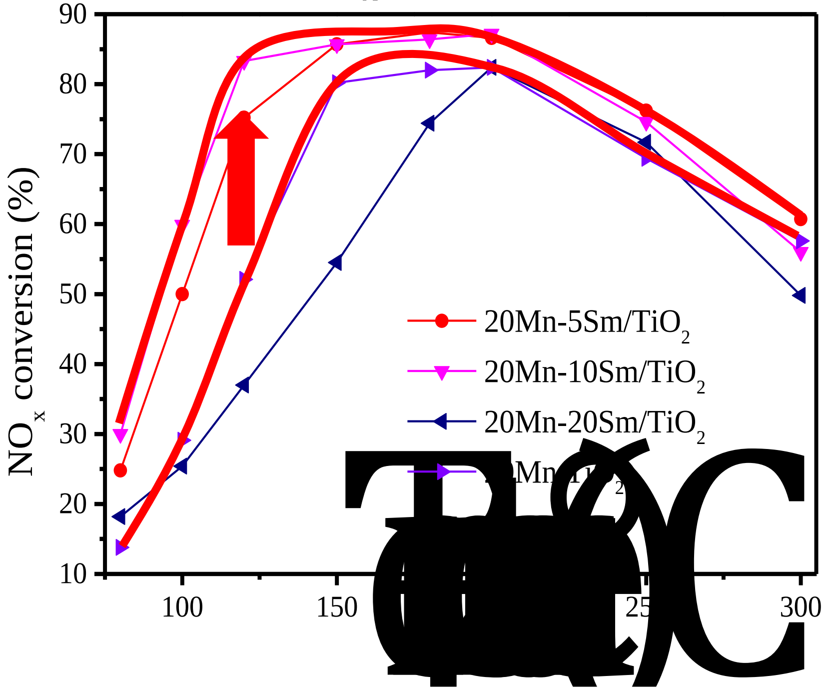
Reaction mechanism

in situ DRIFTS

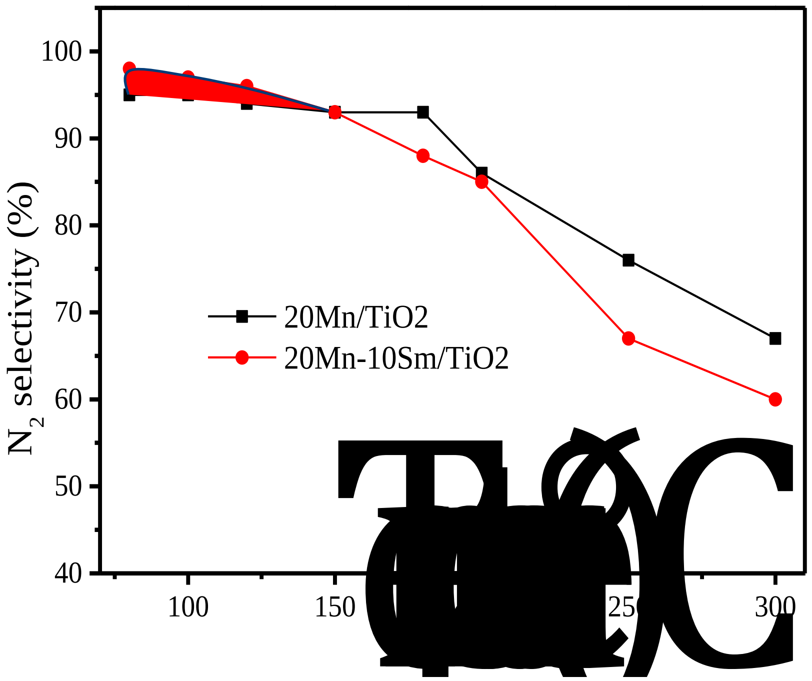
Results and discussion

Catalytic performance

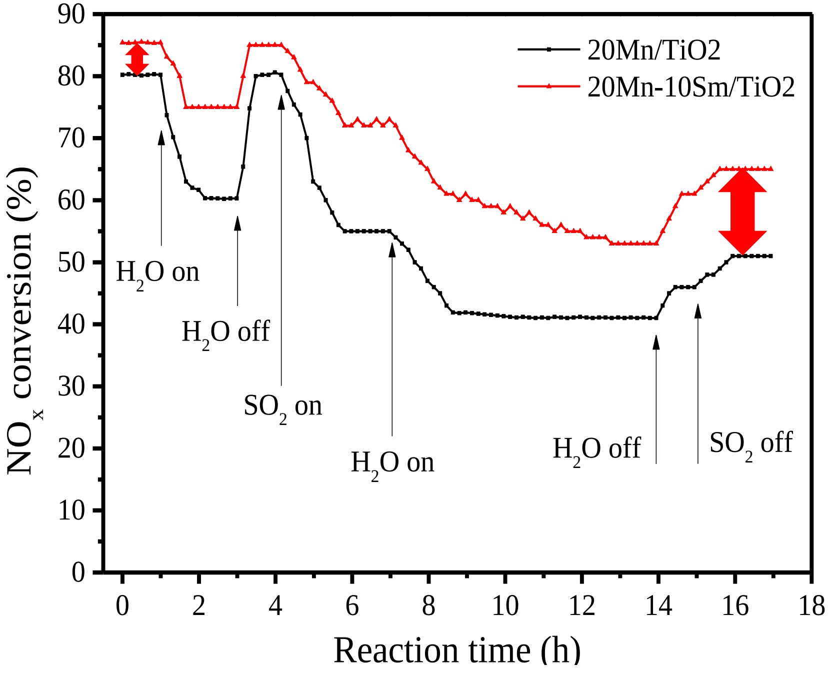
NO_x conversion



N_2 selectivity



Resistance to H_2O and SO_2



Optimum loading : 10%

50% → 85% at 120 °C

Higher N_2 selectivity

Over 95% at 80-150 °C

85% → 70% for Mn-Sm

80% → 55% for Mn

Results and discussion

