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NOTE

Modification of Catalytic Activity by Applied Bias at Gradient Composition CuO/ZnO Heterocontact

Since the 1950s, several researchers have tried to explain the catalytic properties of semiconducting metal oxides from the viewpoint of the electronic theory or the theory of semiconductors (1). However, there are too many exceptions or contradictions in the application of these theories and such studies have been disused until the 1980s (2). However, the electronic theory for catalysts could be a complete theory upon the proposal of any adequate experimental proof.

In the present study, CuO/ZnO heterocontact is fabricated by stacking six layers of CuO/ZnO porous ceramics of different compositions. CuO/ZnO heterocontact is one of the smart sensor materials for selective CO gas sensing. Its gas sensitivity can be controlled by changing the applied bias (3, 4) and the possibility of applied voltage-dependent CO oxidative reaction at the CuO/ZnO interface is suggested. The rate of CO oxidative reaction is measured and the effect of applied bias is studied and discussed. The applicability of the electronic theory to the heterogeneous catalytic reaction is suggested by our experimental results.

Cupric oxide (CuO) and zinc oxide (ZnO) powder (Kojundo Chemical Inc., 99.99% purity) were mixed in the desired proportions with distilled water. They were dried, ground, placed sequentially into a cyclindrical mold, and uniaxially pressed under 9.8 MPa. A powder compact with a gradient composition of CuO_x–ZnO_{1-x} was sintered at 850°C for 3 h in air. Because of its inhomogeneous composition, we were apprehensive of fracturing the specimen during firing. To prevent fracturing the specimen, CuO_x–ZnO_{1-x} layers were stacked between the CuO and ZnO and they worked as the buffer layer. The apparent densities of the pure CuO and ZnO layers were 76% (CuO) and 63% (ZnO) of theoretical and the external view of the as-sintered specimen was that of a truncated cone owing to the gradient in the density of CuO_x–ZnO_{1-x} layers. Ohmic electrodes (silver for CuO and InGa for ZnO) were painted at the back of the specimen and electrodes and lead wires were covered with silica–alumina paste to avoid exposure to the reacting gas stream. A schematic diagram of the prepared CuO/ZnO heterocontact is shown in Fig. 1.

Dried air (P_{O2} = 0.2 atm) with 4142 ppm of CO is the reacting gas and its volumetric flow rate is fixed at 10 ml/min (3.14×10^{-8} mol/min for CO). The composition of the outlet gas is analyzed using gas chromatography. The CO or CO_2 gas concentration is determined using a calibration curve from the analysis of standard gases. The experimental apparatus for the gas phase analysis is shown in Fig. 1.

The texture of the prepared CuO/ZnO heterocontact is sufficiently porous and no other phases are confirmed at the CuO_x–ZnO_{1-x} layers from the X-ray diffraction patterns. The oxidative reaction of CO proceeds at the surface and/or at the interface of the CuO and ZnO particles; product gas (CO_2) is detected above 200°C. Twenty-five to thirty percent of the introduced CO turned to CO_2 at 320°C in the present system. Figure 2 shows the effect of applied voltage on the catalytic activity of CO oxidation at the CuO/ZnO gradient composition heterocontact. The catlytic activity is expressed as the CO_2 concentration in the outlet gas. The catalytic activity is higher when the reverse bias (CuO^-, ZnO^+) is applied. When the applied bias is switched from −1.0 to +1.0 V, the CO_2 rate immediately decreased and the CO_2 concentration in the outlet gas shows about a 10% decrease. This result shows that the catalytic activity of the CuO/ZnO heterocontact can be controlled in a reversible manner by the variation in applied voltage.

Applied voltage dependence of the rate of CO oxidation in the present system is shown in Fig. 3. The amount of CO_2 produced varies as a function of applied voltage and when reverse bias (CuO^-, ZnO^+) is applied, the apparent rate of CO oxidation increases with increasing reverse applied voltage. The observed enhancement in the rate of CO oxidation is about 10%, which is smaller than for non-Faradaic electrochemical modification of the catalytic activity (NEMCA) of the CO oxidative reaction at a Pt catalyst interfaced with ZrO_2 (7, 8). When forward bias (CuO^+, ZnO^-) is applied, the rate of CO oxidation decreases with increasing forward applied voltage and the activity is suppressed by the forward applied voltage.

