

Electronic Supplementary Information for:

Novel proposition on mechanism aspects over Fe-Mn/ZSM-5 catalyst for NH₃-SCR of NO_x at low temperature: rate and direction of multifunctional electron-transfer-bridge and in-situ DRIFTS analysis

Wentao Mu, Jing Zhu, Shen Zhang, Yuyu Guo, Liqing Su, Xingying Li,
and Zhe Li*

College of Chemistry and Chemical Engineering, Taiyuan University of
Technology, Taiyuan 030024, Shanxi, China

*Corresponding author. Zhe Li. Tel/Fax: +86-351-6018975, E-mail: lizhe@tyut.edu.cn

1. Interpretation for samples choice

To seek the regulation of catalytic performances as a function of ferric content meticulously, many catalysts were prepared by co-precipitation method, such as, 0.5Fe-Mn/ZSM-5, 2Fe-Mn/ZSM-5, 5Fe-Mn/ZS-5, 8Fe-Mn/ZSM-5, 10Fe-Mn/ZSM-5, 13Fe-Mn/ZSM-5, 15Fe-Mn/ZSM-5, 16Fe-Mn/ZSM-5, 18Fe-Mn/ZSM-5 and 20Fe-Mn/ZSM-5 catalysts. 10Fe/ZSM-5 and 10Mn/ZSM-5 catalysts were prepared by precipitation method. The NH₃-SCR reaction activities of all catalysts were tested and shown in Figs. S1 and S2. For the most evident regulation of catalytic performance, 10Fe/ZSM-5, 10Mn/ZSM-5, 5Fe-Mn/ZS-5, 10Fe-Mn/ZSM-5, 15Fe-Mn/ZSM-5, 20Fe-Mn/ZSM-5 catalysts were selected to investigate the inherent relation between catalytic performance and amounts of Fe, especially the ratios of metallic ions.

2. Definition of reaction rate

In terms of the method illustrated by Hu et al.,¹ the reaction rate was defined as the mass of reacted NO over unit volume catalysts during per minute ($mg \cdot min^{-1} \cdot mL_{cat}^{-1}$) by assuming that the reaction components were free of diffusion limitations. The rate can be calculated from the following equation:

$$Rate (mg \cdot min^{-1} \cdot mL_{cat}^{-1}) = \frac{C_0 \cdot X \cdot M \cdot F}{V_0 \cdot V_{cat}}$$

where the X is the NO conversion, F is the volumetric flow rate (375 mL•min⁻¹), M is the molar mass of NO (30.01 mg•mmol⁻¹) and C₀ is the feeding concentration of NO (600 ppm). V₀ is the molar volume of gas (22.4 mL•mmol⁻¹), V_{cat} is the catalyst volume (0.5 mL). It should be noted that the conversion of NO was regarded as the NO_x conversion due to the amount of NO₂ in feed gas was so little that can be neglected, and that the rate was in the direct proportion to NO_x conversion X as C₀, M, F, V₀ and V_{cat} were almost constant. The reaction rate was shown in the following Fig. S13.

3. Supporting Figures

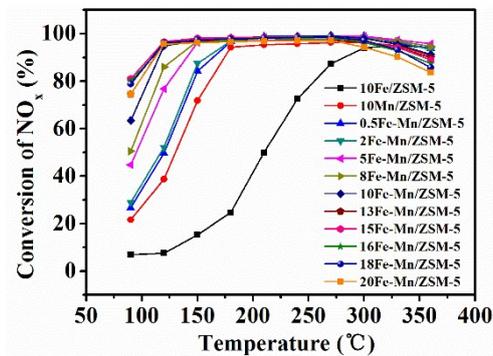


Fig. S1 NO_x conversions as a function of temperature in the NH₃-SCR reaction over prepared catalysts

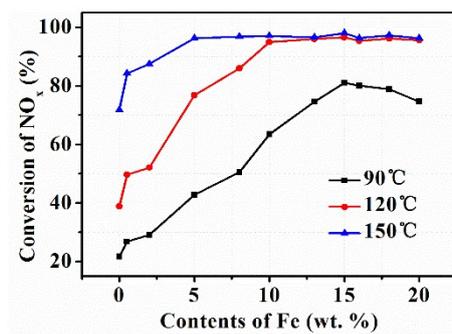


Fig. S2 NO_x conversion over xFe-Mn/ZSM-5 catalysts at 90 °C, 120 °C and 150 °C.

