Hydrogen Storage

Hydrogen Chemisorption on Singly Vanadium-Doped Aluminum Clusters

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Abstract: The effect of vanadium doping on the hydrogen adsorption capacity of aluminum clusters $(Al_n^+, n=2-18)$ is studied experimentally by mass spectrometry and infrared multiple photon dissociation (IRMPD) spectroscopy. We find that vanadium doping enhances the reactivity of the clusters towards hydrogen, albeit in a size-dependent way. IRMPD spectra, which provide a fingerprint of the hydrogen binding geometry, show that H₂ dissociates upon adsorption. Density functional theory (DFT) calculations for the smaller Al_nV^+ (n=2-8,10) clusters are in good agreement with the observed reactivity pattern and underline the importance of activation barriers in the chemisorption process. Orbital analysis shows that the activation barriers are due to an unfavorable overlap between cluster and hydrogen orbitals.

With an ever-growing global energy consumption, the need for a more sustainable and environmentally friendly alternative to our use of fossil fuels becomes increasingly dire. Dihydrogen, H_2 , with a gravimetric energy density roughly three times that of gasoline,^[1] is one such alternative and has been the subject of extensive study.^[2–4] A major drawback, however, is the low volumetric energy density of gaseous hydrogen, which

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urges for other means of storage. For mobile applications, the requirements posited by the U.S. Gov. Department of Energy are rather stringent; by 2020, hydrogen storage materials should have at least 5.5 wt% and 40 gL^{-1} volumetric capacity, with operating and recharging conditions around ambient temperature and pressure. In general, two kinds of hydrogen storage materials can be found in the literature:^[5] 1) highly porous systems such as metal-organic frameworks (MOFs), zeolites, and clathrates,^[6-8] which bind the hydrogen through weak dispersion forces. Much of the effort within this branch of the hydrogen storage research is aimed at increasing the H₂ binding strength to these materials; 2) chemical (metal) hydrides,^[9,10] such as NaAlH₄, MgH₂, LaNi₅H₇, which bind the hydrogen more strongly. For these materials, the focus lies on improving the (de)hydrogenation kinetics, while keeping the weight percentage sufficiently low.

To eventually devise storage media superior to what is currently available, a better understanding of the interaction between hydrogen and potential storage materials is highly desirable. Nanoclusters, whose physico-chemical properties are strongly size-dependent and therefore exhibit a multitude of chemically distinct and possibly reactive sites, are useful model systems for designing more efficient storage media on a larger scale. By studying these clusters in the well-defined experimental conditions (cluster size and composition, charge state) that are characteristic of gas-phase experiments,^[11] one gains more insight in the kinetics and dynamics of hydrogenation reactions of nanostructured materials, which could pave the way towards a sustainable hydrogen economy.

Aluminum is one of the lightest and most abundant metals on earth. It is known to form the bulk metal hydrides alane, AlH₃, and, as mentioned earlier, sodium alanate, NaAlH₄, which have hydrogen weight percentages of 10 and 5.6%, respectively. Despite unremitting efforts,^[12,13] the slow hydrogenation kinetics of both materials limits their use for practical purposes. The bottleneck in the hydrogenation process is a high activation barrier (of the order of 1 eV) in the dissociative reaction pathway, a barrier which is present for bulk as well as small clusters of aluminum.^[14–17] Bogdanović et al.,^[18] however, showed that adding small amounts of titanium strongly enhances the reversible hydrogenation of sodium alanate.^[19] Several computational studies also predict that doping aluminum clusters with transition metals such as Ti, Cr, V, and Co, lowers the activation barriers towards dissociative chemisorption.[20-23] Nonose et al. showed experimentally that this is indeed the case for Co and mentioned similar results for aluminum clus-

Chem. Eur. J. 2017, 23, 15638-15643

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ters doped with Rh and V.^[24] Menezes and Knickelbein,^[25] and later Pramann and co-workers,^[26] showed that unlike for several pure transition metals clusters,^[27] there is no *anti*-correlation between the reactivity of Co doped Al_n clusters and their ionization potential (IP), and attributed the reactivity to geometric or local electronic structure effects. A detailed description of the role of the transition metal in the reaction, however, is still lacking. In this work, we study the reactivity of singly vanadium doped aluminum clusters towards hydrogen by means of mass spectrometry and infrared multiple photon dissociation spectroscopy (IRMPD). For the smaller sizes, we compare density functional theory calculations with the experimental data to rationalize our observations.

