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CATALYTIC REDUCTION OF NO OVER PEROVSKITE-TYPE CATALYSTS

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Abstract – In the present work, we have investigated the reduction of NO by propane over perovskite-type oxides prepared by malic acid method. The catalysts were modified to enhance the activity by substitution of metal into A or B site of perovskite oxides. In addition, the reaction conditions, such as temperature, O_2 concentration, and space velocity have been varied to understand their effects on the catalytic performance. In the $LaCoO_3$ type catalyst, the partial substitution of Ba and Sr into A site enhanced the catalytic activity in the reduction of NO. For the $La_{0.6}Ba(Sr)_{0.4}Co_{1-x}Fe_xO_3$ (x=0-1.0) catalyst, the partial substitution of Fe into B site enhanced the conversion of NO, but excess amount of Fe decreased the conversion of NO. The surface area and catalytic activity of perovskite catalysts prepared by malic acid method showed higher values than those of solid reaction method. The conversion of NO increased with increasing O_2 concentration and contact time. The introduction of water into reactant feed decreased the catalytic activity but the deactivation was shown to be reversible over $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst.

Key words: *Reduction of NO, Perovskite-type Oxides, Malic Acid Method, Effect of Water, Substitution of Ba, Sr and Fe, TPR*

INTRODUCTION

There is a worldwide effort to discover improved solutions for the removal of NO_x emissions [Armor, 1995]. Nitrogen oxides, NO_x, are major air pollutants that cause photochemical smog formation and acid rain. The emission of various nitrogen oxides into our atmosphere occurs on a massive scale. Worldwide, over 30 million tons of NO_x are vented to the earth's atmosphere each year. The public is demanding greater control of the emissions of toxic NO_x into our atmosphere.

It is well known that the major source of NO_x emissions is fuel combustion in automobile engines. Currently, we demands for improved fuel economy and reduced exhaust emissions. Therefore, de-NO_x catalysts, or new aftertreatment systems for the removal of NO_x gases which function also in an oxidizing atmosphere, have to be developed. The reduction of NO_x with hydrocarbons present in the feedstream has drawn attention as a process for the catalytic reduction of NO in the exhaust gas of automobile engines [Iwamoto et al., 1986; Nam, 1995]. Among the catalysts which have been reported, Cu-ion exchanged ZSM-5 is potentially the most effective catalyst for the reduction of NO with hydrocarbons [Iwamoto et al., 1991]. Unfortunately this catalyst shows very poor thermal durability, losing much of the catalytic activity after aging under real exhaust gas conditions on diesel or lean-burn gasoline engines [Monroe et al., 1993]. In addition, Co-ZSM-5 does offer comparable activity with higher hydrocarbons, and it does appear to be much more hydrothermally stable[Armor et al., 1995].

Alumina-based catalysts for the NO_x removal in an excess of oxygen are examined [Iwamoto et al., 1991]. In the development of automotive catalysts, the thermal stability should be essential for a practical application to high-performance automobile engine systems. It was reported that the study of NO reduction with methane over La_2O_3 has been examined under an excess oxygen [Zhang et al., 1994]. The metal oxide catalyst shows high thermal stability but poor activity of NO_x reduction.

Perovskite oxides, which are structurally similar to the mineral of that name ($CaTiO_3$), have long been studied because of technologically important physical characteristics. In 1971, cobaltate perovskites were suggested as substitutes for noble metals in automotive exhaust catalysis [Libby, 1971]. More recently, Teraoka et al. have studied the simultaneous removal of NO and diesel soot over perovskite oxides [Teraoka et al., 1996].

In the present work we study the properties of perovskite-type oxides prepared by malic acid and solid reaction method. We also examine the catalytic activity for NO reduction with propane in the presence of oxygen and the effect of reaction conditions, such as residence time, reaction temperature, especially the effect of water introduced into the feed stream. The studies on the catalytic reduction of NO will be extended additional modified perovskite-type oxides for the simultaneous removal of diesel soot.

