

**Fe and Mn mixed oxide catalysts supported on Sn-modified TiO₂ for selective
catalytic reduction of NO with NH₃ at low temperature**

Zhitao Han^{a†}, Huan Du^{b‡}, Duo Xu^a, Yu Gao^a, Shaolong Yang^c, Liguo Song^a, Jingming Dong^a,

Xinxiang Pan^{a,d}

a. Marine Engineering College, Dalian Maritime University, Dalian 116026, China;

b. China Waterborne Transport Research Institute, Beijing 100088, China;

c. School of Naval Architecture and Ocean Engineering, Huazhong University of Science and
Technology, Wuhan 430074, China;

d. School of Electronic and Information Technology, Guangdong Ocean University, Zhanjiang
524088, China.

Correspondence information: Dr. Zhitao Han, Dalian Maritime University, No.1, Linghai Road,
Dalian 116026, China, hanzt@dlmu.edu.cn, +86 411 8472 3321; Dr. Huan Du, China Waterborne
Transport Research Institute, Beijing 100088, China, duhuan@wti.ac.cn, +86 010 6529 0511.

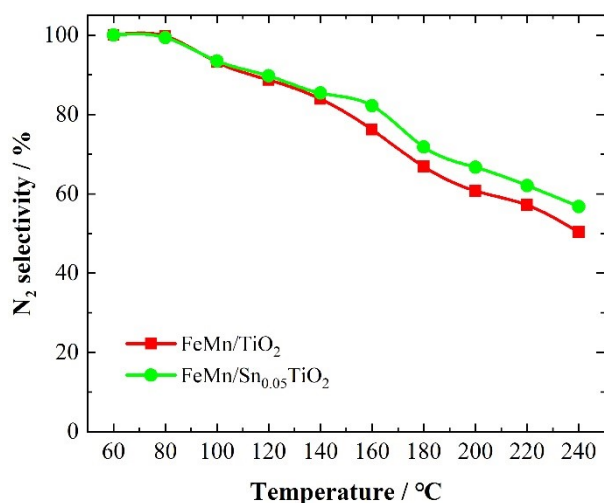


Fig. S1. N₂ selectivities in NH₃-SCR reactions over FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ catalysts (Reaction conditions: 1 mL catalyst, [NO] = [NH₃] = 600 ppm, [O₂] = 5 vol.%, balanced with N₂, GSHV = 30,000 h⁻¹).

SEM and EDS

The samples of TiO₂, Sn_{0.05}TiO₂, FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ were characterized by SEM, and the results were illustrated in Fig. S2. As shown in Fig. S2(a,b), the surface morphology of Sn-modified TiO₂ was more uniform compared with that of pristine TiO₂. As to FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ catalysts, there were no obvious differences in surface morphology observed from the SEM images. The nanoparticles dispersed well, and were uniform in size. It indicated that the introduction of Sn in TiO₂ support imposed little effect on the surface morphology of the prepared catalysts.

The distribution and contents of the elements in the prepared supports and catalysts were evaluated by EDS. The EDS spectra were shown in Fig. S3 and the calculated surface element contents were summarized in Tab. S1. From the EDS spectra of Sn_{0.05}TiO₂ support and FeMn/Sn_{0.05}TiO₂ catalyst, obvious Sn peaks could be observed, which confirmed that transition metal element Sn had been successfully introduced in TiO₂ supports. As shown in Tab. S1, the atomic percentages of Sn and Ti elements on

the surface of $\text{FeMn}/\text{Sn}_{0.05}\text{TiO}_2$ catalyst were 0.52 % and 10.43 %, respectively, resulting in a calculated molar ratio of Sn/Ti was 0.05. This result was very consistent with the design value in preparation process. It implied that the distribution of Sn element in the support of $\text{FeMn}/\text{Sn}_{0.05}\text{TiO}_2$ catalyst was very uniform.

