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Metal Catalysts Supported on Zeolite. I. A Study on Platinum Particles Distribution

Toshihiko KUBO, Hiromichi ARAI, Hiroo TOMINAGA, and Taiseki KUNUGI

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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Zeolite 13Y, loaded with platinum cations by ion exchange, was calcined in the air and subsequently reduced in a hydrogen stream. Hydrogen and carbon monoxide adsorption studies, together with an electron microscopic observation of the catalyst, revealed that the size distribution of platinum particles is controlled by the calcination temperature. The hydrogen chemisorption method gave the average particle diameters, which were in fairly good agreement with the observations made by means of an electron microscope on the catalyst with a platinum particle diameter larger than 20 Å, while trace amounts of hydrogen chemisorption were observed for platinum particles less than 20 Å.

In the preparation of metallic catalysts supported on carriers, the relationship between the size distribution of metallic particles and their adsorptive and catalytic activities has constituted one of the most interesting subjects of study. An incentive to the study from a practical point of view is the need for the efficient utilization of metals, especially of such highly priced ones as those in the platinum group. Several physicochemical techniques, such as X-ray diffraction-line-broadening, electron microscope, and gas chemisorption, have been developed for the dispersion state analysis of the metal. These studies involve the following: the influence of the platinum crystallite size on the selectivity of hydrocarbon reforming,[1] the crystallite size and the specific activity for benzene hydrogenation of platinum/silica catalysts,[2] the influence of the crystallite size on the infrared-active nitrogen adsorption on nickel, palladium and platinum,[3] the preparation of a highly dispersed platinum catalyst supported on silica gel,[4] X-ray adsorption edge study of zeolite supported platinum,[5] the adsorptive and catalytic properties of metal crystallites,[6] and some relations between the structural and catalytic properties of alumina-supported platinum.[7] Echigoya *et al.*,[8] and Shirasaki and Furuoya[9] reported that the temperature of calcining $Pd(NH_3)_4^{2+}$ on silica and silica-alumina in the air affected the size distribution of the palladium crystallites formed by subsequent hydrogen reduction. Further, they studied the dispersion state and the structure of palladium crystallites, in particular of the catalysts calcinined at rather high temperatures (>300°C), by X-ray diffraction-line-broadening, electron microscope, and carbon monoxide chemisorption techniques.

In the present study, we were especially interested in the catalysis of fine platinum particles, such as those less than 20 Å in diameter, on zeolite. The platinum

1) H. J. Maat and L. Moscou, The Third International Congress on Catalysis, Section 2, Paper 5 (1964).
2) T. A. Dorling and R. L. Moss, *J. Catal.*, **5**, 111 (1966).
3) R. Van Hardeveld and A. Van Montfoort, *Surface Science*, **4**, 396 (1968).
4) H. A. Benesi, R. M. Curtis, and H. P. Studer, *J. Catal.*, **10**, 328 (1968).
5) P. H. Lewis, *ibid.*, **11**, 162 (1968).
6) G. C. Bond, The Fourth International Congress on Catalysis, Paper 67 (1968).
7) M. Kraft and H. Spindler, *ibid.*, Paper 69 (1968).
8) E. Echigoya, I. Furuoya, and K. Morikawa, *Kogyo Kagaku Zasshi*, **71**, 1768 (1968).
9) T. Shirasaki and I. Furuoya, *ibid.*, **71**, 1774 (1968).

catalysts were prepared by ion exchange and subsequent calcination in the air, followed by reduction in hydrogen. Particularly, we attempted to establish a method of preparation by which to achieve a desired dispersion state of platinum crystallites, which were analyzed by electron microscope and also by hydrogen chemisorption techniques. The temperature of calcining ion exchanged zeolite in the air was found to be the key factor, whereby the particle size distribution after reduction is affected. The hydrogen chemisorption technique was shown to give an average diameter of particles which is in fairly good agreement with that obtained by electron microscopic examination of the catalyst with a platinum particle diameter of over 20 Å on the average.

Experimental

Catalyst Preparation. Platinum catalysts incorporated with a carrier, zeolite 13Y, were prepared by ion exchange, followed by calcination and reduction. The zeolite of Linde molecular sieves Y type SK-40 was employed. Its analysis indicated a chemical composition of SiO_2 63.5%, Al_2O_3 23.5%, Na_2O 13.0%, Cl 0.05%, and Fe 0.05% by weight.

