Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2020

Supporting Information:

Identifying the Catalyst Chemical State and Adsorbed Species during Methanol Conversion on Copper Using Ambient Pressure X-ray Spectroscopies

Baran Eren,*[a] Christopher G. Sole,[b] Jesús S. Lacasa,[a] David Grinter,[c] Federica Venturini,[c] Georg Held,[c] Cruz S. Esconjauregui,[d] and Robert S. Weatherup,*[bce]

[a] *Department of Chemical and Biological Physics, Weizmann Institute of Science, 234 Herzl Street, 76100 Rehovot, Israel.*

Email: baran.eren@weizmann.ac.il

[b] *Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.*

[c] *Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, United Kingdom.*

[d] *Department of Mechanical Engineering, Kingston University London, Friars Avenue, London SW15 3DW, United Kingdom.*

[e] *Department of Materials, University of Oxford, Parks Road, Oxford, Oxfordshire, OX1 3PH, United Kingdom.*

Email: robert.weatherup@materials.ox.ac.uk

Section S1 – Additional XPS and NEXAFS spectra

In this section, we present supplementary spectra supporting the arguments presented in the main text.

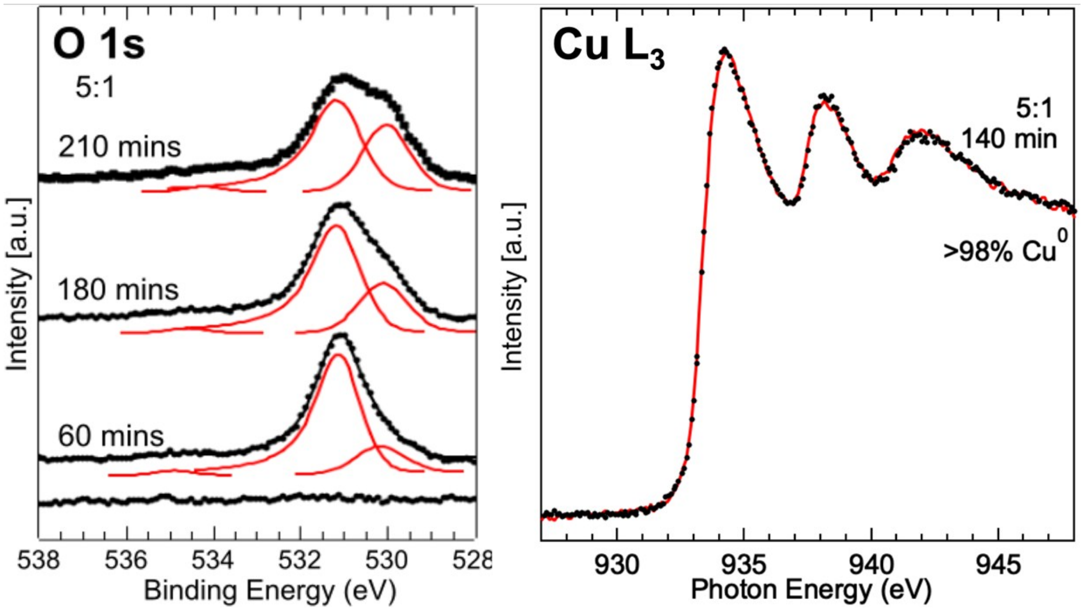

Figure S1 Left: O 1s region of the XPS spectrum acquired in approximately 1 hour, 3 hours, and 3.5 hours after the introduction of both gases (0.15 mbar CH_3OH and 0.03 mbar O_2) into the chamber. The bottom spectrum was acquired in the presence of 0.15 mbar methanol, prior to inclusion of oxygen in the gas mixture. Sample temperature is 200 °C. It is clear that the 530 eV peak increases with time, indicating that the steady-state has not been reached completely. Right: NEXAFS spectrum at the Cu L_3 edge after 2 hours and 20 minutes under the same conditions. The surface remains metallic in the presence of methanol and oxygen even after a long duration of exposure under these conditions.

