

## **Oxygen-Sensing Properties of Spinel-Type Oxides for** Stoichiometric Air/Fuel Combustion Control

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The temperature dependence of electrical resistance of several spinel-type oxides was measured in exhaust gases of air-methane combustion, to evaluate the potential of the oxides as an air/fuel stoichiometric oxygen sensor. The results are discussed in terms of sensitivity and response time at the stoichiometric combustion point. It was found that the sensitivity as well as the response time is markedly affected by point defect structures of the oxide specimens. The response time is also related to the catalytic activity of the oxides for complete oxidation of methane. Among the specimens studied, the  $ZnCr_2O_4 + Cr_2O_3$  (1.0:0.1 molar ratio) is the most promising as the oxygen sensor, because it exhibits the largest resistance changes of more than 3 orders of magnitude and shortest response times of about 0.5 s when the combustion mixture is switched between the air-rich versus fuel-rich composition. [Key words: sensors, spinels, combustion, oxides, electrical resistors.]

#### I. Introduction

NO REDUCE pollutants in exhaust gases from automobile engines, such as hydrocarbons, carbon monoxide, and nitrogen oxides, three-way catalysts are now widely used. But, to attain high efficiency of the catalysts for sufficient reduction of the pollutants, air to fuel ratios (A/F) of the combustion mixtures need to be controlled within a narrow range around the stoichiometric combustion composition. For this purpose, oxygen sensors have been put into practical use. Oxygen partial pressure in the exhaust gases exhibits a drastic change from about 10<sup>3</sup> to 10<sup>-14</sup> Pa<sup>1,2</sup> at the stoichiometric point, leading to dramatic changes in the electrical conductivity of semiconducting oxygen sensors as well as in the emf of solid electrolyte oxygen sensors. Thus, the A/F ratios and then the concentration of pollutants in the exhaust gases can be controlled by utilizing the output signals from the sensors.

An *n*-type semiconductive  $TiO_2$  is a typical oxygen sensor,<sup>1</sup> and investigations have been directed to shortening its response time.<sup>3,4</sup> In addition, *n*-type  $\text{SnO}_2^5$  and  $\text{Nb}_2 \tilde{\text{O}}_5^6$  have been demonstrated to function as the A/F stoichiometric oxygen sensor. As to the potential of mixed oxides, on the other hand, only a few results have been reported, on the perovskite-type oxides.<sup>7,8</sup>

The aim of the present work is to investigate suitable materials among the spinel-type oxides for A/F stoichiometric oxygen sensors, by measuring the temperature dependence of electrical resistance of the oxides in exhaust gases of air-

methane combustion mixtures. The results are discussed in terms of sensitivity and response time at the stoichiometric A/F point, based on point defect structures and catalytic activities of the oxides.

### **II. Experimental Procedure**

## (1) Preparation of Specimen

In preliminary screening tests, several kinds of constituent metal oxides were employed as starting materials: ZnO (>99% pure);<sup>‡</sup> NiO (>99% pure);<sup>‡</sup> Fe<sub>2</sub>O<sub>3</sub> (99% pure);<sup>§</sup> Cr<sub>2</sub>O<sub>3</sub> (99% pure);<sup>§</sup> and MgO, prepared by calcination of MgCO<sub>3</sub>.  $Mg(OH)_2 \cdot 5H_2O$  (extra-pure reagent),<sup>§</sup> at 1100°C for 3 h. Spinel-type oxides were prepared by calcining a mixture of these constituent metal oxides in the desired proportions at 1200°C for 5 h. As an exception, calcination at 1000°C for 5 h was selected for the  $ZnCr_2O_4$  specimen. After calcination, no phases except the desired spinel oxide were detected for all cases by X-ray diffraction with Ni-filtered CuK $\alpha$  radiation. In another procedure, metal nitrates were employed as starting materials in order to improve the sensing properties of MgCr<sub>2</sub>O<sub>4</sub> and ZnCr<sub>2</sub>O<sub>4</sub>. An aqueous solution of a desired mixture of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (reagent grade)<sup>§</sup> with Mg(NO<sub>3</sub>)<sub>2</sub>·  $6H_2O$  (extra-pure reagent)<sup>‡</sup> or  $Zn(NO_3)_2 \cdot 6H_2O$  (extra-pure reagent)<sup>¶</sup> was evaporated to dryness on a hot plate, followed by thermal decomposition at 500°C for 1 h. The resulting solid was ground and calcined at higher temperatures for 5 h, MgCr<sub>2</sub>O<sub>4</sub> at 1000°C and ZnCr<sub>2</sub>O<sub>4</sub> at 900°C. Formation of a single spinel phase was confirmed by X-ray diffraction.

#### (2) Preparation of Sensor Element

The powder of each spinel-type oxide was tightly packed within a  $2 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$  cavity of an alumina substrate whose structure was essentially the same as in the literature,<sup>5</sup> and then sintered at 1200° or 1000°C for 2 h when metal oxides or nitrates, respectively, were employed as starting materials. A pair of Pt wires were embedded as electrodes within the sample compact. The distance between the two Pt wires could be controlled within a negligible error from one sensor element to another by employing small leading holes in the substrates. Thus, differences in the resistance of an individual element at the same condition correspond directly to the differences in conductivity of the specimens.