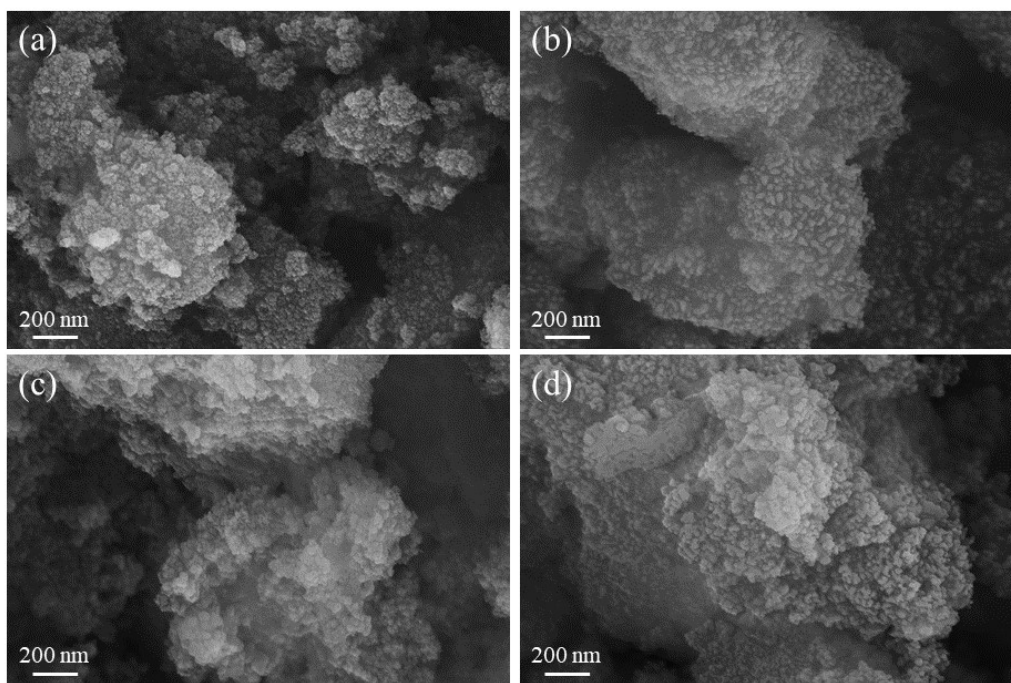
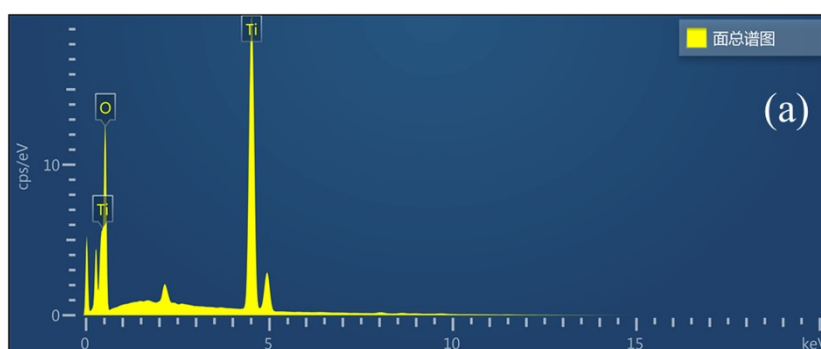


Fig. S2. FESEM images of (a) TiO_2 , (b) $\text{Sn}_{0.05}\text{TiO}_2$, (c) FeMn/TiO_2 and (d) $\text{FeMn}/\text{Sn}_{0.05}\text{TiO}_2$



