Catalysis Letters 44 (1997) 241–245

Highly selective oxidative dehydrogenation of ethane to ethene over layered complex metal chloride oxide catalysts

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Received 24 January 1997; accepted 29 January 1997

Complex metal chloride oxides consisting of bismuth, alkali, alkaline earth, chlorine, and oxygen, were synthesized, characterized structurally, and tested as catalysts for the oxidative dehydrogenation of ethane to ethene with molecular oxygen. The catalysts were prepared by high-temperature solid-state reaction of appropriate mixtures of bismuth chloride oxide, bismuth oxide, alkali chloride, and alkaline earth chloride. We found that the catalysts containing strontium as the alkaline earth constituent and potassium as the alkali constituent were highly active and selective for the oxidative dehydrogenation of ethane. $SrBi_3O_4Cl_3$, which is a fundamental phase of the catalysts, was characterized by single and double chlorine sheets in its layer structure. The catalyst having the composition of $KSr_2Bi_3O_4Cl_6$ showed an extremely high ethene selectivity, more than 90%, even under high oxygen partial pressure conditions and at high molar ratios of oxygen to ethane, and gave 70% yield of ethene at 640°C under an optimized feed gas composition.

Keywords: bismuth chloride oxide catalyst, layer structure, ethane, oxidative dehydrogenation, ethene

1. Introduction

In our previous papers [1–5], we have shown that there is a potentially very large family of oxidative coupling catalysts for methane, all containing bismuth halide oxides and exhibiting a layered structure. We had demonstrated that these catalysts exhibited high catalytic activities for the oxidation of methane, high selectivities to C_2-hydrocarbons, and particularly very high ratio of ethene to ethane. After these findings, we have proposed a reaction mechanism in which the C–H bond of methane is broken radically on surface Cl sites surrounded structurally by metal oxygen sheets, since the activity strongly depended on the type of layer structures and the content of chlorine sheets [6]. The high selectivity seems to be due to high efficiency of the surface chlorine for radical formation and to low reaction probability of the formed methyl radical with oxygen because of high surface concentration of chlorine and of extremely low surface area. From this point of view, one can easily expect very high selectivity to ethene in the oxidative dehydrogenation of ethane as well. In fact, one of the authors has already reported the high selectivity of a complex bismuth chloride oxide for this reaction [7]. We thus further attempted to develop more highly active catalysts based on complex bismuth chloride oxides in order to demonstrate the pronounced selectivity of complex bismuth chloride oxide catalysts for alkane oxidative activation. We then found catalysts based on $SrBi_3O_4Cl_3$ phase, the catalytic performance of which is reported here.

2. Experimental

The prepared catalysts are listed in table 1. All chemicals used for the preparation are commercially available reagent grade. The catalysts were prepared by heating desired mixtures of the relevant chloride, bismuth oxide, and BiClO at 700°C in alumina crucibles for 20 h. The resulting yellow powder was ground before use. Since all the catalysts were synthesized by solid-state reactions at high temperature, the surface area of every sample was less than 1 $m^2\ g^{-1}$ (BET method, N_2 adsorption at liquid N_2 temperature). X-ray powder diffractometry (Cu $K\alpha$ radiation) was used to ascertain phase purity, to determine sub-unit cell dimensions, and to investigate phase change before and after reaction. The RIETAN was used to simulate the structure of the catalysts [8].

The catalytic reaction was carried out in a fixed-bed reactor. The reactor was constructed of a high-purity alumina tube having 11 mm i.d. Two single-walled sealed alumina tubes (6 mm o.d.) were inserted from both sides of the reactor, which were for reducing the empty volumes. One of the sealed ends which was inserted into the catalyst zone served as a thermowell for measuring the reaction temperature, while the other was for supporting the catalysts in the reactor. The catalysts were loaded in the middle part of the reactor, and the amount of catalyst used, unless indicated otherwise, was 4 g, which were diluted by quartz sand (catalyst : quartz sand = 1 : 1 (wt)). All catalytic reactions were carried out at an atmospheric pressure. A feed gas (ethane pressure of 20 kPa, oxygen pressure of 10 kPa) was introduced to the reactor with N_2 as a diluent (total flow rate: 50 ml/min), unless otherwise noted.