Figure 1 shows a mass spectrum of $Al_nV_m^+$ (n=1-18, m=0-3) clusters, before and after interaction with H_2 (Figure 1 a). An expanded view of part of the hydrogenated mass spectrum is shown in the upper right corner. In this letter, the scope of the analysis will be limited to the singly vanadium doped aluminum clusters, the most abundant species in the mass spectra. For these clusters, the fractional distribution of the hydrogenated complexes can be extracted from the mass spectra [Eq. (1)]:

$$[AI_{n}VH_{2p}^{+}]_{frac} = \frac{I(AI_{n}VH_{2p}^{+})}{\sum_{i=0}^{2}I(AI_{n}VH_{2i}^{+})}$$
(1)



Figure 1. Parts of mass spectra of $AI_nV_m^+$ (n = 1-18, m = 0-2) clusters, a) before and after interaction with H₂. An expanded view of a part of the mass spectrum after interaction with H₂ shows the presence of hydrogenated complexes. b) Fractional distribution of hydrogenated AI_nV^+ (n = 1-18) clusters.

with $I(AI_nV_mH_{2p}^+)$ the intensity of the cluster species in the mass spectra. This fractional distribution is plotted in Figure 1 b.

Doping pure aluminum clusters with one vanadium atom changes the clusters' reactivity in a size-dependent way: small AI_nV^+ clusters (n = 1-9) are relatively unreactive towards H_2 , with the exception of Al₂V⁺. Significantly larger reactivities are observed for medium sized clusters (n = 10-16). Especially Al₁₀V⁺ exhibits a drastically increased reactivity. For clusters larger than n = 16 the reactivity decreases again. Experimental work by Lang et al.^[28] suggested that after n = 16, the position of the vanadium dopant in the AI_nV^+ clusters changes from an exohedral to an endohedral site. This structural transformation hypothesis was supported by computational work of Fernandez et al.^[29] The observed decrease in reactivity for the larger sizes then is in line with the assumption that the vanadium dopant acts as a reactive center for H₂ adsorption: for clusters of size larger than $AI_{16}V^+$, the vanadium dopant becomes shielded by a cage of aluminum atoms, thereby impeding the interaction with H₂.

A priori, it is not clear whether the hydrogen molecule dissociates upon adsorption or not. Additionally, the observation that for singly doped aluminum clusters the amount of adsorbed hydrogen molecules is limited to mostly one, could imply that the vanadium atom, which is considered to be the active site,^[30,31] gets poisoned after interaction with the first hydrogen molecule. A tentative answer to both questions can be found by analysis of the IRMPD spectra of the hydrogenated clusters, which provide a fingerprint of the hydrogen binding geometry. A detailed description of this technique can be found in Ref. [32] and a shorter version is included in the Supporting Information. In Figure 2, several low-energy configurational isomers of $Al_{10}VH_2^+$ are plotted together with their calculated IR spectra and the experimental IRMPD spectrum.

The bands observed in the 800–2100 cm^{-1} region for Al_{10}V^+ are related to the stretching modes of atomic hydrogen-metal bonds, meaning that the H₂ molecule dissociates upon adsorption. The feature around 1900 cm⁻¹, for example, corresponds to the stretching mode of a hydrogen atom bound on-top an aluminum atom; the bands at approximately 1350 and 1200 cm⁻¹ correspond to the symmetric and asymmetric stretch of a hydrogen atom bound in a bridge position between a vanadium and an aluminum atom and the frequencies are similar to those for hydrogen bound dissociatively to transition metal (Fe, Co, V, and Ni) clusters.^[33] The spectrum of the lowest energy isomer (iso 1) shows good agreement with the experimental data, although the positions as well as the intensities of a second, almost degenerate isomer ($\Delta E = 0.003 \text{ eV}$) provide an even better match. Because this isomer is structurally more similar to the bare $AI_{10}V^+$ (see Supporting Information), we designate this cluster as the ground state. If there is no considerable energy barrier separating them, both isomers could be present in the molecular beam. The next higher isomer (iso 2, $\Delta E = 0.123$ eV) can be excluded because of the absence of the band at \approx 1900 cm⁻¹. For the fourth isomer (iso 3, $\Delta E = 0.174 \text{ eV}$), the calculated bands are at lower wavenumbers than the experimental ones, and the intensities don't

