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Study of Hydrogen Adsorption by V, V-Ti alloy and V-oxide through ab initio Calculations

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ABSTRACT

The adsorption of hydrogen on surfaces of vanadium, vanadium-titatnium alloy and vanadium oxide was studied by ab initio calculations using Gaussian03 package. The activation and adsorption energies for adsorption were evaluated by scanning potential energy surfaces of respective systems comprising a hydrogen molecule and small cluster consisting of several metal atoms for modelling an alloy surface to reduce computational cost. The surfaces investigated were V(110), V-Ti(110), VO(111) and VO(110), different cluster models being adopted for some surfaces to examine their validities and to find an appropriate cluster model and adsorption site.

By comparing the results obtained by using the alloy and/or compound in different cases, it was found that the activation energy for adsorption is larger for surfaces with an oxygen adlayer than for clean and Ti-covered vanadium surfaces. These findings are in good agreement with experimental observations. It was also demonstrated that different cluster models for a given alloy give similar activation and adsorption energies.

1. Introduction

Vanadium alloys are considered as one of the most promising structural materials for fusion reactors because of their high temperature strength, high thermal stress factor, low activation property and so on [1]. An important concern for this application is the adsorption of hydrogen molecules. Hydrogen is adsorbed on clean vanadium surfaces extremely fast, and then rapidly absorbed by the bulk because of the high diffusivity and solubility of hydorogen atoms in this material[2]. But the environments assumed for their applications will contain some levels of oxygen that can affect the hydrogen adsorption. Vanadium is one of the most sensitive materials to poisoning by impurity gases containing oxygen, carbon and even nitrogen. Consequently the surface of vanadium is easily contaminated by impurity gases even in high vacuum conditions. Surface oxides or contamination layers thus formed act as barriers against the chemisorption of hydrogen isotopes[3, 4, 5]. Therefore they provide effective means to reduce tritium permeation through the structural material as well as the tritium inventory in it. Furthermore, they can enhance the super permeation of tritium atoms and ions generating in the edge plasma region. From this view point, a number of investigations have been carried out to examine the effectiveness of such kind of surface barriers on preventing hydrogen absorption and/or accelating super permeation[6]. The results are, however, rather complicated and hence not well understood, because most of the experiments were done for poly crystlline specimens with different purities and pretreatments under various vacuum conditions.

To understand fundamental roles of these surface barriers on hydrogen absorption and super permeation, the adsorption of hydrogen molecules on the surfaces of V, V-Ti alloy and V-oxide was studied from the first principles in the present study. This is a formidable task that has not been fully achieved in even the simplest case without making several simplifying assumptions. The purpose of our present effort is to undertake ab inito calculations for hydrogen adsorption for the above mentioned mateials by use of small clusters consisting of several metal atoms as the models of crystal surfaces, to examine the validity of small cluster models, and to find effects of such barriers on the adsorption. The computations were performed on a PC workstation by using Gaussian 03[8].

2. Calculation details

2.1. Calculation of potential energy surfaces

For the dissociative adsorption of hydrogen via a bridge site on a metal surface, for example, the following scheme is assumed to be valid

$$H_2 + 2S \overset{K^*}{\rightleftharpoons} S_2H_2^* \xrightarrow{k_f^*} 2SH(a), \tag{1}$$

where H_2 represents a hydrogen molecule, 2S adjacent metal atoms forming a bridge site, $S_2H_2^*$ the activated complex, SH(a) an adsorbed hydrogen atom, K^* the constant for pseudequilibrium between the reactants and acticated complex, k_f^* the rate constant for decompostion of the activated complex. The rate of adsorption is written as[7]

$$\begin{aligned} v_{ad} &= k_f^*[S_2H_2^*]^2 = k_f^* K^*[H_2][S]^2 = (\frac{kT}{h})(\frac{Q^*}{Q_{H_2}Q_{S^2}})\exp(-E_{act}/kT)[H_2][S]^2 && (2) \\ &= k_{ad}[H_2][S]^2, \quad k_{ad} = (\frac{kT}{h})(\frac{Q^*}{Q_{H_2}Q_{S^2}})\exp(-E_{act}/kT) && (3) \end{aligned}$$

where [ ] represents the concentrations of respective species, and k and h are the Boltzmann and the Planck constants, respectively; Q's are partition functions of the activated complex, a hydrogen molecule and a metal atom on the surface, and E_{act} is the difference in the classical energy levels between the reactants and activated complex.

