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# Reactivity of Group 5 Bielement Clusters with $H_2$

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Bielement metal clusters composed of the group 5 elements, $A_nB_m$ (A, B = V, Nb, Ta), were prepared in the gas phase over the wide $n$ and $m$ ranges. We measured reactivities of the attachment reaction of the neutral clusters to $H_2$, which were plotted as a function of a map with $n$ and $m$. The clusters with $n + m = 4$ and 5 were found to be more reactive than the other clusters. The measurement of the ionization energies reveals that there is no strong correlation between the reactivity and the ionization energy. In addition, the reactivities of the cations, $A_nB_m^+$, were also highest at $n + m = 4$ and 5. These findings suggest that the electronic structure does not totally determine the reactivity of the neutral clusters. On the other hand, theoretical calculations for $A_nB_m$ ($n + m = 4$) reported by Metha et al. showed that the optimized geometrical structures of the congener group 5 bielement clusters do not change significantly by changing $n$ and $m$ within $n + m = 4$. Hence, it is highly likely that the pyramidal ($n + m = 4$) and bipyramidal ($n + m = 5$) structures of $A_nB_m$ determine the high reactivity of the clusters.

## Introduction

Metal clusters possess size-dependent chemical and physical properties. The size-dependent properties of single element clusters have been studied intensively and extensively for more than two decades.[1,2] For the multielement metal clusters, the properties depend not only on the size but also on the stoichiometry. Hence, their properties have been investigated for a limited number of clusters due to their complexity.

If one wishes to design clusters that possess a specific chemical and physical attribute, it would be better to use multielement metal clusters and tune the stoichiometry of the clusters to enhance that attribute. However, chemical and physical properties of the multielement clusters generated by mixing the single element clusters are difficult to predict, because there is no established guiding principle. For bulk metals, the Hume−Rothery rules are a set of empirical rules describing the conditions under which an element can dissolve in a bulk metal.[3] The alloy is formed, if the atomic size and electronegativity are similar and the crystal structure is same as those of the atoms of the bulk metal. The rules have been successfully used to predict the formation of bulk alloys. However, it is not known if those rules are still valid for the subnanosized small clusters, composed of 10−20 atoms, nor will the rules predict the properties of the alloys.

Experimentally, the Kaya group is among the pioneers in the research field of the bielement clusters.[4−6] They studied intensively the effect of a heteroatom, when single-element clusters are doped by another elemental atom. The main interest was applicability of the electronic shell model to alloy clusters. The Knickelbein group measured the reactivity and ionization energy of $Al_nCo_m$ clusters,[7−9] finding that there was no correlation between the ionization energy and the hydrogen chemisorption rate constant. In addition, the reactivity of the neutral clusters was similar to that of the cluster ions. Hence, they concluded that the electronic strucure is not enough to explain the reactivity.[9] The Castleman group studied bielement clusters of metal atoms and carbon atoms, finding that $M_8C_{12}$ clusters (M = Ti, V, Nb, etc.) with the caged structure showed significant stabilities when compared with the other stoichiometries.[10−13] However, the preparation of bielement clusters, $A_nB_m$, over the wide $n$ and $m$ ranges, still remains diffcult and uncommon.

In the present study, we focused on the bielement clusters composed of the group 5 (VB) elements. The reactivities with $H_2$ of single-element clusters, $V_n$ and $Nb_n$ are known to exhibit similar size dependences: The reactivity is higher at $n = 4$ and 5. The geometrical structures of the most stable clusters are also similar: $V_5$, $Nb_5$, and $Ta_5$ are known to be the trigonal bipyramids.[14,15] We pose the question; how do the chemical and physical properties change when the group 5 heteroatoms are substituted into an otherewise pure group 5 clusters? We report the reactivity of $A_nB_m$ (A, B = V, Nb, and Ta) with a hydrogen molecule in the gas phase. In addition, ionization energies of $Nb_nV_m$ were measured for all the combination of $n$ and $m$ that were prepared. The reaction mechanism for group 5 bielement clusters is disscussed.

