Supporting Information

Atomic-Scale Cation Dynamics in Monolayer $VO_X/\alpha\text{-}Fe_2O_3$ Catalyst

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Supplementary Methods

Calculation of VO_X coverage.

From BET analysis, the substrate surface area is 6 m^2/g and the weight gain after atomic layer deposition (ALD) is ~ 0.7%. Since 1 monolayer (ML) is defined as 10 V atoms/nm^2, assuming there is 1 g of α-Fe_2O_3 and using 51 g/mol as the V molar mass as well as the Avogadro's constant 6.023×10^{23}, the coverage is given:

$$\frac{(1\times0.7\%/51)\times6.023\times10^{23}}{1\times6}=1.4\times10^{19}\ \text{atoms/m2} = 14\ \text{atoms/nm2} = 1.4\ \text{ML} \qquad \text{(S1)}$$

Determination of the V^{4+}/V^{5+} ratio in the OX VO_X/hematite.

A linear combination fit (Figure S1a) to the oxidized (OX) X-ray absorption near edge spectroscopy (XANES) using that of VO_2 and V_2O_5 gives a rough estimate of 10% V^{4+}. By further assuming two Lorentzian functions for the prepeak shapes of V^{4+} and V^{5+} plus a step function, the pre-edge peak shape of OX is nicely reproduced (Figure S1b), from which V^{4+} is estimated to be *ca*. 6%.

Analysis of V_2O_5 Reference.

The first peaks in EXAFS (Figure 2) appear at remarkably small distances. Careful comparison to the bulk spectra shows that the small peaks around 1 Å are part of the first neighbor EXAFS signals. With this peak included, the V_2O_5 spectrum can be well fit (Figure S) by the orthorhombic V_2O_5 bulk structure with one V-O bond of 1.59 Å and four weight-averaged V-O bonds of 1.85 Å, matching the V-O bond values for bulk V_2O_5. This gives the amplitude reduction factor, S_0^2=0.65.

Analysis and Determination of the second shell intera.

Extended X-ray absorption fine structure (EXAFS) analysis of the interaction at larger distances is not trivial. For V_2O_5, the peak near 3.0 Å (Figure 2), *i.e.*, the second shell, can be well fitted by the V•••V interaction centered at 3.08 Å only after the exhausting search. Therefore, automatic (black box) fitting starting off crystalline structures is proven fruitless. Careful examination of the phases $\sin(2rk+\varphi)$ and amplitudes $f(k)$, which carry chemical information, can provide important insights. Figure S4 compares $2rk+\varphi$ and $f(k)\sin(2rk+\varphi)$ extracted from the V K-edge EXAFS spectra of VO_2, V_2O_5, OX, and RE as well as those of the Fe•••Fe interaction extracted from the Fe K-edge EXAFS from the α-Fe_2O_3 substrate. It is interesting to see the similarity of the phase shapes of the RE and Fe of α-Fe_2O_3. However, the phase of the OX is better aligned with that of VO_2 and V_2O_5. Figure S5 compares the EXAFS oscillations from the second shells, further supporting the conclusion from Figure S4. Therefore, the analyses of the second shells in the OX and the RE was included a V•••Fe interaction. This analysis works nicely for the RE, which is consistent with more coordinated V-O local structure after reduction. Under the reducing condition, V can only get more oxygen by bonding to the oxygen from the substrate and therefore, the V•••Fe interaction becomes pronounced in the EXAFS data. However, this did not work so well for the OX, which could be due to the heavy mixture of V•••V and V•••Fe interactions.