The rate constant k_{ad} is a function of quantum stats of reactants and activated complex. By scanning the potential energy surface for a system consisting of H_2 and metal surface, the products and activated complex can be determined to evaluate the adsorption and activation energies. If the partition functions could be calculated as well, the rate constant k_{ad} is obtained through the ab initio calculations.

The key point for evaluating the rate constant is to find the reaction path connecting the reactants and products through the activated complex in the potenrial energy surface (PES). In the present study, two dimensional PES's were calculated by adopting small cluster models, where the energies were evaluated as funtions of the height of H_2 molecules from the surface and the distance between two H atoms, while the surface structure was assumed to be invariant. Their details are described in section **2.2**. Once the reaction path could be evaluated, the adsorption energy of a hydrogen molecule on the metal surface is calculated by

$$E_{ads} = E_{tot}(2SH) - E_{tot}(metal + H_2), \tag{4}$$

where E_{tot}(metal+H_2) is the total energy of the unit cell with a H_2 molecule in the vacuum region, and E_{tot}(2SH) is the total energy of the unit cell with two adsorbed H atoms on the surface. Similarly, the activation energy of the adsorption is

$$E_{act} = E_{tot}(S_2H_2^*) - E_{tot}(metal + H_2), \tag{5}$$

where $E_{tot}(S_2H_2^*)$ is the energy for forming the activated complex or transition state in the adsorption process.

To evaluate PES for a system consisting of a metal surface and a hydrogen molecule, the present study used the density-functional method, where an extra quadratically convergent SCF (`XQC`) step was performed in case that the first-order SCF was not converged[9]. For vanadium, oxygen and titanium atoms, the Effective Core Potential (ECP) basis sets of Los Alamos ECP plus MBS atomic wavefunctions were applied[10], and a standard 6-31G basic set was used for hydrogen[11]. Then the Kohn-Sham equation was solved by using B3LYP exchange-correlation functions. The B3LYP function is one of the hybrid types. It consists of a careful mixing of Hatree-Fock exchange, Beche's B98 exchange functions and the LYP correlation functions[12, 13].

An example of optional part in a routine input used in the calculation is shown below.

```
Chk=scanV3H2
scan ub3lyp/lanL2dz nosymm guess=(tcheck,mix) iop(2/16=1) extrabasis
scf=(varacc,conver=6,xqc,Fermi,maxcycle=600) test
2D pes scan
```

To find the influence of oxygen and/or titanium atoms deposited on the vanadium surface on hydroge adsorption, clean vanadium surface V(110), vanadium surface covered by oxygen with vanadium structure V/O(110), VO(110,111) and vanadium surface covered by titanium with vanadium structure V/Ti(110), where a hydrogen molecule is assumed to be adsorbed via either a bridge site or on-top site of these surfaces.

2.2. Cluster Models

A given crystal was sliced to a slab comprising a set of given planes with several atomic layers. Then the slab was cut by a plane perpendicular or with a given angle to the plane to make a cluster consisting of several atoms. The cluster was used as a model of the crystal surface to evaluate the potential energy surface (PES) for evaluating the adsorption of a H_2 molecule, where the distance between two hydrogen atoms and the height of the center of H-H bond from the surface were varied for PES calculations. In this case, the mutual distances and angles among the atoms forming the cluster were set equal to those found in the crystal and kept constant; namely, no surface relaxation was accounted for surface formation and also hydrogen adsorption.

2.2.1. Vandadium

Hydrogen adsorption on the clean surface of vanadium was followed for V(110) surface. Vanadium has the body-centered cubic structure with a lattice constant of a=3.028Å, as shown by Fig.1, in which the V(110) lattice plane is drawn. Firstly, the V(110) surface was modeled by clusters containing three or four atoms, which correspond to one- or two-layers thickness. Hereafter, the clusters containing three and four atoms are denoted as V_3 and V_4 clusters, respectively, for convenience. When a hydrogen molecule is adsorbed on the V(110) surface, it would take place via an activated complex formed on the bridge or on-top site with H-H bond oriented parallel to the surface; it should be noted here that the surface is represented by the bond connecting the two vanadium atoms in the first or second layer.