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EXPERIMENTAL

It is well known that the catalytic activity differs according to the preparation method. In this study, we prepared two type of perovskite oxides in order to compare the property of catalysts according to the preparation method. At first in the malic acid method, malic acid was added into mixed aqueous solution of metal nitrates in a desired proportion so as for the molar ratio of malic acid to the total metal cations to be unity. The mixed aqueous solution was controlled at pH 4.0 by addition of ammonia water and then evaporated to dryness with stirring, followed by drying at 150 °C. The precursor was followed by grinding, calcination in air at 200 °C for half h and 350 °C for half h and 600 °C for 12 h. The calcination temperature was determined by the result of thermal analysis of precursors. In addition, the solid reaction method was followed by the literature [Teraoka et al., 1991]. Metal oxides were dried at 120 °C for 2 h and were mixed with $Co(NO_3)_2$ and $Fe(NO_3)_2$. The mixture was grinded in an agate mortar and then was calcined at 1,050 °C for 12 h.

The crystal structures of prepared oxides were examined by powder X-ray diffraction (XRD) with Cu Kα radiation (Rigaku Co. Model DMax) and the BET surface area was measured using BET measuring apparatus (Quanta Chrome Surface Area Analyzer). The sample was pretreated at 200 °C for 1 h before N_2 adsorption. The dead volume of sample port was measured with He gas. In addition, Temperature Programmed Reduction (TPR) was carried out using TCD type detector cell.

Reaction tests were carried out in a continuous flow fixed-bed reactor. The reaction gases, NO (5,000 ppm), C_3H_8 (2,000 ppm), O_2 (14.6 %), He balance, were used. The reactor was made of quartz tube, I.D. of 1.0 cm and 24 cm long, mounted in a tubular furnace. The reaction was carried out at the range of 250-400 °C, the exhaust gas stream temperature. The water was introduced to the system by flowing helium through a gas dispersion tube in a glass saturator containing the liquid. The reactant composition, NO (1,000 ppm), C_3H_8 (1,000 ppm), O_2 (4 %), was controlled by the Helium as a diluent gas. The outlet gas was analyzed by NO_x analyzer.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

After the drying process of the mixed solution of metal nitrates and malic acid at 150 °C, precursor is obtained by following the sol-gel state. If this precursor calcinated at 600 °C directly, a lot of impurities, such as $SrCO_3$, is able to be mixed in the catalyst. It is thought that impurities due to reaction of Sr ion with CO or CO_2 which is formed by decomposition of malic acid all at once. Thus we have to calcinate the precursor stepwise to prevent the formation of impurities. Fig. 1 shows the thermogravimetric analysis of powder precursor in air. TGA peak shows the decrease of weight three times at the range of 150-280 °C, 330-400 °C and 530-620 °C. They are caused by decomposition of NO_3^- and free malic acid, malic complex and $Sr(NO_3)_2$ or $Sr(CO_3)_2$ respectively. This result is confirmed by literature for the citric acid-aided process [Anderson et al., 1979]. The last drop plays an important role in the crystallization of perovskite oxide followed by removal of excess oxygen [Jonker et al., 1953]. Therefore it is important to give enough reaction time in the formation of perovskite structure and the precursor was calcinated at 200 °C for half h, at 350 °C for half h and at 600 °C for 12 h.

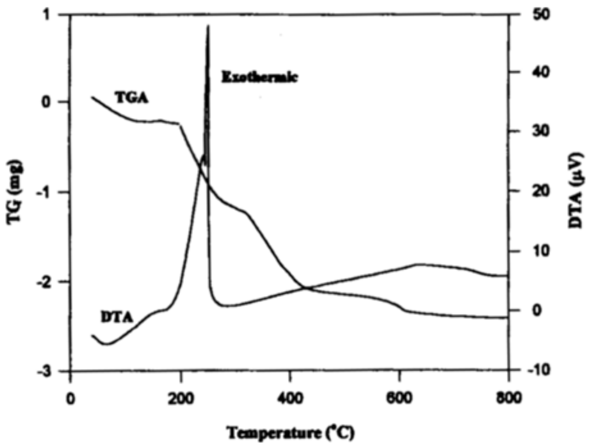

Fig. 1. Thermogravimetric analysis and differential thermal analysis curves for the precursor of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$: heating rate=10 K/min.