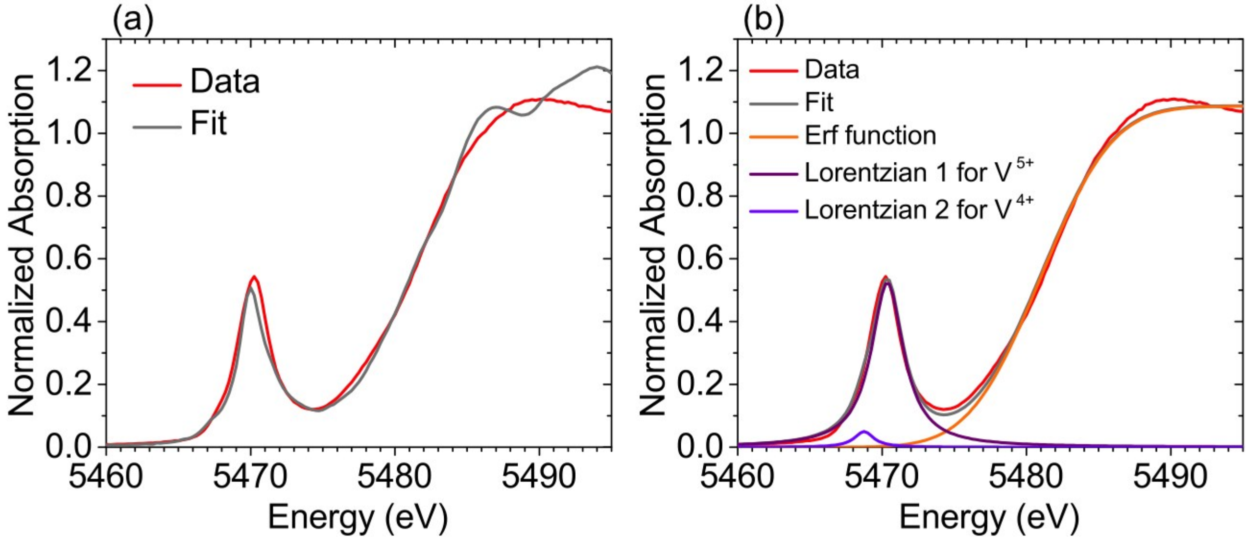

Figure S1. (a) Linear combination fit of the OX XANES spectrum using the XANES data of references VO_2 and V_2O_5, suggesting ca. 10% V^{4+}. (b) Fit of the OX XANES by assuming the Lorentzian core for V^{4+} and V^{5+} plus an erf function. This gives a ca. 6% V^{4+}.

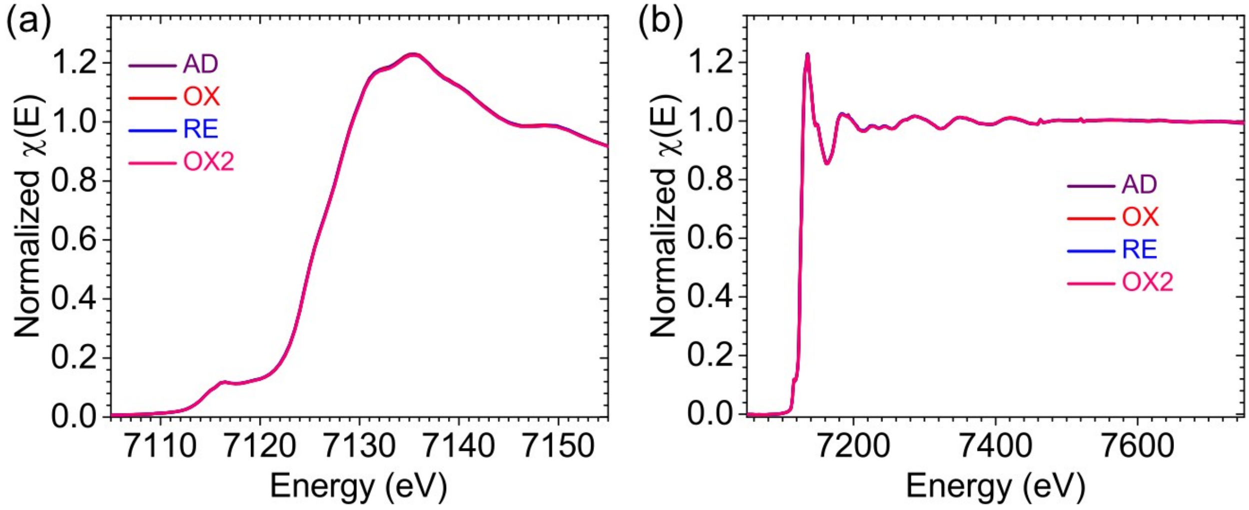

Figure S2. Fe K edge (a) XANES and (b) EXAFS spectra of VO_X/α-Fe_2O_3 at as-deposited (AD), oxidized (OX), reduced (RE) and re-oxidized (OX2) conditions. No change has been observed.