In the V_3 models, triangular and linear geometries were adopted. The V_3 triangular model is constructed by two vanadium atoms labeled by 1 and 2 and one vanadium atom

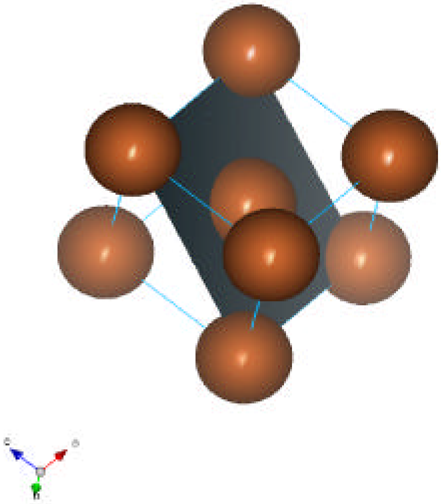

Fig. 1. The body-centered cubic structure of V with a Miller plane (110)

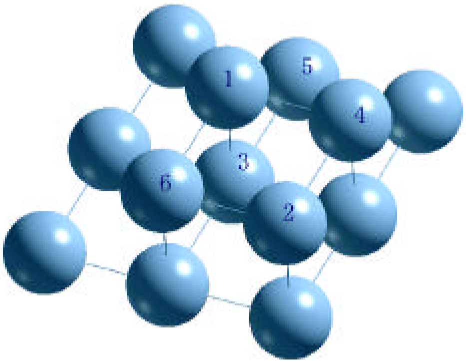

Fig. 2. Arrangement of V-atoms in a two-layer slab of V(110)

labeled by 3 in vanadium 110 substrate as shown in Fig.2, in which vanadium atoms 1, 2, 4, and 6 are in the top layer and the other atoms are in the second layer.

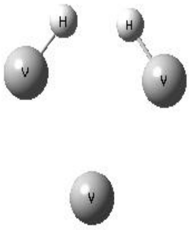

Fig. 3. Adsorption of a hydrogen molecule on a bridge and on-top site on triangular V_3 cluster

The adsorption of a hydrogen molecule through the bridge site of V_3 triangular cluster with H-H bond oriented parallel to the surface are shown by Fig.3, in which the distance between the two vanadium atoms in the top layer is 3.028 Å, the third one is at 2.142 Å under the two atoms.

Three V_3 linear clusters can be also possible for modeling V(110) surface. The first one is the array of vanadium atoms in the [0 1] direction (V_3-linear 1), which is constructed by the vanadium atoms 1, 2, and 3 in top layer of V(110) substrate shown by Fig.4, where the distance between two adjacent atoms is 2.622 Å. The second one is the array in the [1 1] direction and distance between two adjacent atoms is 3.028Å(V_3-linear 2), which is constructed by the vanadium atoms 1, 4, and 5 shown by Fig.4. The third is the one in the [1 -1] direction and the atomic distance is 4.283 Å, but the atoms are too far apart and then this cluster was excluded from inspection. Hereafter, the first two types of linear clusters are denoted as linear model 1 and 2, respectively.

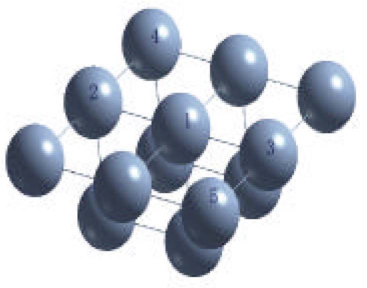

Fig. 4. Another view of the two-layer slub of V(110)

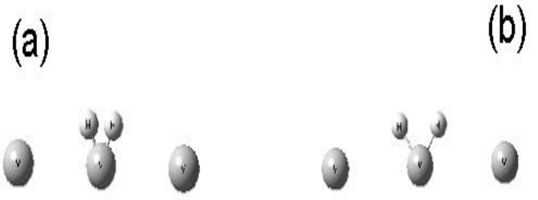

Fig. 5. Adsorption of a hydrogen molecule on on-top sites of linear V_3 cluster

It should be mentioned here that the two hydrogen atoms are in the same plane including the three vanadium atoms for all of V_3 clusters mentioned above. The adsorption of hydrogen molecule by the linear model-1 (a) and -2 (b) are decribed by Fig. 5.

