Making Materials Mesoporous

Mesopores Created by Platinum Nanoparticles in Zeolite Crystals

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Zeolites are important catalytic materials because they have large surface areas, good heat-resistance, solid-state acidity, and molecular-shape selectivity owing to their framework structures.[1,2] Many types of zeolites and related materials have been synthesized and utilized.[3] For example, zeolite Y and zeolite ZSM-5 are used industrially to refine oil and convert methanol into gasoline, respectively. NOx reduction over metal-exchanged zeolite Cu-ZSM-5 has also been examined.[4] In each case, the shape of the channels and pores in the zeolite framework contributes to the catalytic reactions. Synthesis methods and applications for ordered mesoporous materials have also been researched in recent years.[2] These materials are potential catalysts and adsorbents

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because their mesopores are of the same order as the size of many industrially important molecules. Researchers have also attempted to make the amorphous wall surfaces crystalline or add a zeolite-like function to them.[5] Judicious use of micropores (<2 nm diameter) and mesopores (2–50 nm diameter) should enable the reaction field to be accurately controlled so that a wide range of applications can be expected.

The constituents of catalysts undergo various structural changes under actual operating conditions. In the case of automobile catalysts, sintering of the noble metal particles and chemical reactions between the support, particles, and atmosphere occur at high temperature.[6] Understanding such changes on a nanostructural level will provide information for developing high-performance catalyst materials.

Herein, we report the structural changes of a platinum/zeolite catalyst under actual operating conditions. We found that platinum particles penetrated from the surface of the zeolite into its crystalline bulk, with mesopores of about the same size as the platinum particles being formed as if the platinum had tunneled into the structure. This surprising phenomenon has never been observed before in Pt/zeolite catalysts, and might be useful as a technique for controlling the structure of the catalyst. We therefore examined the mesopores in detail to understand their properties better.

Zeolite ZSM-5 ($SiO_2/Al_2O_3 = 1900$) was used as the support in this study. Platinum particles were prepared on the ZSM-5 with a $[Pt(NH_3)_4](OH)_2$ solution. The solution was evaporated to dryness and annealed at 673 K for 2 h in air. The platinum density on the catalyst was 8.4×10^{-5} mol g^{-1}. The prepared catalyst powder was pressed into a pellet, and was exposed to an atmosphere containing gases similar to the actual exhaust gases of an automotive engine (0.11–1.75 % CO, 0.03–0.11 % C_3H_6, 0.19–0.23 % NO, 0.03–2.52 % O_2, 15 % CO_2, 3.0 % H_2O in N_2, total flow-rate $= 0.01$ m^3 min^{-1}.) at 1073 K for 100 h. We examined the nanostructure of the catalyst particles before and after the aging process with a field-emission scanning electron microscope (FE-SEM, Hitachi S-5200) and transmission electron microscopes (TEM, JEOL JEM-2010 and Hitachi HF-2000). The sample for TEM observation was dispersed on a carbon-covered copper mesh. Composition analysis was carried out by energy dispersive X-ray spectroscopy (EDS). Pore volumes were measured by N_2 gas adsorption and desorption experiments using a Shimadzu ASAP-2010 analyzer.

SEM and TEM images of the surface of catalyst particles in the initial state are shown in Figure 1 a and b. EDS confirmed that the small bright particles in Figure 1 a and dark particles in Figure 1 b were platinum. Most of the platinum particles were widely dispersed on the surface of the zeolite crystal, and their size was under 10 nm.

After aging the platinum particles were no longer visible on the surfaces of the zeolite particle, on which many dark spots appeared which looked like holes penetrating the surface (Figure 1 c). Platinum particles about 10 nm in size associated with channels were observed near the surface of the zeolite crystal (Figure 1 d). These characteristic channels seem to be tracks caused by the platinum particles penetrating from the surface of the zeolite crystal into its bulk. The width of the channels is almost equal to that of the platinum particles and the platinum particles are located at the end of the tracks. We assume that the platinum clusters sintered and grew to sizes of about 10 nm on the surface of the zeolite and then penetrated into the zeolite during the aging process.

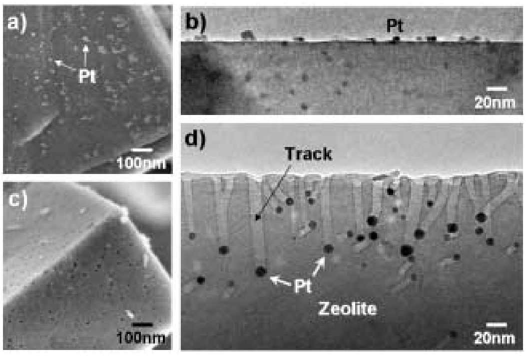

Figure 1. Micrographs of the Pt/ZSM-5 catalyst. a) SEM image of the catalyst particle before aging. b) TEM image near the surface of a catalyst particle before aging. Platinum particles several nanometers in size are distributed over the surface of the zeolite. c) SEM image of the aged catalyst. Many pores are visible on the surfaces. d) The surface of the aged catalyst. All the platinum particles have penetrated into the zeolite. The tracks in the lower part of the image at odd angles to the surface are those formed by particles which have penetrated from other sides of the zeolite crystal.