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Figure 2. Experimental IRMPD cross section vs. calculated IR intensity for energetically low-lying isomers of $Al_{10}VH_2^+$ (blue = Al, red = V, white = H). The upper panel contains the experimental data points in red, together with a three-point running average in black. The lower panels show the calculated harmonic IR spectra of four low-energy configurational isomers. The discrete resonances are artificially broadened by 10 cm⁻¹ to facilitate comparison with the experimental data.

agree well with the experiment. Moreover, the metal framework of iso 2 and iso 3 differs significantly in structure from the calculated bare cluster (Supporting Information), whereas that of the tentative ground state and of iso 1 are very similar. For all calculated isomers of $Al_{10}VH_2^+$, one or two of the hydrogen atoms are bound to a vanadium atom, further corroborating the hypothesis that, at least for this size, the vanadium dopant gets poisoned after adsorption.

Infrared spectra for larger sizes (n = 11, 12, 13, 15), exhibit spectral features in the same wavenumber regime and are included in the Supporting Information. The IR spectra of the few smaller sizes that do adsorb hydrogen, namely AI_nV^+ with n=2, 8, 9 (see Figure 1 b), do not show any discernible IR bands, which could be due to insufficient oscillator strength of the vibrational resonances to desorb the hydrogen. Another explanation could be that the hydrogen for these sizes is mainly bound molecularly, in which case the characteristic vibrations are expected to lie outside our measurement range,^[33,34] that is, below 800 cm⁻¹ (M–(H₂) stretch) and above 2100 cm⁻¹ (H–H stretch).

For the smaller AI_nV^+ sizes (n=2-10), DFT calculations show that the hydrogen molecule first physisorbs on top of a vanadium atom in a precursor state before dissociating into its atomic constituents (structures and properties can be found in the Supporting Information). Table 1 contains calculated properties of selected vanadium doped aluminum clusters, such as the spin multiplicity before adsorption (M_i), the physisorption

Table 1. DFT computational results for selected AI_nV^+ (n=2-10). For each cluster, the initial and final spin multiplicity (M=2S+1), as well as the physisorption energy $E_{ads}(H_2)$ and the chemisorption energy $E_{ads}(2H)$ are listed.

Cluster	Mi	$\mathbf{E}_{ads}(\mathbf{H}_2)$ [eV]	M _f	$\pmb{E_{ads}}(2\pmb{H})~[eV]$
Al_2V^+	5	0.304	5	1.229
$AI_{3}V^{+}$	6	0.212	4	0.756
AI_4V^+	5	0.260	3	0.898
AI_5V^+	4	0.187	4	0.887
AI_6V^+	3	0.279	3	0.594
AI_7V^+	6	0.315	4	0.941
AI_8V^+	5	0.375	5	0.824
AI_9V^+	4	0.349	4	0.847
$AI_{10}V^+$	1	0.109	1	0.928

energy ($E_{ads}(H_2)$), the spin multiplicity after chemisorption (M_f), and the dissociative chemisorption energy ($E_{ads}(2H)$). The values of $E_{ads}(2H)$ suggest that among the smaller clusters, $Al_2VH_2^+$ is the most stable species and hence is expected to be more abundant in the mass spectra, whereas $Al_6VH_2^+$ should be less abundant. Figure 1 b shows that for Al_2V^+ and Al_6V^+ this argument agrees well with the experiment, but for other sizes the situation is less straightforward; $Al_4VH_2^+$, for example, has a relatively high adsorption energy (0.898 eV), but has a low abundance in the mass spectra. Figure 3 explains the reason for this discrepancy: for Al_2V^+ the H₂ chemisorption reaction occurs barrierless, whereas for Al_4V^+ there is an activation barrier of almost 1.4 eV.

