UC Santa Barbara
UC Santa Barbara Previously Published Works

Title
Structure of V2O5·nH2O Xerogels

Authors
Kristoffersen, Henrik H
Metiu, Horia

Peer reviewed

Structure of $V_2O_5 \cdot nH_2O$ Xerogels

Henrik H. Kristoffersen, and Horia Metiu*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, United States

*E-mail: metiu@chem.ucsb.edu, Phone: (805) 893-2256

Keywords

Abstract

Vanadium oxide is a layered compound that forms $V_2O_5 \cdot nH_2O$ xerogel when intercalated by water. The xerogel consists of V_2O_5 bilayers with water between them. The structure of each V_2O_5 layer in the bilayer is close to the structure of a single layer in bulk V_2O_5. However, the distance between the two layers in the bilayer is much smaller than the distance between single layers in the bulk. The xerogel is a Brønsted acid that has been used as an acid catalyst and whose protons are mobile and can be exchanged with other cations. Here we use density functional theory to examine five possible models for the structure of the xerogel. In the model that has the properties established by experiments, the vanadyl groups in the two layers point towards the outside of the bilayer, while in the bulk V_2O_5 they point towards the space between layers. This change in the vanadyl positions allows the two layers to get unusually close to each other. This structure is unstable in the absence of water. Water stabilizes it by reacting with bilayers to form two H_3O^+ ions and one oxygen atom that bridges two vanadium atoms. It is this reaction that confers acidity to the gel.

1. Introduction

V_2O_5 is a widely used catalyst in both industrial[1-3] and academic research[4-6] and has been studied as a possible battery material.[7] Bulk V_2O_5 consists of layers perpendicular to the [001]-crystallographic direction, held together by van der Waals interactions (Figure 1(a)).[8] The bulk structure suggests that it should be possible to find ions or molecules that will intercalate between the V_2O_5 layers and separate them to create thin free-standing two-dimensional systems, such as V_2O_5 double-layers (Figure 1(b)) or V_2O_5 monolayers (Figure 1(c)).

There have been many attempts to create a material consisting of V_2O_5 monolayers by using a variety of exfoliation agents designed to intercalate between the layers and pry them apart.[9] So far, the attempts have resulted in the formation of V_2O_5 gels with the V_2O_5 units in a bilayer structure (Figure 1(d)).[10-13] When water is the only intercalant, the gels are characterized as $V_2O_5 \cdot nH_2O$ xerogels.[14] The properties of $V_2O_5 \cdot nH_2O$ xerogels are described below.

(**1**) X-ray diffraction (XRD) measurements have shown that $V_2O_5 \cdot nH_2O$ xerogels consist of V_2O_5 bilayers (two layers, each having the V_2O_5 stoichiometry) separated by water layers.[15-17] The interpretation of XRD and X-ray absorption fine structure experiments [18-20] indicates that the V-V distance (in the [001] direction) for vanadium atoms located *in different oxide layers of the same bilayer* is ~2.9 Å, which is much shorter than the V-V distance in two layers of bulk α-V_2O_5 (which is 4.4 Å [21]). This makes the bilayer remarkably and unexpectedly thin. The structure of the oxide in the planes forming the bilayer is roughly the same as that of the planes of bulk α-V_2O_5. The formation of such a thin bilayer is possible only if the vanadyl oxygens are õflippedö so that all of them point towards the outside of the bilayer (Figure 1(d)). Our calculations show that, in the absence of water, such bilayer structure has higher energy (0.07 eV per V_2O_5) than the double-layer structure cut from the bulk (Figure 1(b)).
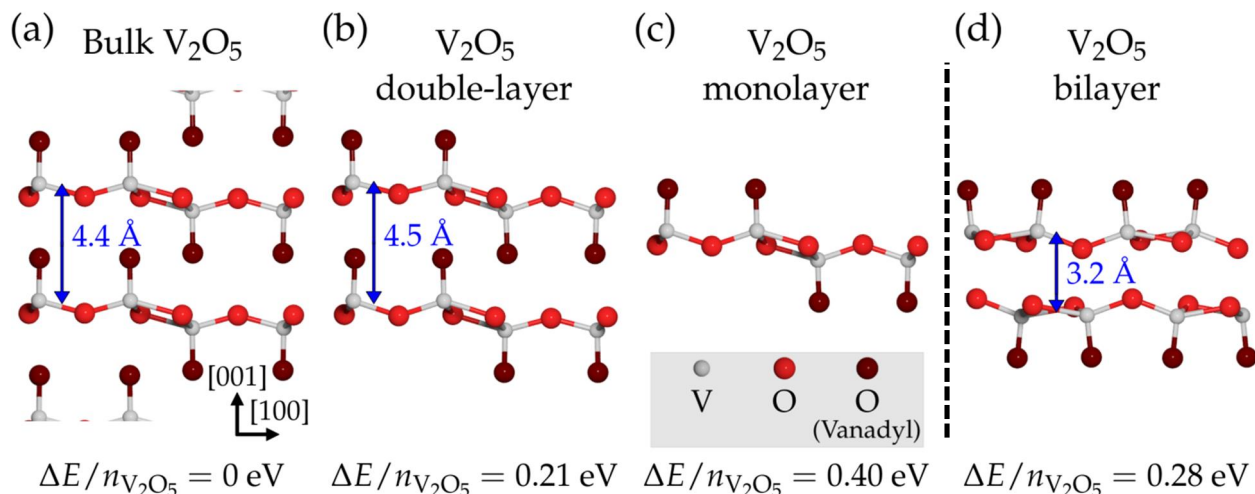
Figure 1. (a) Structure of bulk V_2O_5 viewed to make the layer structure evident. (b) Structure of an isolated double-layer (two layers cut from the bulk and allowed to relax). (c) Structure of an isolated monolayer. (d) Possible structure for the bilayer observed in the gel, but in the absence of water. Note that the vanadyls are õinvertedö. The energy cost of forming the structures (b, c and d) from bulk V_2O_5 are given in the figures (all expressed in eV per V_2O_5).

