Investigation on Reduction Behaviors of SnO$_2$ and SnO$_2$-Supported CuO Sensor Materials by Temperature-Programmed Reduction Method Combined with Resistance Measurement

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(Received May 30, 2016; accepted August 15, 2016)

Keywords: TPR measurement, resistance measurement, semiconductor, tin oxide, copper oxide

Temperature-programmed reduction measurement combined with resistance measurement (TPR&R) was performed to investigate the reduction behavior of the samples containing the semiconductor materials, SnO$_2$ and CuO/SnO$_2$. The four reduction peaks were observed in the H$_2$-TPR profile of SnO$_2$, being assigned to the reductions of surface adsorbed oxygen species, surface lattice oxygen, amorphous SnO$_2$ and bulk SnO$_2$. On the other hand, the H$_2$-TPR profile of CuO/SnO$_2$ was more complicated than that of SnO$_2$. The TPR&R measurement enabled definite assignments of the six reduction peaks of CuO/SnO$_2$: the reductions of (I) Cu$^{2+}$ to Cu$^+$ in highly dispersed copper oxide, (II) bulk CuO to Cu$^0$, (III) Cu$^+$ to Cu$^0$ in highly dispersed copper oxide, (IV) SnO$_2$ lattice oxygen interacting with highly dispersed copper oxide, (V) amorphous SnO$_2$, and (VI) bulk SnO$_2$.

1. Introduction

CuO-doped SnO$_2$ has been reported to be one of the potential materials for CO($^{1-3}$) sensors. We have demonstrated that CuO-doped SnO$_2$ exhibited a response to the small amount of CO involving H$_2$ flow and that its response was related with the oxidation states of Cu and Sn.($^{3}$) Therefore, the investigation of the reduction behavior of CuO-doped SnO$_2$ is significant for understanding the sensor mechanism.

It is well known that temperature-programmed reduction (TPR) measurement is one of the most powerful techniques for elucidating the reduction behavior of a material containing a noble metal, a transition metal oxide, or a lanthanide metal oxide. Numerous TPR studies on copper oxides have been reported, for example, CuO/CeO$_2$,($^{4}$) CuO/Ti$_x$Sn$_{1-x}$O$_2$,($^{5}$) CuO/Al$_2$O$_3$,($^{6}$) Cu-Fe/Al$_2$O$_3$,($^{7}$) and K-Cu/Al$_2$O$_3$,($^{8}$) for clarifying the active copper site for CO oxidation,($^{4,5}$) water–gas shift reaction,($^{6,7}$) NO$_x$ reduction,($^{8}$) among others. Arino et al.($^{9}$) reported that the TPR profile of SnO$_2$ exhibited four reduction peaks at 250, 310, 420, and >470 °C and that the loading of Pt or Pd promoted the reduction of SnO$_2$; that is, four reduction peaks shifted to a lower temperature by loading Pt or Pd on SnO$_2$. A similar result was reported by Pavelko et al.($^{10}$) The TPR profile of a metal oxide

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supported on SnO$_2$ was more complicated than that of a metal oxide supported on a thermally stable material such as Al$_2$O$_3$ and SiO$_2$, because of the contribution of the reduction of SnO$_2$ itself; therefore, the appearance of TPR reduction peaks for SnO$_2$-supported materials remains ambiguous.

In the present study, TPR measurement combined with resistance measurement was carried out to better understand the reduction behavior of the samples containing the semiconductor materials, SnO$_2$ and CuO/SnO$_2$. In addition, X-ray diffraction (XRD) and diffuse-reflectance infrared Fourier transform-infrared (DRIFT-IR) measurements were performed to obtain additional evidence for supporting the assignments of the TPR peaks of SnO$_2$ and CuO/SnO$_2$.

2. Experimental Methods

SnO$_2$ was prepared by the ammonolysis of a solution of tin chloride (Kishida Chem., 99%) according to a previously reported method.$^{11}$ The resulting precipitate was washed repeatedly with deionized water and then calcined at 600 °C for 5 h to yield SnO$_2$. CuO was loaded on SnO$_2$ powder by a conventional impregnation method with an aqueous solution of Cu(CH$_3$COO)$_2$·H$_2$O (Kanto Chem., 99%). The loaded sample was finally calcined at 600 °C for 5 h. The loading amount of CuO was 2–30 wt%. The sample is represented by CuO(x)/SnO$_2$, where $x$ is the loading amount of CuO.