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Table 1
Catalytic performance of layered metal chloride oxides in the oxidative dehydrogenation of ethane at 660°C [a]

Catalyst	Conversion (%)		Selectivity (%)		
	C_2H_6	O_2	C_2H_4	CO	CO_2
$PbBi_3O_4Cl_3$ [b]	51.4	81.5	87.6	4.3	8.1
$SrBi_3O_4Cl_3$	19.5	31.7	89.4	2.5	8.1
$SrBi_3O_4Cl_3 + SrCl_2$	35.2	53.3	89.3	3.7	7.0
$SrBi_3O_4Cl_3 + 2SrCl_2$	43.8	67.3	89.5	4.3	6.2
$SrBi_3O_4Cl_3 + KCl$	35.7	42.7	95.5	1.3	3.2
$SrBi_3O_4Cl_3 + SrCl_2 + KCl$	45.3	64.2	92.2	2.8	5.0
$SrBi_3O_4Cl_3 + 1.5SrCl_2 + KCl$	37.4	46.5	95.4	1.2	3.4
$SrBi_3O_4Cl_3 + SrCl_2 + LiCl$	42.2	54.7	94.1	2.5	3.4
$SrBi_3O_4Cl_3 + SrCl_2 + NaCl$	41.2	53.8	94.7	2.4	2.9

[a] Data were collected after 6 h reaction ([b] data after 1 h reaction). Reaction conditions: catalyst weight 4 g, total flow rate = 50 ml/min, $C_2H_6 : O_2 : N_2 = 10 : 5 : 35$.

It was confirmed that no reaction took place when the reaction was carried out without oxygen or the catalyst. Reaction products were separated with Porapak Q and T and Molecular 13X, and were analyzed using a gas chromatograph equipped with a thermal conductivity detector. N_2 in the feed was used as an internal standard for the calculation of conversion and selectivity. The conversion and selectivities were calculated based on the reacted ethane and the carbon and oxygen balances were nearly 100%.

3. Results and discussion

3.1. Structure of $SrBi_3O_4Cl_3$ phase

The layered bismuth halide oxides generally consist of cation–oxygen layers (cationic) associated with the tetragonal PbO structure, alternating with single or multiple sheets (anionic) of halide ions. The halide layer may also accommodate additional cations in their interstices. Large cations often occur in place of Bi^{3+} and play the same structural role. Since intergrowths are possible at the sub-unit-cell level of single or multiple halogen sheets with the common cation–oxygen layers, there are many structural variants in bismuth halide oxides.

The material, $SrBi_3O_4Cl_3$, which is the fundamental phase of the present catalyst system, is one of the variants of the bismuth halide oxide family and was first reported by Sillen, who assigned this phase X1X2 type on the basis of the XRD data [9]. Schematic structures of the X1X2 type are illustrated in figure 1. The X1X2 type is simply a structurally combined system of X1 having single sheets of chlorine and X2 having double chlorine sheets. In order to confirm the $SrBi_3O_4Cl_3$ material to be X1X2 type phase, we simulated the XRD pattern of the $SrBi_3O_4Cl_3$ material on the basis of the following structural parameters; space group I4/mmm, lattice parameter $a_0 = b_0 = 3.939$ Å, $c_0 = 27.026$ Å. The observed and simulated patterns were compared in figure 2, which clearly reveals that the $SrBi_3O_4Cl_3$ material has X1X2 type structure.

