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Size Distribution of Platinum Dispersed on Charcoal and Its Effect on the Dehydrogenation of 2,3-Dimethylbutane

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Particle size distribution of platinum of varying concentration ranging from 0.12 to 9.33 wt% dispersed on catalytically inactive charcoal was determined by electron microscope. A sharp distribution with a maximum at about 20 Å was obtained for fresh catalysts of platinum concentration below 1.0 wt%. The maximum shifted to about 40 Å for catalysts of higher concentration. Growth of the particle was also observed upon sintering at 650°C.

The catalysts of known size distribution were examined for the dehydrogenation of 2,3-dimethylbutane at 460°C. Overall rate decreased and selectivity with respect to the formation of 2,3-dimethyl-1-butene increased as mean diameter of platinum particle increased. The reaction was thus found to be structure-sensitive. An explanation based on α,β-diadsorbed intermediate on large particles and π-allyl intermediate at sites consisted of lower coordination atoms of smaller particles was suggested.

INTRODUCTION

Since it was pointed out that physical properties of a very fine metallic particle of the size of 50 Å or below might be significantly different from those of bulk metal (*1, 2*), a considerable number of investigations have been reported as to the effect of particle size on catalysis and related phenomena. It is those latter studies that have led Boudart (*3*) to classify a variety of metal catalyzed reactions into two broad categories, demanding and facile. Many reported results have still been often controversial, however, because of ambiguities arising from metal–support interaction and incomplete reduction of metal. Experimental difficulties in evaluating particle size make the situation even more ambiguous. Thus, at present, a given reaction may or may not be structure-sensitive depending on reaction conditions including those at which a given catalyst is prepared and pretreated.

In the present paper, we report the first sharply contrasted electron micrograph of fine platinum particles dispersed on catalytically inactive charcoal. We also report the rate and the selectivity of the dehydrogenation of 2,3-dimethylbutane over the platinum catalysts of which the size distributions are controlled and known with reasonable accuracy. It is thus hoped to render one example to the list of demanding reactions.

EXPERIMENTAL METHODS

Catalysts, 0.12–9.33 wt% platinum on catalytically inactive charcoal, supplied by Nippon Englehard Co., Ltd., were prepared by a conventional impregnation technique. Specific surface area of the charcoal carrier was about 1200 m^2/g. Bulk density of 28–150 meshed catalysts was 0.464–0.484 g/cm^3. Sintering of the catalysts was carried out at 650°C for 2–72 hr in a stream of hydrogen. Finely powdered platinum–charcoal catalysts, both fresh and sintered, were then subjected to electron microscopic observations. Catalysts of 60–100 mesh were used for dehydrogenation. Platinum wire used as representing catalytic behavior of bulk platinum, supplied by Johnson Matthey Chemicals Co., Ltd., was of 0.2 mm in diameter and 200 cm in length.

The sample of the catalysts supported on a plastic film reinforced by carbon was mounted to electron microscope, JEOL Ltd. Model JEM-200A, operated at 200 kV. The magnification of the electron microscope, as determined by the half-spacing (5 Å) of Sericite, was 100,000.

The dehydrogenation of 2,3-dimethylbutane was carried out in a conventional flow apparatus under the following conditions: temperature, 460°C; pressure, 1 atm; hydrogen to 2,3-dimethylbutane feed ratio, 2.2 mol/mol; W/F, 0.004–0.5 g cat hr/mol. 2,3-Dimethylbutane used was gas chromatographically pure except for a trace of 2-methylpentane. Hydrogen was purified by passing over palladium catalyst and drying agent. Products, collected in a trap chilled by methanol–dry ice bath, were composed of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene and were analyzed by the gas chromatographic unit equipped with 90 m squalane capillary column. Other details of the apparatus and procedures were described previously (*4*).

RESULTS AND DISCUSSION

Platinum particle size and its distribution. Chemisorption of hydrogen and carbon monoxide has been extensively studied in an effort to measure exposed surface area and to evaluate average size of finely dispersed metallic particles (*5*, *6*). This approach alone, however, does not give conclusive results, since the number of chemisorbed species per one surface metal atom depends on the dispersion and also on the conditions at which the chemisorption is studied. Our preliminary experiment on the present catalyst along this line has also resulted in quite erratic data.

