Oxidative Dehydrogenation of Ethane over Lanthanum-Substituted Layered Complex Bismuth Chloride Oxide Catalysts

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(Received June 6, 1997; CL-970432)

By the replacement of bismuth ion by lanthanum ion in the cation-oxygen sheet of $SrBi_3O_4Cl_3$ catalyst having a layer structure, c value of the lattice decreased clearly, making the cation-oxygen sheet and the chlorine sheet closer, and the catalytic activity increased prominently for the oxidative dehydrogenation of ethane. The activity increase can be attributed to the enhanced oxidation ability of the cation-oxygen sheet by the introduction of La.

Many studies have shown that substantial amounts of ethene can be produced effectively in the oxidative coupling of methane over chlorine-containing catalysts.[1-7] One of the influence of chlorine in the catalysts seems to be on the conversion of ethane to ethene. Recently, we have investigated a series of layered bismuth chloride oxide catalysts for the oxidative dehydrogenation of ethane to ethene. The extremely high selectivity to ethene even at high ethane conversions is the characteristic point of this catalyst system compared to other halogen-free oxide catalyst systems.[8-10] In our previous papers,[3-7] we found that the catalytic oxidation performance of the metal chloride oxides strongly depends on the environment of chloride ion in the structure, and it is likely that a radical state of surface structural chlorine is involved in the ethane activation. To generate such species effectively, promoting the oxidation ability of the cation-oxygen sheet of bismuth chloride oxide catalyst seems to be very important. For this purpose, we investigated replacement effects of lanthanum ion in the cation-oxygen sheet of $SrBi_3O_4Cl_3$ on the oxidative dehydrogenation of ethane.

The fundamental catalyst studied in the present work has the chemical composition of $SrBi_3O_4Cl_3$ with a layer structure (space group I4/mmm, a =3.933 Å, c =26.986 Å), where the Bi^{3+} and Sr^{2+} ions occupy the same site forming the cation-oxygen sheet and chlorine forms the single and the double sheets (X1X2 type). In the cation-oxygen sheet, it is possible to substitute Bi^{3+} for other cations having large ionic radius, such as rare-earth element, La. The preparative condition for the catalysts is summarized in Table 1. All chemicals used for the preparation were commercially available reagent grade except LaOCl which was prepared by solid-state reaction between La_2O_3 and $LaCl_3$ at 1123 K for 20 h in air. The catalysts were prepared by heating stoichiometric mixtures (see Table 1) of the relevant halides and oxides at 900 °C in alumina crucibles. X-ray powder diffractometry (Cu Kα radiation) was used to ascertain phase purity and to determine sub-unit cell dimensions. The catalytic reaction was carried out in a fixed-bed reactor. The amount of catalyst used was 2g, which were diluted by quartz sands (catalyst : quartz =1:1, weight ratio), the feed composition was C_2H_6: O_2:N_2=1:4:15 (total flow rate: 50ml/min), and the reaction temperature was 640 °C. Reaction products were separated with Porapak Q, T, and Molecular sieve 13X, using a gas chromatograph equipped with a thermal conductivity detector.

The general composition of the catalysts is given by $SrBi_{3-n}La_nO_4Cl_3$, and the catalyst compositions synthesized and tested here are listed in Table 1. The nominal compositions were determined from the amount of the components used in the preparation of the catalysts. With the addition of lanthanum ion to a certain degree ($n \leq 0.75$), it was confirmed by X-ray diffrac-

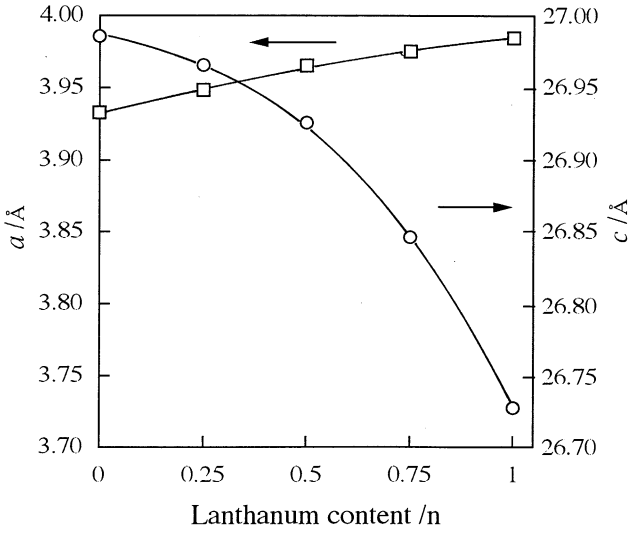

Figure 1. Variation of lattice parameters in the $SrBi_{3-n}La_nO_4Cl_3$ catalysts.(□ :value of a , O:value of c .)