3.2. Oxidative dehydrogenation of ethane over various metal chloride oxide catalysts

BiOCl is a key compound in the synthesis of a variety of metal chloride oxides and the material is constructed by the combination of double chloride ion layer $[Cl_2]^{2-}$ and the metal oxygen layer $[Bi_2O_2]^{2+}$. As previously reported [3] BiOCl is highly active for the methane oxidative coupling reaction and yields ethene selectively and effectively although the structural stability is fairly poor. In accordance with this previous finding, the

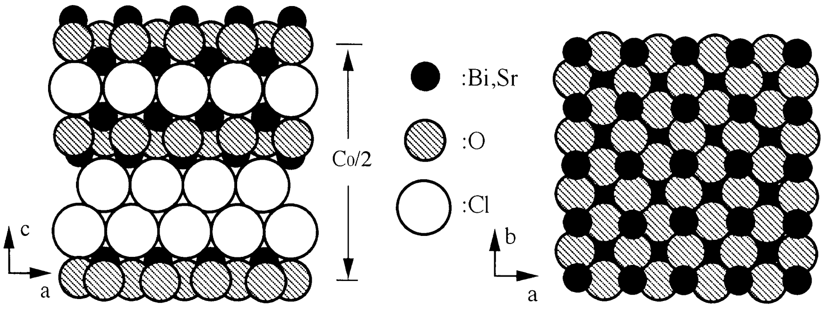

Figure 1. Schematic illustration of X1X2 type structure of $SrBi_3O_4Cl_3$.

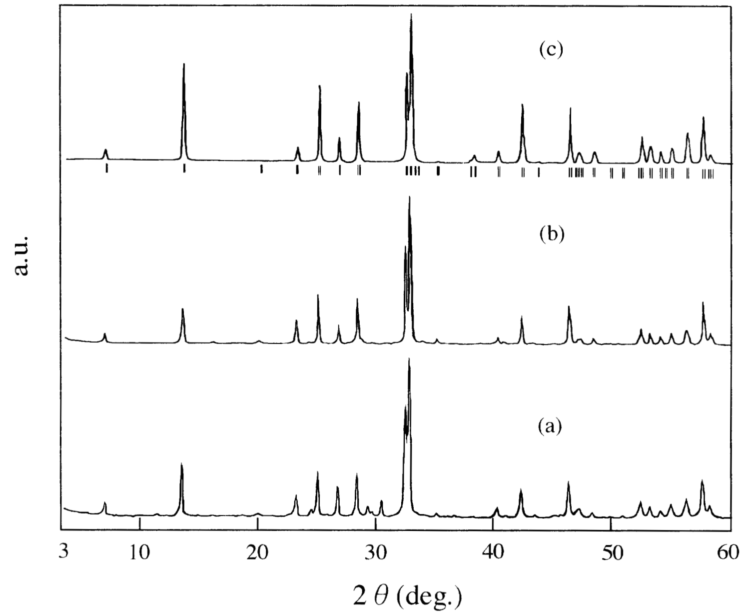

Figure 2. X-ray diffractions. (a) Observed for $SrBi_3O_4Cl_3$, (b) observed for $KSr_2Bi_3O_4Cl_6$, and (c) simulated for the X1X2 type material having the composition $SrBi_3O_4Cl_3$.

BiOCl catalyst also showed a high activity and selectivity in the ethane oxidation to ethene, and a structural decomposition of BiOCl phase was again observed in this reaction. On the other hand, $LiBi_3O_4Cl_2$ and $NaBi_3O_4Cl_2$ catalysts, so-called X1 type phase, which consist of single cation–oxygen layers alternating with single sheets of chloride ions, showed moderate catalytic performance for the ethane conversion and selectivity to ethene but extremely high durability for the reaction.

