

The role of redox property of $\text{La}_{2-x}(\text{Sr,Th})_x\text{CuO}_{4\pm\lambda}$ playing in the reaction of NO decomposition and NO reduction by CO

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Abstract

Two systems of mixed oxides, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 1.0$) and $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$), with K_2NiF_4 structure were prepared. The average valence of Cu ions and oxygen nonstoichiometry (λ) were determined by means of chemical analysis. Meanwhile, the adsorption and activation of nitrogen monoxide (NO) and the mixture of NO + CO over the mixed oxide catalysts were studied by means of mass spectrometry temperature-programmed desorption (MS-TPD). The catalytic behaviors in the reactions of direct decomposition of NO and its reduction by CO were investigated, and were discussed in relation with average valence of Cu ions, λ and the activation and adsorption of reactant molecules. It has been proposed that both reactions proceed by the redox mechanism, in which the oxygen vacancies and the lower-valent Cu ions play important roles in the individual step of the redox cycle. Oxygen vacancy is more significant for NO decomposition than for NO + CO reaction. For the NO + CO reaction, the stronger implication of the lower-valent Cu ions or oxygen vacancy depends on reaction temperature and the catalytic systems (Sr- or Th-substituted). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mixed oxides with K_2NiF_4 structure; Direct decomposition of NO; Reduction of NO by CO; Oxygen vacancy; Lower-valent metallic ion

1. Introduction

Nitrogen oxides (NO_x) are serious pollutants in the Earth's atmosphere in the sense that they are one of the main sources of acid rain [1,2]. The removal of NO_x is one of the key research projects in the protection of our environment and new methods are being developed in many country today [2]. Among them, the direct de-

composition of NO and its reduction with new reductants, instead of NH_3 , is much more attractive. Nitrogen monoxide (NO) is thermodynamically unstable relative to N_2 and O_2 at low temperatures, and therefore, its catalytic decomposition is the simplest and cheapest method for the removal of NO from exhaust streams [1–4]. The catalytic reduction of NO by CO is an important chemical process owing to the need for controlling nitric oxide and carbon monoxide emissions, especially from motor vehicles. The process is advantageous since both components could be removed, leaving harmless carbon dioxide and nitrogen as products.

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It has been reported that the Cu-containing compounds are active catalysts for the reaction of direct decomposition of NO [5,6] and its reduction by CO [7–11]. However, no final conclusion has yet been proposed. For example, London and Bell [8] have reported that the NO–CO reaction proceeds by a redox cycle of Cu^0 and Cu^+ over Cu_2O ; Mizuno et al. [10] and Yasuda et al. [11] found that the La_2CuO_4 -based catalysts having an average oxidation number of copper close to +2 were most active and that the relative activities of the catalysts studied were all well-explained by the mechanism in which the active sites for NO decomposition are coordination-unsaturated in mixed oxide catalysts with K_2NiF_4 -type structure. Halasz et al. [12] have investigated the catalytic activity for the reactions over superconducting and related cuprate catalysts and pointed out that neither the oxidation of CO nor the decomposition of NO is the rate-determining step, but the capacity to adsorb NO may be important. No paper on the comparative study about the similarities and dissimilarities between the direct decomposition of NO and its reduction by CO over mixed oxides with K_2NiF_4 structure has been presented.

K_2NiF_4 -type mixed oxides consist of alternating layers of ABO_3 perovskite and AO rock salt. Some oxide superconductors also belong to this structure. In this structure, it is possible to control the valence of B-site ion by substitution at A-site ion with different valent ions. It means that the variation of redox property of the mixed oxides can be controlled.

In our previous work [13] and reference [14], it has been found that the catalytic activity of oxides with K_2NiF_4 structure is higher than those with single perovskite (ABO_3) structures in some reactions. Recently after systematical study [15–17], we found that Ni-based mixed oxides with K_2NiF_4 structure had higher activity for the direct decomposition of NO.

In this paper, two system of Cu-based mixed oxides $\text{La}_{2-x}(\text{Sr,Th})_x\text{CuO}_{4\pm\lambda}$ with K_2NiF_4 structure were prepared in which the valence of

Cu ions and the oxygen nonstoichiometry (λ) could be controlled by varying the x value regularly in some extent. The catalytic behaviors of NO decomposition and its reduction by CO over these catalysts were investigated and based on the comparison of features for the two reactions, the catalytic mechanisms of both reactions are discussed.

2. Experimental

2.1. Catalyst preparation

The mixed oxides, $\text{La}_{2-x}(\text{Sr,Th})_x\text{CuO}_{4\pm\lambda}$, were prepared by decomposing the amorphous precursors (citrate) as described previously [18]. Briefly, to an aqueous solution of Cu(II), lanthanum (III), thorium (IV) and strontium (II) nitrates with an appropriate stoichiometry, a solution of citric acid 100% in excess was added. The resulting solution was evaporated to dryness, then the obtained precursor was decomposed in air at 300°C, calcined at 600°C for 1 h and finally palletized and calcined once more at 950°C in air for 12 h. The synthesized pellet was pulverized to ca. 40–80 mesh size.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) data were obtained by using an X-ray diffractometer (type D/MAXIIB made in Japan) over the range $5 \leq 2\theta \leq 80^\circ$, at room temperature, operating at 40 kV and 10 mA, using Cu $\text{K}\alpha$ radiation combined with the nickel filter.