In other words, although the formation of $Al_4VH_2^+$ is thermodynamically favorable, it is impeded by the kinetics of the reaction, at least on the timescale of the experiment (i.e. about 100 µs). Figure 3 c shows that for $Al_{10}V^+$ the first step along the reaction coordinate, that is, the dissociation of H_2 , is barrierless as well, in agreement with its high observed abundance in the mass spectra. The small activation barrier (0.2 eV) that separates the initial from the final configuration can be easily overcome by the thermal energy available in the other (32) degrees of freedom of the complex. Calculated pathways for Al_3V^+ , Al_6V^+ and Al_8V^+ (Supporting Information) have activation barriers for the dissociative adsorption of hydrogen onto the clusters of 0.65, 0.15, and 0.12 eV, respectively.

Analysis of the projected density of states (PDOS) and molecular orbitals of the clusters provides insight in the magnitude of these activation barriers. This is illustrated for the complexes with molecularly bound hydrogen $Al_4V(H_2)^+$ and $Al_{10}V(H_2)^+$ in Figure 4. Only the orbitals which have a contribution of the hydrogen s-orbitals are shown in the Figure. The deepest bound states for both clusters are formed by the symmetric and *anti*-symmetric superposition of the doubly occupied H₂ σ -orbital with a cluster s-orbital (which, in turn, consists of the delocalized Al(s) electrons). The other orbitals with



Figure 3. Reaction pathways for the dissociative adsorption of H₂ on a) Al₂V⁺, b) Al₄V⁺ and c) Al₁₀V⁺. Transition states are denoted by a \pm . Initially, at E=0, the hydrogen is bound molecularly. For Al₂V⁺ the dissociative chemisorption reaction is barrierless. For Al₁₀V⁺, the first step along the reaction coordinate is barrierless, followed by a small diffusion barrier towards the final state. For Al₄V⁺, there are two energetic barriers along the reaction coordinate.

H(s) character describe the Kubas interaction^[35] between cluster and H₂: for $Al_4V^+(H_2)$, there is a singly occupied orbital of mainly d-character near the highest molecular orbital (HOMO) level which has a node in between the hydrogen atoms, that is, there is donation of electronic charge from the cluster into the *anti*-bonding σ^* -orbital of H₂. In contrast, the PDOS and orbitals containing H(s) character of $AI_{10}V^+(H_2)$ show that for this cluster there are two orbitals of anti-bonding character, one located near the HOMO level and one around -4 eV, both of which are doubly occupied. This suggests that the destabilization of the hydrogen-hydrogen bond upon physisorption of the H₂ might be stronger for $AI_{10}V^+$ than for AI_4V^+ , leading to a lower activation barrier in the hydrogenation reaction. This weakening of the hydrogen-hydrogen bond by the Kubas mechanism is also visible in the bond distances of $Al_2V^+(H_2)$ and $AI_{10}V^+(H_2)$ compared to other sizes, both have a larger H-H distance, a smaller V-H distance, and less charge transfer from the physisorbed H₂ to the cluster (see Table S2 in the Supporting Information). For other small Al_nV⁺ clusters, similar orbital features can be observed (see Supporting Information), that is, unreactive clusters (n = 3-8) have at most a singly occupied orbital which overlaps with the σ^* H₂ orbital, whereas reactive ones (n=2, 10) have either two or one doubly occupied orbitals of this kind. The above explanation is similar to the ar-



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Figure 4. PDOS and selected orbitals of $AI_4V^+(H_2)$ and $AI_{10}V^+(H_2)$. The orbital isosurfaces correspond to a charge density of approximately $1.10^{-3} e/ a_0^{-3}$.

guments provided by Pino et al.^[15] in their computational study explaining the experimentally observed inertness of pure aluminum clusters towards hydrogen.[16,17] Most of the small pure aluminum clusters have a triplet ground state, and the formation of the hydrogenated clusters, which prefer singlet states, is impeded by a large activation barrier along the pathway. The PES of the singlet states, however, which are initially higher in energy than the triplet states ($\Delta E \approx 0.1 - 0.4 \text{ eV}$), show a smaller and sometimes even negligible barrier. This is explained by double instead of single occupancy of an orbital, which is anti-bonding with respect to the H₂ bond for the singlet states. This argument also explains the observed reactivity of Al₆,^[17] the only reactive pure aluminum cluster, for which the singlet and triplet state were found to be almost degenerate^[15] and with the singlet state even lower in energy in the work of Moc.[36]