The catalysts of the Pt-NaY type were prepared, in this work, according to the following procedure. The zeolite 13Y was degassed by stirring in deionized water, 20 times by weight, at 98—100°C for 2 hr. Then a given amount of aqueous solution of 0.01 mol/*l* $Pt(NH_3)_4Cl_2$ was added slowly, drop by drop; then the resulting mixture was stirred for another 3 hr at 98—100°C. The ion exchanged zeolite was obtained by filtration and washed thoroughly with deionized water until no chloro anion was detected in the filtrate. The zeolite was dried at 110°C for 3 hr, calcined in the air at a given temperature for 3 hr, and then, prior to use, reduced in a hydrogen stream at 500°C for 3 hr to give a zeolite-supported platinum catalyst.

The catalysts of the Pt-NH_4Y type were prepared in the same way except for the pretreatment of the zeolite 13 Y with aqueous NH_4Cl solution to replace the Na^+ with NH_4^+. This treatment was carried out before the ion exchange with $Pt(NH_3)_4^{2+}$.

The platinum contents in the catalysts were determined the colorimetric method proposed by Ayres and Meyer.[10]

Dispersion State Analysis. Electron microscopic observation and chemisorption experiments were carried out in order to characterize the platinum particle size distribution on zeolite.

The electron microscope employed was of Hitachi-HV·11·DS type. A lightly ground catalyst was dispersed in isopropanol; a drop of the suspension was then evaporated on a carbon film to get a specimen which was subjected to observation at a magnification of 108,000 x. Subsequent photographic enlargement to 324,000 x was practicable.

Conventional BET apparatus was used for the chemisorption experiment. The catalyst sample was allowed to stand in a vacuum system ($<10^{-3}$ mmHg) for 2 hr at 400°C. and then it was cooled to 25°C. A given amount of hydrogen was introduced in order to attain a pressure equilibration in 30—60 min at 25°C. Blank tests were made for the carriers, and a trace amount of hydrogen was found to be adsorbed at pressures ranging from 10^{-3} to 10^{-1} mmHg at 25°C. This might possibly be the result of the presence of iron in the zeolite (0.05%). Due calibration was made for the volume adsorption on carriers in order to obtain the net value of adsorption on platinum particles.

Carbon monoxide adsorption on platinum particles was measured by the same procedure as for hydrogen chemisorption.

Results and Discussion

Electron Micrographs. The electron microscopic observation of the catalyst revealed that the platinum particles supported on zeolite varied in their diameter sizes as a function of the calcination temperature in the air. These experimental results are summarized in Table 1.

Catalyst 1, the zeolite carrier, naturally showed no platinum particle. Catalyst 2 indicated only a few particles, ranging from 10 to 15 Å in diameter. Most of the platinum, therefore, would be dispersed in an atomic state and/or in fine particles less than 10 Å in diameter,[11] which is the limit of resolution of the electron microscope employed. It should be noted that 10 Å is close to the largest pore size of the zeolite 13Y. These findings are similar to the observations

TABLE 1. PLATINUM PARTICLE SIZE DISTRIBUTION AS A FUNCTION OF TREATING PROCEDURE

No.	Catalyst	Treating procedure			Platinum particle diameter range (Å)
		Calcination, 3 hr, at	Calcination in the air, at	H_2 reduction, 3 hr, at	
1	0% Pt-NaY	—	500°C	500°C	—
2		—	100	500	15
4	0.24% Pt-NaY	—	300	500	15— 55
6		—	500	500	30—680
10		—	400	500	30— 65
11		—	500	500	15— 75
12	0.28% Pt-NH_4Y	—	600	500	15— 70
13		N_2, 400°C	500	500	40— 60
14		H_2, 500	500	500	60

10) G. H. Ayres and A. S. Meyer, Jr., *Anal. Chem.*, **23**, 299 (1951).

11) P. H. Lewis[5] found that about 60% of the Pt of his Pt-CaY catalyst was soluble in HF. He attributed this to much smaller crystals, although it may have been due to incompletely reduced or reoxidized platinum.

reported by Benesi *et al.*[4] on silica gel-supported platinum catalyst made by ion exchange. Numerous tiny particles ranging from 15 to 55Å in diameter were found on the catalyst 4 (Fig. 1). These particles must exist on the external surface of the zeolite. In the case of the catalyst 6, bulky particles of platinum were noted; their size distribution was from 30 up to 680 Å (Fig. 2). These results suggest that the growth of platinum was accelerated by the temperature of calcination in the air prior to reduction in a hydrogen stream.

