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New Phenomena and Applications by Combination of Metal Oxide and Ultrasound

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Direct synthesis of nanocrystalline novel metals from metal oxides have been investigated by ultrasonic irradiation at room temperature in ethanol. For silver metal, the average particle size of 4nm was successfully prepared on surface of zinc oxide from the silver oxide powder using this process. This reduction was believed to be caused by harmonization of reaction field and materials. By applying this process and choosing the suitable conditions, the nano-sized platinum particles were also prepared on porous cordierite by this sonochemical process. In this paper, the process conditions of the new sonochemical reaction, which can prepare the nano-sized metal particles, were studied for various kinds of substrates, and their mechanisms were discussed.

Key words: Cavitation, Sonochemical process, Nanoparticles, Silver, Platinum

1. INTRODUCTION

In general, the properties of specific energy source determine the course of a chemical reaction. The ultrasonic irradiation differs from traditional energy sources in duration, pressure, and energy per molecule, and it is a unique means on the interaction between energy and matter [1]. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Instead, they are derived principally from acoustic cavitation, which can produce temperatures as high as those on the surface of the sun and pressures as great as those at the bottom of the ocean. Thus, the chemical applications of ultrasound have become an exciting new field of research during the past decade [1-4].

Reseachers now know that the chemical effects of ultrasound are diverse and include substantial improvements in both stoichiometric and catalytic chemical reactions. In some cases, ultrasonic irradiation can increase reactivities by nearly a millionfold. This means that the chemical reaction which takes place under conventional conditions can be amplified by ultrasonic irradiation, that is, effects of concerted amplification [5].

Cavitation by ultrasound radiation in a liquid occurs due to the stresses induced in the liquid by the passing of a sound wave through the liquid [1-4]. A sound wave consists of compression and decompression/rarefaction cycles. Thus, if the pressure during the decompression cycle is low enough, the liquid can be torn apart to leave small bubbles. These cavitation bubbles are the heart of sonochemical process, and these bubbles are subjected to the stresses induced by the sound waves. This causes the bubbles to grow during a decompression phase, and contract or even implode during a compression phase. These bubbles are filled with vapor and gas, and can produce radicals during such implosion. These implosions are important in sonochemical process. Each one of these imploding bubbles can therefore be seen as a microreactor, with high temperature and pressures of several hundreds of atmospheres. Sonochemical process is chemistry assisted and /or enhanced by ultrasound, and then the chemical reactions that take place under more conventional conditions are accelerated, or even yield totally different products. These phenomena can be attributed to either physical or chemical effects of cavitation [6-8]. As the chemical effects of ultrasound, the reaction rates will be enhanced because of the formation of highly reactive radical species formed during cavitation. In liquids, the use of ultrasonic irradiation facilitates the reduction. In general, organic liquid can generate free radicals upon ultrasonic irradiation, and it is easy to reduce metal ions in liquid systems [9,10]. These reactions represent the formation of reducing radicals in liquid systems [9-12]. The chemical effects of ultrasonic irradiation fall into three areas: homogeneous sonochemical efffects of liquids, heterogeneous

sonochemical effects of liquid-liquid or liquid-solid systems, and sonocatalytic effects. In this study, the sonochemical process of nano-sized metal deposition on various kinds of substrates were investigated for the liquid-solid system at room temperature, and the mechanisms were discussed.

2.EXPERIMENTAL PROCEDURE

Ultrasonic irradiation was performed with a sonoreactor (HONDA ELECTRONIC CO. LTD). The output power of the sonoreactor was 22.9kHz, 100W. Ag_2O and PtO_2 were used as starting powders. Both average particle sizes was about 3μm. The powders were immersed in ethanol, which was contained in the beaker, and the beaker was partly submerged with water in the sonoreactor. Powders were irradiated at 20°C by ultrasound together with glass and/or quartz substrates, zinc oxide powder or porous cordierite (30mm×30mm×30mm, 30cell). The obtained products were characterized by X-ray diffraction (RU-200B, Rigaku Co., Tokyo, Japan). A scan rate of 5°/min was used to record the patterns in the 2θ range of 30-80°. The morphology and particle sizes of the products were observed by transmission electron microscopy (TEM, Hitachi Model H-8100) using an accelerating voltage of 200kV. Scanning tunneling microscope (STM, Nano Surf AG, Easy Scan) was also used to characterize the nano-metal particles on the quartz surface deposited by ultrasonic irradiation.

3.RESULT AND DISCUSSION

3-1 Nano-sized silver coating materials

Surface of quartz substrates coated Ag metal by the ultrasonic irradiation is shown in Figure 1. The color of quartz substrates gradually changed from yellow to translucent metallic color alike miller due to the irradiation. These results suggest that the deposition of Ag particles was made on the surface of quartz substrate. The XRD pattern of Ag coating quartz prepared by 180 minutes ultrasonic irradiation is shown in Figure 2. The Ag peaks are clearly observed in this XRD chart. These observations indicate that the Ag_2O was reduced into the Ag metal by the ultrasonic irradiation at room temperature.