The voltage–current characteristics of the CuO/ZnO gradient composition heterocontact are also shown in

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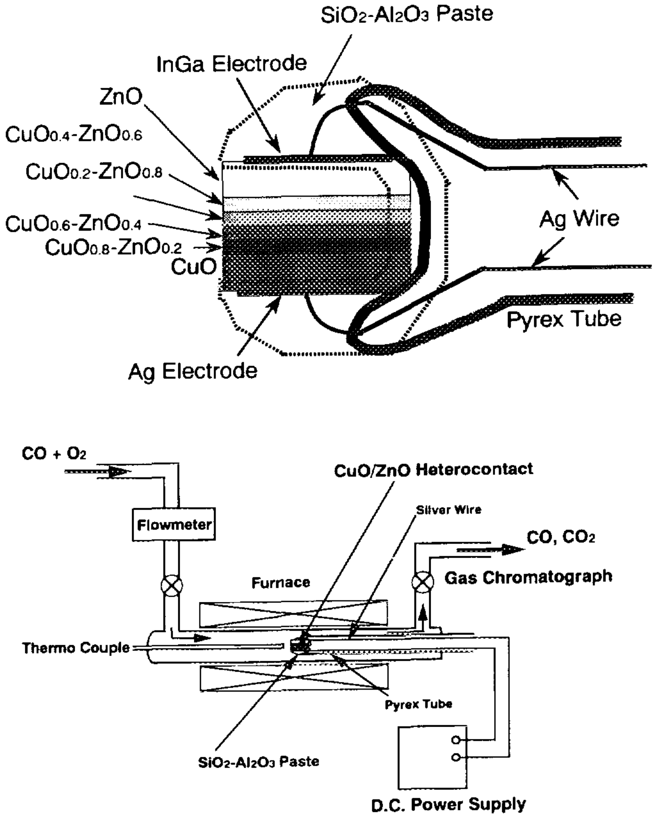

FIG. 1. Schematic diagram of gradient composition CuO/ZnO heterocontact and experimental apparatus. Electrodes and lead wires are covered with silica–alumina paste.

Fig. 3. Generated Joule heat owing to the current flow would be a little larger under forward bias. However, the conversion under forward bias is lower than that under reverse bias and it is concluded that the enhancement of CO_2 uptake under reverse bias is not due to the local heating of the catalyst by the electric current flow. The extent of the conversion of CO by CuO, ZnO, or CuO/ZnO heterocontact is summarized in Table 1. At 320°C, catalytic activity of the CO oxidative reaction of CuO is much higher than that of ZnO and the reaction on the ZnO surface is negligible in the present case. The CO_2 gas detected at the CuO/ZnO heterocontact contains the product of the catalytic reactions at the CuO surface, which is not interfaced with ZnO particles. However, this is not affected by the applied bias. Judging from the applied voltage dependence of the CO_2 uptake shown in Fig. 3, the phenomena would be related to the carrier transport process or variation in surface Fermi level position at the CuO/ZnO interface. However, the former mechanism is thought to be excluded in the present case, because the catalytic activity does not change discontinuously at around zero bias, whereas the polarity of the

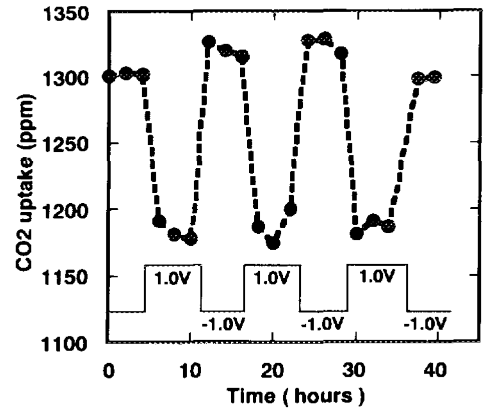

FIG. 2. The effect of applied bias on the catalytic activity of CO oxidation at CuO/ZnO gradient composition heterocontact. The measurements were performed at 320°C. The applied bias is fixed at ±1.0 V. The introduced CO gas concentration is 4142 ppm and catalytic activity is expressed as CO_2 concentration in the outlet gas.