Direct observation by electron microscope seems more promising. It gives information as to both the shape and the size distribution in more unequivocal manner. However, very few successful observations (*7*, *8*) have yet been reported on the practical noble metal catalyst supported on the carrier having large surface area.

Illustrated in Fig. 1 are the electron micrographs of the fresh platinum–charcoal catalysts of varying platinum concentration (Al–A5). These micrographs, especially those of lower platinum concentration, clearly show spherically shaped platinum particles of the diameters as small as 5 Å well dispersed on charcoal carrier.

Arguments have, however, been raised frequently whether the dark spots on the micrographs were those of metal itself or not, especially when metallic component was highly dispersed on the matrix possessing large surface area. We identified them as being due to platinum by the electron diffraction of the dark spots stabilized by sintering. The observed spacings of 2.265 Å (111), 1.969 Å (200), 1.383 Å (220) and 1.186 Å (311) are in agreement with those listed by ASTM. It should be noted that most of the dark spots observed with fresh catalysts were easily destroyed upon irradiation by the electron beam. The fragility suggests that the small platinum particles may be characterized as amorphous aggregates rather than stable microcrystallites.

Illustrated in Figs. 2 and 3 (Al–A5) are the size distribution histograms of plat-

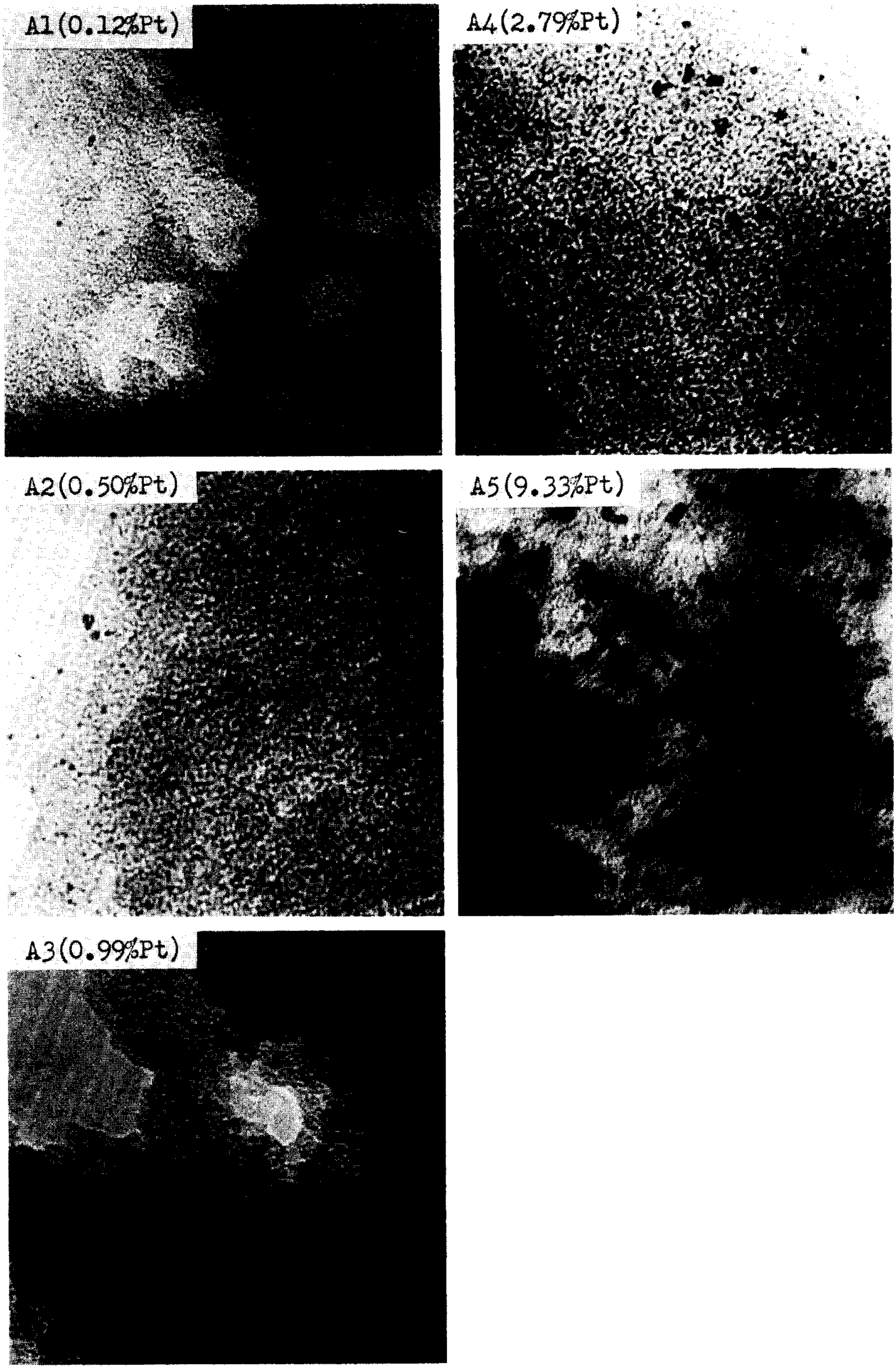

FIG. 1. Electron micrograph of fresh Pt–C catalysts (×500,000).

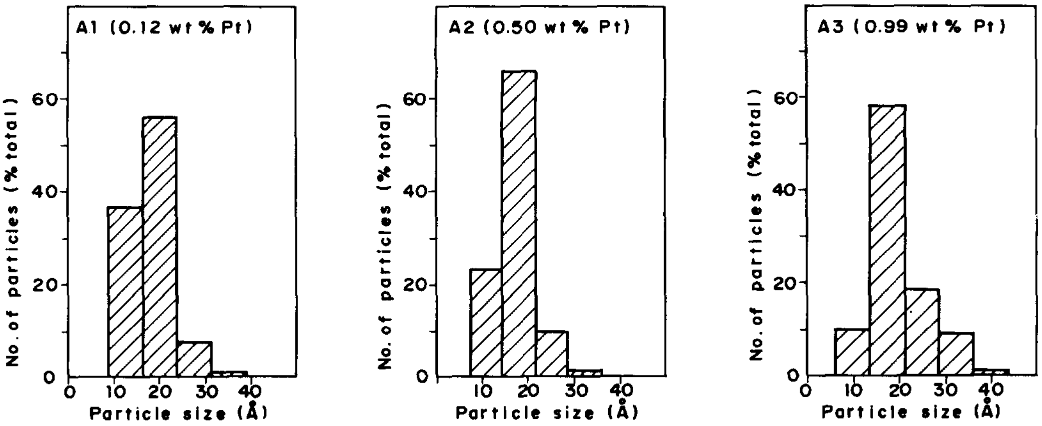

FIG. 2. Size distribution of fresh platinum particles.