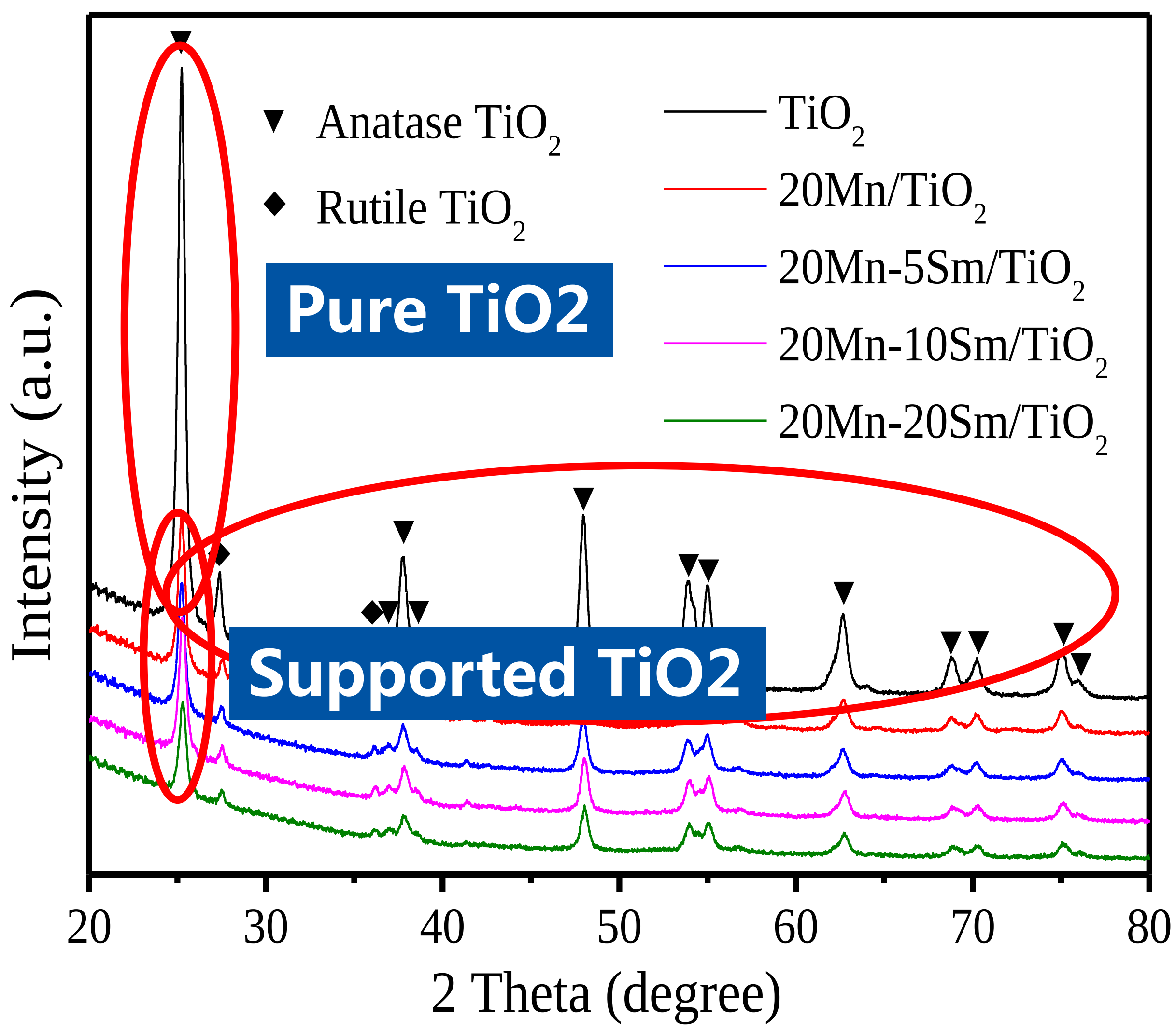
Specific surface area: BET

catalyst	BET surface area (m^2/g)	pore volume (cm^3/g)	average pore size (nm)
TiO_2	50.45	0.24	19.41
20Mn/TiO_2	43.67	0.34	31.55
20Mn-5Sm/TiO_2	45.93	0.30	26.24
20Mn-10Sm/TiO_2	47.69	0.33	27.38
20Mn-20Sm/TiO_2	38.40	0.29	30.67

- The surface areas of Mn-Sm/TiO_2 catalysts increased in the presence of Sm ;
- The doped Sm could promote the dispersion of manganese oxide