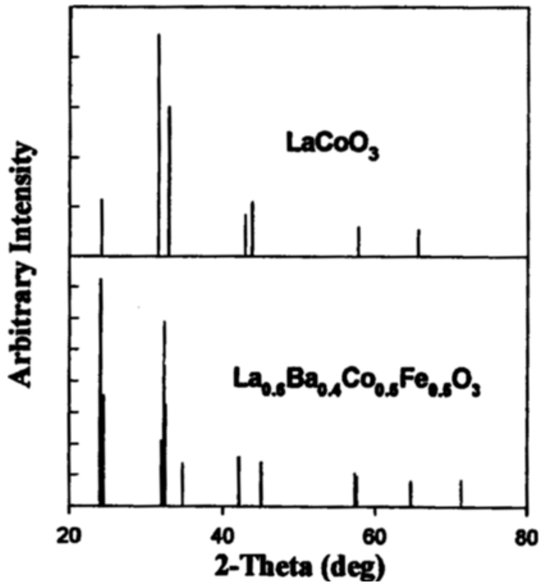

Fig. 2. XRD patterns of perovskite catalysts prepared by malic acid method.

The crystal structures of prepared oxides were examined by XRD and the results are shown in Fig. 2. In spite of preparation method, XRD patterns show large peak at 33° and confirm the formation of perovskite crystalline phase [Anderson et al., 1979].

The surface area of perovskite oxides was measured by BET measuring apparatus. Table 1 shows the surface areas of catalysts by different preparation method. While small surface area is obtained about 1 m^2/g in the catalyst prepared by solid reaction method, large surface areas more than 10 m^2/g are obtained in the catalyst prepared by malic acid method. It is

Table 1. BET surface areas of various perovskite catalysts

Catalyst	Preparation method	Calcining conditions	Surface area (m^2/g)
$LaCoO_3$	Malic acid	600 °C, 12 hr	4.0
$La_{0.6}Sr_{0.4}CoO_3$	Malic acid	600 °C, 12 hr	8.8
$La_{0.6}Sr_{0.4}FeO_3$	Malic acid	600 °C, 12 hr	57.8
$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$	Malic acid	600 °C, 12 hr	20.0
$La_{0.6}Ba_{0.4}CoO_3$	Malic acid	600 °C, 12 hr	5.7
$La_{0.6}Ba_{0.4}FeO_3$	Malic acid	600 °C, 12 hr	26.5
$La_{0.6}Ba_{0.4}Co_{0.8}Fe_{0.2}O_3$	Malic acid	600 °C, 12 hr	7.9
$La_{0.6}Ba_{0.4}Co_{0.5}Fe_{0.5}O_3$	Malic acid	600 °C, 12 hr	12.2
$LaCoO_3$	Solid state rxn	1,050 °C, 12 hr	1.1
$La_{0.6}Ba_{0.4}Co_{0.5}Fe_{0.5}O_3$	Solid state rxn	1,050 °C, 12 hr	0.8
$La_{0.6}Sr_{0.4}CoO_3$	Solid state rxn	1,050 °C, 12 hr	0.8
$La_{0.6}Sr_{0.4}FeO_3$	Solid state rxn	1,050 °C, 12 hr	1.2

thought that the latter is calcinated at lower temperature than the former because malic acid easily makes the complex with transition metal and then it stabilizes the perovskite oxide obtained by the complex at low calcination temperature. In addition, the addition of Fe into B site increases surface area.

2. Effect of Substitution of Metal Ion into A Site

Fig. 3 shows NO conversion with time on stream over $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$. Steady state is obtained relatively fast at almost reaction temperature. In addition, steady state reaches within 20 minute at 300 °C and the activity shows almost constant values. Thus the value of NO conversion is obtained after 1 hr reaction.