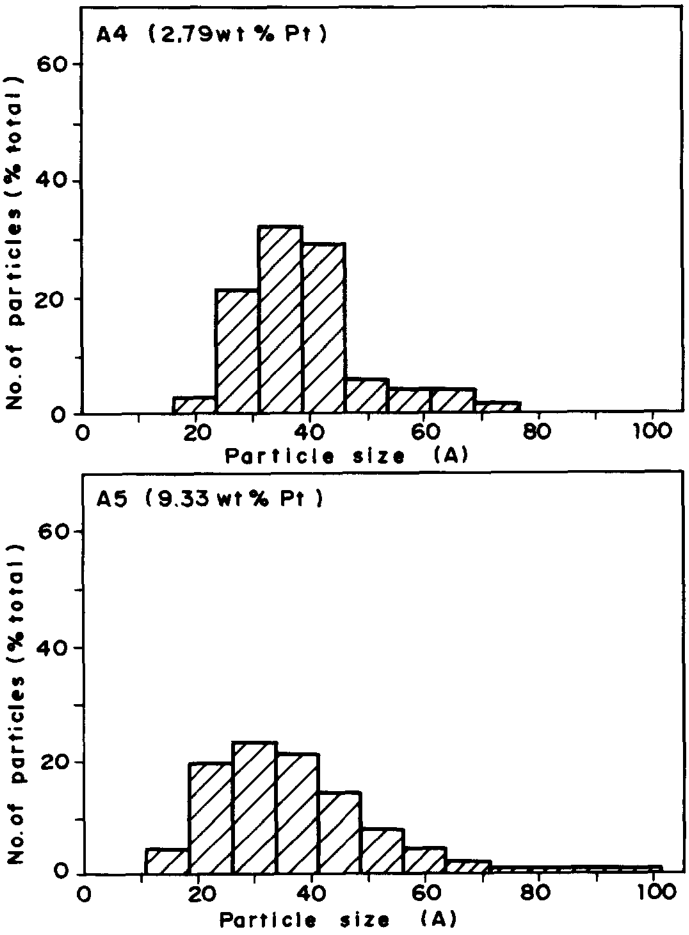

FIG. 3. Size distribution of fresh platinum particles.

inum particles observed as photographic spots appeared in an arbitrarily chosen area of 4×10^6 Å^2 of the micrographs shown in Fig. 1. Because of the limitation drawn by the resolution of the microscope used in the present study and of their minor contribution in the histogram, the particles with diameters less than 8 Å are ignored. This may be justifiable, although indirectly, in view of the absence of particles with diameters less than 20 Å in the sintered sample (see below, Fig. 5) which would show out if the significant amount of the extremely small particles were present in the fresh catalyst. The particle size is sharply distributed in the range between 8 and 40 Å for the fresh catalysts of lower platinum concentration (< 1.0 wt% Pt), whereas the distribution becomes considerably broader toward larger particle size covering the range as large as 110 Å for the catalysts of higher concentration (> 2.5 wt% Pt).

The only successful electron microscopic study which has ever been reported on highly dispersed metallic particles is perhaps that of Pope *et al.* (*7*) on palladium (1 wt%)-charcoal. The trend is similar to the present result except that the size distribution of palladium is considerably broader covering the range from 10 to 200 Å and is bimodal with the second maxima at approximately 80–100 Å which is completely lacking in the present histogram.

The mean diameter based on volume-to-surface ratio, $\bar{d}_{vs}$, of n particles can be defined by the following equation:

$$\bar{d}_{vs} = \sum_i n_i d_i^3 \Big/ \sum_i n_i d_i^2. \qquad (1)$$

The surface area per unit weight, S_w, of spherical particles can then be calculated by the following equation:

$$S_w = 6\bar{d}_{vs}/\rho, \qquad (2)$$

where ρ is the density of platinum. The values of $\bar{d}_{vs}$ and S_w of the fresh platinum-charcoal catalysts of varying platinum concentration calculated by Eqs. (1) and (2) are summarized in Table 1. The specific surface area increases with decreasing platinum concentration and approaches limiting value of about 140 m^2/g at platinum concentration of 0.5 wt%. A similar behavior has been reported on rhodium-SiO_2 catalysts based on the chemisorption of hydrogen and carbon monoxide (*9*).

TABLE 1

MEAN DIAMETER AND SPECIFIC SURFACE AREA OF FRESH PLATINUM PARTICLES

Catalyst	Pt concn (wt%)	$\bar{d}_{vs}$ (Å)	S_w (m^2/g Pt)
A1	0.12	20	140
A2	0.50	20	140
A3	0.99	26	108
A4	2.79	45	63
A5	9.33	48	58

The results described above lead to the conclusion that the conventional impregnation of platinum beyond about 0.5 wt% would only result in the growth of particle size and hence the reduction of the exposed surface area per unit weight of platinum. It is interesting to note that the concentration of noble metals of commercial reforming catalysts has usually been limited to below 0.5 wt%. Unfortunately, no successful electron microscopic observation has been made for the catalysts consisting of more popular oxide carrier.

Illustrated in Fig. 4 (B1–B4) are the electron micrographs of platinum (0.5 wt%)-charcoal catalysts sintered at 650°C for varying sintering time ranging from 2 to 72 hr.

The size distribution of platinum particles of the catalyst containing 0.5 wt% platinum sintered at 650°C for 72 hr is illustrated in Fig. 5 as an example. Summarized in Table 2 are the values of $\bar{d}_{vs}$ and S_w of the sintered platinum particles.

