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## Supporting Information for Publication

### CO and O<sub>2</sub> Adsorption on K/Pt(111)

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### Dosing K on Pt(111)

Potassium was dosed onto the surface at 25 °C for increasing lengths of time using a custom built SAES getter source heated to over 1200 K and positioned in front of the crystal. After outgassing the differential pressure rise was  $2 \times 10^{-9}$  mbar during the course of the depositions, the majority of which was due to hydrogen desorption from the doser. The growth of the potassium adlayer was charted using the Pt<sub>MNN</sub> 69 eV and K<sub>LMM</sub> 272 eV Auger signals. The surface was heated to 550 °C and sputtered and annealed in between each dosing to make certain of the removal of all the potassium used in previous experiments from the surface.

Figure S1 shows two intersecting curves. The growth curve is due to the increasing amount of potassium that is deposited on the crystal surface with increasing time of potassium dose, and the decaying curve is due to the increasing amounts of potassium obstructing the passage of the Auger electrons from the platinum to the electron detecting grids of the retarding field analyser. The curves show that there is a relatively slow initial increase in Auger signal until two minutes potassium surface dose. Between two and three minutes there is a change in slope and large increase in the K signal and consequent reduction in the Pt signal. After this jump there is a slow increase in K signal that appears to tail off towards a maximum with increasing time. This sudden 'jump' in signal is likely due to the adsorbed potassium changing state from ionic to metallic as described in the literature, and in the main text of the paper. As in the chemisorption experiments also described in the main text ~200 s was determined to be the dosing time required for completion of one full potassium

layer (0.33 coverage relative to surface Pt atoms). The curve appears to level off to a shallower slope after the completion of the layer is perhaps characteristic of islands of potassium being formed, which grow in size as further potassium is deposited (Stranski-Krastinov growth mode), rather than the formation of a second complete monolayer. The initial platinum part of the curve (0-2 min) appears to exhibit a linear decrease; however the initial potassium region appears to be curved. It is possible that this is due to the sub-surface incorporation of potassium into the near-surface region as described in the main part of the paper. This might also be responsible for the sudden gradient change between two and three minutes potassium dose as despite the rate of potassium deposition being constant, the surrounding platinum atoms would damp the potassium Auger signal, causing a sudden large potassium signal as subsurface species migrate to surface sites when the critical coverage is reached; however this is unlikely given the shape of the rest of the plot. A further explanation for the gradual tail-off of the Auger spectrum with increasing surface coverage might be that potassium desorbs from the surface at coverages of greater than a monolayer at ambient temperatures as suggested by Somorjai and Garfunkel, who have presented data that appears to show that no further potassium adsorption occurs after one monolayer deposition.

