Prospect of Activating a Photocatalyst by Sunlight - A Quantum Chemical Study of Isomorphically Substituted Titania

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DV-X_α calculations indicated the possibility of shifting the absorption edge of titania to the sunlight region by isomorphic substituting of a transition metal cation for a titanium ion. Among the cations addressed here, Ni^{3+} and V^{5+} reduced the band gap most effectively. The efficiency of the reduction by the substituting cation increased as the radius of the cation decreased.

Titania (titanium dioxide) is used for many industrial purposes such as a pigment, drug, ceramic material, etc. Recently, its applications as a photocatalyst are expected, especially to decompose or detoxify various pollutants by sunlight.[1] Titania, however, can absorb only ultraviolet wavelengths shorter than 380 nm, so that its activity as a photocatalyst is low under sunlight.[2] Anpo et al.[3] reported that they could shift its absorption edge to the visible light region by the ion-implantation of some transition metals in titania bulk. They also confirmed that its photocatalytic activity for the de-NOx reaction under sunlight was promoted by this ion-implantation.[4] The method is, however, so sophisticated that these catalysts may be too expensive to be widely used.

In order to develop a titania-based photocatalyst which can be activated by sunlight, we are trying to modefy titania by the isomorphic substitution method, a conventional method used to prepare solid acid catalysts. As a part of this study, we examined a variation in the band gap of titania by substitution of a transition metal for the titanium ion in anatase or rutile, using the DV-X_α method.[5] Anpo et al.[6] have reported that the isomorphic substitution of V^{4+} or Cr^{3+} occured in the titania implanted with the ion. However, the order of the shift efficiency of most transition metal ions is not yet presented.

Figure 1 shows two calculation models made from the XRD data[7] of two kinds of titania crystals. Clusters of $Ti_{13}O_{50}$ and $Ti_{15}O_{56}$ were used for models of anatase and rutile, respectively. Charge numbers of these clusters were -48 for the former and −52 for the latter. Madelung potentials (+4 for Ti^{4+} and −2 for O^{2-}) at 6954 and 7010 points were used for the calculations of anatase and rutile, respectively, to cancel these charges of the clusters and stoichiometric discrepancy of the models from TiO_2. Titanium ion at the center of the model was substituted by transition metal ions such as V^{3+}, V^{4+}, V^{5+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{2+}, Ni^{3+}, and Rh^{3+} having a similar radius to the titanium ion, without adjusting the total charge number of the model. These ions were thought to be isomorphically substitutable for the ion. The DV-X_α program used for the calculation was Program SCAT provided by the Society for Discrete Variational X_α. The computer used was a Dimension XPS D333 model (Dell Computer Corporation) installed with Windows 98 (Microsoft Corporation).

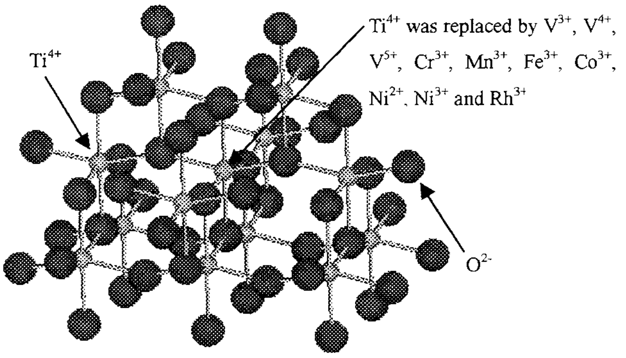

Figure 1(a). Calculation model of anatase.

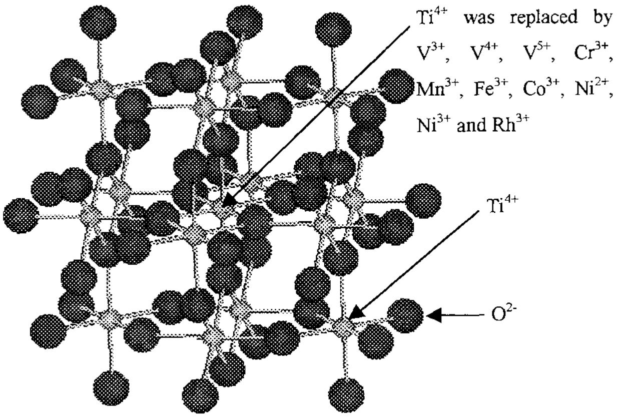

Figure 1(b). Calculation model of rutile.

Figure 2 shows the energy level diagrams calculated for the models of anatase and of the isomorphically substituted one with Mn^{3+} and V^{5+}. A solid line denotes the level occupied by one or two electrons and the broken line is the unoccupied level. To the right side of the energy level, the contribution of an atomic orbital, specified at the bottom of the column, toward the molecular orbital is indicated by the line length. For the model of anatase, it was found that the major component of HOMO near 0.7 eV was the 2p orbital of oxygen and that of LUMO near 4.3 eV was the 3d orbital of titanium. Thus, the band gap for anatase, which was thought to be the difference between HOMO and LUMO, is 3.67 eV. For rutile, the band gap was similarly obtained as 3.29 eV. These values are greater than the experimental ones in the literature[8] (3.23 and 3.02 eV for anatase and rutile, respectively), but they are thought to be within a reasonable error for the quantum chemical calculations and should be improved if we adopt larger clusters.