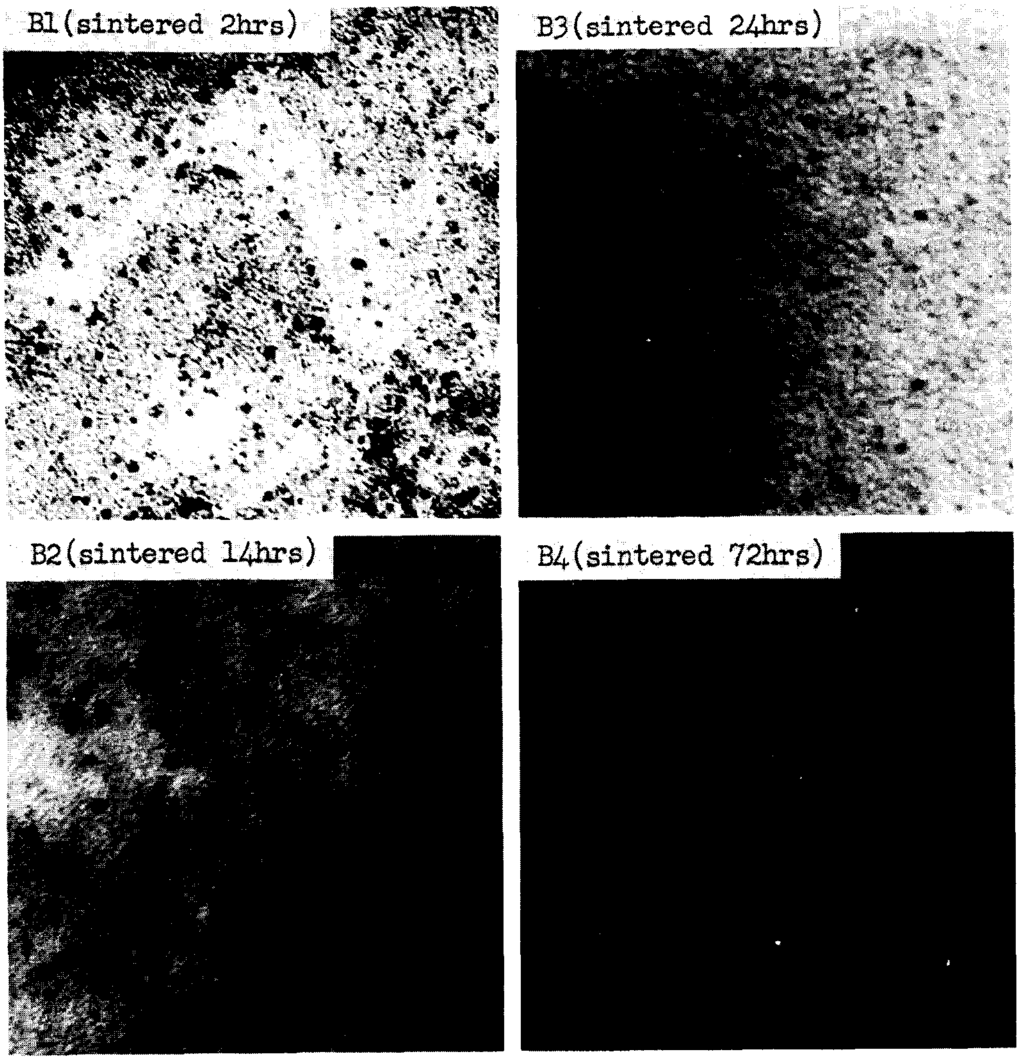

FIG. 4. Electron micrograph of sintered Pt (0.5 wt%)-C catalysts (×500,000).

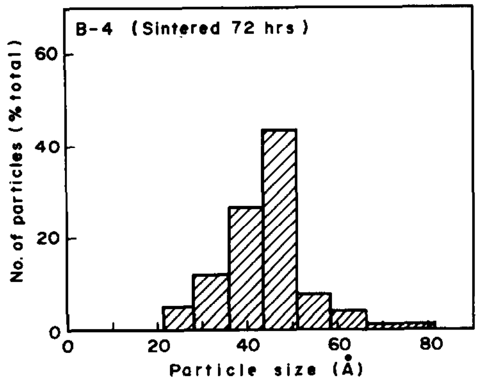

FIG. 5. Size distribution of sintered platinum particles.