#### (3) Measurement of Sensitivity and Response Time

Measurement of oxygen-sensing properties was carried out using a gas-flow apparatus. Air and methane were mixed at an appropriate ratio to obtain a desired air excess ratio  $(\lambda)$ , where  $\lambda$  was defined as

$$\lambda = \frac{\operatorname{air/CH_4}}{(\operatorname{air/CH_4})_{stoich}} \tag{1}$$

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Thus, the stoichiometric point is defined as  $\lambda = 1$ , for which there is just enough oxygen to convert all CH<sub>4</sub> to CO<sub>2</sub> and  $H_2O$ . Two kinds of the gas mixtures with different  $\lambda$  values sandwiching the stoichiometric point were employed:  $\lambda = 1.13$ , corresponding to the lean-burn condition, and  $\lambda = 0.89$  for rich-burn. The gas mixtures were burned at 500°C over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, and the resulting exhaust gases were introduced into a quartz vessel in which a sensor element has been inserted. Water vapor in the exhaust gases, originating from the combustion, was trapped before the vessel. Temperature dependence of the resistance of the specimen was measured in the temperature range of 400° to 800°C. The ratio of the resistance at  $\lambda = 1.13$  to  $\lambda = 0.89$  for *n*-type semiconductive oxides, or the ratio of  $\lambda = 0.89$  to  $\lambda = 1.13$ for *p*-types, at the same operating temperature represents the magnitude of sensitivity in detecting the stoichiometric combustion point, namely, the larger the ratio, the higher the sensitivity. The resistance change was calculated from the voltage change across a load resistor connected in series with the specimen under the applied voltage of 5.0 V dc.

In measurement of response times, the exhaust gas flowing over the specimen was changed quickly to another exhaust gas with a different  $\lambda$  value, and the time required for the output voltage to reach the 80% value of the total change was defined as the response time. The response time was measured both for the  $\lambda = 1.13$  to  $\lambda = 0.89$  change and for the reverse. The former was denoted as "red" response time because reduction of the oxide specimens was induced by the exhaust gas change, while the latter was "ox" because of reoxidation of the reduced oxides.

# (4) Measurement of Catalytic Activity for Methane Oxidation

The surface area of each specimen was measured by the BET method, using nitrogen adsorption isotherms. The catalytic activity of the oxide specimens for complete oxidation of methane was tested in the same gas-flow apparatus. Granules of each specimen (0.2 g) were placed in a fixed bed reactor in the apparatus. An air and methane mixture of  $\lambda = 1$  was fed to the specimen bed at a flow rate of 1800 m<sup>3</sup> · h<sup>-1</sup> (space velocity was about 14 000 h<sup>-1</sup>, the flow rate divided by the catalyst bed volume). The methane conversion was analyzed by gas chromatography<sup>\*\*</sup> with a 5-Å (5 × 10<sup>-1</sup> nm) molecular sieve and a Porapack<sup>+†</sup> Q column. The catalytic activities of the various specimens were evaluated in terms of the conversion of methane at the same reaction temperature.

#### **III. Results and Discussion**

## (1) Sensing Properties

Figure 1 shows the temperature dependence of resistance in three environments and the response time of the ZnFe<sub>2</sub>O<sub>4</sub> specimen. At every temperature, the resistance decreased in the order of air >  $\lambda = 1.13 > \lambda = 0.89$ , suggesting that the specimen was *n*-type semiconductive over the whole oxygen partial pressure range between  $2.1 \times 10^4$  Pa (in air) and about  $10^{-14}$  Pa (in  $\lambda = 0.89$ ),<sup>9</sup> although exact oxygen partial pressures were not measured in this study. As stated previously, the ratio of the resistance at  $\lambda = 1.13$  to that at  $\lambda = 0.89$  at the same temperature represents the sensitivity (k) of the specimen in detecting the stoichiometric point. Thus, it is apparent that the sensitivity is in the magnitude of several hundreds at 400°C and it decreases as the temperature increases. From Fig. 1(b), the "red" response time is much shorter than "ox." But even the "red" times are too long from a practical use, because a response time less than 200 ms was reported for the pellet-type TiO<sub>2</sub> oxygen sensor.<sup>3</sup>



Fig. 1. Temperature dependence of (a) resistance in three environments and (b) response times of  $ZnFe_2O_4$  specimen.

Sensing properties of various spinel oxides prepared from constituent metal oxides are summarized in Table I. The sensitivity is much higher and the response times are much shorter for the *p*-type oxides except for NiCr<sub>2</sub>O<sub>4</sub>. As to the response times, another feature is noted. In the case of *n*-types, the values of "ox" were considerably larger than those of "red." In contrast, the values of "ox" were shorter than those of "red" in the case of *p*-types. The reason for these variations in response times will be discussed later, based on point defect structures of the spinel oxides and the negligibly small catalytic activity of the Pt electrodes used in this study.