The metal-ion components of the catalysts were determined by titration with EDTA and it was confirmed that the metal composition of the products was consistent with those of feed materials. The oxidation states of Cu ions in the catalysts were measured by means of iodometry [19]. The data obtained together with La^{3+} , Th^{4+} and Sr^{2+} contents were used to calculate the nonstoichiometric amount of oxygen (l) in the samples.

The specific surface area of the samples was measured by conventional BET method. The specific surface areas of these series of catalysts are almost the same (ca. 1–2 m²/g).

Temperature-programmed desorption of NO (NO-TPD) or temperature-programmed surface reaction (NO-TPSR) detected by mass spectrometry (MS) was carried out on D-100 type MS (made in Japan). The samples were first heated from room temperature to 900°C at a rate of 30°C/min and kept at 900°C for 1 h in helium. The pretreated sample was first cooled to 200°C and swept with NO (1.5% with helium balanced) for the adsorption of NO for 1 h, and cooled to 80°C in the NO stream for 0.5 h again. Then the sample was swept with helium at a rate of 20 ml/min for 1 h in order to remove the residual NO in the reaction space. Finally, the sample was heated at a rate of 30°C/min in helium for recording the TPD spectra. The process of MS-NO-TPD is similar to that in GC-NO-TPD [15]. In MS-(CO + NO)-TPD, the adsorption of CO + NO was performed at 50°C with CO + NO mixed gas (NO and CO each 4000 ppm, with helium balanced).

2.3. Catalytic activity measurement

The NO + CO reaction was carried out in a flow reactor by feeding a gas mixture of NO:CO = 1:1 (ca. 4000 ppm) and He (balanced) at a flow rate of 22.5 cm³/min over 0.5 g catalyst ($W/F = 1.34$ g s/cm³). The gas composition was analyzed before and after the reaction by an in-line gas chromatography (Pye Panchromatograph made in England) with thermal conductor detector (TCD) and connected with a computer integrator system using molecular sieve 5A column for NO, N₂ and O₂ and Porapak Q column for N₂O and CO₂, respectively. The temperatures of the room for columns and TCD are 50°C and 75°C, respectively. All experiment data were taken after ca. 1–2 h on stream at each temperature when the catalytic reaction practically reached a steady state.

The reaction conditions and the method of the catalytic activity measurement for the direct decomposition of NO are described in Refs. [15–17].

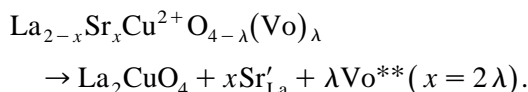
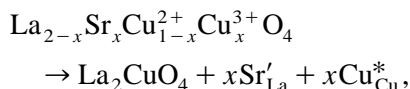
3. Results and discussion

3.1. Defect structure of $La_{2-x}(Sr,Th)_xCuO_{4\pm\lambda}$

The average valence of Cu ions and the contents of Cu³⁺ or Cu⁺ in the two oxide systems were determined by the chemical analysis using the method of iodometry [19]. The oxygen nonstoichiometry (λ) was calculated on the assumption that copper is present as either a mixture of Cu²⁺ and Cu³⁺ in $La_{2-x}Sr_xCuO_{4\pm\lambda}$ system or a mixture of Cu⁺ and Cu²⁺ in $La_{2-x}Th_xCuO_{4\pm\lambda}$ system and other elements are present as La³⁺, Sr²⁺, Th⁴⁺ and O²⁻, respectively [10]. The variation of the average valence of Cu ions and λ vs. x is shown in Fig. 1.

XRD investigation on $La_{2-x}Sr_xCuO_{4\pm\lambda}$ ($0.0 \leq x \leq 1.0$) revealed that the oxides with $0.0 \leq x \leq 0.3$ were single phase with the orthorhombic K₂NiF₄-type structure and that at $x \geq 0.5$, the tetragonal phase, so-called T^* phase [20], was formed in addition to the orthorhombic phase and the amount of the T^* phase increased with an increasing x .