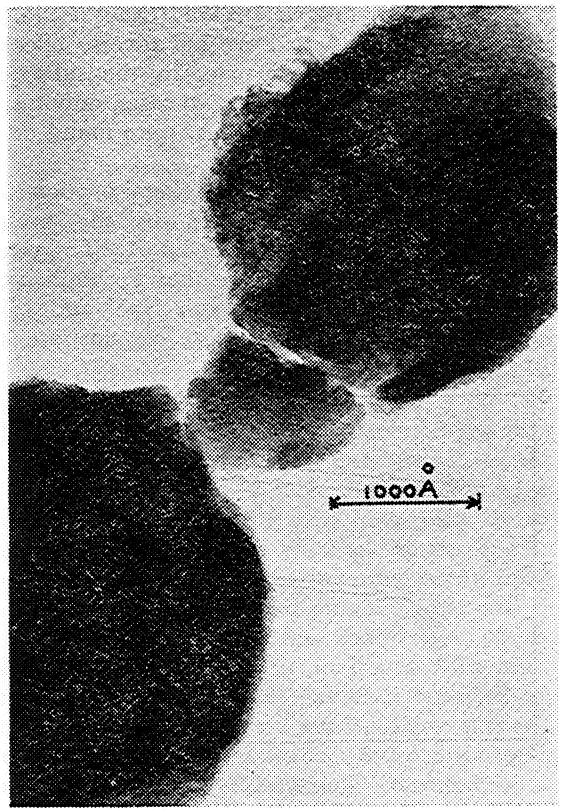

Fig. 1. Electron micrograph of the catalyst 4.

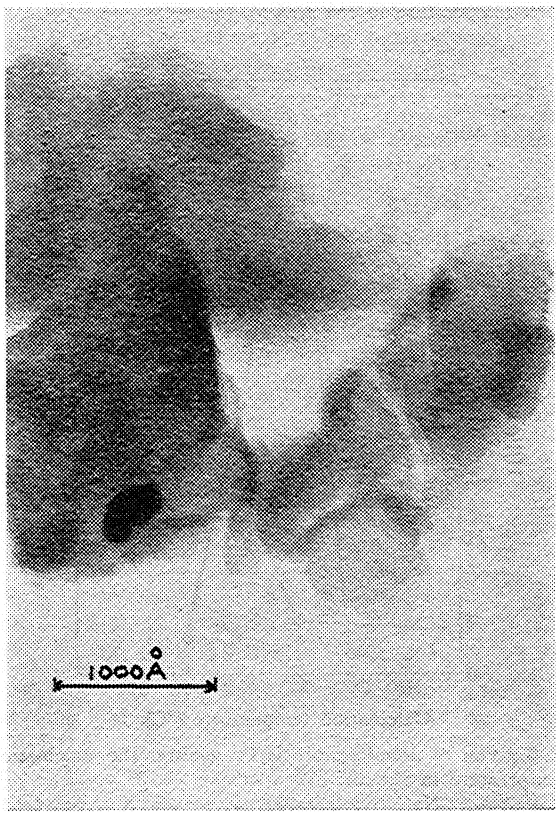

Fig. 2. Electron micrograph of the catalyst 6.

In the cases of the Pt-NH_4Y type catalysts, No. 10 to 12, the platinum particle size distribution seemed less sensitive to the calcination and a fairly good dispersion of platinum on the carrier was still maintained at temperatures ranging from 400 to 600°C. As an example, electron micrograph of the catalyst No. 11

