Complex Metal Halide Oxides (1): Bismuth Chloride Oxides Having Various Structures as Catalysts for Oxidative Coupling of Methane

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Bismuth chloride oxides having four distinct structural types and lanthanum-substituted bismuth chloride oxides were tested as catalysts for the oxidative coupling reaction of methane. Their catalytic properties were compared in relation with their structure. BiClO, which has a layer structure with a double chlorine sheet, so-called X_2 type structure, was most active for the methane conversion but less selective for the formation of C_2 hydrocarbons. The catalyst structure was quite unstable, so that the activity decreased markedly until reaching a constant level, while the selectivity increased. During these changes of the catalytic performance BiClO changed by liberating chlorine to $Bi_{24}Cl_{10}O_{31}$, the so-called Arppe's phase, and then finally to a highly stable and selective Bi_3ClO_4 phase which was constructed with a double metal oxygen sheet and a single chlorine sheet. When more chlorine was removed from Bi_3ClO_4, $Bi_{12}Cl_2O_{17}$, which has quintuple oxide sheets and a single chlorine sheet, was formed as an intermediate phase to be less selective for C_2 hydrocarbons and ultimately Bi_2O_3 was formed with no chlorine, to be nonselective. The substitution of Bi in Bi_3ClO_4 for La caused a decrease of the C_2 selectivity, whereas the $Bi_{3-x}La_xClO_4$ catalysts treated with NaCl brought about a maximum yield of C_2 hydrocarbons.

The functionalizations of alkanes by catalytic oxidation processes with molecular oxygen have recently been of a great interest in solid-state catalysis chemistry.[1—3] Among them the catalytic oxidative coupling of methane has been extensively investigated and many catalysts and processes have been reported so far.[4,5] In our previous papers,[6—9] we have shown that there is a potentially very large family of oxidative coupling catalysts of methane, all containing bismuth and all derived, in one structural form or another, from bismuth chloride oxide, BiClO, having a layered structure. Most of the catalysts have been shown to be monophasic solids and exhibited high catalytic activity for the oxidation of methane and high selectivity to C_2-hydrocarbons.

The bismuth-based halide oxides constitute a large family of layered compounds,[10—19] all of which crystallize into structures consisting of cation-oxygen layer sheets associated with the tetragonal PbO structure, alternating with single or multiple sheets of halide ions. The halide layers may accommodate additional cations in their interstices, if necessary. Large cations such as Na^+ and Ca^{2+} often occur in place of Bi^{3+} and play the same structural role. These are the so-called Sillen phases, X_1, X_2, X_3, and combinations of them, which are regulated with the thickness of halide layer but the metal oxygen layer $[Me_2O_2]^{2+}$ is invariant.

There are reverse structures to the above phases;[14—16] the composition in those structures is regulated by the thicknesses of the metal oxygen layer sheets with an invariant single halide layer. This layered structure consists of the single chlorine sheet and double metal oxygen sheet having a composition, $[Me_3O_4]^+$. The thickness of the metal oxygen sheet is changeable. Thus a highly multiple metal oxygen sheet is possible. The structure of the multiple metal oxygen sheet itself is fluorite, and when no chlorine is contained in layer lattices, the resulting material is bismuth oxide having fluorite structure.

Although there are many structural variants in the complex metal halide oxides, all of which have attractive layer type structures, as just mentioned above, these metal halide oxides have never been investigated systematically as solid-state catalysts. We wish here to report our results on the distinct structures and pronounced catalytic performance of various complex metal halide oxides. The principal focus of the present work is the relationship between structure and catalytic performance. Thus several distinct types of bismuth-based chloride oxides were synthesized and their catalytic performances in the methane oxidation coupling were compared.

