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Layered La-Ba-Cu mixed oxides with perovskite structure as catalyst for NO reduction by CO

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Abstract The mixed oxides, including $LaBa_2Cu_3O_7$, $LaBaCu_2O_5$, $La_4BaCu_5O_{12}$ with perovskite structure, were prepared. The catalysts were characterized by means of chemical analysis, XRD, H_2-TPR. It was found that their structures were layered ABO_3 perovskite structure and they were the active catalysts for the NO reduction by CO. The existance of Cu^{3+} is an important factor to give the catalysts a high activity for the NO reduction by CO.

Keywords: Cu-based mixed oxide, layered ABO_3 structure, NO reduction by CO.

NITROGEN oxides (NO_x) are serious pollutants in the earth's atmosphere in the sense that they are the sources of the acid rain. The development of efficient and simple processes for NO removal is an important problem, and many catalyst-systems have been investigated. Among them, the most interesting ones were the perovskite-type mixed oxides and Cu-based zeolites[1, 2]. ABO_3 oxides ($A = Ln$, $B = Cr$, Mn, Fe, Co, Ni) have been investigated as such or base oxides in multicomponent perovskites for NO reduction by CO[3]. In reference $LaCuO_3$ have not been successfully synthesized, the structures of Cu-based mixed oxides as catalysts are A_2BO_4-type, except the superconductor $YBa_2Cu_3O_7$, the structure of which is three-layered ABO_3-type. In this paper we prepared three types of La-Ba-Cu mixed oxides, whose structures are all layered ABO_3-type. We also studied their activity as catalysts for NO reduction by CO, and found that they have very high activity. Besides, the probable reaction mechanism has been proposed.

1 Experimental

For the preparation of samples and the analysis of the valence of Cu ion refer to refs. [4, 5].

The reaction was carried out in a conventional fixed-bed flow system. A quartz reactor of 6 mm i.d. was used by feeding a gas mixture of NO (7.5×10^{-3}), CO (8.0×10^{-3}) and He (balance) at a flow rate of 33.6 cm^3/min over 0.2 g catalyst. The gas composition was analyzed before and after the reaction by an in-line gas chromatograph (Pye panchromatograph) using molecular sieve 5 A column for NO, N_2 and CO, Porapak Q column for CO_2, N_2O respectively. All experimental data were taken after ca. 1—2 h on stream at each temperature while the catalytic reaction practically reached a steady state. TPR of H_2 was treated at 850℃ for 1 h in oxygen and cooled to room temperature at the same atmosphere. Finally the sample was heated at a rate of

20℃/min in the gas of $H_2$5% + $N_2$95% for recording the TPR spectra.

2 Results and discussion

2.1 Structure and chemical component

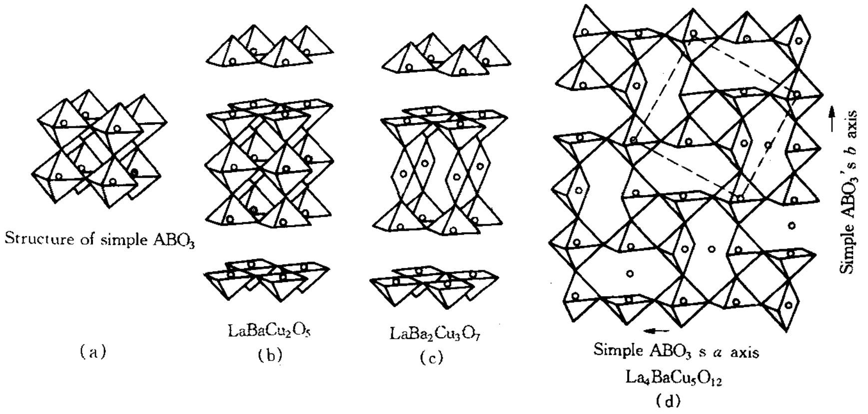
The phase analysis results for the layered cuprates $LaBaCu_2O_5$, $LaBa_2Cu_3O_7$, $La_4BaCu_5O_{12}$ by XRD showed that they are all single-phase with tetragonal perovskite structures and also showed that the atoms are displaced from their ideal positions in the cubic cell, owing to the presence of disordered oxygen vacancies. The average valence states of Cu in samples that were measured by chemical analysis, and the crystal cell parameters are listed in table 1.