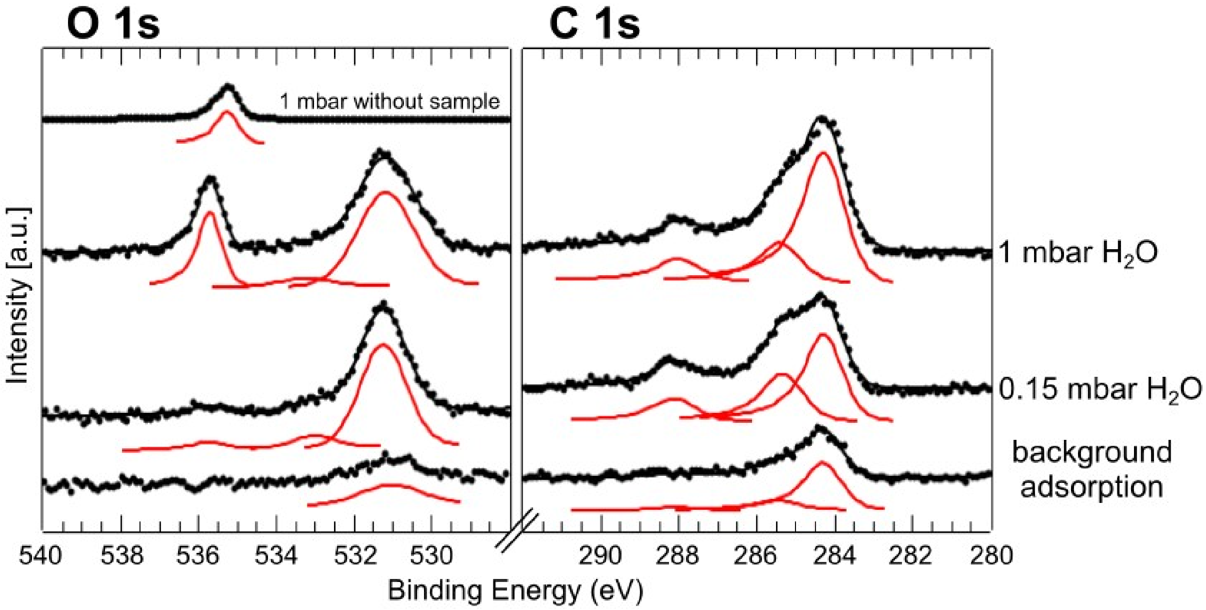

Figure S2 O 1s and C 1s regions of the XPS spectra during water adsorption experiments at ambient water vapour pressures at 200 °C sample temperature. Because of prior experiments with methanol, the measurement chamber and the chamber walls were contaminated with methanol, which adsorbs on the surface as methoxy and formate, best evidenced but the peaks at ~285.2 eV and ~288 eV in the C 1s region. The large 531.3 eV peak has intensity contributions from adsorbed methoxy, formate, and OH on the surface. Molecular water is also present on the surface, as the broad peak at 533.1 eV indicates. Unlike gas phase methanol, gas phase water peak is prominent and appears above 535 eV.

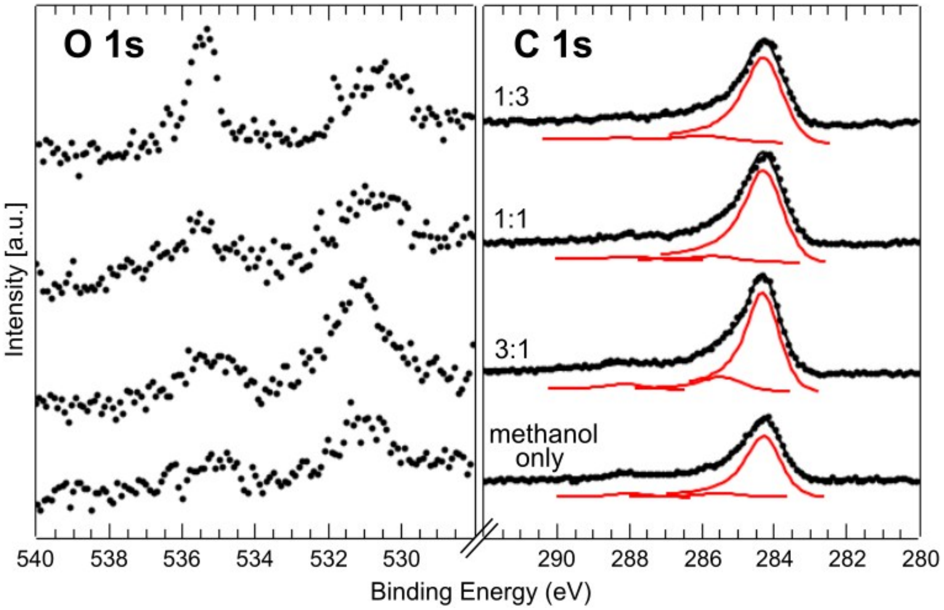

Figure S3 O 1s and C 1s regions of the XPS spectra in the presence of 0.15 mbar CH_3OH mixed with 0.05 mbar, 0.15, and 0.45 mbar of H_2O. Sample temperature is 200 °C. Because of the high pressure of non-oxidising vapours inside the measurements chamber, hydrocarbon contamination accumulating on the sample surface precludes rigorous analysis of the O1s and C1spectra.

