Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Catalytic Oxidation of NO to NO_2 for Nitric Acid Production Using Ag-Promoted MnO_2/ZrO_2 Catalysts

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S1 Gas-phase conversion

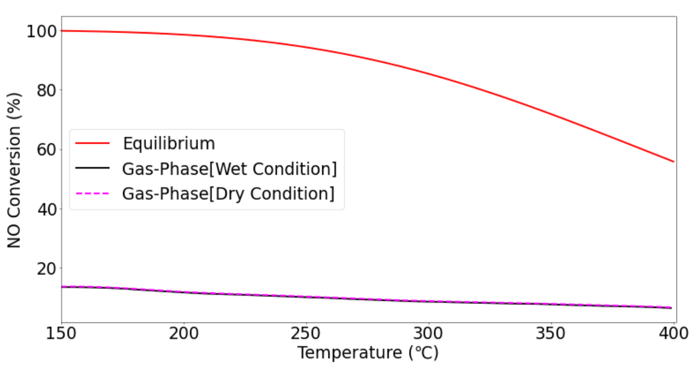


Fig. S1 Gas-phase NO to NO_2 conversion (%) as a function of temperature in both dry (10% NO, 6% O_2 and rest Ar) and wet conditions (10% NO, 6% O_2, 15% H_2O and rest Ar) heated at a rate of 5 °C/min at WHSV= 24,000 $Ncm^3/g_{gcat}h$

S2 Zirconia supported silver conversion

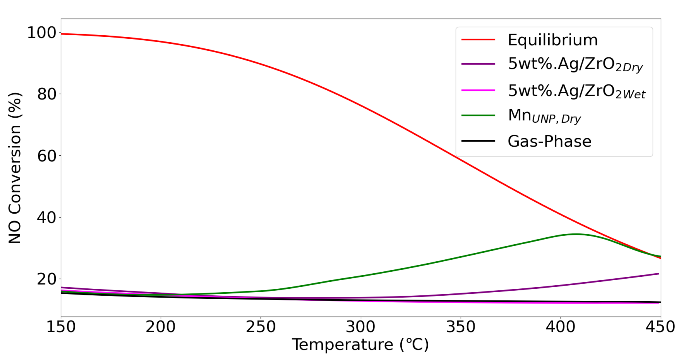


Fig. S2 NO to NO_2 conversion (%) as a function of temperature in dry (10% NO, 6% O_2 and rest Ar) and wet (10% NO, 6% O_2, 15% H_2O and rest Ar) conditions with 5wt.% Ag supported on ZrO_2 in comparison to Mn_{UNP} catalyst in dry (10% NO, 6% O_2 and rest Ar) conditions heated at a rate of 5 °C/min at WHSV= 24,000 $Ncm^3/g_{gcat}h$

5wt.% Ag on ZrO_2 support were prepare by incipient wetness impregnation. The BET surface area was found to be $69m^2/g$. From Fig. S2 it is clear that supported Ag alone have very low NO conversion levels compared to zirconia supported manganese catalysts in the measured temperature range.