In the series of $La_{2-x}Sr_xCuO_{4\pm\lambda}$ ($0.0 \leq x \leq 1.0$) mixed oxides, the deficient positive charge resulting from the substitution of Sr²⁺ for La³⁺ could be balanced either by the formation of higher oxidation state ion at B-site, i.e., Cu²⁺ → Cu³⁺, or by the formation of oxygen vacancy (Vo) [21]. These processes could be explained by the following defect equations:



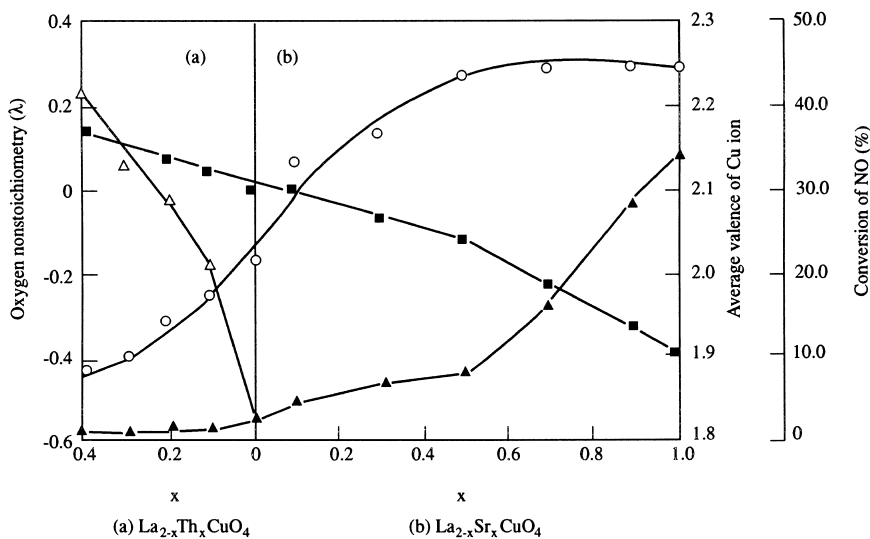
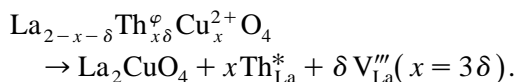
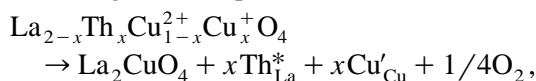


Fig. 1. Average valence of Cu ion (O), oxygen nonstoichiometry (λ , ■) and NO decomposition activity at 850°C (▲, Δ) as a function of x in $\text{La}_{2-x}(\text{Sr,Th})_x\text{CuO}_{4\pm\lambda}$. NO decomposition activity at the steady state (▲) and the initial stage (Δ).

In fact, the two cases often occur at the same time. The analysis results (Fig. 1) show that in the range of $0.0 \leq x \leq 0.5$, the contents of Cu^{3+} increase rapidly and thus, the charge of the mixed oxides is mainly balanced by the increase of Cu^{3+} . In the range of $0.5 \leq x \leq 1.0$, on the other hand, the formation of oxygen vacancies is more pronounced.

In the series of $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$), the surplus-positive charge resulting from the substitution of Th^{4+} for La^{3+} could be balanced either by the formation of lower-valent cation at B-site, i.e., $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, or by causing an excess of oxygen. There are two possibilities for the excess of oxygen. One is O^{2-} ion existing interstitially in the lattice, and the other could exist due to the formation of cation vacancy (denoted by φ). The existence of B vacancy would not be possible, due to the stability of BO_6 polyhedron, and the radius of O^{2-} ion is too large to sit at interstitial sites. So the presence of A-site vacancy is plausible for the oxygen excess structure [22]. Thus, the process

for charge balance can be illustrated by the following defect equations:



In all the Th-substitution oxides, $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.1 \leq x \leq 0.4$), ThO_2 was present along with the K_2NiF_4 -type oxide and the amount of ThO_2 increased with increasing x . As seen from Fig. 1 for the Th-substituted oxides, the average valence of Cu ions is less than 2 and decreases with increasing x . In addition, the oxygen excess increases with increasing x . These results indicate that the formation of Cu^+ ion and A-site vacancy occur simultaneously through the real substitution level x in the K_2NiF_4 structure. It is interesting to note that when La^{3+} ion at A-site was replaced either by lower-valent ion Sr^{2+} or by higher-valent ion Th^{4+} , the average valence of Cu ion and oxygen nonstoichiometry (λ) change

successively with x . In other words, we have succeeded in synthesizing a series of compounds with successive change of valence of Cu ion and oxygen nonstoichiometry.

3.2. MS-NO-TPD (or NO-TPSR)

MS-NO-TPD stands for temperature-programmed desorption of NO detected by mass spectrometer. Strictly speaking, NO-TPD should be called temperature-programmed surface reaction (TPSR), because the adsorbed NO molecule

may react and be converted into other species such as NO_2 , N_2O , N_2 and O_2 during NO-TPD. MS-NO-TPD gave significant information about the adsorption and activation of NO as well as the nature of the catalytic reactions of NO decomposition and reduction over La_2CuO_4 -based catalysts. Fig. 2 shows the MS-NO-TPD chromatograms over LaSrCuO_4 , La_2CuO_4 and $\text{La}_{1.7}\text{Th}_{0.3}\text{CuO}_4$ which are three typical samples in the sense of oxygen nonstoichiometry.

