

A Density-Functional Theoretical Study of Self-regenerating Catalyst

LaFe_{1-x}M_xO₃ (M=Pd, Rh, and Pt)

自己再生触媒 LaFe_{1-x}M_xO₃ (M=Pd, Rh, Pt)に関する第一原理計算による研究

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The growth of metal particles is one of the main reasons of catalyst degradation in the three-way catalyst. Pd containing perovskite catalysts such as LaFe_{0.95}Pd_{0.05}O₃ exhibit excellent durability by suppressing the sintering effect and they can reduce the amount of precious metals dramatically by 70-90%. The perovskite catalysts display quite peculiar behavior. Pd nano-particles are self-regenerated during catalytic reactions by reversibly moving into and out of the perovskite lattice depending on the fluctuations between the oxidative and reductive atmosphere in the emissions. It was concluded that Pd forms a solid-solution with the LaFeO₃ perovskite crystal and partially occupies the Fe site in the oxidative atmosphere, while Pd segregates to form metal particles in the reductive atmosphere. It is very desirable to clarify the mechanism of the self-regeneration of the perovskite catalysts in order to design new ageless catalysts. In this study, we propose a possible scenario of the self-regeneration of precious metal catalyst based on our density functional theory calculations within a generalized gradient approximation.

Phase diagrams and the CALPHAD method for energy materials

カルファド法と状態図のエネルギー材料への適用

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Abstract

Using various thermodynamic quantities of stable / metastable phases obtained

from both the first-principles calculations and experiments, the Gibbs free energy of phases is thoroughly assessed based on simple but adequate thermodynamic models such as the regular solution model and the sublattice model. This procedure is called thermodynamic assessment or CALPHAD (Calculation of Phase Diagrams) method. Since it is based on the thermodynamic models, for extrapolations to temperature, pressure, and compositions (multi-component systems), it provides a good estimate of thermodynamic quantities (Gibbs free energy, heats of reactions, formation enthalpy, specific heat, etc. for the stable and the metastable phases) within the accuracy of the model. Thus, the assessed Gibbs free energy is one of important parameters for dynamic simulations such as phase field method. In this presentation, it will be given an introduction of CALPHAD method, which includes its brief history, various applications, and current/future problems.

First-principles MD study on water structure and redox reactivity of
TiO₂ anatase / water interfaces

「二酸化チタン／水界面における水の構造と酸化還元反応性」

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Abstract

We have investigated the interface properties of the TiO₂ anatase (101) and (001) surfaces "soaked in bulk water" by first-principles density-functional molecular dynamics simulations, aiming at elucidation of photocatalytic reaction mechanism on TiO₂ nanoparticle interfaces in the real working conditions.

We confirmed that only molecular adsorption of water is observed on the (101) surface, while the dissociative adsorption is dominant on the (001). Furthermore we found a novel adsorption structure owing to the presence of bulk water. We then demonstrated "strong and weak hydrogen bonds (HBs)" on the anatase interfaces on the atomic scale. These two types of HBs are in good agreement with the solid-state ¹H-NMR experiment.

We also calculated averaged electronic states in the equilibrium trajectories of the interfaces between TiO₂ anatase (101) and (001) surfaces and bulk water, where many water molecules already adsorb on the surfaces. We found a quantitative difference between them, which may affect the redox reactivity on each surface.

These works are done in collaboration with Dr. M. Sumita (MANA) and Dr. C. Hu (Tokyo Univ. Science). In the talk, the other on-going projects in my group will be introduced.