S3 Short isothermal run

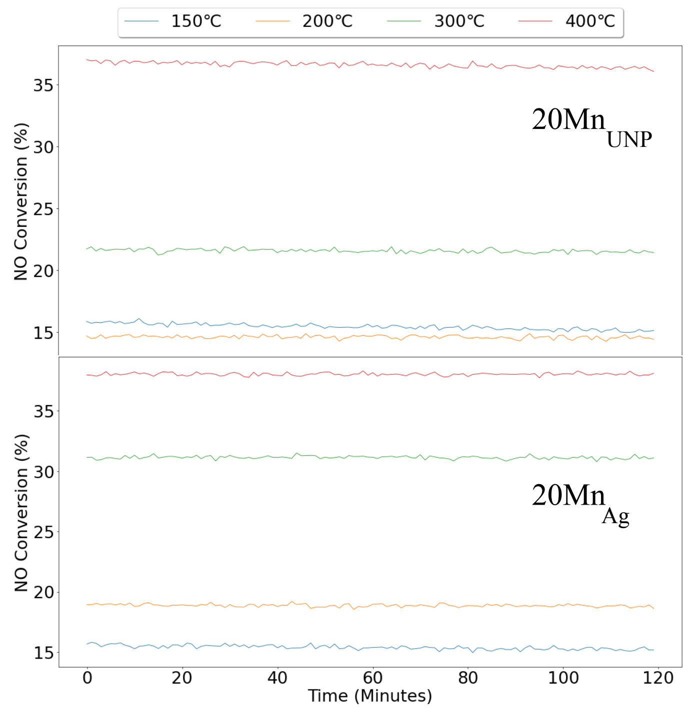


Fig. S3 NO to NO_2 conversion (%) at 150 °C, 200 °C, 300 °C and 400 °C) in wet conditions (10% NO, 6% O_2, 15% H_2O and rest Ar) at WHSV= 24,000 $Ncm^3/g_{gcat}h$

S4 In-situ XAS experiment programme

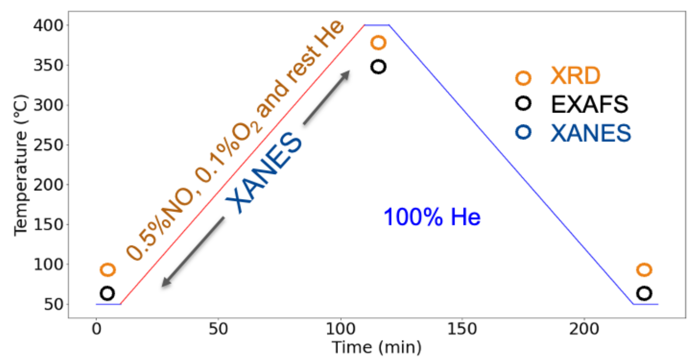


Fig. S4 *In-situ* XAS experiment programme at Mn K Edge with dry NO oxidation temperature scan from 50-400 °C at 5 °C/min rate in 0.5%NO, 0.1%O_2 and He balance at WHSV= 24,000 $Ncm^3/g_{gcat}h$

S5 XAS χ^2 data

Fig. S5 displays χ^2 as a function of wavelength for MnO_2 standard, Mn_{UNP} and Mn_{Ag} fresh catalysts. The signal-to-noise ratio of EXAFS measured (Mn_{UNP} and Mn_{Ag} fresh catalysts) in fluorescence mode is higher when compared to the EXAFS (Mn^{4+} - MnO_2 standard) measured in transmission.

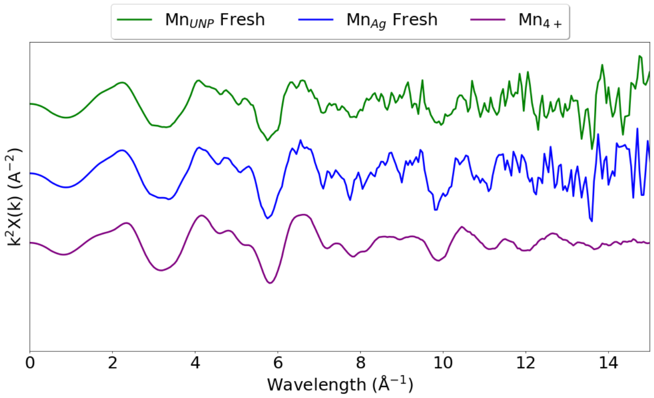


Fig. S5 EXAFS χ^2 as a function of wavelength for MnO_2 standard (measured in transmission mode), Mn_{UNP} and Mn_{Ag} fresh catalysts (measured in fluorescence mode)