In summary, the interaction of singly vanadium doped aluminum clusters with molecular hydrogen was studied experimentally by mass spectrometry and infrared multiple photon dissociation spectroscopy. In contrast to pure aluminum clusters, the vanadium-doped clusters are reactive towards hydrogen, but in a size-dependent way. IR spectroscopy shows that for the most reactive cluster, $AI_{10}V^+$, the hydrogen dissociates upon adsorption but remains (partially) bound to the vanadium atom. For smaller AI_nV^+ clusters, density functional theory calculations demonstrate that the reactivity pattern is not so

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much the result of the energetics of the hydrogenation reaction as of the kinetics, with considerable activation barriers due to unfavorable/insufficient orbital overlap between cluster and molecular hydrogen orbitals. The decrease in reactivity for larger clusters with n > 16 is attributed to cage formation, in which the vanadium dopant occupies an endohedral position in the cluster. Our observations demonstrate the possibility of doping of aluminum with relatively abundant transition metals to improve their reactivity towards hydrogen, but that in the case of a single vanadium dopant only a narrow size range becomes active. Moreover, our results clearly illustrate the feasibility of a detailed understanding of the interaction of hydrogen with materials at the nanoscale, which will be key in realizing the promise of the hydrogen economy.

Experimental Section

The bimetallic vanadium-aluminum clusters were produced in a dual laser ablation (Nd:YAG, 10 Hz, \approx 10–20 mJ per pulse) source setup which has been described in detail elsewhere.^[37] Hydrogen was injected into the source by a separate valve. After formation, the clusters were extracted and detected in a reflectron time-of-flight mass spectrometer. Infrared light (800-2100 cm⁻¹, \approx 50 mJ per pulse) produced by the free-electron laser (FEL) of the Fritz-Haber-Institut der Max-Planck-Gesellschaft^[38,39] was focused onto the clusters through a 2 mm aperture before extraction. When the frequency of the FEL radiation is resonant with an IR-active mode of a cluster, it absorbs several photons, thereby heating the cluster through internal vibrational redistribution. Comparison of spectra with and without IR light shows that the decay channel of the excited clusters is loss of molecular hydrogen (Supporting Information).

DFT calculations were performed in SIESTA,^[40] using the spinpolarized GGA-PBE^[41] exchange–correlation functional. In SIESTA, core electrons were treated with norm-conserving scalar relativistic pseudopotentials in their fully non-local form,^[42] whereas for the valence electrons linear combinations of numerical pseudo-atomic orbitals (PAO) were used (double zeta polarized basis (DZP) set in this work). The equilibrium geometries resulted from an unconstrained conjugate-gradient structural relaxation using the DFT forces until the force on each atom was smaller than 0.001 eV Å⁻¹. The calculation of the dissociation barriers has been performed by the climbing nudged elastic band method^[43] within the VASP^[44] code. The IR spectra were calculated with the ORCA^[45] code (GGA-PBE/def2-TZVP) after re-optimization of the SIESTA structures. The density of states and electronic orbitals were calculated with Quantum Espresso^[46] (GGA-PBE, ultrasoft Vanderbilt core pseudopotentials, plane wave cutoff energy of 200 eV).

Acknowledgements

This work is supported by the KU Leuven Research Council (GOA/14/007). J.V. would like to thank the FWO—Research

Foundation Flanders for a PhD fellowship. P.F. acknowledges CONICyT for a Becas Chile scholarship. E.M.F and L.C.B. thank the Spanish Ministry of Economy (Grants RyC-2014–15261 and FIS2014-59279-P, respectively). A.F. thanks the Deutsche Forschungsgemeinschaft for a Heisenberg grant (FI 893/5).

Conflict of interest

The authors declare no conflict of interest.

Keywords: density functional calculations • hydrogen storage • IR spectroscopy • mass spectrometry • metal clusters

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Manuscript received: September 16, 2017 Accepted manuscript online: September 20, 2017 Version of record online: October 13, 2017