ELSEVIER

Catalysis Today 26 (1995) 79–86

CATALYSIS TODAY

Studies on catalytic and conductive properties of $LaNiO_3$ for oxidation of C_2H_5OH, CH_3CHO, and CH_4

Tzong-Rong Ling, Zu-Bon Chen, Min-Dar Lee *

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106, Taiwan, ROC

Abstract

The oxidation of C_2H_5OH, CH_3CHO, and CH_4 on perovskite-type mixed metal oxide $LaNiO_3$ was conducted in flowing air. The conductivity change of the oxide during oxidation was also measured to ascertain the adaptability of using it as a sensing material. It was demonstrated that the oxidation reaction was accompanied by a loss of oxygen from the lattice and hence a change in conductance of the oxide. The degree of the conductance change depended on the nature and concentration of the gases as well as the oxidizing conditions. These phenomena were more obvious for alcohol and aldehyde than for methane. The temperature was an important factor affecting the sensitivity. The presence of water vapor (the products of hydrocarbon combustion) depressed the oxidation rate, probably owing to the formation of OH species on the oxide and its acting as an electron donor to reduce conductivity. The catalysts were characterized by TPR and TPD techniques. A comparison of oxidation rate and conductance as a function of reactant concentration is discussed.

1. Introduction

Organic vapor combustion and detection are important in environmental protection. Some of the perovskite-type oxides are known to be effective oxidation catalysts [1,2] and sensing materials [3–5]. $LaNiO_3$ (a *p*-type semiconductor [6]) has high electrical conductivity and exhibits oxidation–reduction characteristics [7]. It is known that Ni^{3+} ion is an active center for the hydrocarbon oxidation reaction. At a high enough temperature, the hydrocarbon molecules may interact with the active oxygen accompanied by dissociation and desorption from the surface. During the catalytic reaction, oxygen will be extracted from the lattice, resulting in an oxygen vacancy and consequently a change in the electrical property.

Conductivity measurement is a useful technique widely applied in many areas [8]. The SnO_2 based semiconductor has been used as the commercial gas sensor units for detecting organic vapors and toxic gases [9]. The oxide conductance is a function of gas concentration and temperature. On this metal oxide, the electron donated by the reducing gases (like hydrocarbons) interacts with the surface, and a change in conductivity strongly depends on the reaction behavior. The catalytic oxidation occurs on the oxide surface.

It is known that alcohols are easily oxidized [10] and are more sensitive to gas sensor [11] than other organic compounds, such as aldehydes and alkanes. In general, the oxidation activity of different organics will be more or less influenced by the oxide conductive property. On the basis of this, it is possible to distinguish the types of gas and estimate the sensitivity of gas sensor.

---

* Corresponding author.

0920-5861/95/$0.95
SSDI 0920-5861(95)00099-2

Although sensor materials have been used for a long time, the complexity in the interaction between gas and solid is still not very well understood. In this work, an attempt has been made to gain an insight into the catalytic properties and conductivity changes of $LaNiO_3$ in the oxidation of ethanol, acetaldehyde, and methane.

2. Experimental

2.1. Preparations of catalyst and thick film sensor

$LaNiO_3$ powders were prepared by the sol–gel method. An appropriate amount of ethylene glycol (EG) was added to a mixed metal (atomic ratio, lanthanum:nickel = 1:1) nitrate solution. The sol–gel thus obtained was dried and quickly calcined at a constant temperature of 800°C for 10 min. The perovskite phase was identified by the XRD method. The techniques of thick film sensor preparation were similar to those described in the literature [12]. The synthesized sol–gel was painted on an alumina platelet (5 mm × 10 mm × 0.63 mm). The sample was heated at 800°C for 10 min, as mention above. An electrical contact was made by printing Ag/Pt mixed paste on both sides of the oxide film. The resistance was fixed around 1–5 MΩ at room temperature.

2.2. Characterization of the catalyst

The temperature-programmed reduction (TPR) experiment was conducted in a flow system with 0.1 g of catalyst according to the method described in a previous paper [13]. The TPR profiles were obtained at a heating rate of 10°C/min from room temperature to 850°C (Eurotherm) in a 10% hydrogen/argon gas mixture. During the experiment the water produced was removed by a cooling trap (−88°C). The concentration of effluent was recorded as a function of temperature with a thermal conductivity detector (TCD).

