# Supporting Information

# Redox-Driven Atomic-Scale Changes in Mixed Catalysts: $VO_X / WO_X / \alpha$ -TiO<sub>2</sub>(110)

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#### I. Sample preparation for mixed VO<sub>X</sub> / WO<sub>X</sub> / α-TiO<sub>2</sub>(110) surfaces

Polished rutile  $\alpha$ -TiO<sub>2</sub>(110) (10 × 10 × 1 mm<sup>3</sup>) single crystal substrates were purchased from Crystal GmbH (Germany). To obtain an atomically flat surface, these substrates were loaded into a tube furnace with flowing O2 (~100 sccm) and annealed at 400 °C for 30 min, then 900 °C for 60 min. Prior to ALD, each substrate was immersed in ultrapure water (resistivity >  $10^{18} \Omega$  cm<sup>-1</sup>) for 60 min at 90 °C to hydroxylate the surface. Substrates were then rinsed with 10% HCl, then ultrapure water, and blown dry with nitrogen. The substrates were heated to 300 °C under ultrahigh-purity nitrogen flow at 360 sccm at a pressure of 1 torr for 1 h, then cleaned in situ with flowing ozone. In the ALD reactor<sup>1</sup>, tungsten oxide was deposited first, followed by vanadium oxide. With the sample temperature at 200 °C, the W ALD process began with 10 min exposure of the substrate to Si<sub>2</sub>H<sub>6</sub> at 10 torr, followed by 10 min exposure to WF<sub>6</sub> at 10 torr. Following each exposure, the reactor was evacuated to below 0.05 torr and subsequently purged with ultrahigh-purity nitrogen for 5 min. The process of exposure to Si<sub>2</sub>H<sub>6</sub>, purging with nitrogen, exposure to WF<sub>6</sub>, and finally purging with nitrogen is defined herein as one W ALD cycle. Similarly, for one V ALD cycle, substrates were exposed first to vanadium oxytriisopropoxide at a partial pressure of 0.05 torr for 2 seconds, followed by a nitrogen purge for 5 seconds. The ALD-coated  $\alpha$ -TiO<sub>2</sub>(110) substrates were then exposed to H<sub>2</sub>O<sub>2</sub> at a partial pressure of 0.2 torr for 2 seconds, followed by a nitrogen purge for 5 seconds. For one set of samples, the substrates were ALD-coated with 2 W cycles, followed by 1 V cycle, and for the other set, the substrates were coated with 1 W cycle and then 2 V cycles. Our previous studies<sup>2</sup> showed that the main contamination from the clean substrate was carbon. The above described ozone cleaning procedure removes this carbon contamination. ALD processes could introduce carbon or fluorine<sup>3</sup> (for W growth) contamination, but such contamination is "burned off" after

the first oxidation during the redox processes<sup>2, 3</sup>, thus not affecting results obtained in our studies here.

## II. AFM, XPS, and XSW of VO<sub>X</sub> / WO<sub>X</sub> / α-TiO<sub>2</sub>(110)

Figure S1 shows AFM images of the surface morphology of  $\alpha$ -TiO<sub>2</sub> (110) after the oxygen annealing treatment, after the ALD growth, and after the redox reactions. Silicon AFM tips with a nominal 10 nm radius of curvature and cantilever resonant frequencies of 200 kHz were used with a JEOL-JSPM-5200 scanning probe microscope at the NIFTI facility of NUANCE at Northwestern University. Fig. S1(c) shows the surface of 0.7 ML vanadia mixed with 1.2 ML tungsten oxide (sub-VW) on  $\alpha$ -TiO<sub>2</sub>(110) after a redox reaction cycle. Nanoparticles are observed on the surface, suggesting that high temperature annealing causes some aggregation of surface oxides. Similar results were observed for the 1.1 ML vanadia on 0.6 ML tungsten oxide (ML-VW) case.



**Figure S1.** Atomic-force microscopy images of the  $TiO_2$  (110) single crystal substrate surface. (a) The blank substrate surface after 2-step annealing shows atomically flat terraces with a 3.3 Å vertical step size. (b) After ALD growth of 0.7 ML vanadia on top of 1.2 ML tungsten oxide (the sub-VW case), the flat atomic terraces can still be observed clearly. (c) The same surface after two redox reaction cycles and blowing  $N_2$  gas across the surface shows that nanoparticles were formed.

