Particle Size Effect of Pd on Octane Detection of Hydrothermally Synthesized Pd-SnO_2 Nanoparticles

Takeshi HASHISHIN, Taisuke HATTORI and Jun TAMAKI
Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Introduction

SnO_2 is one of excellent sensing materials for the detection of reducing gases such as H_2, CO, CH_4, C_3H_8, H_2S and so on [1-3]. The fabrication of gas sensing thin film of oxide from sol solution is one of low cost liquid-phase processes and advantageous in the uniformity as well as the chemical stability of oxide film. It is well known that SnO_2 sol solution is hydrothermally synthesized from $SnCl_4$ at 200 °C [4]. The size of SnO_2 grain in the sol is also controllable by hydrothermal conditions and its effects on film structure and H_2S sensing properties are investigated [5]. On the other hand, the surface modification with noble metal and/or metal oxide is the useful and important method for improving the sensing properties. In previous study, we reported that Pd component was hydrothermally added to SnO_2 nanoparticles as a chloride and Pd particles obtained were less visible on SnO_2 nanoparticles, and their sensing properties to hydrocarbon were unity despite of their good sensing properties to 3 ppm H_2S [6].

In this study, Pd added SnO_2 sol solutions were prepared with three preparation methods in order to control the particle size of Pd toward enhancement of sensing properties to octane.

Experimental

Preparation of Pd added SnO_2 sol solutions

Pd added SnO_2 sol solutions were hydrothermally synthesized with following three different methods. The mixed solution of tin chloride ($SnCl_4$) and palladium chloride ($PdCl_2$) was neutralized with ammonium hydrogen carbonate (NH_4HCO_3). The resulting precipitate was washed, filtrated, mixed with aqueous ammonia (pH10.5), and hydrothermally treated at 200 ℃ for 3h (A method). In B method, diamine-dinitro-palladium ($(NH_3)_2(NO_2)_2Pd$) was added to SnO_2 precursor and hydrothermally treated. On the other hand, $(NH_3)_2(NO_2)_2Pd$ was mixed with SnO_2 sol solution for C method. Above preparation processes of Pd added SnO_2 sol solutions are summarized in Fig. 1.

Pd-SnO_2 Sensor for octane detection

The Pd-SnO_2 solutions were dropped on alumina substrate equipped with Au interdigitated electrode, dried, and calcined at 900 ℃ for 3 h to be Pd-SnO_2 thin film gas sensors. The sensors obtained by three preparation methods were placed in a flow apparatus equipped with an electric furnace and the sensing properties to dilute octane (5 ppm) were measured at 250 to 400 °C every 50 °C. The sensor response ($S=R_a/R_g$) was defined as the ratio of resistance in air atmosphere (R_a) to that in octane (C_8H_{10})-containing air atmosphere (R_g).

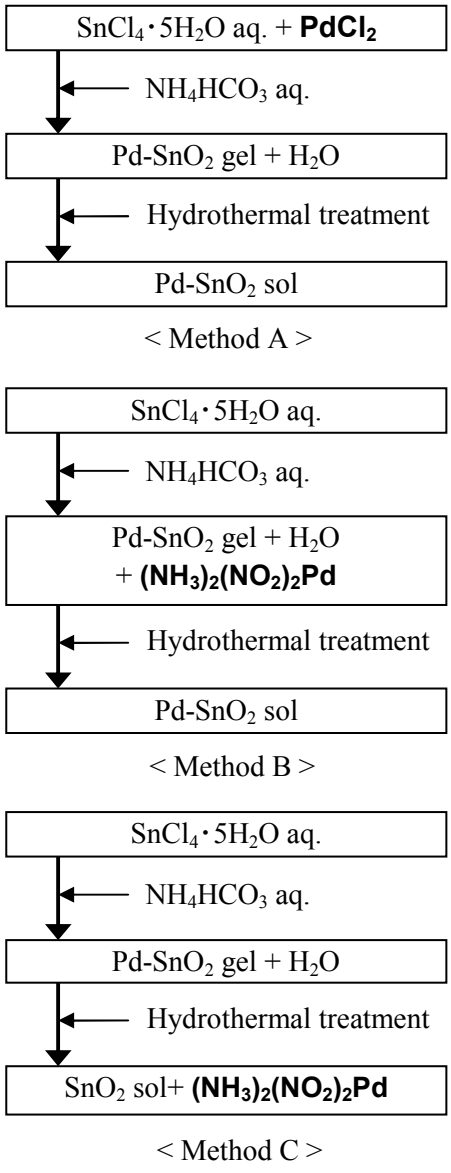

Fig. 1 Three preparation methods of Pd-SnO_2 sol. Pd components were added as a chloride to starting materials (Method A), as a complex before hydrothermal treatment (Method B) and after that (Method C).