Temperature-programmed desorption (TPD) was performed by the method described in our previous paper [14]. A 0.5-g portion of the catalyst was used for each run. After saturation with ethanol or aldehyde vapor or methane gas at room temperature, the desorption was started. The carrier gas used was 40 cm^3/min nitrogen. The concentration profile was obtained with a flame ion detector (FID).

2.3. Catalyst test and conductivity measurement

The catalytic reaction was carried out in a conventional fixed-bed, quartz glass tube flow reactor equipped with a jacket furnace to control the temperature. The feed mixture was composed of O_2 (20 vol.-%), organic vapor (1–4 vol.-%) and a balance of nitrogen. For adjusting the vapor concentration, two streams of N_2 was employed; one was introduced into a bubble saturator to carry out the organic vapor, and the other was used to balance the overall concentration. The downstream flow from the reactor was analyzed by a gas chromatograph equipped with a Porapak Q column (2 m). The space velocity of the reaction mixture was set at 60000 $cm^3/g \cdot h$.

The thick film conductance measurement was performed in a flow type glass chamber. The gaseous flow system was the same as that described above. The sample was adhered to a ceramic heater (50 W) connected to a power supply. Both sides of the sample were joined together with a multimeter (HP34401A) and the data obtained were converted through an interface for computer analysis.

3. Results

3.1. Characterization of $LaNiO_3$

The redox property of the oxide plays an important role in the oxidation of organic compounds and TPR is usually an effective method to obtain this information. Fig. 1 shows the TPR results of $LaNiO_3$. Two peaks of hydrogen consumption with maximum temperatures at 337 and 492°C, respectively, were observed. The reduction of

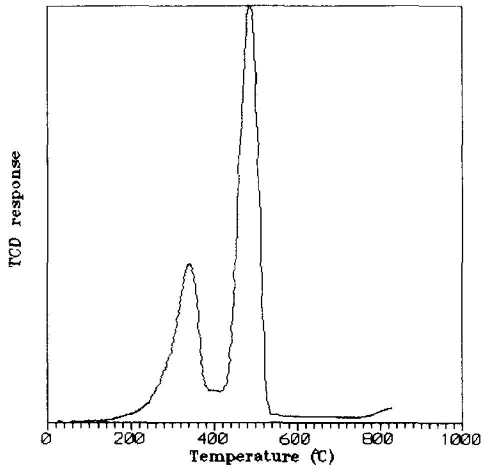

Fig. 1. Temperature-programmed reduction of $LaNiO_3$ at a heating rate of 10°C/min, carrier gas flow-rate is 40 cm^3/min, ($Ar:H_2 = 9:1$), sample weight: 0.1 g.

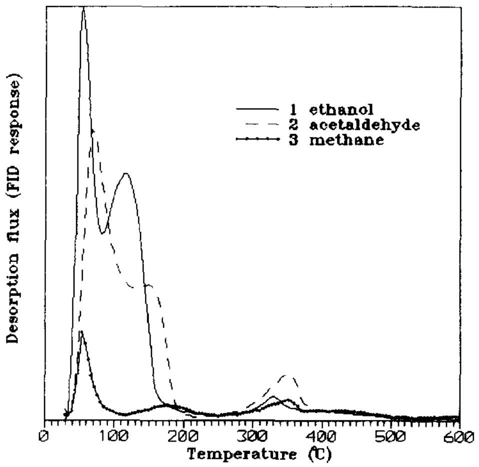

Fig. 2. Temperature-programmed desorption of $LaNiO_3$ after exposure to ethanol, acetaldehyde and methane gas, respectively. Heating rate 10°C/min, carrier gas flow-rate: 40 cm^3/min N_2.

$LaNiO_3$ takes place in two steps. One is $Ni^{3+} \rightarrow Ni^{2+}$, occurring between 150 and 400°C, and the other is $Ni^{2+} \rightarrow Ni^{0+}$, occurring between 400 and 560°C. The ratio of peak areas is around 1:2. This result is similar to that of Tejuca and coworkers [2] and the reactions can be formulated by the following equations:

$$2LaNiO_3 + H_2 \rightarrow La_2NiO_4 + NiO + H_2O \quad (1)$$

$$La_2NiO_4 + NiO + 2H_2 \rightarrow La_2O_3 + 2Ni + 2H_2O \quad (2)$$

These two steps are reversible under some oxidizing condition. In order to compare the adsorbing or desorbing abilities of the organic species on the $LaNiO_3$ surface, TPD studies were performed. As shown in Fig. 2, the strength of adsorption decreased in the order: ethanol $\geq$ acetaldehyde $\gg$ methane. It was also found that some small desorption peaks appear between 300 and 400°C which may be due to the products of oxidation or decomposition of adsorbates. However, the concentrations of desorption products were very low. The results are in agreement with those observed over SnO_2 [15].