S6 Silver edge XANES profiles

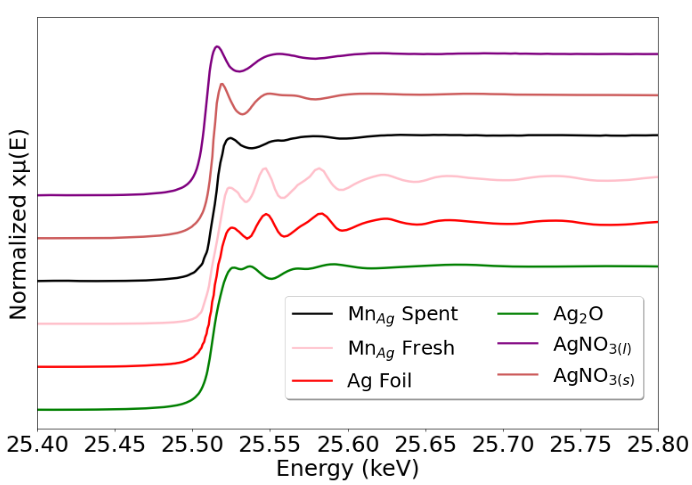


Fig. S6 Mn_{Ag} fresh and spent sample after wet NO oxidation at 400 °C isothermal conditions (10% NO, 6% O_2, 15% H_2O and rest Ar) at WHSV= 24,000 $Ncm^3/g_{gcat}h$, showing *ex-situ* XANES profile compared with different Ag standards collected at the Ag K edge

S7 Simulated equilibrium composition

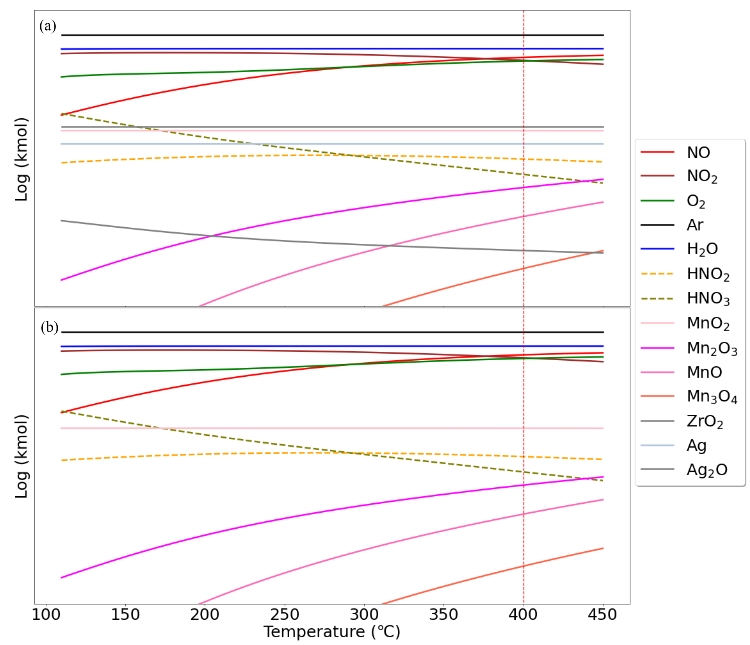


Fig. S7 HSC software simulated equilibrium composition changes for 10% NO, 6% O_2, 15% H_2O and rest Ar with respect to temperature for both (a) Mn_{Ag} and (b) Mn_{UNP} catalysts

Fig. S7 presents simulated equilibrium composition changes for 10% NO, 6% O_2, 15% H_2O and rest Ar with respect to temperature for both Mn_{Ag} and Mn_{UNP} catalysts. For equilibrium composition simulation, HSC 9 software for windows was used[38].

S8 TEM-EDX EELS analysis

This section presents EEL spectra for Mn_{Ag} subjected to longer iso-thermal run at 400 °C. The spectrum is collected from a small region that does not overlap with any ZrO_2. Also, the O K-peak plots have been omitted, and only Mn $L_{2,3}$ edges plots are presented.

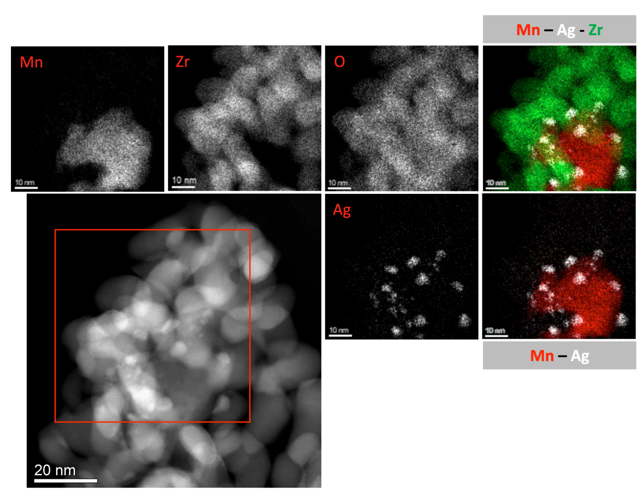


Fig. S8 MAP 1:TEM-EDX image of the spent Mn_{Ag} catalyst sample after 72hrs isothermal wet NO oxidation at 400 °C (10% NO, 6% O_2, 15% H_2O and rest Ar) at WHSV= 24,000 $Ncm^3/g_{gcat}h$ with corresponding EDX elemental-mapping. □ represents mapped region.

