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

Mechanistic Insight into Low Temperature SCR by Ceria-Manganese Mixed Oxide Phases Incorporated into Zeolites

Supporting Information

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Table S1. Textural properties obtained through N_2 physisorption

Sample	BET surface area ($m^2\ g^{-1}$)		Pore volume ($cm^3\ g^{-1}$)	
	Total	Micropore	Total	Micropore
H-SSZ-13	729	667	0.30	0.25
$Ce_{0.7}Mn_{0.3}O_x$/H-SSZ-13	552	509	0.28	0.19
$Ce_{0.7}Mn_{0.3}O_x$	28	n/a	0.54	n/a

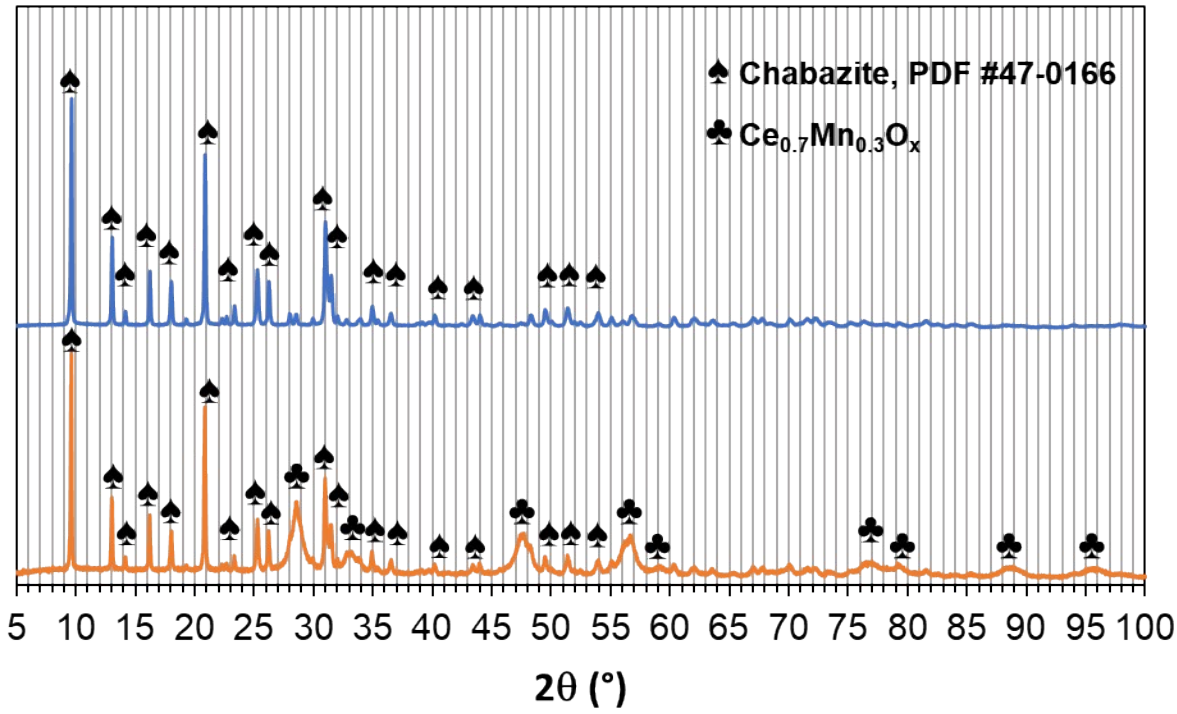

Figure S1. Experimental XRD pattern of H-SSZ-13 (top) and $Ce_{0.7}Mn_{0.3}O_x$/H-SSZ-13 (bottom).