(2) V_2O_5 gels have been created by using a large number of intercalation/exfoliation agents such as ions,[22] molecules, or polymers.[11-13] The same gel can be prepared with water as the only intercalating molecules, by pouring molten V_2O_5 into deionized water and waiting for several days.[17, 23] Experiments have shown that regardless of the intercalation agent used, the structure of the bilayer is the same.[10, 13] Moreover, adding intercalation solution to a gel only increases the distance between the bilayers without affecting the bilayer structure.

(3) We are not aware of any experiment in which a V_2O_5 gel has been created in the absence of water. This suggests that water plays a fundamental role in stabilizing the thin bilayers proposed by the interpretation of the XRD measurements. Thermogravimetric experiments[14] show that there are two kinds of water in the V_2O_5ÉnH_2O xerogels. One leaves the gel at ~120 °C, in an amount that depends on the partial pressure of water in the environment,[24] suggesting that this is in equilibrium with the water vapor. It is very likely that this water originates from the water

3

situated between the bilayers. Some water is lost at ~ 250 °C and we assume that this is water that was bonded to the vanadium oxide in the gel. At 350 °C the gel has lost all water and is converted to crystalline V_2O_5. The results of the thermogravimetric measurements were expressed concisely[14] by the equation

$$V_2O_5 \bullet 1.8H_2O \xrightarrow{120\,°C} V_2O_5 \bullet 0.5H_2O \xrightarrow{250\,°C} V_2O_5 \qquad (1)$$
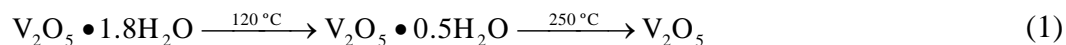
which gives the number of water molecules in the gel per V_2O_5 group. The value of 1.8 can be varied by changing the water vapor pressure.[24] The value of 0.5 water per V_2O_5, present up to a temperature of 250 °C, is independent of the vapor pressure of water.

(4) The V_2O_5 gel is a Brønsted acid[25] and it can be used as an acid catalyst.[26] Solvated protons (H_3O^+) have been measured with IR spectroscopy, the proton conductivity is fairly high, and the protons can be exchanged with other ions.[22] The ion-exchange experiments showed that the gel can release 0.3 H_3O^+ per V_2O_5 group.

In this paper we propose a bilayer model (called õproposed modelö in what follows) that is consistent with the experimental results listed above: it has the correct water-to-vanadium ratio, it has the required short distance between the V atoms in the bilayer, the vanadyl oxygens are õflippedö towards the outside of the bilayer, and one water molecule (in the unit supercell) reacts with V_2O_5 to produce two protons and an oxygen atom bonded to two vanadium atoms of the bilayer. We have examined four additional structures based on suggestions made in the literature and on variations of the model suggested above, and found that they do not have all the properties required for a correct model or have higher energy than the model we propose.

2. Methodology

We studied several models for V_2O_5É1.75H_2O xerogel by use of DFT calculations performed with the Vienna Ab-initio Simulation Package (VASP).[27-30] Exchange-correlation is approximated by the PBE functional[31-32] and a 3 eV DFT+U correction is applied to vanadium *d*-

states.[33] The DFT-D2 correction by Grimme is included to better describe the van der Waals interactions.[34] The calculations used the PAW method and treated explicitly 11 electrons for vanadium, six for oxygen and one for hydrogen.

Every gel model discussed here contains the same number of atoms in the computational cells, namely 8 V_2O_5 units and 14 H_2O molecules. The 8 V_2O_5 units match ($a \times 2b \times c$) bilayer[17] V_2O_5 or ($a \times 2b \times 2c$) bulk[21] -V_2O_5. In both cases, c is perpendicular to the layers. The use of the supercell with $2b$ allows water to have more binding sites to the oxide layers. The stability of the xerogel models are assessed by calculating the energy of the models minus the energy of the proposed model (ΔE_{tot}) (for one computational cell). We also calculate the average water adsorption energy ($\langle E_{ad}(H_2O)\rangle$) compared to bulk -$V_2O_5(s)$ and $H_2O(g)$ (eq 2).