Fig. 4 shows the effect of substitution of metal into A site of $LaCoO_3$. The substitution of Sr or Ba into A site of $LaCoO_3$ increases NO conversion.

The general formula of perovskites is ABO_3. Their crystal structure is relatively simple. The B ions may be catalytically active 3*d*, 4*d* or 5*d* transition metal ions which occupy octahedron. The A ions, which fit into dodecahedral interstices, may be large rare-earth, alkaline-earth, alkali or large ions. Even for a single active metal B center, there is still the freedom to vary its valence and many physical properties by choices of the modifying A ion. In $La_{1-x}Sr_xCoO_3$, oxygen vacancies compensate for the rising Sr content beyond x=0.4 [Jonker et al., 1953]. One phase perovskites $LaNiO_3-\lambda$ ($\lambda\leq 0.25$) have been described but are not very stable.

The reduction of NO by CO and H_2 over perovskite-type catalysts has been classified as an intrafacial process [Voorhoeve et al., 1976]. It was well known that NO adsorbs more strongly on reduced transition metal oxides on oxidized sample [Yao et al., 1973]. An example of an intrafacial process is the reduction of NO, which occurs through dissociative chemisorption on an oxygen vacancy of the perovskite surface.

$$NO+[M\text{-}V_o\text{-}M] \rightarrow N_{ads}+[M\text{-}O\text{-}M]$$

In this reaction, the reduced and oxidized surfaces are symbolized by $[M\text{-}V_o\text{-}M]$ and $[M\text{-}O\text{-}M]$, respectively. N_{ads}, the resulting N fragment, which probably has to be stabilized by interaction with other adsorbates, may react further to form N_2O and N_2 and so forth.

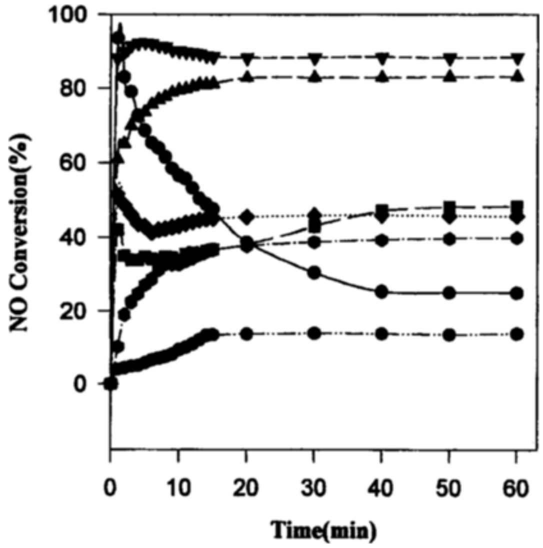

Fig. 3. The effect of reaction time on the conversion of NO over $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$; NO=1,000 ppm, C_3H_8=1,000 ppm, O_2=4%, GHSV=30,000 $hr^{-1.}$
-●-: 250 °C, -■-: 275 °C, -▲-: 300 °C, -▼-: 325 °C, -◆-:
-⬢-: 375 °C, ··●-: 400 °C

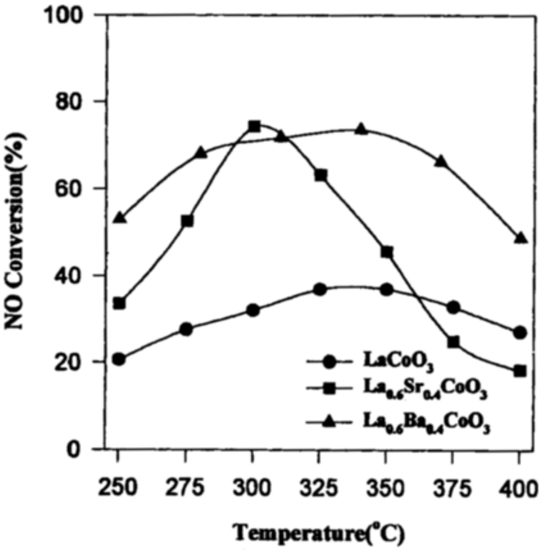

Fig. 4. The effect of reaction temperature on the conversion of NO over perovskite catalysts; NO=1,000 ppm, C_3H_8 =1,000 ppm, O_2=4 %, GHSV=30,000 hr^{-1}.