Thus, the results on the specimens from the constituent oxides indicated that the *p*-type semiconductive  $ZnCr_2O_4$ and MgCr<sub>2</sub>O<sub>4</sub> were more promising as oxygen sensors than the *n*-types. Especially, the  $ZnCr_2O_4$  specimen exhibited the highest resistance change of more than 3 orders of magnitude at the stoichiometric point and the shortest 80% response time of 0.4 s when the  $\lambda$  value was changed from 0.89 to 1.13. To improve the sensing properties,  $ZnCr_2O_4$  and MgCr<sub>2</sub>O<sub>4</sub> were prepared by employing constituent metal nitrates as starting materials so as to reduce the calcination temperature and to enhance the surface area. As a result, the surface area was almost tripled for each case as summarized in Table I. Sensing properties of the two spinels from nitrates at 600°C are also summarized in Table I.

The temperature dependence of resistance in the exhaust gases and the response times for the MgCr<sub>2</sub>O<sub>4</sub> specimen from metal nitrates are shown in Fig. 2. For comparison, the results on the specimen from metal oxides are also plotted in the same figure. The "red" response time was shortened at 500° to 700°C by changing the starting materials. Also, the "ox" response time was significantly improved at 400°C. There is no doubt that the response times are dependent on the following three factors: (1) gas transport through pores within the pellet of the specimen, (2) rate of chemical reaction, that is charge transfer between chemisorbed oxygen and gaseous oxygen at the surface, and (3) mobility of oxide ions in the bulk of the specimen particles.<sup>4</sup> Therefore, the observed improvement in response times may be attributed to the increased surface area or the decreased particle size. But not all the variations in response times can be completely explained by only the surface area or the particle size. Other important factors influencing the response times will be discussed in detail in the next section.

From the results in Fig. 2(a), it was found that the starting materials, in other words the surface area, did not significantly affect the sensitivity of the MgCr<sub>2</sub>O<sub>4</sub> specimen. At every operating temperature, irrespective of the  $\lambda$  value, the resistance decreased in a similar manner by changing the starting materials from metal oxides to metal nitrates. Such decreases in resistance of the specimen may have arisen from a

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Table I.	Sensing 1	Properties and	Catalytic	Activities of	of Several	Spinel-Type	Oxides
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	Starting materials		Sensitivity at 600°C	80% response time at 600°C (s)		Surface	$T_{\rm sorr}^{\dagger}$
Specimens		Semiconductivity	(k)*	Ox	Red	$(m^2 \cdot g^{-1})$	(°C)
MgFe <sub>2</sub> O <sub>4</sub>	Oxides	n	35	117	15	0.16	785
$ZnFe_2O_4$	Oxides	n	170	354	16	0.27	785
$NiFe_2O_4$	Oxides	n	48	228	6		
MgCr <sub>2</sub> O <sub>4</sub>	Oxides	p	1000	0.4	2	1.5	715
$ZnCr_2O_4$	Oxides	p	1800	0.4	1.8	2.1	670
NiCr <sub>2</sub> O <sub>4</sub>	Oxides	, p	28	4	14		
MgCr <sub>2</sub> O <sub>4</sub>	Nitrates	p	750	0.4	0.8	4.7	625
$ZnCr_2O_4$	Nitrates	p	3300	0.35	0.7	6.9	615
$ZnCr_2O_4 + Cr_2O_3$ (1.0:0.1 in molar ratio)	Nitrates	<u> </u>	3800	0.45	0.5	4.8	660

\* $k = R(\lambda = 1.13)/R(\lambda = 0.89)$  for *n*-types,  $k = R(\lambda = 0.89)/R(\lambda = 1.13)$  for *p*-types. <sup>†</sup>Temperature at which conversion level is 80%.

decrease in contact resistance of the MgCr<sub>2</sub>O<sub>4</sub> particles due to the accelerated sintering of fine particles. In both cases of different starting materials, the sensitivity decreased as the temperature rose. Thus, the sensing properties of MgCr<sub>2</sub>O<sub>4</sub> were not improved markedly by changing the starting materials.

The temperature dependence of resistance in the exhaust gases and the response times of two ZnCr<sub>2</sub>O<sub>4</sub> specimens, prepared from metal nitrates and from metal oxides, are shown in Fig. 3. On the whole, the response times were again slightly improved at temperatures higher than 500°C by employing metal nitrates (see Fig. 3(b)). More interesting is the change in sensitivity. When the metal nitrates were employed as starting materials, the resistance in  $\lambda = 1.13$  decreased at every temperature, compared with the oxide starting materials. And the magnitude of the decrease was comparable at every temperature. In  $\lambda = 0.89$ , on the other hand, the resistance decreased slightly at 400° to 600°C, while it increased a little at 700° and 800°C. As a result, the sensitivity was enhanced at temperatures higher than 600°C without any significant deterioration in response times. In addition, this resulted in an increase in the gap between the resistance in  $\lambda = 0.89$  at 800°C and that in  $\lambda = 1.13$  at 400°C, indicating that less compensation is needed for the effect of operating temperature on resistance in its practical use. Thus, it was revealed that ZnCr<sub>2</sub>O<sub>4</sub> was a promising candidate among the specimens studied.