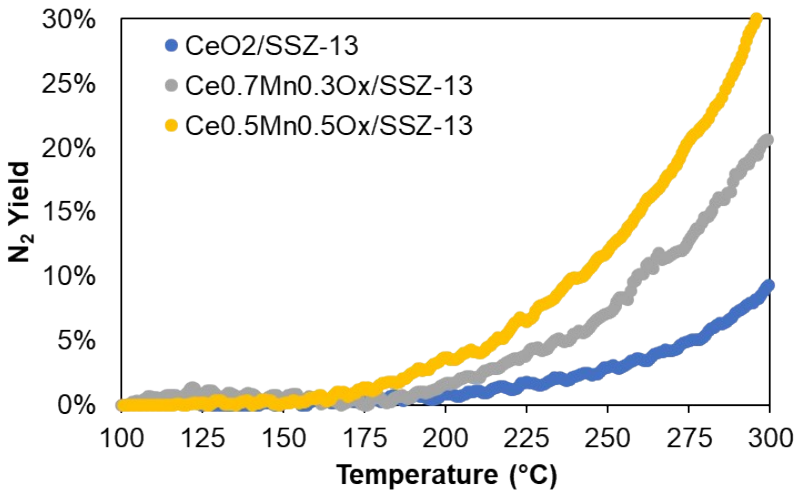

Figure S2. N_2 yield as a function of temperature during NH_3-SCR over $Ce_xMn_{1-x}O_y$/H-SSZ-13 composite catalyst. Reaction conditions: [NO] = 325 ppm; [NO_2] = 6 ppm; [NH_3] = 330 ppm; [O_2] = 15 %; [N_2] = balance; flow rate = 1.5 SLM; GHSV = 1.7e+6 h^{-1}.

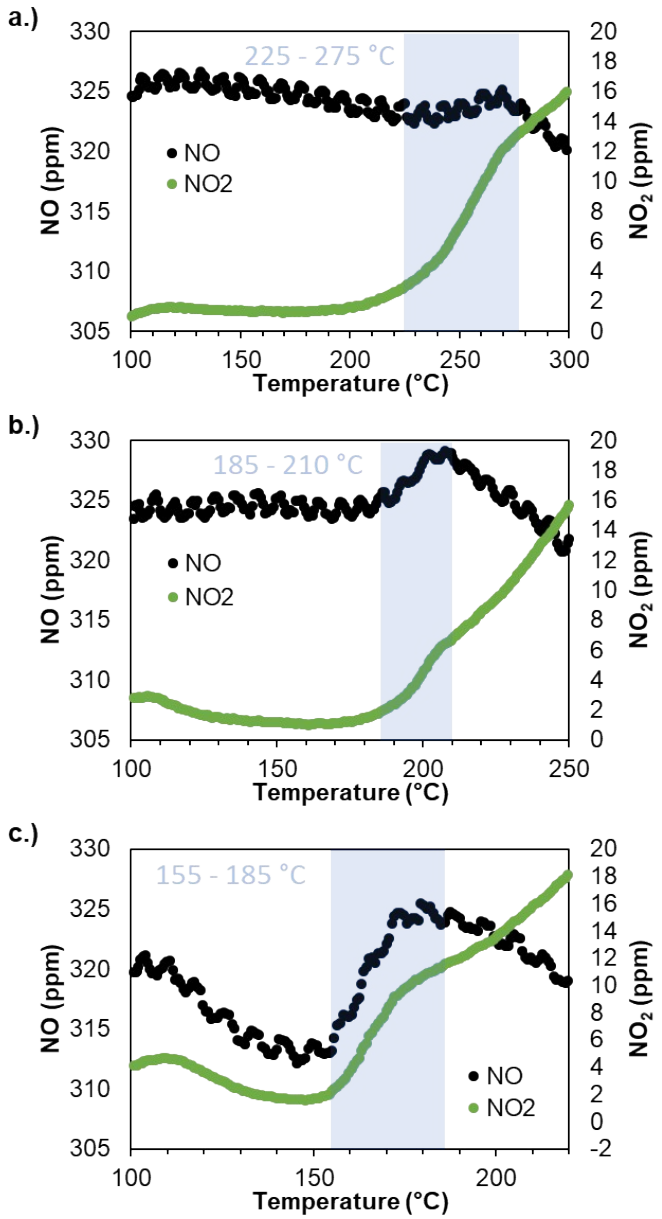

Figure S3. NO and NO_2 concentration profile at the reactor outlet over (a) CeO_2/H-SSZ-13, (b) $Ce_{0.7}Mn_{0.3}O_y$/H-SSZ-13, (c) $Ce_{0.5}Mn_{0.5}O_y$/H-SSZ-13 during NO oxidation with pre-adsorbed NH_3. Reaction conditions: [NO] = 325 ppm; [NO_2] = 6 ppm; [O_2] = 15 %; [N_2] = balance; F = 1.5 SLM; GHSV =1.7e+6 h^{-1}.

