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Selective Detection of Nitrogen Monoxide by the Mixed Oxide of Cr_2O_3-Nb_2O_5

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Several single and mixed oxides were used as sensors for detection of CO, CO_2, NO, and NO_2. The conductivity of $(Cr_2O_3)_{1-x}(Nb_2O_5)_x$ was greatly changed by a contact with 1-1000 ppm of NO, but was unchanged by that with CO or CO_2. The sensitivity to NO was maximum by operating at 573 K using oxide with x=0.1. The influence of CO during detection of NO was negligible at x=0.5.

Oxide semiconductors have been widely used for various chemical sensors.[1-2] Typical examples in practical use are SnO_2 or γ-Fe_2O_3 based oxides for combustible gas sensors.[3] Recently, the sensors for poisonous gases are requested increasingly for security and to avoid air pollution. A small and cheap nitrogen monoxide sensor is one of the important subjects. Although the chemical luminescence method has been popularly employed for NO detection, some materials for NO sensor have been proposed for miniaturization or simplification of the detection system. The NO sensors proposed so far utilize semiconductive properties of oxides[4] or organic thin films,[5-6] a galvanic cell, and a solid electrolyte.[7] Of these types of sensors, oxide semiconductors are advantageous in their stability and cost but generally lack in selectivity. In the present study, we tried to develop the sensitivity and selectivity of NO sensor using several single and mixed oxides. Influences of CO, CO_2, and NO_2 on the detection of NO were also studied.

Mixed oxides were prepared by coprecipitation or evaporation of aqueous solutions of corresponding metal nitrates. The powders thus obtained were calcined at 723 K for 5 h, and then pressed into disks (10 mm in diameter and 0.5 mm thick). After heating at 773 K for 2 h, a Pt paste was applied on both faces of the disks and again fired at 873 K for 30 min. Conductivities of the disks were measured in a flow system with a quartz cell in a temperature range of 473 K to 873 K. Various concentrations of NO, NO_2, CO, and CO_2 were obtained by mixing with dry air. Seebeck coefficients of pellet samples (5 mm x 5 mm x 10 mm) were measured at 573 K. The measurement was performed in a controlled partial pressure of oxygen. Partial pressure of oxygen, which was monitored by yttria-stabilized zirconia oxygen sensor, was controlled either by diluting O_2 with N_2 (1-10^{-4} atm) or by using a gaseous mixture of CO and CO_2 (10^{-10}-10^{-18} atm).

Conductivities of various oxides were measured under a flow of air with or without 600 ppm of NO, NO_2, CO, and CO_2, as summarized in Table 1. The sensitivity of the response is defined as the ratio of the conductivity change of an oxide with gas adsorption to the conductivity in air, $\sigma-\sigma_{air}/\sigma_{air}$, where σ and σ_{air} stand for conductivities in a sample gas and air, respectively. The selectivity of sensors is

Table 1. Sensitivities of metal oxides to 600 ppm of CO, CO_2, NO, and NO_2

Sample	Operation temp / K	$\log(\sigma/S\cdot cm^{-1})$ a)	Sensitivity b) CO	CO_2	NO	NO_2	Surafce area $m^2\cdot g^{-1}$
SnO_2	573	-7.36	1.82	0.00	1.40	0.43	10.4
ZnO	773	-5.86	0.91	0.06	0.78	0.48	10.2
Nb_2O_5	573	-8.06	1.73	0.00	1.37	1.39	4.1
Cr_2O_3	573	-5.56	-0.86	0.00	-0.57	-0.22	3.5
Cr_2O_3-Nb_2O_5	573	-7.13	-0.05	0.00	-0.31	-0.21	6.5
Nb_2O_5-MnO_2	673	-6.31	1.43	0.00	0.29	0.31	2.5
Al_2O_3-ZnO	673	-8.60	6.08	0.09	4.31	5.31	52.7
ZrO_2-ZnO	773	-7.08	1.07	0.03	0.66	0.42	23.7
PbO_2-TiO_2	673	-5.71	-0.35	0.00	-0.57	-0.22	1.9
SnO_2-ZnO	573	-8.31	0.99	0.00	0.45	0.25	23.7
SnO_2-TiO_2	773	-7.68	0.48	0.00	0.39	0.34	11.9
V_2O_5-ZrO_2	773	-6.04	0.62	0.00	0.26	0.30	4.9
Cr_2O_3-ZnO	573	-2.46	-0.09	0.00	-0.06	-0.05	5.3
Nb_2O_5-Al_2O_3	773	-7.64	0.10	0.00	0.12	0.08	28.3