Results and discussion

Crystal structure: XRD



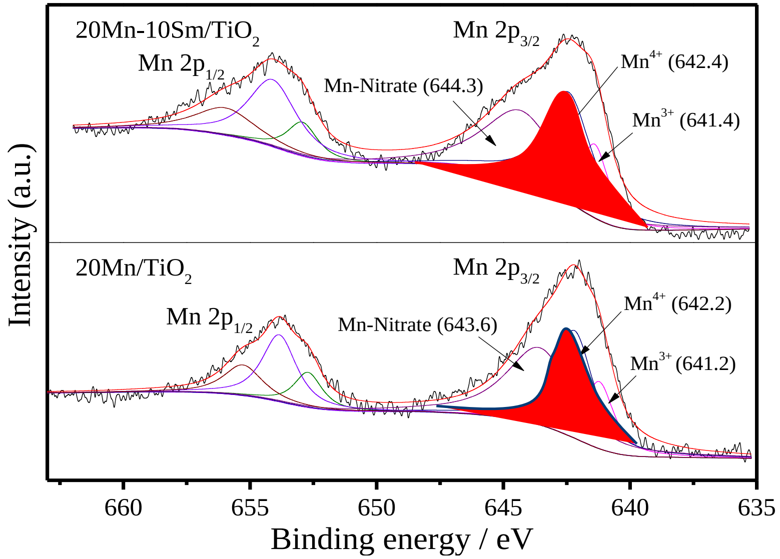
Diffraction peaks of TiO_2 are observed

No Mn and Sm species are detected

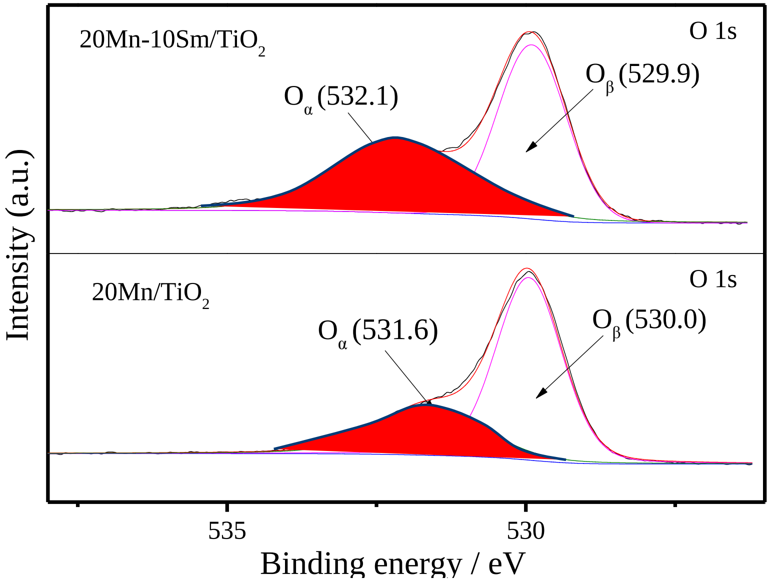
Strong interaction between Mn and Ti

Results and discussion

Oxidation state and surface atomic concentrations: XPS



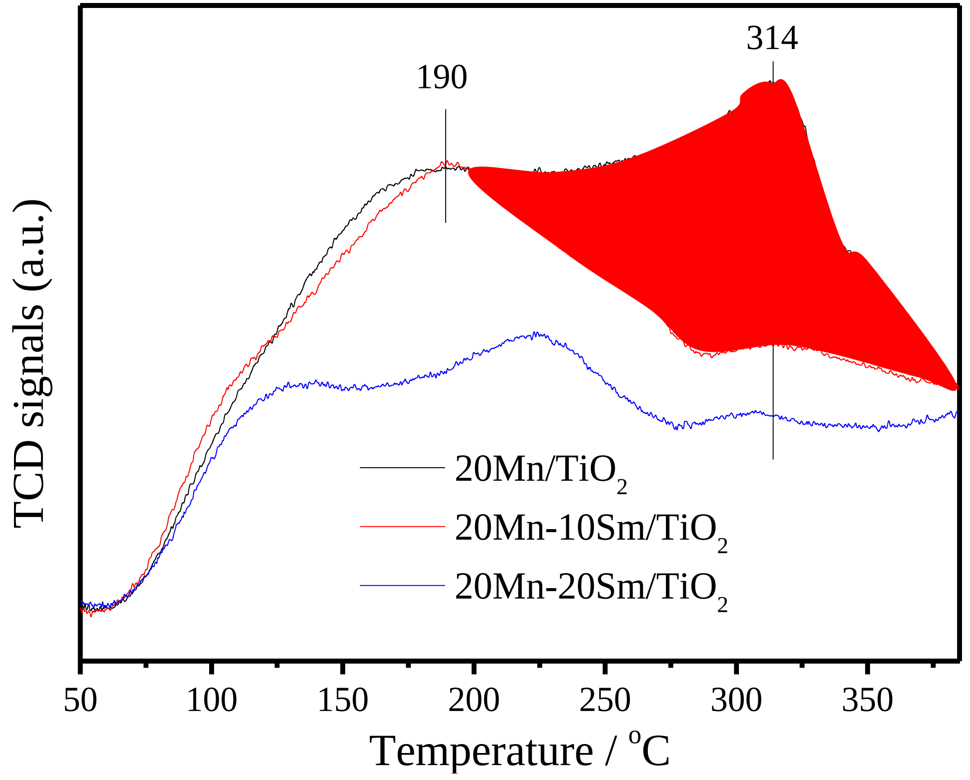
catalyst	surface atom concentration				
	Mn^{4+}/Mn^{3+}	Mn^{4+}/Mn	Mn/Ti	O_α/O_β	O_α/O