$$\langle E_{ad}(H_2O)\rangle = \left(E_{ad}(8V_2O_5 \bullet 14H_2O - 8E(-V_2O_5(s)) - 14E(H_2O(g))\right)/14 \qquad (2)$$

The intercalated water molecules can take a variety of positions, which means that the system will have many local minima. We cannot explore all of them, and to choose relevant water configurations we use *ab initio*, constant temperature, Nosé-Hoover molecular dynamics. We start the molecular dynamics simulation with the system at 600 K and lower the temperature gradually to 250 K. The time step in this calculation is 1 femtosecond and the total time is 10 picoseconds. The energy of the last structure in the simulated annealing is minimized by varying the atomic position and the supercell vectors. This process is repeated five times for each model starting from the relaxed structure of the previous annealing run. The most stable structure generated by such five runs is presented in this paper. The simulated annealing calculations used a plane wave basis with 350 eV energy cutoff, ($1 \times 2 \times 1$) k-points and a spin-paired electronic structure. The structure optimization is performed with 600 eV energy cutoff, ($2 \times 4 \times 2$) k-points and spin polarization. The spin-polarized calculations retain the spin-paired electronic structure. This is expected when there are no oxygen vacancies in the V_2O_5·nH_2O xerogel.[35-36]
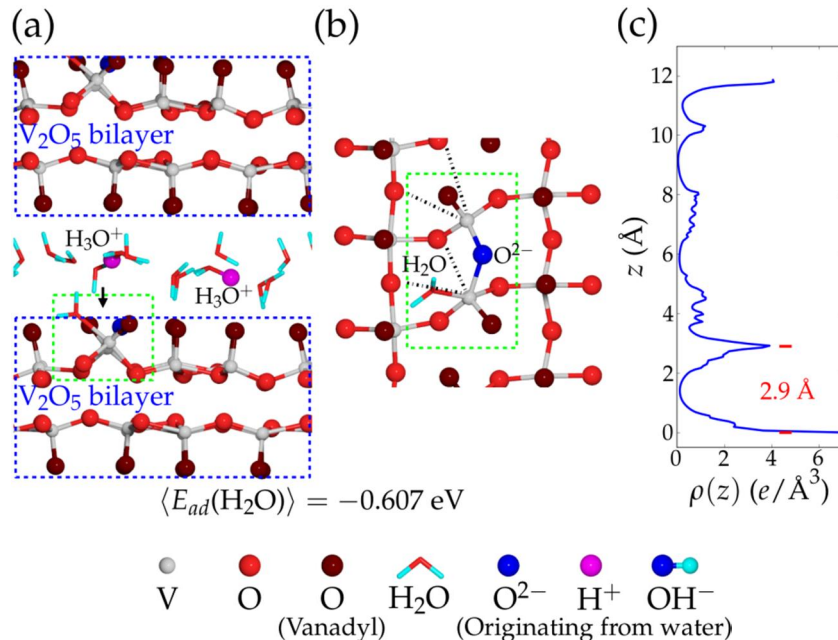
Figure 2. Structure and electron density of the proposed model. **(a)** Side view of two V_2O_5 bilayers (marked by blue dashed rectangles) with 10 H_2O molecules and 2 H_3O^+ (purple hydrogen) in the space between them. Two water molecules have reacted with the oxide to create one molecularly adsorbed H_2O and one adsorbed O atom (blue). The O atom bridges two V atoms. This frees two H atoms that have become the 2 H_3O^+ (purple) in the water layer. The black arrow indicates the view direction in (b) and the green rectangle indicates the atoms shown in (b). **(b)** Top views of the site where the O atom (O^{2-}) from water bridges two V atoms. One water molecule binds to one of the V atoms involved in the bridge such that this V atom obtains a square pyramidal configuration, while the other V atom obtains a tetrahedral configuration. The V-O bonds broken by adsorption are marked with black dashed-dotted lines. **(c)** Total electron charge density ($\rho(z)$) plotted as a function of z. The plot shows that V atoms in the bilayer are separated by 2.9 Å.

3. Proposed gel model

We have studied five structural models and the results of these calculations are reported in Table 1. Based on these calculations we decided that the model called "proposed model" in the table is most likely to represent the structure of V_2O_5·$n$$H_2O$ xerogel. The structure of the proposed model is shown in Figure 2. In the Supporting Information this figure is given in a format that allows it to be rotated for a view from different directions (Figure S1). In all figures