## (2) Factors Influencing Response Times

For improvement of the sensing properties, it is important to get information on the factors influencing the response times. Therefore, the variations in Fig. 2(b) are discussed in detail in this section. It is reasonable to imagine that the chemical reaction at the surface as well as the mobility of oxide ions in the bulk are accelerated as temperature increases. But, contrary to this expectation, the "red" response time was pro-



Fig. 2. Temperature dependence of (a) resistance in the exhaust gases with different  $\lambda$  values and (b) response times of MgCr<sub>2</sub>O<sub>4</sub> specimen:  $(\bigcirc, \bullet)$  prepared from metal oxides;  $(\triangle, \blacktriangle)$  prepared from metal intrates.

longed at 800°C in spite of the increased surface area. In addition, the "ox" response time was not affected by the surface area in the temperature range of 500° to 800°C. In this case, therefore, the above two factors are not considered important in determining the response times.

Another possible factor is the catalytic activity of the sensor element itself. In exhaust gases from automobile engines, there is a certain amount of residual fuel even in a lean-burn region ( $\lambda > 1.0$ ) and also a certain amount of free oxygen even in a rich-burn region ( $\lambda < 1.0$ ).<sup>1</sup> due to incomplete combustion of fuel. Thus, if the catalytic activity is poor, it leads to deterioration of the response time, accompanied by an apparent decrease in sensitivity at the stoichiometric point, because thermodynamic equilibrium in the gaseous phase over the sensor element cannot be achieved rapidly.<sup>4</sup> In this study, however, we believe that the catalytic activity of the  $Pt/Al_2O_3$ is high enough to achieve the equilibrium and that the difference in catalytic activity between the two MgCr<sub>2</sub>O<sub>4</sub> specimens is not an important factor in determining the response time, because the two specimens exhibited almost the same "ox" response times at temperatures higher than 500°C.

Another conceivable factor is the effect of charge defects. Figure 4 shows a schematic diagram of defect concentrations in an MO oxide versus oxygen partial pressure, based on the Kröger–Vink notation.<sup>10</sup> Here, it is assumed that the oxide is likely to contain Schottky-type defects and that it is unintentionally doped with acceptor-type foreign atoms  $F^+$ . In the formulas describing the electrical neutrality conditions in each region of Fig. 4,  $V_{\rm O}$  represents an oxide ion vacancy in the MO lattice, the symbol – denoting two positive charges relative to the O<sup>2-</sup> site, and  $F'_{\rm M}$  is an F<sup>+</sup> ion occupying an M<sup>2+</sup> site, the prime denoting one negative charge relative to



Fig. 3. Temperature dependence of (a) resistance in the exhaust gases with different  $\lambda$  values and (b) response times of  $\text{ZnCr}_2O_4$  specimen:  $(\bigcirc, \bullet)$  prepared from metal oxides;  $(\triangle, \blacktriangle)$  prepared from metal nitrates.



Fig. 4. Defect concentrations in an MO oxide containing unintentional acceptor-type foreign atoms  $(F^+)$  versus oxygen partial pressure.

the  $M^{2+}$  site. A similar, but rather complex, diagram can be drawn for the case of an AB<sub>2</sub>O<sub>4</sub> oxide. But, Fig. 4 is sufficient for discussion of the effect of the concentration of oxide ions. The results in Fig. 2(a) suggest that two MgCr<sub>2</sub>O<sub>4</sub> specimens exhibit *p*-type semiconductivity in the wide range of oxygen partial pressure higher than  $10^{-14}$  Pa. The problem is the transport number of oxide ions at oxygen partial pressures around  $10^{-14}$  Pa. If the transport number is high enough because of a large amount of unintentional impurities (foreign  $F^+$  and/or  $F^{2+}$  ions are able to act as such impurities in the case of an AB<sub>2</sub>O<sub>4</sub> oxide), a  $P_{O_2}$ -independent region of electrical conductivity should appear near the p to n transition point, as easily imagined from Fig. 4. If this is the case for the two MgCr<sub>2</sub>O<sub>4</sub> specimens, the "red" response times should be longer than the "ox" times, since a pair of Pt wire electrodes are not expected to catalyze electron transfer between oxide ions and gaseous oxygen, because of their extremely small surface area, while in the cases of the Pt electrodes of fine particles or of a special kind of perovskite-type oxide electrodes, such electrode-catalyzed electron transfer has been reported.<sup>11,12</sup> Thus, oxide ions would be blocked at the Pt wire/semiconductor interface, leading to polarization at the interface. This would result in a slight increase in resistance of the specimen with the passage of time just after a rapid change in resistance, when the  $\lambda$  value is changed from 1.13 to 0.89, and hence in a relatively long response time. Of course, the contribution of the oxide ion conductivity strongly depends on the starting materials, since the amount of impurities is closely related to them. In addition, a difference between the activation energies for the hole conductivity and for the oxide ion conductivity is also an important factor in evaluating the temperature dependence of the contribution of the oxide ion conductivity. Although the relationship between the conductivity and the oxygen partial pressure as well as the transport number of oxide ions for each specimen were not measured in this study, it is reasonable, referring to the above discussion, to assume that the relatively longer "red" response time observed for the MgCr<sub>2</sub>O<sub>4</sub> specimen prepared from metal nitrates at 800°C arose from the considerable contribution of the oxide ion conductivity. But a question still remains. That is the fact that the "ox" response time was longer than the "red" at 400°C for the MgCr<sub>2</sub>O<sub>4</sub> prepared from metal oxides. This phenomenon cannot be explained by the above discussion and suggests that there is another factor in determining the response time.

