SENSING PROPERTIES AND CATALYTIC DECOMPOSITION TO CHLORINATED HYDROCARBONS OF INDIUM OXIDE BASED GAS SENSORS

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Chlorinated hydrocarbons are typical air pollutants having long-term toxicity. Recently, there are increasing demands for environmental monitoring of chlorinated hydrocarbons in Japan. Thus, the compact gas sensors are needed for this purpose. In this study, the semiconductor gas sensors using In_2O_3-based thin films have been investigated for the detection of 8 kinds of chlorinated hydrocarbons (CCl_4, $CHCl_3$, CH_2Cl_2, C_2Cl_4, C_2HCl_3, 1,1-$C_2H_2Cl_2$, C_2H_3Cl, 1,2-$C_2H_4Cl_2$). As a result, CuO-In_2O_3 sensor could detect CCl_4 with high sensitivity as well as high selectivity. Further, the sensing mechanism to CCl_4 of CuO-In_2O_3 sensor was elucidated by the study on decomposition of CCl_4.

In_2O_3 was prepared from $InCl_3 \cdot 4H_2O$ by wet process. In order to modify with 13 kinds of foreign oxides, In_2O_3 were impregnated with mainly metal acetates. The compact sensor chips equipped with heater were fabricated by using In_2O_3-based powders and subjected to the measurement of sensing properties to 8 kinds of chlorinated hydrocarbons (30 ppm) at 200-400 ℃.

Figure 1 shows the sensitivities (Ra/Rg) of In_2O_3-based sensors to 30 ppm CCl_4. Most of In_2O_3 based sensors showed the sensitivity higher than unity, suggesting the response with resistance decrease. Among these, La_2O_3-, Nd_2O_3-, and NiO-In_2O_3 sensors exhibited high sensitivity to CCl_4. On the other hand, only CuO-In_2O_3 sensor showed the large response with resistance increase (Ra/Rg<1). Further, the CuO-In_2O_3 sensor did not respond to other 7 chlorinated hydrocarbons expect for CCl_4, as shown in Fig. 2, suggesting high selectivity to CCl_4 of CuO-In_2O_3 sensor. When the loading of CuO was changed, the optimal loading was found to be 0.1 wt% and the highest sensitivity of 0.03 (=Ra/Rg) was obtained to 30 ppm CCl_4 at 200 ℃.

In order to elucidate the sensing mechanism of CuO-In_2O_3, CCl_4 decomposition was carried out on In_2O_3 and CuO-In_2O_3. Figure 3 shows the conversion in CCl_4 decomposition on In_2O_3 based catalysts as a function of temperature. The catalytic activity was the lowest for pure In_2O_3 catalyst. The activity slightly increased when 0.01 wt% CuO was added to In_2O_3, and 0.1 and 5 wt% CuO-In_2O_3 showed the highest activity, suggesting that the modification with CuO enhanced the catalytic activity of In_2O_3 in CCl_4 decomposition. The amounts of CO_2 produced in CCl_4 decomposition are shown in Fig. 4. CO_2 was produced even in low conversion range on In_2O_3 and 0.01 wt% CuO-In_2O_3, while any CO_2 was not produced on 0.1 wt% CuO-In_2O_3 until the conversion reached 60% and kept in low level until 95% conversion. CO_2 was moderately observed on 5 wt% CuO-In_2O_3. CCl_4 is decomposed on sensor surface into C and Cl fragments. The C fragment reacts with adsorbed oxygen to form CO_2, inducing the resistance decrease. On the other hand, the Cl fragment is negatively adsorbed on the surface to increase the sensor resistance. On 0.1 wt% CuO-In_2O_3 sensor, CCl_4 is well decomposed into C and Cl fragments. The Cl fragments produce Cl^- adsorbates but the C fragments are not oxidized. The formation of Cl^- adsorbates effectively contribute to the large resistance increase of 0.1 wt% CuO-In_2O_3.

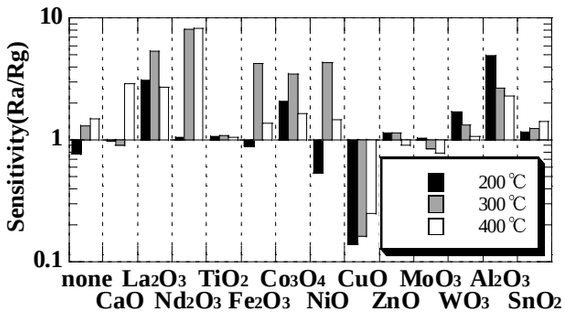

Fig. 1 Sensitivities of In_2O_3 based thin film sensors doped with various metal oxides to 30 ppm CCl_4 at 200-400 ℃.

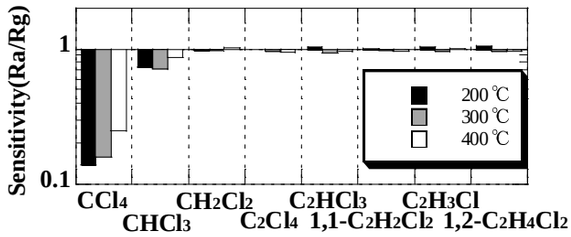

Fig. 2 Sensitivities to 30 ppm various chlorinated hydrocarbons of 5 wt% CuO-In_2O_3 sensor at 200-400 ℃.

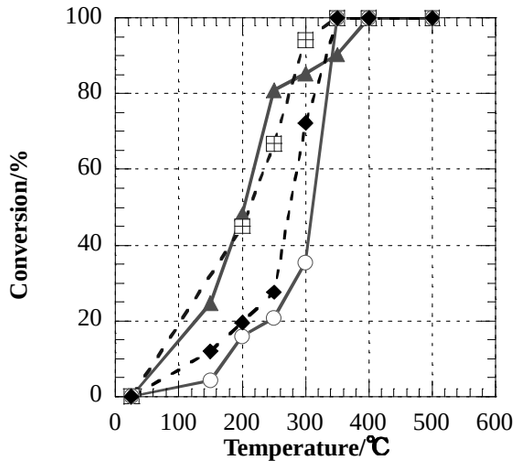

Fig. 3 Conversion in CCl_4 decomposition on In_2O_3 based catalysts as a function of temperature
—○—: In_2O_3, - -◆- -: 0.01 wt% CuO- In_2O_3,
- -⊞- -: 0.1 wt% CuO-In_2O_3,
—▲—:5 wt% CuO-In_2O_3.

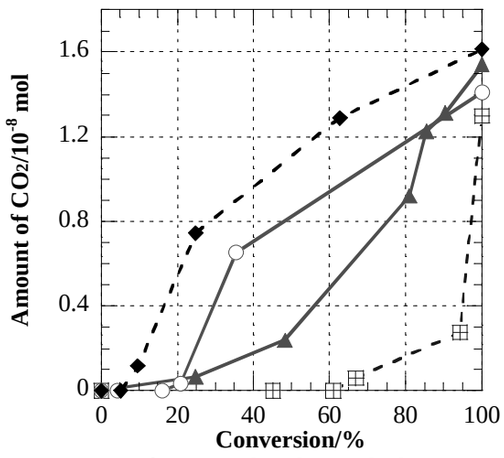

Fig. 4 Amount of CO_2 produced in CCl_4 decomposition on In_2O_3 based catalysts as a function of conversion.
—○—: In_2O_3, - -◆- -: 0.01 wt% CuO- In_2O_3,
- -⊞- -: 0.1 wt% CuO-In_2O_3,
—▲—:5 wt% CuO-In_2O_3.