in this paper, vanadium atoms are gray, the oxygen atoms that do not belong to a vanadyl group are red, the oxygen atoms in the vanadyl groups are brown, and the water molecules are shown schematically by angled red and cyan lines. In all structural figures we display two bilayers and the water-filled space between them. In Figure 2(a) the V_2O_5 bilayers are marked by blue dashed rectangles. One can see that these are similar to the õinvertedö bilayer shown in Figure 1(d), while they are substantially different from the double-layer cut from bulk V_2O_5 (Figure 1(b)). In the absence of water, the inverted bilayer (Figure 1(d)) has higher energy than the double-layer (Figure 1(b)). However, the inverted bilayer shown in Figure 2(a) is stabilized by reactions between water molecules and the oxide. The mean adsorption energy per water molecule is ó0.607 eV. One of the water molecules reacts with the V_2O_5 to create two H_3O^+ ions (shown in purple in Figure 2(a)) located in the space between the bilayers, and an oxygen atom (blue in Figure 2(a,b)) that bridges two vanadium atoms and has the formal charge O^{2-} (Figure 2(b)). The oxygen atom provided by the decomposition of water pulls two vanadium atom out of the position they had prior to the reaction with water; the V-O bonds broken by this pull are shown by dashed-dotted lines (Figure 2(b)). An additional H_2O binds molecularly to one of the vanadium atoms such that this atom regains the bulk square pyramidal coordination (one vanadyl oxygen atom at the apex and four oxygen atoms at the base). The other vanadium atom has obtained a tetrahedral configuration. Both of these structural motifs are consistent with prior calculations of the reconstruction of the V_2O_5 surfaces, which showed that vanadium has a strong tendency to form square pyramidal or tetrahedral coordination.[37]

The proposed model satisfies all the requirements derived from experiments. The variation of the average electron density with the position perpendicular to the bilayer is shown in Figure 2(c). This is consistent with the electron density extracted from the analysis of the XRD measurements. The distance between the layers forming the bilayer is 2.9 Å, which is the same as the distance proposed by analyzing the XRD data.

In this model the system has one H_3O^+ per five H_2O, which corresponds to a pH of ~1. However, the amount of water between the bilayers depends on the water partial pressure.[24] Adding more water provides more water molecules to the gel, which go in the space between the bilayer. We suggest that this between-bilayers water is the one that is in equilibrium with the water vapor and is released at 120 °C in the thermogravimetric measurements.[14] The water released at higher temperature is probably formed by reversing the reaction of water with the vanadium oxide. The protons formed by the water reaction with V_2O_5 interact electrostatically with the O^{2-} formed by the reaction and therefore will tend to stay near the bilayer when water is added between bilayers. They are however free to move along the surface of the bilayer and can therefore be exchanged with other ions or react with NH_3 or pyridine; both effects have been observed experimentally.[22, 38] Furthermore, the formation of protons explains why the gel functions as a Brønsted acid catalyst.[26]

Table 1. Difference in total energy per computational cell (ΔE_{tot}), average H_2O adsorption energy ($\langle E_{ad}(H_2O) \rangle$), intra-bilayer distance and acidity (H^+ per V_2O_5) for the five models considered in this study and compared to experiments.

	ΔE_{tot}	$\langle E_{ad}(H_2O) \rangle$	Intra-bilayer distance	H^+ per V_2O_5
Experiment			2.8 to 2.9 Å [a]	0.3 [b]
Proposed model	0 eV (ref)	−0.607 eV	2.9 Å	0.25
Model A	−0.10 eV	−0.614 eV	3.5 Å	0
Model B	0.29 eV	−0.586 eV	2.8 Å	0.25
Model C	0.33 eV	−0.583 eV	3.0 Å	0.25
Model D	2.16 eV	−0.453 eV	3.2 Å	0

[a] XRD measurements[17, 19]

[b] Ion exchange measurements[22]

4. Other models studied

4.1. Model A. Model A (Figure 3) is constructed from a bulk -V_2O_5($a \times 2b \times 2c$) supercell by introducing 14 H_2O molecules into the space between two double-layers like the ones shown in Figure 1(b). The H_2O molecules arrange themselves such that eight molecules are in the left half and six molecules are in the right half of the supercell (Figure 3(a)). Besides this uneven distribution, the H_2O molecules form an ordered network. The eight vanadium atoms exposed to water act as binding sites for eight H_2O molecules; these õbondsö are shown schematically by the dashed lines in Figure 3(a). The other H_2O molecules form hydrogen bonds with the ones that are õbondedö to the oxide. Figure S2 shows the same structure in rotatable form. The energy of model A is lower than that of the proposed model by 0.10 eV per supercell. The adsorption energy of the 14 water molecules is obtained from the energy of model A, minus the energy of eight bulk -V_2O_5 units, minus the energy of 14 gaseous water molecules. Dividing this energy by 14 gives ó0.614 eV (see Table 1). This energy is also lower than the water adsorption energy in the proposed model. Model A is energetically more favorable than the proposed model. However, it is unacceptable on two counts: no protons are present and the distance between vanadium atoms in the double layer is too large (i.e. 3.5 Å instead of 2.8-2.9 Å). To decide whether model A is more stable than the suggested model, we need to estimate the free energy. This cannot be done without performing Monte Carlo simulations which are beyond the scope of this article. However we suggest that the entropy in the proposed model, in which water moves almost freely between the bilayer, is larger than the entropy of model A. This might make the free energy of the proposed model lower than that of model A, but this conjecture is difficult to prove.
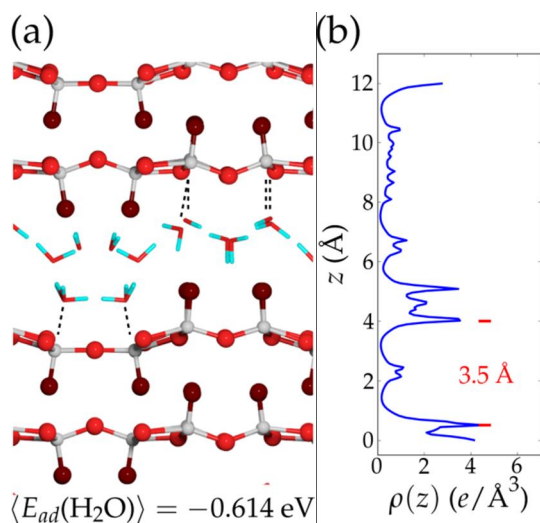
Figure 3. Structure and electron density of Model A. **(a)** Side view of two V_2O_5 double-layers with 14 H_2O molecules intercalated in the space between them. Black dashed lines indicate H_2O molecules bonded to V atoms. **(b)** Total electron charge density ($\rho(z)$) from one computational cell averaged in x and y directions and plotted as a function of z. The x and y directions span the plane of the bottom V_2O_5 layer. The plot shows that no two peaks can explain the 2.9 Å diffraction pattern.