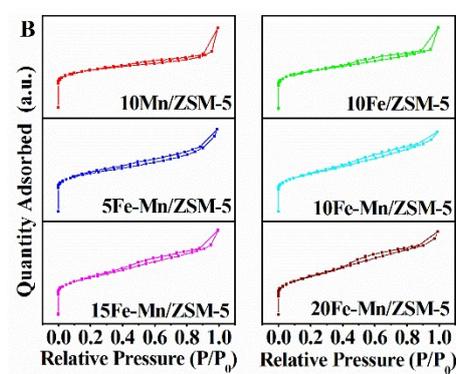
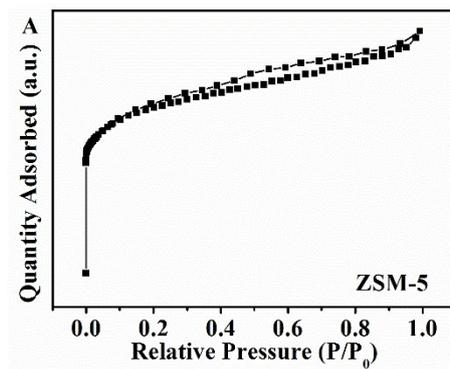


Fig. S3 (A) Nitrogen adsorption/desorption isotherms of the HZSM-5 and (B) Nitrogen adsorption/desorption isotherms of the catalysts.