3.2. Catalytic behavior in the oxidation

$LaNiO_3$ exhibits different catalytic activities in the oxidation of various organic substrates. The oxidation rate of the three reactants under the conditions studied decreased in the order of ethanol $\geq$ acetaldehyde $\gg$ methane. Nevertheless, at temperatures higher than 300°C, the conversion of acetaldehyde was found to rise above that of ethanol (Fig. 3). Generally speaking, the interaction of organic vapor with oxides is an important step in the complete oxidation. The adsorption is usually the rate determining step in the reaction processes at a sufficiently high temperature [16]. The TPD profile in Fig. 2 shows that the adsorption behaviors towards ethanol and acetaldehyde are almost the same, indicating the similarity of

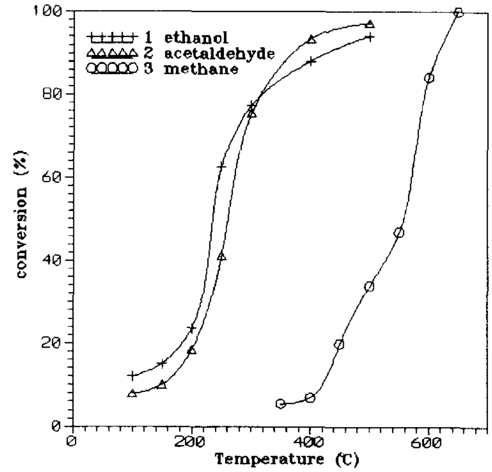

Fig. 3. Comparison of the oxidation of ethanol, acetaldehyde and methane (1 vol.-%) on $LaNiO_3$ in 1 atm pressure, gas flow-rate: 100 cm^3/min (O_2: 20 vol.-%, N_2: 79 vol.-%), catalyst weight 0.1 g.

the adsorption controlling step. The more the reactant is adsorbed, the higher is the conversion observed. Nevertheless, the oxidation rate still depends on the reaction step involving the mechanism, such as the rupture of a double bond, C–H or C–C bond with further rapid oxidation and fragmentation. The temperature also effects the result of decomposition. Water and CO_2 are the final products of complete oxidation. The amounts of both products were found to increase rapidly with elevating temperature as shown in the ethanol oxidation (Fig. 4). At temperature below 150°C, no obvious oxidation product was detected. In contrast, the dissociation starts and partial oxidation occurs at temperature higher than 150°C. The product distribution indicated that acetaldehyde attained a maximum between 200–300°C, whereas detectable ethylene was obtained between 400–500°C. It is suggested that at lower temperatures the dehydrogenation to form aldehyde proceeds more easily than the dehydration to form ethylene. This is unlike the case of the oxidation of acetaldehyde or methane, for which only water and CO_2 were found in the products under the oxidizing atmosphere (about 20 vol.-% O_2). It seems that the products of oxidation will also influence the catalytic property of the oxide.

3.3. *Conductivity change in the oxidation*

Fig. 5 demonstrates the change in resistance of $LaNiO_3$ thick film on exposure to ethanol vapor under a stream of air. The concentration of ethanol was increased successively by 1% at intervals of 10 min. The resistance was found to increase with increasing vapor concentration. The response is slow at 150°C but becomes faster at temperatures higher than 250°C, indicating that the process has to do with chemisorption. The ethanol adsorbed on the surface serves as an electron donor and slowly alters the conductance. With increasing temperature (higher than 150°C), the adsorbate begins to decompose and some oxygen is taken away from the surface (Fig. 4). It was reported that three states of surface oxygen, $O_{2\,ad}^-$(150°C<), O^- (150–350°C) and O^{2-} (>350°C), exist at different temperatures [17]. So it is reasonable to believe that temperature may be a dominant factor controlling the reaction step. The comparison of the resistance vs. time response for ethanol, acetaldehyde and methane (Fig. 6) indicates the occurrence of resistance changes on the $LaNiO_3$. Ethanol and acetaldehyde exhibit a stronger response than methane. Moreover, the interaction of ethanol with oxide proceeds much faster than that of acetaldehyde. In contrast, as the temperature rises to 350°C, the acetaldehyde seemed to attain a larger resistance change than ethanol.