## Experimental Section

Two metal rods were set downstream of the molecular beam from a solenoid pulsed valve (General Valve). Each rod was irradiated with a focused laser pulse (∼10 mJ/pulse) at 532 nm: one from a Quanta Ray GCR-130 and the other from a Continuum Surelite II Nd:YAG laser. We used the group 5 elements (Nb, V, and Ta) as the metal rods. The evaporated atoms by laser ablation were cooled with He gas (>99.99995%; stagnation pressure 9 atm) from the valve, forming bielement neutral clusters, $A_nB_m$ and charged cluster ions, $A_nB_m^{\pm}$. The

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clusters then entered a collision cell filled with a gas mixture of $H_2$ and He, where the clusters reacted with $H_2$. The mixing ratio of $H_2$ to He was prepared at 1 ~ 2%, with He gas used to remove excess energy from the clusters, generated upon attachment of $H_2$ to the clusters. After the collisions of He and $H_2$ in the collision cell, the clusters were introduced into a differentially pumped chamber through a skimmer. When the neutral clusters were monitored, the charged cluster ions were removed from the beam by electrodes equipped positioned immediately after the skimmer. Only the neutral clusters were allowed into the acceleration region, where they were photoionized by an ArF laser pulse at 193 nm from a MPB PSX-100 excimer laser. When charged clusters were monitored, they were introduced directly into the acceleration region. The cluster ions were accelerated by a pulsed electric field for time-of-flight mass analysis. The resolution of the mass spectrometer exceeds 1000, which allows for the observation of the attachment of light hydrogen atoms to $A_nB_m$. When the ionization energies of the neutral clusters were measured, the clusters were ionized by the second harmonic a Continuum Panther EX (216−248 nm) optical parametric oscillator. The ionization laser fluence was kept <500 $\mu$J cm$^{-2}$ to minimize multiphoton processes.

## Results and Discussions

We observed the mass spectrum of clusters with and without $H_2$ in the collision cell. The intensity of nascent $A_nB_m$ decreased and $A_nB_mH_k$ ($k$ = 2, 4) increased as a result of the hydrogen attachment reaction. From the depletion of the $A_nB_m$ intensity, we estimated the relative reactivity of the $H_2$ attachment reaction of $A_nB_m$ for all clusters observed to within an experimental uncertainty of ±20%. Figure 1a shows the relative reactivity for $Nb_nV_m$ with $H_2$ as a color code in a 2D map. As shown along the edges of the map, the size dependences of the relative reactivity in the present study for pure niobium clusters and pure vanadium clusters are very similar to those previously reported:[16−19] $Nb_4$ and $Nb_5$ are most reactive for small niobium clusters (i.e., $n < 10$), while $V_5$ is in the vanadium clusters. In the present study, we found that mixed clusters, $Nb_nV_m$ for $n + m = 4$ and 5, are also reactive with $H_2$, as evidenced by the diagonal red line in the 2D map.

Now, the first issue to be considered is, why is the reactivity highest at $n + m = 4$ and 5? It is known that, if electron donation from the neutral cluster to the antibonding state of $H_2$ initiates the hydrogen attachment reaction, the reactivity of the neutral clusters increases with a decrease in the ionization energy. In order to elucidate the reaction mechanism, we measured the ionization energies of $Nb_nV_m$ (see Table 1). Figure 2 shows the ionization energies as a bar in the 3D map. The ionization energy decreases monotonically with an increase in the total number of the atoms, $n + m$, and rather sharply at $n + m = 9$. Then, it levels off for $n + m \geq 9$. It is worth while mentioning that the ionization energy changes very gradually with $n$ and $m$ as long as $n + m$ is constant. Evidently, there is no significant decrease in the ionization energy at $n + m = 4$ or 5, where the reactivity is the highest, indicating that the electron donation from the clusters to $H_2$ is not bottleneck to the reaction.

