

Supporting Information for

'Carbon Monoxide Adsorption on Manganese Oxide / Cobalt: An Ambient Pressure X-ray Photoelectron Spectroscopy Study'

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Section S1 – SEM images of the Co foil

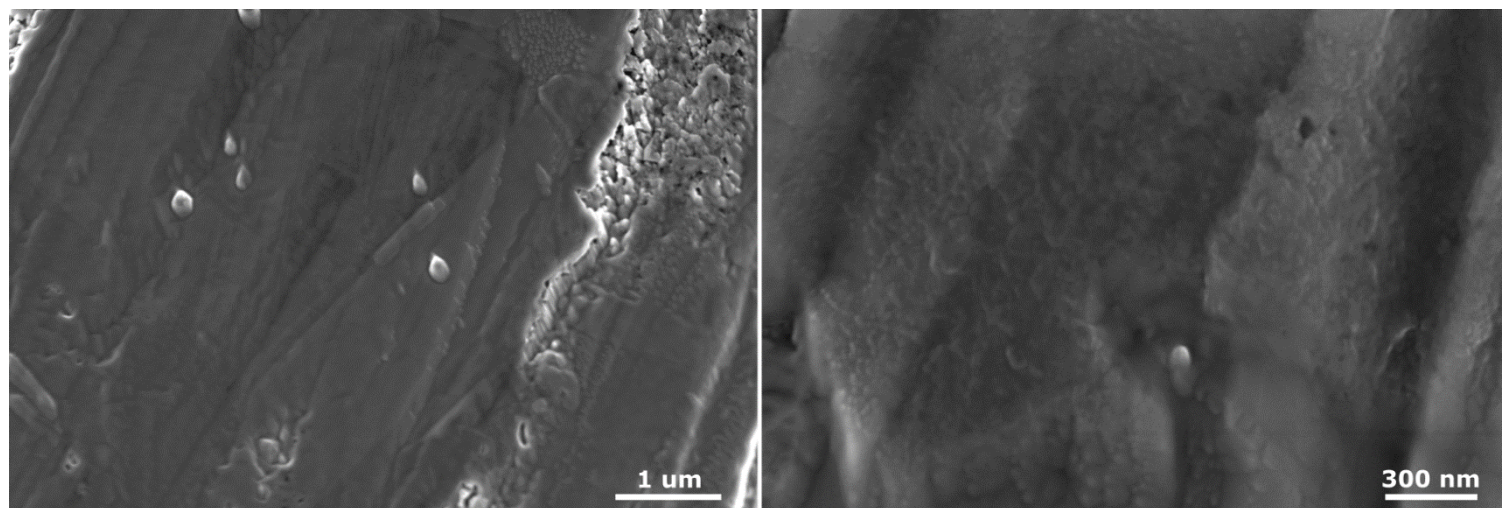


Figure S1. Selected SEM images of course-polished polycrystalline Co foil after 5-6 cycles of sputtering and mild annealing at 200 °C. The surface appears rough in these images, which are representative of the sample surface.

Section S2 – Effects of surface hydrocarbon contamination

Removing adventitious carbon contamination before the beginning of each experiment is essential for CO adsorption. Figure S2b shows that CO cannot adsorb if there is a large amount of adventitious carbon (CH_x). This carbon was removed for each iteration of the experiment by Ar ion sputtering followed by annealing in UHV (Figure 1a top spectrum). Although, the amount of hydrocarbon contamination might appear not high in a survey spectrum (Figure S2a bottom spectrum), this is due to low photoionization cross-section at the C 1s region when an Al $K\alpha$ source is used. It is essential to make sure that the hydrocarbon intensity at ~ 284.4 eV is below the XPS detection limit, or as small as possible.