Table 1. Preparative condition and surface area of lanthanum-substituted bismuth strontium chloride oxide catalysts

No.	Catalyst Composition	Reactant	Structural Phase	Surface Area ($m^2 \cdot g^{-1}$)
1.	$SrBi_3O_4Cl_3$	$1SrCl_2+1Bi_2O_3+1BiOCl$	X1X2	0.2
2.	$SrBi_{2.75}La_{0.25}O_4Cl_3$	$1SrCl_2+1Bi_2O_3+0.75BiOCl+0.25LaOCl$	X1X2	0.3
3.	$SrBi_{2.5}La_{0.5}O_4Cl_3$	$1SrCl_2+1Bi_2O_3+0.5BiOCl+0.5LaOCl$	X1X2	0.4
4.	$SrBi_{2.25}La_{0.75}O_4Cl_3$	$1SrCl_2+1Bi_2O_3+0.25BiOCl+0.75LaOCl$	X1X2	0.3
5.	$SrBi_2LaO_4Cl_3$	$1SrCl_2+1Bi_2O_3+1LaOCl$	X1X2+UP [a]	nd [b]

a: Unknown phase.
b: Not determined.

tion that the catalysts remained in the X1X2 type structure. As pointed out by the result of Table 1, the catalysts were monophasic in the X1X2 structure when n=0, 0.25, 0.5 and 0.75, but as the n increased to 1, another crystalline phase was observed besides the X1X2 structure. The lattice parameter varied regularly with the content of lanthanum. Variations of the sub-unit cell parameters derived from XRD analyses are shown in Figure 1. As increasing the lanthanum content, *a* value along the sheet in the sub-unit cell increased from 3.933 Å (n=0) to 3.985 Å (n=1). Although the *a* value change was very faint because of the slightly larger ionic radius of lanthanum ion than that of bismuth, it is clear that the lanthanum ion invaded into the cation-oxygen sheet by the substitution. On the other hand, the value of *c* representing thickness of the layer structure decreased prominently from 26.986 Å to 26.727 Å. Such the preferential variation in the sub-unit cell parameters is very interesting. The result indicates that the contact of the cation-oxygen sheet and the chlorine sheet became closer, which is because that the thickness of the double chlorine sheet decreases due to the 9-coordination character of La.[11]

The incorporation effect of lanthanum on the oxidative dehydrogenation of ethane is shown in Figure 2. In order to complete the substitution, the catalysts were calcined at 900 °C. Therefore the catalysts were well-sintered and their surface areas were less than 0.5 $m^2 \cdot g^{-1}$ (BET method) as shown in Table 1. All the catalysts exhibited good performance for the formation of ethene. The $SrBi_3O_4Cl_3$ catalyst showed a high selectivity for ethene formation, but the ethane conversion was low. The introduction of lanthanum ion by n=0.25 have given rise no

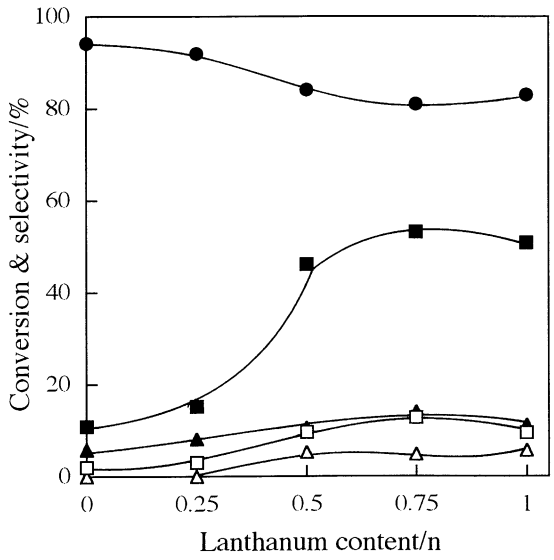

Figure 2. Oxidative dehydrogenation of ethane over $SrBi_{3-n}La_nO_4Cl_3$ catalysts.(□:Conversion of oxygen, ■: Conversion of ethane, ●:Selectivity to ethene, △:Selectivity to CO, ▲:Selectivity to CO_2.)

obvious increase of the catalytic activity. When n=0.5, the conversion of ethane increased markedly. Figure 2 shows that the $SrBi_{2.25}La_{0.75}O_4Cl_3$ catalyst is about 4 times more active than the $SrBi_3O_4Cl_3$ catalyst for the reaction of ethane and a maximum ethane conversion was observed at n=0.75. The selectivity to ethene slightly decreased with the increase of the La content. It is clear from the above results that the replacement by lanthanum promotes the oxidation activity of $SrBi_3O_4Cl_3$ catalyst without diminishing the selectivity for the oxidative dehydrogenation of ethane.

As obtained in Table 1, the surface area of the catalysts has not changed obviously with the addition of the lanthanum ions. It is, therefore, apparent that the surface area of catalyst is not a important factor in the increased ethane conversion. As reported earlier,[5] the catalytic performance strongly depends on the environment of chloride ion in the structure. It was also suggested that the surface chlorine having radical character has to be generated repeatedly in the catalytic oxidation cycle by the prompt action of oxygen species from molecular oxygen activated on the cation-oxygen sheet. We tentatively consider that the increase of the activity by the addition of lanthanum ion in the cation-oxygen sheet results from the increase of the active oxygen species on the lanthanum-containing cation-oxygen sheet for the chlorine radical regeneration, because molecular oxygen can be activated much easily on the lanthanum sites. The lanthanum-substituted $SrBi_{3-n}La_nO_4Cl_3$ catalysts were slightly less selective than the $SrBi_3O_4Cl_3$ catalyst at any ethane conversions, which might be due to that ethene is oxidized progressively to CO and CO_2 by the active oxygen formed on the lanthanum-containing cation-oxygen sheet of the catalyst.

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