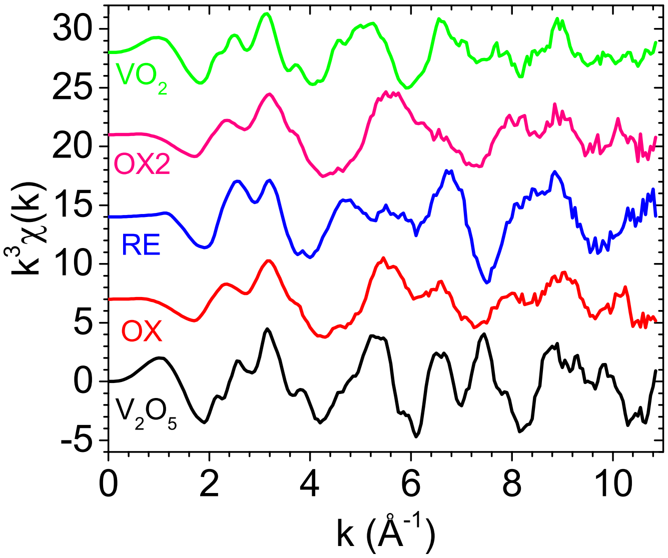

Figure S3. The data for vanadium K-edge EXAFS spectra in k space for V_2O_5 (black) and VO_2 (green) reference powders, and VO_X/α-Fe_2O_3 in oxidized (OX, red), reduced (RE, blue) and re-oxidized (OX2, pink) conditions. Clearly OX is quite different from RE, but has some similarity to OX2.

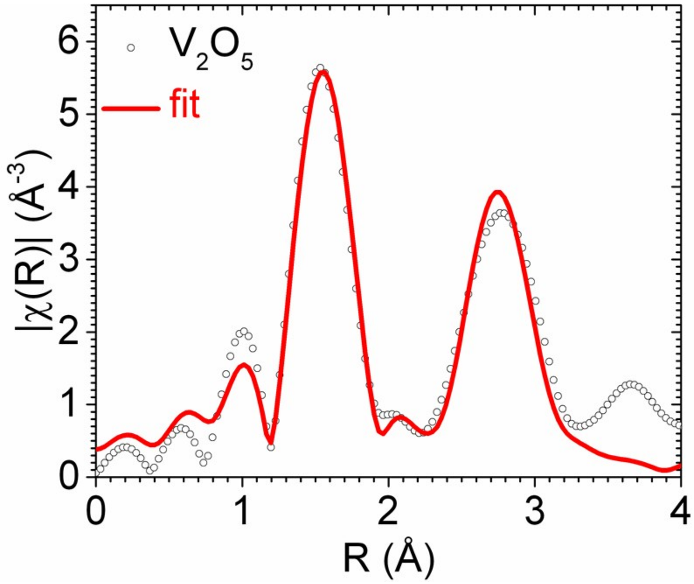

Figure S4. The EXAFS data and fit for V_2O_5 reference.