It can be seen from Fig. 2a that LaSrCuO_4 , in which a large amount of oxygen vacancy exists,

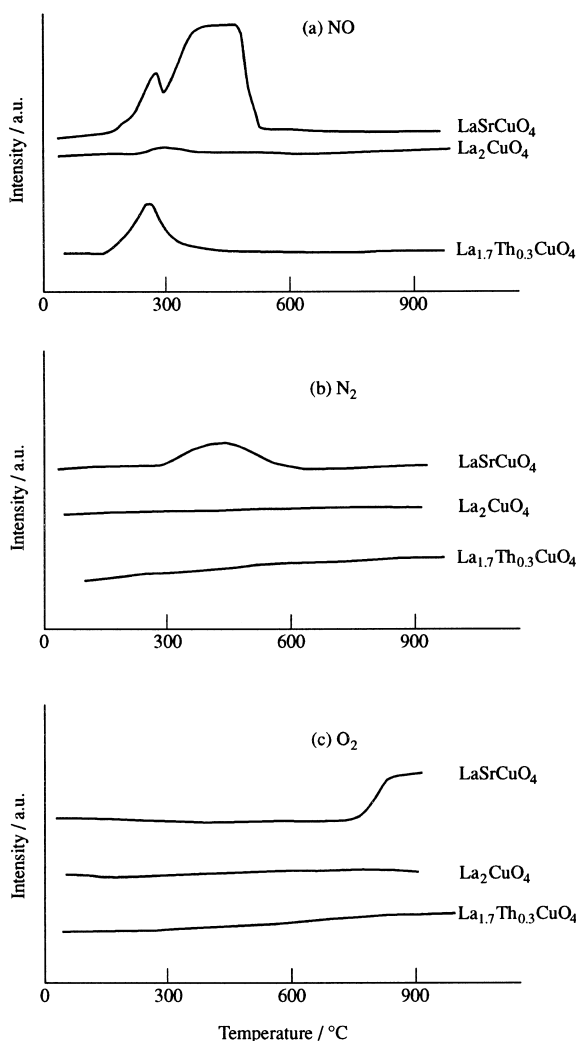


Fig. 2. MS-NO-TPD chromatograms of NO, N_2 and O_2 over LaSrCuO_4 , La_2CuO_4 and $\text{La}_{1.7}\text{Th}_{0.3}\text{CuO}_4$.

has two desorption peaks of NO (mass number: 30), i.e., smaller one at lower temperature and larger one at higher temperature, while for oxygen excess La_2CuO_4 and $\text{La}_{1.7}\text{Th}_{0.3}\text{CuO}_4$, on the other hand, only a small desorption peak at lower temperature was observed. The desorption of N_2 was observed only from LaSrCuO_4 (Fig. 2b) on which a large amount of NO was adsorbed. These results indicated that the adsorption of NO is one of the indispensable steps for the activation and decomposition of NO molecules.

As shown in Fig. 2c, only oxygen-deficient LaSrCuO_4 showed the desorption peak of lattice oxygen at high temperature. There may be two reasons to cause the desorption of lattice oxygen in NO-TPSR. The first reason is due to the high mobility of lattice oxygen and good reversible adsorption–desorption property of lattice oxygen for LaSrCuO_4 in the presence of a large amount of oxygen vacancy. The second reason is as follows: During the adsorption of NO at lower temperature, as discussed in our previous works [15,16], a part of the adsorbed NO molecules was decomposed into N_2 and O_2 , and the nitrogen was desorbed, while the oxygen was still adsorbed on the catalysts, since the temperature is lower than that necessary for desorption of the oxygen. At higher temperature, the adsorbed oxygen would be desorbed. The mass chromatograms of O_2 over LaSrCuO_4 in CO-TPD and (CO + NO)-TPD were similar to that in the NO-TPD. So the first reason would be the main reason to cause the desorption of lattice oxygen for LaSrCuO_4 sample.

The desorption peak of NO_2 (mass number: 46) has not been observed in MS-NO-TPD. This results show that it is difficult to form NO_2 species during the process of adsorption and desorption of NO on 1 h and, and on the other hand, NO_2 may be converted into NO and O_2 when desorbed at high temperature.

We also investigated the adsorption and activation of NO during the co-adsorption of NO + CO. The desorption profiles of NO in NO + CO-TPD are similar to those in the NO-TPD

(Fig. 2a) (figures of (NO + CO)-TPD are omitted). It shows that the adsorption of NO molecule not only has some priority over that of CO, but also is stronger than that of CO. It seems that the adsorption of NO plays a decisive role in the activation and reduction of NO by CO. It was supported by the activity measurement results in the following part and in Ref. [10].

3.3. Catalytic behavior in NO decomposition

The variation of catalytic activity for NO decomposition over $\text{La}_{2-x}(\text{Sr,Th})_x\text{CuO}_{4\pm\lambda}$ with reaction temperature at 850°C is shown in Fig. 3. LaSrCuO_4 showed the high and stable catalytic activity for NO decomposition. On the other hand, $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$) showed the high activity at the initial stage, but it rapidly deactivated with reaction time. Since pure ThO_2 was inactive for NO decomposition, activity of the system certainly originates from the Th-substituted K_2NiF_4 -type phase.