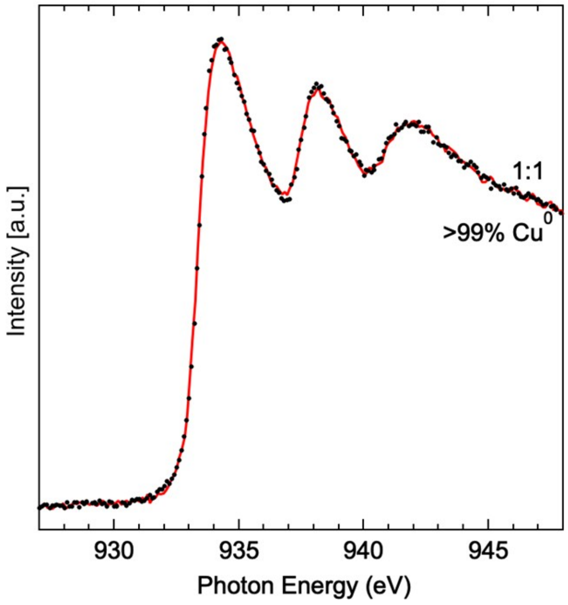

Figure S4 NEXAFS spectrum at the Cu L_3 edge in the presence of 0.15 mbar CH_3OH and 0.15 mbar H_2O at 200 °C. The surface is metallic.

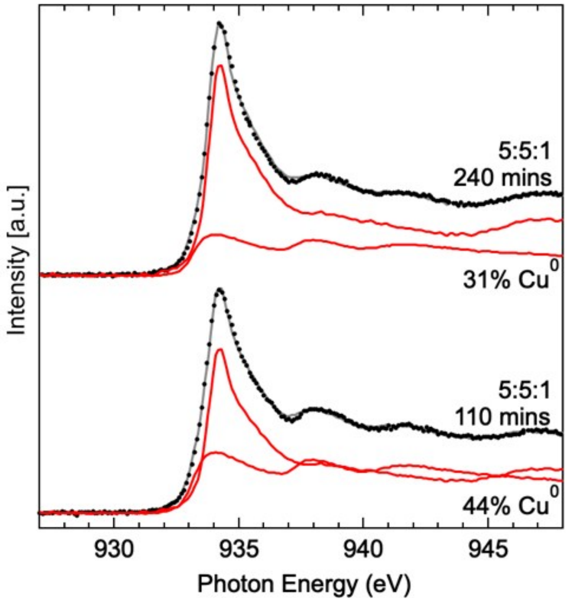

Figure S5 NEXAFS spectrum at the Cu L_3 edge after 1 hour and 50 minutes and after 4 hours in the presence of (0.15 mbar CH_3OH, 0.15 mbar H_2O, and 0.03 mbar O_2) at 200 °C. The surface continues to oxidise with time.

Section S2 How to keep the partial pressure ratio stable with 3 gases?

An important technical issue during these experiments is sustaining the pressure ratio between three gases unchanged throughout the course of acquiring each set of XPS and NEXAFS spectra. Typical gas dosing and pumping configurations in a typical AP-XPS beamlines are shown in Figure S6. Gas dosing is then typically performed as follows:

1- Open the leak valve and insert one gas (mbar/Torr range) while the valve to the turbo pump is closed so that the chamber is only slowly pumped through the AP-XPS analyser nozzle and differentially pumped X-ray source (if present).

2- Make sure the pressure is stable over a few minutes.

3- Insert the second gas. Make sure the total pressure is stable over a few minutes.

4- Insert the third gas. Make sure the total pressure is stable over a few minutes.

It is however extremely challenging to maintain the partial pressures ratios the same over the course of the ~30 min measurement time as slight accuracies in the adjustment of very small flows using the leak valves will result in the partial pressures drifting with time (e.g., the partial pressure of one gas might be creeping up while another is going down).