To confirm more details the formation of Ag coating on the quartz substrates, STM observation was carried out. Figure 3 shows a STM image of the Ag coating glass prepared by 180 minutes ultrasonic irradiation. The thickness of this uniform coating was estimated to be under 50nm. Figure 4 shows a TEM image of the Ag particles formed on the zinc oxide powder with the average particle size of 100nm by the sonochemical process. It was clearly conformed from this picture that the deposited Ag particle was of nanometer size and homogeneously dispersed on the surface of powders. The average size was under 5nm. This observation indicates that the ultrasonic irradiation plays an important role in

Figure 1. Quartz substrates coated Ag from Ag_2O by the sonochemical process at room temperature

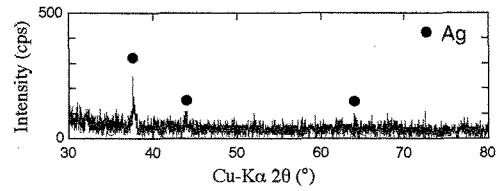

Figure 2. XRD pattern of the quartz substrate coated the Ag metal for 180 minutes irradiation.

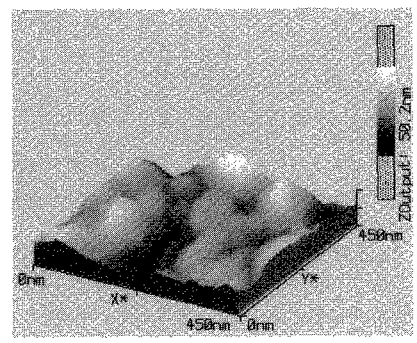

Figure 3. STM image of the Ag coated quartz for 180 minutes irradiation.

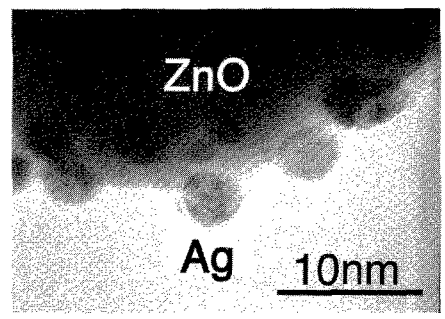

Figure 4. TEM image of ZnO powder deposited the Ag metal by sonochemical process.

the reduction of Ag_2O to Ag. In this case, reducing radicals are not concerned with reduction of Ag_2O because of liquid-solid system. It is considered that driving force of reduction is shock wave in cavitation. When cavitation occurs in a liquid near a solid surface, the cavity collapse changes dramatically the dynamics of energy [13,14]. When the powders exist like the experiment in this study, therefore, it induces the jet formation. In the case of liquid-powder (Ag_2O-EtOH) slurries, the shock waves created by cavitation can create high-velocity collisions. Close to a solid boundary, cavity collapse is very asymmetric and generates high-speed jets of liquid. The potential energy of the expanded bubble is converted into kinetic energy of a liquid jet that moves through the bubble's interior and penetrates the opposite bubble wall. These jets hit the surface with tremendous force [13-15]. In this study, during ultrasonic irradiation, it is considered that the cavity collapsing near the extended Ag_2O particles drives high speed jets of liquid into the surface of Ag_2O. It is observed that the liquid jets drive into the surface with high-velocity [15]. These phenomena have great importance for understanding of the reduction of Ag_2O. The turbulent flow and shock waves produced by intense ultrasound can drive metal particles together at sufficiently high speeds to cause effective melting at the point of collision. Such collisions are capable of inducing striking changes in surface texture, composition, and reactivity. Hot spot reaction represents the directly reduction by cavitation. This phenomenon produces a newly exposed and highly heated surface, which makes the reduction of Ag_2O easy rapidly. The nucleation of Ag occurred in solution and then growth and immobilization of the Ag particles would proceed on another powders or substrates.

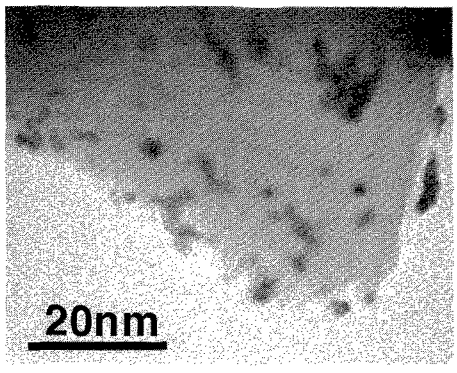

Figure 5. TEM image of the nano-sized Pt metal particles deposited from PtO_2 on cordierite surface at room temterature.

3-2 Application

We applied this phenomenon to PtO_2 and prepared platinum supported porous cordierite by ultrasonic irradiation. A TEM image is shown in Figure 5. It was observed that the nano-sized platinum particles were formed on cordierite. The particle shape and size are able to control by condition (e.g. irradiation time, irradiation wavelength and solution). Generally, the Pt metal supported materials are made by soaking the porous support into aqueous solutions of nitrates, and calcining at high temperatures to produce metal particle. In the case using nitrates, NO_x is formed during works. On the other hand, this method only generates O_2 at room temperature. It is very worthy to note that this process is of low environmental impact.

4.SUMMARY

In this study we proposed new phenomena by the concerted amplification and its applications. And the deposit ion of the Ag and Pt nano-sized particle from the metal oxides on various materials was successfully made by the sonochemical process at room temperature. This fact means that the chemical and physical reactions, which take place under conventional conditions, can be amplified by the ultrasonic irradiation. There is no doubt that the most important parameter in sonochemical effects, which were observed in reduction of metal oxides, is cavitation induced by the ultrasonic irradiation. It is expected that this sonochemical process can be applied to obtain the nano-sized metal particles supported materials by adjusting conditions. In final, it is worthy to specially note that this process is very simple, safety, and clean.

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