The above discussion also explains why n-type semiconductive specimens tend to exhibit a longer "ox" response time (see Table I). From the diagram in Fig. 4, it is easy to imagine that in the case of the n-type oxides the contribution of oxide ion conductivity is dominant at higher oxygen partial pressures (the lean-burn region) rather than at the lower partial pressures (the rich-burn region), if the concentration of oxide ion vacancies is high enough. The influence of the oxide ion conductivity on the response time would be a minor subject if the catalytic activity of the electrodes were high enough. But, the influence still remains as a serious problem in determining the sensitivity at the stoichiometric point. For example, if the specimen exhibits the *p*-to-*n* transition at a certain oxygen partial pressure in the range of 10<sup>4</sup> to 10<sup>-14</sup> Pa or exhibits a  $P_{O_2}$ -independent conductivity region in the same oxygen partial pressure range, the sensitivity would become smaller than the value calculated by assuming that the formula  $\sigma \propto P_{O_2}^{\pm 14}$  can be set up for the specimen.<sup>9</sup>

## (3) Attempts to Improve Sensing Properties by Doping

Among the specimens studied,  $ZnCr_2O_4$  was the most promising as an oxygen sensor. Taking the above discussion into consideration, some attempts were made to improve the sensing properties of the  $ZnCr_2O_4$  specimen, by 5 mol% partial substitution of  $Mg^{2+}$  ions for  $Cr^{3+}$  in  $ZnCr_2O_4$ , as well as by addition of the 10 mol% excess constituent metal oxides to  $ZnCr_2O_4$ . These specimens were prepared from metal nitrates for all the cases. These experiments were aimed also at evaluating the effect of charge defects in the  $ZnCr_2O_4$  lattice on the sensing properties.

Figure 5 shows the temperature dependence of resistance in the exhaust gases with two different  $\lambda$  values and the response times of the ZnCr<sub>1.95</sub>Mg<sub>0.05</sub>O<sub>4.8</sub> specimen. For comparison, the results on ZnCr<sub>2</sub>O<sub>4</sub> from metal nitrates are also plotted in the same figure. By the 5 mol% partial substitution of Mg<sup>2+</sup> for Cr<sup>3+</sup>, the resistance significantly decreased over the whole temperature range in  $\lambda = 0.89$ . Also it decreased in  $\lambda = 1.13$ , but the magnitude of the decrease was relatively small compared with the case of  $\lambda = 0.89$ . As a result, the sensitivity became poor by the partial substitution. In addition, the "red" response time became longer and ranged between 4 and 10 s. Although the partial substitution did not offer any improved properties, these results support the above discussion that the oxide ion conductivity possibly influences the sensitivity as well as the response times.

From the resistance changes both in  $\lambda = 0.89$  and in  $\lambda = 1.13$ , it is likely true that Mg<sup>2+</sup> ions partially substitute the Cr<sup>3+</sup> sites, producing a considerable amount of fully ionized oxygen vacancies as follows:

$$2 \text{MgO} \xrightarrow{\text{Cr}_2\text{O}_3} 2 \text{Mg}'_{\text{Cr}} + 2 \text{O}_0^{\times} + V_0^{\cdot}$$
(2)

Under an atmospheric environment, it is reasonable to consider that gaseous oxygen preferentially reacts with these



Fig. 5. Temperature dependence of (a) resistance in the exhaust gases with different  $\lambda$  values and (b) response times of  $ZnCr_{1.95}Mg_{0.05}O_{4-\delta}$  and  $ZnCr_2O_4$  specimens:  $(\blacksquare, \square) ZnCr_{1.95}Mg_{0.05}O_{4-\delta}$ ;  $(\triangle, \blacktriangle) ZnCr_2O_4$ .

oxygen vacancies to produce neutral oxygen sites and mobile holes. Thus, we have

$$V_{\rm O}^{``} + \frac{1}{2} {\rm O}_2(g) \to {\rm O}_{\rm O}^{\times} + 2{\rm h}^{``}$$
 (3)

This reaction is essentially the same as the following reaction:

$$Zn^{2+}Cr_{1.95}^{3+}Mg_{0.05}^{2+}O_{3.975}^{2-} + 0.0125O_2(g) \rightarrow Zn^{2+}Cr_{1.90}^{3+}Cr_{0.05}^{4+}Mg_{0.05}^{2+}O_4^{2-}$$
(4)

The Cr<sup>4+</sup> ions can act as positive hole sites and contribute to p-type conduction. Thus, the decrease in resistance in  $\lambda = 1.13$  can be explained by the increased concentration of positive holes. In the case of  $\lambda = 0.89$ , on the other hand, the decrease in the resistance cannot be fully attributed to the same mechanism, because the magnitude of the decrease was larger than in  $\lambda = 1.13$ . Another reason for the significant decrease may be the effect of oxide ion conductivity. Oxygen partial pressure in the exhaust gas of  $\lambda = 0.89$  is considered to be on the level of  $10^{-14}$  Pa. In such a low oxygen partial pressure, the reverse reaction of Eq. (3) likely occurs, leaving a considerable amount of oxygen vacancies. Under such a condition, the oxide ion conductivity is no longer negligible. As a result, with a decrease in oxygen partial pressure, the conductivity exhibits less decrease than that expected for a *p*-type semiconductor. The changes in resistance shown in Fig. 5(a) were in good agreement with this prediction. As discussed before, the prolonged "red" response time can be attributed to both the considerable oxide ion conduction in the rich-burn region and the poor catalytic activity of the Pt wire electrodes used in this study.