$$N_{ads}+NO_{ads} \rightarrow N_2O$$

$$2N_{ads} \rightarrow N_2$$

The V_o is restored by a reducing agent, hydrocarbon, in the gas,

$$[M\text{-}O\text{-}M]+HC \rightarrow [M\text{-}V_o\text{-}M]+CO,\ CO_2$$

It is understandable from the mechanism that the number of oxygen vacancy in the surface is important for the rate of NO conversion. It is thought that the number of V_o increases and then NO conversion also increases in the substitution of Sr or Ba into A site.

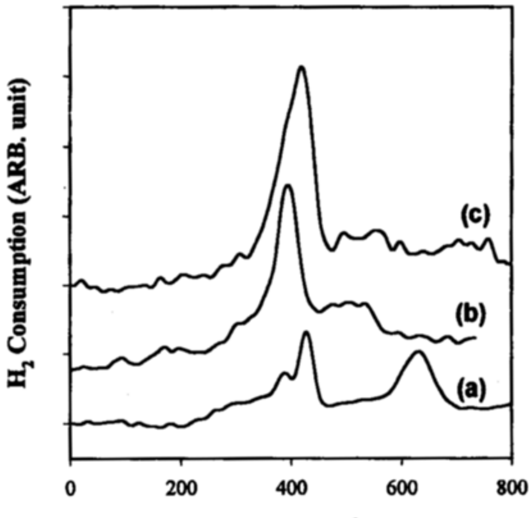

Fig. 5. TPR profiles measured for various perovskite type oxides calcined at 600 °C for 12 hrs (Heating rate=10 K/min, gas mixture=7.5 % H_2/N_2).
(a) $LaCoO_3$, (b) $La_{0.6}Ba_{0.4}CoO_3$, (c) $La_{0.6}Sr_{0.4}CoO_3$

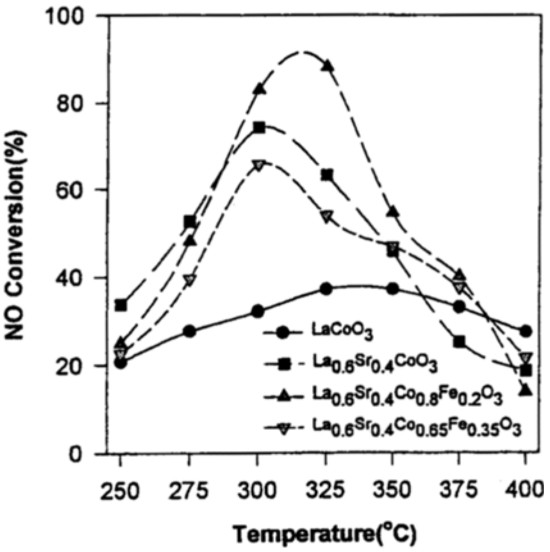

Fig. 6. The effect of reaction temperature on the conversion of NO over perovskite catalysts: NO=1,000 ppm, C_3H_8 =1,000 ppm, O_2=4 %, GHSV=30,000 hr^{-1}.

Fig. 5 shows the TPR results of various perovskite oxides. The $LaCoO_3$ shows two kinds of reduction peaks at 400 °C and 610 °C, respectively but in the substitution of Sr or Ba, the peak size increases at low temperature and disappears at high temperature. This results suggests that the substitution of Sr or Ba gives rise to easy reduction of oxides and form oxygen vacancies of surface and then increase the catalytic activity of NO reduction.

3. Effect of Substitution of Metal Ion into B Site

Fig. 6 shows the effect of substitution of Sr into A site and Fe into B site of $LaCoO_3$. The substitution of Sr into A site enhances catalytic activity and that of Fe into B site also enhances the activity at the substitution ratio=0.2 but catalytic activity decreases at substitution ratio=0.35. In addition, the maximum activity appears at the range of 300-325 °C over all catalysts.

