Supplementary material

Dual Role of Mn in Regulating Structural and Functional Sites of Ag-based Catalysts for Selective Catalytic Oxidation of High-concentration NH_3

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Text S1 Characterization methods and instruments operation

The computerized PANalytical Empyrean diffractometer used to perform powder X-ray diffraction (XRD) experiments has a Cu Kα radiation source, and the accompanying test condition parameters: in cooperation with the PIXcel detector, the angle range of the test was 10-90°, the step size was 0.026°, and the time consumed per step was 44.625s

In situ Fourier transform infrared spectroscopy (FTIR) experiments were performed on the Thermo Nicolet iS-50 in transmission mode, equipped with a high vacuum chamber with a base pressure of less than 5×10^{-8} mbar, to detect the content of OH groups over different sample surfaces

The Thermo Nicolet iS-50 FTIR instrument performs *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and is equipped with an MCT/A detector to detect the NH_3-SCO reaction mechanism of different samples, using Harrick *in situ* cells during the experiment, and recording the spectral range within 4000-600 cm^{-1}, maintaining a resolution of $4cm^{-1}$, and the cumulative number of scans is 32. The samples were first pretreated for 30 min at 500 °C under a 20 vol% O_2/N_2 (285.7mg/L O_2) mixture atmosphere. The sample was then purged with pure N_2 and cooled to the desired temperature. Background spectra were collected simultaneously until the new spectrum coincided with the previous one.

Scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectrometer (EDS) for elemental mapping images were measured on the FEI talos f200s to observe the microstructure of

the samples in detail, and equipped with an accelerating voltage of 200 kV

In situ Raman spectra were collected by Renishaw in Via Raman Spectrometer. It is equipped with an *in situ* reaction chamber. At the same time, an air-cooled 633 nm laser with an output power of 150 mW was utilized as the excitation source

The Brunauer-Emmett-Teller (BET) method was used to determine and analyze the N_2 adsorption-desorption isotherm and pore size distribution curves of the samples by physical adsorption instrument (NOVA 2000e).

The elemental compositions of Ag, Mn and O were analyzed using X-ray Photoelectron Spectroscopy (XPS), which was obtained with Thermo Fisher Scientific K-Alpha electron spectroscopy.

To perform H_2 temperature-programmed reduction (H_2-TPR) experiments, a Micromeritics AutoChem II 2920 unit is required. First, all samples were pretreated at 500 °C in a 20% O_2/Ar (285.7 mg/L O_2) atmosphere for 30 min, followed by cooling to 50 ℃ with Ar and continuing to purge for 20 min. Next, a 10% H_2/Ar (8.93mg/L H_2) flow was heated from 50℃ to 800℃ at a rate of 5℃/min to obtain a reduction curve. Throughout the process, H_2 consumption is continuously monitored using a Thermal Conductivity Detector (TCD).

For NH_3 temperature-programmed desorption (NH_3-TPD) experiments, the same instrument used for H_2-TPR described above was used. Samples were first pretreated at 500 ℃ in a 20% O_2/Ar (285.7mg/L O_2) atmosphere for 30 min and then cooled to 50 ℃. After 30 min of purging with Ar, the atmosphere was converted to NH_3 for 60 min for adsorption, then switched to Ar purge again for 30 min. Finally, the sample was

heated to 800 ℃ at a heating rate of 5 ℃/min.

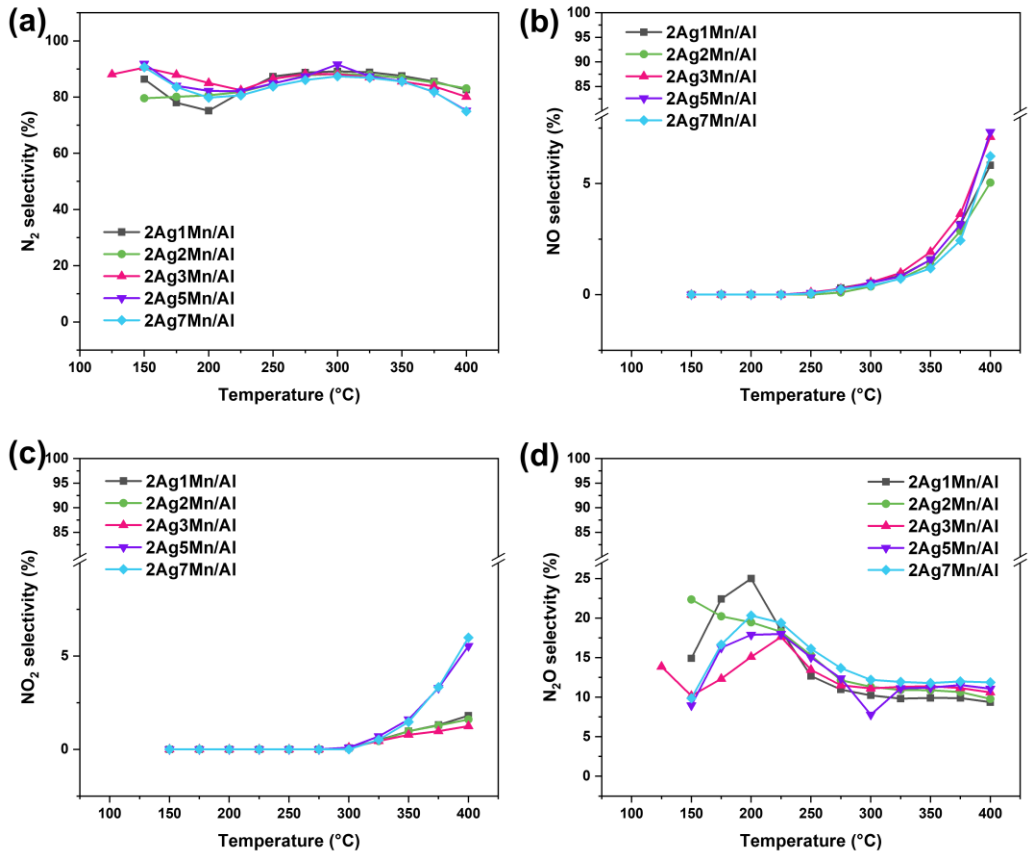

Fig. S1. Product selectivity of 2AgxMn/Al catalysts: (a) N_2 selectivity; (b) NO selectivity; (c) NO_2 selectivity; (d) N_2O selectivity.

