SUPPORTING INFORMATION FOR:

Structure and Reactivity of a Model Oxide Supported Silver Nanocluster Catalyst Studied by Near Ambient Pressure X-ray Photoelectron Spectroscopy

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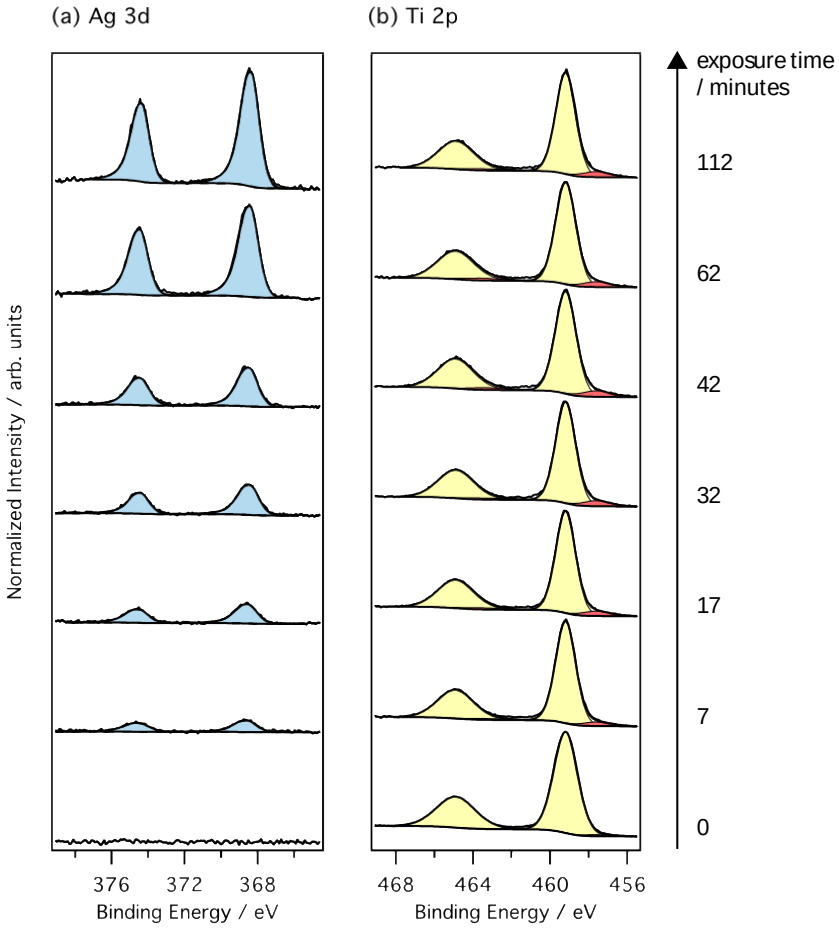
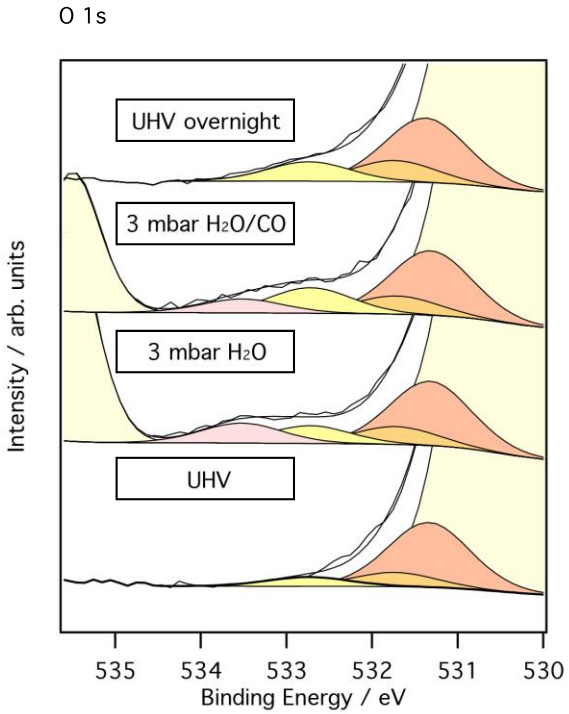
Figure S1. Core level photoelectron spectra for (a) Ag 3d and (b) Ti 2p



Complete set of Ag 3d XPS core-level spectra (a) with the corresponding Ti 2p core-level spectra (b) (*hv* = 1 keV) showing, from bottom to top, an increasing Ag coverage. The spectra are normalized to the intensity of the Ti 2p $Ti^{4+}{}_{3/2}$ peak at 459.2 eV.

Figure S2. Enlarged Core level NAP-XPS spectra for O 1s showing components due to H2O and CO exposure in more detail.



O 1s core- level NAP-XPS spectra recorded at UHV, under exposure to 3 mbar H_2O, under exposure to 3mbar H_2O/CO and at UHV the following day. The O 1s spectra highlight the high binding energy shoulder shown in Figure 4 of the main manuscript for clarity.

The assignment of the fitted peaks for the O 1s, Ti 2p and Ag 3d is given below in Table S1. The gas phase O 1s peaks are not included in the table. These occur at 535.5 eV (H_2O) and 538.2 eV (CO).

Table S1. Binding energy and assignment of Ti 2p, O 1s and Ag 3d XPS core-level peaks.

		UHV		3 mbar H_2O		3 mbar H_2O/CO		UHV-next day	
Species	**Assignment**	**BE / eV ± 0.1 eV**	**% ±1%**	**BE \ eV ± 0.1 eV**	**% ±1 %**	**BE / eV ± 0.1 eV**	**% ±1 %**	**BE \ eV ± 0.1 eV**	**% ±1 %**
Ti $2p_{3/2}$	**Ti^{3+}**	457.7	7.3	457.7	6.3	457.7	6.7	457.7	5.2
	TI^{4+}	459.2	92.7	459.2	93.7	459.2	93.3	459.2	94.8
O 1S	**TIO_2**	530.4	88.0	530.4	84.3	530.4	84.1	530.4	86.2
	$O_{intrinsic}$[1]	531.4	8.8	531.3	8.4	531.3	8.4	531.3	8.6
	O_{defect}/OH_{ads}	531.8	1.9	531.7	2.3	531.7	2.4	531.7	2.6
	$O_{defect}/CO_{ads}/OH_{ads}$	532.7	1.2	532.7	2.0	532.7	3.3	532.7	2.1
	H_2O	-	0	533.5	2.6	533.5	1.8	-	0
Ag $3d_{5/2}$	**$Ag^{\delta+}$/Ag(III)**	-	0	-	-	367.6	5.5	367.6	0
	Ag(0)	368.4	100	368.4	100	368.4	89.0	368.4	100
	$Ag(III)_{satellite}$	-	0	-	0	371.4	5.5	371.4	0

(1) Jackman, M. J.; Thomas, A. G.; Muryn, C. Photoelectron Spectroscopy Study of Stoichiometric and Reduced Anatase TiO_2(101) Surfaces: The Effect of Subsurface Defects on Water Adsorption at Near-Ambient Pressures. *J. Phys. Chem. C* **2015**, *119*, 13682–13690.