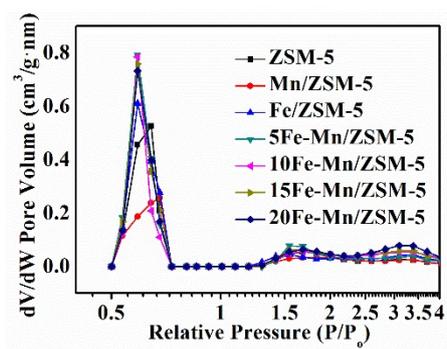


Fig. S4 Pore size distributions of ZSM-5 and catalysts

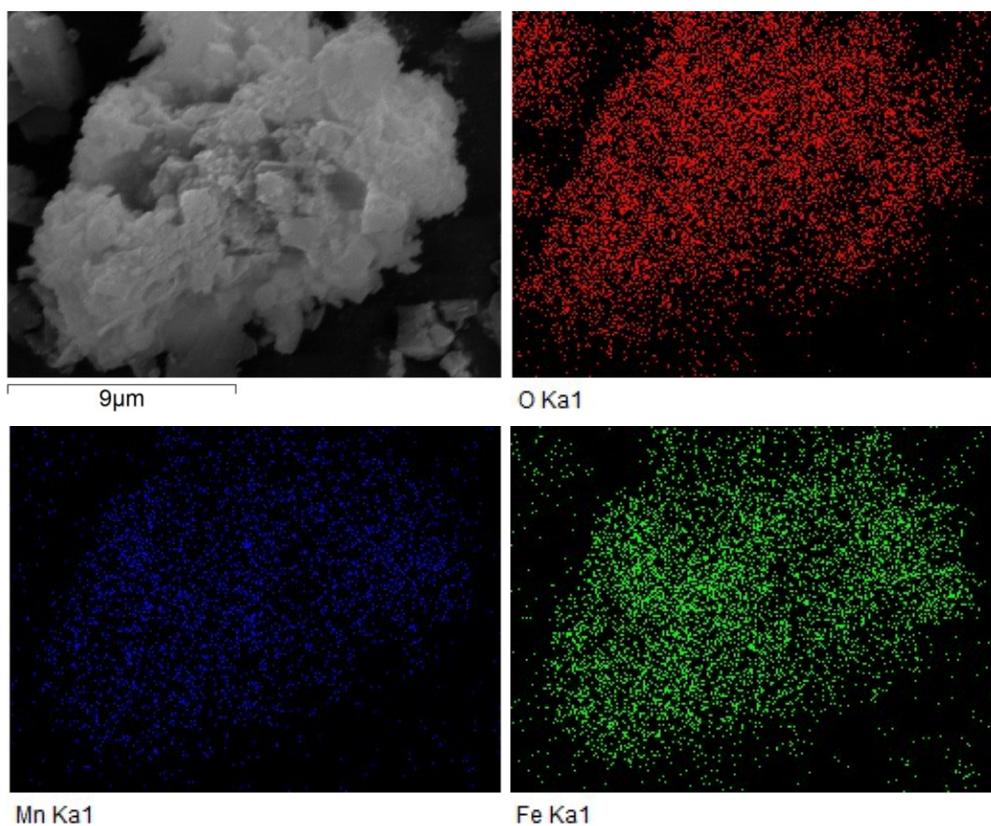
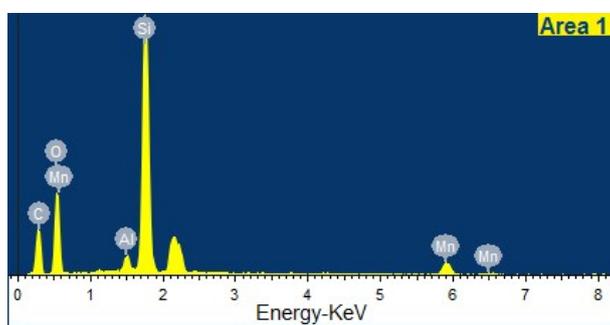
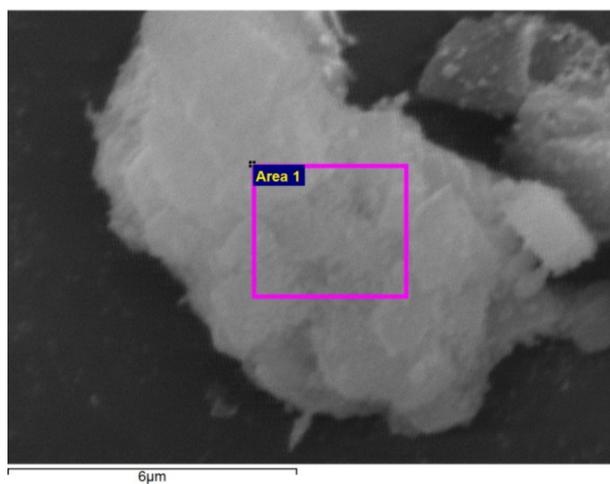
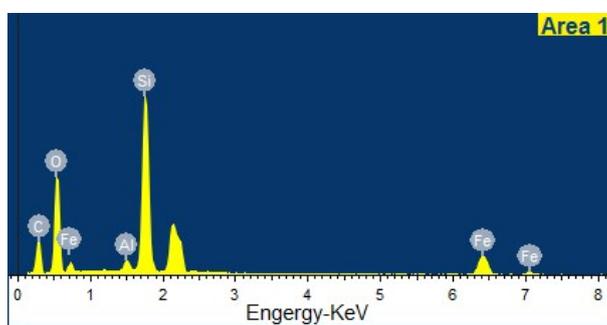
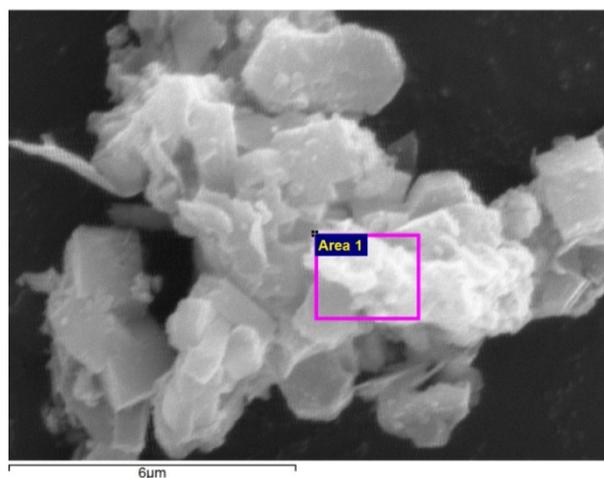


Fig. S5 EDS elemental mappings of O, Fe and Mn over 20Fe-Mn/ZSM-5 catalyst.