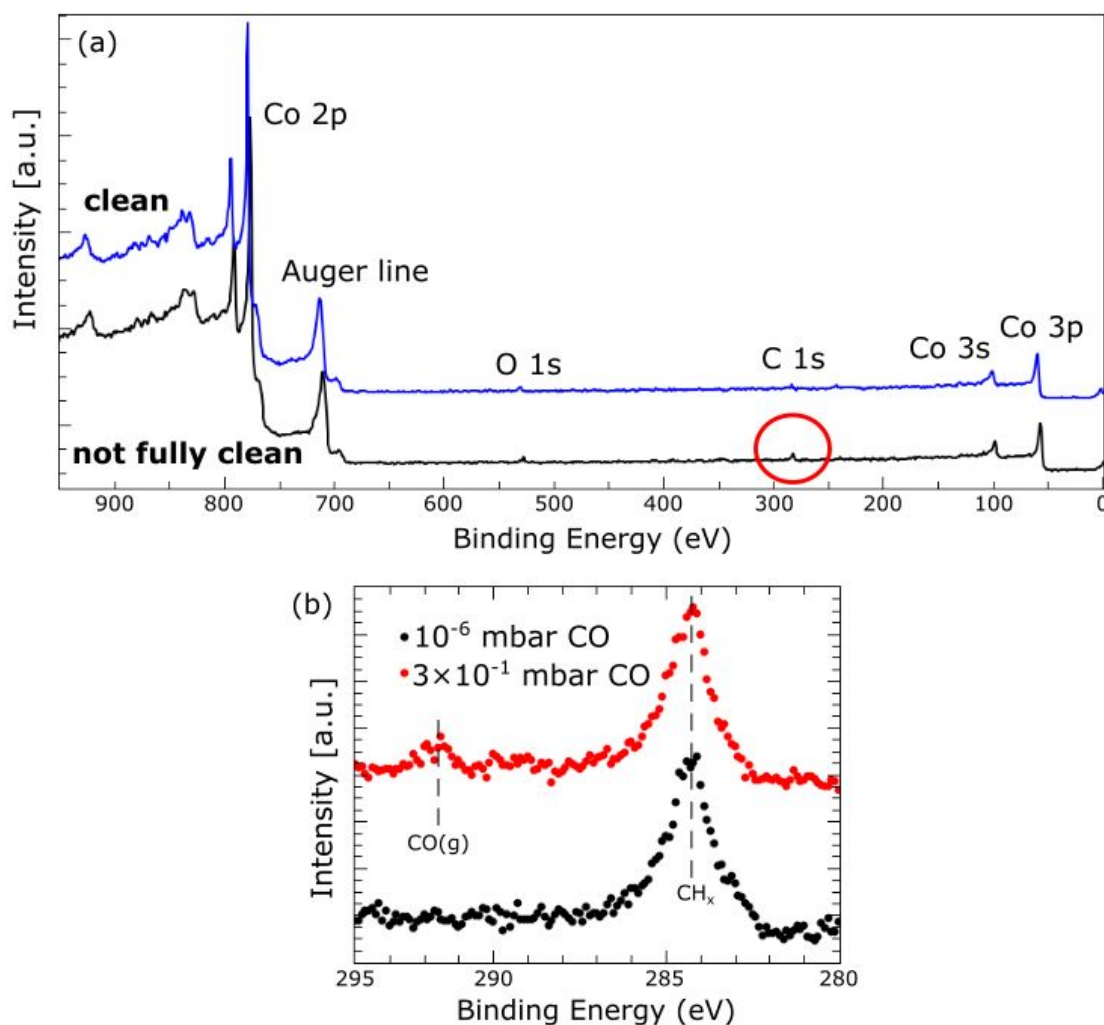


Figure S2. (a) Bottom spectrum - Survey spectra of Co foil after a few cycles when the surface is still not fully cleaned, top spectrum – after the hydrocarbon peak is below the detection limit both in the survey spectrum and in the C 1 region. (b) C 1s spectra on a CH_x -covered Co surface in the presence of CO. No CO adsorbs on the surface.

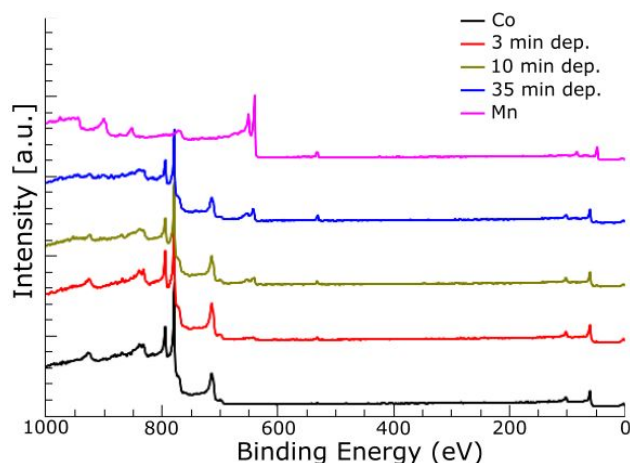


Figure S3. Survey spectra after different surface preparation procedures. No hydrocarbon or other contamination is discernible.

Section S3 - C 1s spectra and analysis

The C 1s spectra shown in Figure S4 are used for the CO adsorption analysis in the main text. The explanation of the peak positions is in the figure caption.