We also measured the reactivity of cationic $Nb_nV_m^+$ with $H_2$ (Table 2).[21] Figure 3a shows the relative reactivity of the $H_2$ attachment reaction of $Nb_nV_m^+$ as a color code. There is also a diagonal red line in the 2D map showing that $Nb_nV_m^+$ at $n + m = 4$ and 5 are highly reactive. Although the electronic structure of cationic $Nb_nV_m^+$ is different from that of neutral $Nb_nV_m$, the reactivity depends on the stoichiometry of the clusters, regardless of the charge, indicating that the electronic structure does not totally determine the reactivity of the clusters.[9,17,18,24]

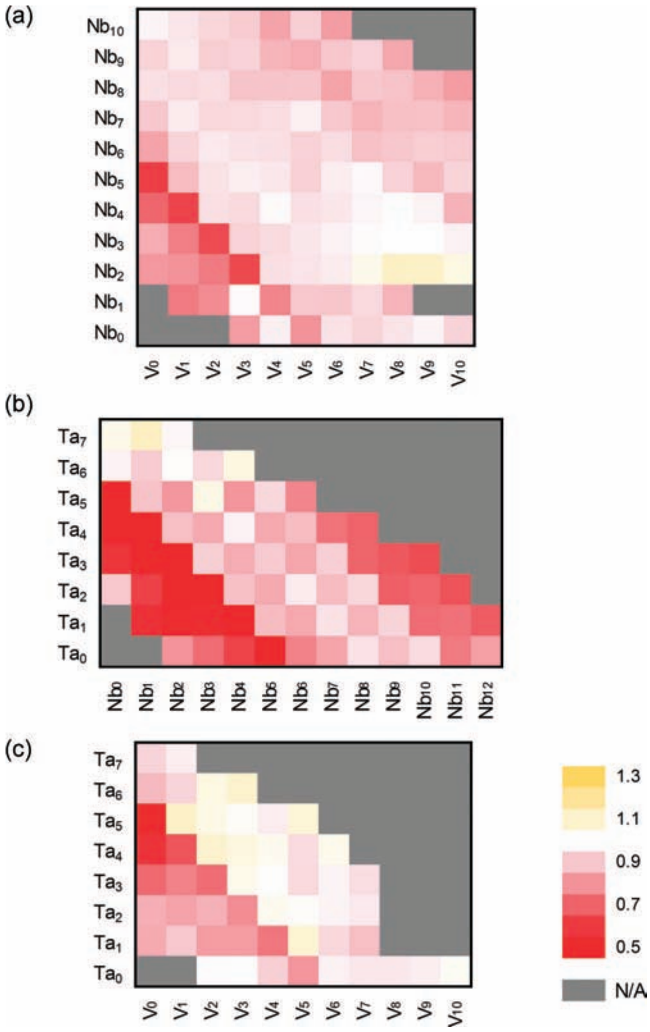

**Figure 1.** Relative reactivity for neutral bielement clusters with $H_2$ shown by a color code: (a) $Nb_nV_m$, (b) $Nb_nTa_m$, and (c) $Ta_nV_m$.

The second question to be considered is, why doesn't the reactivity to $H_2$ change drastically, when the niobium atoms in the cluster are replaced by the same number of the vanadium atoms? The replaceability must relate to the fact that niobium and vanadium are congener elements. This conjecture is supported by the observations of Nb−Ta and Ta−V clusters, which are composed of the same group 5 elements. They show similar stoichiometry dependences of the reactivity (see Figures 1b,c and 3b,c): $Nb_nTa_m^{+/0}$ for $n + m = 4$ and 5 and $Ta_nV_m^{+/0}$ for $n + m = 5$ are reactive with $H_2$, as evidenced by the diagonal lines in the maps.

