

## Dispersion of Platinum in Pt/ZSM-5 Zeolites

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The dispersion of Pt in reduced Pt/ZSM-5 zeolites has been studied using electron microscopy and hydrogen chemisorption. Upon activation in O<sub>2</sub> at 200°C and reduction in H<sub>2</sub> at 400°C, 6- to 15-Å Pt agglomerates, most of which can fit in the channels and channel intersections in the bulk of the zeolite, are formed. However, they show little ability to chemisorb hydrogen (H/Pt = 0.33). Activation at 350°C prior to reduction produces mainly 20- to 25-Å metal particles, most of which are presumably located on the external surface of the zeolite, and these have a higher ability for hydrogen chemisorption (H/Pt = 0.69). Upon raising the activation temperature to 450°C prior to reduction, larger metal crystallites (mainly 30–55 Å diameter) are obtained. They are also presumably located on the external surface of the zeolite and chemisorb hydrogen only to a small extent (H/Pt = 0.35). © 1992 Academic Press, Inc.

### INTRODUCTION

The importance of metal dispersion in the efficient use of metal catalysts has been well established. Zeolite supports have gained increased importance in the preparation of highly dispersed supported metals. Indeed, several reports and reviews have been published on the use of faujasites (Y-zeolite in particular), with the pore system linking large cavities, as support for Pt and other metals (1–12). However, little is known about the dispersion of metals in pentasil (ZSM-5 and ZSM-11 in particular), pore systems of which do not link large cavities. The present paper therefore aims at giving a picture of the various dispersion, adsorption properties, and possible location of Pt in ZSM-5 zeolite, stress being laid on the variation of these parameters as a function of thermal treatment. Transmission electron microscopy and hydrogen chemisorption measurements were used for this purpose.

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### EXPERIMENTAL METHODS

#### A. Materials

Pt was introduced into domestically synthesized H-ZSM-5 (Na<sub>0.14</sub>H<sub>5.26</sub>Al<sub>5.4</sub>Si<sub>90.6</sub>O<sub>192</sub>) by ion exchange using a dilute aqueous solution ( $2.0 \times 10^{-3}$  M) of Pt (NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> salt, which provides Pt (NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> cations. The quantity of noble metal solution used was calculated to yield 0.5 wt% of Pt in the final catalyst (reduced). The solution was stirred at room temperature for 24 h, filtered, washed free of Cl<sup>-</sup> ions with deionized water, and dried overnight at 110°C.

#### B. Thermal Treatments

The thermal treatments (activation and reduction) were performed either in the hydrogen chemisorption or in the catalytic reactor system (13). A series of small samples (ca. 0.4 g) of the dried zeolite (0.25–0.5 mm fraction) was slowly heated (1 or 2°C/min) in a flow of oxygen (3 liters/h) up to different activation temperatures ranging from 200 to 450°C. The catalysts were maintained at these temperatures for 2 h and allowed to cool to room temperature in a purge of N<sub>2</sub> gas. Reductions

were then performed in flowing hydrogen (3 liters/h) by slowly raising the temperature at 2°C/min to 300°C and at 1°C/min to 400°C. The samples were maintained at this temperature for 1 h and then allowed to cool in flowing hydrogen or argon. The samples of 0.5 wt% Pt/ZSM-5 catalyst thus obtained were subsequently used for the various measurements, i.e., electron microscopy (EM) and hydrogen chemisorption.

### C. Electron Microscopy Measurements

The samples were examined using a Philips EM-400T high-resolution transmission electron microscope equipped with a microprobe system. A small amount of each sample was lightly ground and subsequently dispersed ultrasonically in acetone. A drop of the suspension was then evaporated on a "holey" carbon film, predeposited on standard copper grids. Specimens thus obtained were subjected to observation at magnifica-

tions ranging from 280,000 to 480,000 $\times$  with the microscope operated at 100 kV. Subsequent enlargements (600–1,000,000 $\times$ ) using thin photographic paper were practicable. The size of the metal particles was determined using a TGZ-3 particle size analyzer.

### D. Hydrogen Chemisorption Measurements

The chemisorption experiments were carried out using the dynamic pulse technique. Hydrogen chemisorption was measured on all the samples at 25°C in a continuous flow adsorption system similar to that described by Freel (14). Details of the experimental technique and calculation of volumes chemisorbed are given elsewhere (13).