4.2. Model B. The structure of model B is shown in Figure 4(a and b) together with the variation of the electron density in the direction perpendicular to the slab (Figure 4(c)). In model B, four water molecules react with the bilayer to create a number of species: two oxygen atoms originating from water (blue in the Figure 4(a, b)) each bridge two vanadium atoms in the bilayer. These two sites are both identical to the single adsorption site in the proposed model. Oxygen adsorption releases four protons of which two are present in the water layer between bilayers as H_3O^+ ions (shown in purple in Figure 4(a)), and two bind to an oxygen atom that was part of a vanadyl group prior to the bonding of the two hydrogen atoms (marked $2H^+$ and shown in green in Figure 4(a)). In order to bind the bridging oxygen atoms, the vanadium atoms break the V-O bonds shown as dashed-dotted lines in Figure 4(b); by this we mean that the V-O distances along the dotted line have increased substantially. One of the vanadium atoms in each bridge makes a bond with a water molecule. The two vanadium atoms in the bridge form

10

(roughly) a tetrahedral and a square pyramidal structure, which are the motifs favored in most V_2O_5 compounds.

Model B has all the desired features: water reacts to produce protons and the vanadium atoms in the layers forming the bilayer are separated by 2.8 Å (Figure 4(c)), which is consistent with the experiments. However this model has higher energy than the proposed model (by 0.29 eV per supercell).
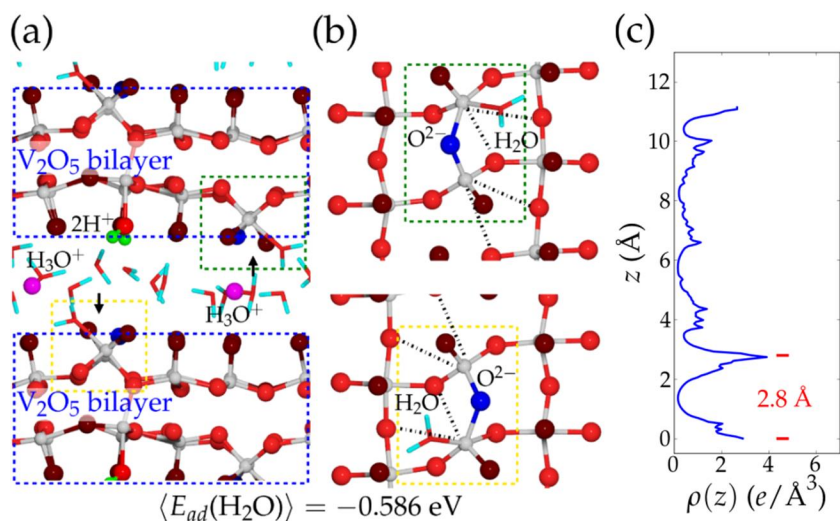

Figure 4. Structure and electron density of model B. **(a)** Side view of two V_2O_5 bilayers (marked by blue dashed rectangles) with 8 H_2O molecules and 2 H_3O^+ (purple hydrogen) in the space between them. Four water molecules have reacted with the oxide to create two molecularly adsorbed H_2O and two O atoms (shown in blue). Each O atom bridges two V atoms. This frees four H atoms, two of which have become the $2H_3O^+$ (purple) in the water layer and two ($2H^+$, green) bind to a vanadyl oxygen to form what might be regarded as a water molecule bound to V. The black arrows indicate the view directions in (b) and the green and yellow dashed rectangles indicate the atoms shown in (b). **(b)** Top views of the two sites where O atoms (O^{2-}) from water bridges two V atoms. At both sites one water molecule binds to one of the V atoms involved in the bridge such that this V atom obtains a square pyramidal configuration, while the other V atom obtains a tetrahedral configuration. The V-O bonds broken by adsorption are marked with black dashed-dotted lines. **(c)** Total electron charge density ($\rho(z)$) plotted as a function of z. The plot shows that V atoms in the bilayer are separated by 2.8 Å.