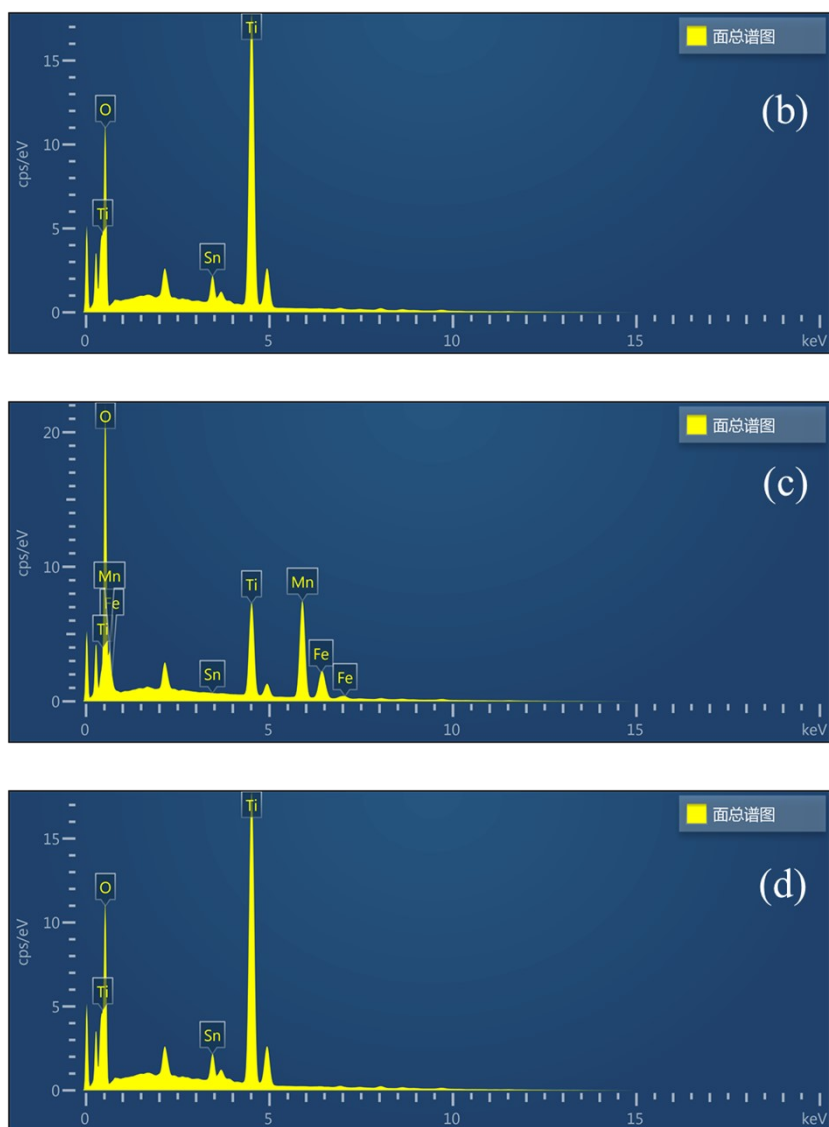


Fig. S3. EDS pictures of (a) TiO₂, (b) Sn_{0.05}TiO₂, (c) FeMn/TiO₂ and (d) FeMn/Sn_{0.05}TiO₂

NH₃-TPD

NH₃-TPD tests were performed to investigate the influence of Sn doping in TiO₂ on the surface acidity of the prepared catalysts. NH₃-TPD profiles of FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ catalysts were shown in Fig. S4. There were two obvious desorption peaks in NH₃-TPD spectra of both catalysts. The desorption peaks in the low-temperature region (< 250 °C) belonged to the weak acid sites, while the desorption peaks in the high-temperature region (> 250 °C) belonged to the strong acid sites.

Comparatively speaking, the desorption peak area of FeMn/Sn_{0.05}TiO₂ catalyst was obviously larger than that of FeMn/TiO₂ catalyst. It indicated that the strengths of both weak acid sites and strong acid sites over Sn-modified FeMn/TiO₂ catalyst had been distinctively enhanced. Yao et al. reported that the enhancement of weak acid sites was helpful to promote the low-temperature activity of SCR catalysts [1]. The results demonstrated that the introduction of Sn in TiO₂ support could promote the strength of weak acid sites on catalyst surface, thus improving the SCR activity of FeMn/TiO₂ catalysts at low temperature.

