Supplementary Information

Atomic Structure and Special Reactivity Toward Methanol Oxidation of Vanadia Nanoclusters on TiO_2(110)

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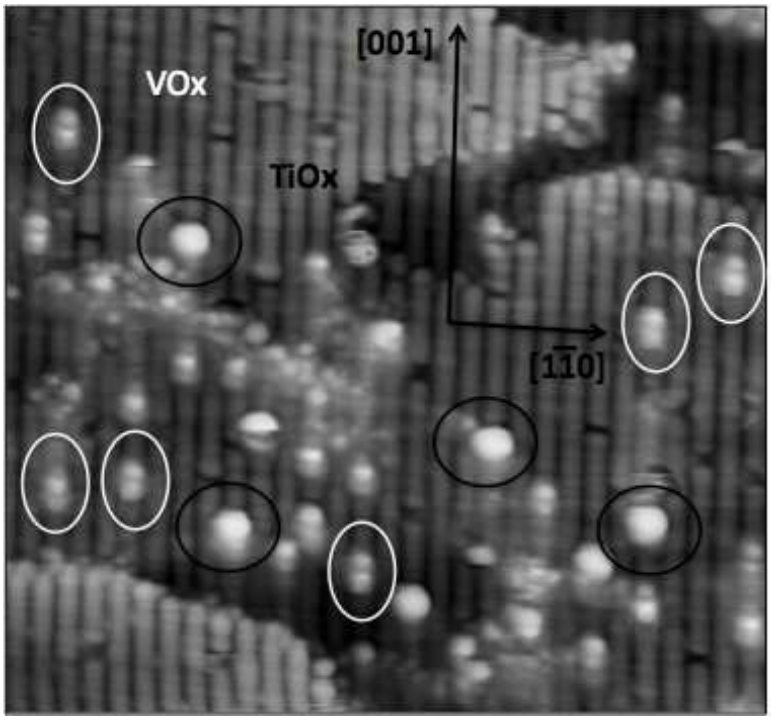

Figure S1. STM image (20 nm x 20 nm 1.9 V, 0.63 nA) of the VO_x(0.3 ML)/TiO_2(110) system. White circles correspond to VO_x NCs growing aligned with the substrate [001] crystallographic direction, black circles correspond to TiO_2 metastable structures formed during O_2 exposure.

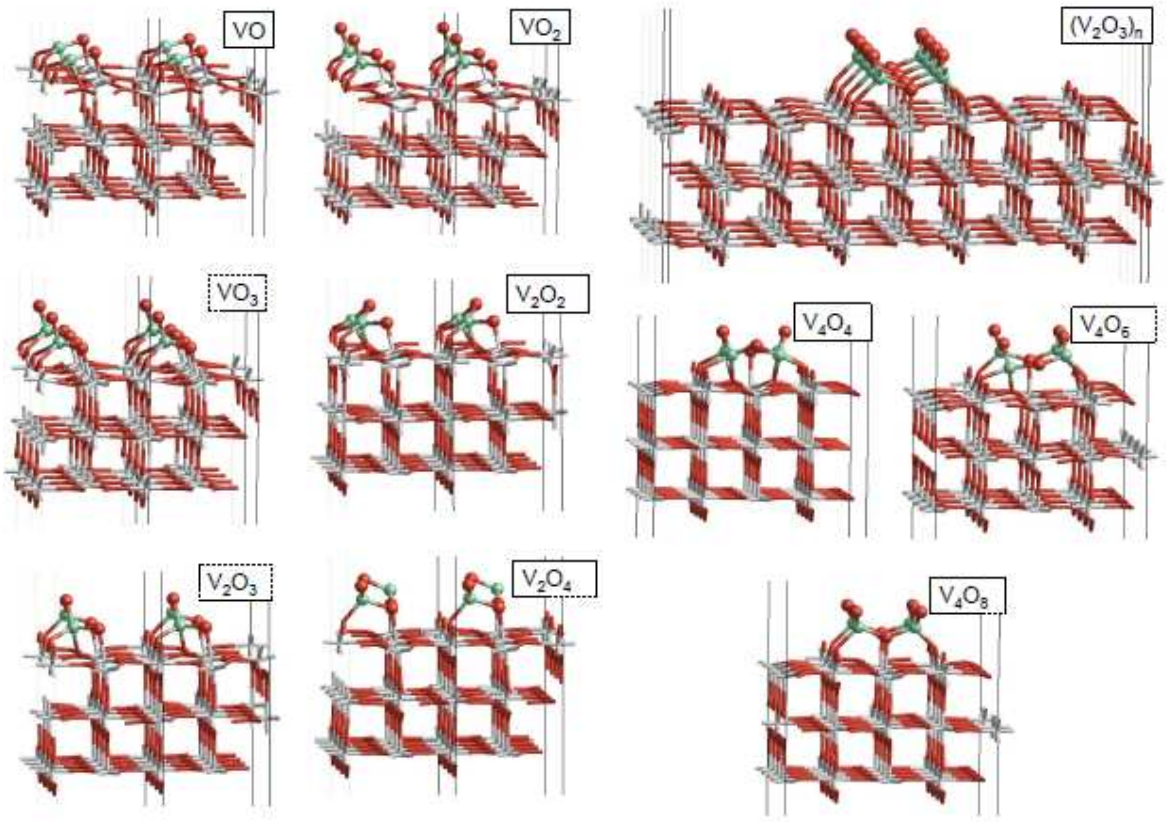

Figure S2. Sketches of the structures for the most stable supported clusters for each stoichiometry and size, as determined by the DFT-GGA calculations.