## RESULTS

### A. Electron Microscopy Studies

On the zeolite activated at 200°C prior to hydrogen reduction at 400°C, very small

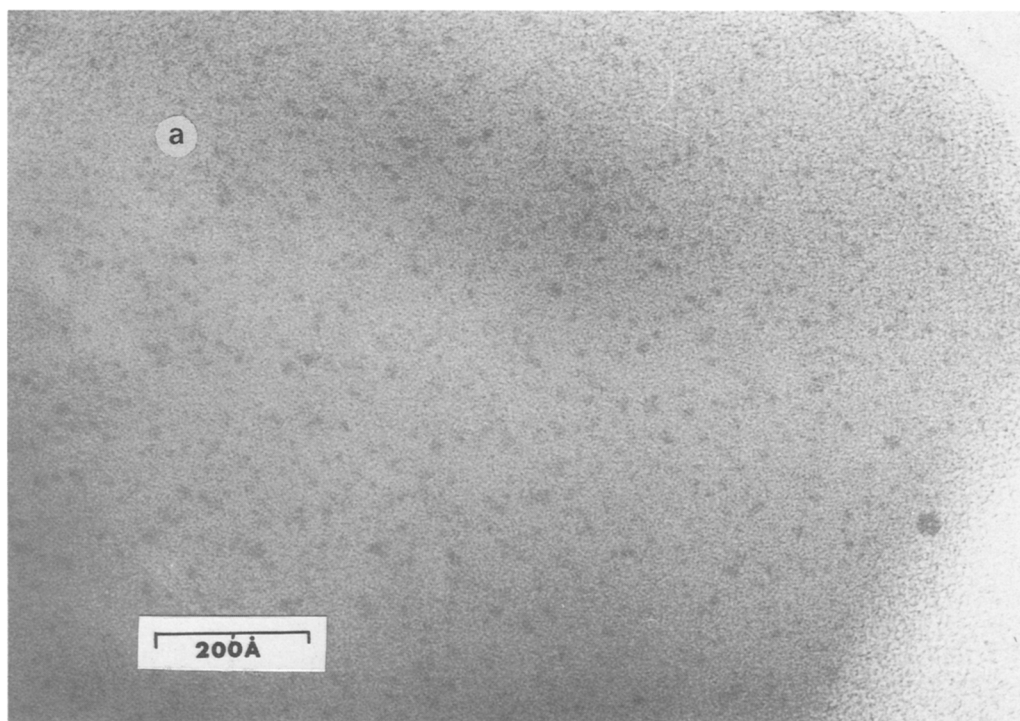


FIG. 1. Electron micrographs of Pt on ZSM-5 after activation in O<sub>2</sub> at (a) 200, (b) 350, and (c) 450°C, followed by reduction in H<sub>2</sub> at 400°C.