The overall trends in NO and NO_2 selectivity for the 2AgxMn/Al series catalysts are consistent. The 2Ag3Mn/Al catalyst exhibits slightly higher NO selectivity in the high-temperature range compared to other catalysts. However, its NO_2 selectivity is significantly lower than that of the other catalysts. Additionally, the N_2O selectivity of 2Ag3Mn/Al remains consistently low at low temperatures. Upon heating to 250°C, although it fails to maintain a low N_2O selectivity, it stabilizes between that of 2Ag1Mn/Al and 2Ag7Mn/Al, overall, it demonstrates optimal N_2O selectivity across the entire temperature range. By comparing the catalytic products selectivity of different Ag and Mn ratios in the 2AgxMn/Al series, the molar ratio of 2:3 is determined to be optimal for Ag and Mn.

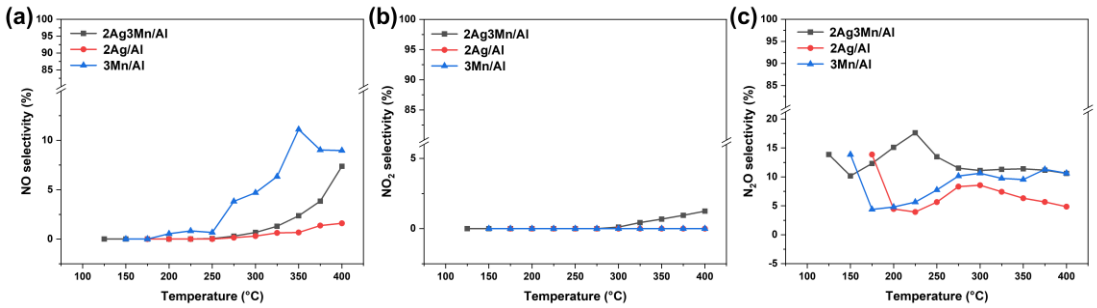

Fig. S2. Product selectivity of 2Ag/Al, 3Mn/Al and 2Ag3Mn/Al catalysts: (a) NO; (b) NO_2; (c) N_2O.

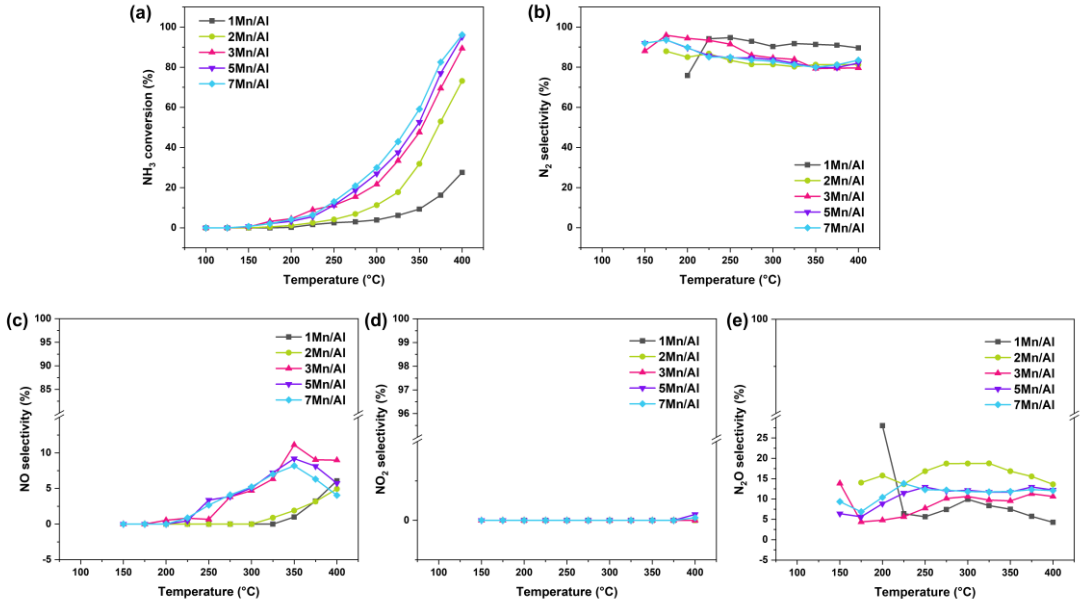

Fig. S3. Active test results and product selectivity of xMn/Al catalysts: (a) Active test results; (b) N_2 selectivity; (c) NO selectivity; (d) NO_2 selectivity; (e) N_2O selectivity.

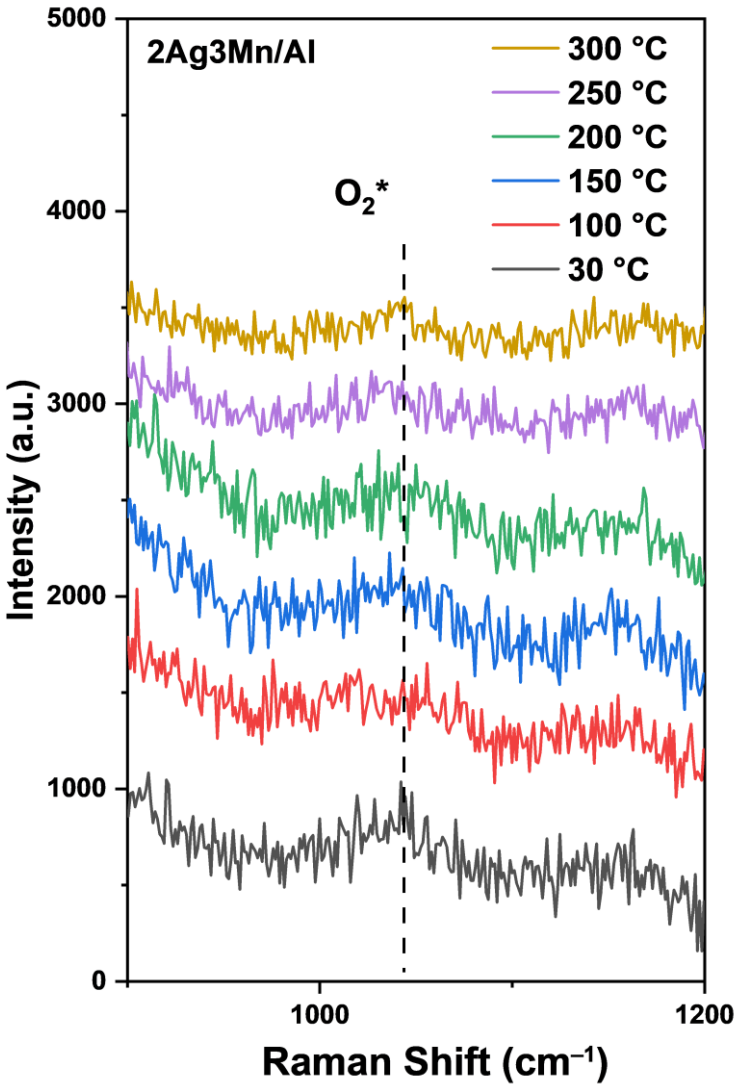

Fig. S4. Locally amplified *in situ* Raman spectra under 10 vol% O_2/N_2 (142.9mg/L O_2) at different temperature of 2Ag3Mn/Al.