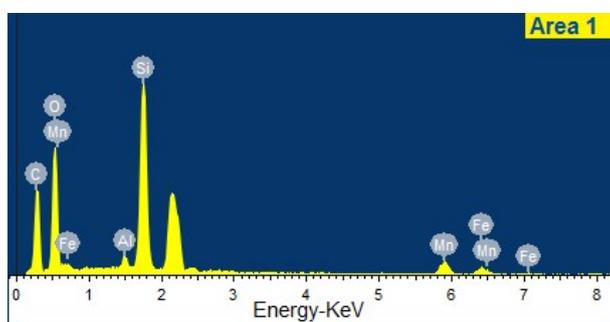
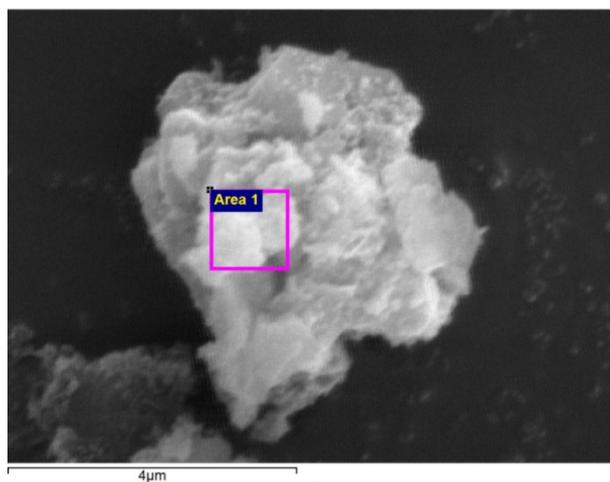
Element	Wt. %	At. %
C K	37.40	49.05
O K	39.60	38.99
Al K	1.02	0.60
Si K	18.48	10.36
Mn K	3.50	1.00
Total	100.00	100.00

Fig. S6 SEM image and elemental concentrations determined by EDS over 10Mn/ZSM-5 catalyst.



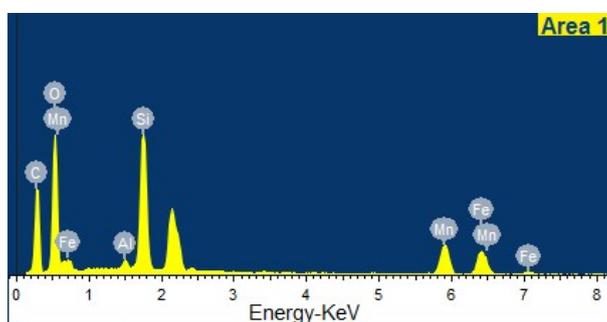
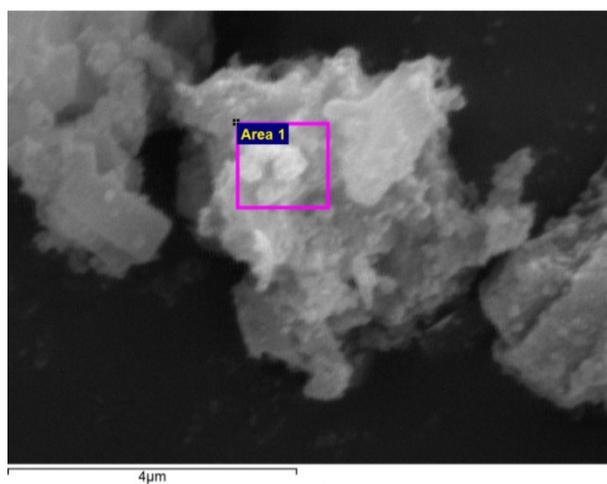
Element	Wt. %	At. %
C K	29.26	40.08
O K	46.77	48.08
Al K	0.96	0.59
Si K	15.39	9.01
Fe K	7.62	2.24
Total	100.00	100.00

Fig. S7 SEM image and elemental concentrations determined by EDS over 10Fe/ZSM-5 catalyst.