Metha and co-workers calculated the lowest energy structures for pure- and mixed-metal tetramers comprised of the group 5 elements: The structures for $Nb_4$ and $Ta_4$ are tetrahedra with $T_d$ symmetry and singlet multiplicity.[25] The structures for mono-substituted tetramers, $NbV_3$, $TaV_3$, $Nb_3V$, $Nb_3Ta$, $Ta_3V$, and $NbTa_3$, are thought of as a hetroatom sitting atop an equilateral homonuclear triangle, whereas the structures for $Ta_2V_2$ and $Nb_2V_2$ are almost tetrahedral, and $Nb_2Ta_2$ has an open *arachno* structure. In addition, a trimetallic cluster, $NbTaV_2$, was found to have a closed almost tetrahedral structure with all bond lengths being 2.3−2.5 Å. These calculations suggest that atoms of the group 5 elements tend to mix together, and the mixed-metal clusters do not change significantly from the geometrical structures of the pure clusters.

**TABLE 1: Ionization Energies, $E_i$ (eV), Observed for $Nb_nV_m$[a]**

| | | Nb | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| V | 0 | | | | 5.79(0.06) | 5.60(0.05) | 5.40(0.06) | 5.33(0.06) | 5.33(0.06) |
| | 1 | | >5.74 | 5.70(0.10) | 5.46(0.05) | 5.41(0.05) | 5.39(0.05) | 5.30(0.05) | 5.3(0.1) |
| | 2 | | 5.64(0.05) | 5.40(0.05) | 5.43(0.05) | 5.40(0.05) | 5.32(0.05) | 5.30(0.08) | 5.1(0.1) |
| | 3 | 5.49(0.05) | 5.55(0.05) | 5.42(0.05) | 5.35(0.05) | 5.28(0.05) | 5.30(0.10) | 5.10(0.12) | 5.05(0.15) |
| | 4 | 5.63(0.05) | 5.43(0.05) | 5.34(0.05) | 5.27(0.05) | 5.30(0.03) | 5.05(0.05) | 5.08(0.12) | 5.0(0.1) |
| | 5 | 5.47(0.05) | 5.40(0.05) | 5.23(0.05) | 5.30(0.05) | 5.03(0.08) | 5.10(0.08) | 5.04(0.12) | 5.0(0.1) |
| | 6 | 5.37(0.05) | 5.25(0.05) | 5.28(0.05) | 5.07(0.08) | 5.0(0.1) | 5.02(0.08) | 5.0(0.2) | |
| | 7 | 5.24(0.05) | 5.30(0.05) | 5.06(0.06) | 5.0(0.1) | 5.0(0.1) | 5.0(0.1) | | |
| | 8 | 5.30(0.05) | 5.15(0.08) | 5.06(0.08) | 5.0(0.1) | 5.0(0.1) | | | |
| | 9 | 5.18(0.06) | 5.1(0.1) | 5.0(0.1) | 4.9(0.1) | | | | |
| | 10 | 5.15(0.06) | 5.0(0.1) | 5.0(0.1) | 4.9(0.1) | | | | |
| | 11 | 5.0(0.1) | 4.9(0.1) | 4.9(0.1) | | | | | |
| | 12 | 5.1(0.1) | 4.9(0.1) | 4.9(0.1) | | | | | |
| | 13 | 4.9(0.1) | 5.0(0.1) | | | | | | |
| | 14 | 5.0(0.1) | | | | | | | |
| | 15 | 4.9(0.2) | | | | | | | |

[a] Values in parentheses are estimated experimental errors.