The length of the tracks caused by platinum-particle penetration sometimes reached several hundreds of nanometers. Most platinum particles appear to have moved in a straight line in directions usually parallel to the crystal faces of the zeolite ZSM-5. Powder X-ray diffraction of the zeolite before and after aging produced the diffraction patterns of zeolite ZSM-5 in both cases, with no significant differences between them.

A thin sample including a section of the track along which a platinum particle migrated was prepared for TEM observation by Ar^+ ion polishing. The cross section of the track in the thin sample was observed to produce a very bright contrast about 10 nm in diameter. No contrast corresponding to an amorphous region was observed around it. From the EDS analysis, we confirmed that apart from the platinum particle the channel was vacant. In other words, the channel corresponds to a mesopore in the zeolite. The gas absorption–desorption experiments also showed that mesopores had been formed (see Supporting Information). The total volume of the measured mesopores agrees well with the volume estimated from the amount of loaded Pt, particle size, and the length of the mesopores.

TEM observation under a very low-intensity electron beam is one of the most effective techniques for studying the fine structure of materials, such as zeolites, which are easily damaged by electron-beam irradiation.[7] We applied this technique to determine the crystal condition of the zeolite around the “mesopore” formed by the platinum particle.

Figure 2 a is a TEM image of a mesopore observed from the [100] direction of the zeolite ZSM-5. This image indicates that the region of the zeolite around the mesopore is in the crystalline state. Figure 2 b is a micrograph of a mesopore

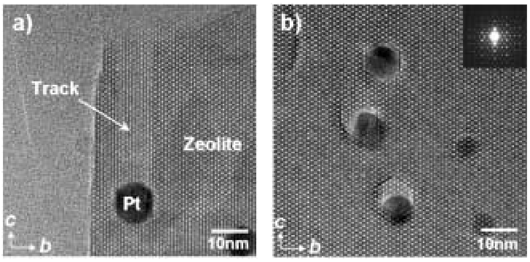

Figure 2. TEM images of mesopores formed by platinum particles in the aged catalyst. Both images were taken along the [100] zone axis. a) The region around the mesopore remains crystalline. b) The width of the mesopore is almost equal to that of a platinum particle. The walls of the mesopore are formed from zeolite crystal facets.

viewed normal to its long axis. This micrograph shows that the width of the mesopore is almost equal to that of the platinum particle. A characteristic feature of all mesopores is their internal walls are constructed from facets of the zeolite crystal.

The high-resolution TEM image in Figure 3 shows a typical cross section of a mesopore observed along the [010] zone axis. This micrograph reveals that the crystal structure of the zeolite ZSM-5 is maintained right up to the edges of the mesopore. By comparison with the structural model in Figure 3b viewed along the same direction, we can see that the apexes of the hexagonal mesopore correspond to the main channels of the zeolite's 10-ring. The sides of the hexagonal mesopore correspond to {100} planes and {101} planes of the zeolite ZSM-5. The surfaces of the mesopores were found to be terminated by rows of atoms from the split main channels and the neighboring 5- and 6-rings as shown in Figure 3b. This configuration corresponds to planes of high atomic density, so that the stability of the observed facets can be explained in terms of the greater number of chemical bonds that must be broken compared to in less dense planes of the same orientation.

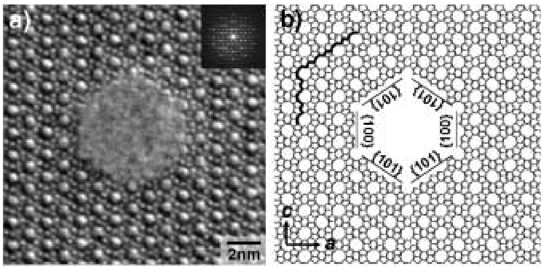

Figure 3. a) HR-TEM image of the cross section of a mesopore observed along the [010] zone axis compared with a structural model (b) see main text for details.

When observed along the [010] axis of the ZSM-5, the mesopore cross-sections tended to be hexagonal (Figure 3). Cross sections observed along the [100] axis were also hexagonal with the mesopores bounded by {010} and {011} planes (see Figure 2b). When viewed along these two axes, large channels 0.51–0.56 nm in diameter which are arranged regularly can be seen.[3] We consider these to be easy directions for making hexagonal tunnels. When observed along the [001] axis, the cross section was an irregular polygon, with {100} and {010} planes forming the long sides. Such irregular polygons were rarely observed, however, and most mesopores grew perpendicular to the [001] direction. When projected along the [001] axis, material density varies periodically along the x and y axes. Such a configuration can result in mesopores whose cross sections are polygons containing {100} and {010} planes. The cross-sectional shapes of mesopores formed by platinum particles therefore seem to strongly reflect the framework structure of the zeolite.