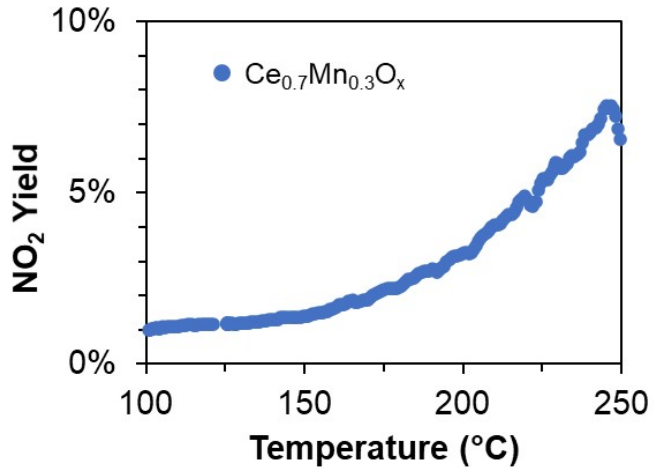

Figure S4. NO oxidation activity over bulk $Ce_{0.7}Mn_{0.3}O_y$ with pre-adsorbed NH_3. No curvature change is observed, unlike the mixed oxide supported on zeolite. Reaction conditions: [NO] = 325 ppm; [NO_2] = 6 ppm; [O_2] = 15 %; [N_2] = balance; F = 1.5 SLM; GHSV =4.6e+6 h^{-1}.

