

Figure S1: Adsorption / desorption isotherms of calcined (SBAc) and uncalcined (SBAa) SBA-15.



Figure S2: Pore size distribution of calcined (SBAc) and uncalcined (SBAa) SBA-15.



Figure S3: N₂ Adsorption/desorption isotherms of 10Mn-MIa before and after acid treatment



Figure S4: N_2 Adsorption/desorption isotherms of of 20Mn-MIa before and after acid treatment



Figure S5: N₂ Adsorption/desorption isotherms of 30Mn-MIa before and after acid treatment



Figure S6: Scheme illustrating the "pore network effect" generating ink bottle pores^[32]



Figure S7: Pore size distribution (offset by 0.4 cm³.g⁻¹.nm⁻¹) of 10Mn-MIa before and after acid treatment



Figure S8: Pore size distribution (offset by 0.4 cm³.g⁻¹.nm⁻¹) of 20Mn-MIa before and after acid treatment



Figure S9: Pore size distribution (offset by 0.4 cm³.g⁻¹.nm⁻¹) of 30Mn-MIa before and after acid treatment



Figure S10: A/(A+B) ratio as a function of Mn wt %



Figure S11: XPS spectra of Si 2p for 20 and 30 Mn-MIa before and after acid treatment



Figure S12: XPS spectra of Mn 3s for 20 and 30 Mn-MIa before and after acid treatment (* : gain x3)



Figure S13: Example of the decomposition of Mn 2p_{3/2} envelope for 20Mn-MIa



Figure S14: Example of the decomposition of Mn $2p_{3/2}$ envelope for 20Mn-MIa-AT

| Compound | Peak 1 | | Peak 2 | | Peak 3 | | Peak 4 | | Peak 5 | | | Peak 6* | | | | | | |
|--|-----------------|------|--------|---------------|--------|------|---------------|------|--------|---------------|------|---------|---------------|-----|------|---------------|-----|-----------------|
| | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM |
| Mn(II), MnO | left to vary | 23.7 | 1.5 | Peak 1 + 0.97 | 27.6 | 1.5 | Peak 1 + 1.9 | 21.8 | 1.5 | Peak 1 + 2.85 | 12.2 | 1.5 | Peak 1 + 3.99 | 5.7 | 1.5 | Peak 1 + 5.74 | 9.0 | left to vary |
| Mn(III), Mn ₂ O ₃ | left to vary | 18.8 | 2.05 | Peak 1 + 1.1 | 44.4 | 2.05 | Peak 1 + 2.37 | 25.2 | 2.05 | Peak 1 + 3.87 | 8.5 | 2.05 | Peak 1 + 5.49 | 3.1 | 2.05 | | | |

Table S1: Fitting parameters used to simulate the Mn 2p_{3/2} envelope for xMn-MIa samples inspired from the work of M. Biesinger ³⁸

* : MnO satellite

 $\label{eq:solution} \textbf{Table S2}: Fitting parameters used to simulate the Mn 2p_{3/2} envelope for $xMn-MIa-AT$ samples inspired from the work of M. Biesinger 38 results a statement of the statement of t$

| Compound | Peak 1 | | | Peak 2 | | Peak 3 | | Peak 4 | | Peak 5 | | | Peak 6* | | | | | |
|-----------------------------|-----------------|------|------|---------------|------|--------|------------------|--------|------|------------------|-----|------|------------------|-----|------|------------------|------|-----------------|
| | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM | eV | % | FWHM |
| Mn(II), MnO | left to vary | 34.4 | 1.6 | Peak 1 + 1.2 | 26.2 | 1.6 | Peak 1 + 2 | 16.9 | 1.6 | Peak 1 + 2.9 | 8.6 | 1.6 | Peak 1 + 7.5 | 3.5 | 1.6 | Peak 1 + 5 | 10.4 | left to vary |
| Mn(IV), MnO ₂ | left to vary | 43.7 | 1.75 | Peak 1 + 0.86 | 27.5 | 1.75 | Peak 1 + 1.56 | 16.1 | 1.75 | Peak 1 + 2.31 | 9.6 | 1.75 | Peak 1 + 3.16 | 0.5 | 1.75 | Peak 1 + 4.16 | 2.6 | 1.75 |

* : MnO satellite.