Results and discussion

The sol solutions prepared by A method were colorless clear solutions when Pd content was less than 5 wt%. Thus, Pd particle was not observed in Pd-SnO_2 film (Fig. 2 (a)), suggesting the tiny Pd particles loaded on SnO_2 particles (ave. 20 nm). On the other hand, the film had Pd particles ca. 100 nm in which the Pd content was increased to 10 wt%, as shown in Fig. 2 (b). However, the X-ray diffraction patterns of this film did not also show an existence of Pd, suggesting Pd component going out as a black precipitate at the bottom of the SnO_2 sol solution. Fig. 2 (c) and (d) respectively show the films prepared by B and C methods, in which respective films had large Pd particles ranging from 200 to 1500 nm and ca. 300 nm in diameter.

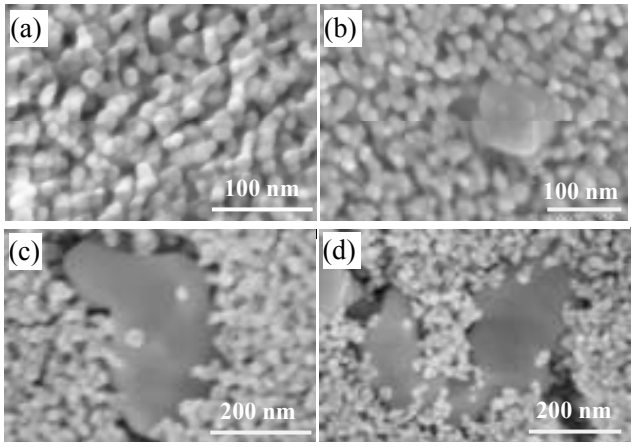

Fig. 2 SEM images of Pd-SnO_2 film obtained from 1.0 wt% $PdCl_2$ via method A (a), 10.0 wt% $PdCl_2$ via method A, 1.0 wt% $(NH_3)_2(NO_2)_2Pd$ via method B (c), and 1.0 wt% $(NH_3)_2(NO_2)_2Pd$ via method C (d).

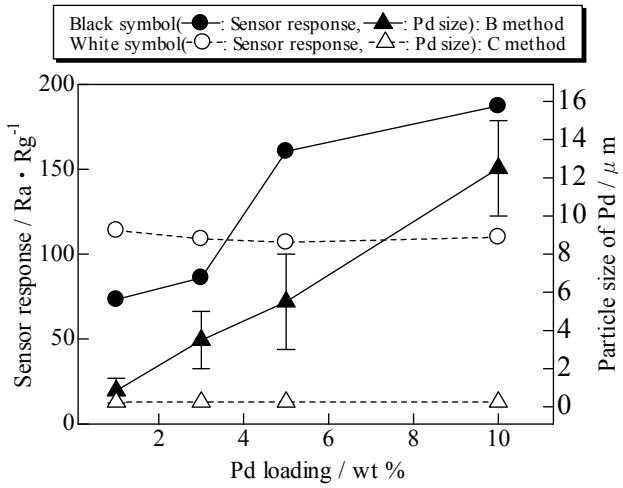

Fig. 2 Particle size effect of Pd on sensor response to 5 ppm octane as a function of Pd loading.

The sensor response to 5 ppm octane at 300 ℃ of Pd-SnO_2 sensor with 1-5 wt% Pd was almost the same as that of pure SnO_2 sensor. While, the Pd-SnO_2 sensors with large Pd particles (prepared by A method with 10wt% Pd, B and C methods) showed high sensor responses, suggesting that the sensor response to octane was increased with increasing Pd particle size. The Pd particle size of Pd-SnO_2 nanoparticles obtained by B method and their sensor response to 5 ppm octane at 300 ^oC were increased with increasing Pd loading, as shown in Fig. 2. Especially, the sensor response of Pd-SnO_2 nanoparticles increased steeply between 3 and 5 wt%. The x-ray diffraction patterns of Pd-SnO_2 nanoparticles with more than 5 wt% Pd loading show PdO 110 diffraction peak near 41.95 deg. It is well known that the p-n junction promotes electronic interaction between p-type PdO and n-type SnO_2 and PdO particles can influence the whole SnO_2 surface electronically [1]. Thus, it can be explained that sensor response is improved by loading Pd more than 5 wt % in Fig. 2. On the other hand, the Pd particle size of Pd-SnO_2 nanoparticles obtained by C method was almost 300 nm and their sensor responses were also unity. As the Pd loading was more than 3 wt%, the PdO diffraction peaks existed in their x-ray diffraction patterns. The relative intensity of diffraction peak of PdO 110 to SnO_2 110 was almost same in Pd loading more than 3 wt% although the relative intensity of Pd 111 to SnO_2 110 increased with increasing Pd loading. This denotes that PdO dominant the electronic sensitization of Pd-SnO_2 sensor, leading to higher sensor response.

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