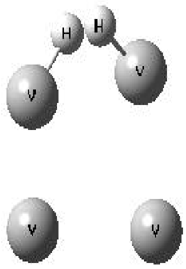

Fig. 6. Adsorption of a hydrogen molecule on a bridge site of V_4 cluster

In the V_4 model as shown by Fig.2, there are two vanadium atoms (1 and 4) in [1 0] direction at the top-layer and two atoms (3 and 5) in [0 1] direction at the second layer, and the distance between two vanadium atoms in the same layer is 2.622 Å. The line connecting the center of the former and the center of the latter is perpendicular to the (110) surface, and the angle between the plane perpendicular to the surface decided by the former and the plane perpendiculat to the V(110) surface decided by the latter is 70.53 degree. In this case, two hydrogen atoms and the two vanadium atoms at the top layer were assumed to be in the same plane, as shown by Fig. 6.

2.2.2. V-Ti alloy

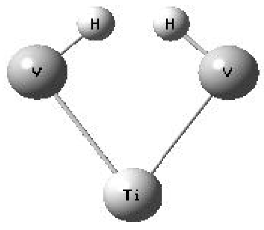

Fig. 7. Adsorption of a hydrogen molecule on a bridge site of V_2Ti or VTi_2 cluster

For the adsorption of hydrogen by V-Ti alloy, it was assumed that a 50%V-50%Ti alloy has the same crystal structure and lattice constant as those of V. The cluster models adopted here were V_2Ti and VTi_2. As for the former (schematically drawn in Fig.7), a hydrogen molecule was assumed to be adsorbed via the brdige site consisting of two adjacent V atoms, and for the latter via the brdige site comprising two adjacent Ti atoms. These clusters correspond to the model of V_3 shown in Fig.3. In the present study, however, only the adsorption for the latter is reported.

2.2.3. Vandadium oxide

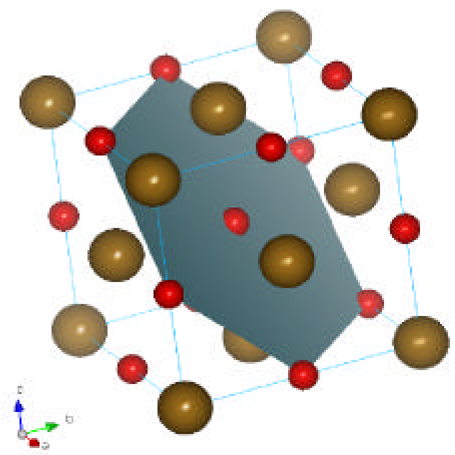

Fig. 8. The NaCl structure of VO with a Miller plane (111)

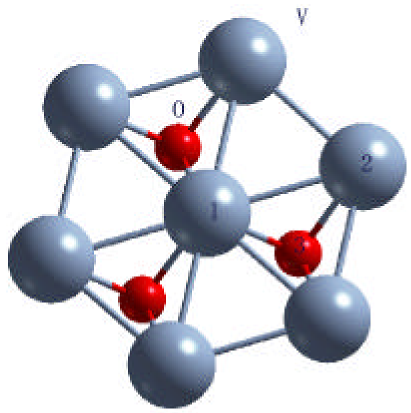

Fig. 9. Arrangement of V- and O-atoms in a two-layer slab of VO(111)

The VO(111) surface was examined for the adsorption by VO of NaCl structure shown by Fig.8, for which the V_2O and VO_2 clusters were adopted as models. The former, which is constructed by two vanadium atoms 1 and 2 in the first layer and one oxgen atom labeled by 3 as shown by Fig.9, assuming that the adsorption takes place on vanadium sites.

In this case (V_2O), hydrogen atoms are not in the plane decided by the two vanadium atoms and the one oxygen atom as seen in Figs.9 and 10. The angle between the plane decided by V_2-H-H and the plane decided by V-V-O is 39.23 degree. The distance between two vanadium atoms is 2.894 Å, and the distance between the oxygen atoms and the center of two vanadium atoms is 1.447 Å. The VO_2 model has the same geometric structure as V_2O, as shown in Fig.9, expect that two oxygen atoms come at the tope layer, and a vanadium atom is at the second layer.

