Application of microwave to the synthesis of nanosized metal and alloy catalysts on titanium dioxide supports

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Abstract. Nanosized Pd and PdAu x alloy particles were deposited on various titanium dioxides (TiO2; anatase + rutile, anatase, and rutile) using a simple and unique microwave-assisted method. The structure of the obtained samples was characterized by X-ray diffraction (XRD), N2 adsorption-desorption and X-ray absorption fine structure (XAFS) methods. Results of XAFS indicated that PdAu x alloy particles had formed on TiO2 supports. Catalytic activity was estimated by a direct synthesis reaction of hydrogen peroxide (H2O2) from hydrogen and oxygen gases at room temperature. A high reaction rate could be obtained using these PdAu x alloy catalysts compared with conventional Pd catalysts.

1. Introduction
Microwave dielectric heating has attracted a great deal of attention as a new and promising method in organic and inorganic syntheses [1]. It is widely accepted that microwave irradiation enables rapid, uniform and energy efficient heating. This heating is also applicable to the simple preparation of metallic nanostructured materials [2]. For example, Ru, Ag, Pt, PtNi, Cu nanoparticles, ZrO2, Ag nanowires and zeolites have been prepared using microwave heating [3-9]. As a supported system, carbon-supported and polymer stabilized colloids have been synthesized [10-13]. Recently, the microwave synthesis of Au and Pd nanoparticle catalysts on CeO2 supports and their high catalytic activities for the CO oxidation reaction were reported [14]. Although a large number of studies dealing with the preparation of metal colloids and clusters have been reported, no reports exist concerning the microwave-assisted synthesis of metal particles supported on titanium dioxides (TiO2).

Many reports describe a direct synthesis of hydrogen peroxide (H2O2) from hydrogen and oxygen gases using Pd and PdAu nanoparticles on supports [15-19]. H2O2 is a very important industrial oxidant and is currently produced by the sequential hydrogenation and oxidation of an alkyl anthraquinone as an intermediate. There are problems associated with the anthraquinone route and these include the cost of the quinone solvent system and the requirement for periodic replacement of anthraquinone due to hydrogenation.

In this work, nanosized Pd metal and PdAu x alloy particles were prepared using microwave irradiation on three types of TiO2 with different crystal phases (anatase + rutile, anatase and rutile) as support materials. The obtained catalysts were characterized by XRD, BET and XAFS measurements. Additionally, the direct synthesis of H2O2 from hydrogen and oxygen gases at room temperature was performed and their catalytic activity is discussed.
2. Experimental

2.1. Materials
Three types of TiO₂ were used as supports, JRC-TIO-4 (equivalent to Degussa P-25; anatase : rutile = 7 : 3), JRC-TIO-6 (rutile) and JRC-TIO-8 (anatase) were kindly supplied from the Japan Catalysis Society of Japan. PdCl₂ and HAuCl₄ were purchased from Wako Pure Chemical Ind., Ltd.

2.2. Preparation and characterization of catalysts
The Pd metal precursor and various titanium oxide materials were irradiated by microwave (500 W, 2450 ± 30 MHz, MWO-1000S, Tokyo Rikakikai Co. Ltd.) for 15 min with stirring. After centrifugation the sample was dried at 383 K for 12 h, calcined at 723 K for 5 h and reduced by H₂ (20 mL/min) at 473 K for 1 h. The specific surface area measurement was performed using a BEL-SORP max (Bel Japan, Inc.) at 77 K. The sample was degassed under vacuum at 473 K before data collection. X-ray fluorescence measurements were performed using an EDX-720 (Shimadzu). Au L₃-edge XAFS spectra were recorded using a fluorescence-yield collection technique at the beam line BL01B1 station with an attached Si (311) monochromator at SPring-8, JASRI, Harima, Japan (prop. No. 2008A1366, 2008A1457). EXAFS data were normalized by fitting the background absorption coefficient around the energy region higher than the edge of about 35–50 eV with the smoothed absorption of an isolated atom. EXAFS data were examined using the Rigaku EXAFS analysis program. Fourier transformation (FT) of k³-weighted normalized EXAFS data were performed over the 3 Å < k/Å⁻¹ < 12 Å range to obtain the radial structure function. To compare catalytic activities of Pd and PdAuₓ alloy catalysts (0.1 g) were prepared by microwave irradiation. The direct synthesis of hydrogen peroxide (H₂O₂) from hydrogen and oxygen (80 mL/min, H₂ : O₂ = 1 : 1) was carried out under atmospheric pressure at room temperature.

