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HYDROGENATION OF ETHYLENE ON SMALL PALLADIUM PARTICLES

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Activation energy for hydrogenation of ethylene on small palladium particles, which were prepared by vacuum evaporation of palladium onto a graphite plate, has been revealed to decrease with decreasing palladium particle size.

Model catalysts which are prepared by vacuum evaporation of metals onto flat substrates, such as mica sheet, SiO_2 film, carbon film (C), and Al_2O_3 film have been used to reveal the catalytic or adsorptive properties of supported metal catalysts.1-4) These catalysts can offer clean surfaces with high densities of particle number adoptable to measurements by UPS (ultraviolet photoelectron spectroscopy) and other techniques using UHV system. In the previous papers, the authors have reported that the activation energy for H_2-D_2 exchange reaction on Pd/C,3) Pd/SiO_2,5) and Pd/mica6) catalysts decreased with increasing palladium particle size. Moreover, we have shown the UPS valence band spectra of Pd/$SiO_2$7) and Pd/Gr (graphite)8) model catalysts.

In the present study, the properties of palladium model catalysts for hydrogenation of ethylene have been examined in order to reveal whether any effect of palladium particle size should exist or not.

The graphite plate support (10 mm x 10 mm x 1 mm) was prepared by cutting high-purity polycrystalline graphite rod (Nippon Carbon Co. EG-36H). After polishing with an emery paper and washing in acetone, the surface of the support was smoothly planed with a clean edge of a slide glass. Preparation of Pd/Gr model catalysts and subsequent catalytic activity measurements were performed in an ion-pumped glass UHV system as described elsewhere.5) Palladium particles were obserbed by TEM (transmission electron microscopy) after the catalytic activity measurements, and three examples are shown in Fig.1. The particle size was controlled by the amount of palladium evaporated. Neither any heat-treatment in vacuum nor in hydrogen was done after the evaporation of palladium onto the graphite plate. The palladium islands did not so homogeneously distributed over the polycrystalline graphite plates, compared with the cases of Pd/C, Pd/SiO_2, and Pd/GC (glassy carbon).9) The reaction process of the hydrogenation of ethylene was followed with a quadrapole mass-filter (Spectrum Scientific, SM-800) connected to the reaction cell which was described in a previous paper.5) The rate constant was calculated as follows.

If the hydrogenation of ethylene obeys a first order law for hydrogen pressure, the rate constant k is given by

$$k = (1/t)\ln(P^{\circ}_{H_2}/P_{H_2}), \qquad (1)$$

where $P^{\circ}_{H_2}$ and P_{H_2} are hydrogen pressures at t = 0 and t = t, respectively. When the initial pressure of hydrogen is equal to that of ethylene, P_{H_2} can be presented as $(P^{\circ}_{H_2} - P_{C_2H_6})$. Therefore, the rate constant becomes

$$k = (1/t)\ln(1 - P_{C_2H_6}/P^{\circ}_{H_2})^{-1}. \qquad (2)$$

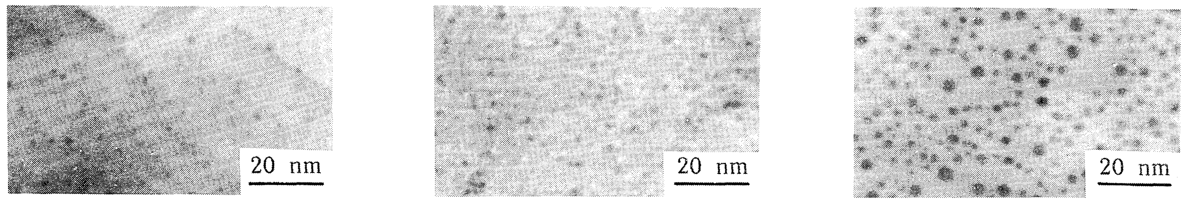
On presenting the ratio of peak height at 26 (mass number) to that at 30, on a mass spectrum of a mixture of C_2H_4, C_2H_6 and H_2, as $R = M_{30}/M_{26}$, we obtain following equations, $P_{C_2H_6} = (R/R_\infty)P^{\circ}_{C_2H_4} = (R/R_\infty)P^{\circ}_{H_2}$, where R_∞ is the peak height ratio at final state of the reaction. Finally k is written as

$$k = (1/t)\ln[R_\infty/(R_\infty - R)]. \qquad (3)$$

Most of the kinetic data in this experiment obeyed the Eq. 3, with an error less than 10%.