By normalizing the C 1s peak intensities to the total Cu 2p + Mn 2p areal intensities, we obtained the normalized CO intensities shown in Figure S5. All the spectra were corrected for photoionization cross sections (using Scofield sensitivity factors for Al K α excitation: 0.01367 for C 1s, 0.2591 for Co 2p, and 0.1878 for Mn 2p [S1]). The Co 2p to Mn 2p intensity is adjusted for the analyzer transmission function (1.2:1 at the kinetic energies of these two species). However, it is not straightforward to convert this ratio to a nominal coverage because the inelastic mean free path (IMFP) of photoelectrons originating from C species is higher than those of Co 2p and Mn 2p (i.e., more bulk sensitive).

It can be seen in Figure S5 that the CO coverage is increasing with increasing pressure, with the exception of two cases: At 1 mbar, there is a decrease in CO coverage, where Co is covered with a small and moderate amount of MnO_x. This behavior is because the adsorption sites are blocked by OH adsorption, as discussed in the main text.

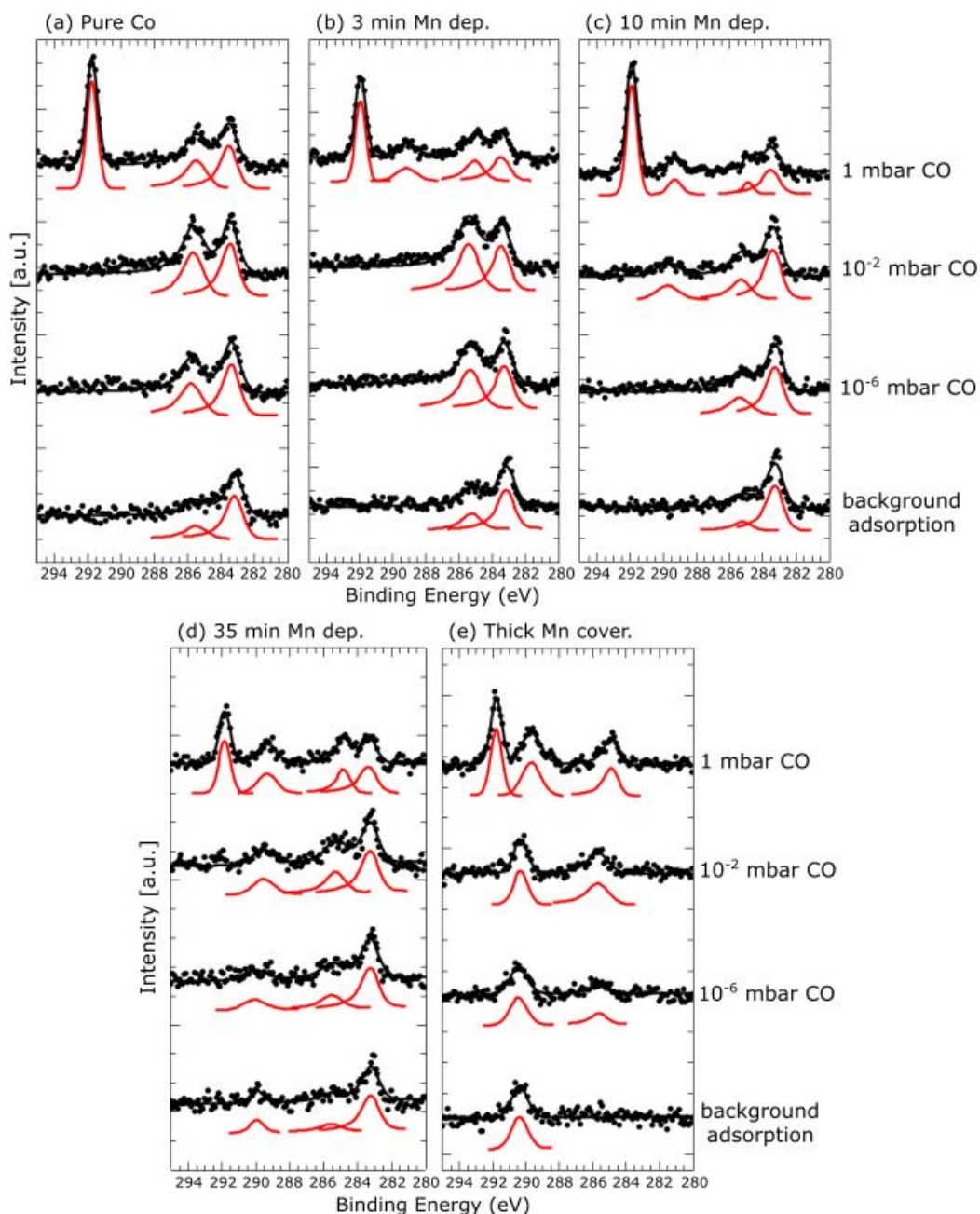


Figure S4. Acquired C1s spectra (black dots), Gaussian-Lorentzian fits for each peak (solid red lines, some are asymmetric), and the sum of the fits (solid black line), presented as a function of CO pressure for the different surfaces. The peak that is above 291 eV, which can only be observed in the presence of 1 mbar CO, is the gas phase CO, and its exact position depends mainly on the work function. The peak at 283.4 eV is due to carbide contamination inside the Co foil. CO species appear at two different positions: The peak at 284.8-285.8 eV is due to CO adsorbed on a metal, mostly on metallic Co. The position of this peak can be observed at lower binding energies, below 285 eV in some cases, at higher CO pressures due to Mn₂O₃ formation. The second CO peak appears at 288.2 eV-290.5 eV, which is CO adsorbed on an oxide.

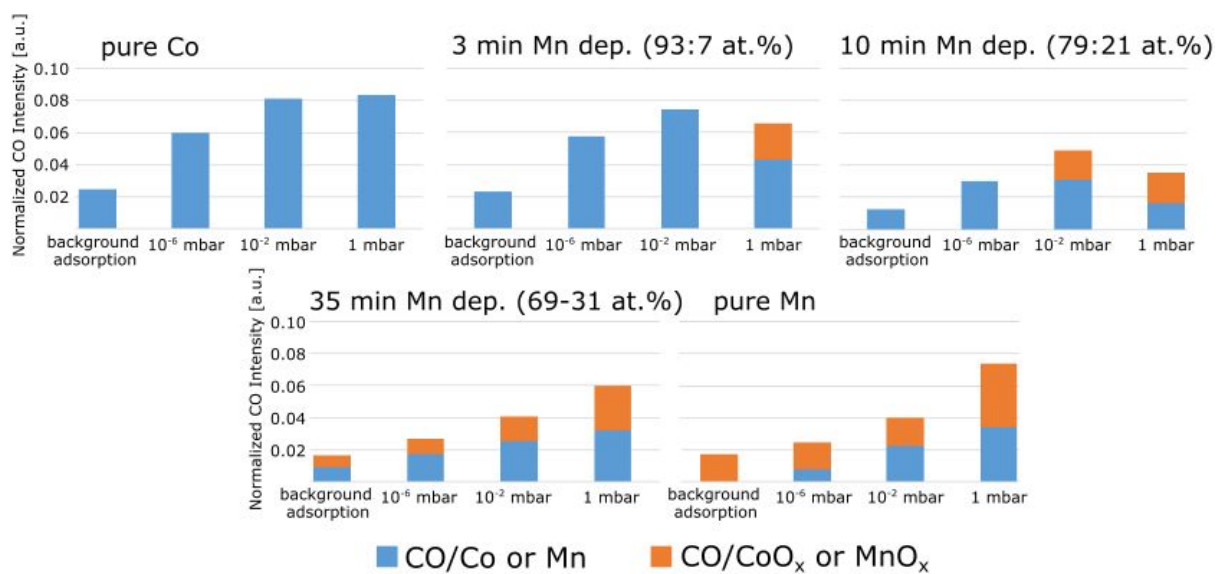


Figure S5. Normalized CO intensity on each surface under different CO pressures. Blue is CO on metal sites (mostly Co), and orange is CO on oxide sites (mostly MnO_x).