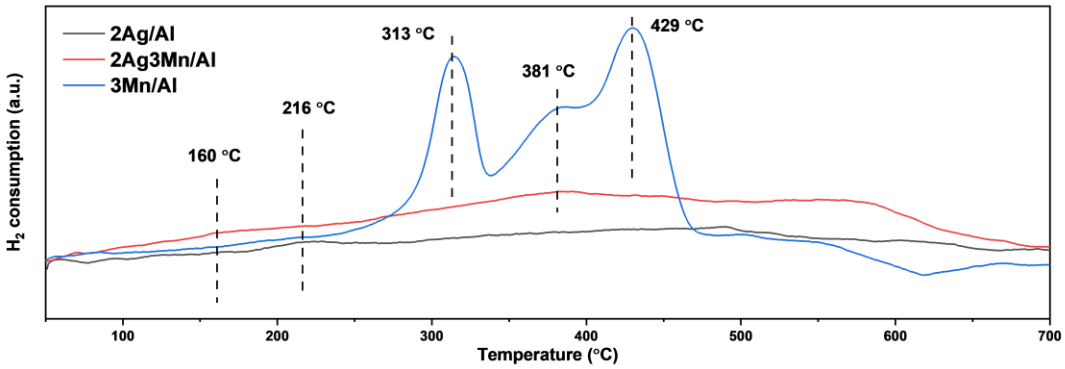

Fig. S5. H_2-TPR curves of 2Ag/Al, 2Ag3Mn/Al, and 3Mn/Al catalysts.

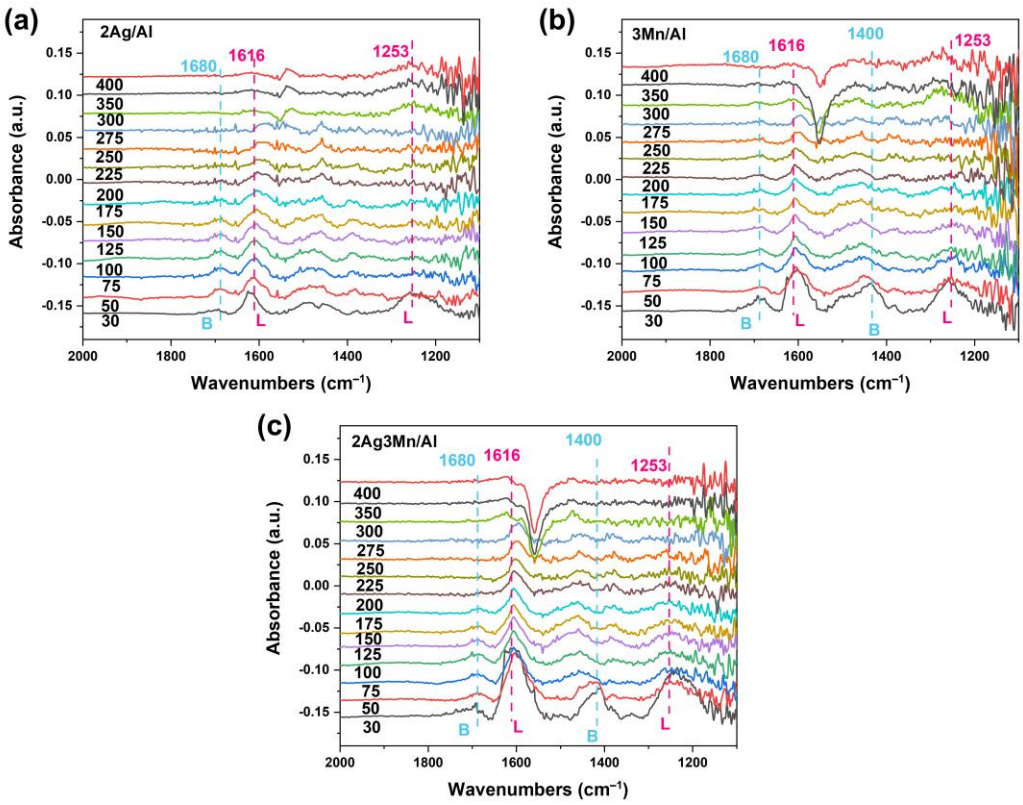

Fig. S6. *In situ* DRIFTS of NH_3 desorption in (a) 2Ag/Al, (b) 3Mn/Al and (c) 2Ag3Mn/Al.

