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The Catalytic Properties of the Pd/Mica Model Catalyst

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Synopsis. The apparent activation energy of an H_2–D_2 exchange reaction on a Pd/mica model catalyst system increased with the decrease in the particle size of palladium. The activity pattern as a function of the mean particle size was of a volcano-type, with a maximum at a particle size around 1.2 nm.

The effects of the metal-particle size on the catalytic properties of supported metal catalysts have not been clearly revealed. Most of the investigations which have aimed at revealing the size effects have been performed with catalysts prepared by the impregnation method. However, they have had the following difficulties: (1) the observation of small metal particles on supports (Al_2O_3, SiO_2 or active carbon) by TEM (transmission electron microscopy) is not easy; (2) the surface cleanness of metal particles on the support cannot be well guaranteed, and (3) the application of UPS (ultraviolet photoelectron spectroscopy) to reveal the valence-band structure of catalysts is substantially impossible.

The model-catalyst method will be able to overcome those concomitant problems. Many investigations with model catalysts have been performed using an UHV (ultra-high vacuum) system; however, scarcely no experiments which have examined both metal-particle size and catalytic-activity measurements have been made.[1–6]

In this study, palladium was evaporated onto a mica sheet in an UHV system, and its catalytic activity for an H_2–D_2 exchange reaction was measured *in situ*.

Experimrental

The features of the apparatus used for the preparation of the model catalysts and for the subsequent measurements of their catalytic activities have been described elsewhere.[7] The apparatus was capable of being evecuated to the pressure of 10^{-9} Torr (1 Torr=133.3 N m^{-2}). A cleaned mica-sheet support and a TEM mesh were set in the UHV chamber. The TEM sheet mesh was composed of fine mica powder fixed on evaporated carbon film which was held on a copper sheet mesh (#400). The mount of palladium evaporated was monitored by means of a quartz-thickness monitor (ANELVA EVM-32B). A transmission electron microscope (Japan Electron Optics, JEM-200-CX, bright field) was adopted for the observation of the palladium particles on the mica-sheet support.

Results and Discussion

Figure 1 shows some typical electron micrographs of the model catalyst, in which one can see palladium particles ranging in size from the observation limit of 0.6 nm to approximately 3 nm. The mean thickness $\bar{D}$ signifies the thickness of the palladium layer if the deposits were dense and did not form any island structure. The effective surface areas of these palladium catalysts were estimated by assuming all the palladium particles to be half-spheres.

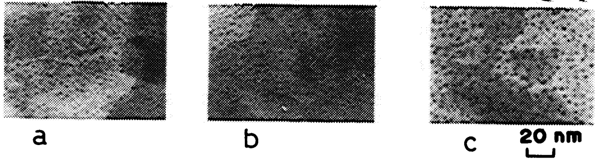

Fig. 1. Typical electron micrographs of Pd/mica model catalysts.
Mean thickness $\bar{D}$; a: 0.25 nm, b: 0.41 nm, c: 0.54 nm.

The H_2–D_2 exchange reaction on this Pd/mica model catalyst system obeyed a first-order reaction under the present experimental conditions. Figure 2 shows the specific activity towards the H_2–D_2 exchange reaction ($P_{H_2}=P_{D_2}=2.8\times10^{-2}$ Torr, 25°C) of this catalyst system as a function of the mean palladium-particle size. The activity pattern is of a "volcano" type, with a maximum at a particle size around $\bar{d}=1.2$ nm ($\bar{d}$ signifies the mean diameter of the palladium particles). Such an activity pattern has been found not only for the Pd/C and Pd/SiO_2 model catalyst systems in the H_2–D_2 exchange reaction reported elesewhere[7,8] but also for a Rh/SiO_2 powder catalyst system in benzene reduction.[9] Therefore, a hemispherical palladium particle with a diameter of 1.2 nm may be said to consist of about 30 atoms. Below $\bar{d}=1.2$ nm, the specific activity decreased rapidly with the decrease in $\bar{d}$. There-

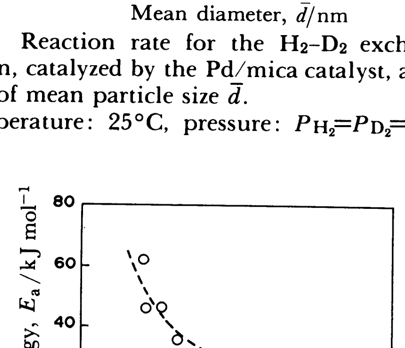

Fig. 2. Reaction rate for the H_2–D_2 exchange reaction, catalyzed by the Pd/mica catalyst, as a function of mean particle size $\bar{d}$.
Temperature: 25°C, pressure: $P_{H_2}=P_{D_2}=2.8\times10^{-2}$ Torr.