Experimental

Catalyst Preparation and Characterization. All monophasic crystalline catalysts tested here were prepared by solid-state reaction, except Bi_2O_3 which was a commercial product. All were used as catalysts after calcination in air at 1073 K. The preparative conditions for each catalyst are summarized in Tables 1 and 2. All chemicals used for the preparation are commercially available reagent grade except LaClO, which was prepared by solid-state reaction between La_2O_3 and $LaCl_3$ at 1123 K for 20 h in air. The desired catalysts were prepared in the main by heating an exactly or closely stoichiometric mixture of relevant halides (NaCl and $BiCl_3$), Bi_2O_3, La_2O_3, and BiClO at the desired temperatures in alumina crucibles or in sealed silica tubes. BiClO was prepared by calcination of $BiCl_3$ in air at 923 K for 20 h, followed by reheating at 1123 K for 20 h in a sealed silica tube. The Arppe's phase sample, $Bi_{24}Cl_{10}O_{31}$, was synthesized with the mixture (1 : 1) of BiClO and Bi_2O_3 at 1173 K for 5 h in a sealed silica tube. The starting mixture consists of Bi_2O_3 in a slightly higher amount than the ideal composition required for the Arppe's phase. The resulting sample normally contains a small amount of free Bi_2O_3, although most of the excess Bi_2O_3 reacted with the silica tube during the preparation. The Bi_3ClO_4 sample was prepared from exactly the same mixture for the Arppe's phase synthesis but under the different heating conditions; a lower temperature, 1073 K and a longer heating duration, 10 h in a sealed silica tube. The lanthanum-substituted Bi_3ClO_4 samples, $Bi_{3-x}La_xClO_4$ (x=0.75—2), were obtained by heat-treating the desired mixtures of BiClO, La_2O_3, and Bi_2O_3 under the same condition as the Arppe's phase because the higher temperature is necessary for the formation of the solid-solution. The $Bi_{12}Cl_2O_{17}$ sample was synthesized with the mixture (2 : 5) of BiClO and Bi_2O_3 at 923 K for 70 h in a sealed silica tube. The $Bi_{3-x}La_xClO_4$–NaCl (x=0—2) samples were crystallized from the mixture consisting of desired amounts of BiClO, La_2O_3, Bi_2O_3, and NaCl at 1173 K for 20 h in an alumina crucible. All the materials were sintered and well-crystallized powders. All the synthesized materials were ground in an agate motor before use as catalysts and all their surface areas were less than 1 $m^2 g^{-1}$. 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 use. More structural analyses were carried out with SAED patterns and HREM images of the samples. In general, monophasic materials were subjected to catalytic testing.

Catalytic Testing. Measurements of the catalytic performance of the bismuth-based chloride oxides in the oxidative coupling of methane were carried out using a fixed-bed reactor with a conventional gas flow system under atmospheric pressure. The reactor was made of highly pure alumina: 35 cm length and 11 mm inner diameter. Two one-side sealed alumina tubes (6 mm o.d.) were inserted from the two sides of the reactor; the both were for reducing the empty volumes and the one of which the sealed end was inserted into the catalyst zone served as a thermowell for measuring the reaction temperature, while the other was also for supporting the catalysts in the reactor. The powder catalysts (1 g) diluted with 5 g of quartz chips (total volume; 6 ml) were loaded in the middle of the reactor. A reactant mixture of methane (99.9% research grade, 20 kPa) and oxygen (10 kPa) was introduced to the reactor (993 K) with nitrogen as a diluent (SV at STP; 50 $m g^{-1} min^{-1}$). The catalyst zone was heated up to 993 K at the rate of 10 $K min^{-1}$ in the flow of the reactant mixture. After the reactor temperature reached 993 K, the catalytic performance data were collected as a

Table 1. Preparative Conditions and Lattice Parameters of Various Bismuth Chloride Oxides