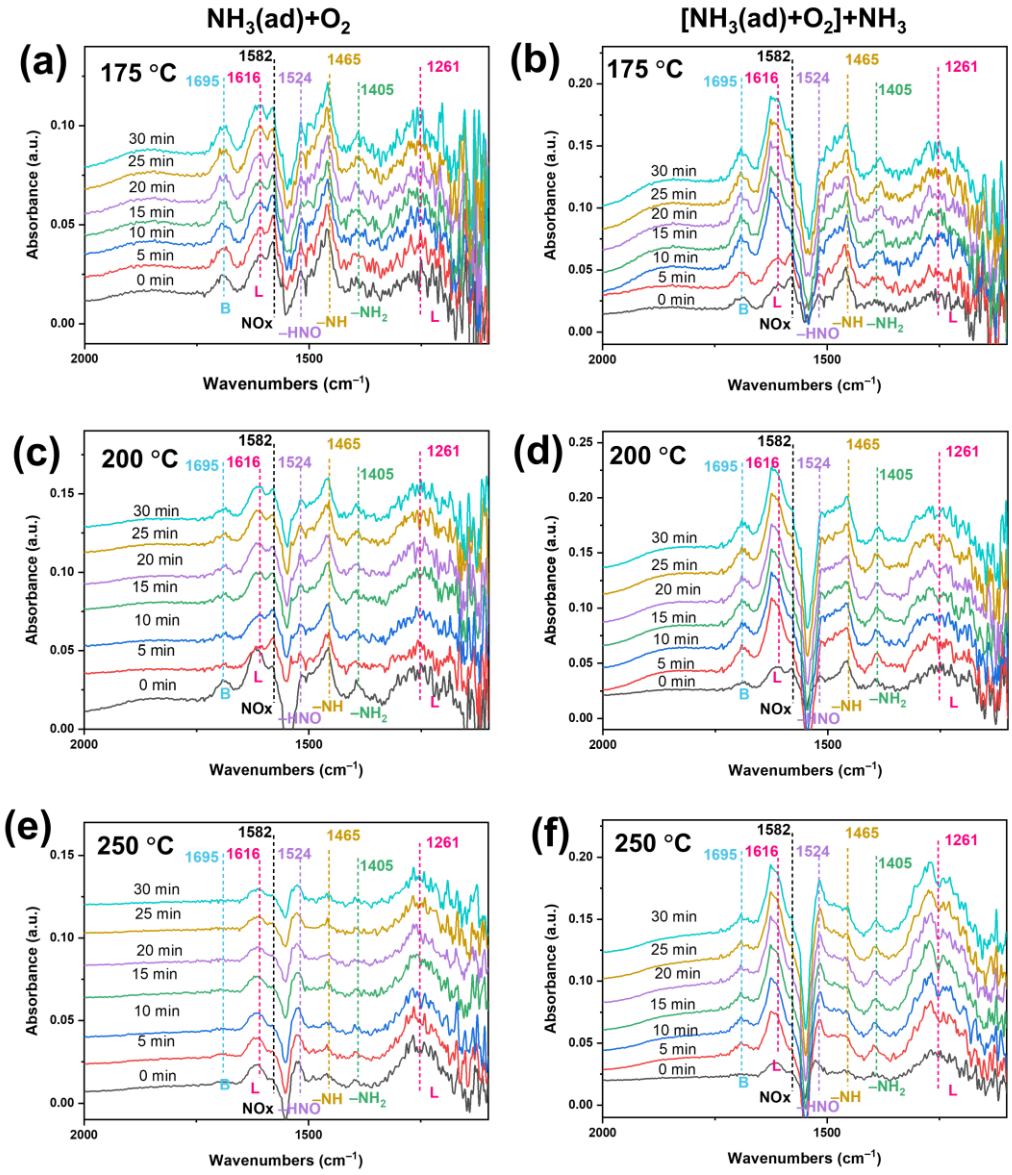

Fig. S7. *In situ* DRIFTS of 2Ag/Al pre-adsorbed NH_3 reacted with O_2 for 30 min at different temperatures, and the *in situ* DRIFTS of 7.5mg/L NH_3 followed after O_2 after 30 min of reaction with pre-adsorbed NH_3. (a, b) 175 °C; (c, d) 200 °C; (e, f) 250 °C.

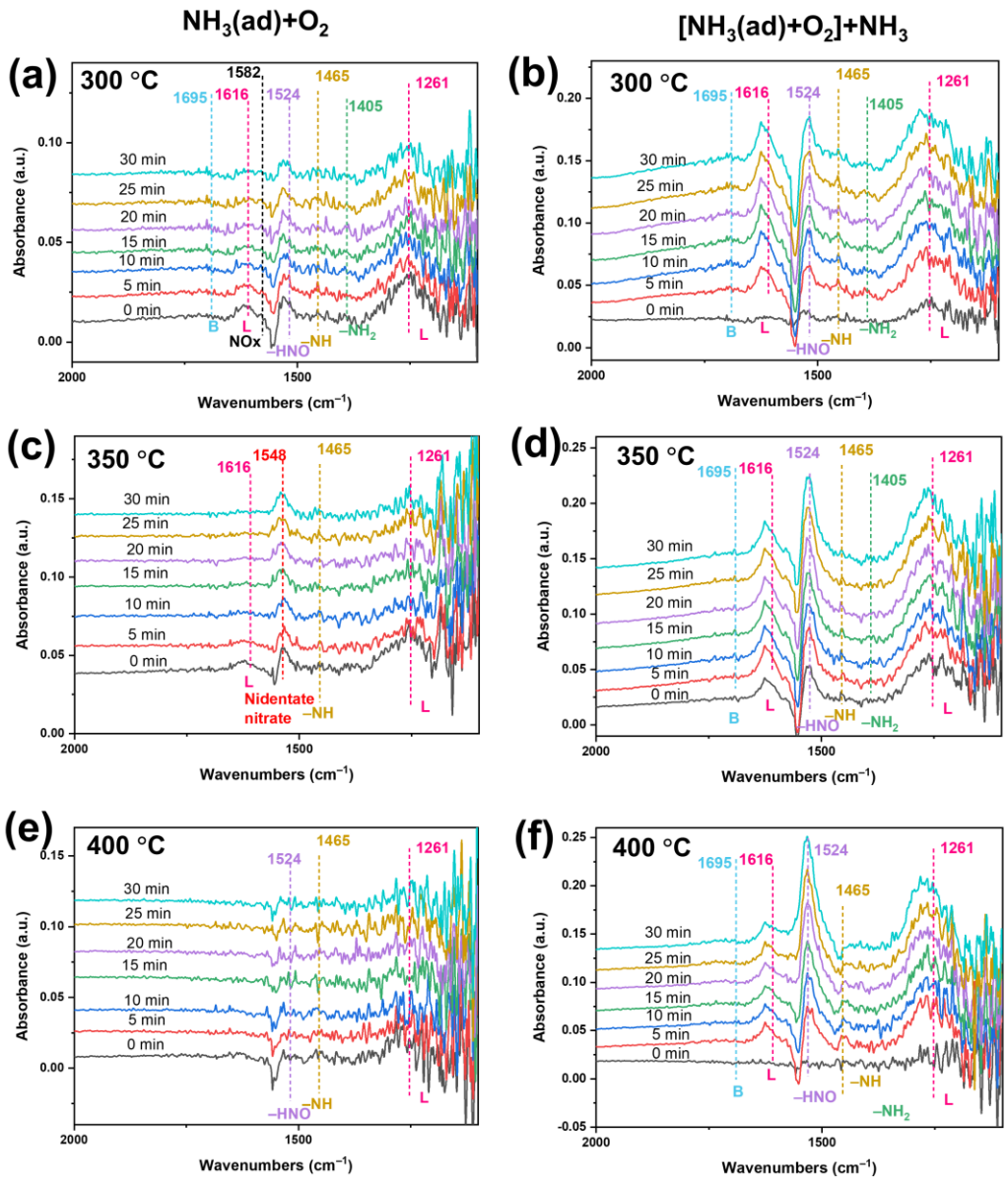

Fig. S8. *In situ* DRIFTS of 2Ag/Al pre-adsorbed NH_3 reacted with O_2 for 30 min at different temperatures, and the *in situ* DRIFTS of 7.5mg/L NH_3 followed after O_2 after 30 min of reaction with pre-adsorbed NH_3. (a, b) 300 °C; (c, d) 350 °C; (e, f) 400 °C.