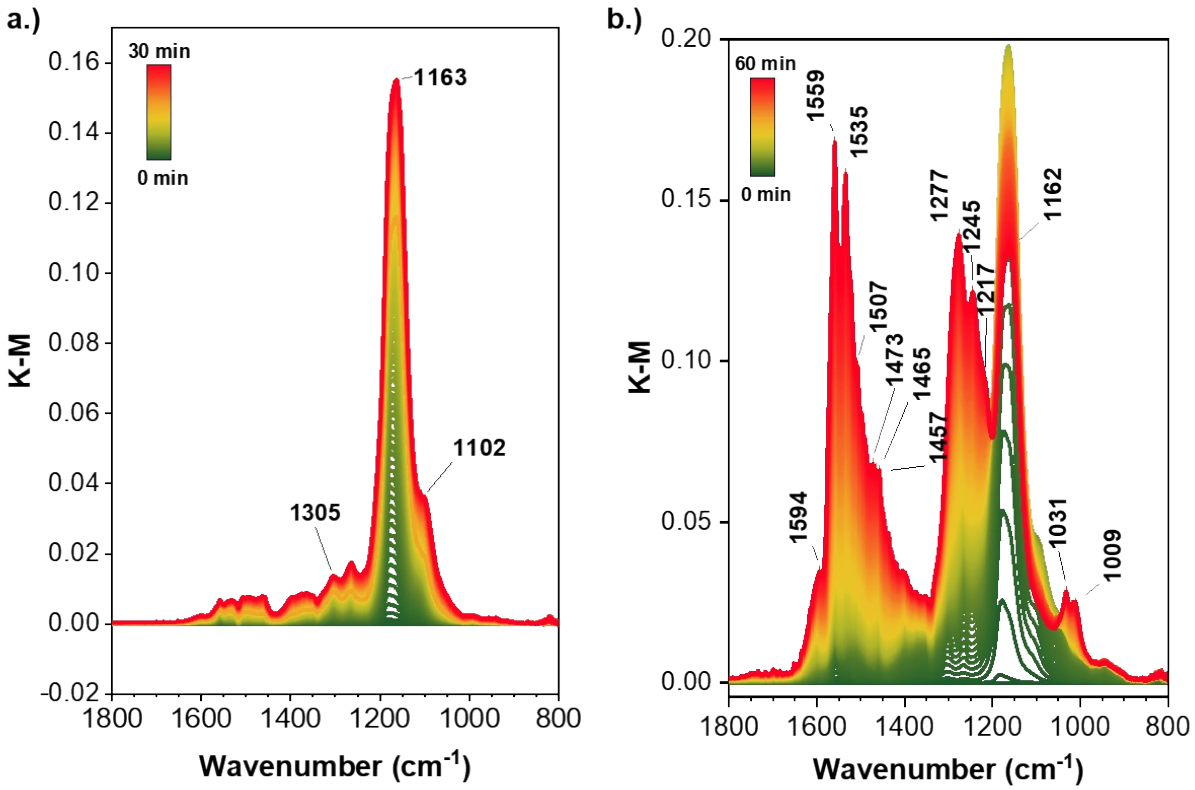

Figure S5. DRIFTS recorded during exposure of $Ce_{0.7}Mn_{0.3}O_x$ bulk oxide to a.) NO and b.) NO + O_2 at 150 °C. The catalyst was pre-treated with 2% O_2 at 500 °C for 15 min, followed by He purge for 45 min at 500 °C prior to each measurement. Conditions: [NO] = 350 ppm; [O_2] = 2%; F = 100 mL min^{-1}. For (a), the bands

at 1163 cm^{-1} and 1305 cm^{-1} were attributed to symmetric nitrites. The band at 1102 cm^{-1} was attributed to hyponitrites. [1]