Catalyst	Preparative conditions				Structural informations					
		Temp	Soak	Crucible	Thickness of	Thickness of	Sub-unit cell parameters			
Composition	Reactant	K	time/h		Cl sheet	Me–O sheet	a (Å)	b (Å)	c (Å)	Crystal group
BiClO	$BiCl_3$	923	20	Alumina						
		1123	20	Sealed quartz	2	1	3.89	—	7.37	$P4/mmm$
$Bi_{24}Cl_{10}O_{31}$	$1Bi_2O_3+1BiClO$	1173	5	Sealed quartz	1	1, 2	29.4	3.97	9.99	
							$\beta=88.77$			Monoclinic
Bi_3ClO_4	$1Bi_2O_3+1BiClO$	1073	10	Sealed quartz	1	2	5.69	5.64	18.56	
							$\beta=91.5$			Momoclinic
$Bi_{12}Cl_2O_{17}$	$5Bi_2O_3+2BiClO$	923	70	Sealed quartz	1	5	3.83	—	35.46	$P4/mmm$
Bi_2O_3	Bi_2O_3	1073	5	Alumina	0	∞	5.52	—	—	Fluorite

Table 2. Preparative Conditions and Lattice Parameters of Lanthanum-Substituted Bismuth Chloride Oxides Which Are Isotypic to Bi_3ClO_4 Consisting of Double Oxygen Sheet and Single Chlorine Sheet

Catalyst		Preparative conditions				Structural informations (Space group: $P4/mmm$)	
			Temp	Soak	Crucible	Sub-unit cell parameters	
Composition	x	Reactant	K	time/h		a (Å)	c (Å)
$Bi_{3-x}La_xClO_4$		$(1-x/2)BiO_2O_3+1BiClO$					
	0.75	$+x/2La_2O_3$	1173	5	Sealed quartz	3.98	9.12
	1.0					4.03	9.04
	1.5					3.98	9.12
	2.0					4.04	9.23
$Bi_{3-x}La_xClO_4$		$(1-x/2)Bi_2O_3+1BiClO$					
NaCl	0.5	$+x/2La_2O_3+1NaCl$	1173	20	Alumina	3.98	9.23
	1.0					4.03	9.04
	1.5					3.98	9.12
	2.0					4.04	9.23

function of time on stream. The reaction products were analyzed with Porapak T (3 m) and Parapak Q (1.5 m) at 313 K for CO_2, C_2H_4, and C_2H_6, and Molecular sieve 13X (2 m) at 303 K for O_2, N_2, CO, and CH_4 in a gas chromatograph (TCD). The selectivity and yield of the products were calculated on the basis of the carbon number of methane reacted. In all the catalytic runs, the carbon balances and oxygen balances were more than 98%. It was confirmed that no reaction took place without catalysts under the above reaction conditions.

Results

Catalytic Performance of BiClO, $Bi_{24}Cl_{10}O_{31}$ (Arppe's Phase), and Bi_3ClO_4. The above three distinct types of bismuth-based chloride oxides, having different structures, were synthesized and then tested for the oxidative coupling of methane. The XRD patterns of these fresh samples are shown in Fig. 1 (a), (b), and (c), respectively and the subunit cell parameters derived from the XRD analyses and their reasonable space groups or crystal groups are listed in Table 1. Their schematic structures are also represented in Fig. 2. First, BiClO is a well-known X_2 type phase and in its structure single cation-oxygen sheets alternate with double chlorine sheets (Fig. 2 (a)). The BiClO catalyst showed a high catalytic activity for the methane conversion as shown in Fig. 3 (a). This catalyst was, however, rather unstable; the catalytic activity decreased rapidly with the progressive liberation of chlorine from the lattice (1.2 mmol HCl from 1 g BiClO during 6 h reaction),[9] whereas the selectivity to C_2-hydrocarbons increased from 35% at the beginning to 56% at the steady state. Obviously, this lack of long-term stability of the most chlorine containing solid[20—22] catalysts that normally display high performance is a potentially grave disadvantage. Nevertheless, from the structural point of view, there are some interesting features.