When 10 mol% excess ZnO was added to the ZnCr<sub>2</sub>O<sub>4</sub> specimen, almost the same behavior of variations in sensing properties was observed, as shown in Fig. 6. Namely, the resistance decreased more significantly in  $\lambda = 0.89$  than with the case of  $\lambda = 1.13$ , and the "red" response time was prolonged, while the "ox" response time was not significantly changed. These results suggest a possibility that the excess ZnO is partially soluble in the ZnCr<sub>2</sub>O<sub>4</sub> lattice by the following equation, although the X-ray diffraction measurement indicated the existence of two phases, ZnCr<sub>2</sub>O<sub>4</sub> and ZnO, in the specimen:

$$3\text{ZnO} \xrightarrow{\text{ZnC}_{12}\text{O}_4} \text{Zn}_{\text{Zn}}^{\times} + 2\text{Zn}_{\text{Cr}}' + 3\text{O}_0^{\times} + V_0^{\circ}$$
(5)

In contrast to the above, when the 10 mol% excess  $Cr_2O_3$  was added to the  $ZnCr_2O_4$  specimen, the sensitivity was significantly improved without any significant change in the response times, as shown in Fig. 7. The resistance in  $\lambda = 1.13$ 



Fig. 6. Temperature dependence of (a) resistance in the exhaust gases with different  $\lambda$  values and (b) response times of ZnCr<sub>2</sub>O<sub>4</sub> + 10 mol% excess ZnO and ZnCr<sub>2</sub>O<sub>4</sub> specimens: ( $\Box$ ,  $\blacksquare$ ) ZnCr<sub>2</sub>O<sub>4</sub> + 10 mol% excess ZnO; ( $\triangle$ ,  $\blacktriangle$ ) ZnCr<sub>2</sub>O<sub>4</sub>.



**Fig. 7.** Temperature dependence of (a) resistance in the exhaust gases with different  $\lambda$  values and (b) response times of  $ZnCr_2O_4 + 10 \text{ mol}\%$  excess  $Cr_2O_4$  and  $ZnCr_2O_4$  specimens: ( $\Box$ ,  $\blacksquare$ )  $ZnCr_2O_4 + 10 \text{ mol}\%$  excess  $Cr_2O_3$ ; ( $\triangle$ ,  $\blacktriangle$ )  $ZnCr_2O_4$ .

decreased over the whole operating temperature range by the addition of excess Cr<sub>2</sub>O<sub>3</sub>. Especially, the decrease in resistance was more pronounced at temperatures higher than 700°C (phenomenon I). On the other hand, the resistance in  $\lambda = 0.89$  remained unchanged at temperatures higher than 700°C (phenomenon II) in spite of the addition, whereas it decreased at temperatures lower than 600°C. Owing to these two phenomena, the addition of 10 mol% excess Cr<sub>2</sub>O<sub>3</sub> resulted in an increase in the sensitivity at temperatures higher than 600°C and also in the enlargement of the gap between the resistance in  $\lambda = 0.89$  at 800°C and that in  $\lambda = 1.13$ at 400°C. The gap enlargement is favorable because the  $ZnCr_2O_4 + Cr_2O_3$  (1.0:0.1 molar ratio) specimen does not demand any strict compensation for the effect of operating temperature on the resistance in practical use. Thus, it was found that the  $ZnCr_2O_4 + Cr_2O_3$  specimen was the most suitable for the A/F stoichiometric oxygen sensor among the specimens studied.

The role of the excess  $Cr_2O_3$  is of interest. From the results shown in Fig. 7(a), the following defect reaction is plausible, although two phases,  $ZnCr_2O_4$  and  $Cr_2O_3$ , were identified in the specimen:

$$x \operatorname{Cr}_2 \operatorname{O}_3 \xrightarrow{Zn \operatorname{Cr}_2 \operatorname{O}_4} x V_{Zn}'' + 2x \operatorname{Cr}_{\operatorname{Cr}}^{\times} + 3x \operatorname{O}_0^{\times} + 3x V_0''$$
(6)

This is essentially the same as the following reaction:

$$x \operatorname{Cr}_{2}^{3+} \operatorname{O}_{3}^{2-} + \operatorname{Zn}^{2+} \operatorname{Cr}_{2}^{3+} \operatorname{O}_{4}^{2-} + \frac{x}{2} \operatorname{O}_{2}(g)$$
  
$$\rightarrow \operatorname{Zn}^{2+} \operatorname{Cr}_{2}^{3+} \operatorname{Cr}_{4x}^{4+} \operatorname{O}_{4(1+x)}^{2-}$$
(7)

Therefore, the decrease in resistance by the addition of excess  $Cr_2O_3$  was attributed to increased positive holes (see Eq. (3)).