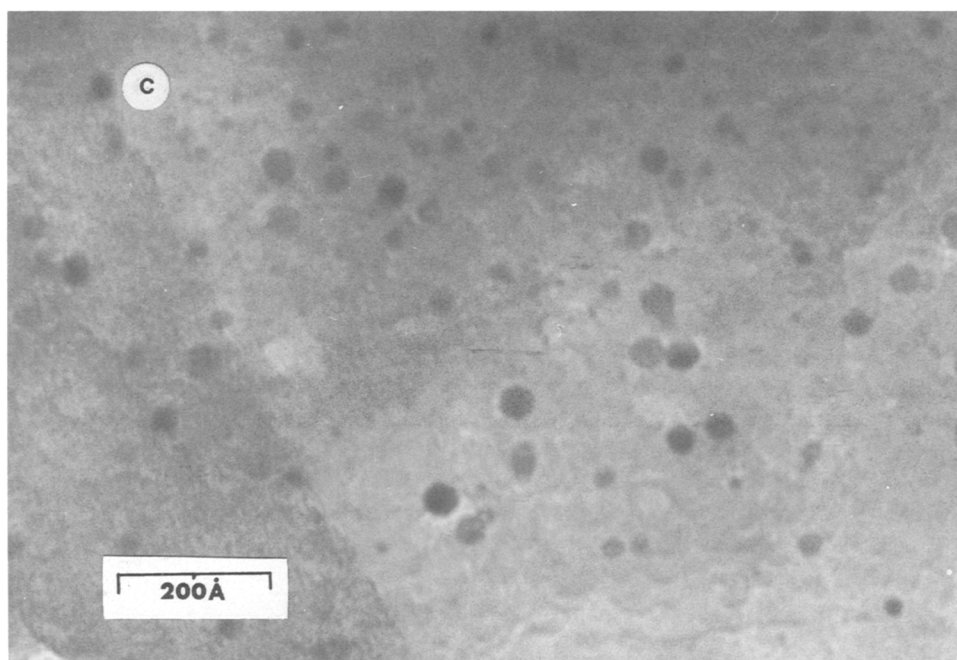
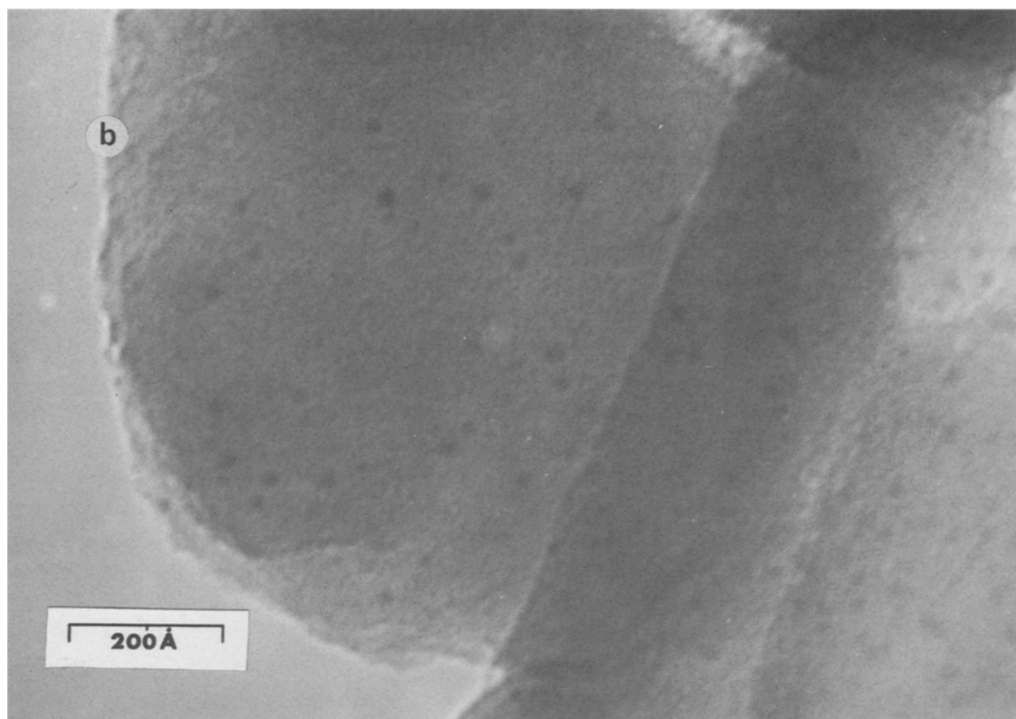


FIG. 1—Continued

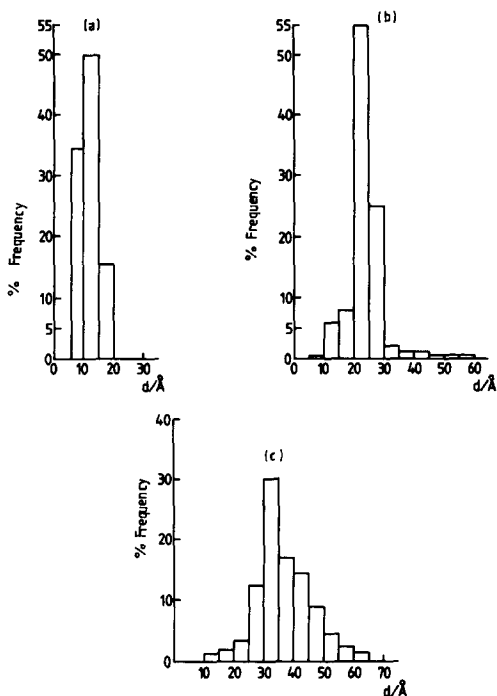


FIG. 2. Size distribution of Pt particles in 0.5% Pt/ZSM-5. (a) O<sub>2</sub>-200°C, (b) O<sub>2</sub>-350°C, (c) O<sub>2</sub>-450°C. All samples subsequently reduced in H<sub>2</sub> at 400°C.

particles of Pt with sizes ranging from 6 to 15 Å are observed (Figs. 1a and 2a). The majority of these particles has sizes in the range 8–15 Å. In the case of activation at 350°C, EM examination of the sample indicates that the sizes of Pt particles formed range from 6 to 60 Å (Figs. 1b and 2b), but most of them have sizes in the range 20–25 Å. On the sample activated at 450°C, fairly large Pt crystallites are formed. Particle size measurements indicate that, although the overall size distribution is 10–60 Å, the predominant size range is, indeed, 30–55 Å (Figs. 1c and 2c).