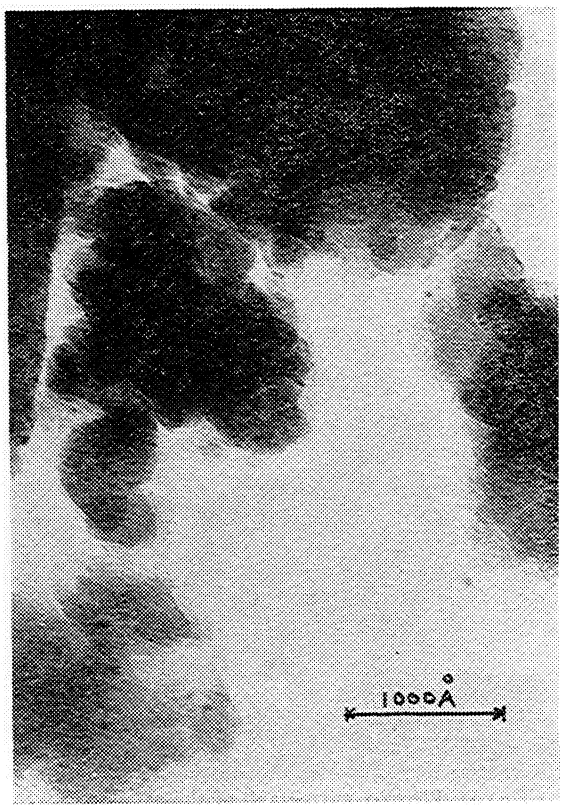

Fig. 3. Electron micrograph of the catalyst 11.

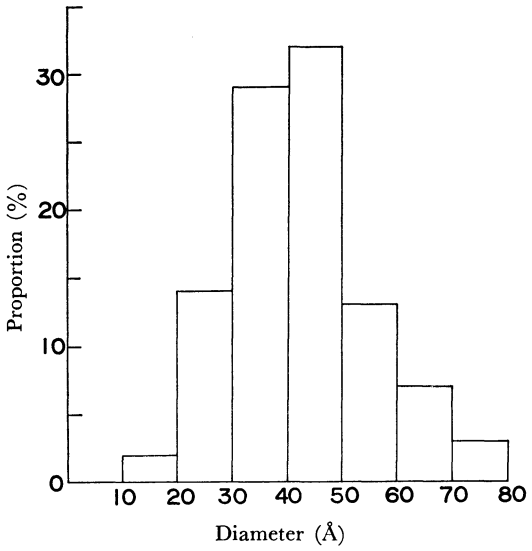

Fig. 4. Size distribution of platinum particles on the catalyst 11.

is shown in Fig. 3, while its particle size distribution is presented in Fig. 4.

The different susceptibilities to the calcining temperature between the Pt-NaY Type and the Pt-NH_4Y type supposedly has some connection with the changes in the crystal structure and electric field of the latter in calcination. That is, at temperatures near 300°C the ammonium ion decomposes into ammonia to leave a proton, while at higher temperatures, near 500°C water is eliminated by the combination of the hydroxyl group with the proton and a defect is formed in the lattice.[12] No definite explanation, however, has yet been developed to account for the above difference.

Fig. 5. Electron micrograph of the catalyst 13.

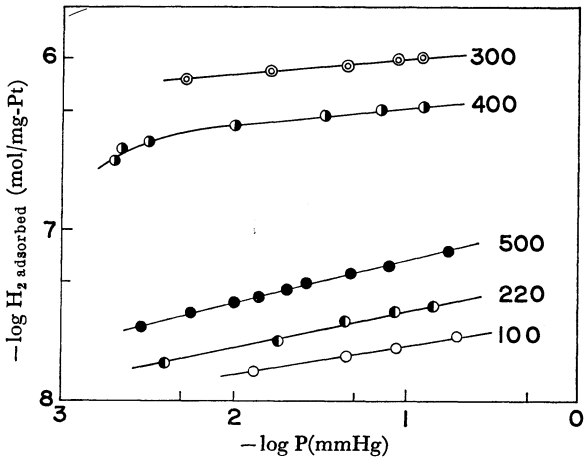

Fig. 6. Freundlich-type hydrogen adsorption isotherms of the Pt-NaY type catalysts. Numerals indicate the calcination temperature in the air.

The pretreatment of ion exchanged zeolites, of both the Pt-NaY and Pt-NH_4Y types, before calcination in the air, by heating in a nitrogen stream (catalyst No. 13) or in a hydrogen stream (catalyst No. 14) respectively, was found to have an adverse effect on the growth of platinum particles in the subsequent calcination in the air. In these two cases, only a small number of tiny particles, 40—60 Å, were found on the carrier (Fig. 5).