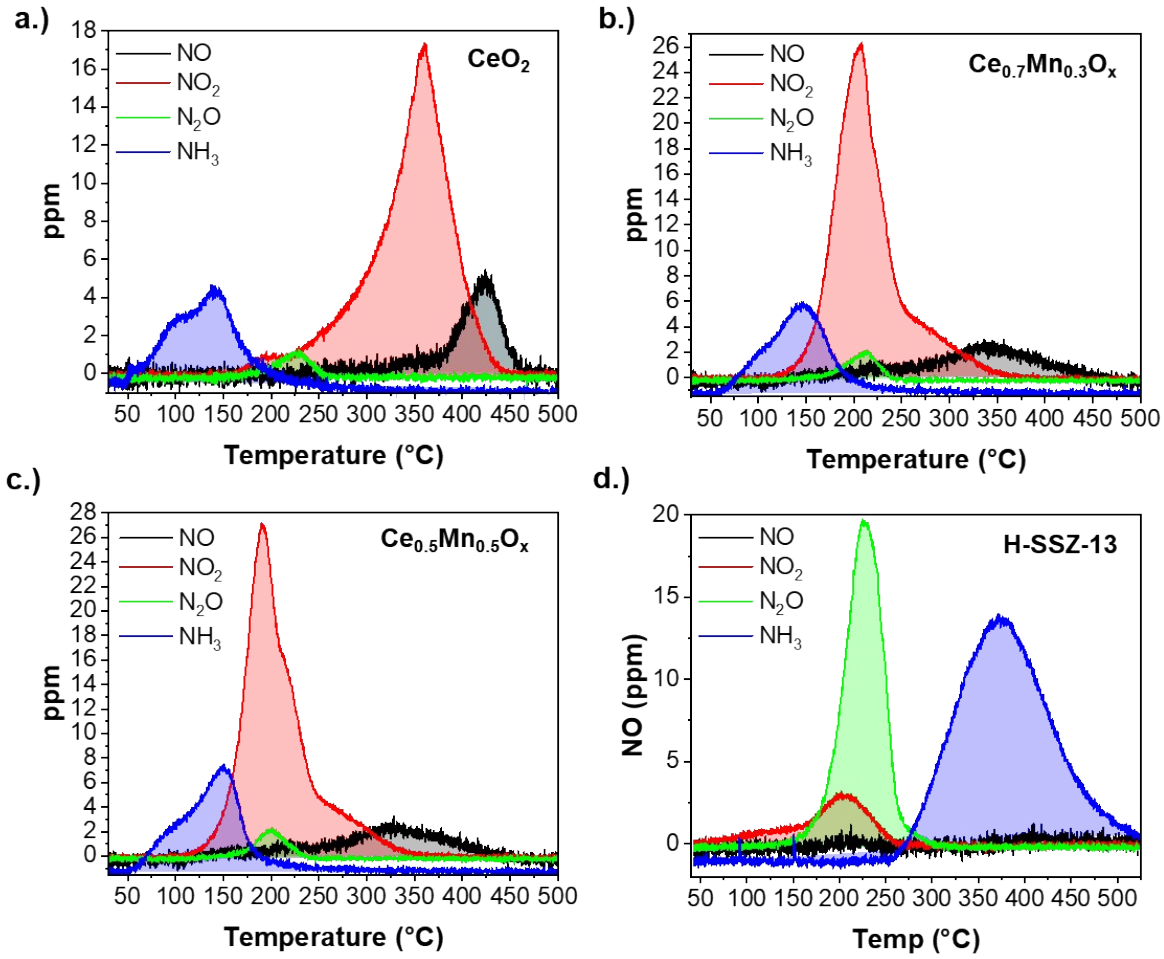

Figure S6. Ammonium nitrate decomposition products observed during heating in N_2 over bulk oxide catalysts. The shaded areas represent the integrated areas used in Figure 3a. The NO evolved in (a-c) is a thermodynamic effect derived from NO_2 dissociation to NO and O_2. For (a), the temperature that NO_2 evolved likely reflects the ability of the ceria surface to store NO_x as opposed to the temperature at which ammonium nitrate decomposes.[2] From panel (a) we assume that in the absence of NO_x storage, the NO_2 desorption leading edge would have been around 175 °C, about 40-50 °C higher than for the Mn-based catalysts. Conditions: $[NH_4NO_3]$ = 15 wt. %; β = 10 °C min^{-1}; F = 1 SLM.