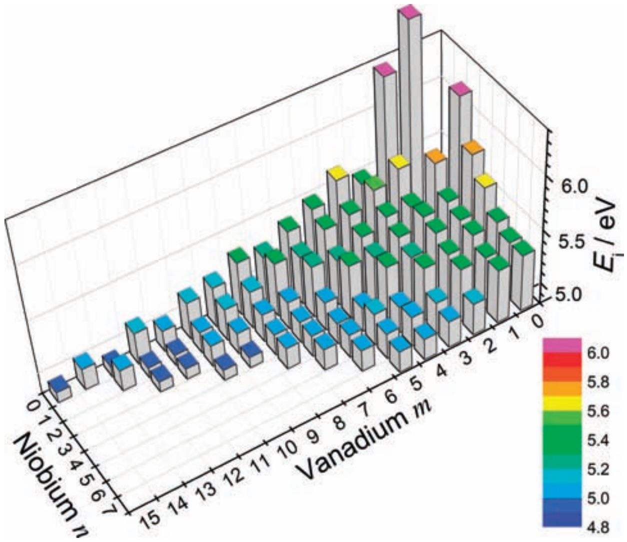

**Figure 2.** Ionization energy of $Nb_nV_m$. For Nb, $Nb_2$, and $V_2$, reported values are used.[20]

**TABLE 2: Rate Constants for the Reactions of $Nb_nV_m^+$ with $H_2$ Normalized to the Rate Constant of $Nb_2V_2^+$**

| | | V | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
| Nb | 0 | | | | 0.6 | 1.0 | 1.0 | 0.7 |
| | 1 | | | 0.5 | 1.1 | 0.9 | 0.2 | |
| | 2 | 0.4 | 0.5 | 1.0 | 0.7 | 0.1 | | |
| | 3 | 0.3 | 1.0 | 0.8 | 0.4 | | | |
| | 4 | 1.5 | 1.3 | 0.7 | | | | |
| | 5 | 1.8 | 0.9 | | | | | |
| | 6 | 0.9 | 0.2 | | | | | |
| | 7 | 0.4 | | | | | | |

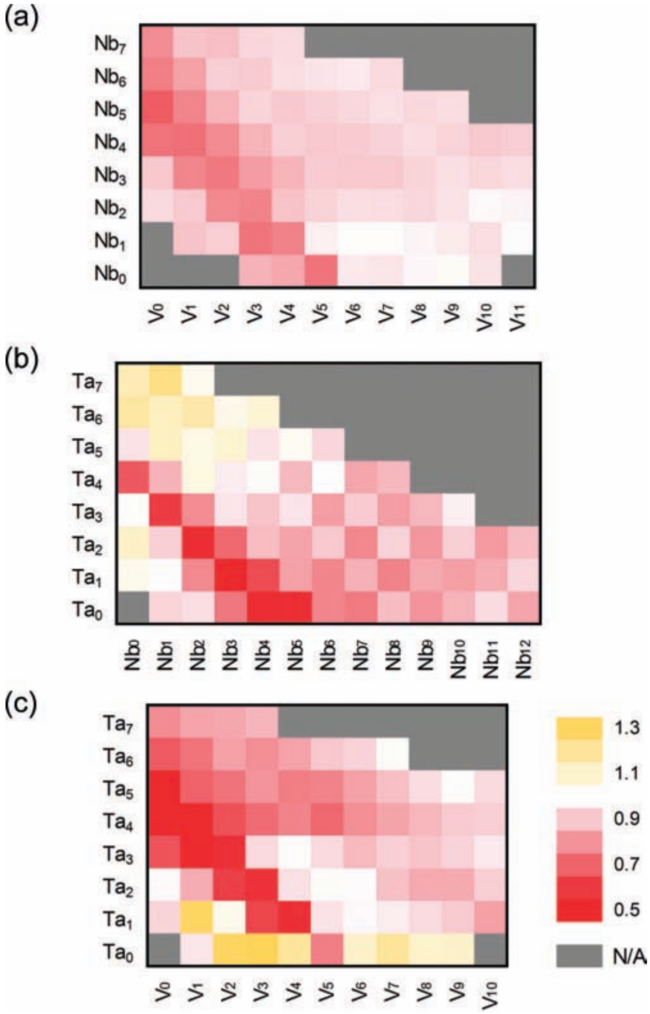

**Figure 3.** Relative reactivity for cationic bielement clusters with $H_2$ shown by a color code: (a) $Nb_nV_m^+$, (b) $Nb_nTa_m^+$, and (c) $Ta_nV_m^+$, respectively.

