HREM IMAGING OF SMALL Pt CLUSTERS DISPERSED IN Y-ZEOLITES

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Received 20 November 1989; accepted 21 February 1990

HREM, small Pt clusters, zeolites

High resolution electron microscopy (HREM) has been used to study dispersed Pt clusters in NaY- and USY-zeolites. All the samples contained 0.8% Pt and were reduced at temperatures of 300 °C, 500 °C and 650 °C. The size of the Pt clusters ranged from a few Å up to ~ 30 Å. When the incident electron beam was sufficiently strong, it caused some of the extremely small metal clusters to sinter. This was usually accompanied by zeolite damage. This in-situ sintering must be taken into consideration when interpreting the particle size distribution results obtained solely by TEM, especially for particles that are smaller than 10 Å. The minimum phase contrast imaging condition is demonstrated to be more appropriate than optimum defocus for detecting the extremely small Pt clusters inside the zeolite structures.

1. Introduction

The importance of zeolites as a catalytic material in petrochemical processing has been known for many years [1]. TEM has been shown to be very valuable in characterizing catalysts made up to zeolites containing dispersed metals [2,3]. The crystal structures of zeolites can be considered as framework aluminosilicates which are made up of a three-dimensional network of AlO4 and SiO4 tetrahedra linked to each other by sharing all of the oxygens [4]. The general formula of a zeolite for the crystallographic unit cell can be written as: $M_{x/n}[\text{AlO}_2]_x[\text{SiO}_2]_y,$ where $M$ is the cation of valence $n$, $w$ is the number of water molecules. Zeolite Y, along with X and faujasite, has a FCC lattice with an $a_0$ of about 24.74 Å. The unit cell contains 192 (Si, Al)O4 tetrahedra. The structural units are the so-called $\beta$-cage and double 6-ring which are polyhedral arrangements of (Si, Al)O4 tetrahedra. The structure can be simply visualized as a diamond structure with the replacement of each C atom by the $\beta$-cage which is tetrahedrally joined to other $\beta$-cages through the double 6-ring unit [4].

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When catalytic metals are introduced into the zeolite matrix, it is important to determine the distribution of the metals. It would be especially informative if we can visualize small metallic clusters inside the open channels and the zeolite cages [5]. The orientational relationship, if any, between the metals and the zeolite structures would be an important clue to the catalytic behavior of a particular catalyst [6]. This presents a great challenge to the HREM technique because (1) the metal clusters of interest are very small (on the order of 10 Å or less), the strong phase contrast produced by the zeolite structure could easily obscure their contrast, and (2) the deterioration of the zeolite structure is rapid under HREM imaging conditions.

There are many studies on the crystal structures and defects of various zeolites by HREM [7–12]. However, the application of this technique has been limited mainly by the sensitivity of the nonconducting zeolites to electron beam damage [13,14]. Efforts have been made to develop methods for stabilizing the zeolite structures for TEM observations. Successful results have been achieved in some cases [15,16]. In this paper we will report some HREM studies of the small Pt clusters dispersed in the zeolite structures of 0.8% Pt/NaY and 0.8% Pt/USY catalysts.

2. Experimental

The catalysts were prepared by the incipient wetness impregnation of NaY zeolite with an aqueous solution of Pt(NH$_3$)$_4$(NO$_3$)$_2$ to provide 0.80 g Pt per 100 g zeolite. Each catalyst was dried overnight in a vacuum oven at 100 °C, heated at 5 °C per minute from room temperature to 150 °C in flowing dry air, heated at 5 °C per minute from 150 °C to 290 °C in a flowing mixture of 75% air and 25% steam, held at 290 °C in the flowing air stream mixture for two hours, and cooled to room temperature in dry air. The samples were then divided into three portions and reduced in H$_2$ at 1 atmosphere pressure. The $^{129}$Xe NMR results and chemisorption results were presented in a previous publication [17]. The TEM samples were prepared by two methods, direct dispersion and ultramicrotomy. The zeolite powders were ground in an agate mortar and suspended in ethanol. After being further dispersed in the ultrasonic agitator, a drop of the suspension was put on a holey carbon grid and allowed to dry in air. This method for preparing catalyst TEM samples has been described by many authors [2,5,8].

All the HREM work was carried out in a JEOL JEM-200 CX with a top-entry stage and point resolution of 2.5 Å. The images were recorded at 200 kV and magnifications of either 100,000 or 130,000. The electron beam intensity was kept as low as possible with the selection of spot size 4 to minimize the beam damage to the zeolites. The samples were also examined at 400 kV with the JEOL JEM-4000EX but appeared to be more stable at 200 kV than 400 kV.