

10-28-2002

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## Publication Info

*Applied Physics Letters*, Volume 81, Issue 18, 2002, pages 3449-3451.

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Publisher's Version: <http://link.aip.org/link/doi/10.1063/1.1518158>

DOI: 10.1063/1.1518158

PACS: 61.46.-w, 61.43.Gt, 81.05.Rm, 81.07.Bc, 82.33.Ln, 82.75.Fq, 82.60.Qr, 82.30.Vy, 07.07.Df, 82.80.-d

## Distributions of noble metal Pd and Pt in mesoporous silica

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(Received 9 July 2002; accepted 9 September 2002)

Mesoporous silica nanostructures have been synthesized and loaded with Pd and Pt catalytic noble metals. It is found that Pd forms small nanoclusters (3–5 nm) on the surface of the mesoporous structure whereas Pt impregnation results in the inclusion of Pt nanostructures within the silica hexagonal pores (from nanoclusters to nanowires). It is observed that these materials have high catalytic properties for CO–CH<sub>4</sub> combustion, even in a thick film form. In particular, results indicate that the Pt and Pd dispersed in mesoporous silica are catalytically active as a selective filter for gas sensors. © 2002 American Institute of Physics. [DOI: 10.1063/1.1518158]

Recently, nanostructured mesoporous materials have attracted much attention for the development of catalytic systems.<sup>1,2</sup> The base mesoporous materials have often been modified by adding noble metals or metal oxides in order to improve their physical and chemical properties.<sup>3–6</sup> In particular, mesoporous silica has been widely used as the base material to develop chemical gas sensors.<sup>7,8</sup> Mixtures of mesoporous silica and SnO<sub>2</sub> have also been explored to improve the response of gas sensors.<sup>9</sup>

Since Seiyama *et al.*<sup>10</sup> introduced the possibility to use chemical sensors for gas sensing, several studies have focussed on sensing materials that exhibit dramatic changes in conductivity as gas composition is changed. To date, SnO<sub>2</sub> is the most widely used oxide as the base material for semiconductor gas sensors (SGS).<sup>11,12</sup> Further, it is also well known that the introduction of noble metals, such as platinum and palladium, improves SGS selectivity and decreases device operating temperatures.<sup>13,14</sup> However, gas sensor selectivity and stability are two main problems to be solved. The electrical properties of semiconductors are influenced not only by the interaction with the target gas, but also by many gas molecules having similar physicochemical properties. Moreover, undesired gas molecules may be adsorbed on the oxide surface, leading to drift in sensor response. The influence of interfering gases can be avoided by using active filters capable of catalytically transforming the interfering species to innocuous gases, hence hindering the active gases from reaching the sensor surface. In this letter, we report our initial findings in our effort to mesoporous silica as selective filter for gas sensors. There are mainly three different kinds of mesoporous molecular sieves used in catalysis.<sup>2</sup> The first one is the so-called M41S family of silica and aluminosilicates. The second one is the hexagonal mesoporous silica HMS and MSU families. The third family is exemplified by the hexagonal SBA-15 materials. Here we have selected the SBA-15 mesoporous silicas because they have long range order, large monodispersed mesopores and thicker walls,

which make them more thermally and hydrothermally stable than previous materials. In the present work, we characterize and model SBA-15 mesoporous silicas loaded with Pt and Pd.

SBA-15 mesoporous silica was synthesized following procedure reported by Zhao *et al.*<sup>15,16</sup> Pd and Pt additives were introduced into mesoporous silica by impregnation of the SBA-15 silica with 0.01 M aqueous solution of palladium chloride and ammonium tetrachloroplatinate, followed by slow evaporation of water.

The as-synthesized mesoporous silica adopted the well-known SBA-15 structure, as shown in transmission electron microscopy (TEM) micrographs (Fig. 1). The obtained material has a hexagonal array of mesopores with a lattice constant of 9.18 nm. The mesopores are arranged in structures grouping few hundred pores with lengths up to 2 μm. These