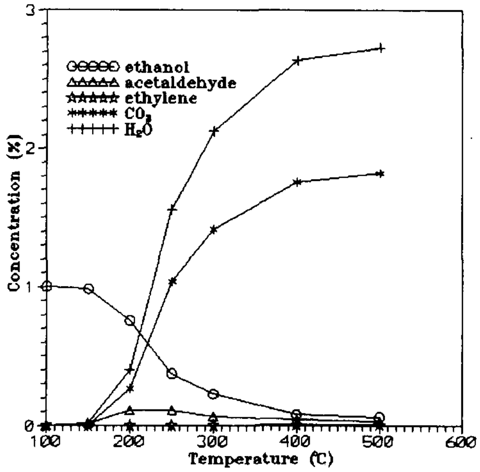

Fig. 4. Product distribution of ethanol oxidation on $LaNiO_3$. Gas flow-rate 100 cm^3/min. O_2: 20 vol.-%, N_2: 79 vol.-%, catalyst weight: 0.1 g WSHV = 60000 $cm^3/g \cdot h$.

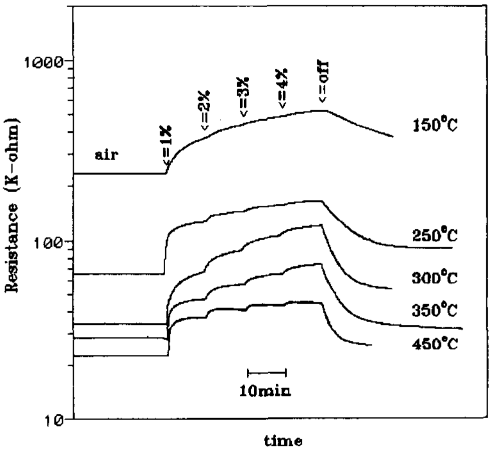

Fig. 5. Time dependence of the resistance of a $LaNiO_3$ thick film by step change of ethanol concentration (1, 2, 3 and 4 vol.-%) in flowing air 500 cm^3/min.