3. Results and discussion
From the elemental analysis of samples, it was found that the precursor of Pd metal can be successfully deposited on all three types of TiO₂ supports under microwave irradiation of the TiO₂ powder slurry in an aqueous PdCl₂ solution without using any reducing reagents or surfactants. The surface area of support and the loading amount of metals are summarized in Table 1. The amount of Pd loading was not proportional to the surface area of supports. It was found that the amount of Pd loading depended on the crystal phase and that the rutile phase allowed easier loading than the anatase phase. In addition, alloy particles were successfully prepared on three types of TiO₂ by the same procedure using two different metal salt precursors (PdCl₂ and HAuCl₄). In this binary system, a similar trend was observed for the deposition of Pd metal particles on each type of TiO₂ support but the amount of Au metal particles increased with increasing surface area of TiO₂ supports.

The X-ray absorption fine structure (XAFS) was performed to investigate formation of the PdAuₓ alloy particle on TiO₂ supports by the microwave irradiation method. Figure 1 shows Au L₃-edge Fourier Transform of Extended X-ray Absorption Fine Structure (FT-EXAFS) spectra of samples. Au foil and PdAu₃ were used as reference materials. The spectrum of each sample was similar to that of PdAu₃ but different to that of Au foil. PdAuₓ alloy particles were thus formed on TiO₂ supports by the

| Table 1. The surface area of supports and the amount of metal loading. |
|-------------------------------------------------|
| Support (Phase of TiO₂) | Surface area of supports (m²/g) | Pd (wt%) | Pd / Au (wt%) |
|-------------------------|---------------------------------|----------|---------------|
| TIO-4 (anatase + rutile)| 50                              | 0.42     | 0.34 / 0.40   |
| TIO-6 (rutile)          | 100                             | 0.78     | 0.44 / 0.82   |
| TIO-8 (anatase)         | 338                             | 0.51     | 0.39 / 1.12   |
microwave irradiation method. As shown in Figure 2, the bulk Au foil sample showed a characteristic white line [20] whereas there was no intrinsic white line for PdAuₙ samples. These results suggest that in this microwave irradiation method a nucleus of metal alloy nanoparticles is created. Concerning the structure of the PdAuₙ alloy particles, it is reasonable to consider that most of the Au atoms are preferentially deposited in the core region while the Pd atoms are preferentially deposited in the shell region. Because the reduction rate of Au ions is faster than that of Pd ions they are reduced first and constitute the core [21]. Alloy particles were thus formed by the reduction of Pd ions on the surface of the Au core.

To compare the catalytic activity of Pd and the PdAuₙ alloy that was deposited on TiO₂, synthesis of H₂O₂ from hydrogen and oxygen gases was carried out under atmospheric pressure and at room temperature, as shown in Figure 3. The PdAuₙ alloy deposited on TiO₂ (anatase + rutile) catalyst showed the highest activity among the examined catalysts. We found that the anatase phase was better than the rutile phase. For PdAuₙ alloy catalysts, catalytic activities of all supports were increased by Au addition. Although the amount of loaded Au metal was different for each TiO₂ support, a similar catalytic enhancement was observed for all PdAuₙ catalysts. These results suggest that the amount of loaded Au does not significantly affect the catalytic activity but Au addition was effective for the synthesis of H₂O₂.

4. Conclusions
Nanosized Pd and PdAuₙ particles were successfully deposited on various titanium dioxides using a
A simple and unique microwave irradiation method. Results of XAFS spectra indicated that the obtained PdAu$_x$ particles formed an alloy structure. These catalysts were used for the direct synthesis of H$_2$O$_2$ from hydrogen and oxygen gases. The PdAu$_x$ that was deposited on titanium dioxide comprised a mixed phase of anatase and rutile and exhibited the highest activity for this catalytic reaction.

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