Chemisorption. Hydrogen chemisorption on platinum catalysts was measured in the pressure range from 10^{-3} to 10^{-1} mmHg at 25°C. The results, shown in Figs. 6 and 7, indicate that Freundlich-type adsorption isotherms hold for both NaY and NH_4Y type catalysts. These figures also demonstrate that

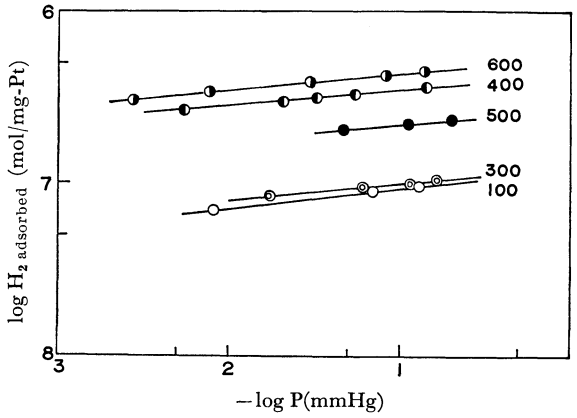

Fig. 7. Freundlich-type hydrogen adsorption isotherms of the Pt-NH_4Y type catalysts. Numerals indicate the calcination temperature in the air.

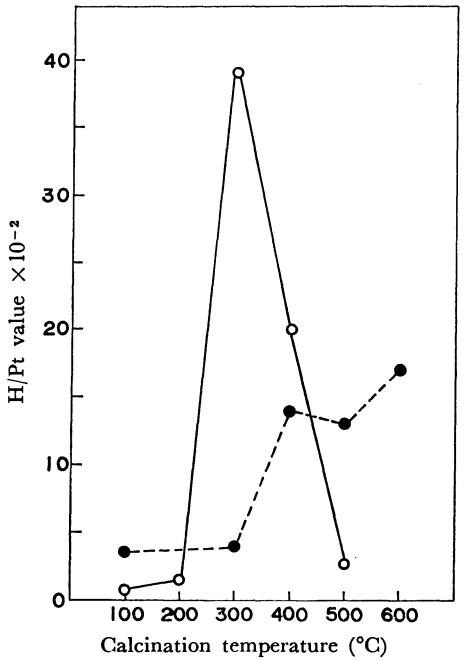

Fig. 8. Plot of atomic ratio H/Pt against the calcination temperature in the air.
—○— Pt-NaY type catalyst.
--●-- Pt-NH_4Y type catalyst.

12) D. N. Stamires and J. Turkevich, *J. Amer. Chem. Soc.*, **86**, 749 (1964).

the volume of hydrogen chemisorption is dependent upon the calcining temperature in the air. The dependency is shown more clearly in Fig. 8, where the number of hydrogen atoms chemisorbed per platinum atom loaded is plotted against the calcination temperature.

Based on the chemisorption data, the average diameter of the platinum particles was calculated. Two assumptions were involved in the calculation, that is, that the platinum particles are in a uniform sphere and that a hydrogen molecule dissociatively chemisorbs covering two platinum atoms. The average diameter is, consequently, given by $6V/S$, where V and S denote the total volume and the total surface area of platinum loaded respectively. S is given by the number of hydrogen atoms adsorbed times the unit area per platinum atom, namely, 8.09Å^2, which is the average the site densities of (100), (110), and (111) of the platinum crystal.[13]

Tables 2 and 3 present the calculated results. The diameters in parentheses, for catalysts 2, 3, 8, and 9, which were calcined at low temperatures, do not seem realistic because no such large particle as those calculated was found by electron microscope inspection. Rather, this could be regarded as meaning that the loaded platinum existed either near atoms or fine particles with diameters less than 10 Å which had little ability to chemisorb hydrogen. In this connection, an interesting fact has been reported by Van Hardeveld and Van Montfoort.[3] They carried out a study of infrared-active nitrogen adsorption on nickel supported on silica. The study consisted of an infrared spectroscopic investigation of the adsorbed nitrogen and of an electron microscopic determination of the metal particle size distribution. They found that the infrared-active adsorption was measurable only if the nickel crystallites were within the range of 15—70 Å. It was also stated that this applies not only to nickel but also to platinum and palladium.

Carbon monoxide adsorption on platinum particles was measured in the same way as hydrogen adsorption. The results are summarized in Figs. 9 and 10. In the case of the Pt-NaY type catalysts, the Freundlich-type adsorption isotherms were found to hold for carbon monoxide, the amount being dependent on the size of the platinum particles.