Section S4 - Metallic Co to CoO ratio based on Co 2p_{3/2} spectra

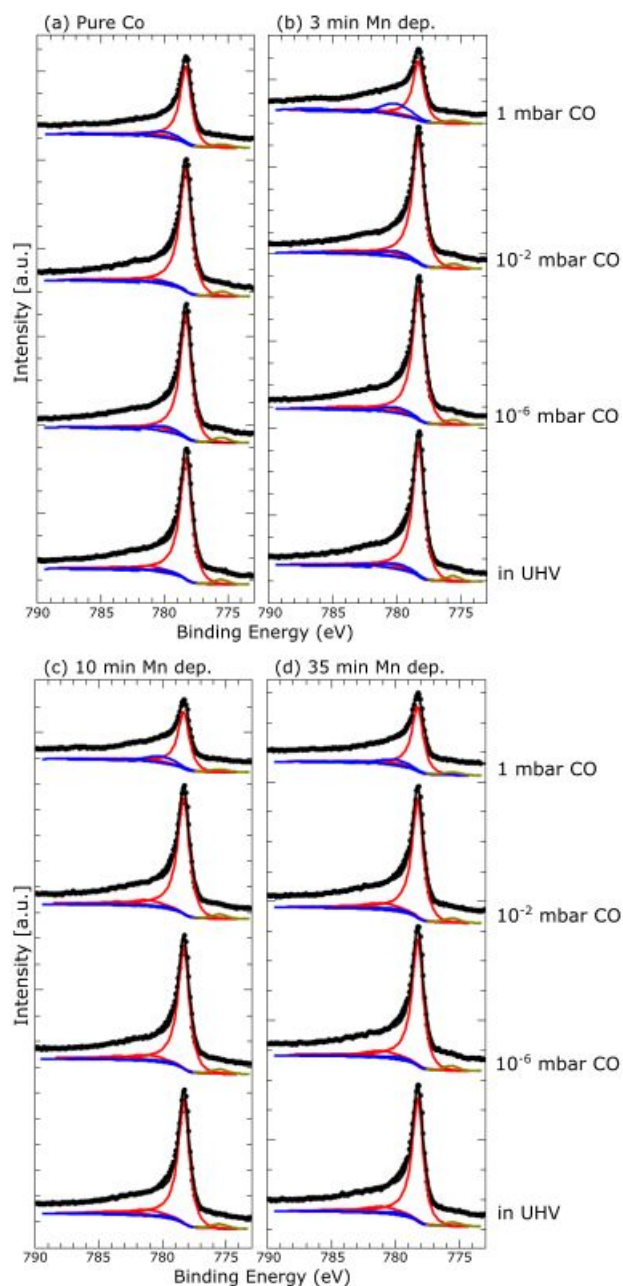


Figure S6. Co 2p_{3/2} spectra fit with 7 components. The yellow curve is an Auger line of Co. Red curves are asymmetric and represent metallic Co with the main peak at 778.3 eV and two weak satellites at higher binding energies. The symmetric and broader blue curves represent CoO, with the main peak at 780.1 eV and two satellites at higher binding energies. Fitting of these spectra were done in accordance with Ref. [S2].

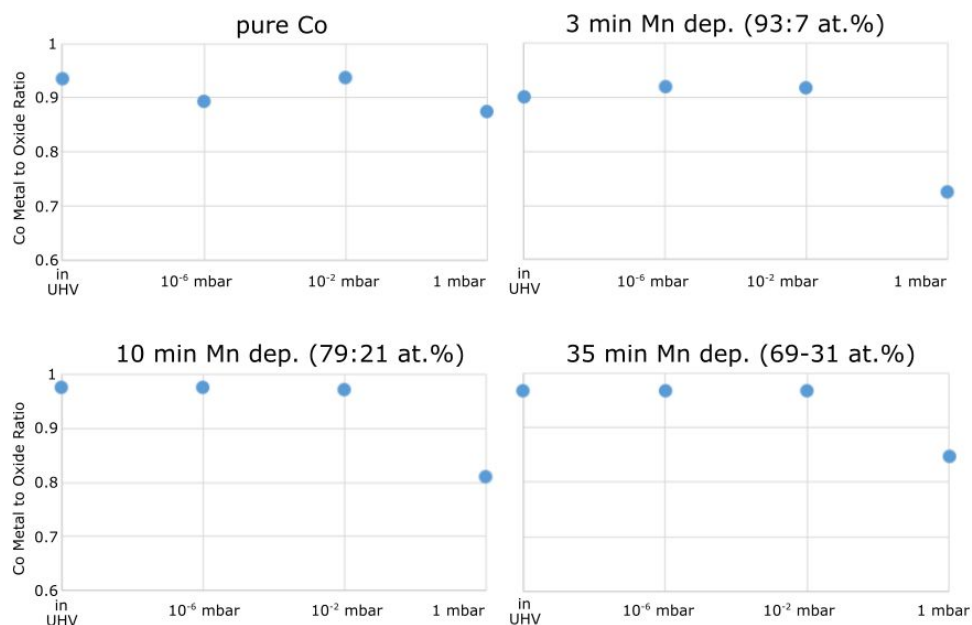


Figure S7. Metallic Co to CoO ratio obtained using the fits presented in Figure S6. We observe a slight oxidation at 1 mbar CO, which is counter-intuitive because CO is a reducing gas. However, as we presented in our previous work [S3], CO can only reduce CoO above 150 °C in this pressure range. At room temperature, water vapor in the background starts oxidizing the surface [S3]. These water vapor molecules originate from desorption from the chamber walls, as the adsorption of CO initiates significant desorption at higher pressures.