In the micrograph of Figure 4a, lattice fringes from the {101} planes of the ZSM-5 and mesopores along the planes were observed. While still observing this region, we tilted the sample about the [101] direction. The apparent length of the mesopores decreased with increasing tilt angle, until the cross sections of the mesopores and their Pt particles perfectly coincided in most cases at an angle of 0.29 radians (Figure 4b). In this position, the incident electron beam was aligned with the [010] direction of the zeolite. This result indicates that hexagonal mesopores about 80 nm in length formed selectively along the [010] axis of the ZSM-5 crystal. It can be seen that the mesopores in Figure 4 marked P1 and P2 both formed in the [010] direction of the ZSM-5, while the platinum particles moved in the reverse direction. Hence, they appear to have penetrated into the zeolite crystal along the [010] axis but from opposite surfaces of the particle. By examining several other particles, we confirmed that mesopores formed mainly along the [100] and [010] axes.

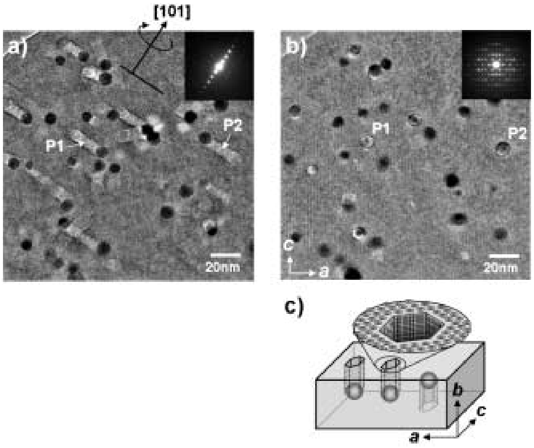

Figure 4. TEM images of mesopores and platinum particles. a) Most of the mesopores formed along the {101} plane of the ZSM-5, the diffraction pattern of which is also shown. b) The crystal tilted by 0.29 radians, observed along the [010] zone axis of ZSM-5. The mesopores mainly formed along the [010] direction. c) Schematic diagram of the zeolite surface.

The mechanism of the phenomenon reported here is considered to be as follows: The width of the mesopores is equivalent to the diameter of the platinum particles, and the framework structure of the zeolite is not perturbed by the presence of a mesopore. This feature suggests that the mesopores formed by selective reaction with atoms in the zeolite structure at the interface between the platinum and zeolite. Under hydrothermal conditions siloxane bonds in zeolites are broken and recombined.[8] When silica is heated in contact with silicon, carbon, hydrogen, or a hydrocarbon at high temperatures, SiO is given off as a gaseous product.[9] The surfaces of the platinum particles act as catalytic reaction sites, so that water forms on them by reaction between the molecules in the atmosphere during aging according to Equation (1):

$$C_mH_n + (m + n/4)O_2 \rightarrow m\,CO_2 + (n/2)\,H_2O \qquad (1)$$

Heat is also generated by this reaction. Water and hydrogen can also be formed by other catalytic reactions. Around a single platinum particle there are a greater number of active agents, such as radicals produced by catalytic reactions, water and hydrogen reaction products, and active H^+ and OH^- ions (from the dissociation of these products as well as from Si–OH terminating species of the zeolite) than in other regions. It is likely that these active agents at high temperature cause the decomposition of siloxane bonds at the interface between the platinum particle and zeolite. It is conceivable that broken zeolite components diffuse out of the system in forms of SiO or $Si(OH)_4$ because no amorphous phases were observed around the mesopores by electron microscopy, and because the mesopores increased in volume according to gas absorption–desorption measurements. While the decomposition of the siloxane bonds gradually progresses at the interface between platinum and the zeolite, the platinum particle itself tends to remain in contact with the zeolite because this is the most energetically stable position. As a result, the platinum particle gradually penetrates into the zeolite.

The mesopores formed along particular directions in the zeolite ZSM-5 crystal, and their walls were formed from specific ZSM-5 crystal faces. Such shape selectivity during the mesopore formation process can be explained as follows: There is a spatial distribution in the densities and directions of siloxane bonds in the framework of zeolite. Vacancies are most easily formed by the decomposition and removal of siloxane bonds in directions where the bond density is lower. The platinum particle continues to “eat” its way into the zeolite, but the final shape of the mesopore is strongly influenced by the framework structure of the zeolite. In addition, the structure of the zeolite may also affect the diffusion rates of reactants to the reactive interface.

Formation of mesopores using carbon during synthesis of zeolites or by generation of noble-metal particles has been reported.[10,11] However, the shapes of the mesopores and their arrangement could not be controlled. With a technique based on the phenomenon reported here, it might be possible to control the shape and size of the mesopores by altering the size of the platinum particles, the processing time, the type of zeolite, and the crystal orientation of the support material. Such a technique would produce materials for applications in which both structure-controlled mesopores and micropores based in a zeolite framework are needed, such as fine catalysts, adsorbents, and nano-ordered devices, with high precision and efficiency.

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