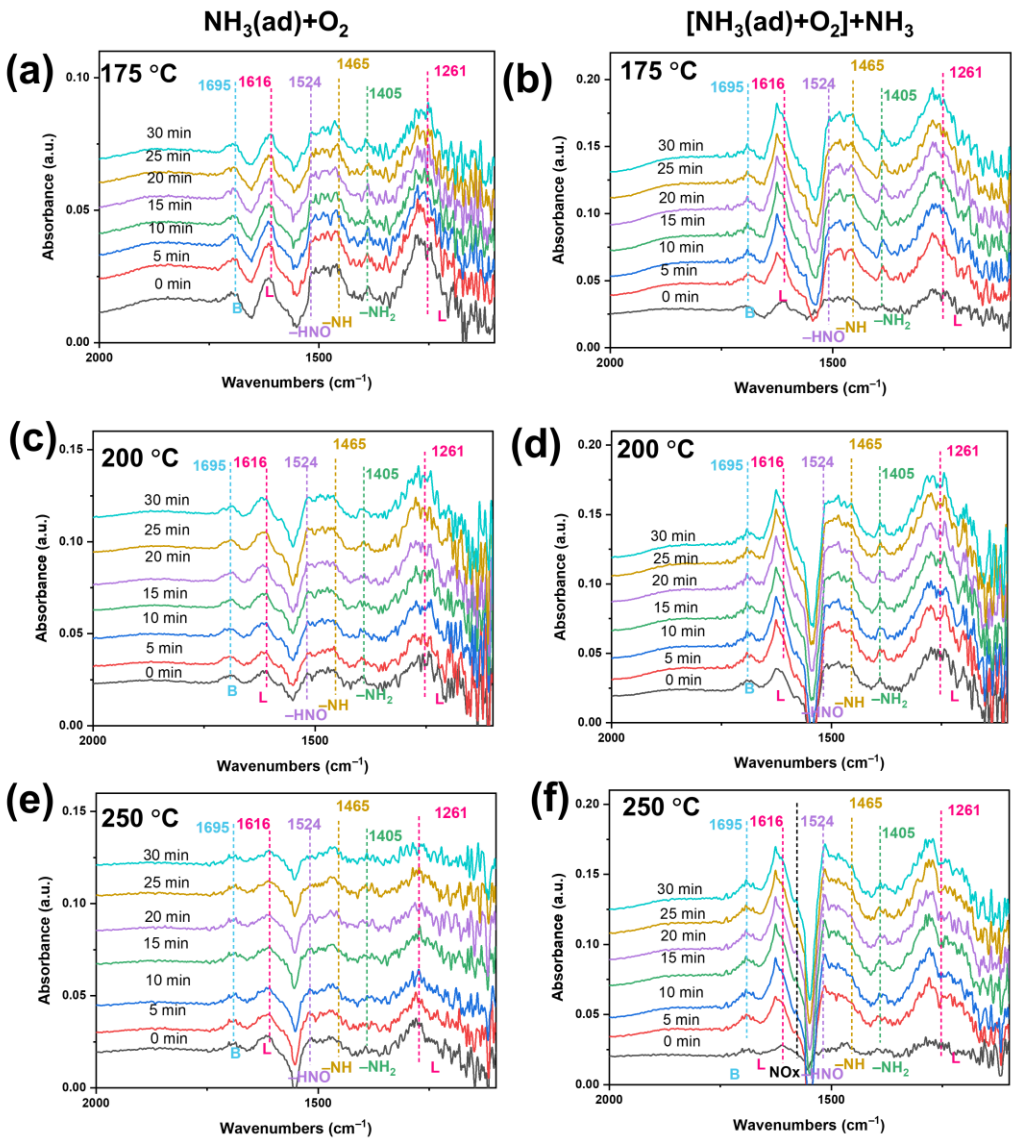

Fig. S9. *In situ* DRIFTS of 3Mn/Al pre-adsorbed NH_3 reacted with O_2 for 30 min at different temperatures, and the *in situ* DRIFTS of 7.5mg/L NH_3 followed after O_2 after 30 min of reaction with pre-adsorbed NH_3. (a, b) 175 °C; (c, d) 200 °C; (e, f) 250 °C.