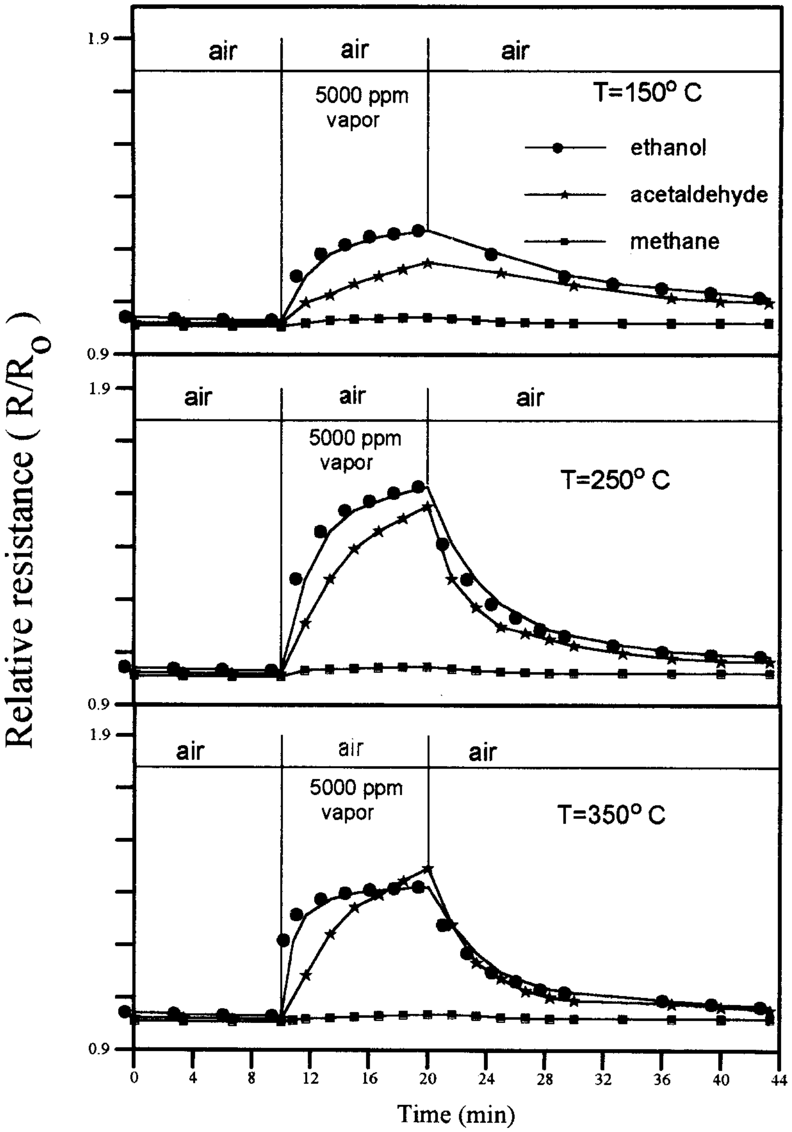

Fig. 6. Time dependence of the relative resistance of a $LaNiO_3$ thick film which was exposed to 5000 ppm of ethanol, acetaldehyde and methane for 10 min at 150°C, 250°C and 350°C in flowing air 500 cm^3/min, R: resistance, R_o: original resistance.

3.4. Influence of water vapor on catalytic and conductive properties

Water vapor is one of the major products of hydrocarbon combustion. Due to its large quantity and high polarity, the water vapor is easily adsorbed on the surface, competes with reactant for the active site, and inhibits the oxidation of the reactant. As can be seen from Fig. 7, the conversion of ethanol decreased with increasing H_2O concentration. Water vapor also acts as an electron donor, which may interact with holes and active oxygen O^- ion to produce OH species and then reduce the activity and conductance of oxides [15].

$$H_2O + O_s^- + (h^\cdot) = 2OH_s \qquad (3)$$

Fig. 8 shows that the resistance is slowly changed with H_2O concentration. The reaction is very slow as an adsorption process.

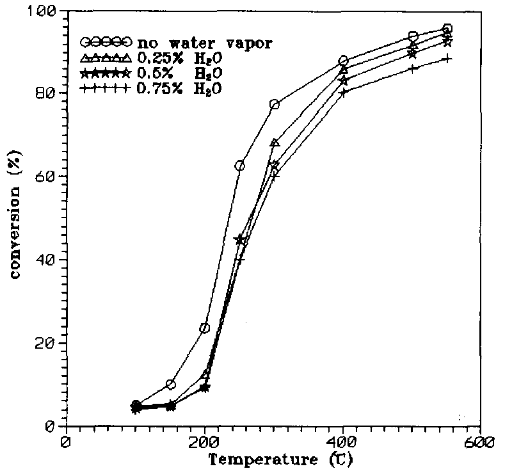

Fig. 7. Effect of the various water vapor concentration in oxidation of ethanol over $LaNiO_3$. Gas flow-rate: 100 cm^3/min (ethanol: 1 vol.-%, O_2: 20 vol.-%, N_2: balance); catalyst weight: 0.1 g WHSV = 60000 cm^3/g·h.

3.5. Correlation between reaction rate and conductance

The rate of catalytic oxidation is often described by a power law kinetic equation $r = k[O_2]^m[Org]^n$. The oxidation of ethanol on $LaNiO_3$ was observed under the reaction conditions of one atmospheric pressure, oxygen concentrations 5–20 vol.-% and ethanol 1–4 vol.-%, and at 350°C. The m and n values were experimentally found to be 0.12 and 0.98, respectively. Fig. 9 shows the comparison of the rate and relative resistance. It seems that r is proportional to $[ethanol]^1$ and $(R-R_o)/R_o$ to $[ethanol]^{0.67}$. The effect of water was also observed from Fig. 10; the rate of ethanol oxidation was depressed and the resistance of oxide increased with water vapor concentration. However, an increase in temperature decreased the adsorption of water vapor on the oxide.