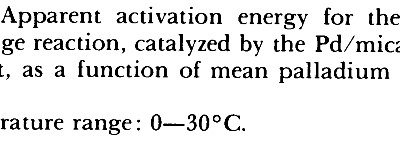

Fig. 3. Apparent activation energy for the H_2–D_2 exchange reaction, catalyzed by the Pd/mica model catalyst, as a function of mean palladium particle size $\bar{d}$.
Temperature range: 0—30°C.

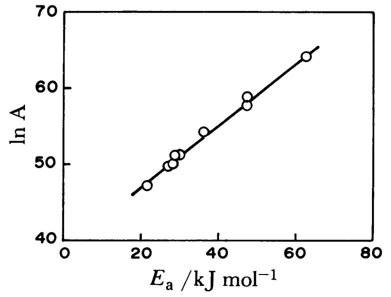

Fig. 4. Compensation effect for the H_2–D_2 exchange reaction, catalyzed by the Pd/mica model catalyst. The A means the preexponential factor in the Arrhenius equation.

fore, the contribution to the catalytic activity of the palladium particles below the observation limit of the electron microscopy (0.6 nm) must be extremely low.

Figure 3 shows the apparent activation energy of the reaction on this Pd/mica model catalyst system as a function of the mean particle size $\bar{d}$. It must be noted that the apparent activation energy gradually decreased with the increase in $\bar{d}$ from *ca.* 60 kJ mol^{-1} at $\bar{d}$ = 1.0 nm to *ca.* 20 kJ mol^{-1} at $\bar{d}$ = 2.4 nm. This tendency must not be directly affected by problems in determining the surface area of the catalyst. As with the specific activity, this tendency is analogous to the results of the Pd/C and Pd/SiO_2 model catalyst systems.[7,8] As shown in Fig. 4, a compensation effect between the apparent activation energy E_a and the preexponential factor A in the Arrenius equation exists for this H_2–D_2 reaction on the Pd/mica model catalyst system. This suggests that the reaction mechanism in this system is the same in all these palladium catalysts, while the activation energy differs.

As has been reported by many previous investigators, including us,[2,3,6] the valence band as well as the 3d levels of small particles of palladium shift to a higher binding energy from the bulk values with a decrease in the particle size. The shift of the valence band to a higher binding energy must be caused by either the intrinsic property of the very small metal particles or the support effect. The former effect has been proved by some investigators[6] on the basis of calculations; the latter effect is now under investigation by the present authors using various catalyst supports. In any event, the increase in the binding energy of the valence-band electrons in palladium particles with the decrease in the particle size must result in the decrease in the adsorption energy of hydrogen on the palladium particles. If this is the case, the increase in the apparent activation energy for the H_2–D_2 exchange reaction with the decrease in the particle size is likely to be caused by an increase in the activation energy for the dissociative adsorption of hydrogen. The rate-determining step of this H_2–D_2 exchange reaction has not been kinetically examined; however, we have pointed out that linear relationships exist between the catalytic activities of a hydrogen-recombination reaction or an H_2–D_2-exchange reaction and the amount of strongly adsorbed hydrogen (probably dissociative) on the cleaned first-transition metal wires as well as the cleaned Cu-Ni alloy plates.[10] On the other hand, the density of low-coordinated surface atoms rapidly increased with the decrease in the particle size.[11] If low-coodinated surface sites were more catalytically active than the higher-coordinated surface atoms, the catalytic activity would increase with the decrease in the particle size. However, the apparent activation energy increases with the decrease in the particle size, an activity maximum appeared at a certain particle size. In order to make a more decisive explanation, an *in-situ* investigation of adsorption and UPS studies using other supports are now being made.

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References

1) D. L. Doering, J. T. Dickinson, and H. Poppa, *J. Catal.*, **73**, 91, 104 (1982).

2) M. G. Mason, L. J. Gerenser, and S. T. Lee, *Phys. Rev. Lett.*, **39**, 288 (1977).

3) Y. Takasu, R. Unwin, B. Tesche, A. M. Bradshaw, and M. Grunze, *Surf. Sci.*,**77**,219 (1978).

4) J. F. Hamilton and R. C. Baetzold, *Science*, **205**, 1213 (1979).

5) M. Arai, T. Ishikawa, and Y. Nishiyama, *J. Phys. Chem.*, **86**, 577 (1982).

6) M. G. Mason, *Phys. Rev. B*, **27**, 748 (1983).

7) Y. Takasu, K. Kasahara, Y. Matsuda, and I. Toyoshima, *Nippon Kagaku Kaishi*, **1984**, 1011.

8) Y. Takasu, T. Akimaru, K. Kasahara, Y. Matsuda, H. Miura, and I. Toyoshima, *J. Am. Chem. Soc.*,**104**, 5249 (1982).

9) W. F. Graydon and M. D. Langan, *J. Catal.*, **69**, 1890 (1981).

10) Y. Takasu and Y. Matsuda, *Electrochim. Acta*, **21**, 133 (1976).

11) J. R. Anderson, "Structure of Metallic Catalysts," Academic Press, London (1975).