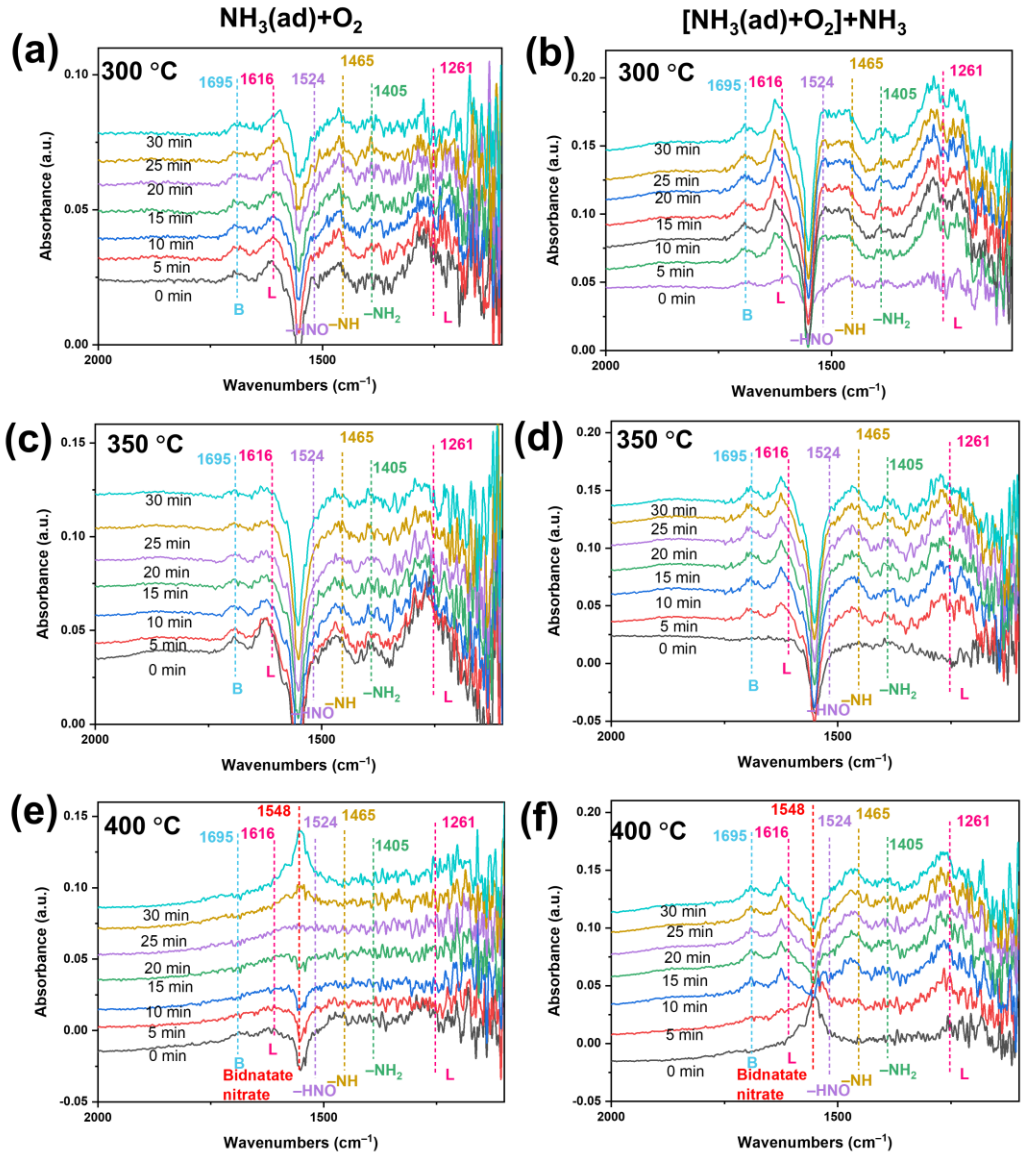

Fig. S10. *In situ* DRIFTS of 3Mn/Al pre-adsorbed NH_3 reacted with O_2 for 30 min at different temperatures, and the *in situ* DRIFTS of 7.5mg/L NH_3 followed after O_2 after 30 min of reaction with pre-adsorbed NH_3. (a, b) 300 °C; (c, d) 350 °C; (e, f) 400 °C.

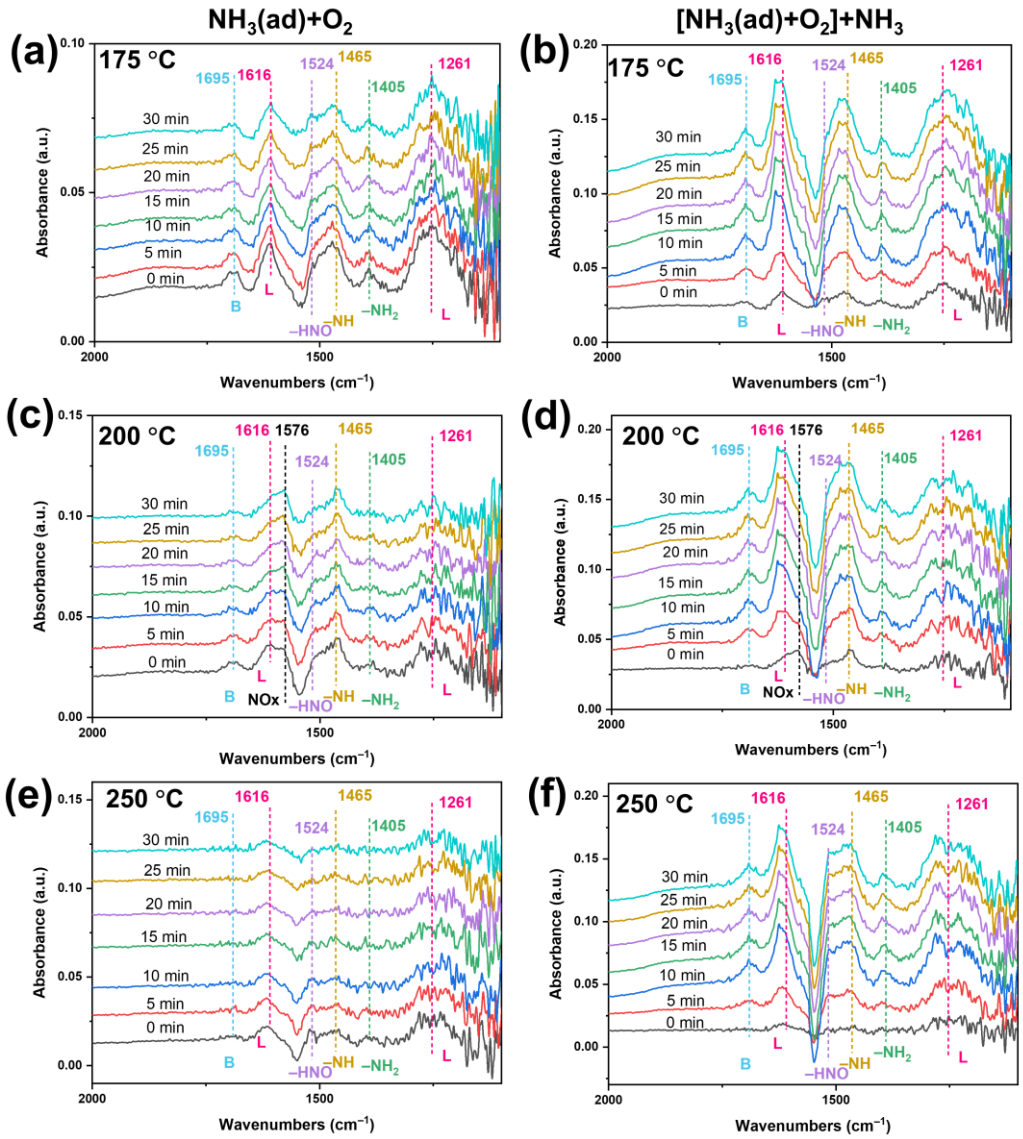

Fig. S11. *In situ* DRIFTS of 2Ag3Mn/Al pre-adsorbed NH_3 reacted with O_2 for 30 min at different temperatures, and the *in situ* DRIFTS of 7.5mg/L NH_3 followed after O_2 after 30 min of reaction with pre-adsorbed NH_3. (a, b) 175 °C; (c, d) 200 °C; (e, f) 250 °C.