From table 1 the average valence of Cu ions of $LaBaCu_2O_5$ and $LaBa_2Cu_3O_7$ is similar, but that of $La_4BaCu_5O_{12}$ is higher than them. This is different with the change of average valence state of B ions in the general $A_xA'_{1-x}BO_3$ perovskite-like mixed oxides. Khan proposed[6] that the structure is made of two "element-like" fundamental compounds $BaCu^{2+}O_2$ and $LaCu^{3+}O_3$. Both $LaCu^{3+}O_3$ and $BaCu^{2+}O_2$ are structurally unstable, but the existence of $BaCu^{2+}O_2$ can make $LaCu^{3+}O_3$ stable while $BaCu^{2+}O_2$ can exist stably in the structure only in the situation that the concentration of Ba is small. So the average valent state of Cu ions of $La_4BaCu_5O_{12}$ is far higher than others.

Table 1 The valence of Cu ion and structure data of $La_{1-x}Ba_xCuO_{3-\lambda}$

	La/Ba ratio (rel. to 1 Cu)	Cu^{3+} content (%)	Average valence of Cu	Crystal	Cell parameter
				a(Å)	c(Å)
$LaBa_2Cu_3O_7$	0.17	13.7	2.14	3.910	12.033
$LaBaCu_2O_5$	0.50	12.9	2.13	3.924	11.643
$La_4BaCu_5O_{12}$	0.80	21.8	2.22	8.653	3.863

The studies of the superconductor showed that the copper can exist as Cu^{1+}, Cu^{2+} or Cu^{3+} in the structure of layered ABO_3, and they can take octahedral (CuO_6), pyramidal (CuO_5) or square plane (CuO_4) coordination with oxygen[7]. So the Cu-based mixed oxides can have different structures, different valence of Cu ion(figure 1[8]).



(a) (b) (c) (d)

Fig. 1. Schematic comparison of structures of three samples and simple ABO_3.

In fig. 1 (a) is the structure of simple ABO_3-type mixed oxide. Its crystal cell parameter has a relationship of $a = b = c = a_p$. In contrast, we can find the structures of $LaBaCu_2O_5$ and $LaBa_2Cu_3O_7$ are both 3-layered ABO_3-type. We also can find the evidence from table 1. Their crystal cell parameters have the relationship $a = b = a_p$, $c = 3a_p$. The crystal cell parameter of $La_4BaCu_5O_{12}$ differs from others. Its relationship is $a = b = \sqrt{5}a_p$, $c = a_p$. Its structure is 5-layered ABO_3-type in the a and b axes of the simple ABO_3-type.

2.2 Activity to NO reduction by CO

The catalytic activity for NO + CO was measured as function of reaction temperature. Temperature rose from room temperature to 300℃, keeping the reaction for 1—2 h or more to achieve steady activity data, and then dropping from 300 to 140℃ at 20℃ intervals. The results are shown in fig. 2. In the process of rising reaction temperature, the activity of the catalyst increased monotonously with rising temperature. When the reaction was carried out at 300℃, the activity of catalyst is very high. The conversion of NO is above 90%. The most active one is $La_4BaCu_5O_{12}$, with its conversion of NO being already 88% at 240℃. It is the best result about this type of catalyst and reaction in the references. During the reaction, we observed that there was a little N_2O among products besides N_2 and CO_2, but its yield was only about 5% at 300℃, so the selectivity of catalysts is also good.