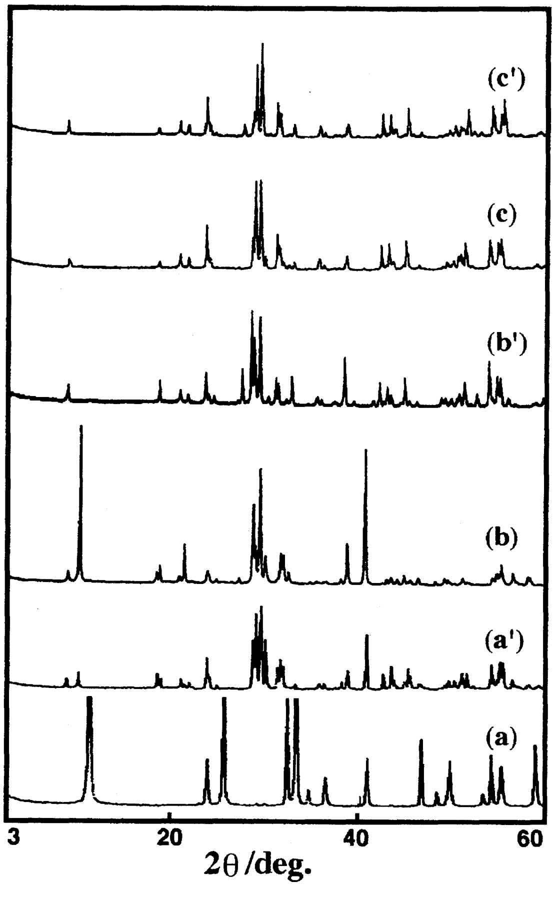

Fig. 1. XRD patterns (Cu$K\alpha$ radiation) of (a) fresh BiClO, (a′) used BiClO catalyst, (b) fresh Arppe's phase, $Bi_{24}Cl_{10}O_{31}$, (b′) $Bi_{24}Cl_{10}O_{31}$ after use for the reaction, (c) fresh Bi_3ClO_4 and (c′) its used sample.

As can be seen Fig. 1 (a′) which shows the XRD patterns of the BiClO catalyst used, the layer structure with the double chlorine sheet was completely destroyed after the catalysis for 6 h because of the remarkable liberation of chlorine. The observed resulting phases were $Bi_{24}Cl_{10}O_{31}$, the so-called Arppe's phase and Bi_3ClO_4; the former is regarded as chlorine deficient and oxygen sufficient analogue of X_2 and in the proposed structure a part of the chloride ion sheet originally presented in the X_2 type is replaced with oxide layer, forming zigzag staking sheets (Fig. 2 (b)) and the latter is closely related to the Arppe's structure but without the zigzag staking sheet, that is, the structure is a simple layered structure consisting of the single chlorine sheet and double metal oxygen sheet having a composition: $[Bi_3O_4]^+$ (Fig. 2 (c)).[15]

We then tested activities of these mono-phasic catalysts prepared separately by the solid-state reaction. Figure 3 (b) and (c) exhibit the catalytic performance changes of the prepared $Bi_{24}Cl_{10}O_{31}$ and Bi_3ClO_4 as a function of time on stream, respectively, and their phase changes during the reaction were also examined by XRD as shown in Fig. 1 (b), (b′), (c), and (c′). Phase formations were ascertained by the comparison of the observed XRD patterns with JCPDS data. The HREM study for the Bi_3ClO_4 sample also clearly proved the presence of double metal oxygen sheets. The $Bi_{24}Cl_{10}O_{31}$ catalyst showed a relatively high activity for methane conversion at the beginning of the reaction; this activity only slightly decreased with the reaction time. The selectivity was little changed. During the methane oxidation, the Arppe's phase completely disappeared and, in place of it, the Bi_3ClO_4 phase appeared as a sole phase. On the other hand, the Bi_3ClO_4 catalyst appeared to be rather poor active but superior in the stability, since no phase change was formed during the reaction (Fig. 1 (c), (c′)).