We then tried to test the X1X2 type material because it can be expected that the X2 type phase could be stabilized by the structural combination with highly stable X1 type unit without diminishing the high catalytic performance of the X2 type. We synthesized $PbBi_3O_4Cl_3$ and $SrBi_3O_4Cl_3$ as catalysts and their catalytic performances are summarized in table 1. The $PbBi_3O_4Cl_3$ catalyst showed very high activity for the ethane oxidation and good selectivity as expected from the activity of the X2 type structural unit. The catalyst was, however, very unstable under the catalytic oxidation conditions, so that the activity decreased readily accompanying with the structure decomposition in a short reaction period. The reason for this is not known at present. On the other hand, the $SrBi_3O_4Cl_3$ catalyst exhibits good catalytic performance for the oxidative dehydrogenation of ethane. Particularly important is the extremely high structural stability of this catalyst: There was no detectable change in the X1X2 structure of the catalyst, by XRD measurements, before and after the reaction.

By taking the above-shown catalytic performance and stability of each catalyst into account, we selected the $SrBi_3O_4Cl_3$ catalyst for further modification to improve these catalytic properties. We tried to modify the $SrBi_3O_4Cl_3$ catalyst by the addition of $SrCl_2$ and alkali chlorides since it can be expected that excess addition of such metal chlorides can minimize the formation of amorphous metal oxides or other phase impurities which causes lower selectivities in the catalytic reaction. The catalytic performance data are listed in table 1. These materials seem to be multi-phasic since excess amounts of metal chlorides were added, although very weak diffractions ascribable to strontium chloride were observed only. It was confirmed that neither $SrCl_2$ nor alkali chloride show any activity for the ethane oxidation themselves. In the case of the catalysts containing excess $SrCl_2$ only, the main X1X2 type crystalline structure was formed with a very little amount of the additional phase ascribed to crystalline $SrCl_2$. In the case of the catalysts containing both $SrCl_2$ and alkali chloride, on the other hand, no additional phases (like $SrCl_2$, LiCl, NaCl, or KCl) were detectable except the basic X1X2 phase. These phase analysis data suggest that the excess $SrCl_2$ and alkali chloride (LiCl, NaCl, KCl) are distributed on the surface of $SrBi_3O_4Cl_3$ in thin film form. All the catalysts exhibited high performance for the formation of ethene in the oxidative dehydrogenation of ethane, as can seen in table 1. In particular, the extremely high catalytic performance was attained using the catalysts prepared by adding $SrCl_2$ and alkali chloride (LiCl, NaCl, KCl). The ethane conversion increased from 19.5 to 42%, and the ethylene selectivity also increased from 89.4 to 94.1% for the $LiSr_2Bi_3O_4Cl_6$ catalyst. With the addition of $SrCl_2$ and KCl or $SrCl_2$ and NaCl, the same promotion effect was obtained. Highest among these modified catalysts is the $KSr_2Bi_3O_4Cl_6$ catalyst, in which 92% selectivity for ethene is achieved at 45% ethane conversion. The extremely high selectivity even at high ethane conversions is the characteristic feature of this catalyst system compared to other halogen-free oxide catalyst systems [10–14].

Structural stability of the $LiSr_2Bi_3O_4Cl_6$, $NaSr_2Bi_3O_4Cl_6$, and $KSr_2Bi_3O_4Cl_6$ catalysts were also investigated by XRD. After reaction for 6 h, a little of the new crystalline phase appeared in the $LiSr_2Bi_3O_4Cl_6$ and $NaSr_2Bi_3O_4Cl_6$ catalysts, although the main X1X2 structure still persisted. According to our earlier research [1], this additionally formed phase was identified as X1X3 phase. In contrast to these catalyst, there was no detectable phase change in the $KSr_2Bi_3O_4Cl_6$ catalyst before and after the reaction, showing a very high structural stability. Summarizing the above results, the $KSr_2Bi_3O_4Cl_6$ catalyst has the highest catalytic performance for the oxidative dehydrogenation of ethane and structural stability.