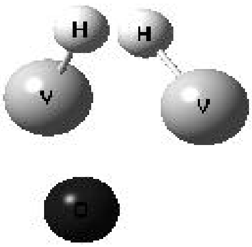

Fig. 10. Adsorption of a hydrogen molecule on bridge sites of triangular V_2O cluster

But the calculation for the latter, which has two oxgen atoms in the first layer and one vanadium atom in the second layer of VO surface, did not converge well, and then the result is not described here.

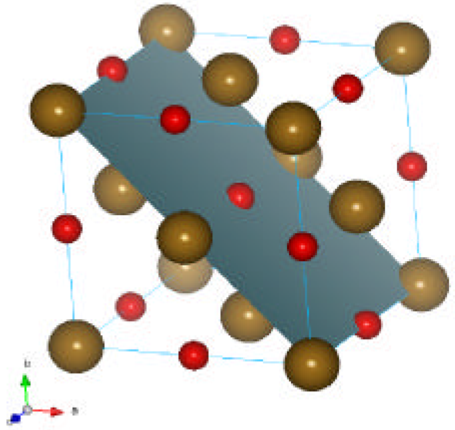

Fig. 11. The NaCl structure of VO with a Miller plane (110)

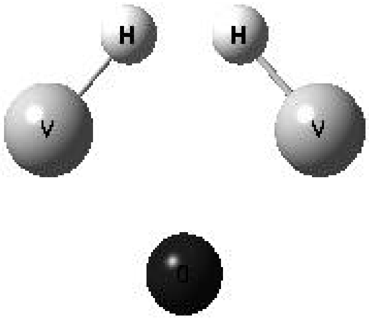

Fig. 12. Adsorption of a hydrogen molecule on a bridge site of triangular V_2O cluster for modeling VO(110)

In addition to VO(111), the adsorption of hydrogen on VO(110) was also studied by scanning the PES of the systems consisting V_2O and two hydrogen atoms. The VO(110) surface is shown by Fig.11, in which vanadium atoms 1, 2 in the first layer and oxygen atom 3 in the second layer is modelled to V_2O model(VO-V_2O(110)). In this system, all atoms are in a plane, i.e. the plane containing two vanadium and one oxygen atoms, and two hydrogen atoms is perpendicular to the surface. Figure 12 shows the parallel approach of a hydrogen molecule to the bridige sites of V_2O cluster for VO(110).

3. Results and discussion

As mentioned above, for all of the models two dimensional PESs were calculated by Gaussian 03; namely, the energy was evaluated as a function of the distance between two hydrogen atoms and the height of the center of two hydrogen atoms from the surface, where the geometry of the substrate was set invariable throughout the PES calculation. Some of them are presented in this section as examples. Figure 13 represents the 3D- (a) and contour (b) mapping of the PES for V(110) by Model 1, the parallel approach of H_2 on the trianglular V_3 cluster shown in Fig.3, where `Half rHHx` is the half of the distance betweem two H-atoms, `Height` indicates the distance between the center of the H-H bond and the surface, both in Åunit, and `E` is the energy in the Hartree unit. It was found that the activation and adsorption energies were 0.106 eV and -0.454 eV, respectively. Figures 14 shows the PES of the adsorption of hydrogen molecule via the on-top site of V_3 linear model 1 with H_2 oriented parallel to the V(111) surface, for which the resulted activation