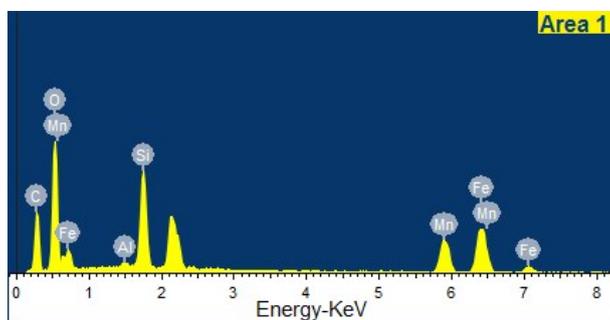
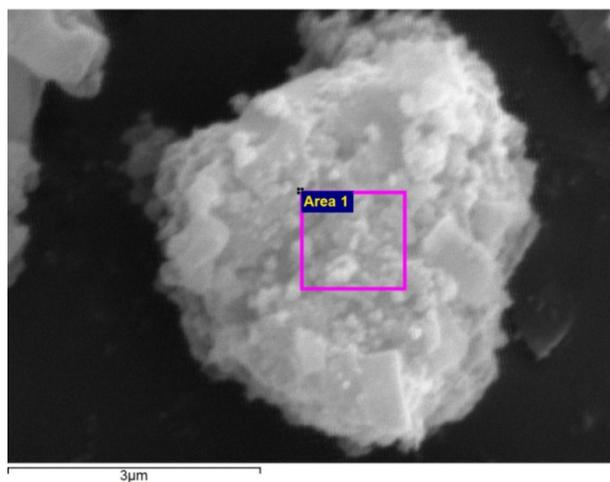
Element	Wt. %	At. %
C K	37.87	48.71
O K	44.96	43.41
Al K	0.65	0.37
Si K	10.72	5.90
Mn K	3.78	1.06
Fe K	2.01	0.55
Total	100.00	100.00

Fig. S8 SEM image and elemental concentrations determined by EDS over 5Fe-Mn/ZSM-5 catalyst.



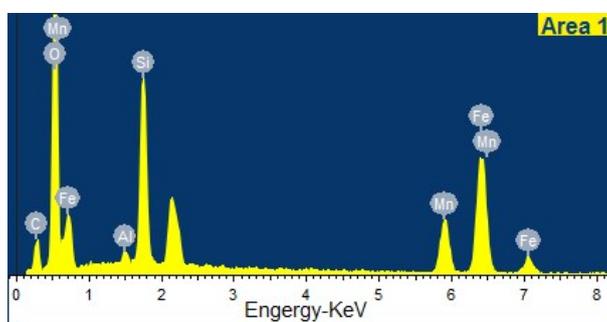
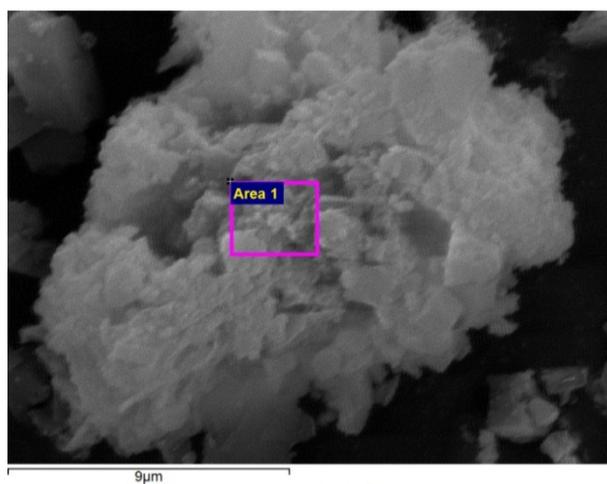
Element	Wt. %	At. %
C K	34.83	47.49
O K	42.30	43.29
Al K	0.49	0.30
Si K	8.01	4.67
Mn K	7.47	2.23
Fe K	6.90	2.02
Total	100.00	100.00

Fig. S9 SEM image and elemental concentrations determined by EDS over 10Fe-Mn/ZSM-5 catalyst.