4.3. Model C. In model C, two water molecules have reacted with the vanadium oxide and produced two H_3O^+ ions, located in the water layer between the two bilayers, and two hydroxyl groups bound to vanadium (Figure 5(a)). The two vanadium atoms that bind the hydroxyls are located at different layers in the bilayer. The formation of the V-OH bond causes the breaking of two V-O bonds at each adsorption site (dashed-dotted lines in Figure 5(b)). The V-OH groups are not similar: in one the vanadium atom has a square pyramidal coordination and in the other, a tetrahedral coordination. These are two of the favorite coordinations vanadium takes when forming V_2O_5 compounds. This model has all the features observed experimentally i.e. acidity and the short distance between the vanadium atoms in the bilayer (Figure 5(c)), but the model has higher energy than the proposed model (by 0.33 eV per supercell). Model C is an example of a system that can seamlessly adsorb the protons from the water layer by converting the two adsorbed OH[6] into two adsorbed H_2O. However, this does not happen in any of the relaxed structures from the five annealing runs.
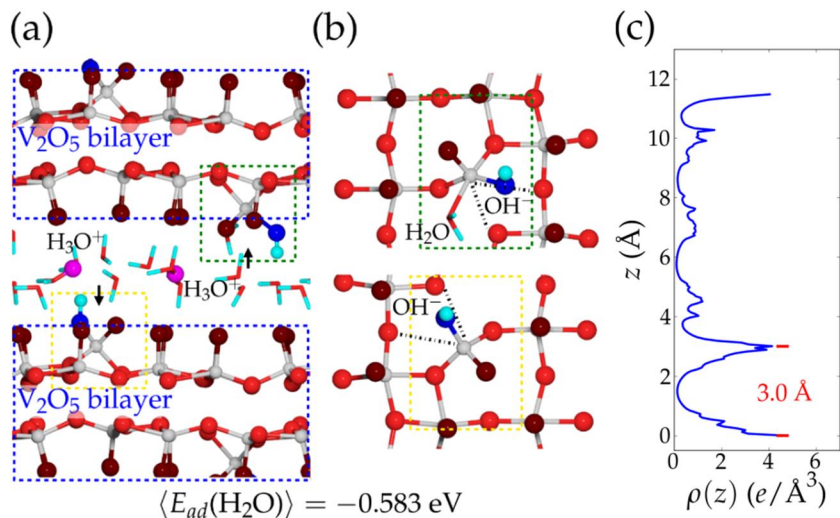

(a)   (b)   (c)

$\langle E_{ad}(H_2O) \rangle = -0.583$ eV

Figure 5. Structure and electron density of model C. **(a)** Side view of two V_2O_5 bilayers (marked by blue dashed rectangles) with 9 H_2O molecules and 2 H_3O^+ (purple hydrogen) in the space between them. Three water molecules have reacted with the oxide to create one molecularly adsorbed H_2O and two hydroxyls bonded to vanadium (dark blue oxygen and cyan

hydrogen). This frees two H atoms that become the $2H_3O^+$ in the water layer. The black arrows indicate the view directions in (b) and the green and yellow dashed rectangles indicate the atoms shown in (b). **(b)** Top view of the two adsorption sites. One V atom binds H_2O and OH^6 and obtains a square pyramidal configuration and one V atom binds OH^6 and obtains a tetrahedral configuration. The V-O bonds broken by the adsorption are marked with black dashed-dotted lines. **(c)** Total electron charge density ($\rho(z)$) plotted as a function of z. The plot shows that V atoms in the bilayer are separated by 3.0 Å.
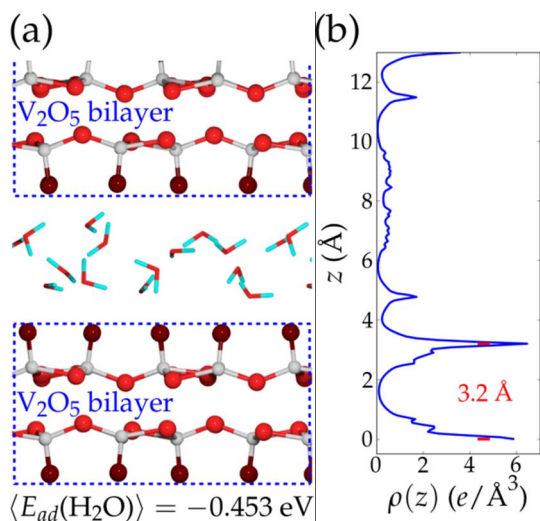

Figure 6. Structure and electron density of model D. **(a)** Side view of two V_2O_5 bilayers (marked by blue dashed rectangles) with 14 H_2O molecules in the space between them. No H_2O molecules have reacted with the oxide. **(b)** Total electron charge density ($\rho(z)$) from one computational cell averaged in x and y directions and plotted as a function of z. The x and y directions span the plane of the bottom part of the bilayer. The plot shows that vanadium atoms in the bilayer are separated by 3.2 Å.