It was well known that oxygen ion moves through the lattice vacancy in the perovskite-type oxides and the mobility of ion increases and then the activation energy of anion mobility decreases as the lattice vacancy increases [Cook et al., 1991]. Consequently the oxygen vacancies increase followed by removal of oxygen by reducing agent at surface as the mobility of oxygen ion increases in the lattice. In the TPR results of $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$, the addition of Fe gives rise to move the peak position of α-oxygen species to low temperature [Moon et al., 1996]. It is reported that the α-oxygen species are not only strongly bonded to Co or Fe but reversible oxygen species which are concerned in reduction of oxygen by freely moving in the lattice of metal oxides. Therefore the expansion of lattice by addition of Fe gave rise to easily occur the reduction of oxygen by lowering the bond energy between α-oxygen species and metal [Moon et al., 1996].

With the increase of Fe content, it is difficult to reduce oxygen owing to other factors except for lattice expansion. Moon et al. reported that the content of irreversible oxygen increased with the increase of Fe content followed by holding the peripheral oxygen in the lattice [1996], and then α-oxygen species decreased relatively. As is shown in Fig. 6, the catalytic activity decreases according to the decrease of α-oxygen species in the Fe content≥0.35.

Fig. 7 shows the effect of substitution of Ba into A site and Fe into B site of $LaCoO_3$.

The substitution of Ba into A site also enhances catalytic activity and that of Fe into B site shows the maximum activity at the substitution ratio=0.5. It can be explained as same reason before. In addition, the high activity appears at large range temperature compared to $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$. This result suggests that $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst is better in the real

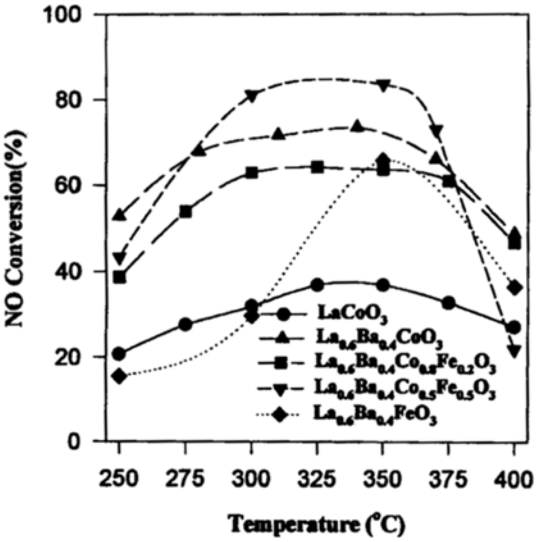

Fig. 7. The effect of reaction temperature on the conversion of NO over perovskite catalysts; NO=1,000 ppm, C_3H_8=1,000 ppm, O_2=4 %, GHSV=30,000 hr^{-1}.

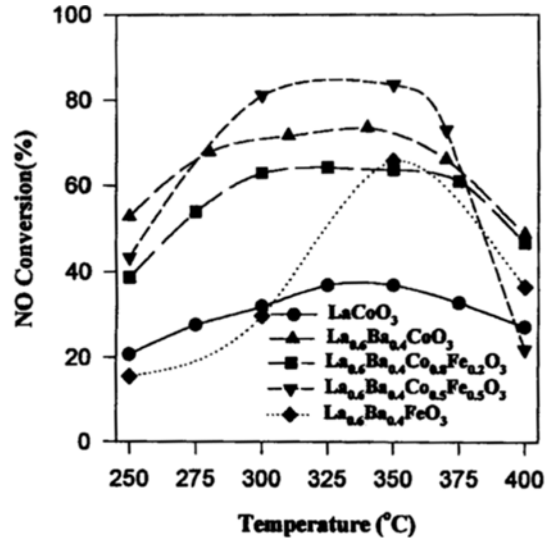

Fig. 8. The effect of reaction temperature on the conversion of NO over perovskite catalysts; NO=1,000 ppm, C_3H_8 =1,000 ppm, O_2=4 %, GHSV=30,000 hr^{-1}, M-A: malic acid mothod, S-S: solid reaction method.

exhaust gas condition than $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$.