Figure 3 shows the H_2-TPR curves of three samples. There are two reduction peaks on the TPR curves of all samples. The corresponding temperatures are about 350℃ and 600—700℃ after samples were reduced. It was discovered that the colour of all samples changed from black to red. The XPS results do not clearly show that Cu ion was reduced to Cu_2O or metal Cu. The reduction could be divided into two steps: the first step corresponds to the reduction of $Cu^{3+} \rightarrow Cu^{2+}O$ referring to the first peak on the H_2-TPR curve; the second corresponds to $Cu^{2+} \rightarrow Cu_2O$ or $Cu^{2+} \rightarrow Cu$ referring to the second peak. Fig. 4 shows the relation between the conversion of NO at 240℃ and the area of the first peaks on the H_2-TPR curve. We discover that the existence of Cu^{3+} is an important factor to make the catalyst highly active for NO reduction by CO. A tentative mechanism of NO reduction by CO over layered perovskite structure oxides is proposed as follows:

$$Cu^{3+} - O^{=} - Cu^{3+} + CO \rightarrow Cu^{2+} - \square - Cu^{2+} + CO_2$$

$$Cu^{2+} - \square - Cu^{2+} \rightarrow Cu^{3+} - \boxed{e} - Cu^{2+}$$

$$Cu^{3+} - \boxed{e} - Cu^{2+} + NO \rightarrow Cu^{3+} - NO^{-} - Cu^{2+}$$

$$Cu^{3+} - NO^{-} - Cu^{2+} \rightarrow Cu^{3+} - O^{=} - Cu^{3+} + 1/2N_2$$

Here the notation of $Cu^{3+} - \boxed{e}$ has been generally described as an F-center.

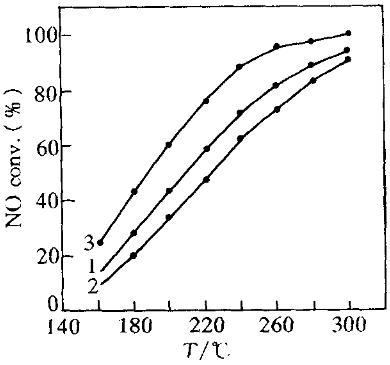


Fig. 2. Conversion of NO vs. reaction temperature. 1, $LaBa_2Cu_3O_7$; 2, $LaBaCu_2O_5$; 3, $La_4BaCu_5O_{12}$.

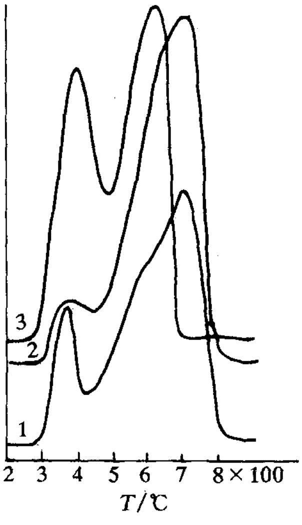


Fig. 3. H_2-TPR curves of $La_{1-x}Ba_xCuO_{3-\lambda}$. 1, $LaBa_2Cu_3O_7$; 2, $LaBaCu_2O_5$; 3, $La_4BaCu_5O_{12}$.

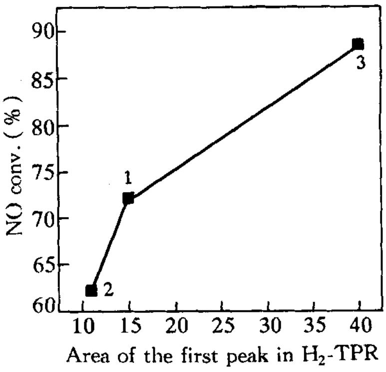


Fig. 4. Conversion of NO vs. the first peaks on the TPR curves. 1, $LaBa_2Cu_3O_7$; 2, $LaBaCu_2O_5$; 3, $La_4BaCu_5O_{12}$.

2.3 The role of Ba ion in the catalyst

In our laboratory we also prepared the perovskite-like La-Sr-Cu oxides and La-Th-Cu oxides with A_2BO_4 structure. We found that their activities for NO reduction by CO were much poorer at 300℃ than La-Ba-Cu mixed oxides and their activities became good until 500℃. We also found that their structure was K_2NiF_4-type. In our system, Ba ion takes the Sr(Th)'s place, the structure changes to layered ABO_3-tyep. Maybe this is a reason of the high activity. Another reason may be the existence of $BaCuO_2$