Section S5 - Raw spectra: Co 3p – Mn 3p, Mn 2p, and Co 2p Regions

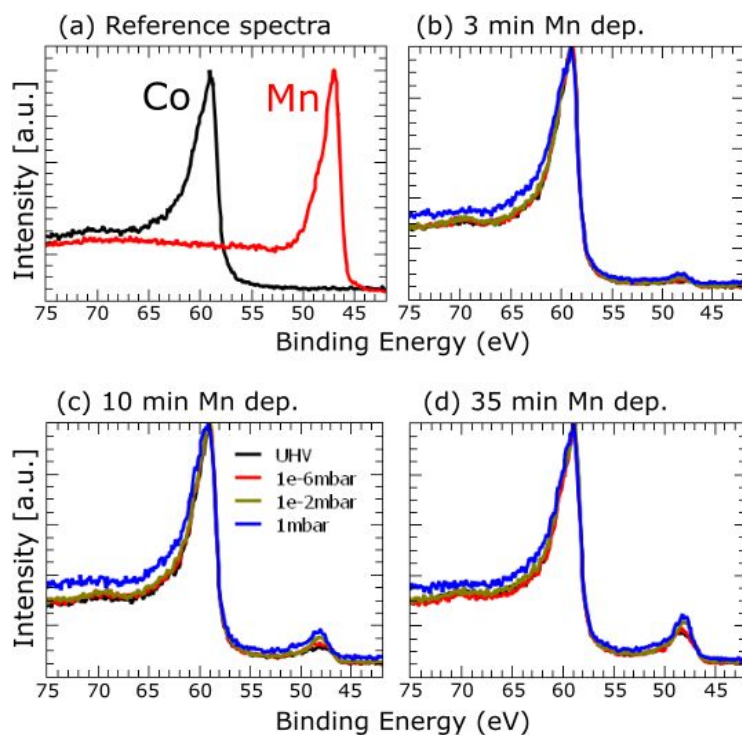


Figure S8. The Co 3p – Mn 3p core level spectra. Because the kinetic energy of the photoelectrons is over 1400 eV, the spectra are sensitive to the subsurface. Since the binding energies of Co 3p and Mn 3p electrons are similar, the intensities can be compared directly as the IMFPs are more or less the same. In all cases, there are only small changes that originates from the changes in the background and the lineshapes. Mn 3p to Co 3p intensity ratio remains the same within a 2%.

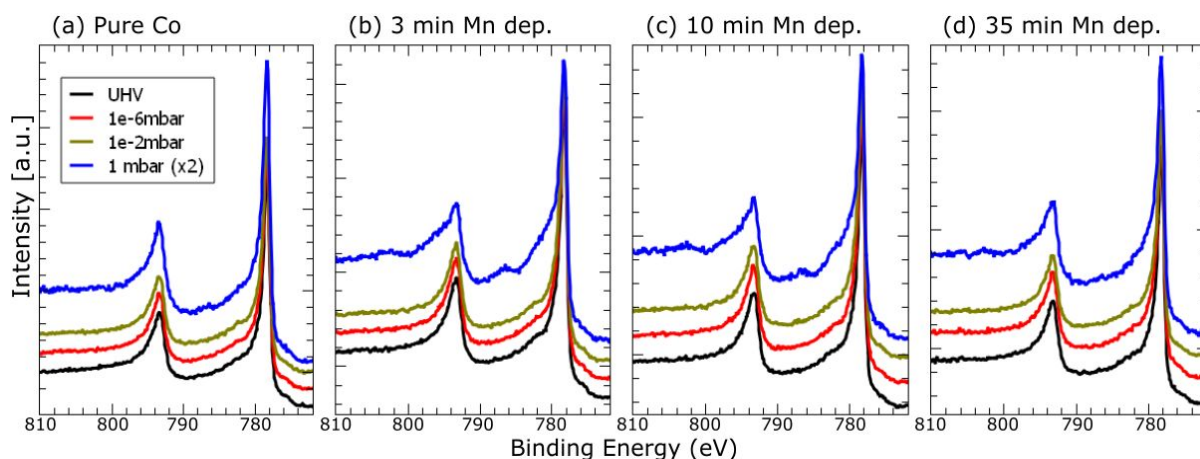


Figure S9. Co 2p spectra of all the surface preparations containing Co. There is no Co 2p signal for the fully covered Mn surface. The spectra were collected at UHV (black), 10^{-6} mbar CO (red), 10^{-2} mbar CO (dark yellow), and 1 mbar CO (blue).