Figure S15: H₂-TPR profiles of 10Mn-MIa before and after acid treatment



Figure S16: H₂-TPR profiles of 20Mn-MIa before and after acid treatment



Figure S17: H₂-TPR profiles of 30Mn-MIa before and after acid treatment



Figure S18: TGA/DSC curves of 20Mn-MIa sample

| Samples | Mn (wt%*) | H ₂ -consumption (mmol/g) | $n_{\rm H2}/n_{\rm Mn}$ | Mn AOS | | |
|-------------|--------------|--------------------------------------|-------------------------|--------|--|--|
| 10Mn-MIa | 9.41 | 0.071 | 0.04 | 2.1 | | |
| 20Mn-MIa | 19.18 | 1.223 | 0.35 | 2.7 | | |
| 30Mn-MIa | 26.64 | 1.471 | 0.3 | 2.6 | | |
| 10Mn-MIa-AT | 2.38 | 0.334 | 0.77 | 3.5 | | |
| 20Mn-MIa-AT | 8.61 | 0.943 | 0.60 | 3.2 | | |
| 30Mn-MIa-AT | 10.93 | 1.738 | 0.87 | 3.8 | | |
| *: From ICP | | | | | | |

 $\textbf{Table S3:} H_2\text{-}TPR \text{ data for the $xMn-MIa$ samples before and after acid treatment}$



Figure S19: HR-TEM of 10Mn-MIa (A and C) and 20Mn-MIa (B and D)



Figure S20: TEM and HR-TEM of 10-MIa-AT (A and C) and 20MIa-AT (B and D). The insert of Fig. 20(C) excludes the external particles

| T ₉₀ ∕ °C | T ₅₀ | r_s^1 | |
|-------------------------|---|---|--|
| / C | / C | | |
| 218 | 183 | 17 | |
| 176 | 144 | 11.5 | |
| 182 | 141 | 9.5 | |
| 230 | 205 | 30 ² | |
| 160 | 125 | 51.2 | |
| 165 | 122 | 39.7 | |
| | T ₉₀ / °C 218 176 182 230 160 165 | $\begin{array}{c c} T_{90} & T_{50} \\ / ^{\circ} C & / ^{\circ} C \\ \hline 218 & 183 \\ 176 & 144 \\ 182 & 141 \\ \hline 230 & 205 \\ 160 & 125 \\ 165 & 122 \\ \hline \end{array}$ | |

Table S4: Catalytic properties of the fresh and acid-treated xMn-MIa catalysts

 $^1\!\!:$ expressed in mmoles of HCHO converted into CO_2 per mole of Mn and per hour at 130 $^\circ C$; 2: at 170 $^\circ C$



Figure S21: Plots of HCHO conversion as a function of time for 20Mn-MIa-AT in dry and humid air (RH= 50%) at 130 °C during 70 h.



Figure S22: Wide-angle XRD patterns of fresh and used 20Mn-MIa-AT under dry or moisture condition



Figure S23: Adsorption / desorption isotherms (offset by 400 $\text{cm}^3.\text{g}^{-1}$) of fresh and used 20Mn-MIa-AT under dry or moisture condition



Figure S24: Pore size distribution (offset by 0.4 cm³.g⁻¹.nm⁻¹) of fresh and used 20Mn-MIa-AT under dry or moisture condition



Figure S25: H₂-TPR profiles of fresh and used 20Mn-MIa-AT in dry and humid air



Figure S26: Evolution of infra-red spectra of fresh and used 20Mn-MIa-AT under dry or moisture condition