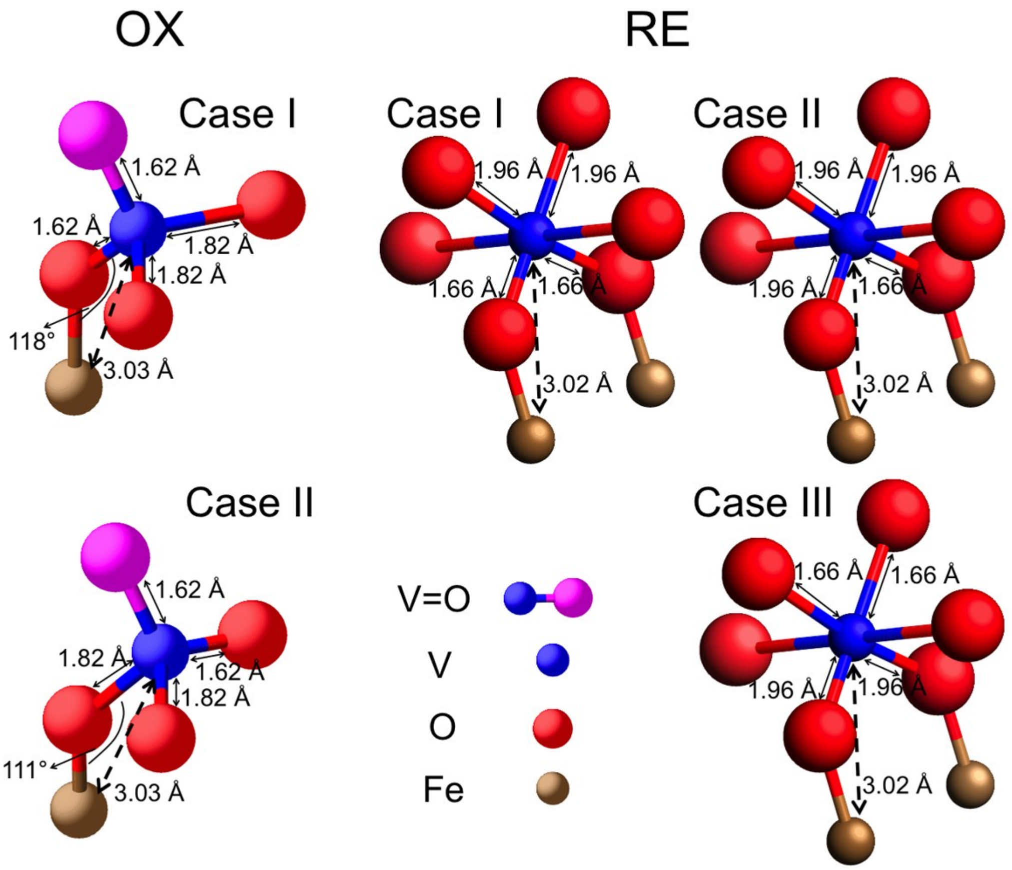

Figure S5. The bond lengths and assignments for oxidized (OX) and reduced (RE) VO_X samples supported on α-Fe_2O_3 hematite powder. For a VO_4 tetrahedral unit in OX, the V=O bond and one V-O bond in either V-O-Fe (case I) or V-O-V (case II) are 1.62 Å, the rest V-O bonds in either V-O-V or V-O-Fe are 1.82 Å, and V•••Fe is 3.03 Å. The angle of V-O-Fe is calculated to be 118° based on the 1.62 Å of V-O bond and 1.91 Å of Fe-O bond in α-Fe_2O_3. For a VO_6 octahedral unit in RE, V•••Fe is 3.02 Å but there are three different cases for V-O bond assignments.

