# Orbital Correlation Diagram for Understanding Surface Reactions

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In this talk, an orbital correlation diagram is proposed for the purpose of understanding and predicting a surface reaction. To deal with the electronic structure of a surface, one may need to rely on a cluster model or a surface slab model. Band (crystal) orbitals calculated at the Γ point in the reciprocal space for the unit cell of the slab model with periodicity are found helpful for the construction of the correlation diagram. By using the diagram thus established, the C–H bond activation reaction of methane on an $IrO_2$ surface is investigated. The energy level of the $d_{z2}$ orbital of a coordinatively unsaturated Ir atom in the surface is found to be important for determining the activation barrier of the reaction. The activation energy can be reduced by lowering the energy level of the $d_{z2}$ orbital. Conversely, a rise in the energy of the $d_{z2}$ orbital leads to an increase in the activation barrier. To make the $d_{z2}$ orbital energy change, the concept of mixed-anion compounds is adopted. The replacement of an oxide with a different anion allows one to tune the crystal field splitting of metal oxides. $IrO_2$ doped with F as an axial ligand yields a lower-lying $d_{z2}$ orbital level, while the orbital goes up in energy when $IrO_2$ is doped with N. This trend is consistent with what is expected from the electronegativity of each dopant. A perfect inverse linear correlation is found between the activation energy of the reaction and the electronegativity as shown in Figure 1. By changing the dopant, one may have control over the reactivity of $IrO_2$.[1)]

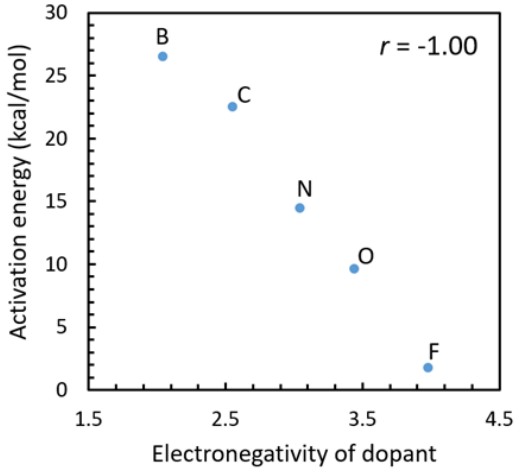


**Figure 1.** The activation energy of C-H bond dissociation of methane on doped $IrO_2$ is plotted as a function of the electronegativity of the dopant (Pauling's scale). *r* denotes the Pearson's correlation coefficient. O corresponds to the undoped system.

1) Tsuji, Y.; Yoshizawa, K. *J. Phys. Chem. C* **2020**, *124*, 17058.