A schematic view of the experimental apparatus for TPR measurement combined with the resistance measurement is shown in Fig. 1. The redox behavior and the change in the sample resistance can be measured using this apparatus. This new combined method is named “TPR&R” hereafter. The element for measuring sample resistance was fabricated by the following method.$^{11}$ The sample powder was dispersed in deionized water, and the resulting paste was painted on an alumina tube (1.2 mm $\phi$) with a pair of Pt wire electrodes attached. The element with the sample was located in the middle of a quartz tube (9 mm $\phi$) and the sample resistance was determined by measuring the voltage of external resistance, as shown in Fig. 1.

For TPR measurement, the sample powder was pressed and sieved in the range of 212–500 µm. 0.2 g of the granular sample was placed near the element for measuring sample resistance (Fig. 1).

![Fig. 1. Schematic view of experimental apparatus of TPR&R measurement.](image-url)
The amount of H₂ consumed was monitored using a gas chromatograph (Shimadzu, GC-8AIT) with a thermal conductivity detector (TCD).

Prior to TPR&R measurement, the samples were pretreated at 500 °C for 3 h in air. TPR&R measurement was carried out by flowing 5 vol% H₂ + N₂ (50 cm³·min⁻¹) in the temperature range of 50–450 °C at a heating rate of 2 °C·min⁻¹.

DRIFT-IR spectra were recorded while flowing pure N₂ at room temperature or 50 vol% H₂ (N₂ balance) at 50, 300, and 350 °C with a Perkin Elmer Spectrum One spectrometer. Powder XRD analysis was performed to determine the crystalline phase of samples using a Rigaku RINT2200HF diffractometer with CuKα radiation.

3. Results

3.1 XRD profiles of CuO/SnO₂ and SnO₂ samples

The XRD profiles of CuOₓ/SnO₂ and SnO₂ samples are shown in Fig. 2. The strong peaks assigned to the tetragonal crystal phase of SnO₂ were observed at 33, 37, and 39°. For CuOₓ/SnO₂ with a small loading amount of CuO, there were no detectable XRD peaks induced from CuO crystallites. As the loading amount of CuO increased, the crystal phase of CuO became apparent at 35, 38, and 49°, and these peaks of CuO were intensified. The XRD results suggest that CuO is highly dispersed on SnO₂ when the loading amount of CuO is smaller than 5 wt%, and the excess loading of copper (more than 5 wt%) forms bulk CuO, which can be reflected in the XRD pattern. The crystalline sizes of SnO₂ and CuO in CuOₓ/SnO₂, which were estimated from SnO₂(101) and CuO(002) XRD peaks using the Scherrer’s equation, are summarized in Table 1, being less dependent on the loading amount of CuO.

![Fig. 2. XRD patterns of (a) SnO₂, (b) CuO(2)/SnO₂, (c) CuO(5)/SnO₂, (d) CuO(8)/SnO₂, and (e) CuO(15)/SnO₂. ○: SnO₂ and □: CuO.](image-url)
3.2 DRIFT-IR spectra of SnO$_2$

The in situ DRIFT-IR spectra of SnO$_2$ exposed to 50 vol% H$_2$ + N$_2$ at 50, 300, and 350 °C for 2 h are shown in Fig. 3. The spectra shown in Fig. 3 represent the change in the spectra before and after the respective treatments, that is, the negative peak indicates the decrease in the amount of surface species accompanying desorption and/or decomposition. The DRIFT-IR spectra of SnO$_2$ exposed to 50 vol% H$_2$ + N$_2$ at 300 and 350 °C showed a strong negative peak in the region assigned to Sn–O–Sn stretching vibration (750–2000 cm$^{-1}$). The result suggests that SnO$_2$ was reduced by 50 vol% H$_2$ + N$_2$ at the temperature above 300 °C.