In other words, the problem is very low leak and pumping rates, meaning that small absolute inaccuracies in the set flows are large relative to the flows involved. The stability of the partial pressures can be significantly improved by operating the leak valves at much more open positions while simultaneously pumping the gases at a much higher rate. This can be achieved by adding an adjustable butterfly valve to the pumping line (Figure S7), which is controlled electronically to achieve a desired pressure using a conventional proportional-integral- differential (PID) controller. We operate now as follows:

1- Insert one gas (1e-5 to 1e-4 mbar/Torr range) with the valve to the turbo pump fully open.

2- Make sure the pressure is stable over two minutes.

3- Insert the second gas with the desired partial pressure ratio. Make sure the total pressure is stable over half a minute.

4- Insert the third gas with the desired partial pressure ratio. Make sure the total pressure is stable over half a minute.

4- Close the gate valve to turbo. Let the pressure creep up to the desired total pressure, and open the butterfly valve with the target pressure set at the desired total pressure. The PID-controlled butterfly valve will now adjust to retain this total pressure.

5- After XPS measurements are finished, the butterfly valve can be fully opened to pump down to low pressures, before fully opening the main valve to the turbo pump and then closing the butterfly valve. By then removing each gas one by one, it is possible to confirm that the partial pressure ratio initially set with the leak valves whilst in the 1e-5 to 1e-4 mbar/Torr range has been maintained. This last step provide confirmation that the approach for maintaining the ratio of gases has been successful.

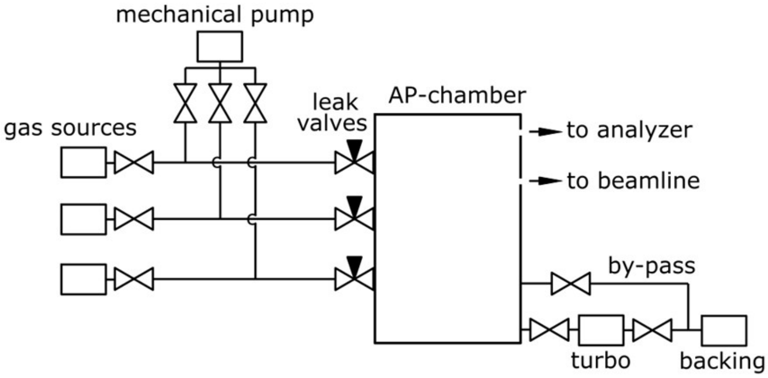

Figure S6 Typical gas dosing and pumping scheme used in most of the AP-XPS beamlines. Pumping rates are very slow and only through two nozzles, one to the AP-XPS analyser and the other one to the beamline. In some beamlines, there is instead an X-ray transparent SiN_x window between the beamline and the measurement chamber (AP-chamber), meaning the chamber is only pumped by the AP-XPS analyser.

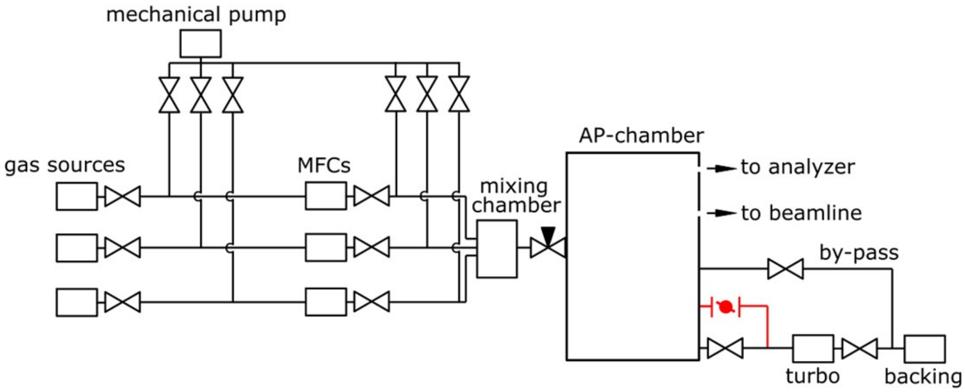

Figure S7 Alternative approach to dosing and pumping gases in the measurement chamber. Higher gas flow rates through the leak valves reduce the relative contribution of errors in the flow rate. Higher pumping rates are needed to achieve the same total pressure, which is then controlled using a butterfly valve (red part).