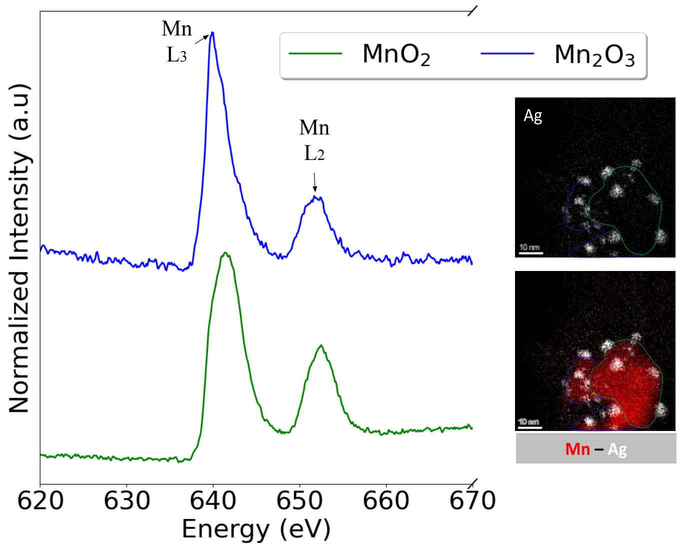


Fig. S9 EEL spectra obtained for TEM-EDX image presented in Fig. S8 at Mn $L_{2,3}$ edges (vertically displaced for more clarity). The presence of both MnO_2 and Mn_2O_3 were found in the mapped region.

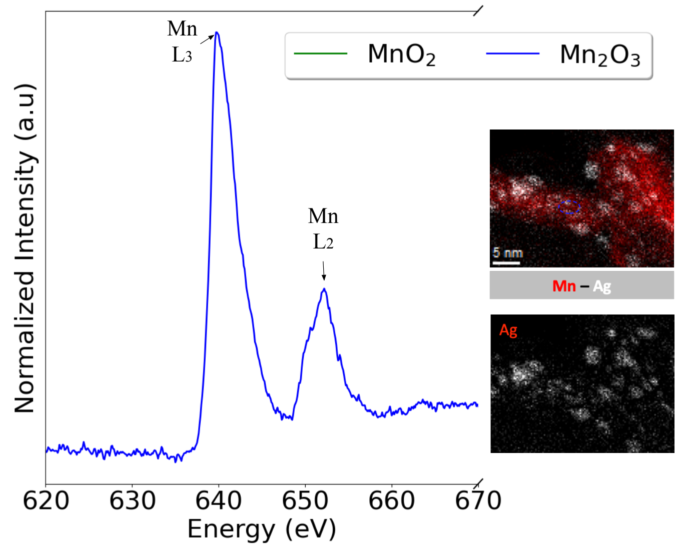


Fig. S11 EEL spectra obtained for TEM-EDX image presented in Fig. S10 at Mn $L_{2,3}$ edges. The presence of only Mn_2O_3 was found in the mapped region.