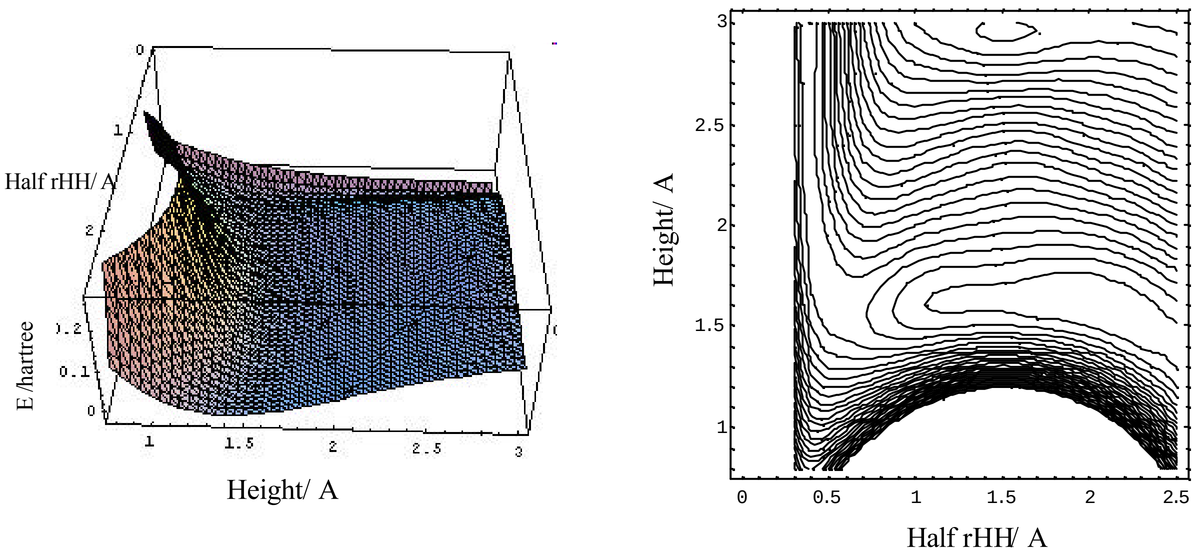

Fig. 13. 3D- and contour-mapping of the PES for triangular V_3 cllluster shown by Fig.3

and adsorption energies are 0.083 eV and -1.288 eV, respectively. Fig.15 shows the PES for the hydrogen adsorption via the bridege site of V_2O clulster modeling with H_2 oriented parallel to the VO(111) surface, in which the resulted activation and adsorption energies are 0.638 and -0.407 eV, respectively.

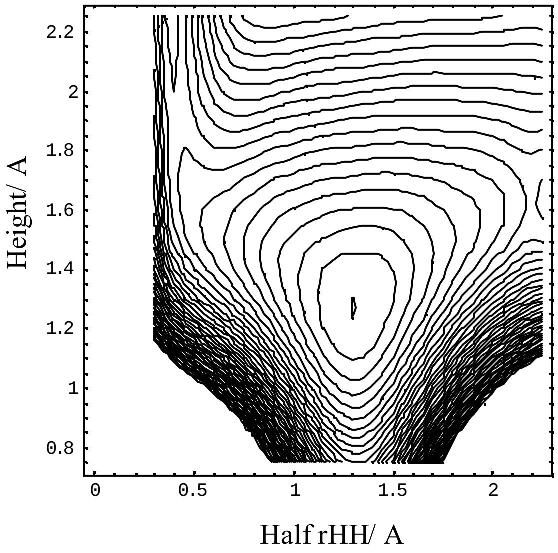

Fig. 14. Contour map of the PES for V_3-linear 1 shown by Fig.5 (a)

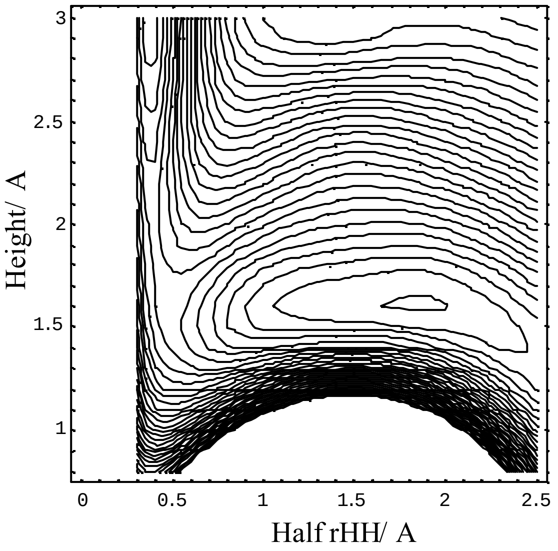

Fig. 15. Contour map of the PES for V_2O cluster shown by Fig.10

Although other PES's for other cluster models will not be shown here, calculated activation and adsorption energies are summarized in Table 1 along with their structures. As seen in the table, the hydrogen adsorption on the V(110) surface requres relatively small activation energies about 0.1 eV or below as seen for triangular V_3 and V_3-linear 1 models, but the adsorption via the on-top site of V_3-linear 2 does not likely occur because of a noticeably higher activation energy. It should be mentioned here that the adsorption via the bridge site of V_4 gave very similar activation energy with that for the triangular V_3 cluster along with the similarity of adsorption energy, although the structures of activated and adsorbed states differ a little from those for triangule V_3 cluster. As for the alloying with Ti, the activation enery for Ti_2V cluster seems a little higher than that for triangular V_3, although the structure of activated complex is very similar to that of triangular V_3. These results suggest that hydrogen adsorption on V(110) surface takes place most likely via the bridge site or the on-top site of the atomic array in [01] direction, and the alloying with Ti does not change significantly the activation energy. Further details in the activation energy as well as heat of adsorption, however, should be compared by calculations applying much larger clusters.