3.3 TPR&R profiles of SnO$_2$ and CuO/SnO$_2$

The TPR&R profiles of SnO$_2$ and CuO(x)/SnO$_2$ samples (x = 2, 5, 8, 15, and 30) are shown in Fig. 4. The overlapping reduction peaks in the TPR profiles shown in Figs. 4(a)–4(f) were deconvoluted, as shown in Figs. 4(a')–4(f'), respectively. SnO$_2$ provided four TPR peaks centered at 230 (peak α), 300 (peak β), 370 (peak γ), and >400 °C (peak ω) [Figs. 4(a) and 4(a')]. A similar result was reported by Arino et al. The reduction peaks α and β were accompanied by a decrease and an increase in resistance, respectively, whereas the reduction peaks γ and ω contributed less to the change in resistance.

Table 1

| Sample          | Mole of CuO loaded$^a$ (μmol) | Crystallite size$^b$ of SnO$_2$ (nm) | Crystallite size$^b$ of CuO (nm) | Amounts of H$_2$ consumption$^c$ (μmol) |
|-----------------|-------------------------------|-------------------------------------|----------------------------------|----------------------------------------|
|                 |                               |                                     |                                  | Peak I  | Peak II | Peak III | Peak IV |
| CuO(2)/SnO$_2$  | 57                            | 21                                  | —                                | 29 (145)| —   | 32 (213) | 41 (250) |
| CuO(5)/SnO$_2$  | 142                           | 23                                  | 42                               | 64 (137)| 17 (183)| 70 (212) | 110 (240) |
| CuO(8)/SnO$_2$  | 228                           | 19                                  | 36                               | 53 (151)| 110 (242)| 57 (212) | 104 (266) |
| CuO(15)/SnO$_2$ | 438                           | 23                                  | 36                               | 48 (146)| 345 (237)| 42 (216) | 94 (254) |
| CuO(30)/SnO$_2$ | 848                           | 19                                  | 31                               | 41 (140)| 769 (226)| 42 (203) | 51 (266) |

$^a$The weight of the material for TPR measurement was unified to be 0.2 g.

$^b$The crystallite size was estimated using Scherrer’s equation.

$^c$The numerical values in parenthesis indicate the temperatures of peak top.

Fig. 3. DRIFT-IR spectra of SnO$_2$ after exposure to 50 vol% H$_2$/N$_2$ at (a) 50, (b) 300, and (c) 350 °C for 2h.
Fig. 4. TPR&R profiles of (a) SnO$_2$, (b) CuO(2)/SnO$_2$, (c) CuO(5)/SnO$_2$, (d) CuO(8)/SnO$_2$, (e) CuO(15)/SnO$_2$, and (f) CuO(30)/SnO$_2$, and the deconvolution curves of TPR profile for (a') SnO$_2$, (b') CuO(2)/SnO$_2$, (c') CuO(5)/SnO$_2$, (d') CuO(8)/SnO$_2$, (e') CuO(15)/SnO$_2$, and (f') CuO(30)/SnO$_2$. 

Temperature (°C)  
Amount of H$_2$-consumption (μmol)  
Amount of H$_2$-consumption (arb. unit)  
Sensor resistance (Ω)
Figure 4(b) shows the TPR&R profile of CuO(2)/SnO$_2$. The TPR profile of CuO(2)/SnO$_2$ was more complicated than that of SnO$_2$. The TPR profile of CuO(2)/SnO$_2$ consisted of six reduction peaks represented by peaks I–VI, as shown in Fig. 4(b). A similar TPR&R profile was obtained for CuO(5)/SnO$_2$ [Figs. 4(c) and 4(c')] and CuO(8)/SnO$_2$, CuO(10)/SnO$_2$, and CuO(30)/SnO$_2$ with higher Cu loading [Figs. 4(d)–4(f) and 4(d’)–4(f’)] were slightly different from those of CuO(2)/SnO$_2$ and CuO(5)/SnO$_2$ with lower Cu loading; the position of peak II shifted to a higher temperature.