### B. Hydrogen Chemisorption Studies

The volume of hydrogen chemisorbed per gram of metal and the ratio H/Pt are plotted in Fig. 3. The ratio H/Pt for the sample activated at 200°C is 0.33 and increases to 0.69 for the sample activated at 350°C. However,

H/Pt sharply decreases to 0.35 for the sample activated at 450°C.

Based on the hydrogen chemisorption data, the average diameter of the Pt particles ( $\bar{d}_{vs}$ ) can be calculated assuming that the metal particles are spherical and that a hydrogen molecule dissociatively chemisorbs on 2 Pt atoms,

$$\bar{d}_{vs} = \frac{6\Sigma V_i}{\Sigma S_i},$$

where  $V_i$  is the volume and  $S_i$  is the surface area of dispersed platinum ( $S$  is given by the number of H atoms times the unit area per Pt atom, namely 8.39 Å (15)). The corresponding surface average diameter ( $\bar{d}_s$ ) can be estimated from electron microscopy data, using the expression (15)

$$\bar{d}_s = \frac{\Sigma N_i d_i^3}{\Sigma N_i d_i^2},$$

where  $d_i$  is the diameter of particle and  $N_i$  is each diameter increment. The results from

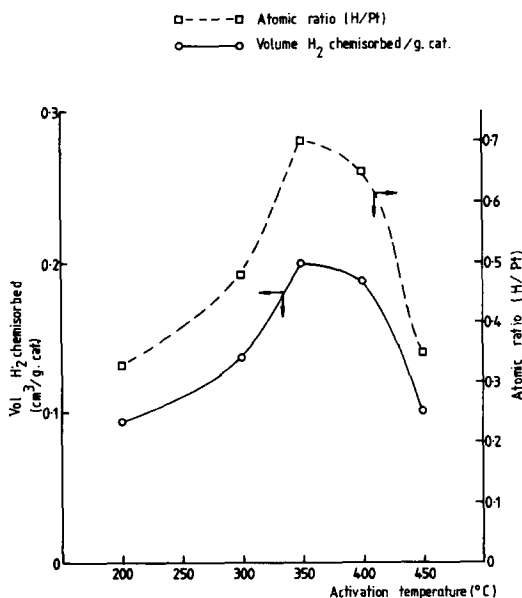


FIG. 3. Plots of volume of hydrogen chemisorbed and of the atomic ratio (H/Pt) against the activation temperature in oxygen.

TABLE 1

Comparison of Pt Particle Sizes in 0.5% Pt/ZSM-5 Determined by Means of H<sub>2</sub> Chemisorption and Electron Microscopy

Activation <sup>a</sup> temperature in O <sub>2</sub> (°C)	Average diameter ( $\bar{d}_{vs}/\text{Å}$ ) from H <sub>2</sub> chemisorption	Average diameter ( $\bar{d}_s/\text{Å}$ ) from electron microscopy
200	34.4	10.9
300	23.5	—
350	16.1	22.5
400	17.1	—
450	31.7	38.7

<sup>a</sup> Following activation in O<sub>2</sub>, all the catalysts were reduced in H<sub>2</sub> at 400°C.

the two sets of calculations are presented in Table 1.

## DISCUSSION

### A. Pt Dispersion in Pt/ZSM-5 Zeolite

The results in Figs. 1 and 2 clearly show that Pt particles supported on ZSM-5 zeolite vary in their sizes as a function of the activation temperature in O<sub>2</sub>. Previously, other workers (5–7, 9–12) obtained similar results with Pt supported on other zeolites (X- and Y-types). Although ZSM-5 has no large cavities like those in X- and Y-zeolites, its structure (16), however, contains channels (5–6 Å wide) and channel intersections (9–10 Å wide).