$20Mn/TiO_2$	2.08	36.81%	0.21	0.38	27.75%
$20Mn\text{-}10Sm/TiO_2$	2.46	41.57%	0.43	0.54	35.10%



- The presence of Sm could inhibit the crystallization of manganese oxide ;
- Mn could incorporate into lattice structure of TiO_2;
- The addition of Sm could promote the surface active oxygen species.

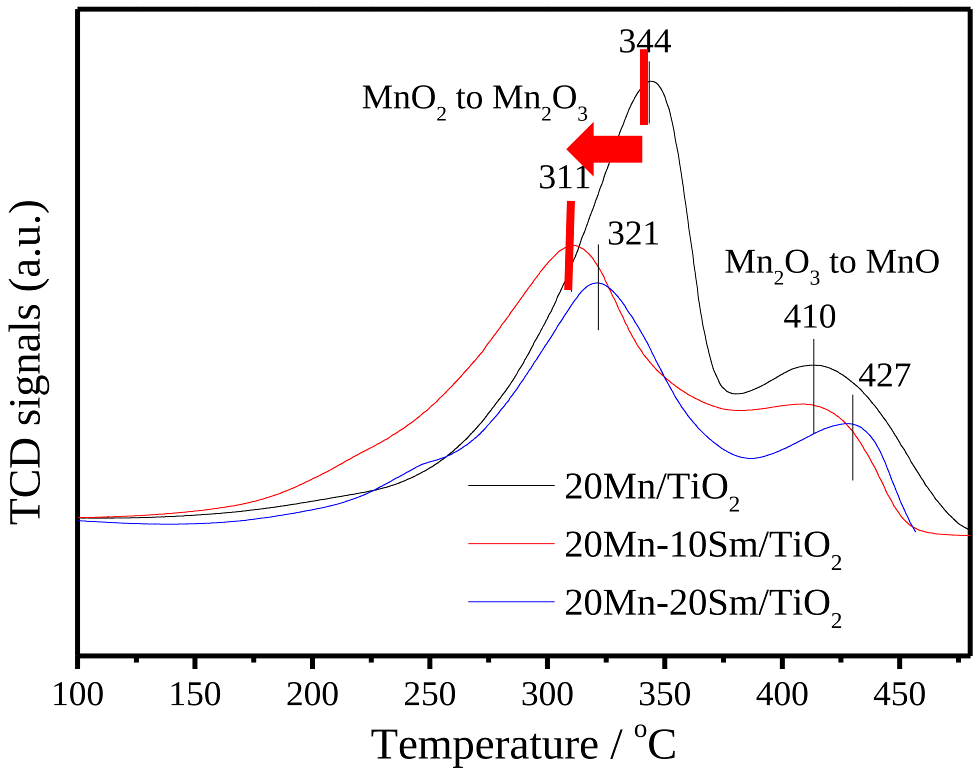
Results and discussion

Acidity: NH_3-TPD



- Lewis acid site might not be the main factor in low-temperature NH_3-SCR of NO_x over these catalysts.