However, the increase in the sensitivity was not explained only by this mechanism. In the formula representing the dependence of the electrical conductivity on oxygen partial pressure for the semiconductive oxides,  $\sigma \propto P_{O_2}^{1/m}$ , the value of m can vary from 4 to 6, depending on whether the conduction process is extrinsic or intrinsic, that is, depending on the amount of impurities in the lattice. It is easy to imagine that the sensitivity at the stoichiometric point decreased with an increase in m value (see Fig. 3). A more important factor in the case of a semiconducting A/F stoichiometric oxygen sensor is the oxygen partial pressure at which the conduction process is changed from extrinsic to intrinsic. If the transition point is lower than the oxygen partial pressure of 10<sup>3</sup> Pa or less, the sensitivity becomes small. Therefore, the reason for phenomenon I may be attributed to the extension of the extrinsic conduction process to a higher oxygen partial pressure range due to formation of  $Zn^{2+}$  vacancies by the addition of excess  $Cr_2O_3$ . On the other hand, the reason for phenomenon II is not clear at present.

## (4) Effect of Catalytic Activity of the Sensor Materials on Sensing Properties

Figure 8 shows the relation between conversion of CH4 and the reaction temperature when a mixture of methane and air was oxidized over the sensor materials in granular form. The broken line indicates the result of the blank reaction without the materials. It is noted that the catalytic activities of *n*-type specimens,  $ZnFe_2O_4$  and  $MgFe_2O_4$ , were negligibly small, while all the *p*-type specimens showed relatively high activities. To find any relationship between the sensing properties and the catalytic activities, some fundamental data are summarized in Table I. The  $T_{80\%}$  value is the temperature at which the conversion of CH<sub>4</sub> attains 80%. Broadly, it is apparent in Table I that the larger the surface area, the higher the catalytic activity. But, from the comparison of characteristics between the  $ZnCr_2O_4$  and  $ZnCr_2O_4 + Cr_2O_3$  specimens, it is suggested that the sensitivity is not affected by the catalytic activity of the specimen, as long as the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is used to prepare the exhaust gas. In a practical application to automobile engines, however, the ZnCr<sub>2</sub>O<sub>4</sub> family offers the potential that excellent performance can be realized without a Pt catalyst, owing to its high catalytic activity.

In contrast, there is a tendency for both the "red" and the "ox" response times to become shorter with an increase in catalytic activity. But, this fact does not mean directly that the catalytic activity of the Pt/Al<sub>2</sub>O<sub>3</sub> used to prepare the exhaust gas is not high enough and that a certain amount of residual fuel exists even in the lean-burn region and also a certain amount of free oxygen in the rich-burn region. Instead, this fact suggests that the catalytic activity of the specimen is closely related to the reactivity of the chemisorbed oxygens at the oxide ion vacancy sites and/or that of lattice oxygens, because the p-type semiconductive specimens likely involve a certain amount of oxide ion vacancies and then chemisorbed oxygens at these sites in an atmospheric environment. And it was reported in measurement of temperature-programmed desorption spectra of oxygen<sup>13,14</sup> that such chemisorbed oxygens tend to desorb at temperatures up to 600°C in flowing helium. Thus, it is supposed that the rate of



Fig. 8. Temperature dependence of CH<sub>4</sub> combustion over several specimens: ( $\bigcirc$ ) ZnFe<sub>2</sub>O<sub>4</sub> prepared from metal oxides; ( $\bigcirc$ ) MgFe<sub>2</sub>O<sub>4</sub> prepared from metal oxides; ( $\triangle$ ) MgCr<sub>2</sub>O<sub>4</sub> prepared from metal oxides; ( $\triangle$ ) MgCr<sub>2</sub>O<sub>4</sub> prepared from metal nitrates; ( $\square$ ) ZnCr<sub>2</sub>O<sub>4</sub> prepared from metal nitrates.

charge transfer between gaseous oxygen and chemisorbed oxygen at the surface or, in turn, the mobility of oxide ions in the bulk, increases as the catalytic activity of the specimen increases. As a result, a shorter response time can be realized when the specimen with a higher catalytic activity is employed as a sensor material. On the whole, the catalytic activity of the specimen is also one of the factors in determining the response times, but the behavior observed in this study cannot be completely explained only in terms of the catalytic activity, as described before.

#### **IV.** Conclusions

From comparison of the sensing properties of several spineltype oxides, an interesting feature could be observed that *n*-type specimens tended to exhibit the shorter "red" response time than the "ox" response time, while p-types exhibited a reverse tendency. These phenomena could be explained fairly well by combination of the effect of the oxide ion conductivity, which arose from foreign impurities, and the reduced activity of the Pt wire electrodes. This assumption was confirmed by the longer response times of the  $ZnCr_{1.95}Mg_{0.05}O_{4-\delta}$  specimen, especially in "red," than those of the  $ZnCr_2O_4$  specimen. Influence of the oxide ion conductivity on the response times may be eliminated by employing highly active electrodes instead of Pt wire and/or by a supporting Pt catalyst on the sensor specimen. Even when highly active electrodes are employed, however, the influence of oxide ion conductivity on the sensitivity at the stoichiometric point still remains as a serious problem.