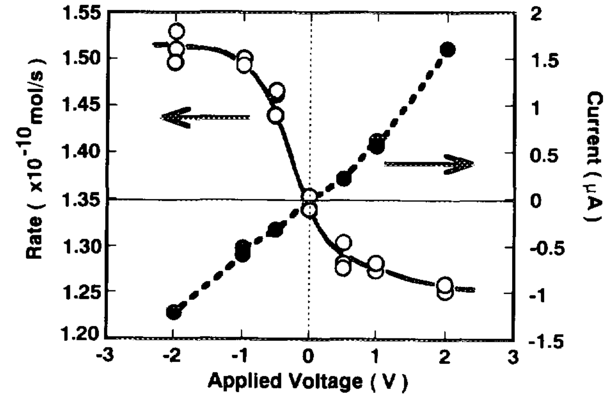

FIG. 3. The relation between the apparent rate for CO oxidation, applied current, and applied voltage at the CuO/ZnO gradient composition heterocontact. The measurements were performed at 320°C. The introduced CO gas concentration is 4142 ppm and its flow rate is 5.23×10^{-10} mol/s.

TABLE 1

Extent of Conversion of CO to CO_2 for CuO, ZnO, and Gradient Composition CuO/ZnO Heterocontact

Specimen	CO_2 uptake (ppm)	Conversion (%)
CuO (powder)[a]	3688	88.4
ZnO (powder)[a]	303	3.1
CuO/ZnO heterocontact	1067	25.8
Blank test	223	—

Note. Concentration of introduced CO gas is 4142 ppm (3.14×10^{-8} mol/liter).

[a] The powder specimen (3g CuO or ZnO) is mounted on a quartz plate. The specific surface areas are 0.375 m^2/g for CuO and 1.11 m^2/g for ZnO, respectively. The powder specimens are used after heat treatment at 850°C for 3 h in air.

applied bias and the direction of carrier transport are inverted at zero bias.

A relation between the catalytic activity and the Fermi level position of the metal oxide catalysts has been suggested since the 1950s (5, 6). Schwab explained the variation in activation energy of CO oxidative reactions at several metal oxides by considering the variation in Fermi level positions (9). The oxidative reaction of CO on CuO proceeds by the Rideal mechanism at 320°C (see Ref. 10) and the reaction rate of CO oxidation r is expressed as

$$r = \alpha \, [O^{-}] P_{\mathrm{CO}},$$

where α is a constant and $[O^{-}]$ and P_{CO} are the surface concentration of singly ionized adsorbed oxygen (O^{-}) and the CO partial pressure, respectively. The adsorbed oxygen species O^{-} is much more reactive with CO than O^{2-} or other adsorption species (11). According to the theory of Wolkenstein, the amount of ionized adsorbed oxygen depends on the surface Fermi level position and the reaction rate increases with increasing the surface Fermi level in the band gap (6). In the application of this theory to the case of the CuO/ZnO heterocontact, the surface Fermi level must be varied with applied bias.

The capacitance–voltage (C–V) relation of the CuO/ZnO heterocontact does not depend on the reverse applied voltage and an S–I–S (semiconductor–insulator–semiconductor) structure can be supposed as the model of CuO/ZnO. Assuming the S–I–S structure, the surface Fermi level of CuO would rise and the enhancement of catalytic activity of CO oxidation over CuO is suggested. The relation between the rate of CO oxidation and applied voltage (Fig. 3) would reflect part of the calculated E_s–r (Surface Fermi energy (E_s)–rate of the CO oxidation (r)) curve proposed by Wolkenstein.

The variation in Fermi level position at the CuO/ZnO contacted interface may be a reasonable explanation of the variation in catalytic activity of CuO/ZnO heterocontact. Though the heterocontact in the present study is a special reaction field, our results provide evidence for the validity of the application of electronic theory to the CO oxidation reaction and possibly other chemical reactions at semiconductor heterogeneous catalysts.

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