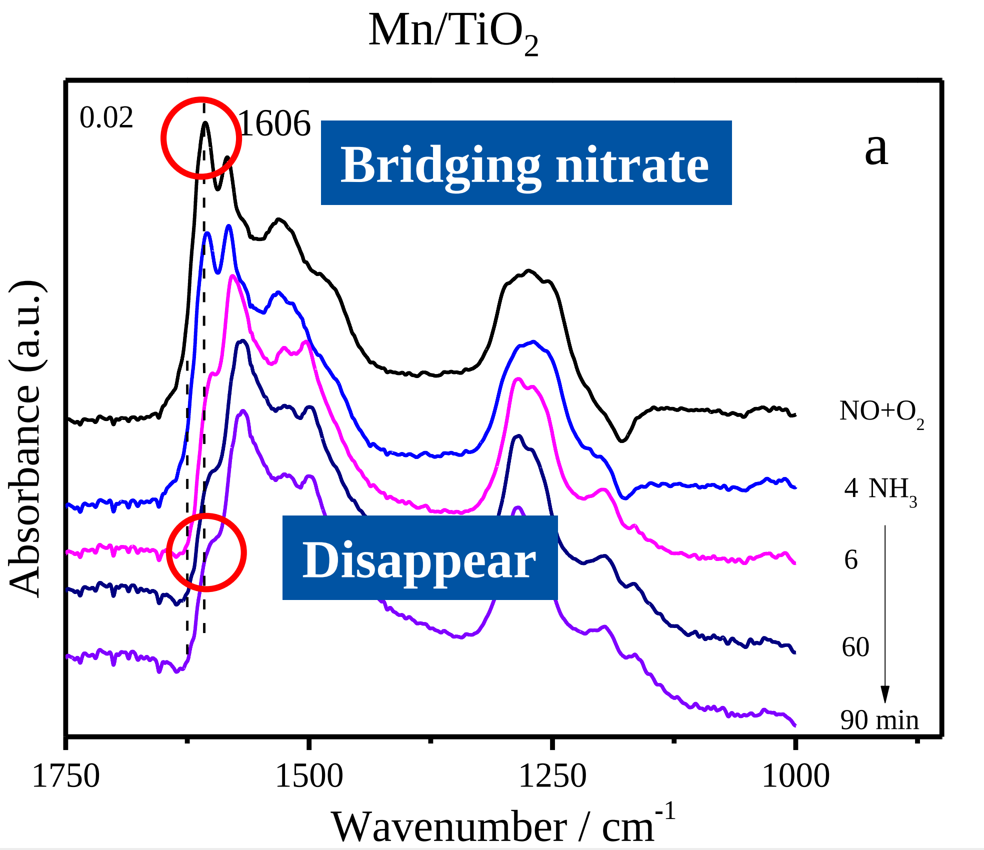
Redox property: H_2-TPR

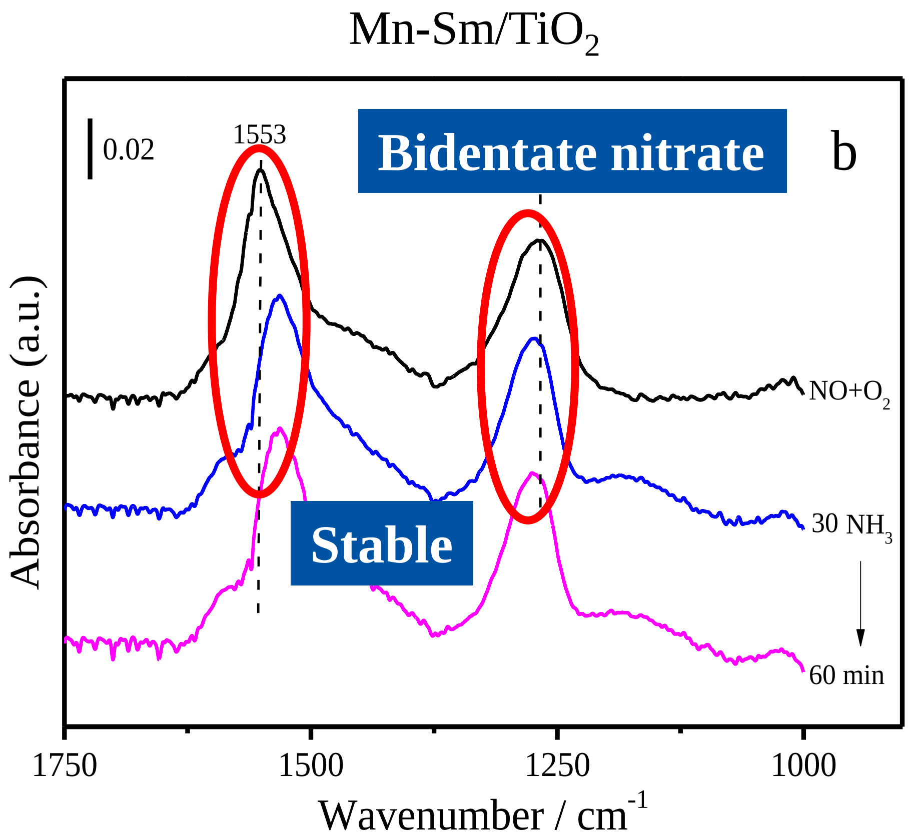


- The reducibility may be play an important role in low-temperature SCR activity.