XP spectra were collected with an Omicron ESCA probe using monochromated Al K $\alpha$  X-rays. A low-energy electron flood gun was used to compensate photoionization-induced surface charging effects. Adventitious carbon 1s (284.8 eV) was used as the reference to calibrate the XP spectra. The chemical states of V and W in mixed catalysts are determined by the binding energy (BE) of W 4f<sub>7/2</sub><sup>4-6</sup> and V 2p<sub>3/2</sub><sup>7</sup>, and the binding energy difference (BED) of V 2p<sub>3/2</sub> to O 1s.<sup>7</sup> The BED of the W 4f<sub>5/2</sub> and W 4f<sub>7/2</sub> doublet peak is set to be 2.1 eV. Table S1 lists the BE and BED values for V and W.

**Table S1:** Values taken from Refs.<sup>4-7</sup> for the V  $2p_{3/2}$  and W  $4f_{7/2}$  binding energies (BE) and the binding energy differences (BED) of V  $2p_{3/2}$  to O 1s.

Element	<b>V</b> 2p <sub>3/2</sub> <sup>7</sup>			<b>W</b> 4f <sub>7/2</sub> <sup>4-6</sup>		
<b>Chemical states</b>	+5	+4	+3	+6	+5	+4
BE (eV)	517.2	516.3	515.6	35.6	34.5	33.1
BED (eV)	12.9	13.8	14.6			

For X-ray standing wave (XSW) experiments, the incident photon energy was set to 7.00 keV for observing V K XRF and 13.00 keV for W L XRF by the beamline Si (111) high-heat-load monochromator. The beam was conditioned further with either Si (111) or (220) channelcut postmonochromator crystals. (See Refs. <sup>8</sup> and <sup>9</sup> for more details on the XSW experimental setup.) The ALD-coated single crystal substrates were mounted inside a Be dome gas reaction chamber as shown in Figure S2. A Vortex EM silicon drift diode (SDD) detector was used to collect X-ray fluorescence spectra. Tables S2 and S3 list the measured XSW Fourier components  $f_H$  and  $P_H$  for the oxidized (OX), reduced (RD), and re-oxidized (OX2) surfaces of the sub-VW and ML-VW samples, respectively. These model-independent values were determined by fits of the normalized XSW yield equation

$$Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)}f_H \cos(v(\theta) - 2\pi P_H), \quad (S1)$$

where  $R(\theta)$  is the crystal reflectivity, and  $v(\theta)$  is the phase of the reflected X-ray wave. By inserting these measured sets of  $f_H$  and  $P_H$  into Eq. (S2)<sup>10</sup>, an atomic density map can be generated for either V or W at each redox processing step, as shown in Figs. 3 and 4.

$$\rho(\mathbf{r}) = 1 + 2 \sum_{\substack{\mathbf{H}=-\mathbf{H}\\\mathbf{H}\neq 0}} f_H \cos\left[2\pi \left(P_H - \mathbf{H} \cdot \mathbf{r}\right)\right].$$
(S2)

To better understand the V and W distributions and their adsorption heights in the (110) surface normal direction in the OX, RD, and OX2 conditions, a two-site model described in Eq. 1 is used to perform a least-squares fit. Tables S2 and S3 also list the model-predicted values,  $f_{\rm H}^{\rm C}$  and  $P_{\rm H}^{\rm C}$ , for comparison to the XSW measured values.



**Figure S2.** (a) Photograph showing the top view of the beryllium dome reaction chamber mounted on a 5-circle diffractometer at the APS 5ID-C end station. The 0.25 mm thick Be hemisphere has a 25.4 mm radius, a boron-nitride interior and exterior surface coating, and is brazed to a water-cooled stainless-steal flange. Also shown in the lower-half of the picture is the XRF detector snout. (b) Inside the beryllium dome, a  $5 \times 5 \times 1$  mm<sup>3</sup> hematite single crystal sample (rather than rutile TiO<sub>2</sub> as used in the present study) is held by two stainless steel clips to a pyrolytic boron nitride heating plate (Momentive Performance Materials Quartz, Strongsville, Ohio, part no. HTR1001).