The results indicate that the growth takes place predominantly for those smaller platinum particles which are originally amorphous and fragile.

Dehydrogenation of 2,3-dimethylbutane. Catalytic behavior of the platinum–charcoal catalysts of varying platinum particle size was examined by the reaction of 2,3-dimethylbutane at 460°C. The reaction was revealed to be sufficiently selective to form either 2,3-dimethyl-1-butene or 2,3-dimethyl-2-butene under the present experimental conditions. The charcoal used as carrier was also proved to be inac-

TABLE 2
MEAN DIAMETER AND SPECIFIC SURFACE AREA OF SINTERED PLATINUM PARTICLES

Catalyst	Sintering time (hr)	$\bar{d}_{vs}$ (Å)	S_w (m²/g Pt)
A2	0	20	140
B1	2	32	87
B2	14	35	79
B3	24	41	69
B4	72	48	58

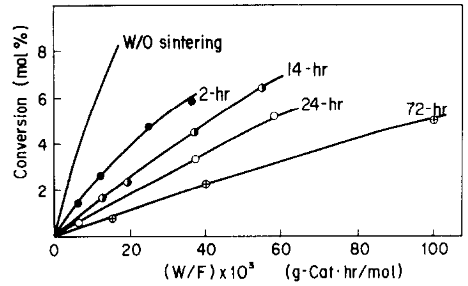

FIG. 7. 2,3-Dimethylbutane dehydrogenation over sintered catalysts.

tive. Illustrated in Figs. 6 and 7 are the relations of conversion vs time factor for a series of fresh catalysts (A1–A5) and of sintered catalysts (B1–B4), respectively. The values of the initial reaction rate, r, are calculated using the following equation:

$$r = \frac{1}{1+a}\frac{dx}{d(W/F)}, \qquad (3)$$

where a is the molar ratio of hydrogen to 2,3-dimethylbutane, x the conversion and W/F the time factor in hr g cat mol^{-1}. These values can then be converted to those based on exposed surface area of platinum using the values listed in Tables 1 and 2, and are plotted against mean diameter of the platinum particles as illustrated in Fig. 8. The initial reaction rate increases exponentially as mean particle diameter reduces from 50 to 20 Å. Illustrated also in Fig. 8 are the ratio of surface metal atoms to the total number of metal atoms [broken curve (b)] and the fraction of the surface atoms of lower coordination numbers in an infinite octahedral (111) face [broken curve (a)], both of which have been suggested by Boudart (*3*) as indices of dispersion.

Parallelism observed between the experimental rate data and the indices of dispersion indicates that the platinum catalyzed dehydrogenation of 2,3-dimethylbutane is strongly influenced by the existence of lower coordinated corner atoms (*10*) and hence structure-sensitive.

As illustrated in Fig. 9, the fraction of 2,3-dimethyl-1-butene in the dehydrogenated product decreases with conversion and reaches thermodynamic equilibrium composition (*4*). Deviation from the equilibrium composition at lower conversion is more pronounced when catalysts of either higher platinum concentration or longer sintering time are used. Illustrated in Fig.

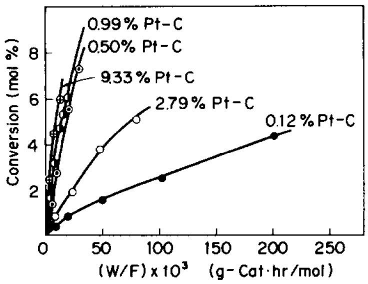

FIG. 6. 2,3-Dimethylbutane dehydrogenation over fresh catalysts.

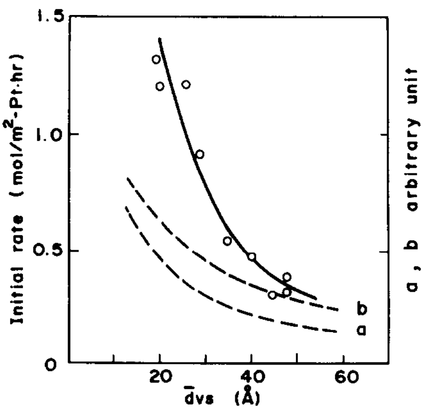

FIG. 8. Effect of particle size on reaction rate.