From the two facts that the initial activity and selectivity of the prepared $Bi_{24}Cl_{10}O_{31}$ catalyst are almost comparable to those of the BiClO catalyst just after the initial rapid deactivation and that the $Bi_{24}Cl_{10}O_{31}$ phase is not so stable under the reaction condition because of easy disappearance of this phase, while the resulting Bi_3ClO_4 phase is quite stable, it is obvious that $Bi_{24}Cl_{10}O_{31}$ is the intermediate phase of the phase transformation of BiClO during the deactivation of the activity. The phase transformation can be written as follows:

$$24\mathrm{BiClO}\ (+7\mathrm{O}, -14\mathrm{Cl}) \longrightarrow \mathrm{Bi_{24}Cl_{10}O_{31}} \qquad (1)$$

$$\mathrm{Bi_{24}Cl_{10}O_{31}}\ (+\mathrm{O}, -2\mathrm{Cl}) \longrightarrow 8\mathrm{Bi_3ClO_4}. \qquad (2)$$

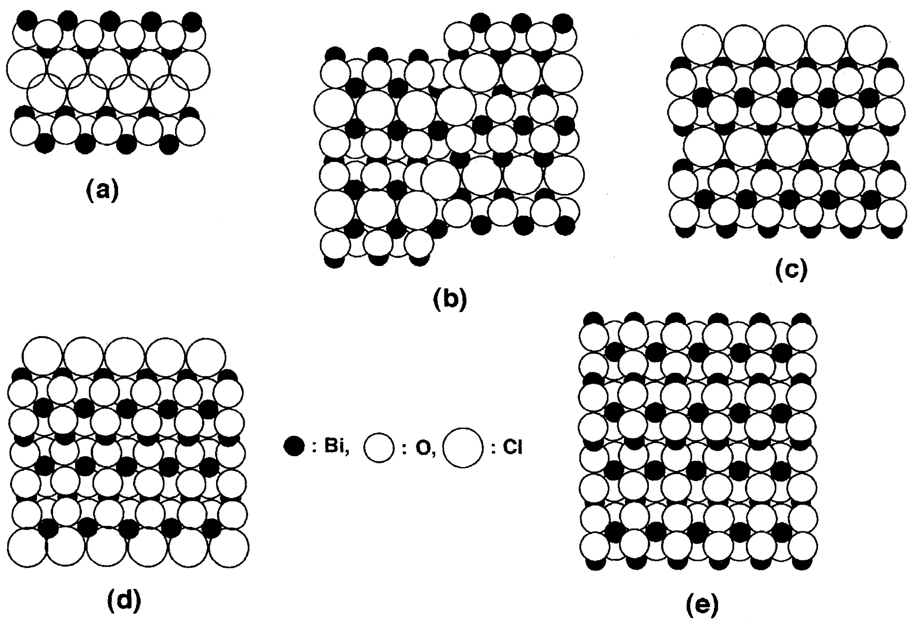

Fig. 2. Schematic representation of four distinct types of bismuth chloride oxides, (a) BiClO, (b) $Bi_{24}Cl_{10}O_{31}$, (c) Bi_3ClO_4, (d) $Bi_{12}Cl_2O_{17}$, and (e) Bi_2O_3.

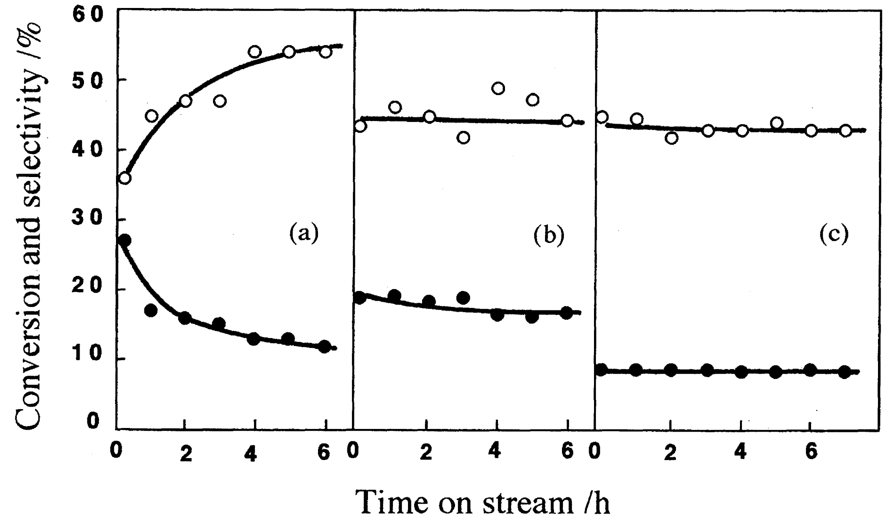

Fig. 3. Oxidative coupling of methane over (a) BiClO, (b) $Bi_{24}Cl_{10}O_{31}$, and (c) Bi_3ClO_4 catalysts (1 g) at 993 K. Methane conversion (●) and selectivity to C_2-hydrocarbons (○) are plotted as the function of time on stream.