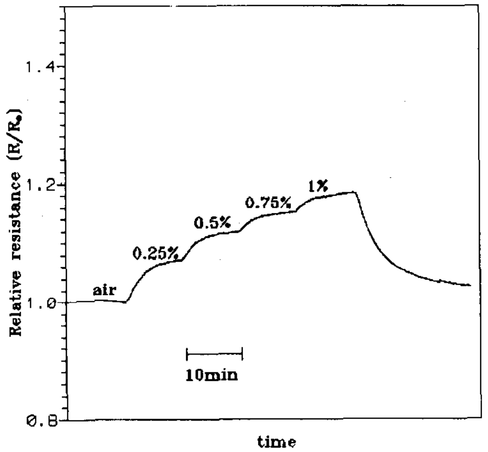

Fig. 8. Time dependence of the relative resistance of a $LaNiO_3$ thick film at 350°C and different concentrations of water vapor (0.25, 0.5, 0.75 and 1 vol.-%) in flowing air 500 cm^3/min.

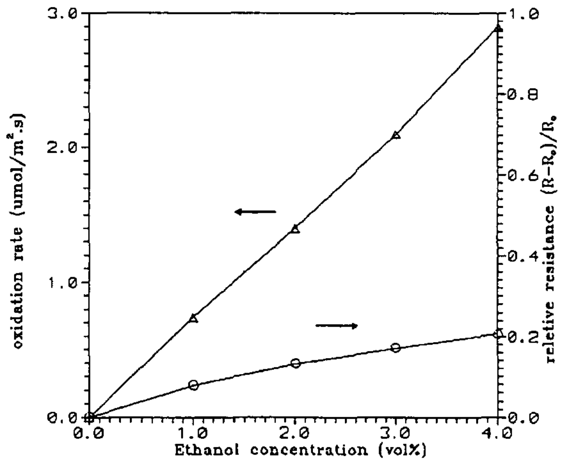

Fig. 9. Comparison between the oxidation rate of ethanol and the resistance change of a $LaNiO_3$ thick film at 350°C, total gas flow: 100 cm^3/min (O_2 = 20 vol.-%, N_2: balance), R: resistance, R_o: original resistance.

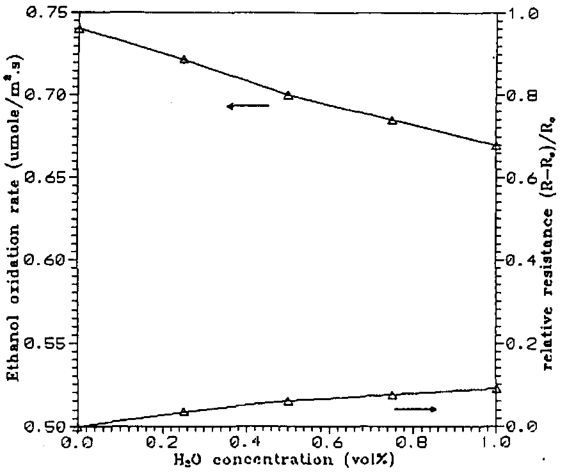

Fig. 10. Comparison of water effect between oxidation rate of ethanol (1 vol.-%) and relative resistance change $(R-R_o)/R_o$ at 350°C, gas flow-rate: 100 cm^3/min (O_2 = 20 vol.-%, N_2 = balance).

4. Discussion

$LaNiO_3$, in which the Ni^{3+} ions are d^7, has metal-like conductivity [7]. Generally speaking, semiconductors may be classified according to their electron donor or acceptor levels as follows [17]:

	Oxidizing condition, e.g. oxygen added	Reducing condition, e.g. oxygen reduced
n-Type	Resistance rise	Resistance fall
p-Type	Resistance fall	Resistance rise

Bockris and Otagawa [6] and Yannopoulos [12] reported that the perovskite $LaNiO_3$ belongs to a *p*-type semiconductor. This is consistent with our observation. Losing of oxygen ions decreases its *p*-type conductivity. The charge compensation is generated by ion vacancies in the oxide. The conductivity become lower when it is reduced to $LaNiO_{3-\delta}$, in which a 2-δ fraction of the Ni ions is changed into the 2+ state [10]. The extent of oxygen deficiency is reversible. According to this property, it is suitable for sensing oxygen as well as reducing gases including organic vapor. Catalytic oxidation on perovskite-type oxides proceed through the redox scheme [10,18]. It is reasonable to assume that oxidation of organics in this case occurs on the surface of sensing oxide thus