The gas adsorption behavior of hydrogen or carbon

Table 2. The average diameter of platinum particles calculated from hydrogen chemisorption (Pt-NaY type)

Cat. No.	Calcin. temp. °C	Mol adsorbed at 10^{-1} mmHg mol/g-cat	Atomic ratio, H/Pt	Average diameter, Å
2	100	5.3×10^{-8}	8.6×10^{-3}	(1312)
3	220	8.5×10^{-8}	1.4×10^{-2}	(820)
4	300	2.4×10^{-6}	3.9×10^{-1}	29
5	400	1.3×10^{-6}	2.0×10^{-1}	55
6	500	1.6×10^{-7}	2.7×10^{-2}	425

Table 3. The average diameter of platinum particles calculated from hydrogen chemisorption (Pt-NH_4Y type)

Cat. No.	Calcin. temp. °C	Mol adsorbed at 10^{-1} mmHg mol/g-cat	Atomic ratio, H/Pt	Average diameter, Å
8	100	2.7×10^{-7}	3.7×10^{-2}	(302)
9	300	2.8×10^{-7}	3.9×10^{-2}	(286)
10	400	9.8×10^{-7}	1.4×10^{-1}	82
11	500	9.2×10^{-7}	1.3×10^{-1}	87
12	600	1.2×10^{-6}	1.7×10^{-1}	66

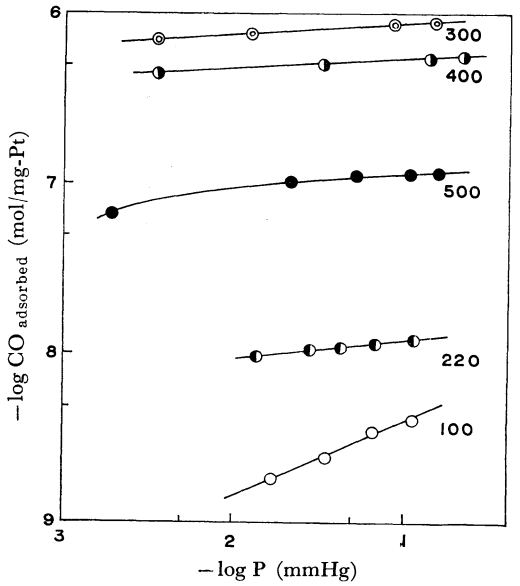

Fig. 9. Freundlich-type carbon monoxide adsorption isotherms of the Pt-NaY type catalysts. Numerals indicate the calcination temperature in the air.

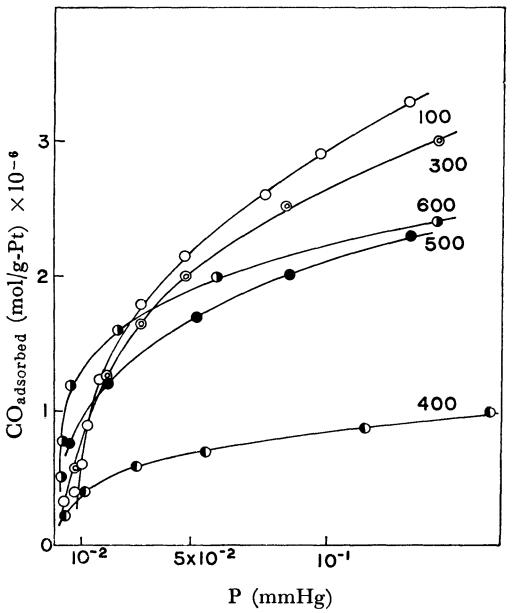

Fig. 10. Carbon monoxide adsorption isotherms of the Pt-NH_4Y type catalysts. Numerals indicate the calcination temperature in the air.

13) H. Chon, R. A. Fisher, E. S. J. Tomezsko, and J. G. Aston, The Second International Congress on Catalysis, Section 1, Paper 3 (1960).

