Electronic Supplementary Information

Synergistic effect of VO_x and MnO_x surface species for improved performance of $V_2O_5/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ catalysts in low-temperature NH₃-SCR of NO

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SI-A XRD analysis



Figure SI-1. X-ray diffraction patterns of pure $Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ supports (A) and 5% V₂O₅/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta} catalysts (B).

SI-B Surface and pore site analysis



Figure SI-2: N_2 adsorption (filled symbols) and desorption isotherms (open symbols) of pure supports (A) and supported vanadium catalysts (B).



Figure SI-3. XP spectra in the region of the O 1s peaks of $Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ supports (left) and 5% $V_2O_5/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ catalysts (right).



Figure SI-4. XP spectra in the region of the Mn 2p peaks of $Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ (x = 0.1; 0.2) supports and 5% V₂O₅/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta} catalysts.

The Mn 2p XPS spectra contain two main peaks $(2p_{1/2} \text{ and } 2p_{3/2})$ and a satellite feature at above 647 eV. The Mn $2p_{3/2}$ peaks at 640.9± 0.3, 641.9 ± 0.3 and 643.4 ± 0.3 eV can be ascribed to Mn²⁺, Mn³⁺ and Mn⁴⁺ species, respectively, while the satellite feature (647 eV) corresponds to Mn²⁺.



Figure SI-5. XP spectra in the region of the Ce 3d peaks of $Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ supports and 5% $V_2O_5/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ catalysts.

All Ce 3d spectra show the typical peaks for $3d_{5/2}$ (v, v", v"") and $3d_{3/2}$ (u, u", u"") core electrons of Ce⁴⁺. Especially the u" peak at 917.7 eV is a fingerprint for Ce⁴⁺ (see ref. 43 of the main manuscript). The lowest binding energy in all samples was between 882 and 883 eV which is characteristic for tetravalent Ce. No v⁰ peak of Ce³⁺, expected between 880 and 881 eV, was observed. Therefore, the presence of trivalent Ce can be excluded.



Figure SI-6. XP spectra in the region of the Ti 2p peaks of $Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ supports and 5% $V_2O_5/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ catalysts.





SI-D H₂-TPR analysis

Table SI-1: H ₂ consumption and maximum temperature derived				
from H ₂ -TPR profile of pure supports $Ce_{0.5}Ti_{0.5-x}Mn_xO_{2-\delta}$ and				
vanadium containing catalysts V/Ce $_{0.5}$ Ti $_{0.5-x}$ Mn $_x$ O $_{2-\delta}$.				
Samples	H ₂ consumption /	T _{max} /		
	µmol.g⁻¹	°C		
Ce _{0.5} Ti _{0.5} O _{2-δ}	1334.6	445.3		
$Ce_{0.5}Ti_{0.45}Mn_{0.05}O_{2-\delta}$	1544.1	432.0		
$Ce_{0.5}Ti_{0.4}Mn_{0.1}O_{2-\delta}$	1709.2	369.8		
$Ce_{0.5}Ti_{0.3}Mn_{0.2}O_{2-\delta}$	2238.9	375.8		
$V/Ce_{0.5}Ti_{0.5}O_{2-\delta}$	1786.1	531.0		
$V/Ce_{0.5}Ti_{0.45}Mn_{0.05}O_{2-\delta}$	1961.9	541.1		
$V/Ce_{0.5}Ti_{0.4}Mn_{0.1}O_{2-\delta}$	2130.0	506.1		
$V/Ce_{0.5}Ti_{0.3}Mn_{0.2}O_{2-\delta}$	2767.5	503.3		

SI-E FTIR analysis



Figure SI-8. In situ DRIFT spectra of the V-containing catalysts (region of the 2v overtone of V⁵⁺=O) recorded at 175°C: after pretreatment (initial), 45 min exposure to 0.1 % NH₃/He flow and after subsequent flushing with He.



Figure SI-9. In situ DRIFT spectra of the V-containing catalysts (region of the 2v overtone of $V^{5+}=O$) recorded at 175°C: after pretreatment (initial), 45 min exposure to 0.1 % NO, 5 % O₂/He at 175 °C, followed by flushing with He, and subsequent exposure to 0.1 % NH₃/He flow.

SI-F EPR analysis



Figure SI-10. N₂ formation and NO reduction detected by mass spectrometric analysis of the effluent gas stream during NH₃-SCR over 4 catalysts V/Ce_{0.5}Ti_{0.5-x}Mn_xO_{2- δ} (x=0; 0.05; 0.1; 0.2) at 200 °C, carried out parallel to the operando EPR measurements.



Figure SI-11: In-situ-EPR spectra at 150 °C of support $Ce_{0.5}Ti_{0.45}Mn_{0.05}O_{2-\delta}$ (A) and catalyst V/Ce_{0.5}Ti_{0.45}Mn_{0.05}O_{2-\delta} (B) after 1 h pretreatment in O₂ flow at 300 °C and cooling to 150 °C in Ar flow, subsequent exposure for 30 min each to 0.1% NH₃/Ar, 0.1% NO, 5% O₂/Ar and total SCR feed flow (flushing with Ar between subsequent steps).



Figure SI-12: In-situ-EPR spectra at 150 °C of support $Ce_{0.5}Ti_{0.4}Mn_{0.1}O_{2-\delta}$ (A) and catalyst V/Ce_{0.5}Ti_{0.4}Mn_{0.1}O_{2- δ} (B) after 1 h pretreatment in O₂ flow at 300 °C and cooling to 150 °C in Ar flow, subsequent exposure for 30 min each to 0.1% NH₃/Ar, 0.1% NO, 5% O₂/Ar and total SCR feed flow (flushing with Ar between subsequent steps).