For isomorphically substituted titania, on the other hand, a new energy level due to the substituting metal cation was ob-

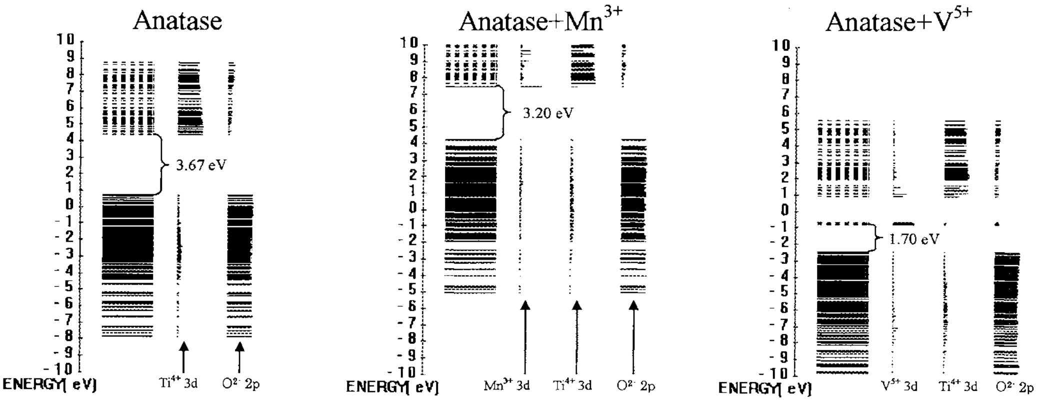

Figure 2. The energy level of anatase, anatase+Mn^{3+} and anatase+V^{5+}

served near the 3d(Ti) level except for Ni^{3+} and V^{5+}. The major component of the new orbital was the 3d or 4d orbital of the cation. The level was containing 0, 1 or 2 electrons. In case of 1 or 2 electrons, the level will make a weak isolated band in the long wavelength region on the basis of excitation from the level, since the concentration of the substituting metal cation is very low. Therefore, in the same manner for the original titania, the band gap for the substituted one is thought to be the difference between the new level and that of the 2p orbital of oxygen. The difference between the two band gaps of the substituted and the original titanias are listed in Table 1.

Table 1. The change of band gap with anatase and rutile after substituted by transition metal ions

Centered metal ion	Ionic radius/ Å	Band gap/eV	
		Anatase	Rutile
Ti^{4+}	0.75	0.00	0.00
Ni^{2+}	0.83	-0.69	-0.23
Rh^{3+}	0.81	-0.26	+0.12
Fe^{3+}	0.79	-0.41	-0.06
Mn^{3+}	0.79	-0.47	-0.12
V^{3+}	0.78	+0.11	+0.23
Cr^{3+}	0.76	-0.20	+0.16
Co^{3+}	0.75	-0.50	-0.38
Ni^{3+}	0.74	-1.22	-1.21
V^{4+}	0.72	-0.30	-0.45
V^{5+}	0.68	-1.97	-2.68

As seen from the table, the band gaps are mostly decreased by the isomorphic substitution for both crystal types. The order of the shift efficiency of the transition metal ions for anatase are as follows: $\mathrm{V^{5+}>Ni^{3+}>Ni^{2+}>Co^{3+}>Mn^{3+}>Fe^{3+}>V^{4+}>Rh^{3+}>Cr^{3+}>V^{3+}}$. V^{5+} and Ni^{3+} exhibited such unusually large effects as -1.22 and -1.97 eV for anatase and -1.21 and -2.68 eV for rutile, respectively. These values seem to be too large, and it is likely caused by our neglecting structural deformation of the models, resulted from the substitution of ions.

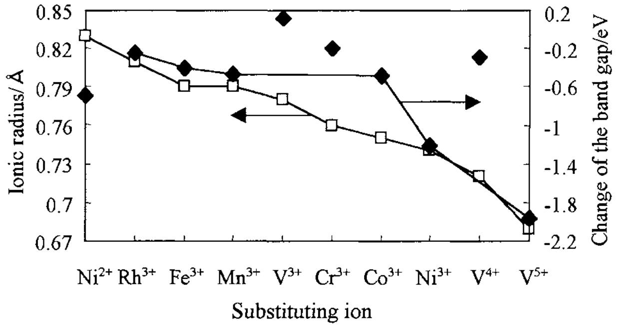

Figure 3. The relationship between the ionic radius and the change of the band gap (anatase).

Figure 3 shows the relation between ionic radii of the transition metals and the decreases in the band gaps. Except for some cations, we can see that the band gap decreases with decreasing the cation size. In fact, we could confirm that a decrease in the size increases the covalent bond character between the cation and the oxygen (as Fajans' rule tells us), so that it will probably increase the interaction of the 3d or 4d orbital of the metal and the 2p orbital of the oxygen. Unfortunately, structural optimization of the substituted models was not carried out because the DV-X$_\alpha$ method does not give the total energies with enough accuracy. We believe the optimization of the model will give more reasonable results for Cr^{3+}, V^{4+}and Ni^{2+}.

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