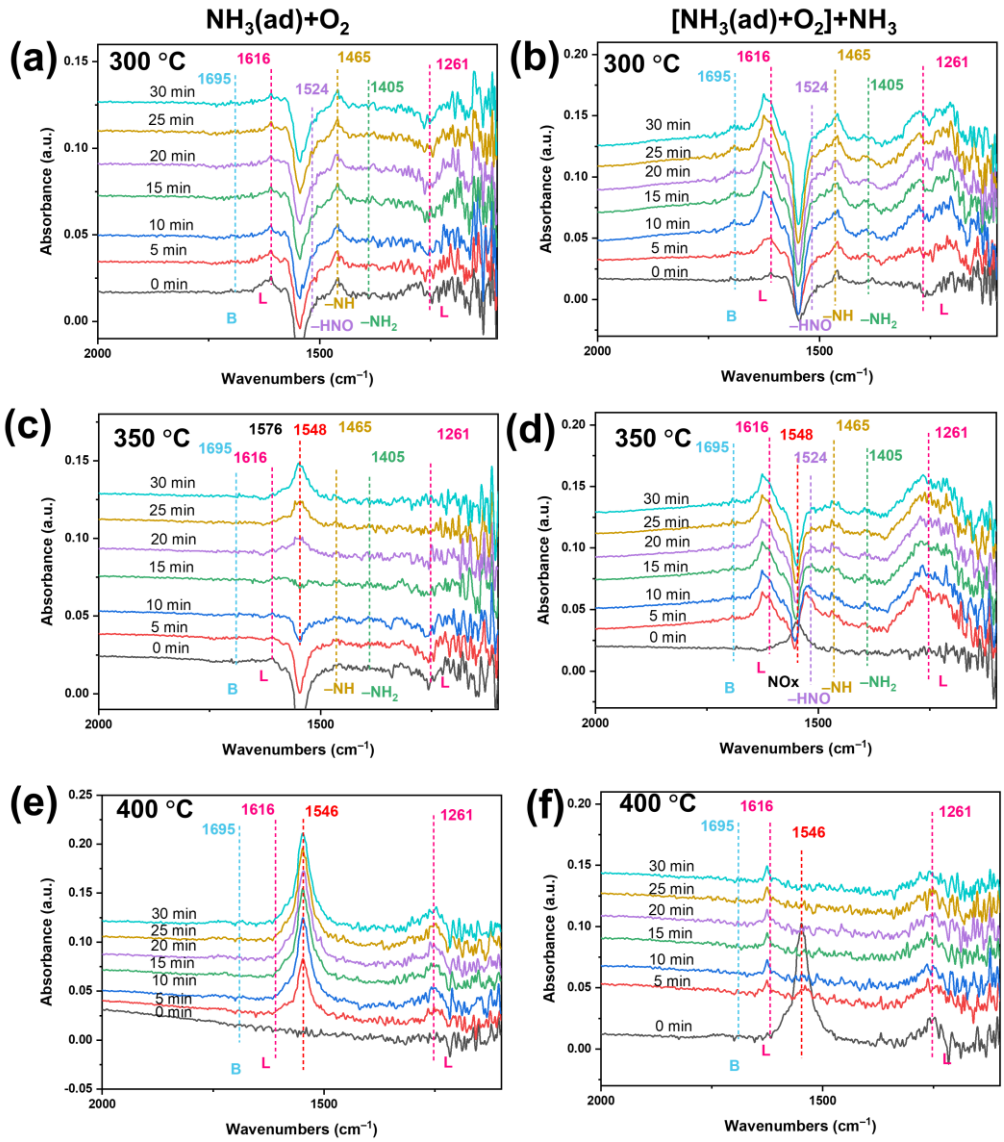

Fig. S12. *In situ* DRIFTS of 2Ag3Mn/Al pre-adsorbed NH_3 reacted with O_2 for 30 min at different temperatures, and the *in situ* DRIFTS of 7.5mg/L NH_3 followed after O_2 after 30 min of reaction with pre-adsorbed NH_3. (a, b) 300 °C; (c, d) 350 °C; (e, f) 400 °C.

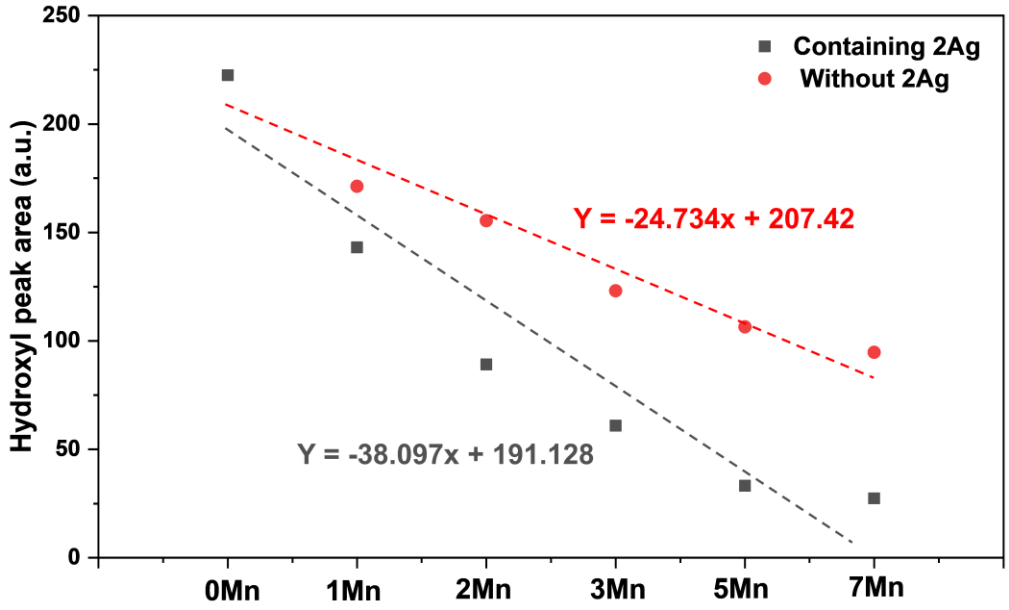

Fig. S13. Correlation between Mn loading and hydroxyl peak area for 2AgxMn/Al and xMn/Al catalysts.