Although this phase transformation can take place even by heat treatment in an air, the transformation during the catalytic reaction was faster than that in air only. Therefore, it seems likely that the water that was formed by the catalytic oxidation of methane involves or accelerates the phase transformation; presumably surface hydrogens produced in the course of the reaction normally react with the surface oxygen species to give water, but can also react with the surface chlorine anions to form liberating hydrogen chloride, resulting in the rapid phase transformation. Simply, the results indicate that the stability of the bismuth chloride oxides is strongly dependent on their structures. Nevertheless, taking into account that the formed hydrogen chloride is not involved in the activation of methane,[23] we can speculate that the reactivity or stability of lattice chloride anion, which may change with the structural layer unit of bismuth chloride oxides, is strongly concerned with the catalytic activity and selectivity in the oxidative coupling of methane.

A Comparison between Catalytic Performance and Structure of Bismuth Chloride Oxides. We thus further compared four distinct types of bismuth chloride oxides and Bi_2O_3 in terms of the conversion of methane, selectivity to C_2-compounds, and ethylene/ethane ratio in Table 3. For BiClO and $Bi_{24}Cl_{10}O_{31}$ catalysts both values obtained at the beginning and at the steady state of the reaction are listed because of their activity decreases. The $Bi_{12}Cl_2O_{17}$ structure is closely related to that of Bi_3ClO_4; both have a single chlorine sheet but different thickness of oxide sheet. If we take

Table 3. Catalytic Performance of Bismuth Chloride Oxides Having Different Structures in the Oxidative Coupling of Methane

Catalyst	Thickness of Cl sheet	Thickness of Me–O sheet		Observed phase	Conversion/% Methane	Conversion/% O_2	Selectivity to C_2-compounds/%	Yield of C_2-compounds/%	Ethylene / Ethane
BiClO	2	1	Fresh	BiClO	29.8	90.6	35.3	10.5	13
			Used	$Bi_{24}Cl_{10}O_{31}+Bi_3ClO_4$	11.7	20.6	55.5	6.5	2.3
$Bi_{24}Cl_{10}O_{31}$	1	1, 2	Fresh	$Bi_{24}Cl_{10}O_{31}$	19.1	40.5	43.4	8.3	2.7
			Used	Bi_3ClO_4	16.3	33.8	48.9	8.0	2.0
Bi_3ClO_4	1	2	Fresh	Bi_3ClO_4	8.6	17.0	45.6	3.9	1.0
$Bi_{12}Cl_2O_{17}$	1	5	Fresh	$Bi_{12}Cl_2O_{17}$	8.4	18.0	39.6	3.3	0.6
Bi_2O_3	1	∞	Fresh	Bi_2O_3	6.7	22.7	18.4	1.2	0.4

the X_1 type consisting of single chlorine and oxide sheets as a reference, the thickness of metal oxygen sheet along c direction of sub-unit cell increases stepwise by about 2.9 Å with increasing the thickness of the sheet;[24] the thickness was calculated to be $n=5$ as in Table 3 from the observed c_0 value. The ideal structure of this sample is shown in Fig. 2 (d). In this sample, however, a superstructure was observed from the SAED patterns and HREM images, 2-fold along the [110] and 16-fold along [−110] directions of the sub-unit cell. Therefore, the real unit cell will be orthorhombic with $a\approx5.76$, $b\approx45.3$, and $c\approx35.7$ Å. Although the basic structure is of shown in Fig. 2 (d), more structural investigations are obviously needed to confirm the structure. Full details will be reported elsewhere. The last sample, Bi_2O_3, has a fluorite structure, where no chlorine sheet exists, as shown in Fig. 2 (e), so that we can consider this sample to be a extreme of bismuth chloride oxide catalysts. These two catalysts were highly stable, showing constant catalytic performance as one can easily expect on the basis of the above-mentioned results, and therefore no XRD patterns were illustrated in Fig. 1.