a) Conductivity in air. b) Sensitivity=$(\sigma-\sigma_{air})/\sigma_{air}$.

discussed by comparing the cross sensitivity at a given concentration of each gas. Tin and zinc oxides, which are well-known as sensors for combustible gases, underwent large change in conductivity with adsorption of NO, though the conductivity changes were larger for CO than for NO. All the single metal oxides listed in Table 1 did not achieved a sufficient selectivity for NO detection. The conductivity of every metal oxide examined here was unchanged by introduction of CO_2. The conductivities of Cr_2O_3-ZnO, Nb_2O_5-Al_2O_3, SnO_2-TiO_2, and V_2O_5-ZrO_2 were unchanged with an exposure to either NO, NO_2, CO, or CO_2. Mixing of oxides sometimes gave rise to enhancement of the sensor performance. Especially, the sensitivity to CO was six times larger for Al_2O_3-ZnO than that for single ZnO. The high sensitivity of Al_2O_3-ZnO appears to result from its large surface area, increasing adsorption amount, and low conductivity. Although Al_2O_3-ZnO and ZrO_2-ZnO were sensitive to NO, these oxides are not adequate for a

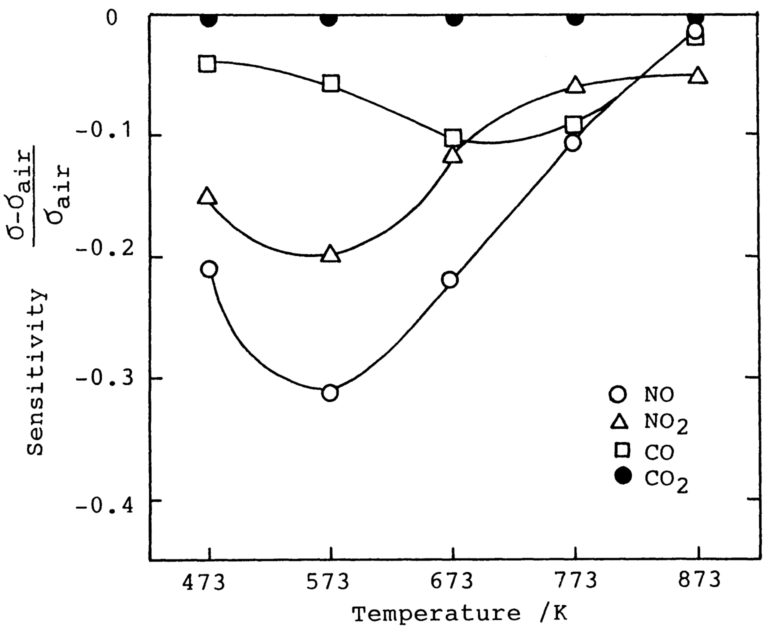

Fig. 1. Temperature dependence of sensitivity of Cr_2O_3-Nb_2O_5 to NO, NO_2, CO, and CO_2. (gas concentration 600 ppm)

selective NO sensor because of their higher sensitivity to CO. The conductivity of Cr_2O_3-Nb_2O_5 was largely changed with adsorption of NO and NO_2 at 573 K, but were unaffected with that of CO and CO_2. Further study was focused on the Cr_2O_3-Nb_2O_5 system as a NO sensor.

