

Supporting Information

Mechanism of the effect of H₂O on the low temperature selective catalytic reduction of NO with NH₃ over Mn-Fe spinel

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1. Experimental

1.1 Catalytic test

The ratios of NO_x and NH₃ conversion, the amount of N₂ formed, and N₂O selectivity were calculated using the following equations:

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \quad (\text{S1})$$

$$\text{NH}_3 \text{ conversion} = \frac{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \quad (\text{S2})$$

$$\text{N}_2 \text{ formed} = [\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}} \quad (\text{S4})$$

$$\text{N}_2\text{O selectivity} = \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NH}_3]_{\text{in}} + [\text{NO}_x]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_x]_{\text{out}}} \quad (\text{S4})$$

Where, [NH₃]_{in}, [NO_x]_{in}, [NH₃]_{out}, [NO_x]_{out} and [N₂O]_{out} were the concentrations of NH₃ and NO_x (including NO and NO₂) in the inlet, and the concentrations of NH₃, NO_x and N₂O in the outlet, respectively.

1.2 In situ DRIFT study

In situ DRIFT spectra were recorded on another FTIR spectrometer (Nicolet 6700) equipped with a smart collector and an MCT detector by accumulating 32 scans with a resolution of 4 cm⁻¹.¹

2. Results

2.1 In situ DRIFT study

After the adsorption of 500 ppm of NH₃ at 120 °C for 30 min, Mn-Fe spinel was mainly covered by coordinated NH₃ bound to the Lewis acid sites (at 1603 and 1190 cm⁻¹) and ionic NH₄⁺ bound to the Brønsted acid sites (1669 and 1440 cm⁻¹) (shown in Fig. S1a).²⁻⁴ The negative peak at 1340 cm⁻¹ was assigned to residual SO₄²⁻ on Mn-Fe spinel after water washing, which was covered by NH₄⁺.⁵⁻⁷ After the further introduction of 500 ppm of NO and 2% of O₂, adsorbed ammonia species gradually diminished (shown in Fig. S1a). Meanwhile, adsorbed H₂O (at 1620 cm⁻¹) appeared, which is the typical product of NO reduction.² Furthermore, adsorbed NO_x cannot be observed during the remarkable decrease of adsorbed NH₃ species in the first 1 min. They suggest that the reaction of adsorbed ammonia species with gaseous NO (i.e. the Eley-Rideal mechanism) contributed to NO reduction over Mn-Fe spinel. At last, Mn-Fe spinel was mainly

covered by monodentate nitrite (at 1608 cm^{-1}), monodentate nitrate (at 1548 cm^{-1}), and bidentate nitrate (at 1584, 1530, 1277 and 1230 cm^{-1}).^{4,8}

After the adsorption of 500 ppm of NO and 2% of O₂ at 120 °C, monodentate nitrite (at 1608 cm^{-1}), monodentate nitrate (at 1548 cm^{-1}), and bidentate nitrate (at 1584, 1530, 1277 and 1230 cm^{-1}) appeared on Mn-Fe spinel (shown in Fig. S1b). After NH₃ was introduced, the band at 1608 cm^{-1} corresponding to monodentate nitrite and the band at 1548 cm^{-1} corresponding to monodentate nitrate gradually decreased (shown in Fig. S1b). It suggests that the reaction of adsorbed monodentate nitrite/monodentate nitrate with adsorbed NH₃ on the adjacent sites (i.e. the Langmuir-Hinshelwood mechanism) contributed to NO reduction over Mn-Fe spinel. However, the bands at 1584, 1531, 1277 and 1230 cm^{-1} corresponding to bidentate nitrate shifted to 1566, 1507, 1286 and 1246 cm^{-1} due to the reaction with adsorbed ammonia species (shown in Fig. S1b).⁴ However, their intensities did not decrease after the further introduction of NH₃/N₂. It suggests that the reaction between ammonia and bidentate nitrate did not contribute to NO reduction over Mn-Fe spinel due to the stronger binding energy of bidentate nitrate with the interface.⁸ The similar result was reported on MnO_x-CeO₂ by Qi and Yang.⁹ Meanwhile, coordinated NH₃ (at 1603 and 1190 cm^{-1}) and ionic NH₄⁺ (1669 and 1440 cm^{-1}) were observed on Mn-Fe spinel. Previous research demonstrated that the product of nitrate route was N₂O, while that of the nitrite route was N₂.¹⁰ Therefore, N₂O formation over Mn-Fe spinel during the introduction of NH₃/N₂ to NO+O₂ pretreated Mn-Fe spinel mainly resulted from the reaction of adsorbed monodentate nitrate with adsorbed NH₃.