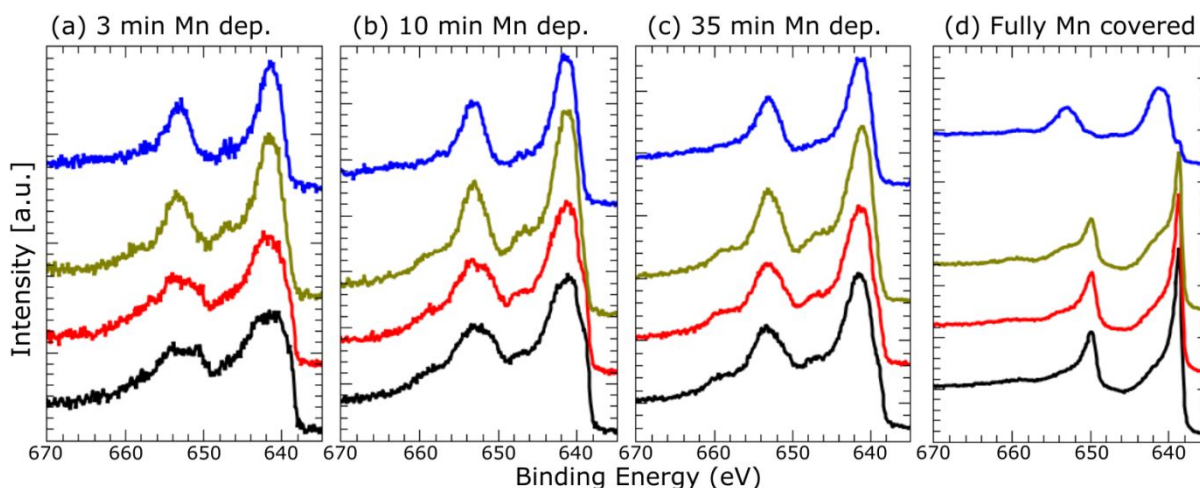


Figure S10. Mn 2p spectra of the surface preparations that contain Mn. The color-coding is the same as that in Figure S9. As-deposited Mn is a mixture of metallic Mn (638.8 ± 0.1 eV) and oxidic Mn (641.3 ± 0.1 eV), with more of the former at higher Mn surface populations (e.g., mostly metallic in (d)). Oxidic Mn (as deposited) is either MnO or Mn_2O_3 , according to the binding energy. The strong satellite feature at ~ 647 eV suggests MnO to be the dominant oxide species. In the presence of CO, the metallic peak disappears, and the satellite feature diminishes. Both suggest a transformation to Mn_2O_3 from a $\text{MnO} + \text{Mn}$ mixture. Although this behavior appears counter-intuitive, the reason for this oxidation is background H_2O in the gas phase causes both Co (explained in Ref. [S3] and in the caption of Figure S7) and Mn to oxidize. The oxidation is more severe for Mn than for Co.