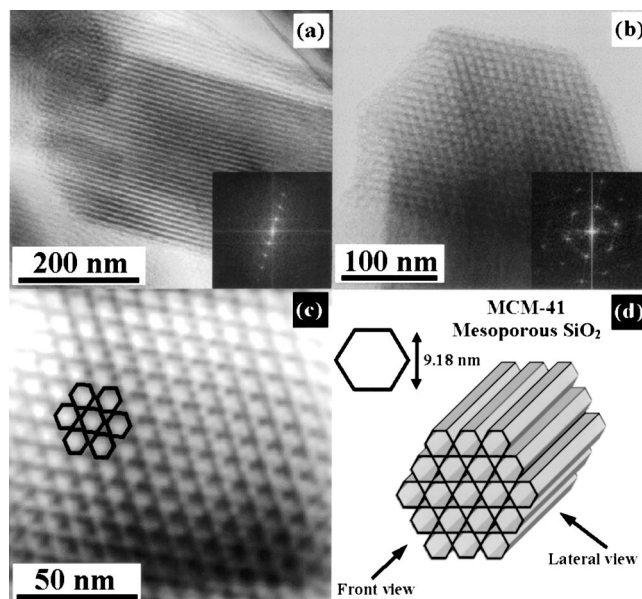


FIG. 1. (a) Lateral bright-field TEM view of a typical mesoporous aggregate. Few hundred pores compose every aggregate. The inset corresponds to the digital diffractogram of the TEM image. (b) Front TEM view of a silica mesoporous aggregate with its corresponding digital diffractogram as inset. (c) Filtered TEM image enhancing the pores hexagonal structure. (d) Model of the SBA-15 mesoporous silica found in our samples.

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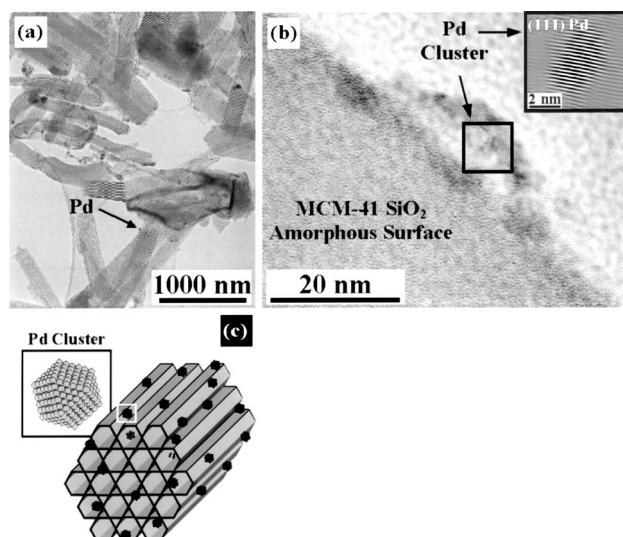


FIG. 2. (a) General TEM view of the Pd modified silica mesoporous material. (b) HRTEM micrograph of a Pd nanocluster placed on the mesoporous surface. The inset shows the filtered (111) Pd planes of the selected nanocluster. (c) Model proposed for the nanocluster dispersion in the Pd modified mesoporous silica. Nanoclusters used in the model are the 561-atom Pd cuboctahedrons (with  $\sim 3$  nm lateral size).

structures provide large surface areas up to  $800 \text{ m}^2/\text{g}$ . Furthermore, the Pt and Pd impregnated mesoporous  $\text{SiO}_2$  still has sufficiently large resistivity; it has no influence on the electrical conductivity of the active sensing layer.

In order to make the materials catalytically active, the mesoporous silica was loaded with Pd and Pt compounds. These Pt and Pd modified SBA-15 mesoporous silicas were deposited over  $\text{SnO}_2$  layers to obtain high selective SGS devices. It was found that, at an appropriate operating temperature, sensors covered with a layer of the Pt/Pd loaded mesoporous silica did not respond to changes in concentration of CO when it was exposed to  $\text{CH}_4$ -CO mixtures, demonstrating high selectivity to  $\text{CH}_4$ . Nevertheless, the  $\text{SiO}_2$ :Pt filter behaved quite differently from the  $\text{SiO}_2$ :Pd filter. While the  $\text{SiO}_2$ :Pt filters were effective in diminishing/eliminating the CO interference in the entire temperature range ( $250$ – $450^\circ\text{C}$ ) studied, the  $\text{SiO}_2$ :Pd filters were effective only in the high-temperature range ( $350$ – $450^\circ\text{C}$ ) and were not effective in the low-temperature range ( $250$ – $350^\circ\text{C}$ ).