The sensitivity of the Cr_2O_3-Nb_2O_5 element depended on the operation temperature as shown in Fig. 1. The sensitivity to NO was maximum at 573 K and decreased with either increasing or decreasing temperature. On the other hands, sensor became sensitive to CO with increasing temperature up to 673 K. It is obvious that the optimum operation temprature of Cr_2O_3-Nb_2O_5 is about 573 K from the requests of sensitivity and selectivity.

The sensitivity of Cr_2O_3-Nb_2O_5 is examined as a function of the concentrations of NO, NO_2, CO, and CO_2 at 573 K in Fig. 2. The sensitivity of Cr_2O_3- Nb_2O_5 decreased with increasing concentrations of NO, NO_2, and CO, but the sensitivity to NO was the largest among these gases. Therefore, the Cr_2O_3-Nb_2O_5 sample is selective and sensitive enough for detection of NO. With introducing 600 ppm of NO abruptly, 80% of the steady response was attained within 50 s. Subsequent purge with air restored 80% of the original level within 90 s.

The Seebeck coefficient of Cr_2O_3-Nb_2O_5 was obtained from thermoelectromotive force as a function of partial pressure of oxygen (Fig. 3). The equimolar oxide of Cr_2O_3-Nb_2O_5 possessed positive Seebeck coefficient in the P_{O_2} range of 10^{-17} to 1 atm. This agreed with observed p-type response with introduction of a small amount of CO, NO, and

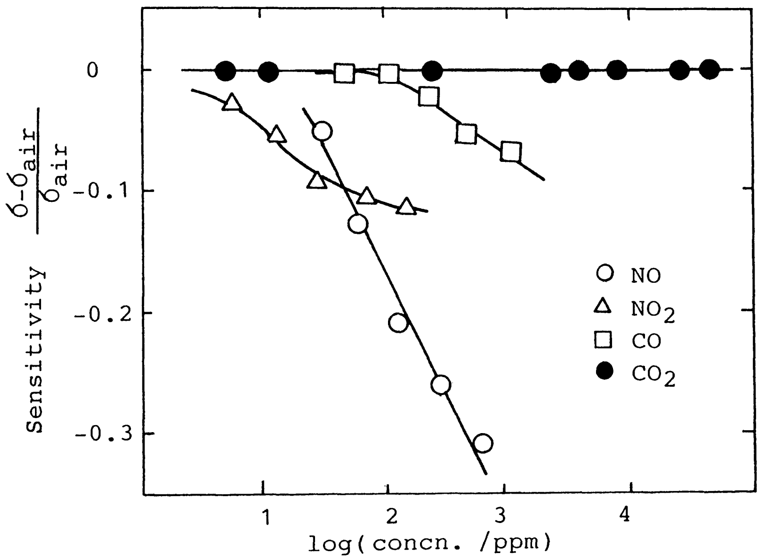

Fig. 2. Dependence of Cr_2O_3-Nb_2O_5 sensitivity on concentration of NO, NO_2, CO, and CO_2 in air. (operation temperature 573 K)