Results and discussion

Reaction of NH_3 with pre-adsorbed NO + O_2: In situ DRIFTS



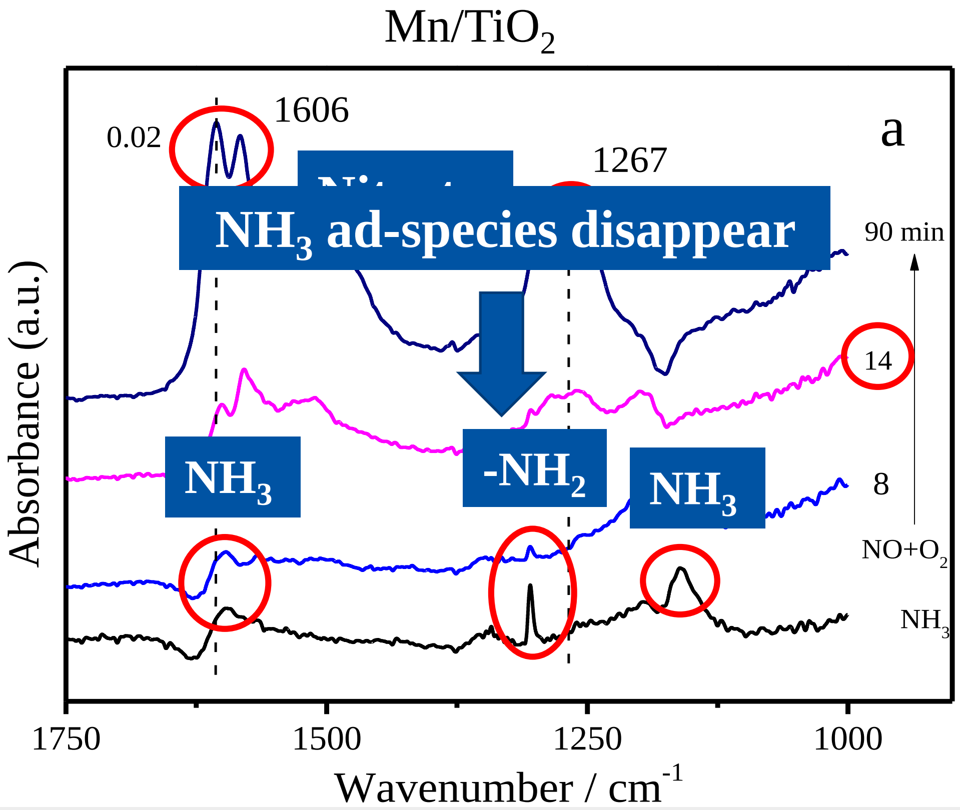


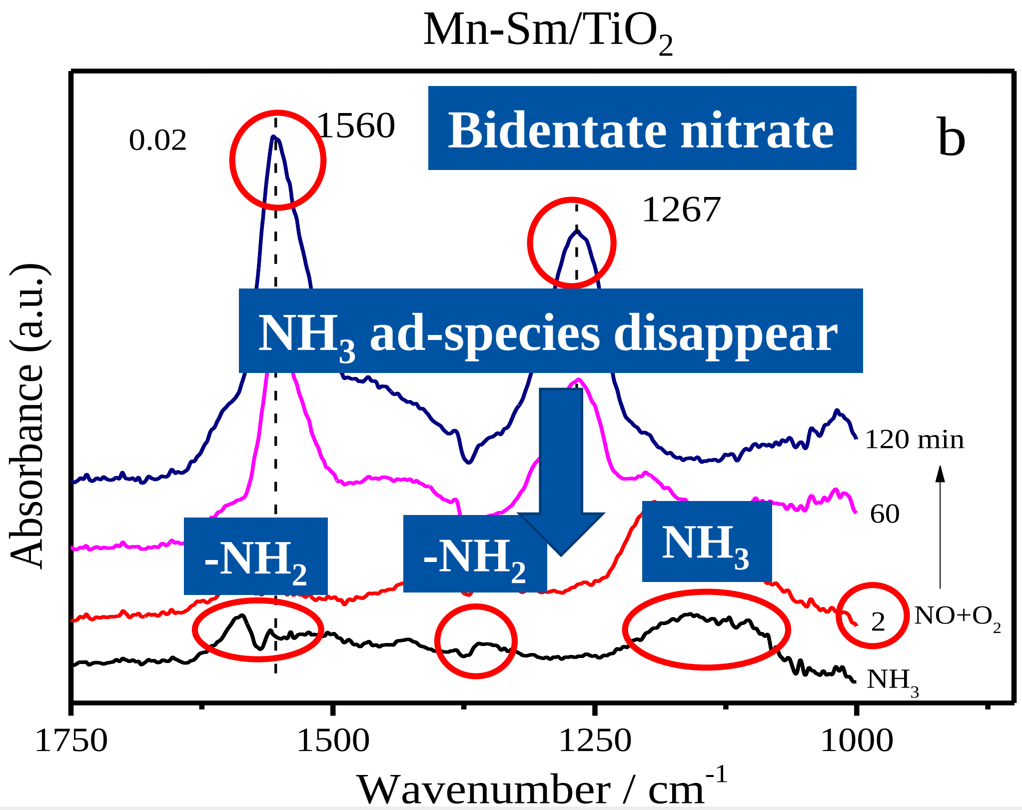
- The bridging nitrates are the main active nitrate species;
- The SCR reactions over the Mn/TiO_2 catalyst can proceed through L−H mechanism.

- The bridging nitrates were not formed on the surface of Mn-Sm/TiO_2 catalyst;
- The SCR reactions over the Mn-Sm/TiO_2 catalyst can not happen via L−H mechanism.