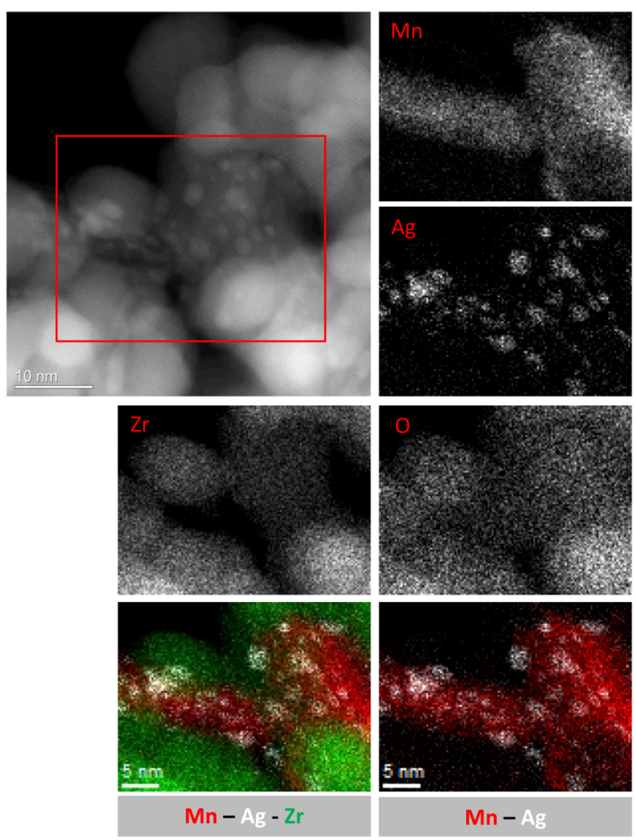
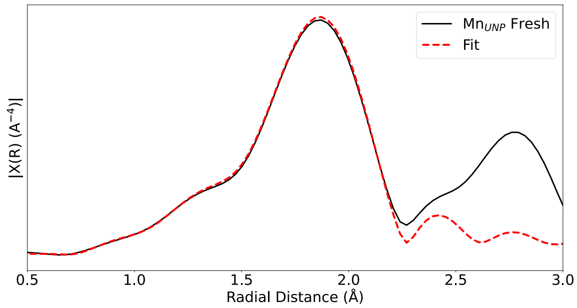
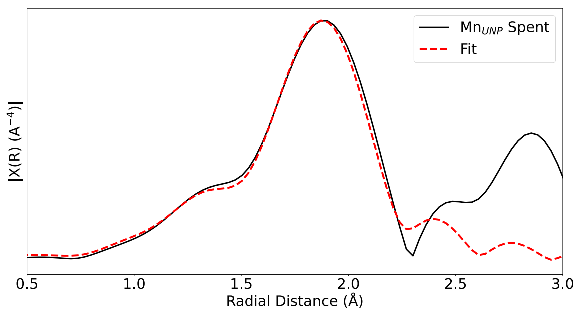


Fig. S10 MAP 2:TEM image of the spent Mn_{Ag} catalyst sample after 72hrs isothermal wet NO oxidation at 400 °C (10% NO, 6% O_2, 15% H_2O and rest Ar) at WHSV= 24,000 $Ncm^3/g_{gcat}h$ with corresponding EDX elemental-mapping. □ represents mapped region

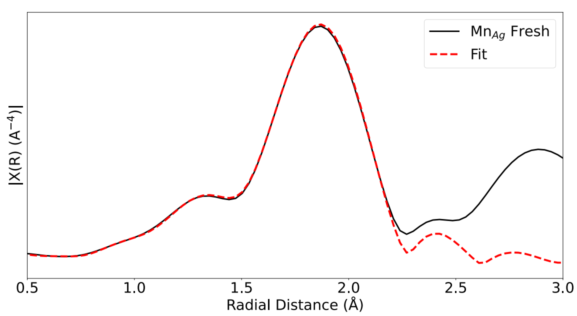
S9 R space EXAFS



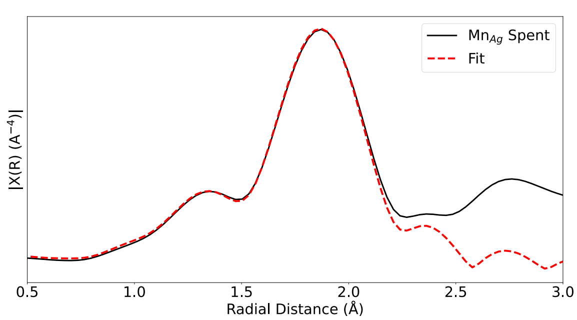
Mn_{UNP} fresh [-] catalyst sample



Mn_{UNP} spent [-] catalyst sample



Mn_{Ag} fresh [-] catalyst sample



Mn_{Ag} spent [-] catalyst sample

Fig. S12 R space EXAFS fits for fresh and spent catalyst samples of Mn_{UNP} and Mn_{Ag} after dry NO oxidation [—Data and - - Fit]