Element	Wt. %	At. %
C K	28.66	42.35
O K	41.74	46.29
Al K	0.34	0.22
Si K	5.69	3.59
Mn K	9.50	3.07
Fe K	14.07	4.47
Total	100.00	100.00

Fig. S10 SEM image and elemental concentrations determined by EDS over 15Fe-Mn/ZSM-5 catalyst.



Element	Wt. %	At. %
C K	14.71	24.28
O K	47.81	59.23
Al K	0.68	0.50
Si K	8.19	5.78
Mn K	9.16	3.30
Fe K	19.46	6.91
Total	100.00	100.00

Fig. S11 SEM image and elemental concentrations determined by EDS over 20Fe-Mn/ZSM-5 catalyst.

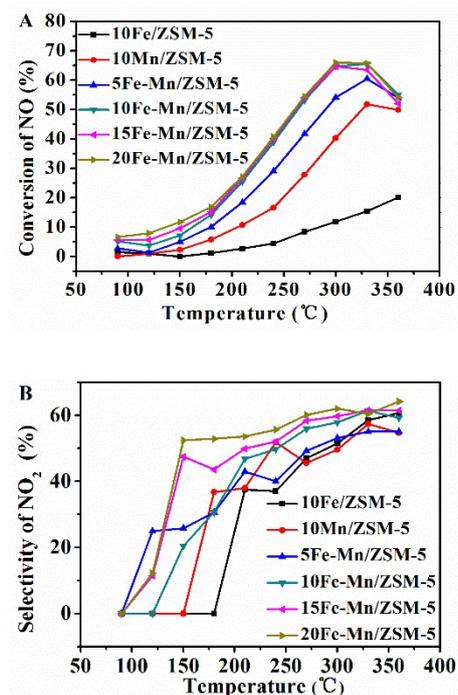


Fig. S12 (A) Conversions of NO as a function of temperature in NO oxidation measurements. (B) Selectivity of NO₂ as a function of temperature in NO oxidation measurements.

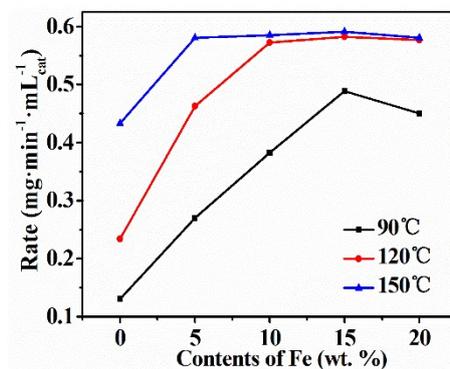


Fig. S13 Reaction rate of xFe-Mn/ZSM-5 catalyst at 90°C, 120°C and 150 °C.

4. H₂-TPR characterization analysis

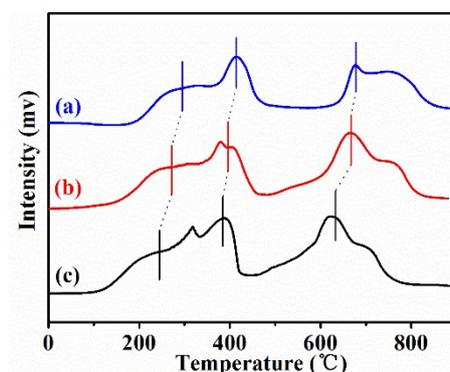


Fig. S14 H₂-TPR profiles of (a) 10Fe-Mn/ZSM-5, (b) 15Fe-Mn/ZSM-5 and (c) 20Fe-Mn/ZSM-5 catalyst.

Fig S14 revealed the H₂-TPR profiles of 10Fe-Mn/ZSM-5, 15Fe-Mn/ZSM-5 and 20Fe-Mn/ZSM-5. The reduction temperatures of catalysts with poorer Fe contents were lower than those of containing higher Fe contents. As the increment of Fe as well as the ratios of metallic ions, the reduction peak shifted to lower temperature implying that the redox ability of catalysts were heightened.^{2,3} On the other hand, the results were line with the XPS analysis that the relevant amount of metallic ions with higher valence increased as the Fe contents improved.³ Therefore, the higher redox ability was along with the higher ratios of metallic ions, which could promote the redox reaction over catalysts to facilitate the formation of intermediates as evidenced by the NO_x-intermediates storage shown in Table 6 in the paper.