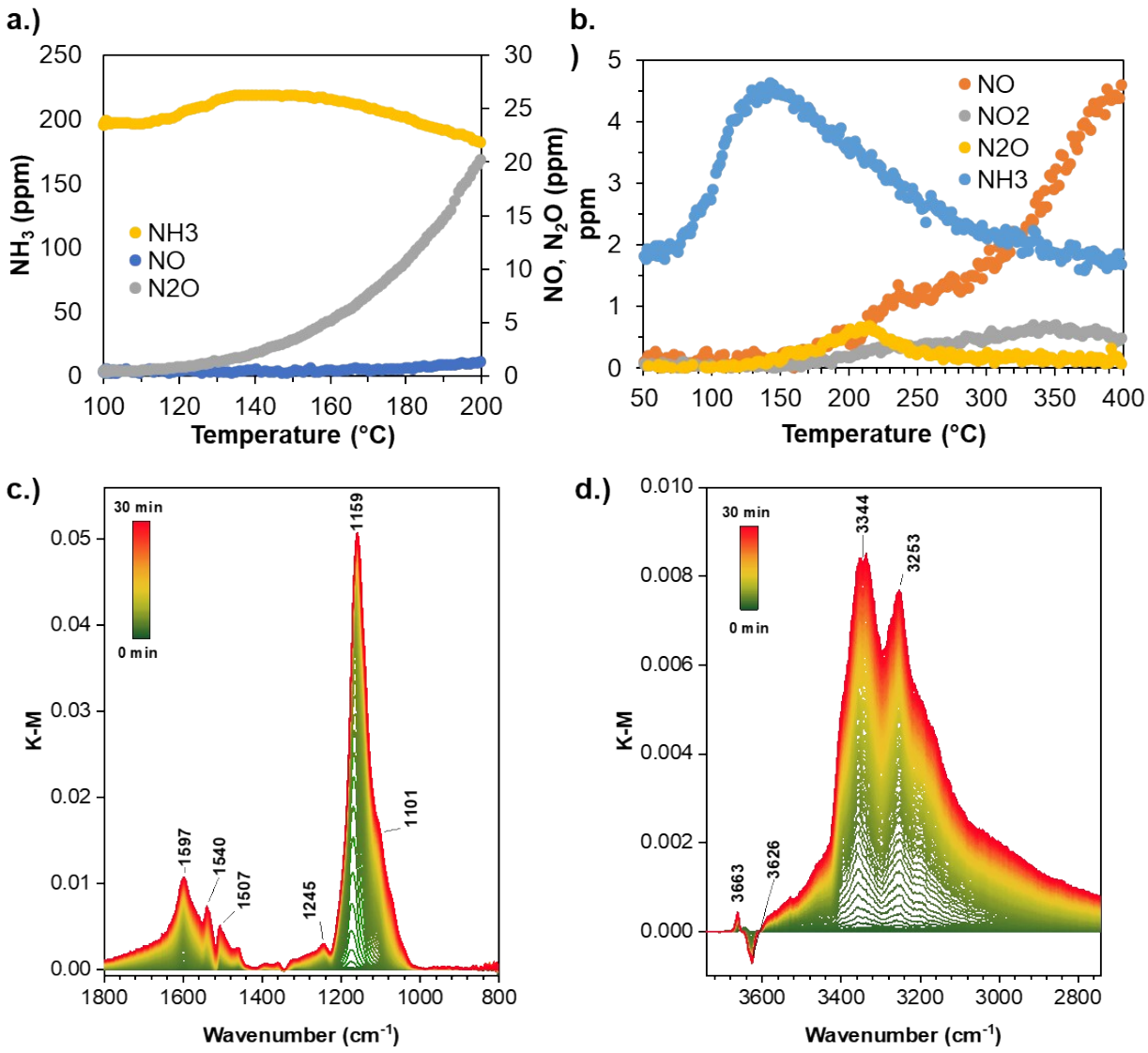

Figure S7. a.) Light-off profile obtained by flowing NH_3 over bulk $Ce_{0.7}Mn_{0.3}O_y$. Conditions: [NH_3] = 200 ppm; [N_2] = balance; β = 5 °C min^{-1}; F = 1 SLM. b.) NH_3 temperature programmed desorption (TPD) over bulk $Ce_{0.7}Mn_{0.3}O_y$. The catalyst was heated to 500 °C in 15 % O_2 for 0.5 h, followed by cooling under He, admittance of 350 ppm NH_3 for 0.5 h at 50 °C, and heating at 10 °C min^{-1} under 1 SLM N_2. c.) DRIFTS recorded during exposure of bulk $Ce_{0.7}Mn_{0.3}O_x$ to NH_3 at 150 °C in the 1800-800 cm^1 region. The bands at 1159 cm^{-1} and 1597 cm^{-1} were attributed, in part, to NH_3 adsorbed at Lewis acid.[3] The other labelled bands were attributed to NO_x species. The shoulder at 1101 cm^{-1} suggests the presence of hyponitrite.[1] d.) DRIFTS recorded during exposure of bulk $Ce_{0.7}Mn_{0.3}O_x$ to NH_3 at 150 °C in the 3730-2750 cm^{-1} region. The bands spanning 3350-3250 cm^{-1} are attributed to adsorbed NH_3.