The relation between the steady state catalytic activity for NO decomposition and oxide composition is depicted in Fig. 1. For the series of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ catalysts, the concentration of Cu^{3+} increases rapidly but the catalytic activity increases slowly in the range of $0.0 \leq x \leq 0.5$ with increasing x . In the range of $0.5 \leq x \leq 1.0$, however, the concentration of Cu^{3+} keeps almost constant but the concentration of oxygen vacancy and the catalytic activity of NO decomposition increase rapidly. Evidently, it shows that the activity of NO decomposition is closely related to the oxygen vacancy. It can thus be recognized that oxygen excess $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ without oxygen vacancy shows very low NO decomposition activity at the steady state.

As shown in Fig. 3, $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ showed the high initial activity which increased with increasing x . The parallelism between the concentration of Cu^+ and the initial activity suggested that Cu^+ has high ability for the activation of NO through the following reaction: $\text{Cu}^+ + \text{NO} \rightarrow [\text{Cu}^{2+} - \text{NO}^-]$. Because the N–O

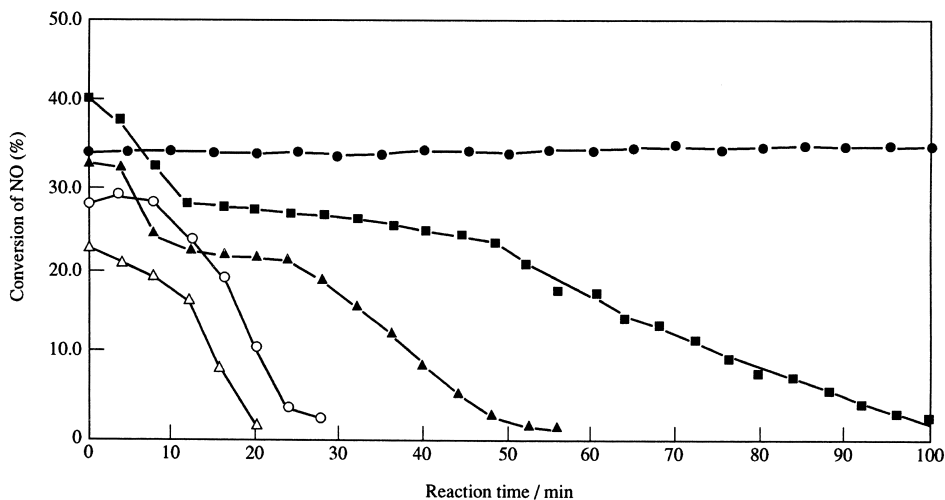
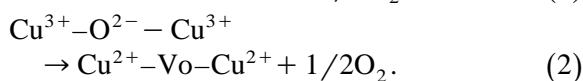
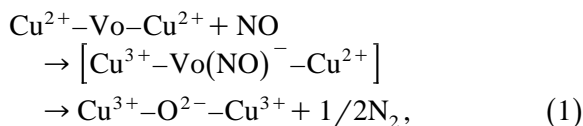


Fig. 3. Variation of catalytic activity for NO decomposition at 850°C with reaction time. (Δ) $\text{La}_{1.9}\text{Th}_{0.1}\text{CuO}_4$, (\circ) $\text{La}_{1.8}\text{Th}_{0.2}\text{CuO}_4$, (\blacktriangle) $\text{La}_{1.7}\text{Th}_{0.3}\text{CuO}_4$, (\blacksquare) $\text{La}_{1.6}\text{Th}_{0.4}\text{CuO}_4$, (\bullet) LaSrCuO_4 .

bond orders of NO^- (2.0) is lower than those of NO (2.5) and NO^+ (3.0), the $\text{N}=\text{O}$ bond for NO^- is easier to break [23,24]. The Cu species on or near the surface might be easily oxidized by O from NO molecule, resulting in the rapid deactivation.

As stated above, the stable activity for NO decomposition is parallel to the amount of oxygen vacancy. The presence of oxygen vacancy is very important not only for the adsorption and activation of NO molecule, but also for increasing the mobility of lattice oxygen which, in turn, is beneficial to the regeneration of the active site for NO decomposition.

On the basis of above discussion and in similarity to that in Ni-based mixed oxide catalysts [15], oxygen vacancy and the easy redox change between Cu^{2+} and Cu^{3+} play important roles in NO decomposition and a tentative mechanism of NO decomposition over these Cu-based mixed oxides could be proposed as follows:



3.4. Catalytic behavior in the reaction of NO + CO

3.4.1. Results of activity measurement

The catalytic activities of $\text{La}_{2-x}(\text{Sr}, \text{Th})_x\text{CuO}_{4\pm\lambda}$ for the reaction of NO + CO were measured as a function of reaction temperature from 300°C to 600°C. The profiles of the conversion of NO and CO vs. temperature are very similar for all the catalysts examined and N_2 was a sole reduction product of NO in the temperature range examined. At each temperature, the reaction was kept for 1–2 h to achieve steady activity. The temperature dependence of the NO conversion over $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ is shown in Fig. 4. The catalytic activity of all the samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.1 \leq x \leq 1.0$) increases with rising temperature. The catalytic activity in the reaction of NO + CO is higher for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.7 \leq x$) and tends to decrease with decreasing x .

