Topics

Application of Molecular Orbital Calculation for Analysis of Adsorption State on Supported Noble-Metal-Particle Catalysts

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Recently, trends in research on theoretical computation at the molecular level are changing. Molecular computation has thus far pursued the expansion of the computation scale by developing the theory and method and improving computer performance. Now there are signs that effective computational forecasting can be done by developing models with an awareness of the hierarchyin the nature. Substances, which look homogeneous to the naked eye, can be observed as groups of atoms through a high-resolution electron microscope. The problem is the composition of a material that looks different depending on the scale of the space under observation. In other words, new trends are aimed at creating an effective method of forecasting physical properties of material by combining organically characteristic methods in several scales of space. Standard computation methods are being sought in several systems of materials[1, 2].

Supported noble-metal-particle catalysts are materials consisting of noble metal particles of several dozens to several hundred A in grain diameter supported by a support of porous oxides. They are typical examples of materials whose physical properties are characterized by the electronic state of the admolecules, the supported state of the noble metal particles, the porosity of the support and other hierarchical structures. It is impossible to discuss the grain size and support effects of admolecules in the electronic state using conventional methods. This paper introduces a computational model we developed by being aware of the above-mentioned hierarchy, and presents the results of evaluation using this model to determine the dependence of vibration frequency in CO, Here, the on-top adsorption of CO molecule on Pt particulate surface is investigated, on the grain diameter and dielectric constant of the support.

Fig. 1 shows the computation model. We determined image charges so that the boundary conditions at which the electrostatic potential on the surface of a hemispherical metal conductor and on the surface of a planar dielectric substance become equal and in continuity with the vacuum side.

We calculated the electronic state of PtCO using an originally-coded molecular orbital computation program (density functional method + effective core potential method). From this, we estimated the electrostatic induction energy based on the above-mentioned model using the gross charge of C and O obtained and corrected the energy of the PtCO molecule.

Fig. 2 shows the analytical results of the vibration frequency shift of CO. We also show the results of an experiment[3] conducted with Rh particulates supported by alumina after adding 26 cm^{-1} to the value. The figure shows well the trends in changing vibration frequency shift to grain diameter. In addition, the figure shows that a observable support effect appears depending on the difference of the dielectric constant of the support.

The model used in the present study is a classical

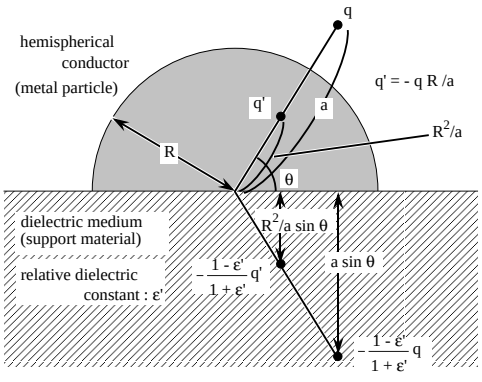

Fig. 1 Model for electrostatic induced-energy calculation (hemispherical conductor model). q: charge of an atom of adsorbed molecule. a: distance between the position of charge q and the center of hemispherical conductor. θ: polar angle of the position of charge q. R: radius of hemispherical conductor. ε': relative dielectric constant of support material.

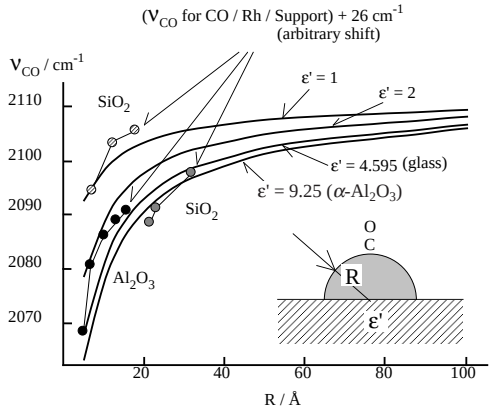

Fig. 2 Dependence of adsorbed CO molecule vibrational frequency, ν_{CO}, on particle radius, R, and relative dielectric constant of support matrial, ε', for supported Pt particle system.

electromagnetic model preconditioned on a uniform conductor and dielectric. Therefore, justifiability is lost as the grain diameter approaches atomic size. Conversely, we can expect better approximation as the grain diameter increases. Therefore, we can state that this model is ideal for an area we failed to examine using conventional methods. Computation of the electronic state in an uneven field was realized by burying adsorbent particulates in an environment that is calculated by the classical electromagnet method.

An example of particulate computation, which was thus far impossible, has been introduced by combining the computational methods in different spatial scales. It is thought that such computation procedures may rapidly increase in importance in the future for calculating the physical properties of materials.

References

1) NEOD "High Performance Material Design Platform" Project (generally called ‘DOI Project’, 1998 to 2001, studies on polymer materials).

2) Nakano, A., Kalia, R.K. and Vashishta, P.: "Introduction of Trends in Studies on Ceramics and Semiconductor Systems." Solid-state physics, 35-1(2000), 1-12

3) Mori, Y., Mori, T., Miyamoto, A., Takahashi, N., Hattori, T., and Murakami, Y.: J. Phys. Chem., 93(1989), 2039

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