According to the Hume–Rothery rules for alloy formation of bulk metals, it is important to compare the electronegativity and the atomic radius of the elements forming multielement compounds. The electronegativity (Pauling) of the V, Nb and Ta atoms are 1.63, 1.60, and 1.50, respectively, while and the atomic radius (Slater) of the V, Nb, and Ta atoms are 135, 145, and 145 pm, respectively. It is highly likely that these similar values allow for the ready substitution of atoms for the group 5 elements. Indeed, Nb and Ta which have the same atomic radii are the best combination in terms of the reactivity. The maps of the Nb–Ta clusters (see Figures 1b and 3b) exhibit clear diagonal lines, suggesting that the different clusters with the same $n + m$ value have a similar reactivity to $H_2$. This finding suggests that $n + m$ is a good number to describe the properties of the Nb–Ta clusters.

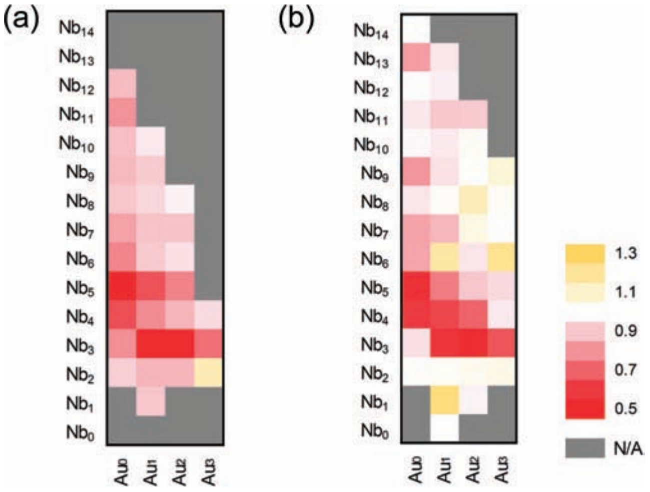

**Figure 4.** Relative reactivity for bielement clusters with $H_2$ shown by a color code: (a) $Nb_nAu_m$ and (b) $Nb_nAu_m^+$, respectively.

On the other hand, Au with the electronegativity of 2.54 is not in the same group of V, Nb, and Ta according to the Hume−Rothery rules. We measured the reactivity of the mixed cluster, $Nb_nAu_m^{+/0}$, with $H_2$, and found that stoichiometry dependence is different from that of the group 5 bielement metal clusters (see Figure 4): $Nb_nAu_m$ with $n = 3$ and 5 are reactive regardless of $m$, although $Nb_3$ is not so reactive. There is no explicit diagonal line in the map. It seems that gold atoms behave as the spectators in $Nb_nAu_m$ as well as promoters of the reaction. The role of the Au atoms is an issue for further investigation.

To conclude, we prepared group 5 bielement clusters in the gas phase over a wide range in stoichiometries. The reactivity of the neutral clusters with a $H_2$ was measured for each cluster with a different stoichiometry, and was plotted on a 2D map. The clusters $A_nB_m$ (A, B = V, Nb, Ta) for $n + m = 4$ and 5 were found to be highly reactive for the every combination of group 5 elements. The stoichiometry dependence of the reactivity of $Nb_nV_m$ does not correlate with the ionization energy and is quite similar to that of cationic $Nb_nV_m^+$. On the other hand, it is known that the geometrical structure of the mixed clusters does not change by substitution of the elements according to theoretical calculations. Hence, we concluded that the specific geometrical structure of the group 5 bielement clusters is more responsible for the reactivity than the electronic structure.

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