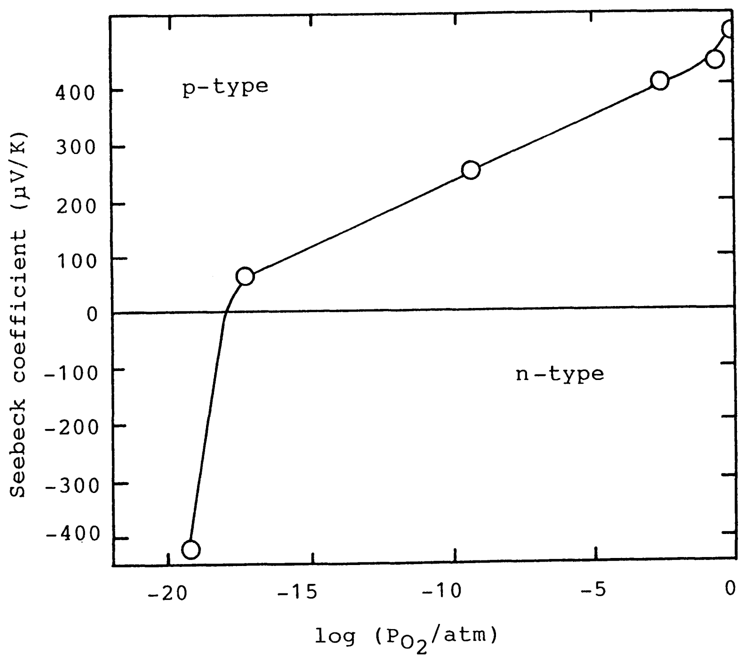

Fig. 3. Dependence of Seebeck coefficient of Cr_2O_3-Nb_2O_5 on partial pressure of oxygen. (Cr_2O_3 : Nb_2O_5 = 5 : 5)

NO_2, as mentioned above. Seebeck coefficient decreased monotonously and the sample changed into n-type semiconductor at very low P_{O_2} (10^{-18} atm).

The composition dependence of sensitivity as well as conductivity in air of the system $(Cr_2O_3)_{1-x}(Nb_2O_5)_x$ are shown in Fig. 4. The oxide system of $(Cr_2O_3)_{1-x}(Nb_2O_5)_x$ was insensitive to CO_2 over the whole composition range. It is noted that with increasing x, the sign of sensitivity was reversed at about x=0.7. Namely, the conductivity of sample decreased by a contact with NO, NO_2, or CO at x=0.5, while it increased at x=0.7. Since pure Cr_2O_3 and Nb_2O_5 are p- and n-type semiconductors, respectively, the change of the sign occurs at intermediate composition. The sensitivity to NO was the highest at x=0.9, but almost zero at x=0.7. On the other hand, the sensitivity to CO was very small around the equimolar composition. The oxide with x=0.9 was sensitive to NO, though this sensor was also sensitive to CO and NO_2. When the selectivity is required for NO detection, one should choose the sample with x=0.5. The sensitivity and selectivity of sensor elements were greatly enhanced by mixing of Cr_2O_3 and Nb_2O_5. This mixed oxide system is excellent in its selectivity for detection of NO.

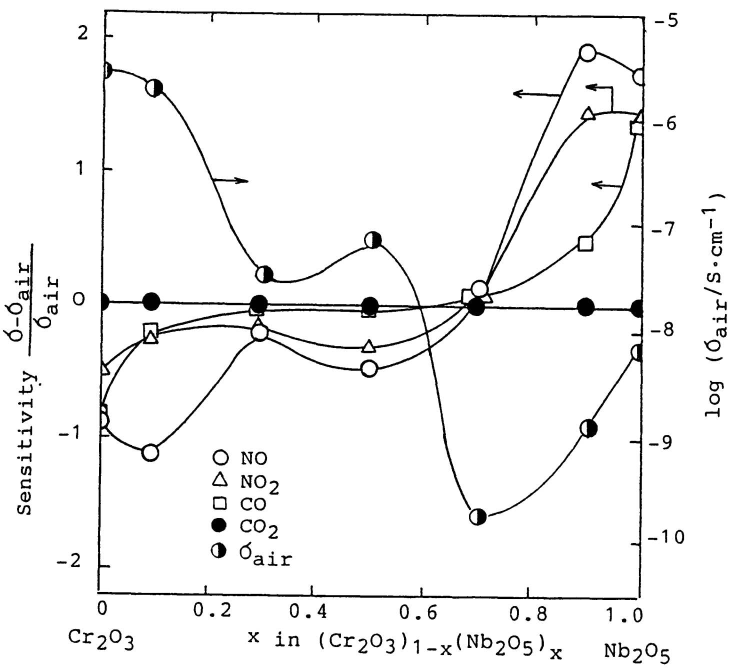

Fig. 4. Effects of oxide composition on the sensitivity of $(Cr_2O_3)_{1-x}(Nb_2O_5)_x$ mixed oxides. (operation temperature 573 K, gas concentration 600 ppm)

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