**Table S2**: Summary of XSW experimental results from the as deposited (AD), oxidized (OX), reduced (RD), and re-oxidized (OX2) surface treatments of the 0.7 ML  $VO_X / 1.2$  ML  $WO_X / \alpha$ -TiO<sub>2</sub> (110) (sub-VW) sample.  $f_H$  and  $P_H$  are experimentally measured coherent fractions and coherent positions, respectively, and  $f_H^C$  and  $P_H^C$  are least-square determined best fit values. The top part of the table is the summary for V results and the lower part of the table is the summary for W results.

hkl		110	101	200	111	211	210	220	301
V									
AD	$f_H$	0.23(4)							
	$P_H$	-0.07(3)							
OX	$f_H$	0.30(1)	0.46(1)	0.30(6)	0.2(1)	0.31(5)			
	$f_H^C$	0.33	0.44	0.32	0.42	0.21			
	$P_H$	-0.16(1)	-0.05(1)	-0.14(3)	0.28(6)	-0.21(2)			
	$P_H^C$	-0.16	-0.09	-0.16	0.44	-0.16			
RD	$f_H$	0.60(5)	0.42(8)	0.27(6)	0.32(8)	0.36(6)			
	$f_{H}^{C}$	0.45	0.42	0.41	0.27	0.35			
	$P_H$	0.04(2)	0.01(4)	-0.12(3)	0.30(4)	-0.19(3)			
	$P_H^C$	-0.07	-0.03	-0.07	0.40	-0.10			
OX2	$f_H$	0.24(2)	0.43(7)						
	$f_H^C$	0.27	0.37						
	$P_H$	-0.16(1)	-0.12(3)						
	$P_H^C$	-0.14	-0.09						
W									
AD	$f_H$	0.13(1)	0.12(1)	0.06(1)	0.11(2)	0.05(1)			
	$P_H$	0.10(8)	-0.12(8)						
OX	$f_H$	0.30(1)	0.24(1)	0.36(1)					
	$f_H^C$	0.29	0.27	0.24					
	$P_H$	0.02(1)	-0.11(1)	-0.19(1)					
	$P_H^C$	-0.22	-0.11	-0.22					
RD	$f_H$	0.21(1)	0.22(1)	0.32(1)	0.30(2)	0.16(1)	0.16(1)	0.08(2)	0.13(1)
	$f_H^C$	0.30	0.26	0.25	0.12	0.18	0.11	0.17	0.12
	$P_H$	-0.03(1)	-0.09(1)	-0.01(1)	0.28(1)	-0.04(1)	0.68(1)	0.07(4)	0.02(2)
	$P_H^C$	-0.04	-0.02	-0.04	0.45	-0.07	0.43	-0.09	-0.07
OX2	$f_H$	0.25(1)	0.28(1)	0.31(1)	0.16(1)	0.18(1)	0.14(1)	0.09(1)	0.14(1)
	$f_{H}^{C}$	0.29	0.27	0.25	0.14	0.17	0.16	0.15	0.13
	$P_H$	-0.04(1)	-0.15(1)	-0.10(1)	0.39(1)	-0.06(1)	-0.37(1)	-0.15(1)	-0.12(1)
	$P_{H}^{C}$	-0.07	-0.04	-0.07	0.52	-0.10	-0.49	-0.13	-0.10

**Table S3:** Summary of the XSW experimental results from the as deposited (AD), oxidized (OX), reduced (RD), and re-oxidized (OX2) surface treatments of the 1.1 ML  $VO_X / 0.6$  ML  $WO_X / \alpha$ -TiO<sub>2</sub> (110) (ML-VW) sample. The top part of the table is the summary for V results and the lower part of the table is the summary for W results.