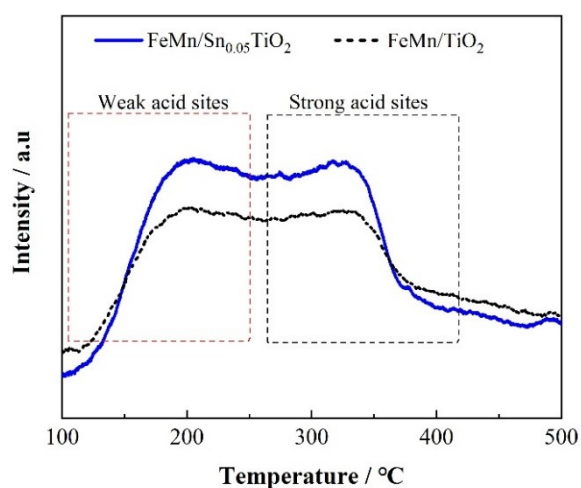


Fig. S4. NH₃-TPD profiles of FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ catalysts

Tab. S1. Surface element contents of the prepared supports and catalysts

Sample		O	Ti	Mn	Fe	Sn	Total
TiO ₂	wt (%)	42.73	57.27	0	0	0	100
	atomic ratio (%)	69.08	30.92	0	0	0	100
Sn _{0.05} TiO ₂	wt (%)	40.59	53.09	0	0	6.32	100
	atomic ratio (%)	68.60	29.97	0	0	1.44	100
FeMn/TiO ₂	wt (%)	32.86	19.02	39.16	8.96	0	100
	atomic ratio (%)	61.78	11.96	21.45	4.83	0	100
FeMn/Sn _{0.05} TiO ₂	wt (%)	28.17	15.43	46.17	8.34	1.89	100
	atomic ratio (%)	57.01	10.43	27.21	4.84	0.52	100

Tab.S2. Textural properties of the prepared supports and catalysts

Catalyst	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
TiO ₂	75.6	0.18	6.8
Sn _{0.01} TiO ₂	78.9	0.18	6.3
Sn _{0.05} TiO ₂	62.0	0.16	7.4
Sn _{0.1} TiO ₂	80.7	0.18	6.7
Sn _{0.2} TiO ₂	108.2	0.20	5.3
FeMn/TiO ₂	53.6	0.14	7.6
FeMn/Sn _{0.01} TiO ₂	62.4	0.16	7.5
FeMn/Sn _{0.05} TiO ₂	53.6	0.15	8.1
FeMn/Sn _{0.1} TiO ₂	59.3	0.15	7.5
FeMn/Sn _{0.2} TiO ₂	71.7	0.16	6.5
FeMn/TiO ₂ -S	48.0	0.19	10.9
FeMn/Sn _{0.05} TiO ₂ -S	50.3	0.15	8.8

Tab. S3. Reduction temperatures and H₂ consumption values of FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ catalysts before and after SO₂ resistance tests

Catalyst	Peak temperature (°C)			H ₂ consumption (cm ³ /g STP)
	Peak-1	Peak-2	Peak-3	
FeMn/TiO ₂	323	421	479	161.6
FeMn/Sn _{0.05} TiO ₂	323	429	687	245.4
FeMn/TiO ₂ -S	361	459	652	216.6
FeMn/Sn _{0.05} TiO ₂ -S	359	4354	486	261.5

Tab. S4. Surface atomic ratios of FeMn/TiO₂ and FeMn/Sn_{0.05}TiO₂ catalysts before and after SO₂ resistance tests

Catalyst	Mn (%)	Fe (%)	O (%)	Ti (%)	S (%)	N (%)	Mn ⁴⁺ /Mn ⁿ⁺ (%)	O _α /(O _β + O _α) (%)
FeMn/TiO ₂	14.26	4.76	45.56	5.55	-	-	27.2	23.9
FeMn/Sn _{0.05} TiO ₂	12.85	4.44	46.67	7.34	-	-	30.8	26.4
FeMn/TiO ₂ -S	16.16	4.93	49.28	3.96	2.12	1.83	28.3	25.7
FeMn/Sn _{0.05} TiO ₂	13.11	4.89	50.65	7.67	1.93	1.68	40.8	33.7

Tab. S5. Comparison of some reported FeMn/TiO₂ catalysts in terms of NO conversion efficiencies and SO₂ resistance

Catalysts	Reaction condition	NO conversion	SO ₂ resistance	Reference
FeMn/Sn _{0.05} TiO ₂	NO = NH ₃ = 600 ppm, O ₂ = 5%, GHSV = 30000 h ⁻¹ , flow rate 500 mL/min, SO ₂ = 100 ppm (when	95.9% (@100°C)	84.4% (@200°C, 3 h)	This work