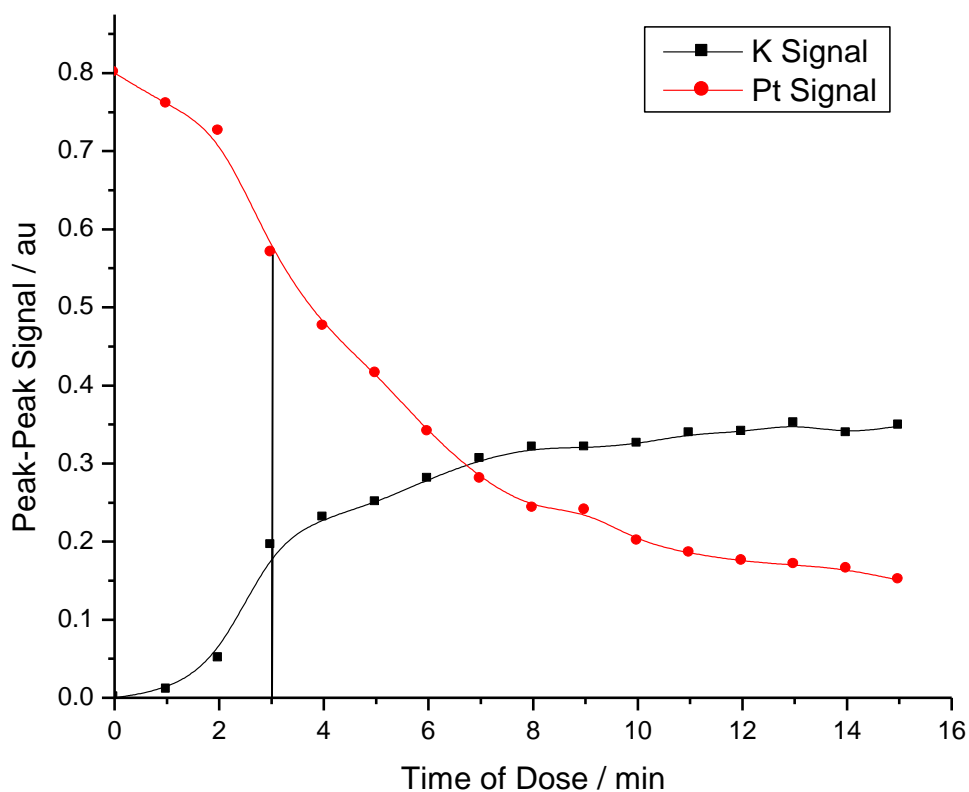


Figure S1 – the change in the relative Auger signals of K and Pt with increasing K surface coverage.

### Oxygen/potassium codosing

Some experiments were carried out in a separate machine equipped with XPS facilities. Here the K and oxygen were co-dosed to minimize contamination, since that UHV machine had a relatively poor background pressure varying between 5 – 10 x 10<sup>10</sup> mbar, depending on previous history.

The XPS below shows the O(1s) and K(2p) regions and shows the K(2p<sub>3/2</sub>) peak at ~ 293.2, characteristic of oxidized potassium, K<sup>+1</sup>. At high doses of oxygen, the O(1s) shows two peaks, the main one at ~532 eV, with a lower binding energy shoulder indicative of a peak at ~ 529.5 eV. The latter then is likely to be associated with atomic oxygen, probably bound to Pt (but influenced by K from the TPD in the main text), whereas the former is likely to be a peroxidic-like state. For comparison, see the table S1 below showing literature data for potassium oxides.

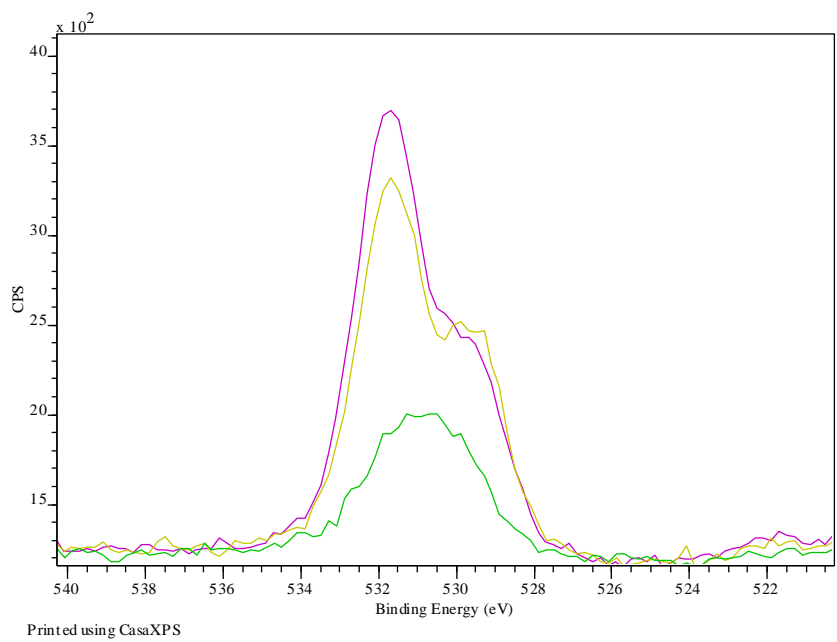


Fig S2a. O(1s) spectra after co-dosing oxygen and K on Pt(111) at 573K and O<sub>2</sub> pressures of  $1 \times 10^{-8}$  mbar for 6, 14 and 22 mins