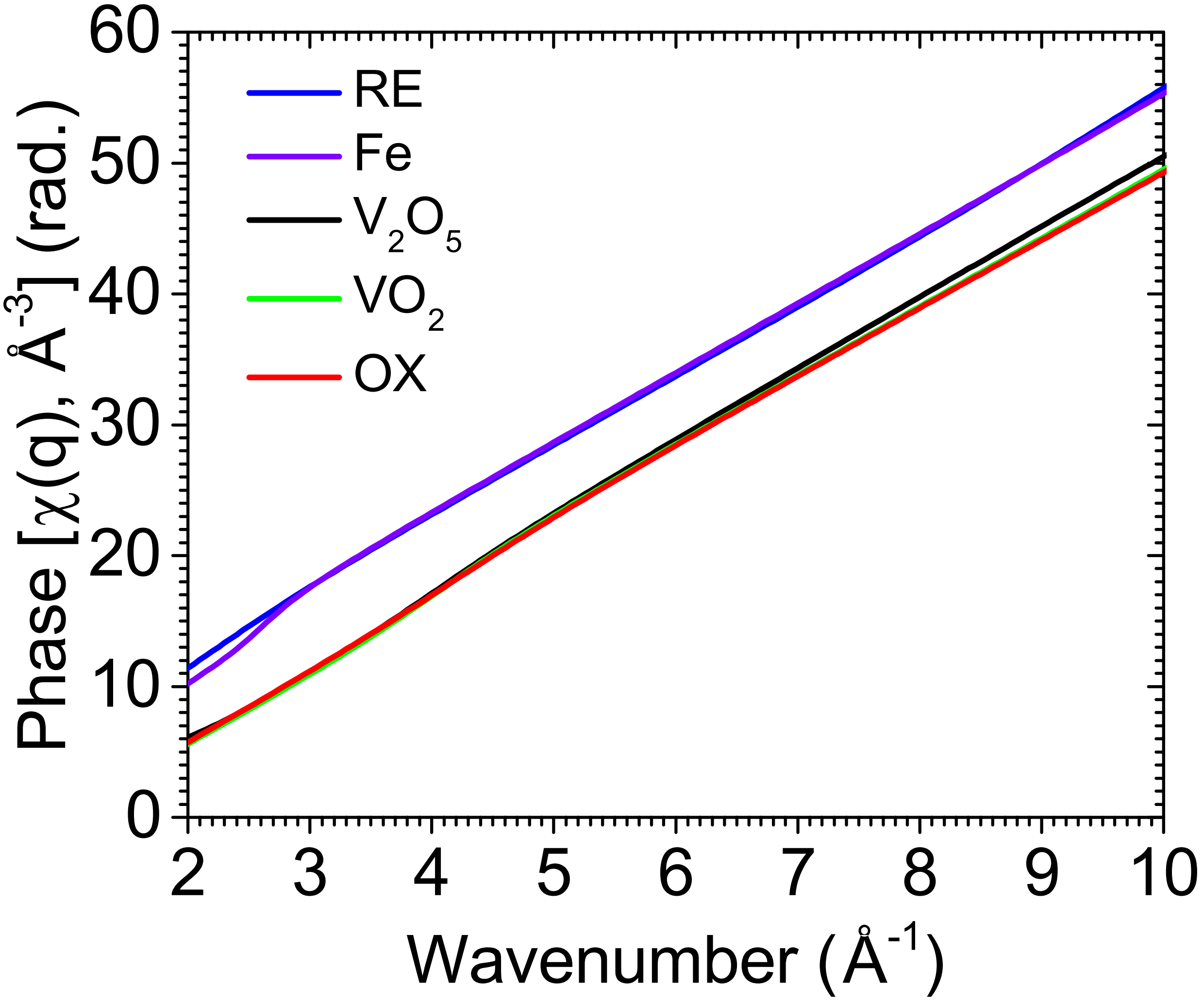

Figure S6. The EXAFS phases extracted from the second peaks in Figure 2 for V_2O_5, VO_2, OX, Re and Fe from the substrate hematite α-Fe_2O_3. The data are vertically displaced for clarity. The phases of RE and Fe in α-Fe_2O_3 compares quite well, while the phase of OX is better aligned with that of VO_2 and V_2O_5.

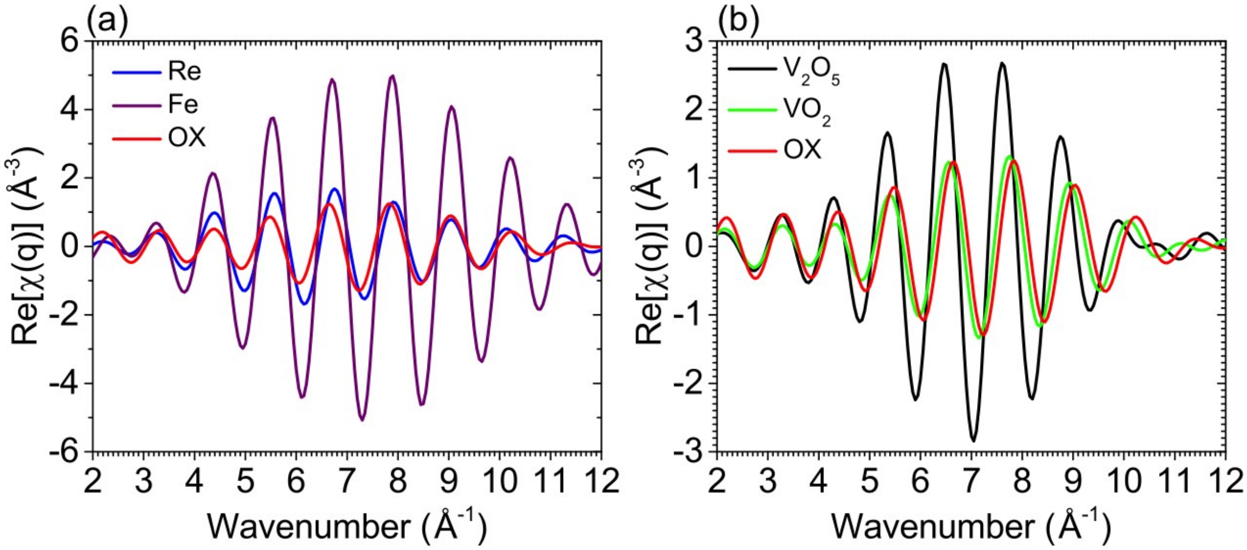

Figure S7. Comparison of the second shell EXAFS oscillations of (a) the Fe-Fe interaction measured from the hematite substrate at the Fe K edge, obtained by the inverse Fourier transforms. This illustrates further the likelihood of the sample containing more V•••Fe interaction after reduction. Clearly, the EXAFS of the OX is out of phase. (b) Comparison of the second shell EXAFS oscillations of the OX to those extracted from the VO_2 and V_2O_5 EXAFS data by the inverse Fourier transforms. The differences are seemingly due only to the differences in the distances.

Reference:

(1) Keller, D. E.; Koningsberger, D. C.; Weckhuysen, B. M. *Journal of Physical Chemistry B* **2006**, *110*, 14313.