4.4. Model D. This model was proposed by Yamamoto and co-workers[15-16] and further validated by Kanatzidis and co-workers.[17] It consists of the inverted bilayers (with õflippedö vanadyls) with all the water molecules between them (Figure 6(a)). This model is less satisfactory than the proposed model. The energy difference between model D and the proposed model is 2.16 eV per supercell and the average H_2O adsorption energy of model D is only ó0.453 eV (Table 1). The distance between V atoms in the two layers of the bilayer is 3.2 Å (Figure 6b). This is a 10%

overestimation of the 2.9 Å found in experiments, which is not unreasonable for DFT calculations at the PBE+D2 level of accuracy.[39] However, it may also indicate that this model is not complete. In addition, model D does not explain the observed acidity. We note that model D was only annealed from 400 K to 250 K over a 10ps time span. Simulated annealing at 600 K resulted in non-reversible formation of OH[6] adsorption sites similar to those observed in model C and the release of protons to the water layer. This confirms the instability of model D.

4.5. Summary. Based on the existing experiments we have required that a promising model for the V_2O_5·$n$$H_2O$ xerogel must satisfy the following conditions. 1. It should consist of bilayers in which the distance between the vanadium atoms in the two layers is 2.8-2.9 Å, to agree with the XRD measurements. 2. It should be a Brønsted acid, to agree with proton transport experiments, ion exchange experiments, and infrared experiments, which all show the presence of H_3O^+. 3. It should have the lowest energy among all the models satisfying the first two conditions. Given the fact that water in this system is amorphous, it is not possible to examine all imaginable models. We have used ab initio molecular dynamics with temperature annealing to generate likely configurations, whose energy was then minimized. One could never exclude the possibility that we have missed some of the possible structures.

In all models whose properties resemble those found in experiments, water reacts with the vanadium oxide to generate hydronium ions located in the water layer in the space between bilayers. This explains the origin of the acidity. In the lowest energy structure that satisfies all the requirements, one water molecule reacts with the bilayer to produce two hydronium ions and an oxygen atom that bridges two vanadium atoms. The vanadium atoms forming this bridging structure each break two of the V-O bonds present before the reaction with water. One of the vanadium atoms in the bridge binds an additional water molecule. In the resulting configuration this vanadium has a square pyramidal conformation and the other has a tetrahedral conformation; these two conformations are common in many V_2O_5 compounds. It appears that water is an

essential ingredient and we are not aware of any experiments in which a water-free intercalation agent has been used for making a gel.

Supporting Information Available: Comparison of the cell parameters for the presented models to those obtained in the XRD experiment; rotatable figures for the models; figures showing the development of average H_2O adsorption energy and unit cell volume along the five annealing-optimization cycles for each model. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes

The authors declare no competing financial interest.

References
(1) Bartholomew, C. H.; Farrauto, R. J. *Fundamentals of Industrial Catalytic Processes*; Wiley & Sons: Hoboken, NJ, 2006.
(2) Lloyd, L. *Handbook of Industrial Catalysis*; Springer: New York, 2011.
(3) Rase, H. F. *Handbook of Commercial Catalysts: Heterogeneous Catalysts*; CRC Press: Boca Raton, 2000.
(4) Carrero, C. A.; Schloegl, R.; Wachs, I. E.; Schomaecker, R. Critical literature review of the kinetics for the oxidative dehydrogenation of propane over well-defined supported vanadium oxide catalysts. *ACS Catal.* **2014,** *4*, 3357-3380.

(5)   Wachs, I. E. Recent conceptual advances in the catalysis science of mixed metal oxide catalytic materials. *Catal. Today* **2005,** *100*, 79-94.

(6)   Wachs, I. E. Catalysis science of supported vanadium oxide catalysts. *Dalton Trans.* **2013,** *42*, 11762-11769.

(7)   Whittingham, M. S. Lithium batteries and cathode materials. *Chem. Rev.* **2004,** *104*, 4271-4302.

(8)   Londero, E.; Schröder, E. Role of van der Waals bonding in the layered oxide V_2O_5: First-principles density-functional calculations. *Phys. Rev. B* **2010,** *82*, 054116.

(9)   Nicolosi, N.; Chhowala, M.; Kanatzidis, M. G.; Strano, M. S.; Coelman, J. N. Liquid exfoliation of layered materials. *Science* **2013,** *340*, 1420-1438.

(10)   Liu, Y. J.; Schindler, J. L.; DeGroot, D. C.; Kannewurf, C. R.; Hirpo, W.; Kanatzidis, M. G. Synthesis, structure, and reactions of poly(ethylene oxide)/V_2O_5 intercalative nanocomposites. *Chem. Mater.* **1996,** *8*, 525-534.

(11)   Aldebert, P.; Baffier, N.; Gharbi, N.; Livage, J. Intercalation de solvants organiques polaires dans la structure lamellaire des gels de V_2O_5. *Mater. Res. Bull.* **1981,** *16*, 949-955.

(12)   Kanatzidis, M. G.; Wu, C. G.; Marcy, H. O.; DeGroot, D. C.; Kannewurf, C. R. Conductive polymer/oxide bronze nanocomposites. Intercalated polythiophene in vanadium pentoxide (V_2O_5) xerogels. *Chem. Mater.* **1990,** *2*, 222-224.