All samples of CuO($x$)/SnO$_2$ showed much higher resistance than SnO$_2$ at low temperature (50–150 °C). With increasing temperature, the sample resistance markedly decreased to 180–220 °C, together with the appearance of peak I, and then slightly increased. In the intermediate temperature range (180–300 °C), the change in the sample resistance of CuO($x$)/SnO$_2$ was dependent on the amount of CuO loaded on SnO$_2$. The high resistance augmentation was observed for CuO(8)/SnO$_2$.

In the high temperature range (>300 °C), the sample resistance was less sensitive to temperature, although the reduction peaks V and VI were observed.

4. Discussion

4.1 Assignments of reduction peaks in TPR profile of SnO$_2$

TPR studies of SnO$_2$-based materials have been reported by several researchers$^{(9-12)}$. Sasiakala et al.$^{(12)}$ reported that a series of TPR peaks observed at low temperature were assigned to the reduction of the SnO$_2$ surface. Pavelko et al.$^{(10)}$ reported that the reduction peaks of SnO$_2$ below 450 °C were attributed to the reduction of not only the surface but also the subsurface of SnO$_2$. Thus, the assignment of the TPR reduction peak to SnO$_2$ is still controversial; therefore, we attempted to assign the TPR reduction peaks of SnO$_2$ by TPR&R measurement.

The α peak in Fig. 4(a), accompanied by a significant decrease in sample resistance, can be assigned to the reduction of anionic surface-adsorbed oxygen species such as O$_2^-$ and O$^-$ because of the following reason. When the anionic surface-adsorbed oxygen species that trapped electrons from SnO$_2$ are reacted with H$_2$ gas, the electrons from the anionic species are donated to SnO$_2$, resulting in the decrease in the sample resistance. A similar explanation concerning the TPR peak was reported by Marikutsa et al.$^{(13)}$

In contrast to the α peak, the β peak observed at 300 °C was accompanied by an increase in sample resistance. DRIFT-IR spectra shown in Fig. 3 demonstrated that SnO$_2$ was partially reduced when the SnO$_2$ sample was exposed to 50 vol%H$_2$ + N$_2$ at 300 °C. Therefore, the β peak may be assigned to the reduction of the lattice oxygen of SnO$_2$, probably near the surface. The presumable interpretation of resistance augmentation is as follows. The lattice oxygen of SnO$_2$ was reduced to form SnO, which is a p-type semiconductor. The p-type SnO forms a p–n heterojunction with an unreduced n-type SnO$_2$ bulk, resulting in the increase in sample resistance. Although there is no direct evidence of SnO formation in this study, Kulshreshtha and Gadgil$^{(14)}$ reported the formation of SnO as an intermediate phase during the H$_2$ reduction of SnO$_2$.

During the appearance of the γ peak, no change in sample resistance was observed so that the assignment of the γ peak is difficult from TPR&R measurement. The assignment of the γ peak will be discussed in the following section.
The intensity of the ω peak was markedly increased at >400 °C. This suggests that the reduction of the lattice oxygen in SnO₂ progressively proceeded with increasing reduction temperature. This assumption was supported by the DRIFT-IR result that the negative peak derived from ν(Sn–O–Sn) became large with increasing reduction temperature (Fig. 3). Therefore, the ω peak can be assigned to the reduction of bulk SnO₂.

4.2 Assignments of reduction peaks in TPR profiles of SnO₂-supported CuO

As shown in Figs. 4(b)–4(f) and 4(b′)–4(f′), CuO(x)/SnO₂ samples exhibited six reduction peaks, peaks I–VI, regardless of the loading amount of CuO. As can be seen in Figs. 4(b)–4(f), it is clear that peak I of all the CuO(x)/SnO₂ samples was accompanied by the marked decrease in resistance. The initial high resistance of CuO(x)/SnO₂ samples (>10⁹ Ω) may be derived from n-SnO₂/p-CuO heterojunctions between the supported p-type CuO grains and the n-type SnO₂ grains. Upon exposure to H₂ gas in TPR&R measurement, the barrier height of n-SnO₂/p-CuO heterojunctions decreases markedly because of the partial reduction of p-CuO to CuO₁−ₓ, probably leading to a marked decrease in resistance. Therefore, peak I can be assigned to the reduction of CuO.