5. Effects of SO₂ and GHSV on catalytic activities over 15Fe-Mn/ZSM-5 catalyst.

5.1 Effects of GHSV on catalytic activities over 15Fe-Mn/ZSM-5 catalyst.

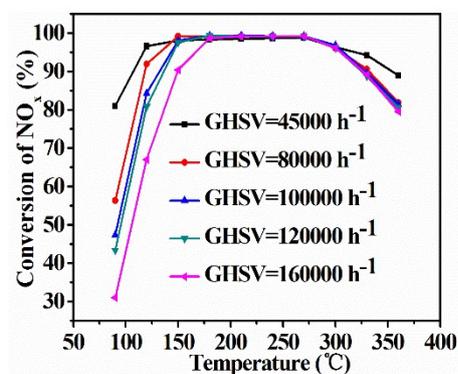


Fig. S15 Conversion of NO_x over 15Fe-Mn/ZSM-5 catalyst under different GHSV, with the evaluating condition: 600 ppm NO, 600 ppm NH₃, 5.0 vol. % O₂, and with the N₂ as balance.

Fig. S15 showed that conversion of NO_x over 15Fe-Mn/ZSM-5 could achieve 90% at approximate 130 °C under GHSV=120,000 h⁻¹, while Kim et al.⁴ indicated that the temperature to achieve the same conversion of NO_x was above 150 °C under GHSV=100,000 h⁻¹. However, the conversion of NO_x over 15Fe-Mn/ZSM-5 catalyst decreased significantly when the GHSV achieved 160,000 h⁻¹, which may be due to so shorter contact time that the rate of electrons transfer between NO and O₂ utilizing the METB was limited seriously resulting in the lower production of reactive species.

5.2 Effects of SO₂ on catalytic activities over 15Fe-Mn/ZSM-5 catalyst.

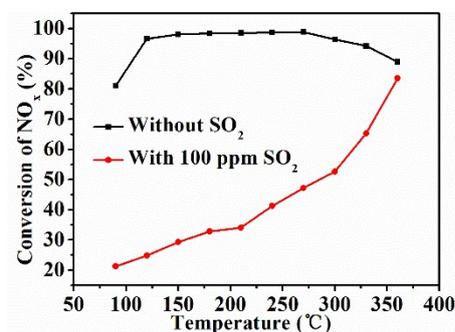


Fig. S16 Effects of SO₂ on the conversion of NO_x over 15Fe-Mn/ZSM-5 catalyst, with the evaluating condition: 0.5 mL catalysts, 600 ppm NO, 600 ppm NH₃, 100 ppm SO₂ (when needed), 5.0 vol. % O₂, and the N₂ as balance with a flow rate of 375 mL • min⁻¹ (GHSV=45,000 h⁻¹)

Obviously, 15Fe-Mn/ZSM-5 showed quite low resistance to SO₂, especially the temperature below 270 °C with the conversion less than 50%. It has been demonstrated that the low temperature deactivation was primarily caused by the formation of ammonium sulfate species, as well as the competitive adsorption between SO₂ and NO_x through the formation of active metal sulfates.⁵ Then, Chang et al. hold that the decrease of NO_x conversions below 250 °C was mainly due to the blocking of the active sites by the formation of metal sulfates and ammonium sulfates.⁶ Moreover, the formation of active metal sulfates, was regarded as the the main deactivation route over MnO_x/Al₂O₃ catalysts.⁷ Therefore, on the basis of the proposed mechanism as shown in Schemes 3 and 4 in the paper, the deactivation of SO₂ may be due to the formation of manganese sulfates or ferric sulfates which were so stable that resulted in the poisonous effects on active manganese and ferric ions. Then, the poisonous effects of SO₂ can limit the electrons transfer to lessen the production of linear nitrites and monodentate nitrates seriously inducing quite worse catalytic performance, especially at low temperature.

References:

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