Considering this pore system, the influence of the activation temperature on Pt dispersion in Pt/ZSM-5 is tentatively suggested to be due to the position of Pt<sup>2+</sup> ions (formed from the decomposition of Pt(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> cations) in the zeolite prior to reduction in H<sub>2</sub>. When the ion-exchanged ZSM-5 is activated at low temperature (200°C), Pt<sup>2+</sup> ions presumably occupy positions in the channels and channel intersections of the zeolite. Upon reduction at 400°C, Pt atoms form 6- to 15-Å agglomerates, most (if not all) of which remain occluded in these channels and channel intersections in the bulk of the zeolite. Part of the zeolite framework

around the few particles larger than 10 Å is probably destroyed in order to accommodate them. A similar suggestion was made by Gallezot *et al.* (5) to explain the accommodation of 15- to 20-Å Pt crystallites in the bulk of Y-zeolite with supercages 13 Å in diameter.

In the case of activation at a higher temperature (350°C), most of the Pt<sup>2+</sup> ions probably migrate into positions in the pore system near pore mouths. Upon reduction at 400°C, metal atoms gradually migrate to the external surface of the zeolite, where they form large particles (mainly 20–25 Å in size). A further rise in activation temperature to 450°C probably causes most of the Pt<sup>2+</sup> ions to migrate out of the pore system to the external surface of the zeolite crystals, where, during reduction, metal atoms sinter rapidly to give the large crystallites (mainly 30–55 Å in size). The dependence of Pt dispersion on the location of Pt<sup>2+</sup> ions in zeolites (which is a function of the temperature of activation in O<sub>2</sub>) was previously demonstrated for Pt/Y zeolites by Gallezot *et al.* (5, 6) and by Sachtler and co-workers (10–12).

### B. Chemisorption Properties of Pt Particles on ZSM-5 Zeolite

The results in Fig. 3 show clearly that the volume of hydrogen chemisorbed by Pt/ZSM-5 and, hence, the dispersion (H/Pt) are dependent upon the activation Pt temperature in O<sub>2</sub>, thus confirming previously published results (5, 7, 10, 11) on the chemisorption properties of Pt supported on other zeolites (e.g., Y-zeolite). However, for the catalyst activated at 200°C, there is a considerable discrepancy between the sizes calculated from hydrogen chemisorption and from electron microscopy data (Table 1). Since Pt crystallites with diameter up to 34.3 Å were rarely detected on this catalyst in the electron microscope, the large  $\bar{d}_{vs}$  obtained is due to low chemisorption by the 6- to 15-Å agglomerates. Hence, only an "apparent Pt dispersion" would be measured by hydrogen chemisorption for this catalyst.

However, it should be noted that in this range of size, nearly all the metal atoms are exposed and should chemisorb hydrogen with  $H/Pt = 1$ . Gallezot *et al.* (5) and Tzou *et al.* (10, 11) found  $H/Pt = 1$  for Pt agglomerates in the size range 5–13 Å supported on Y-type zeolites.

Two interpretations can be tentatively proposed to explain the discrepancy observed for the small Pt agglomerates in Pt/ZSM-5:

(i) The low hydrogen adsorptive ability of the 6- to 15-Å Pt agglomerates may be due to electron deficiency effects arising from a partial electron transfer between Pt atoms and Lewis acid sites on the ZSM-5 support (17, 18).

(ii) Some of the Pt agglomerates occluded in the zeolite bulk are probably not accessible to hydrogen.

Indeed, some Pt agglomerates fitting in the channels (5–6 Å wide) and channel intersections (9–10 Å wide), perhaps near pore mouths, can block access by molecular hydrogen (with kinetic diameter of 2.89 Å) to other metal agglomerates located further in the interior of the zeolite pore system, thereby resulting in low hydrogen adsorption by the catalyst.

As for the catalysts activated at 350 and 450°C, there is less disagreement between hydrogen chemisorption and electron microscopy results since most of the Pt particles or crystallites are on the external surface of the zeolite crystals and are thus accessible to hydrogen. The slight differences observed are probably due to errors (5–10%) incurred in the assumptions used for calculating the average diameter from these data. The  $H/Pt$  ratios of 0.69 and 0.35 found respectively for these catalysts (Fig. 3) are, more or less, consistent with the sizes of the metal particles or crystallites observed on them.

#### CONCLUSION

This study has shown that the various states of dispersion and possible location of Pt in ZSM-5 zeolite matrix strongly depend

on the temperature of activation (or pretreatment) of the ion-exchanged zeolite in  $O_2$  prior to reduction in  $H_2$ . The results in this work also show that 6- to 15-Å Pt agglomerates, which are small enough to be lodged in the intracrystalline pore system of ZSM-5, are obtained but they chemisorb hydrogen only to a small extent. Whether this is due to an intrinsic property of these small metal agglomerates and/or to their inaccessibility to hydrogen is a question that needs to be cleared up.

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