While a complete set of sensor performance measurements will be reported elsewhere,<sup>17</sup> it is important to control and characterize the dispersion of catalysts (Pt and Pd) in mesoporous silica in order to understand the physical and chemical changes introduced by the catalysts. TEM and high-resolution TEM (HRTEM) have been used to determine the distribution of Pd and Pt, which may play a decisive role in influencing the behavior of the two types of active filters.

For a palladium impregnated mesoporous silica ( $\text{SiO}_2$ :Pd) as shown in Fig. 2(a), the Pd was distributed on the surfaces of the mesoporous silica as randomly distributed nanoclusters with diameters of about 3 nm. Shown in Fig. 2(b) is a Pd cluster lying on the surface of an amorphous silica mesopore. It is noticed that palladium clusters are not oxidized and adopt the typical face-centered-cubic bulk structure (after HRTEM analysis). This suggests that the Pd

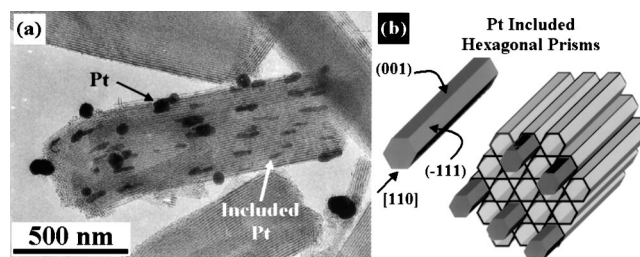


FIG. 3. (a) Bright-field TEM view of a Pt modified mesoporous silica composite. Notice that there is Pt on the composite surface, and Pt that has been included inside the pores. (b) Pt modified mesoporous silica model with the platinum adopting nonregular hexagonal prism morphology.

nanoclusters may adopt the well-known cuboctahedral morphology,<sup>18,19</sup> as shown in Fig. 2(c) inset.

Unlike  $\text{SiO}_2$ :Pd where Pd nanoclusters are found primarily on the surfaces of the mesoporous structures, it seems that, in  $\text{SiO}_2$ :Pt, the Pt clusters are found inside the pores. An extensive TEM study of the Pt impregnated mesoporous silica ( $\text{SiO}_2$ :Pt) indicated that Pt is deposited at two different locations. On one hand, Pt can be found as in the case of Pd, forming metal nanoclusters on the surface of the mesoporous silica. On the other hand, Pt can also be found along the silica mesopores as small nanoclusters for low Pt loadings or as Pt hexagonal prisms (nanowirelike structures) occupying the entire pores for high Pt loadings (Fig. 3). As the amount of Pt inside the pores increased, Pt nanoclusters grow until the pores are completely filled with Pt. Once the cluster has reached the pore size, it can only grow along the pore, adopting a nonregular hexagonal structure with  $\{001\}$ ,  $\{00-1\}$ ,  $\{-111\}$ ,  $\{-11-1\}$ ,  $\{1-11\}$ , and  $\{1-1-1\}$  lateral facets and growing along the  $[110]$  Pt direction [Fig. 3(b)]. This form of Pt distribution is undesirable for gas filters, since the hexagonal prisms would block the gas paths through the mesoporous structures. However, other researchers have recently described this phenomenon as an excellent method for metal nanowire production.<sup>20</sup> In our case, by carefully controlling and limiting the metal nanocluster size, we can obtain a perfect flow of the gas through the pores to catalytically filter and select the target gas for our sensor device.

It is therefore concluded that Pd is preferentially distributed as small clusters outside the mesoporous structure, leading to small catalytically active surface area (about  $15 \text{ m}^2/\text{g}$ ) and exhibiting small catalytic effect. On the other hand, Pt is preferentially distributed not only on the surface but also into the fine pores, resulting in large catalytically active area (up to  $800 \text{ m}^2/\text{g}$ ) and exhibiting large catalytic effect. When the loading of Pt is too high, however, the formation of nanowire may block the structural canals for gas transport. In addition to the different catalytic properties of Pd and Pt, preferential distribution displayed by Pt and Pd may greatly influence the response of sensors modified with Pd and Pt impregnated filters under CO- $\text{CH}_4$  gas flow. Thus, it is crucial to control the distributions of noble metals in mesoporous silica in order to optimize the selectivity of gas sensors.

The authors wish to gratefully acknowledge partial support of this project by the Georgia Institute of Technology Molecular Design Institute, under prime Contract No. N00014-95-1-1116 from the Office of Naval Research.

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