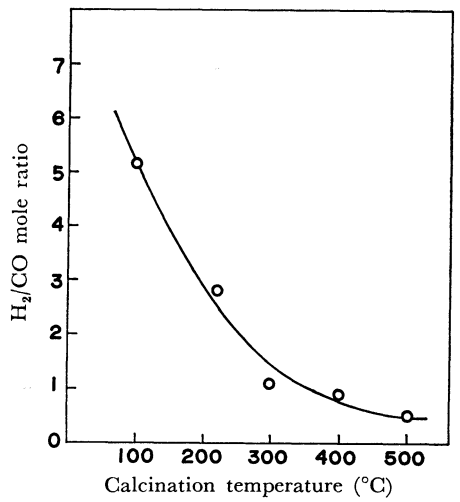

Fig. 11. The ratio of hydrogen and carbon monoxide adsorption on the platinum particles of the P-NaY type catalysts.

monoxide towards platinum particles may change according to their size distribution. This is suggested in Fig. 11, where the amount of hydrogen or carbon monoxide adsorption, at 10^{-1} mmHg and at room temperature, on the platinum supported on NaY zeolite is plotted against the calcining temperature, which has been shown to determine effectively the platinum particle size distribution. Those catalysts which are calcined at low temperatures, and which can consequently be supposed to have fine parparticles, adsorb larger amounts of hydrogen that of carbon monoxide, while those calcined at high temperatures, and having large particles, adsorb less hydrogen than carbon monoxide. The ratio of these two adsorption amounts is given in Table 4. Larger platinum particles, probably more than *ca.* 20 Å in diameter, are shown to have equal number of adsorptive sites for both of the gases by the fact, as is generally recognized, that hydrogen adsorbs in a dissociative fashion, while carbon monoxide does so in a linear form. This is shown by the fact that the ratio, H_2/CO in mole, in Table 4 approaches 0.5 with a rise in the calcining temperature. The reason why the catalyst calcined at a low temperature adsorbs much more hydrogen than carbon monoxide has not yet been made clear;[14] the fact, however, may be accepted that changes in the catalyst preparation procedure and/or conditions generally lead to a catalyst the surface of which is different in gas adsorption susceptibility as a result of some change in its physico-chemical properties, such as lattice defect and work function, in addition to merely physical properties, such as surface area.

TABLE 4. THE RATIO OF HYDROGEN AND CARBON MONOXIDE ADSORPTION ON THE PLATINUM PARTICLES OF THE Pt-NaY TYPE CATALYSTS

Cat. No.	Calcin. temp., °C	H_2/CO
2	100	(5.2) a)
3	220	2.9
4	300	1.2
5	400	0.9
6	500	0.5

a) The ratio is supposed to be slight reliable, because the amount of carbon monoxide on platinum is little.

14) G. C. A. Schuit and L. L. Van Reijen, "Advances in Catalysis," Vol. 10, ed. by Academic Press, New York and London (1958), p. 250.

On the other hand, the Pt-NH_4Y type catalysts were characteristically distinguished in their adsorptive properties from NaY type catalysts. Carbon monoxide on the carrier was extremely large. Figure 10 shows that the adsorption on the Pt-NH_4Y type carrier was also affected by the calcination temperature in the air.

In conclusion, dispersion state analysis by hydrogen chemisorption gives a result which is in virtual agreement with that obtained by electron microscopic observation with respect to the catalyst with an average particle size over approximately 20 Å in diameter. For the catalyst calcined at low temperatures, however, the hydrogen adsorption method possibly gives rise to a false result. This seems to suggest that the loaded platinum is dispersed in atoms or in fine particles which lose the metallic properties to adsorb hydrogen, supposedly in a more or less cationic state as a result of the pronounced effect of the surrounding oxygen atoms in zeolite. Carbon monoxide adsorption has generally been used to evaluate the metal surface and compared with the catalytic activity. However, the discrepancy between hydrogen and carbon monoxide adsorptions, observed in this study for the platinum fine particles, suggests that the hydrogen chemisorption method is more useful for predicting the catalytic activity, especially for reactions where hydrogen is involved.

These experiments have suggested that, for obtaining a properly dispersed platinum catalyst which has an excellent ability to chemisorb hydrogen, the temperature of calcining the ion exchanged zeolite is one of the most important key factors in the catalyst preparation.

The mechanistic interpretation of the action of oxygen in the calcination of $Pt(NH_3)_4^{2+}$ ion exchanged zeolite to promote the growth of platinum to form crystallites is an interesting subject; it is now under investigation in this laboratory.

For the catalysts calcined at low temperatures, the platinum particles dispersed in atoms or in fine particles, or both, lose their metallic properties to adsorb hydrogen, and supposedly gain a cationic character as a result of the pronounced effect of the surrounding oxygen atoms in zeolite.

A good parallelism that was found to exist between the amount of hydrogen adsorption, which depends on the dispersion states of platinum particles, and their catalytic activities of hydrogenation will be reported in the following paper.

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