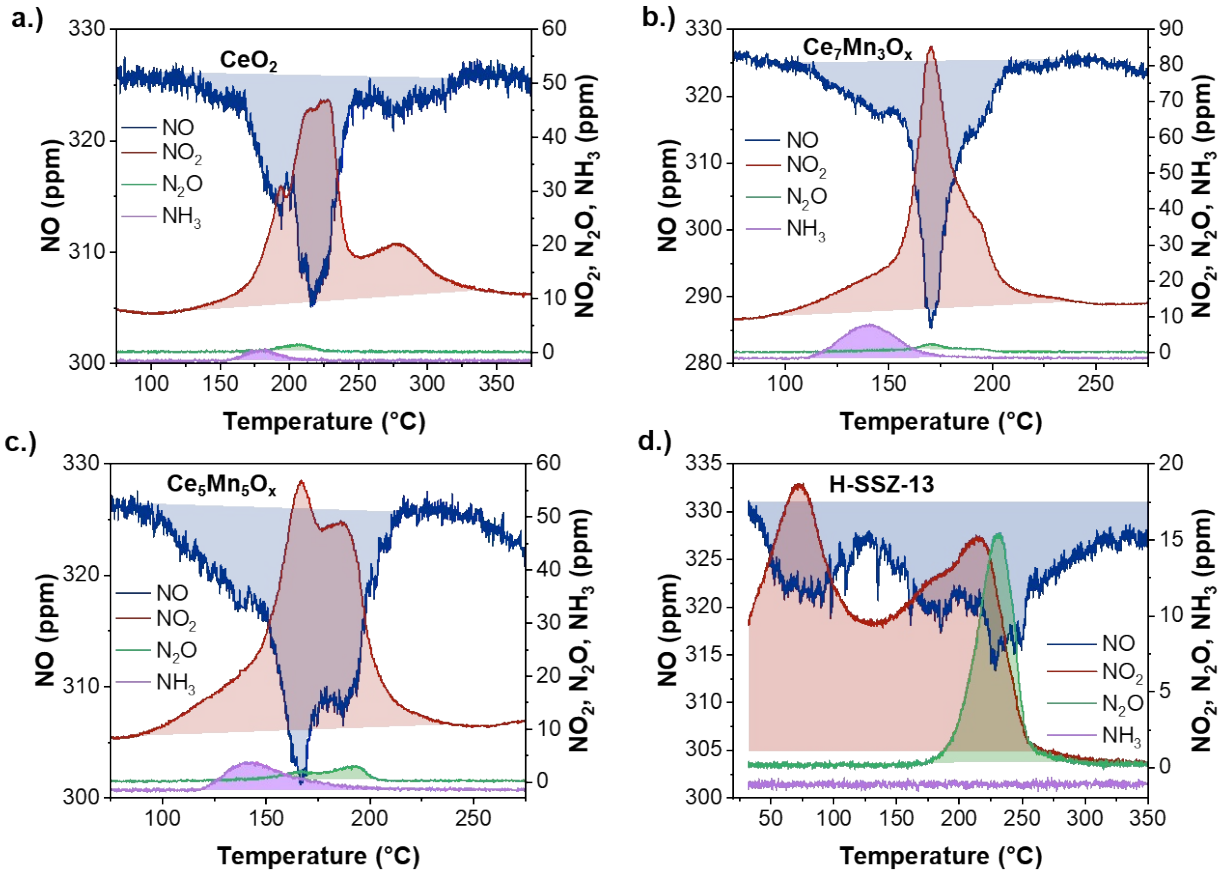

Figure S8. Temperature programmed surface reaction between NO and NH_4NO_3 over bulk oxide catalysts. The shaded areas represent the integrated areas used in Figure 3b. Conditions: [NH_4NO_3] = 15 wt. %; [NO] = 325 ppm; β = 10 °C min^{-1}; F = 1 SLM.