Fig. 5 summarized the temperature dependence of the conversion of NO over ThO_2 and the mixed oxides $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$). ThO_2 was almost inactive for the NO + CO reaction in the temperature range examined and the catalytic activity for the NO + CO reaction

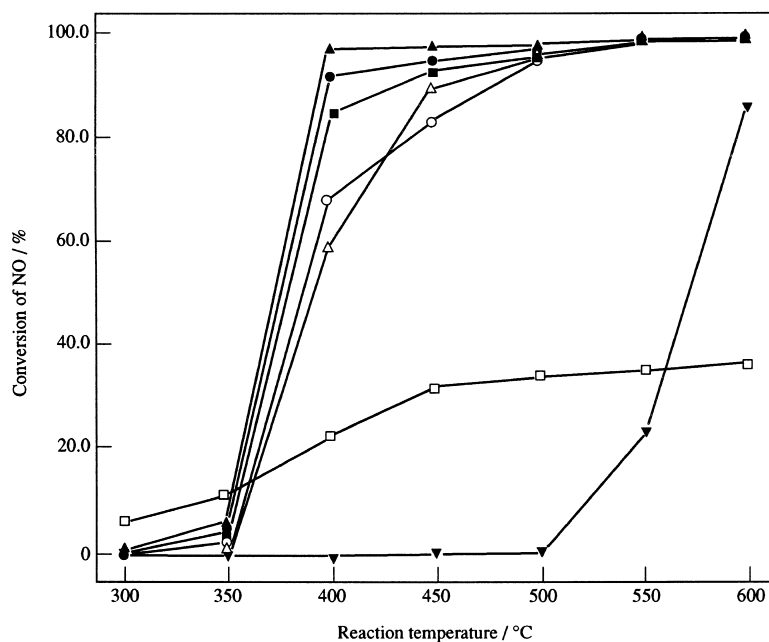


Fig. 4. Effect of reaction temperature on the conversion of NO of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ in the reaction of NO + CO. $x = 0$ (▼), 0.1 (□), 0.3 (○), 0.5 (△), 0.7 (■), 0.9 (●), 1.0 (▲).

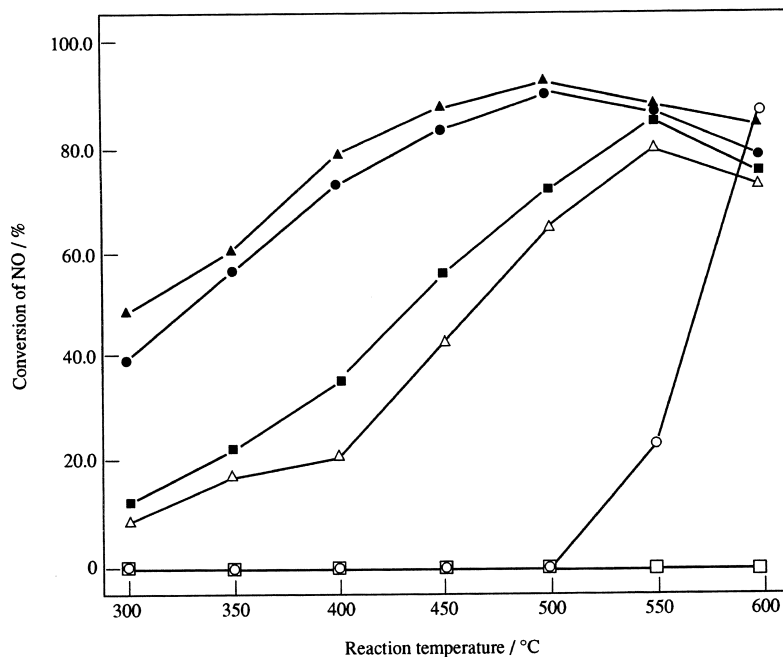


Fig. 5. Effect of reaction temperature on the conversion of NO over $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ in the reaction of NO + CO. $x = 0$ (○), 0.1 (△), 0.2 (■), 0.3 (●), 0.4 (▲), ThO_2 (□).

over $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ increased with increasing x .

3.4.2. Rate-determining step and reaction mechanism

The relationship between the conversion of NO with the substitution degree of La^{3+} by Sr^{2+} or Th^{4+} over mixed oxide $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.1 \leq x \leq 1.0$) and $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$) in the reaction of $\text{NO} + \text{CO}$ is shown in Fig. 6. Comparing Figs. 1 and 6, it can be seen for the system, $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$), that both the conversion of NO and the contents of lower-valent Cu ion increase with the increase of substitution degree x . It means that catalytic activity for NO + CO reaction would be related to the lower-valent Cu ion (Cu^+ in the Th-substituted oxide). In the series of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.1 \leq x \leq 1.0$) catalysts, the variation of NO conversion can be divided into two regions, i.e., the lower temperature range ($\leq 400^\circ\text{C}$) and the higher temperature range ($> 400^\circ\text{C}$). In the former range, the average valence of Cu ion increases, while the