hkl		110	101	200	111	211
V						
AD	$f_H$	0.19(5)	0.1(1)			
	$P_H$	0.25(8)				
OX	$f_H$	0.29(4)	0.18(5)	0.27(4)		
	$f_H^C$	0.28	0.23	0.21		
	$P_H$	-0.14(2)	-0.08(4)	-0.22(2)		
	$P_H^C$	-0.18	-0.09	-0.18		
RD	$f_H$	0.53(7)	0.62(9)	0.1(1)	0.7(2)	0.3 (1)
	$f_H^C$	0.45	0.60	0.43	0.47	0.18
	$P_H$	0.01(3)	0.03(3)	-0.1 (3)	-0.28(3)	-0.10(6)
	$P_H^C$	-0.03	-0.02	-0.03	-0.27	-0.06
OX2	$f_H$	0.38(7)	0.39(9)		0.4(2)	0.48(9)
	$f_H^C$	0.45	0.44		0.09	0.40
	$P_H$	-0.1(3)	-0.13(3)		0.02(9)	-0.13(3)
	$P_H^C$	-0.10	-0.05		0.00	-0.16
W						
AD	$f_H$	0.29(1)	0.25(1)	0.21(1)	0.24(1)	0.17(2)
	$P_H$	0.05(4)	0.07(5)	-0.06(3)	0.17(4)	0.05(5)
OX	$f_H$	0.45(1)	0.28(1)	0.43(2)	0.06(2)	0.31(2)
	$f_H^C$	0.41	0.36	0.34	0.06	0.24
	$P_H$	0.04(1)	0.05(1)	0.90(1)	0.45(7)	0.07(1)
	$P_H^C$	0.04	0.02	0.04	0.51	0.06
RD	$f_H$	0.46(1)	0.44(1)	0.54(3)	0.11(3)	0.45(3)
	$f_H^C$	0.45	0.46	0.45	0.08	0.44
	$P_H$	0.03(1)	0.00(1)	0.01(1)	0.38(4)	0.12(1)
	$P_H^C$	0.05	0.02	0.05	0.39	0.07
OX2	$f_H$	0.25(1)	0.26(2)			
	$f_{H}^{C}$	0.25	0.24			
	$P_H$	0.03(1)	0.04(1)			
	$P_H^C$	0.04	0.02			

#### III. XPS and XSW measurement of 1.0 monolayer (ML) W on α-TiO<sub>2</sub>(110)

For pure ML W ALD growth, similar blank rutile ( $\alpha$ -TiO<sub>2</sub>) (110)-terminated single crystals were used. After atomically flat surfaces were produced by O<sub>2</sub> annealing, 2 ALD cycles of W were performed on  $\alpha$ -TiO<sub>2</sub> (110). The W coverage, 1.0 ML, was determined by a side-by-side X-ray fluorescence (XRF) comparison with a standard sample calibrated by Rutherford backscattering.

XP spectra were taken for the sample at the AD, OX, and RD conditions. Fig. S3 shows the XPS analysis of W in each redox processing step. The chemical states of W are determined according to W 4f binding energies.<sup>4-6</sup> No change is observed, indicating that W does not reduce during the redox reaction.



**Figure S3**: W 4f XP spectra of 1.0 ML  $WO_X / \alpha$ -TiO<sub>2</sub> (110) in as-deposited (AD), oxidized (OX), and reduced (RD) states with a 45° electron emission angle. No chemical state change of W is observed.

For the X-ray standing wave (XSW) measurements, the sample was placed on a ceramic heating stage inside a beryllium dome gas reaction cell that was mounted on a four-circle diffractometer at the Advanced Photon Source (APS) 33ID-D station. An incident photon energy

of 13.00 keV was selected with a diamond (111) monochromator, and the beam was conditioned further with either Si (111) or (220) channel-cut postmonochromator crystals. A Vortex EM silicon drift diode (SDD) detector was used to collect X-ray fluorescence spectra at each angle position of each scan through each *hkl* Bragg reflection. The OX and RD surface conditions were achieved by annealing at 400 °C for 30 min in O<sub>2</sub> and 2% H<sub>2</sub> in helium at 760 Torr, respectively. Fig. S4 shows the XSW data for seven different (*hkl*) planes. Table S4 lists a set of measured  $f_H$ and  $P_H$  values derived from data shown in Fig. S4 when the surface is at the RD condition. The same sets of  $f_H$  and  $P_H$  values were obtained for the OX and 2<sup>nd</sup> oxidized (OX2) condition. These values match reasonably well for the surface at OX, RD and OX2 conditions, indicating that W is very stable in the redox reaction and has no structural change.