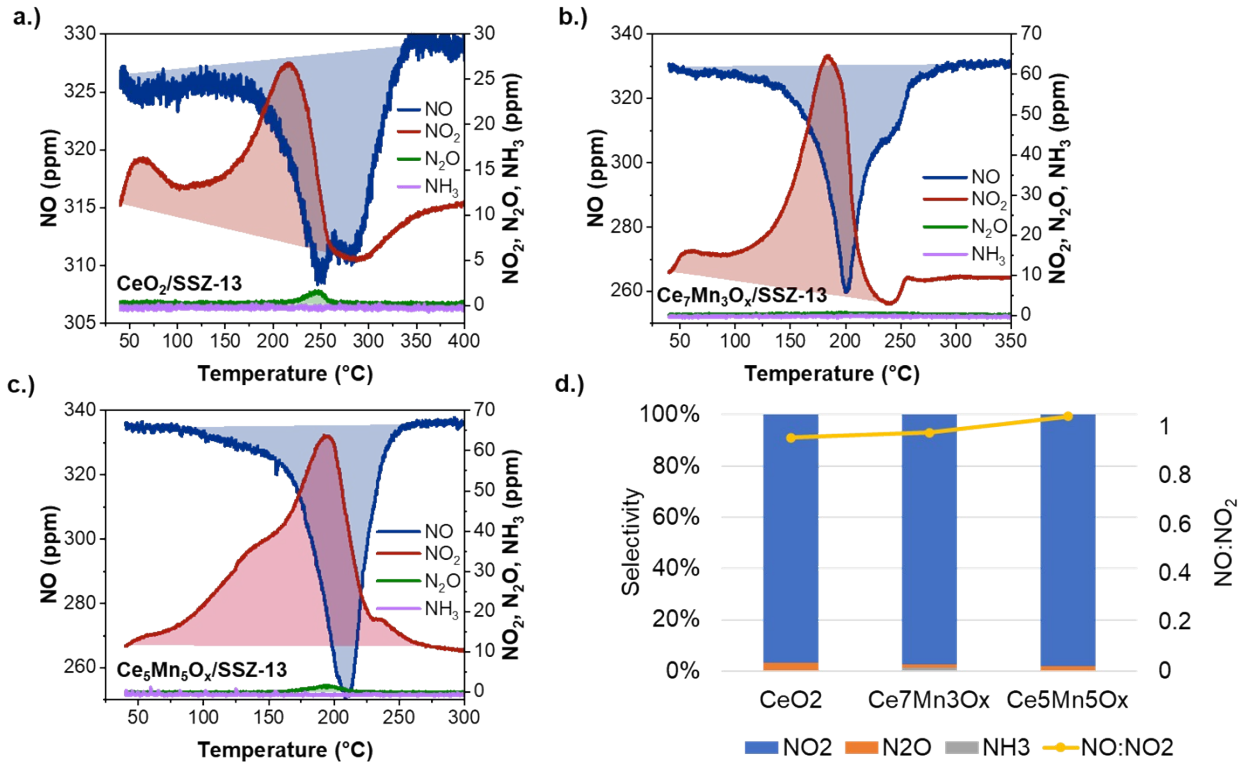

Figure S9. Temperature programmed surface reaction between NO and NH_4NO_3 over zeolite-supported mixed oxide catalysts. The shaded areas represent the integrated areas used in for the histogram in (d). Conditions: [NH_4NO_3] = 15 wt. %; [NO] = 325 ppm; β = 10 °C min^{-1}; F = 1 SLM.

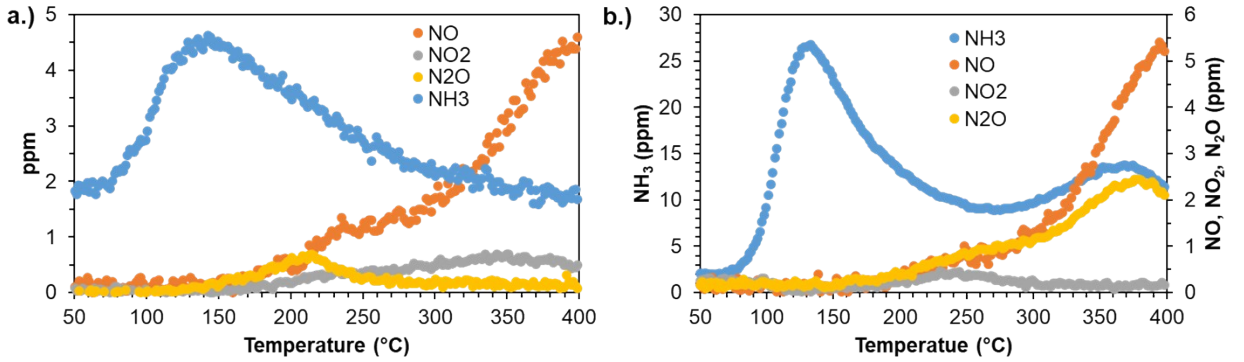

Figure S10. NH_3 temperature programmed desorption (TPD) over a.) bulk $Ce_{0.7}Mn_{0.3}O_y$ and b.) $Ce_{0.7}Mn_{0.3}O_y$/SSZ-13. Both catalysts were heated to 500 °C in 15 % O_2 for 0.5 h, followed by cooling under He, admittance of 350 ppm NH_3 for 0.5 h at 50 °C, and heating at 10 °C min^{-1} under 1 SLM N_2.

References:

1. Mihaylov, M. Y.; Ivanova, E. Z.; Vayssilov, G. N.; Hadjiivanov, K. I., Revisiting ceria-NOx interaction: FTIR studies. *Catal. Today* **2020,** *357*, 613-620.
2. Kim, Y.; Hwang, S.; Lee, J.; Ryou, Y.; Lee, H.; Kim, C. H.; Kim, D. H., Comparison of NO_x Adsorption/Desorption Behaviors over Pd/CeO_2 and Pd/SSZ-13 as Passive NO_x Adsorbers for Cold Start Application. *Emission Contr. Sci. Technol.* **2019,** *5*, 172-182.
3. Zhang, L.; Pierce, J.; Leung, V. L.; Wang, D.; Epling, W. S., Characterization of Ceria's Interaction with NO_x and NH_3. *J. Phys. Chem. C* **2013,** *117*, 8282-8289.