(13)   Petkov, V.; Parvanov, V.; Trikalitis, P.; Malliakas, C.; Vogt, T.; Kanatzidis, M. G. Three-dimensional structure of nanocomposites from atomic pair distribution function analysis: Study of polyaniline and (polyaniline)$0.5V_2O_5 \cdot 1.0H_2O$. *J. Am. Chem. Soc.* **2005,** *127*, 8805-8812.

(14)   Livage, J. Vanadium pentoxide gels. *Chem. Mater.* **1991,** *3*, 578-593.

(15)   Yao, T.; Oka, Y.; Yamamoto, N. Layered structures of vanadium pentoxide gels. *Mater. Res. Bull.* **1992,** *27*, 669-675.

(16)   Yao, T.; Oka, Y.; Yamamoto, N. Layered structures of hydrated vanadium oxides. Part 2. Vanadyl intercalates (VO)$V_2O_5 \cdot nH_2O$. *J. Mater. Chem.* **1992,** *2*, 337-340.

(17)   Petkov, V.; Trikalitis, P. N.; Bozin, E. S.; Billinge, S. J. L.; Vogt, T.; Kanatzidis, M. G. Structure of $V_2O_5 \cdot nH_2O$ xerogel solved by the atomic pair distribution function technique. *J. Am. Chem. Soc.* **2002,** *124*, 10157-10162.

(18)   Aldebert, P.; Baffier, N.; Gharbi, N.; Livage, J. Layered structure of vanadium pentoxide gels. *Mater. Res. Bull.* **1981,** *16*, 669-676.

(19)   Legendre, J.-J.; Aldebert, P.; Baffier, N.; Livage, J. Vanadium pentoxide gels:: II. Structural study by x-ray diffraction. *J. Colloid Interface Sci.* **1983,** *94*, 84-89.

(20)   Giorgetti, M.; Passerini, S.; Smyrl, W. H.; Berrettoni, M. Evidence of bilayer structure in V_2O_5 xerogel. *Inorg. Chem.* **2000,** *39*, 1514-1517.

(21)   Enjalbert, R.; Galy, J. A refinement of the structure of V_2O_5. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1986,** *42*, 1467-1469.

(22) Livage, J.; Barboux, P.; Badot, J. C.; Baffier, N. Ionic properties of vanadium pentoxide gels. *MRS Online Proceedings Library Archive* **1988,** *121*, 167-177.

(23) Müller, E. Herstellung kolloider Vanadinsäure nach einer neuen Dispersionsmethode. *Zeitschr f. Chem. und Ind. der Kolloide* **1911,** *8*, 302-303.

(24) Kittaka, S.; Ayatsuka, Y.; Ohtani, K.; Uchida, N. Interlayer water molecules of vandium pentaoxide hydrate. Part 1. Phase equilibrium with water vapour at a relative pressure higher than 0.005. *J. Chem. Soc., Faraday Trans. 1* **1989,** *85*, 3825-3832.

(25) Livage, J. Sol-gel chemistry and electrochemical properties of vanadium oxide gels. *Solid State Ionics* **1996,** *86–88, Part 2*, 935-942.

(26) Kishimoto, N.; Matsunami, E. Method of catalyzing a gas phase reaction using an acid-base catalyst composed of vanadium pentoxide hydrate US Patent 6,479,710 B2, 2002.

(27) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **1993,** *47*, 558-561.

(28) Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal--amorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994,** *49*, 14251-14269.

(29) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996,** *54*, 11169-11186.

(30) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996,** *6*, 15-50.

(31) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996,** *77*, 3865-3868.

(32) Perdew, J. P.; Burke, K.; Wang, Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys. Rev. B* **1996,** *54*, 16533-16539.

(33) Wang, L.; Maxisch, T.; Ceder, G. Oxidation energies of transition metal oxides within the GGA+U framework. *Phys. Rev. B* **2006,** *73*, 195107.

(34) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006,** *27*, 1787-1799.

(35) Gharbi, N.; Sanchez, C.; Livage, J.; Lemerle, J.; Nejem, L.; Lefebvre, J. Mixed-valence poly(vanadic acid) gels. *Inorg. Chem.* **1982,** *21*, 2758-2765.

(36) Cezar, A. B.; Graff, I. L.; Varalda, J.; Schreiner, W. H.; Mosca, D. H. Oxygen-vacancy-induced room-temperature magnetization in lamellar V_2O_5 thin films. *J. Appl. Phys.* **2014,** *116*, 163904.

(37) Kristoffersen, H. H.; Metiu, H. Reconstruction of low-index a-V_2O_5 surfaces. *J. Phys. Chem. C* **2015,** *119*, 10500-10506.

(38) Ruiz-Hitzky, E.; Casal, B. Interlayer adsorption of ammonia and pyridine in V_2O_5 xerogel. *J. Chem. Soc., Faraday Trans. 1* **1986,** *82*, 1597-1604.

(39) Björkman, T.; Gulans, A.; Krasheninnikov, A. V.; Nieminen, R. M. Are we van der Waals ready? *J. Phys.: Condens. Matter* **2012,** *24*, 424218.