At last, the IR spectra during the SCR reaction (i.e. 500 ppm of NH₃, 500 ppm of NO and 2% of O₂ were simultaneously introduced) at 120 °C were recorded. As shown in Fig. S1c, adsorbed H₂O (at 1620 cm^{-1}), coordinated NH₃ (at 1603 and 1190 cm^{-1}), ionic NH₄⁺ (at 1669 and 1440 cm^{-1}) adsorbed bidentate NO₃⁻ (at 1584 cm^{-1}) and adsorbed NH₄NO₃ (at 1507 and 1246 cm^{-1}) were all observed. Previous study has demonstrated that bidentate nitrate on the surface mainly resulted from the further oxidation of adsorbed NO₂⁻.¹¹ Therefore, the presence of bidentate nitrate on the surface indicates that the formation of NO₂⁻ on Mn-Fe spinel, which was rapidly reacted with NH₃. Therefore, both the Langmuir-Hinshelwood mechanism and the Eley-Rideal mechanism contributed to NO reduction over Mn-Fe spinel.

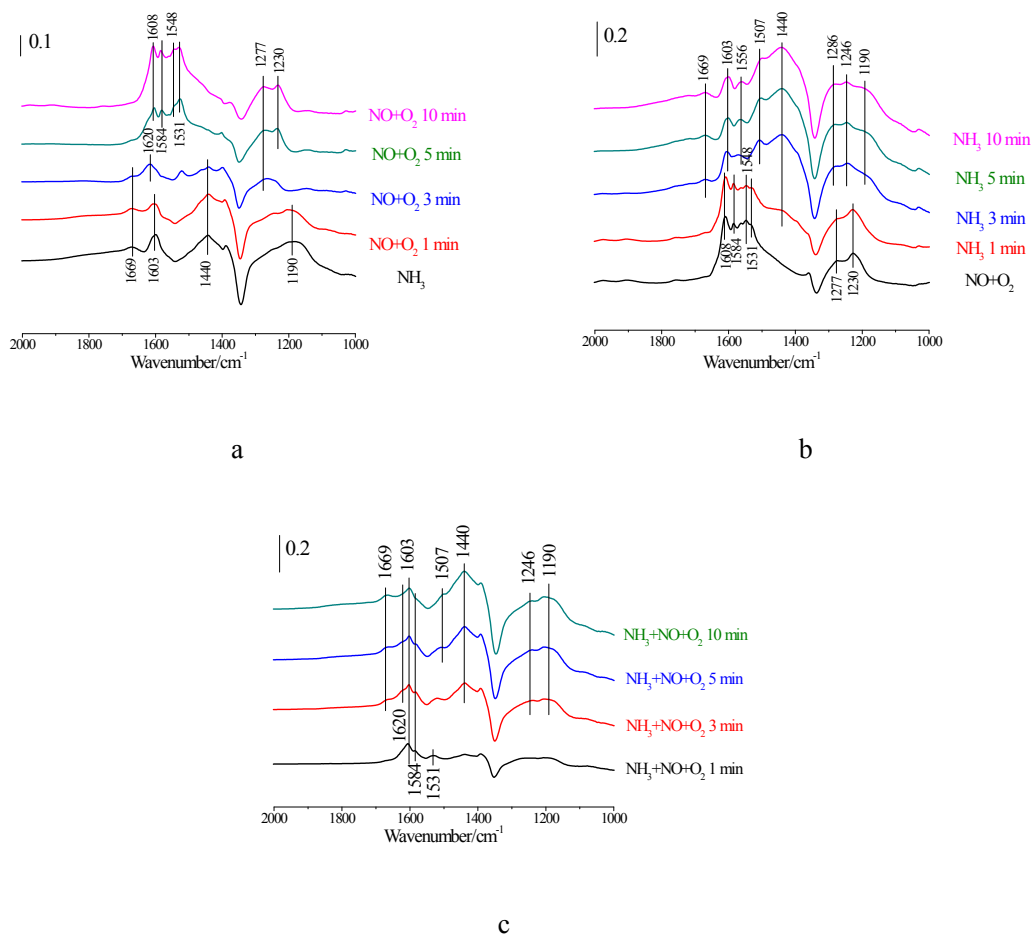


Fig. S1 (a), DRIFT spectra taken at 120 °C upon passing NO+O₂ over NH₃ presorbed Mn-Fe spinel; (b), DRIFT spectra taken at 120 °C upon passing NH₃ over NO+O₂ presorbed Mn-Fe spinel; (c), DRIFT spectra taken at 120 °C upon passing NH₃+NO+O₂ over Mn-Fe spinel.

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