4. Effect of Preparation Method of Catalysts

It is well known that the catalytic activity differs according to the preparation method. In this study, we prepared two type of perovskite oxides in order to compare the property of catalysts according to the preparation method. The result is shown in Fig. 8.

The catalyst prepared by malic acid method shows higher activity than that prepared by solid reaction method. In addition, the former shows the maximum activity at lower reaction temperature compared to the latter (350 °C). It is thought that the active site of the former increases owing to their high surface area. Therefore this result suggests that the catalyst prepared by malic acid method can be used effectively in the reduction of NO.

5. Effect of Reaction Conditions

It is well known that NO reduction is strongly promoted by oxygen [Iwamoto et al., 1991]. In Fig. 9, the effect of oxygen concentration on the NO conversion over $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ is shown. As is shown, the addition of oxygen into the gas feed has a dramatic effect on the NO conversion performance of the catalyst. This result suggests that the oxygen plays an important role on the reduction of NO. The similar results were shown by other authors [Montreuil et al., 1992; Monroe et al., 1993]. It is thought that partially oxygenated hydrocarbon species are capable of reducing NO under oxidizing conditions. In addition, such partially oxygenated species perform NO conversion in the absence of gas phase molecular oxygen. NO conversion increases with increasing of O_2 concentration, but it is expected that NO conversion will decrease at high O_2 concentration owing to decreasing of hydrocarbon.

The effect of space velocity on the NO conversion over $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ is examined and the result is shown in Fig. 10. In this case, different space velocity was obtained by changing the mass of catalyst while holding the volumetric flow rate constant. The NO conversion decreases with increasing space velocity, that is, deceasing contact time between catalyst and reactants. The similar results are shown over almost metal oxide catalysts [Torikai et al., 1991]. Therefore in real exhaust gas condition, the catalytic activity on the space velocity is considered to be very important.

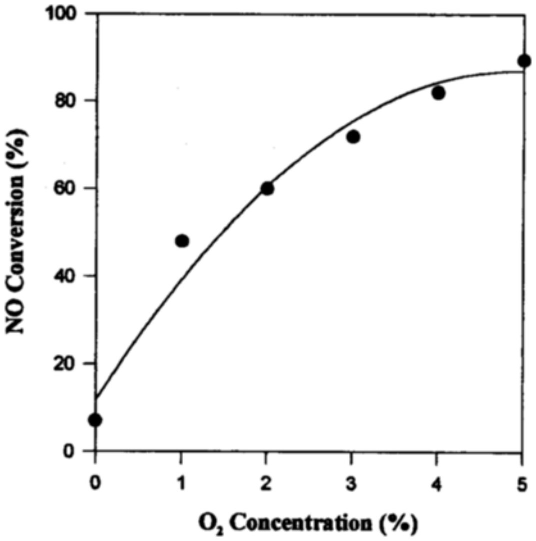

Fig. 9. The effect of oxygen concentration on the NO conversion over $La_{0.6}Ba_{0.4}Co_{0.5}Fe_{0.5}O_3$ catalyst: NO=1,000 ppm, C_3H_8=1,000 ppm, T_R=350 °C.

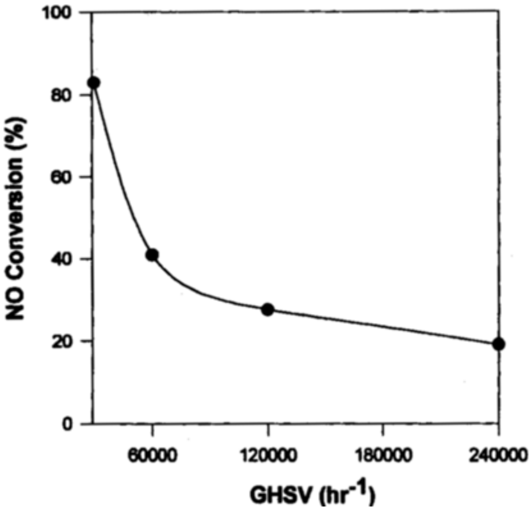

Fig. 10. The effect of space velocity on the NO conversion over $La_{0.6}Ba_{0.4}Co_{0.5}Fe_{0.5}O_3$ catalyst: NO=1,000 ppm, C_3H_8= 1,000 ppm, T_R=350 °C, O_2=4 %.