Section S6 - O 1s Region and Its Analysis

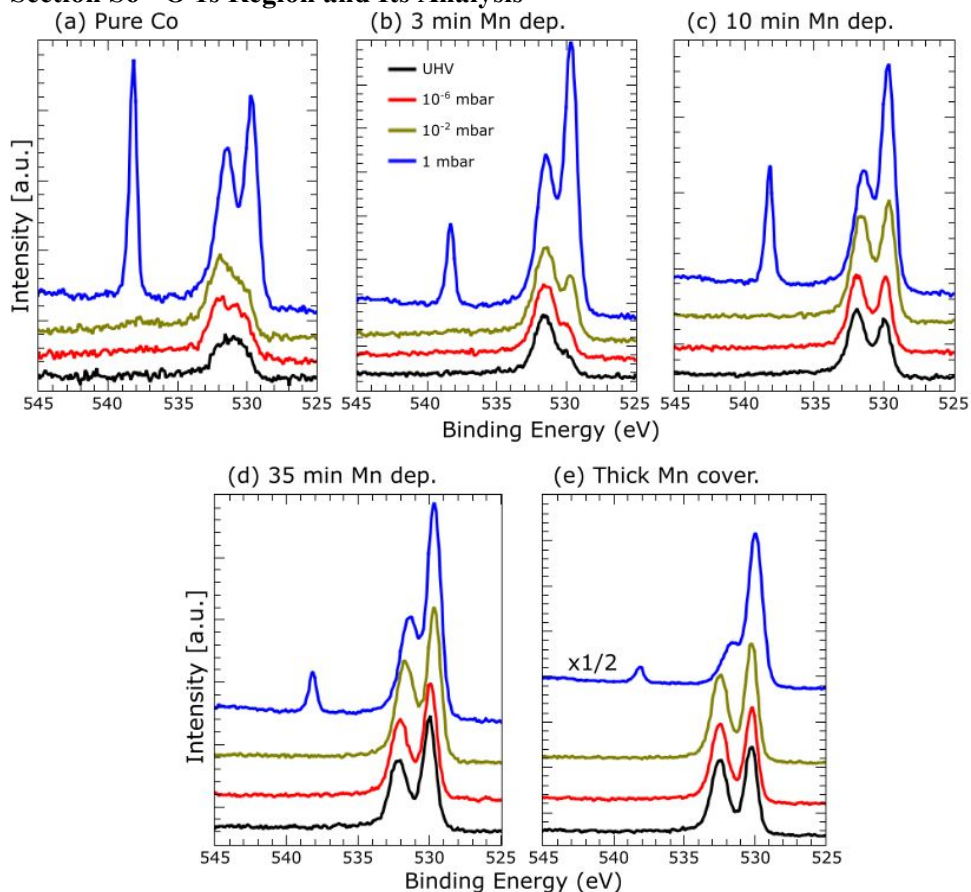


Figure S11. O 1s spectra of all the surface preparations collected at UHV and several CO pressures. The sharp peak at binding energies greater than 538 eV is due to the gas phase CO. The peak at 529.6-529.9 eV is due to adsorbed oxygen or lattice oxygen. The peak at 531.6-532.3 eV is due to a convolution of adsorbed CO and OH species.

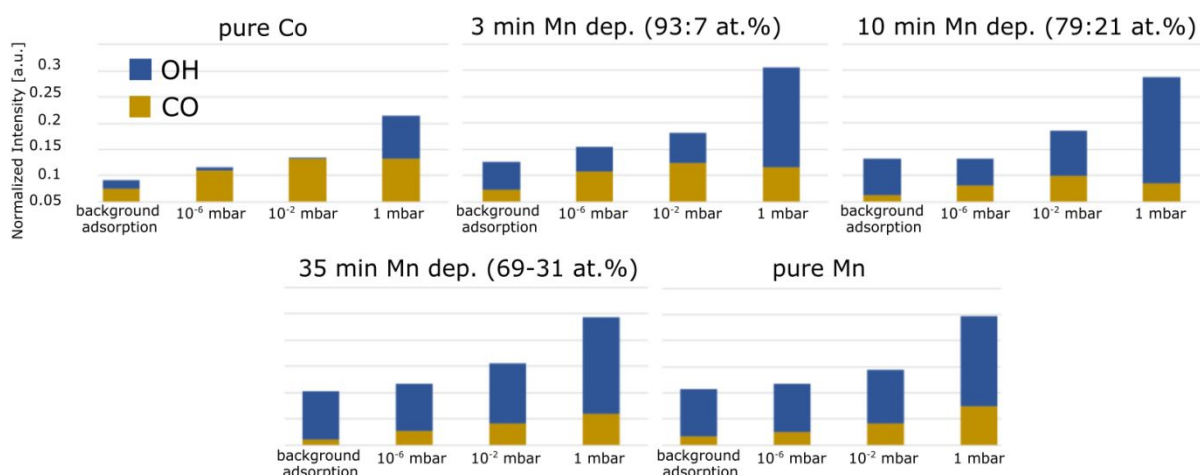


Figure S12. Constructed CO (golden) and OH (dark blue) normalized intensities on the surface by using O 1s to C 1s ratio of gas phase CO to estimate the OH amount.

References:

- [S1] Scofield, J. H. Hartree-Slater Subshell Photoionization Cross-sections at 1254 and 1487 eV. J. Electron Spectrosc. 1976, 8, 129-137.
- [S2] Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni. Appl. Surf. Sci. 2011, 257, 2717–2730.
- [S3] Wu, C. H.; Eren, B.; Bluhm, H.; Salmeron, M. Ambient-Pressure X-ray Photoelectron Spectroscopy Study of Cobalt Foil Model Catalyst under CO, H₂, and Their Mixtures. ACS Catalysis 2017, 7, 1150.