Table 1. Energies and structures of activated and adsorbed states for different clusters; calculated with `scf=(Vshift=200,conver=8,xqc,Fermi,maxcycle=600)`

Cluster	Activated state			Adsorbed state		
	Energy(eV)	Half-rHH(Å)[a]	Height(Å)[b]	Energy(eV)	Half-rHH(Å)[a]	Height(Å)[b]
V_3-triangle	0.11	0.60	1.60	-0.45	2.05	1.60
V_3-linear 1	0.08	0.42	1.95	-1.29	1.31	1.31
V_3-linear 2	0.29	0.42	1.86	-1.22	1.53	0.76
V_3-Ti_2V	0.16	0.60	1.65	-0.41	2.12	1.70
V_4	0.07	0.44	1.65	-0.41	1.90	1.60
V_3-V_2O[c]	0.66	0.53	1.55	-0.23	2.21	1.53
VO-V_2O(110)	0.78	0.53	1.75	-0.24	1.73	1.72
VO-V_2O(111)	0.64	0.40	1.95	-0.41	1.76	1.65

[a]: half-length of H-H distance

[b]: height of the center of the H-H bond from the surface

[c]: pseud-oxide, where the bottom V was replaced by O of the triangular V_3 cluseter

On the contracy, considerably larger activation energies were obtained for the adsorption via the bridge sites of VO(111) and VO(110); they are 0.64 and 0.78 eV for V_2O(111) and V_2O(110) clusters, respectively. But as for the heat of adsorption, two cluster models of VO gave rather small values; they are comparative or even smaller in comparison with those observed for triangular V_3 and Ti_2V clusters, and apparently smaller than those for linear V_3 clusters. This is because the site for adsorption in this case is similarly a vanadium atom on the surface. Larger heat of adsorption can be expected for oxygen sites.

All of the above mentioned results indicate that the features of hydrogen adsorption on vadadium and vanadium covered by oxygen obtained by cluster models are in good agreement with experimental observations that the rate of hydrogen ab/adsorption by vanadium is drastically decreased with the presence of adsorbed oxygen or oxide film on the surface[2]. In addtion, it is shown that there is no significant difference among the activation energies of hydrogen adsorption on the different models, as seen for the triangular V_3 and V_4 as well as other combinations not described here. It is noted here, however, that the exact values of activation energy and the heat of adsorption along with the structures of activated complex and adsorbed speceis should be discussed by more precise calculations with periodic boundary conditions.

4. Conclusions

The adsorption of hydrogen on the surfaces of vanadium, vanadium-titatnium alloys and vanadium oxides was modeled by simple clusters comprising three or four atoms and the potential energy surfaces were calculated by ab initio calculations using Gaussian03 package. The surfaces investigated were V(110), V-Ti(110), VO(111) and VO(110), where different cluster models were adopted for some of the surfaces to examine their validities and to find an appropriate cluster model. The calculation indicated that hydrogen adsorption takes place most easily via the on-top site of the atomic array in [1 0] direction on V(110) surface, and a hydrogen atom is stably adsorbed at the midpoint between the two vanadium atoms in the array. On the other hand, the presence of oxygen on the surface will significantly hinder the adsorption owing to the notable increase in the activation energy. These features are in good agreement with experimental observations that the rate of hydrogen ab/adsorption by vanadium is drastically decreased with the presence of adsorbed oxygen or oxide film on the surface.

The present calculations also showed that simple cluster models consisting of a few atoms can give usefull information of the influence of crystal faces exposed to hydrogen, effect of alloying, and consequence of surface poisoning by oxygen, sulfer and others on hydrogen adsorption by metals. However, more accurate geometric models are necessary to obtain precise values of activation and adsorption energeis as well as structure of activation and adsorption species.

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