$$\mathrm{Org} + O_o^x + (2h^{\cdot}) \rightarrow \mathrm{Org{-}O} + V_o^{\cdot\cdot} \quad (5)$$

$$V_o^{\cdot\cdot} + 1/2O_2 \rightarrow O_o^x + 2h^{\cdot} \quad (6)$$

where O_o^x is lattice oxygen without excess charge, $V_o^{\cdot\cdot}$ is oxygen vacancy with two positive charge and h is electron holes with positive charge. If both the organics and oxygen concentration are constant, the rates of these two reactions depend solely on the activity of organics, which is also directly related to δ in $LaNiO_{3-\delta}$. For various organic compounds, the δ values attained at steady state would be different. From the resistance observation, the values of δ of alcohol and aldehyde are larger than that of methane. The rates of both reactions are temperature dependent. The overall reaction was expressed as

$$\mathrm{Org} + 1/2O_2 \rightarrow \mathrm{Org{-}O} \rightarrow \mathrm{decompose} \quad (7)$$

From the results of the oxidation reaction, alcohol and aldehyde show a higher combustion rate than that of methane. It may imply that they have a faster reduction rate (Eq. 5) than that of methane.

5. Conclusions

In the catalytic oxidation over $LaNiO_3$, ethanol vapor proceeded much easier than that of acetaldehyde or methane and showed a stronger response in the conductance change. At a high oxidation rate, ethanol strongly interacted with the oxide surface and extracted a large amount of oxygen.

The production of water vapor was unavoidable in the oxidation procedures. Water vapor acted as an electron donor and inhibitor. It competed for the active sites with the reactants during oxidation.

The activity of oxidation of organics on $LaNiO_3$ was closely related to the conductive property of the solid. Both of them depended on the kinds and partial pressure of organics, adsorption properties, and temperature. It was proposed that the catalytic oxidation and chemisorption of organics involved the charge transfer and therefore led to a decrease in hole concentration and to an increase in resistance on the oxide. Although a conductivity mechanism is not proposed at present, the conductivity change still provides some information which is worthy of further investigation.

Acknowledgements

Financial support of this work by the National Science Council (Grant No. NSC82-0402-E002-373) is gratefully acknowledged.

References

[1] P.J. Gellings and H.J.M. Bouwmeester, Catal. Today, 12 (1992) 1.
[2] J.L.G. Fierro, J.M.D. Tascon and L.G. Tejuca, J. Catal., 93 (1985) 83.
[3] H. Obayashi, Y. Skura and T. Gejo, J. Solid State Chem., 17 (1976) 299.
[4] T. Arakawa, H. Kurachi and T. Shiokawa, J. Mater. Sci., 20 (1985) 1207.

[5] Y. Teraoka, H.M. Zhang, K. Okamoto and N. Yamazoe, Mater. Res. Bull., 23 (1988) 51.

[6] John O'M. Bockris and T. Otagawa, J. Electrochem. Soc., 131 (1984) 290.

[7] H. Obayashi and T. Kudo, Jpn. J. Appl. Phys., 14 (1975) 330.

[8] J.M. Herrmann and J. Disdier, Catal. Today, 20 (1994) 135.

[9] D. Kohl, Sensor and Actuators, 18 (1989) 71.

[10] T. Kudo, Catal. Today, 8 (1990) 263.

[11] C.-C. Chang, Ph.D dissertation, Department of Chemical Engineering, National Cheng Kung University, 1993, p. 15.

[12] L.N. Yannopoulos, Sensor and Actuators, 12 (1987) 263.

[13] M.-D. Lee, W.-S. Chen and H.-P. Chiang, Appl. Catal. A: General, 101 (1993) 269.

[14] W.-S. Chen and M.-D. Lee, J. Chin. Inst. Chem. Eng., 123 (4) (1992) 233.

[15] T. Seiyama, Chemical Sensor Technology, Kodansha Ltd., Tokyo, 1991, Vol. 1, p. 30.

[16] J.R. Anderson and M. Boudart, Catalysis Science and Technology, Vol. 3, 1982, p. 117.

[17] P.T. Moseley, J.O.W. Norris and D.E. Williams, Techniques and Mechanism in Gas Sensing, Adam Hilger, 1990, p. 53.

[18] N.P. Maksimovich, Sensors and Actuators: B, 13–14 (1993) 600.