3.3. Partial pressure dependency

With the aim of optimizing the reaction conditions, we conducted the ethane oxidative dehydrogenation over the $KSr_2Bi_3O_4Cl_6$ catalyst under different partial pressures of ethane and oxygen at 640°C. The results are shown in figures 3 and 4, respectively. The ethane conversion decreased with increasing the partial pressure of ethane. The important point is again the selectivity; the ethene selectivity is quite high at high partial pressures of ethane, simply because the conversion is low, but is still more than 80% even at very high conversion levels. This clearly indicates that the catalyst is intrinsically selective for oxidative dehydrogenation and is not very effective for oxygen insertion to intermediate products. Then, we applied a high oxygen pressure condition, as shown in figure 4. In fact, the oxygen pressure has a positive effect for ethane oxidative dehydrogenation: the higher the oxygen pressure, the higher the ethane conversion, without decreasing the ethene selectivity drastically.

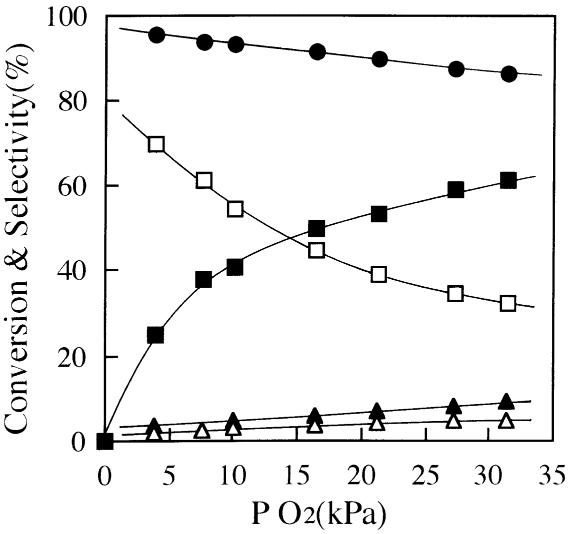

Figure 4. Partal pressure effect of oxygen on the oxidative dehydrogenation of ethane at 640°C over the the $KSr_2Bi_3O_4Cl_6$ catalyst (2 g). P(ethane) = 4.6 kPa(const.). Symbols as in figure 3.

3.4. Effect of reaction temperature

Under a chosen reaction condition ($C_2H_6/O_2/N_2 = 1/4/15$) on the basis of the above observation, the effect of the reaction temperature on the ethane conversion and the ethene selectivity was studied using the $KSr_2Bi_3O_4Cl_6$ catalyst. Results are shown in figure 5. The reaction began at about 560°C. 23% ethane conversion and 98% ethene selectivity were attained at 580°C. The ethane conversion raised with increasing the reac-

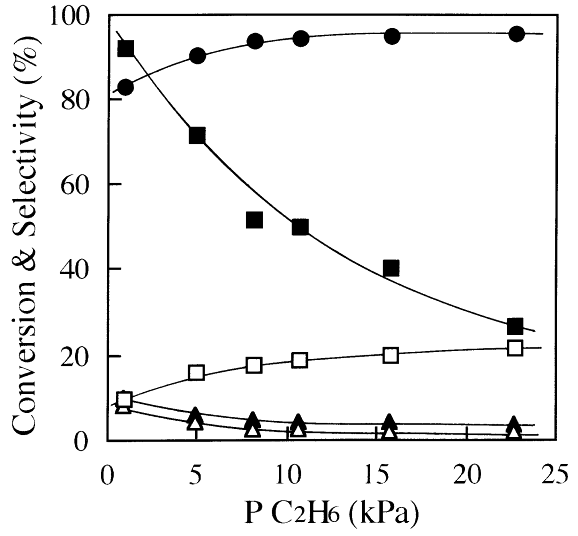

Figure 3. Partal pressure effect of ethane on the oxidative dehydrogenation of ethane at 640°C over the $KSr_2Bi_3O_4Cl_6$ catalyst (2 g). $P(O_2)$ = 20.3 kPa(const.). Conversion of ethane (■) and oxygen (□), and selectivities to ethene, (●), CO_2 (▲), and CO (△).