On the whole, activities of the sensor specimens for catalytic combustion of methane correlated with the response times. This means that the rate of charge transfer between gaseous oxygen and chemisorbed oxygen at the surface, or in turn the mobility of oxide ions in the bulk, increases as the catalytic activity of the specimen increases. Thus, it was assumed that the catalytic activity was one of the most important factors in determining the response times. On the other hand, there was no definite correlation between the catalytic activity and the sensitivity. In a practical application to automobile engines, however, it is supposed that the catalytic activity of the sensor materials themselves is also an important factor in determining the sensitivity, because their higher catalytic activity makes it possible to achieve thermodynamic equilibration of the exhaust gases without any Pt catalyst.

The most promising sensing properties could be realized with the  $ZnCr_2O_4 + Cr_2O_3$  (1.0:0.1 molar ratio) specimen. The role of the excess  $Cr_2O_3$  was assumed to extend the extrinsic conduction process to a higher oxygen partial pressure range especially at higher operating temperatures by producing the  $Zn^{2+}$  vacancies in the lattice. Thus, it is concluded that the point defect structure is the most important factor in determining the sensitivity as well as the response times.

#### References

<sup>1</sup>T.Y. Tien, H. L. Stadler, E. F. Gibbons, and P. J. Zacmanidis, "TiO<sub>2</sub> as an Air-to-Fuel Ratio Sensor for Automobile Exhausts," *Am. Ceram. Soc. Bull.*, **54** [3] 280-82 (1975).

Bull., 54 [3] 280-82 (1975). <sup>2</sup>Y. Shimizu, Y. Fukuyama, H. Arai, and T. Seiyama, "Oxygen Sensor Using Perovskite-Type Oxides—Measurements of Electrical Characteristics," ACS Symp. Ser., 309, 84-100 (1986).

 tics, "ACS Symp. Ser., 309, 84-100 (1986).
 <sup>3</sup>E. M. Logothetis and W. J. Kaiser, "TiO<sub>2</sub> Film Oxygen Sensors Made by Chemical Vapour Deposition from Organometallics," Sens. Actuators, 4, 333-40 (1983).
 <sup>4</sup>A. L. Micheli, "Fabrication and Performance Evaluation of a Titania Au-

<sup>4</sup>A. L. Micheli, "Fabrication and Performance Evaluation of a Titania Automotive Exhaust Gas Sensor," *Am. Ceram. Soc. Bull.*, **63** [5] 694–98 (1984).
<sup>5</sup>K. Ihokura, K. Tanaka, and N. Murakami, "Use of Tin Oxide Sensor to

Control a Domestic Gas Heater," Sens. Actuators, 4, 607-12 (1983). <sup>6</sup>H. Kondo, H. Takahashi, T. Takeuchi, and I. Igarashi, "Nb<sub>2</sub>O<sub>5</sub> Thin-

<sup>o</sup>H. Kondo, H. Takahashi, T. Takeuchi, and I. Igarashi, "Nb<sub>2</sub>O<sub>5</sub> Thin-Film Oxygen Sensor"; pp. 185–90 in Proceedings of Third Sensor Symposium, IEEE of Japan, Tsukuba, Japan, 1983.

<sup>7</sup>Y. Yamamura, Y. Ninomiya, and S. Sekido, "An Element Sensitive to Stoichiometric Composition of Exhaust Gas"; pp. 187–92 in Proceedings of International Meeting on Chemical Sensors, Kodansha Ltd., Tokyo, Japan, 1983.

<sup>8</sup>Y. Shimizu, Y. Fukuyama, T. Narikiyo, H. Arai, and T. Seiyama,

"Perovskite-Type Oxides Having Semiconductivity as Oxygen Sensors,"

Chem. Lett., 377-80 (1985).
 <sup>9</sup>Y. Shimizu, Y. Fukuyama, C. Yu, and H. Arai, "A Lean-Burn Oxygen Sensor Consisting of a Dual-Disc Semiconductor," Sens. Actuators, 14, 319-

<sup>10</sup>F. A. Kröger and H. J. Vink, "Relationship between the Concentrations of Imperfections in Crystalline Solids," *Solid State Phys.*, 3, 307 (1956).
 <sup>11</sup>H. Arai, K. Eguchi, and T. Inoue, "The Effect of Electrode on the Re-

sponse of Oxygen Sensor with CeO2-Based Solid Electrolytes"; pp. 689-92

in Proceedings of Transducers '87, IEEE of Japan, Tokyo, Japan, June, 1987. <sup>12</sup>Y. Teraoka, H. M. Zhang, K. Okamoto, and N. Yamazoe, "Mixed Ionic-Conductivity of La<sub>1-x</sub>Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3- $\delta$ </sub> Perovskite-Type Oxides," *Mater Res. Bull.*, **23**, 51–58 (1988). <sup>13</sup>N. Yamazoe, Y. Teraoka, and T. Seiyama, "TPD and XPS Study on Ther-

mal Behavior of Adsorbed Oxygen in La1-xSrxCoO3," Chem. Lett., 1767-70

(1981).
 <sup>14</sup>C. Yu, Y. Shimizu, and H. Arai, "Investigation on a Lean-Burn Oxygen Sensor Using Perovskite-Type Oxides," *Chem. Lett.*, 563–66 (1986).