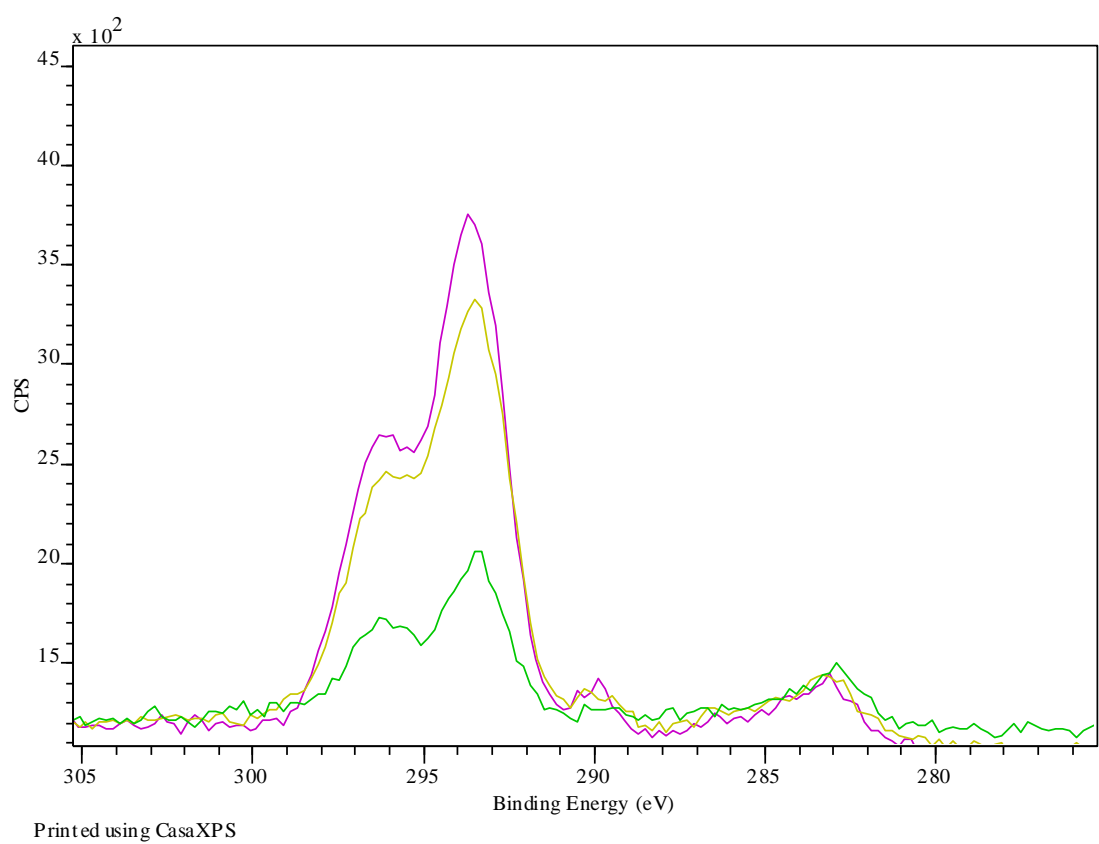


Figure S2b K(2p) XPS spectra, as in fig 2a.

**Table S1.** Literature values of oxygen binding energies for different chemical states associated with K

Substrate	BE in K <sub>2</sub> O	BE in K <sub>2</sub> O <sub>2</sub>	BE in KO <sub>2</sub>	BE in K <sub>2</sub> O <sub>3</sub>	Ref
Si(111)	528.3 on the surface (O <sub>2</sub> exp < 4L) 527.2 under the surface (O <sub>2</sub> exp > 4L)	531.0	534.3	532.0	2
Diamond (100)		531.1	534.2	534.2	3
HOPG		531.4 low coverage	534.2 high coverage		4
Ni(100)	529.5				5
NiO+K on Ag(100)	529.6	532.2	534.0		6

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