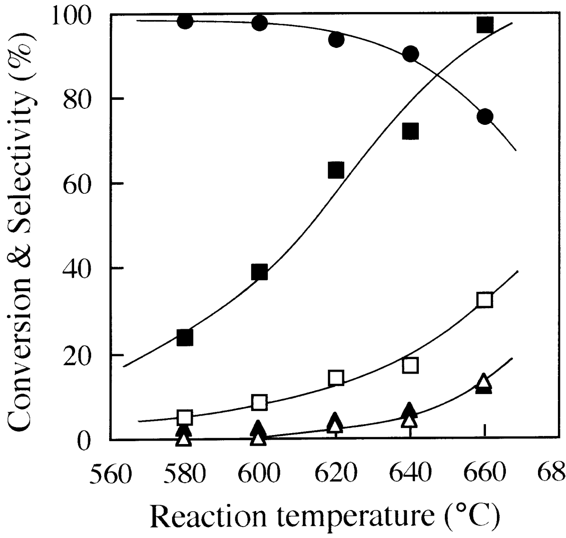

Figure 5. Oxidative dehydrogenation of ethane over the $KSr_2Bi_3O_4Cl_6$ catalyst (2 g). Feed composition: $C_2H_6/O_2/N_2 = 1/4/15$, total flow rate: 50 ml min^{-1}. Symbols as in figure 3.

tion temperature, and then at 660°C, ethane was almost completely converted, at which temperature the ethene selectivity decreased to 76%. It should also be noted from the result in figure 5 that the extent of selectivity decrease is differently depending on the temperature range between 580 and 660°C. The ethane conversion increased to 72% from 25% and the selectivity for ethene slightly decreased to 90% from 98% in the range of 580–620°C. However, when the reaction temperature was up to 640°C, the selectivity decreased to 75% rapidly. We consider that above 640°C a non-catalytic oxidation occurs in the present reaction condition, since at low temperature (< 600°C) carbon dioxide was the sole by-product, whereas at higher reaction temperature the selectivity toward carbon monoxide increased and began higher than that to carbon dioxide (> 650°C). Ethene seems to convert into carbon monoxide in a gas-phase reaction at a high temperature in the presence of molecular oxygen [15].

3.5. Durability of the catalytic performance

At the initial stage of the reaction, the activity is reduced to some extent and then the conversion and selectivity become stable for more than 6 h. Although this catalyst was found to be stable and not quickly deactivated within the limited testing time, in accordance with that there was no detectable phase change before and after the reaction, the catalyst surface seems to be partly damaged because we observed the evolution of a small amount of hydrogen chloride from the catalyst into the outlet. Such surface damage is not detectable by XRD measurement but will obviously cause deactivation in a further stage. Therefore we are now trying to design many integrated materials on the basis of the layered metal chloride oxide structure in order to develop high-performance alkane oxidation catalysts since halogen-containing catalysts are reported highly effective for alkane oxidative dehydrogenation in many cases [16–18].

4. Conclusion

A series of layered bismuth strontium chloride oxide catalysts was investigated for the oxidative dehydrogenation of ethane. The materials that have layer sequences given by $[SrBi_3O_4][Cl_2][Cl]$, where Bi^{3+} and Sr^{2+} ions occupy the same site, showed good activity and selectivity for ethene. The addition of $SrCl_2$ and alkali chloride enhanced the catalytic performance of $SrBi_3O_4Cl_3$. 70% yield of ethene has been attained in the oxidative dehydrogenation of ethane at 640°C over the catalyst having a composition of $KSr_2Bi_3O_4Cl_6$ and the crystalline structure was unchanged.

Acknowledgement

Part of this work has been carried out as a research project of The Japan Petroleum Institute commissioned by the Petroleum Energy Center with the subsidy of the Ministry of International Trade and Industry.

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