catalytic activity decreases with increasing x . It should be pointed out that in this temperature range, the catalytic activity increases with decreasing average valence of Cu ions irrespective of substituted cations (Sr or Th). According to the characteristics of the molecular structure for NO and CO [23], it could be thus concluded that the lower the valence of metallic ion, the easier the formation of $\text{M}^{(n+1)+} \rightarrow \text{O}^-$ species. So the lower-valent metallic ion would play a decisive role in the activation of NO molecule. Oppositely, metallic ion with higher valence (i.e., hole) would play an important role in the activation of CO. Although the CO molecule has a molecular structure similar to that of NO, it is easy for CO molecule to be adsorbed on the hole over the mixed oxides and to form CO^+ [25], i.e., the electron was transferred to the higher-valent metallic ion. Therefore, the lower-valent metallic ion is unfavorable for the adsorption and activation of CO molecule. Based upon the above discussions, it can be thus concluded that the activation of NO by lower-valent Cu ion, especially Cu^+ , is more important than

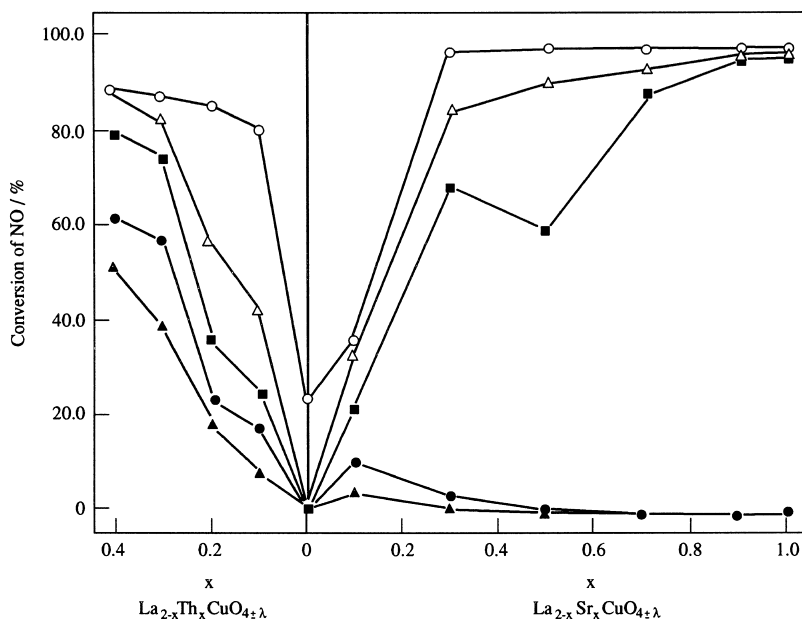
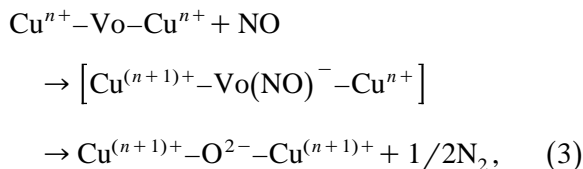
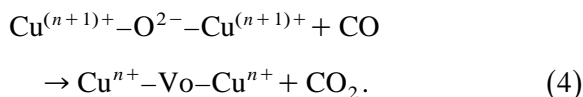


Fig. 6. Effect of substitution of La by Sr or Th on the conversion of NO in the reaction of $\text{NO} + \text{CO}$. (▲) 300°C , (●) 350°C , (■) 400°C , (△) 450°C , (○) 550°C .

the activation of CO at lower temperature range. The mechanism of the reaction of NO + CO over mixed oxide catalyst at lower temperatures could be proposed as follows:



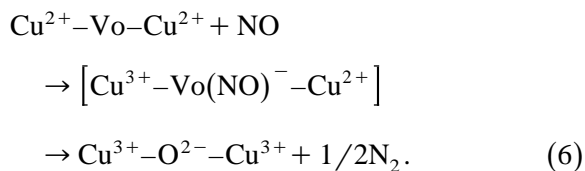
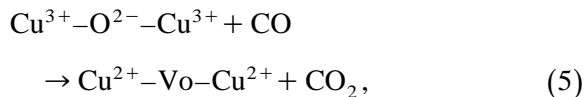
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Comparing with the mechanism of NO decomposition, it could be seen that the rate-determining step under low temperature is the same, i.e., activation of NO (see Eqs. (1) and (3)). The only difference between two reactions is the regeneration of the active center, one by thermal (Eq. (2)), and the other by reductant (Eq. (4)).