**Figure S4**: In situ XSW scans and fits for the 1.0 ML  $WO_X / \alpha$ -TiO<sub>2</sub>(110) surface in the reduced (RD) condition from seven different hkl TiO<sub>2</sub> Bragg reflections: (110), (101), (111), (220), (200), (211) and (210). Each frame shows the relative incident-angle dependence of the experimental X-ray reflectivity (open circles) and W L $\beta$ XRF yield (open squares). The solid lines correspond to dynamical diffraction theory-based fits of Eq. (S1) to the data. <sup>8, 11, 12</sup>

Of the seven hkl Fourier components measured for 1.0 ML W /  $\alpha$ -TiO<sub>2</sub>(110), only the h+k+l=2n+1 (111) and (210) are sensitive to the lateral positional differences between the atop (AT) and bridging (BR) sites. The small Fourier amplitude measured for each of these two reflections ( $f_H < 0.1$ ) implies that the occupation and displacement are essentially identical between these sites. When the Fourier components of either the (111) or (210) reflections are included along with the other five reflections in a least-squares global fit of the occupations and vertical displacements based on Eq. 1, qualitatively different results emerge. We conclude that the amplitudes corresponding to the (111) and (210) reflections are too small to indicate any difference in occupancy or vertical displacement between the two sites and that the corresponding measured coherent positions are likely erroneous. In light of this, we use a leastsquares global fit based on an equivalent two-site model with the constraint that  $c_{AT} = c_{BR}$  and  $z_{AT} = z_{BR}$  in Eq. 1. XSW Fourier components from only the (110), (101), (200), (211), and (220) reflections are included as being nonzero in amplitude. The results from this 1.0 ML W case are given in Table S5 along with previously published data for 0.38 ML WO<sub>x</sub>/ $\alpha$ -TiO<sub>2</sub>(110).<sup>6</sup> From these values, the model-dependent Fourier components ( $f_H^C$ ,  $P_H^C$ ) are back-calculated and shown to agree well with the experimental measurements (Table S4). The bridging and atop W atoms sit about 0.10 Å above the bulk-like sites. While the 0.38 ML W case also shows equal occupancy between the two sites, there is a significant vertical displacement (0.35 Å) of the bridging W atoms from the bulk-like rutile sites. Note that in the 0.38 ML case,  $f_{111} = 0.23$ , indicating significant differences between the two sites.<sup>6</sup> XSW therefore reveals coverage-dependent effects for the atomic arrangement of W on this model catalyst surface.

**Table S4:** XSW measured hkl Fourier amplitudes,  $f_H$ , and phases,  $P_H$ , for 1.0 ML  $WO_X/\alpha$ -TiO<sub>2</sub>(110) in the reduced condition. The calculated values  $f_H^C$  and  $P_H^C$  are determined from the best fit of an equivalent two-site model similar to the one described in Eq. 1 with values taken from Table S5. The (111) and (210) Fourier amplitudes are set to zero in the fit. Values are similar for the oxidized states, indicating no measurable structural changes through the redox cycle.

hkl	110	101	200	111	211	210	220
$f_H$	0.42(1)	0.45(2)	0.39(2)	0.07(3)	0.32(2)	0.06(2)	0.36(1)
$f_H^C$	0.43	0.41	0.40	0	0.36	0	0.35
$P_H$	0.10(1)	0.02(1)	0.02(1)	0.15(6)	0.04(1)	0.61(7)	0.04(1)
$P_H^C$	0.03	0.02	0.03		0.05		0.06

**Table S5:** Least-squares fit model parameters determined from XSW data and Eq. 1 for the W occupation fractions,  $c_X$ , and heights,  $z_X$ , above the bulk TiO (110) plane for 1.0 ML and 0.38 ML<sup>6</sup> WO<sub>X</sub> /  $\alpha$ -TiO<sub>2</sub> (110), respectively. For comparison, Ti in bulk  $\alpha$ -TiO<sub>2</sub> has  $z_{BR} = z_{AT} = 3.25$  Å. The W correlated fraction ( $\Sigma c = c_{BR} + c_{AT}$ ) is also listed.

W cov.	C <sub>BR</sub>	<i>c</i> <sub>AT</sub>	Σc	<i>z</i> <sub>BR</sub> (Å)	<i>z</i> <sub>AT</sub> (Å)	$\sigma(\text{\AA})$
1.0 ML	0.23(1)	0.23(1)	0.46(2)	3.35(1)	3.35(1)	0.18(2)
0.38 ML	0.36(7)	0.38(8)	0.74(9)	3.60(8)	3.28(8)	0.22(4)

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