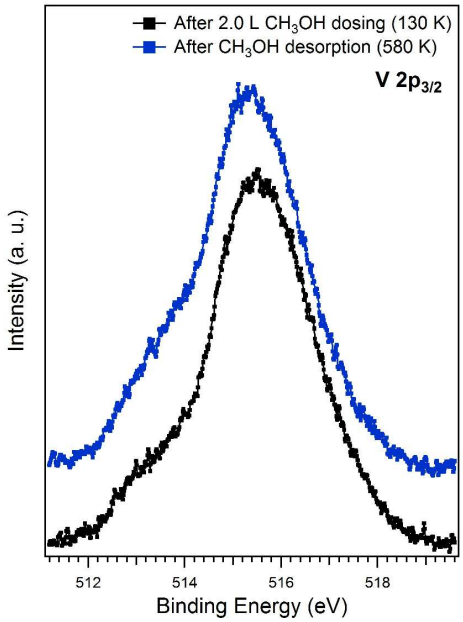

Figure S3. V 2p XPS peaks collected immediately after a 2.0 L CH_3OH dosing on VO_x(0.3 ML)/TiO_2(110) at 130 K (black curve) and after the complete CH_3OH desorption at 580 K (blue curve)

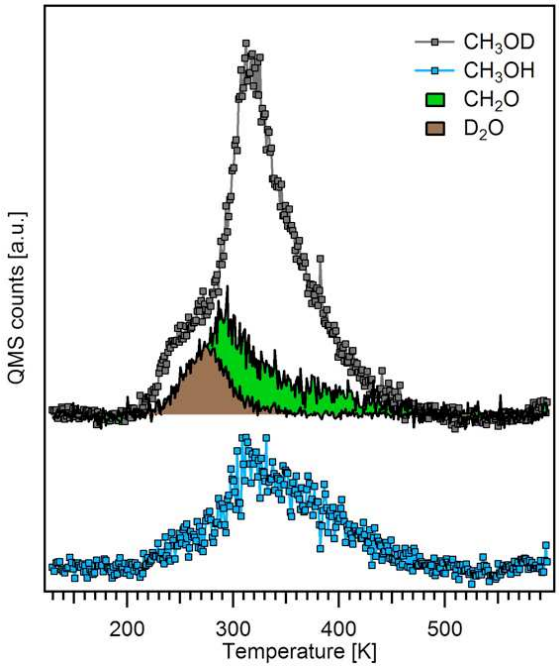

Figure S4. TPD data showing methanol, formaldehyde and labeled water (D_2O) desorption peaks after a 2.0 L methanol dosing at LT on a clean TiO_2(110) substrate prepared by annealing in po_2=5.0*10^{-8} mbar at 473 K. All peaks result to be shifted to lower temperature than those obtained from VO_x NCs (Figure 3a): methanol at 310 K, formaldehyde at 290 K and D_2O at 275 K. A conversion yield of about 15% with respect to MODH reaction has been calculated based on all the desorbed carbon containing species.

S5 Computational Details

Density functional calculations were performed using both the generalized gradient approximation (GGA) and the so-called GGA + *U* approach. In both cases, the Perdew-Burke-Ernzerhof (PBE)[1] exchange-correlation functional was adopted. In the DFT + *U* calculations, U = 3 was adopted for both Ti and V atoms. The interaction between the valence electrons and the ion cores was modelled by means of ultrasoft pseudopotentials.[2] To increase the accuracy of the calculations, small cores were used, including 1s electrons for O, and 1s and 2p electrons for Ti and V. The smooth part of the wave function was expanded in plane waves, with a kinetic energy cutoff of 25 Ry, while the cutoff for the augmented electron density charge was 200 Ry. Slab models typically included 3 TiO_2 layers. V_yO_x species were placed only on the top surface, whereas the bottom three atomic layers kept frozen throughout all the calculations. The theoretical (PBE) lattice constants were adopted for the substrate.[3] This setup was tested in previous work on VO_x layers on TiO_2(anatase).[4,5] The Brillouin zone (BZ) of 1x2 supercells was sampled with 4x4 Monkhorst-Pack grids of points, whereas equivalent grids were adopted for larger supercells.

(1) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(2) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
(3) Lazzeri, M.; Vittadini, A.; Selloni, A. *Phys Rev B* **2001**, *63*, 155409.
(4) Vittadini, A.; Selloni, A. *J. Phys. Chem. B* **2004**, *108*, 7337.
(5) Vittadini, A.; Casarin, M.; Sambi, M.; Selloni, A. *J. Phys. Chem. B* **2005**, *109*, 21766.