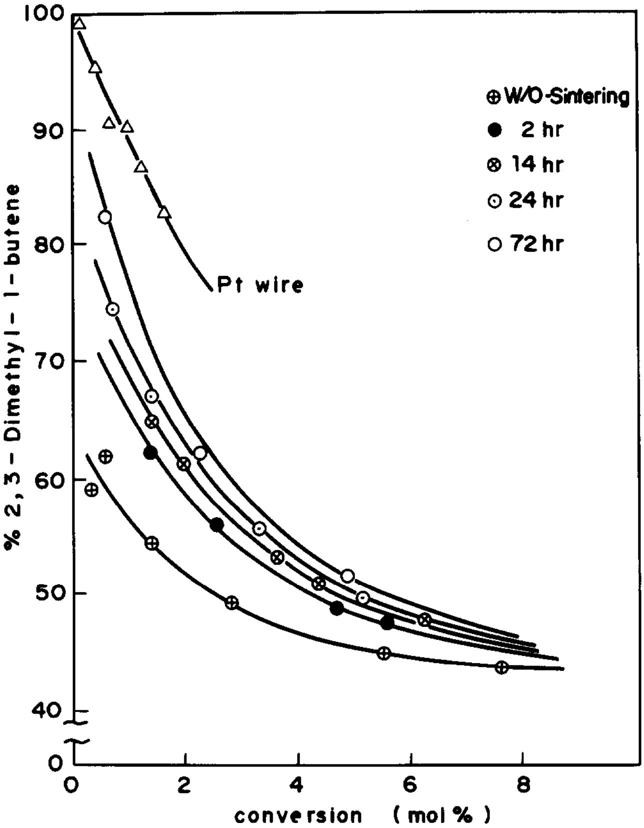

FIG. 9. Selectivity of 2,3-dimethyl-1-butene.

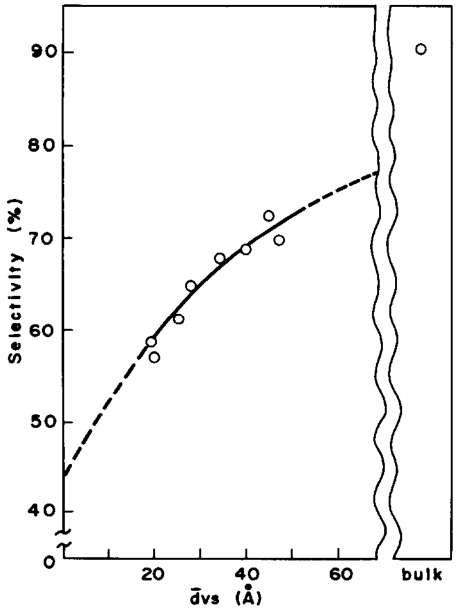

FIG. 10. Effect of particle size on selectivity.

10 is the 2,3-dimethyl-1-butene selectivity at the conversion of 1% observed with catalysts of varying platinum particle size.

Results of the reaction over platinum wire are also illustrated in Figs. 9 and 10 for comparison, and are in conformity with those obtained with the present catalysts if the wire is regarded as a catalyst of infinite particle size. The trend observed can be accounted for by assuming π-adsorbed or α,β-diadsorbed intermediate depending on the size of platinum particle. Platinum atoms of lower coordination numbers favor the formation of π-olefin and π-allyl chemisorbed intermediates in the hydrogenolysis (*11*). If this holds in the present system, the dehydrogenation through π-allyl chemisorbed intermediate to produce equilibrium mixture of butenes takes place faster on the catalyst having smaller platinum particles. As the particles grow, more common α,β-diadsorbed intermediates become important. It is reasonable to suppose, in this latter case, that 1,2-diadsorbed state which produces only 2,3-dimethyl-1-butene is the favorable chemisorbed intermediate due to the relative stability of its monoadsorbed precursor (*4*).

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