At higher temperatures, the variation of the catalytic activity of the two systems of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.1 \leq x \leq 1.0$) and $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$) shows an inflection point at the sample of La_2CuO_4 . It shows that the mechanism for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.1 \leq x \leq 1.0$) may be different from that for $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$). Generally higher temperatures are favorable for the transfer of lattice oxygen (O^{2-}), i.e., for the lattice oxygen to participate in the catalytic reaction cycle. But it depends on the nature of the catalyst whether the lattice oxygen takes part in the reaction cycle or not. As discussed above, for the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.3 \leq x \leq 1.0$) catalysts, in which a large amount of oxygen vacancy exists, the mobility of lattice oxygen is higher and it is easy for lattice oxygen to participate in the catalytic reaction cycle. Moreover, the presence of higher oxidation state ion (i.e., hole) is advantageous to the adsorption and oxidation of CO. Thus at higher temperatures, the tentative mechanism of the NO + CO

reaction over $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ with the $\text{Cu}^{2+}/\text{Cu}^{3+}$ redox couple could be illustrated as follows:fast



For oxygen excess $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$), the mobility of lattice oxygen is low and therefore, their participation is difficult. It seems that the activation of NO by Cu^+ (in the presence of reductant CO) is also important over $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ even at higher temperature range.

It can be imagined that, from the energetic point of view, the lower temperature is favorable for the adsorption of NO molecule over the mixed oxides, but unfavorable for the activation and dissociation of NO molecule. So the dissociation of NO molecule is the rate-determining step at lower temperature. Evidently, the lower-valent metallic ion would play an important role. On the other hand, the higher temperature is favorable for the activation for dissociation of NO molecule, but unfavorable for the adsorption of NO molecule. As discussed above, the adsorption of NO is very important for the reaction of the direct decomposition of NO and its reduction by CO. So the adsorption of NO would play a determining role at higher temperature. It has been reported in our recent works [15,26] on the adsorption and the direct decomposition of NO that the presence of oxygen vacancy is favorable for the adsorption of NO and the adsorption amount of NO is correlated with the amount of oxygen vacancy present. Oxygen vacancy can provide the adsorption sites of NO. Moreover, even more important is the mobility of lattice oxygen which, in turn, is beneficial for the regeneration of active site.

Therefore, the catalytic activity is related to the oxygen vacancy and its content at high temperature in the Sr-substituted oxides.

The results shown in Fig. 1 show that the average valence of Cu ion is more than and less than +2, in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ and $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$, respectively. This indicates that the redox couples of $\text{Cu}^{3+}/\text{Cu}^{2+}$ and $\text{Cu}^{2+}/\text{Cu}^+$ would be responsible for the catalytic cycle in Sr- and Th-substituted systems, respectively. In the unsubstituted La_2CuO_4 , however, the average valence of Cu ion is 2.02 and therefore, almost all the Cu ions exist as Cu^{2+} . The absence of Cu^+ and oxygen vacancy, both of which are important for the activation of NO, might be the reason why La_2CuO_4 sample has the lowest activity in the whole temperature region.

3.5. The comparison between NO decomposition and NO reduction by CO

Comparing the catalytic behavior of NO decomposition with that of the reduction of NO by CO over these Cu-based mixed oxides, evidently, there are some similarities and dissimilarities.

Both the reactions follow redox mechanisms consisting of two catalytic reactions: oxidation and reduction. Oxygen vacancy and lower-valent Cu ion both play important roles in the two reactions, but whichever is more important in the catalysis depends on the type of the reaction, temperature and catalytic systems.

Oxygen vacancy is more important for NO decomposition than that for NO + CO reaction. In NO + CO reaction, the activation of NO on Cu^+ is important over $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ below 400°C and $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ at 350–550°C. Over $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ above 400°C, oxygen vacancy and mobility of lattice oxygen become more important.

As shown by the measured results of steady state and “initial” activity for NO decomposition [15], NO molecule can be activated even at lower temperature region (200–500°C). It means

that the former half catalytic cycle, i.e., the reduction (activation) of NO to NO^- can proceed at lower temperature (Eq. (1)). However, the latter half catalytic cycle, i.e., the regeneration of active center (Eq. (2)) is difficult. In the NO decomposition reaction, the regeneration of the active center occurs by the thermal desorption of oxygen, while in the NO + CO reaction, it occurs by the reduction with CO. This is the reason why reaction temperature of NO + CO reaction is lower by about 500°C than NO decomposition.

4. Summary

In this study, two systems of mixed oxides $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 1.0$) and $\text{La}_{2-x}\text{Th}_x\text{CuO}_{4\pm\lambda}$ ($0.0 \leq x \leq 0.4$) with K_2NiF_4 structure by varying x values were prepared and the average valence of Cu ions and oxygen nonstoichiometry could be successively controlled by the substitution level of Sr and Th. The catalytic behaviors of these catalysts in the reactions of direct decomposition of NO and its reduction by CO were investigated. The activity measurements demonstrated that Cu-based mixed oxides with K_2NiF_4 structure are active catalysts for the reaction of NO + CO. The results of MS-TPD for NO or (NO + CO) indicate that the adsorption of NO is very important for the decomposition of NO and its reduction by CO. The redox-type catalytic mechanism of the reactions for NO decomposition and NO + CO over these oxide catalysts were proposed and the variation of activity and reaction mechanism could be explained by the types and concentration of defects (oxygen vacancy and valence state of Cu).

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