Figure 2 shows the apparent activation energy for the hydrogenation of ethylene (0 - 50 °C, $P_{H_2} = P_{C_2H_4} = 0.67$ Torr) on the Pd/Gr model catalyst system as a function of numerical mean diameter of palladium particles. The graphite was inactive to the catalytic hydrogenation of ethylene under the experimental conditions. The activation energy for H_2-D_2 exchange reaction on Pd/C model catalyst system (0 - 50 °C, $P_{H_2} = P_{D_2} = 0.028$ Torr)3) was also drawn for comparison. As is shown in Fig.2, the activation energy for the former decreases with the decrease of palladium particle size, while that for the H_2-D_2 exchange reaction increases. It must be noted that an evident size effect was found to exist in the hydrogenation of ethylene over the surface of small palladium particles. In order to explain why the activation energy for the hydrogenation decreased with the palladium particle size, we must consider either contributions of the valence band or of the geometry of surface atoms on the palladium particles. As shown in Fig.2, the valence band levels (the peak energy of the state density) of small palladium particles progressively shifted to a higher binding energy compared with bulk metal as the particle size decreased.8) The increase in the binding energy of the valence band electrons in palladium particles would affect the adsorption energy of adsorbed species, such as ethylidine10) or other species, on the palladium particles. The adsorption strength of the adsorbed species must affect the energetics of its hydrogenation. On the other hand, the density of low co-ordinated surface atoms and stepped surfaces rapidly increases with decreasing the particle size. If such low co-ordinated surface atoms and stepped surfaces (they increase with the decrease in particle size) were more catalytically active than the higher co-ordinated surface atoms,11) the hydrogenation of the adsorbed species must be affected by the palladium particle size. But, it is difficult at present to determine which effect is the dominant factor in the catalytic properties of palladium particles, the geometry of surface palladium atoms or the electronic state of palladium particles, because both of them change with the decrease in palladium particle size.

The specific activity, on the other hand, appeared to exhibit a maximum at a particle size of $\bar{d} = 1.3$ nm at a rate of $k_m = 2 \times 10^{17}$ molecules $cm^{-2}s^{-1}$ at 20 °C, in which a hemisphere model was used to estimate the surface area based on the



(a) (b) (c)

Fig.1. Transmission electron micrographs of the Pd/Gr model catalysts.

The amount of palladium evaporated : (a); 0.3×10^{15} Pd atom cm^{-2}, (b); 1.5×10^{15} Pd atom cm^{-2}, (c); 4×10^{15} Pd atom cm^{-2}.

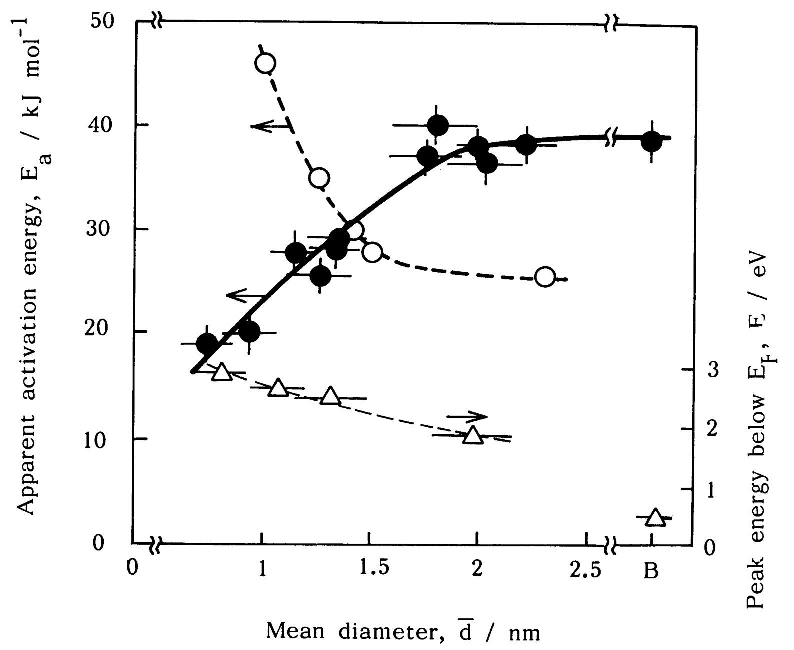


Fig.2. The apparent activation energy of the Pd/Gr model catalyst system for the hydrogenation of ethylene.

● : $C_2H_4 + H_2$ on Pd/Gr model catalyst (this work); ○: H_2-D_2 exchange reaction on Pd/C model catalyst (Ref.3); △: the peak energy of the valence band of Pd/Gr model catalyst (Ref.8). Evaporated palladium formed almost bulk-like film at point B.

transmission electron micrograph. The specific activity decreased with increasing the palladium particle size; however, there is some uncertainty in the determination of the surface area due to the observation limit of the TEM (ca. 0.6 nm), especially for the samples having a mean diameter less than $\bar{d}$ = 1.3 nm.

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