Catalysts	Reaction condition	NO conversion	SO ₂ resistance	Reference
	used)			
FeMn/TiO ₂	NO = NH ₃ = 1000 ppm, O ₂ = 3%, GHSV = 20000 h ⁻¹ , flow rate 2 L/min, catalyst 4 mL, SO ₂ = 200 ppm (when used)	100% (@150°C)	80% (@150°C, 35 min)	[2]
FeMn/TiO ₂	NO = NH ₃ = 600 ppm, O ₂ = 3%, GHSV = 50000 h ⁻¹ , flow rate 300 mL/min, SO ₂ = 100 ppm (when used), H ₂ O = 3%(when used)	65% (@100 °C)	84% (@180 °C, 5 h)	[3]
FeMn/TiO ₂	NO = NH ₃ = 1000 ppm, O ₂ = 2%, catalyst 2.5 g, flow rate 100 mL/min	88% (@100 °C)	No data	[4]
HoFeMn/TiO ₂	NO = NH ₃ = 0.08%, O ₂ = 5%, GHSV = 20000 h ⁻¹ , flow rate 100 mL/min, SO ₂ = 200 ppm (when used), H ₂ O = 15% (when used)	85% (@100 °C)	80% (@120 °C, 4h)	[5]
PrFeMn/TiO ₂	NO = NH ₃ = 1000 ppm, O ₂ = 7%, GHSV = 30000 h ⁻¹ , flow rate 1 L/min, SO ₂ = 100 ppm (when used)	85 (@120 °C)	95% (@200 °C, 3h)	[6]
FeCoMnCe/TiO ₂	NO = NH ₃ = 500 ppm, O ₂ = 6%, GHSV = 12000 h ⁻¹ , flow rate 400 mL/min, SO ₂ = 200 ppm (when used)	85% (@100 °C)	96% (@200 °C, 7h)	[7]
Mn/Fe-Ti	NO = NH ₃ = 500 ppm, O ₂ = 6%, GHSV = 12000 h ⁻¹ , flow rate 100 mL/min, SO ₂ = 60 ppm (when used) H ₂ O = 8% (when used)	59% (@100 °C)	83% (@200 °C, 700 min)	[8]
FeMnW/TiO ₂	NO = NH ₃ = 600 ppm, O ₂ = 15%, GHSV = 240000 h ⁻¹ , flow rate 150 mL/min	68% (@100 °C)	No data	[9]

References:

- [1] X. J. Yao, Y. Xiong Y, W. X. Zou, L. Zhang, S. G. Wu, X. Dong, F. Gao, Y. Deng, C. J. Tang, Z. Chen, L. Dong, Y. Chen, *Appl Catal B-Environ.*, 2014, **144**, 152-165.
- [2] B.Q. Jiang, Z.B. Wu, Y. Liu, S.C. Lee, W. K. Ho, *J. Phys. Chem. C.*, 2010, **114**, 4961-4965.
- [3] B.X. Shen, T. Liu, N. Zhao, X.Y. Yang, L.D. Deng, *J Envir Sci.*, 2010, **22**, 1447-1454.
- [4] G. Qi, R. T. Yang, *Appl Catal B-Environ.*, 2003, **44**, 217-225.
- [5] Y. Zhu, Y. Zhang, R. Xiao, T. Huang, K. Shen, *Catal. Commun.*, 2017, **88**, 64-67.
- [6] X. X. Hou, H. P. Chen, Y. H. Liang, X. Yang, Y. L. Wei, *Catal. Lett.*, 2020, **150**, 1041-1048.
- [7] F. M. Wang, B. X. Shen, S. W. Zhu, Z. Wang, *Fuel.*, 2019, **249**, 54-60.
- [8] S. Yang, F. Qi, S. Xiong, H. Dang, Y. Liao, P. K. Wong, J. Li, *Appl Catal B-Environ.*, 2016, **106**, 570-580.
- [9] J. Shi, Z. H. Zhang, M. X. Chen, Z. X. Zhang, W. F. Shang, *Fuel.*, 2017, **210**, 783-789.