The amounts of H₂ consumed for peaks I and III were increased with increasing loading amount of CuO, reaching a maximal value for CuO(5)/SnO₂, and then decreased with the further increase in the loading amount of CuO (Table 1). In addition, the amount of H₂ consumption for peak I was almost equal to that for peak III. Therefore, it is presumable that peaks I and III come from the reduction of identical CuO species. As can be seen in Fig. 2, the XRD pattern of CuO(2)/SnO₂ exhibited no visible diffraction peak because of the high dispersion of CuO, whereas peaks I and III were clearly observed in Fig. 4(b). As a result, peaks I and III were tentatively assigned to the reduction of Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰, respectively, of highly dispersed CuO.

\[
\text{Peak I: } 2\text{CuO} + \text{H}_2 \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}
\]

\[
\text{Peak III: } \text{Cu}_2\text{O} + \text{H}_2 \rightarrow 2\text{Cu}^0 + \text{H}_2\text{O}
\]

As shown in Fig. 2, the increase in the loading amount of CuO from 8 to 30 wt% resulted in the increase in the intensity of the diffraction peaks of CuO. Table 1 shows that the amount of H₂ consumption for peak II was increased with increasing CuO loading from 8 to 30 wt%, and the total amounts of H₂ consumption for peaks I, II, and III corresponded to the amount of H₂ consumption required for the complete reduction of CuO to metallic Cu. Therefore, peak II can be assigned to the reduction of bulk CuO.

Interestingly, the behavior of peak IV was similar to those of peaks I and III, suggesting that peak IV was related to highly dispersed CuO. In addition, the sample resistance increased together with the appearance of peak IV. Since the total amount of H₂ consumption for peaks I, II, and III corresponded to that of the complete reduction of CuO to metallic copper, the origin of peak IV cannot be explained by the reduction of CuO species. Liu et al. reported that the CuO fine particles in intimate contact with cerium oxide showed “strong interaction” and promoted the surface reduction of cerium oxide. Considering this report, peak IV is probably assigned to the reduction of the surface lattice oxygen of SnO₂ interacted with highly dispersed CuO. The increase in sample resistance may be derived from the p–n heterojunction of reduced SnO₂ with the p-type semiconductor with an unreduced SnO₂ bulk with the n-type semiconductor.
The temperatures giving peaks V and VI were almost the same as those giving peaks γ and ω in Fig. 4(a), respectively. This result implies that peaks V and VI are identical to peaks γ and ω, respectively. As mentioned in a previous section, peak ω (peak VI) can be assigned to the reduction of bulk SnO₂. The assignment of peak γ (peak V) could not be clarified in the present study; however, Park et al.\(^{17}\) pointed out that the TPR peak of a SnO₂/Al₂O₃ catalyst below 450 °C was assigned to the reduction of amorphous SnO₂.

The present TPR&R measurement proved the reduction of SnO₂ with several overlapping peaks in the temperature range of 200–300 °C. In addition, the stepwise reduction of highly dispersed CuO \(+2 \rightarrow +1 \rightarrow 0\) was clarified and the resulting reduced copper species was found to play a role as a promoter of the reduction of SnO₂.

5. Conclusions

The resistance measurement was combined with TPR measurement (TPR&R) to assign the reduction peaks in the TPR profiles of SnO₂ and CuO(x)/SnO₂. Using TPR&R, the four reduction peaks in TPR profile of SnO₂ at 230, 300, 370, and >400 °C could be assigned to the reduction of oxygen species adsorbed on SnO₂, lattice oxygen of SnO₂ near the surface, amorphous SnO₂, and bulk SnO₂, respectively. In the TPR profile of CuO(x)/SnO₂, the experimentally observed six peaks, peaks I–VI, were found to be attributed to the reductions of (I) Cu²⁺ to Cu⁺ in highly dispersed copper oxide, (II) bulk CuO to Cu⁰, (III) Cu⁺ to Cu⁰ in highly dispersed copper oxide, (IV) SnO₂ lattice oxygen interacting with highly dispersed copper oxide, (V) amorphous SnO₂, and (VI) bulk SnO₂. Thus, TPR&R measurement is one of the powerful methods enabling the definite assignment of the reduction peaks of materials containing a semiconductor such as SnO₂ and CuO(x)/SnO₂.

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