6. Effect of Water Introduced into Feed Gas

Since any combustion process is going to produce almost 16 % water vapor, one must focus on a catalyst that is stable for long times in such wet environments. However no outstanding catalyst has been known to be stable in such conditions.

We examined the effect of water on the catalytic activity and the result is shown in Fig. 11. The catalytic activity decreases under the wet environment over perovskite-type oxides. However $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst shows to have high-

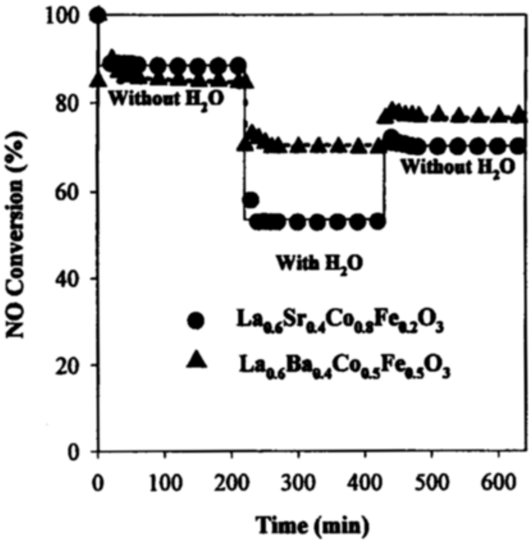

Fig. 11. Reversibility of perovskite catalyst deteriorated by water vapor: NO=1,000 ppm, C_3H_8=1,000 ppm, O_2=4 % H_2O =5 vol%, T_R=325 °C.

er stability than $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$ catalyst. It is thought that the former has higher resistance to water vapor than other reported catalyst.

It is well known that added water prohibits reactants from reacting with active metal by dealumination of the skeletal structure of zeolites [Iwamoto et al., 1994]. Actually, this weakness has blocked the practical use of zeolite catalyst. It is known that added water has different function in the metal oxide compared to zeolite [Nam et al., 1995]. It was reported that water prohibited from adsorption of reactants followed by competitive adsorption with reactants in the active site. In the perovskite-type oxide, it is thought that water in the reactants also decreases the active site of catalyst. In addition, it was reported that this deactivation was reversible, that is, the activity was recovered in the stoppage of water introduction [Nam et al., 1995].

As is shown in Fig. 11, the initial activity of $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst is almost recovered compared to $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_3$ catalyst. This suggests that deactivation by water is reversible over $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst. In addition, it is thought that $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst deserves to be commercialized in the removal of NO_x.

CONCLUSIONS

The following results are drawn from the reduction of NO by propane over perovskite-type oxides.

1. In the $LaCoO_3$ type catalyst, the partial substitution of Ba, Sr into A site enhanced the catalytic activity in the reduction of NO.
2. In the $La_{0.6}Ba(Sr)_{0.4}Co_{1-x}Fe_xO_3$ (x=0-1.0) catalyst, the partial substitution of Fe into B site enhanced the conversion of NO, but excess amount of Fe decreased the conversion of NO.
3. The surface area and catalytic activity of perovskite catalysts prepared by malic acid method showed higher values than those of solid reaction method.
4. In the $La_{0.6}Ba(Sr)_{0.4}Co_{1-x}Fe_xO_3$ catalyst, the conversion of NO increased with increasing O_2 concentration and contact time.
5. The introduction of water into reactant feed decreased the catalytic activity but the deactivation was shown to be reversible over $La_{0.6}Ba_{0.4}Co_{1-x}Fe_xO_3$ catalyst.

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