Results and discussion

Reaction of NO + O_2 with pre-adsorbed NH_3: In situ DRIFTS



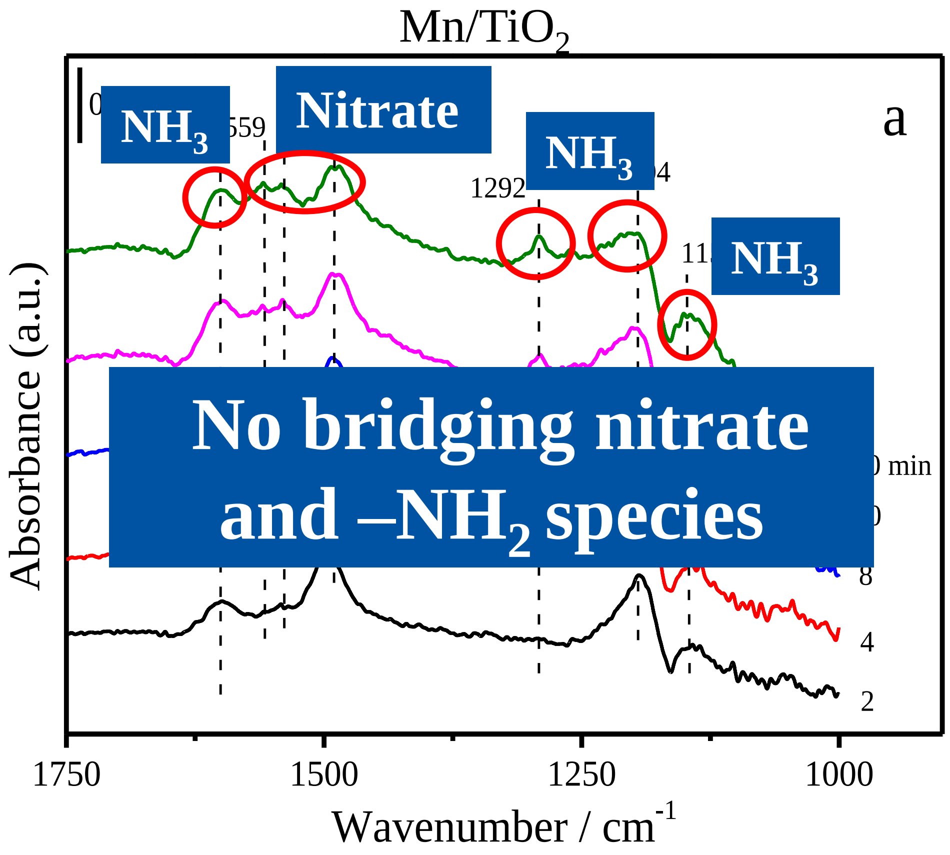


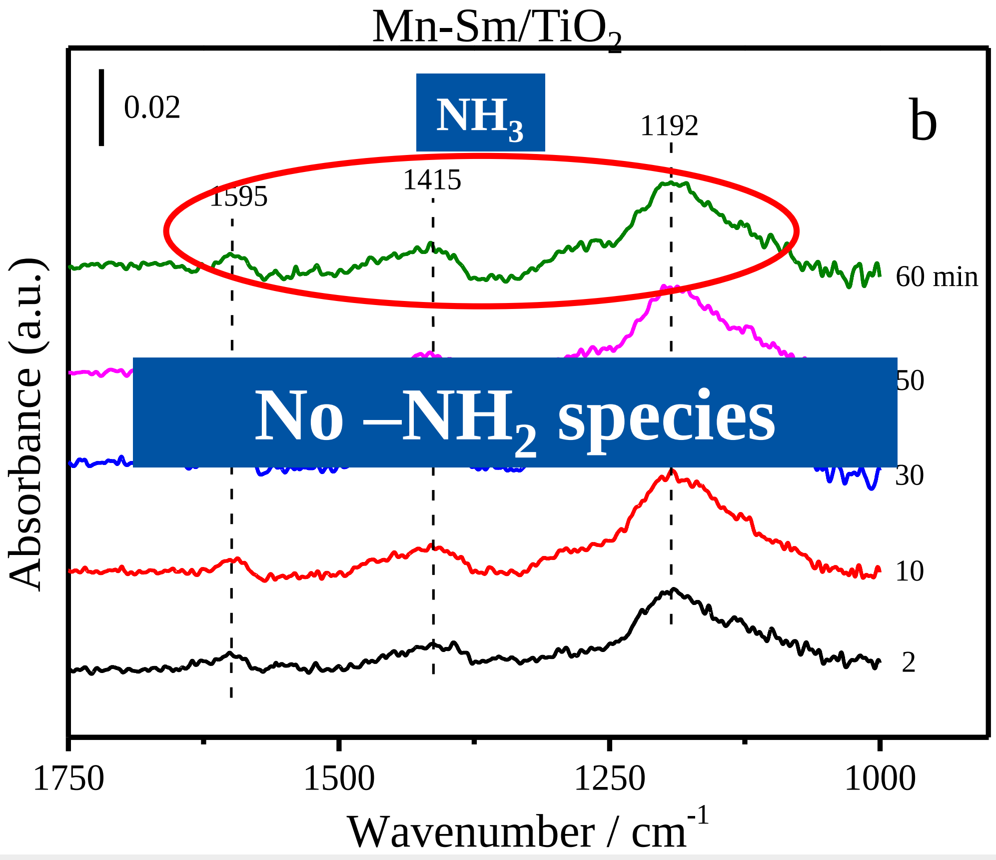
- All bands of coordinated NH_3, NH_4^+ and $-NH_2$ species disappeared gradually after exposure to NO + O_2;
- The SCR reactions over the Mn/TiO_2 catalyst can proceed through E−R mechanism.

- The reaction of preadsorbed NH_3 with NO + O_2 on Mn-Sm/TiO_2 catalyst was significantly faster than that over Mn/TiO_2 catalyst;
- The Sm modified catalyst possessed more $-NH_2$ species than Mn/TiO_2 catalyst.

Results and discussion

Adsorption and reaction of NH_3 + NO + O_2: In situ DRIFTS





- The co-existence of the NH_3 ad-species and NO_x ad-species are observed;
- The reactive bridging nitrate and the $-NH_2$ and NH_4^+ intermediates are all absent.

- The adsorption of NO can not happen in the presence of NH_3;
- The formed $-NH_2$ species quickly reacted with gaseous NO to produce N_2 and H_2O.

Conclusions

- The best 20Mn-10Sm/TiO_2 catalyst achieved almost 85% NO conversion with a GHSV of 60000 h^{-1} at 120 °C;
- The presence of Sm can improve the dispersion of manganese oxide and the relative concentration of surface oxygen (O_α);
- The SCR reaction mechanism changed by inhibiting the formation of bridging nitrate in the presence of Sm and the reactions can proceed only through Eley-Rideal mechanism;
- The enhanced oxygen transport after introduction of Sm boost the reaction rate.

THANKS FOR YOUR LISTENING!