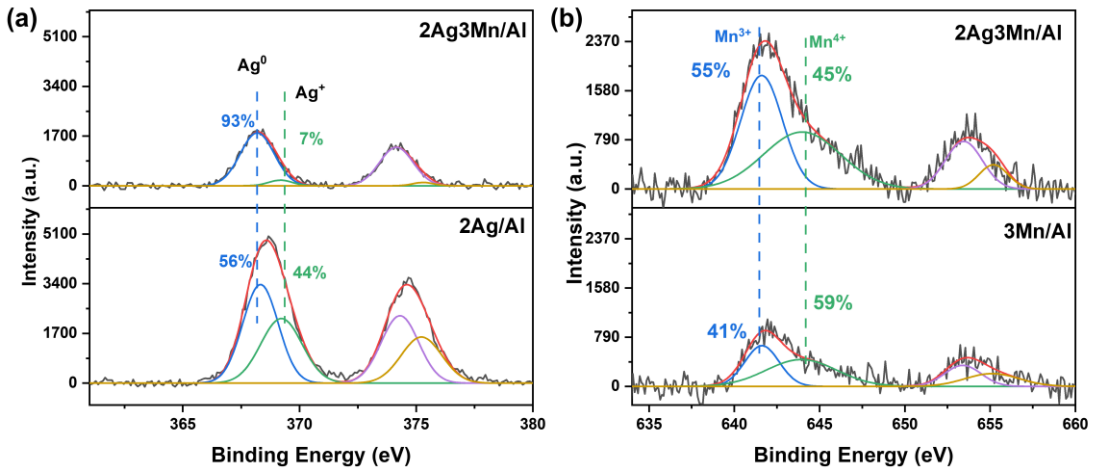

Fig. S14. XPS spectra of 2Ag/Al, 3Mn/Al and 2Ag3Mn/Al. (a) Ag 3d; (b) Mn 2p.

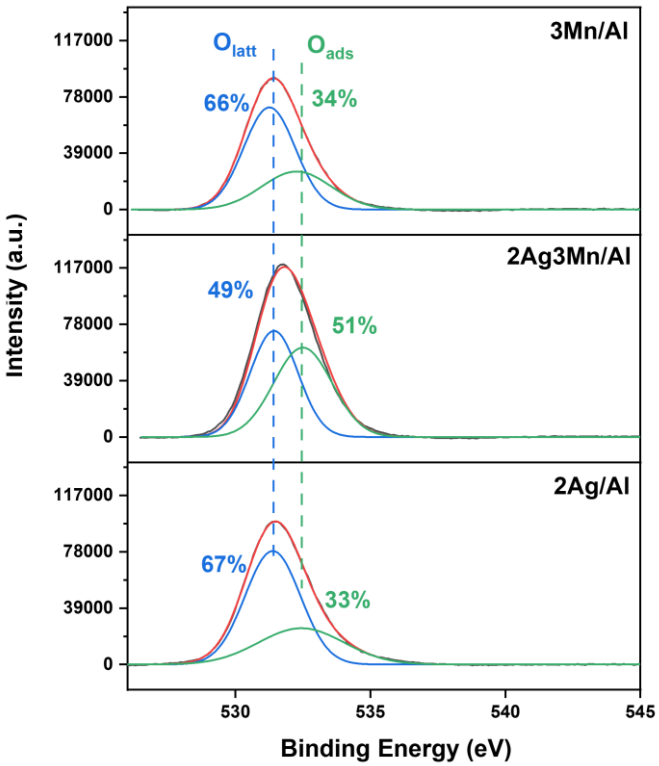

Fig. S15. O 1s XPS spectra of 3Mn/Al, 2Ag3Mn/Al, and 2Ag/Al.

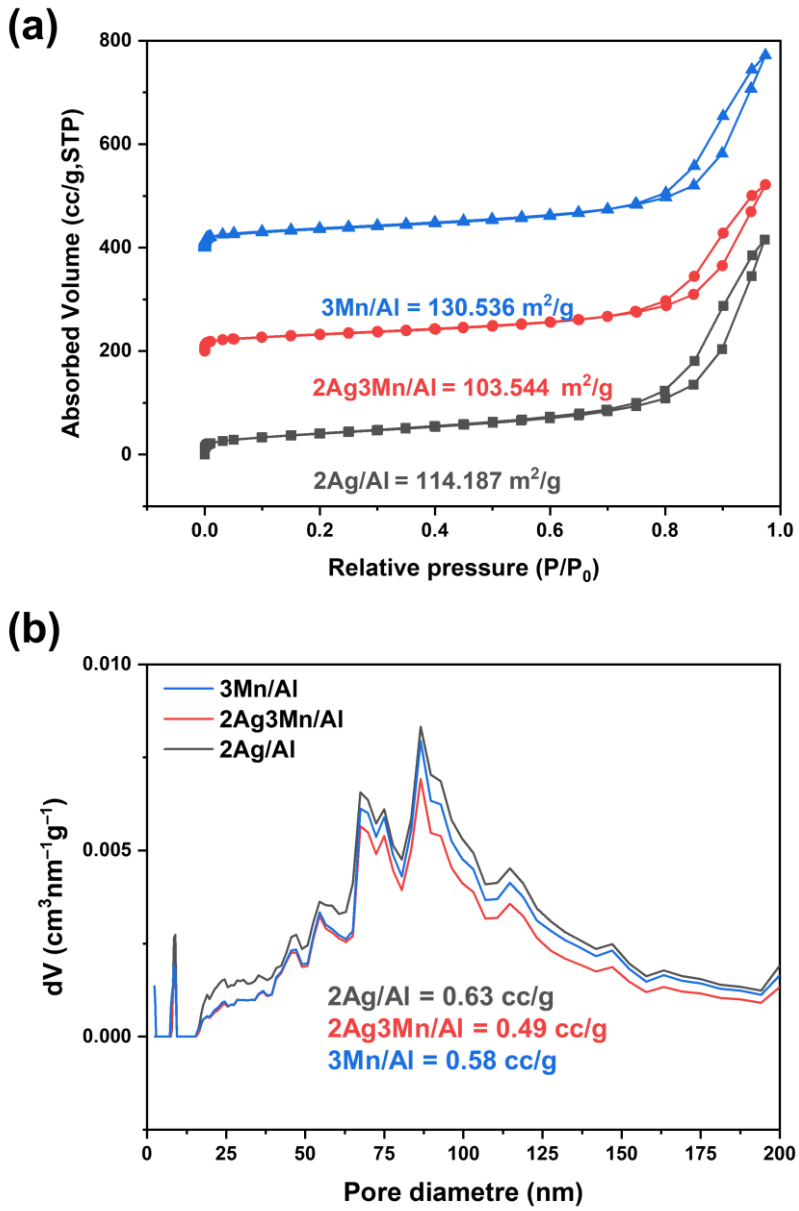

Fig. S16. N_2 adsorption−desorption isotherms and pore-size distribution curves of the 2Ag/Al, 3Mn/Al and 2Ag3Mn/Al. (a) BET; (b) pore-size distribution.