Although it is not easy to evaluate precisely the intrinsic activity of the BiClO catalyst because of the rapid deactivation as described above, it is reasonable that this catalyst is characterized as the highest in activity for the methane conversion, yield of C_2-hydrocarbons, and ethylene/ethane ratio. The evaluation of the selectivity of this catalyst is still not achievable because of large differences in the conversions for each catalyst. The same situation also happens on the Arppe's phase catalyst but more easily the initial values can be taken for the intrinsic activity of this catalyst.

Before proceeding to the activity comparison, we have to refer to the activity differences between the same phase catalysts. The results showen in Fig. 3 appear to have an discrepancy: Since the sample of the Arppe's phase catalyst used had the Bi_3ClO_4 phase as ascertained by XRD, the catalytic activity at the steady state should coincide with the activity of the prepared Bi_3ClO_4 catalyst and also should have activity similar to that of the BiClO catalyst at the 6 h reaction. However the facts were different; the activity of the Bi_3ClO_4 phase from the Arppe's phase was higher than those of the others. The activity difference would be explicable as follows: Because all well-sintered samples had surface areas less than 1 $m^2\,g^{-1}$, it is not meaningful to compare the catalysts on the basis of surface area. As mentioned earlier, the phase transformation of BiClO takes place with the liberation of large portions of chloride anions from the lattice (Eq. 1). Since this transformation occurs very quickly when the catalytic reaction takes place at the same time, the surface must be seriously damaged, causing the drastic deactivation. This might be the reason why the activity difference has been observed even though the deactivated sample had the active Arppe's phase with the Bi_3ClO_4 phase. On the other hand, the reason for the activity of the Arppe's phase catalyst at the steady state being higher than that of the prepared Bi_3ClO_4 catalyst seems to be that the Arppe's phase is intrisically highly active due to its zigzag structure and its active surface may be retained even after the bulk phase change during the catalysis because of small amounts of chloride anion liberation (Eq. 2). There has been observed a small difference in the selectivity to C_2-hydrocarbons for each of three catalysts as shown in Fig. 3, so that no discussion may be necessary about it.

Now, we can compare the catalytic performance of the bismuth chloride oxides in the oxidative coupling of methane. The catalysts were in the following orders in terms of the activity (methane conversion, selectivity, and ethylene/ethane ratio),

$$\mathrm{BiClO} > \mathrm{Bi_{24}Cl_{10}O_{31}} > \mathrm{Bi_3ClO_4} > \mathrm{Bi_{12}Cl_2O_{17}} > \mathrm{Bi_2O_3},$$

the chlorine content (or in the reverse of the thickness of oxide sheet),

$$\mathrm{BiClO} > \mathrm{Bi_{24}Cl_{10}O_{31}} \geq \mathrm{Bi_3ClO_4} > \mathrm{Bi_{12}Cl_2O_{17}} > \mathrm{Bi_2O_3},$$

and the stability

$$\mathrm{BiClO} < \mathrm{Bi_{24}Cl_{10}O_{31}} < \mathrm{Bi_3ClO_4} = \mathrm{Bi_{12}Cl_2O_{17}} = \mathrm{Bi_2O_3}.$$

The observed parallelism between the orders of the thickness of oxide sheet and the stability is quite natural, because structural deformations in which chlorine is liberated from the lattice inevitably are easier for a sample having thinner oxide sheets. In other words, the bond strength between chlorine anion and metal oxygen sheet might be weaker when the catalyst consists of thinner oxide sheets. We therefore think that such weakly bound chlorine in the layered lattice is highly reactive for activating methane. An apparent relationship can be seen between the orders of the thickness of oxide sheet and the catalytic activity; the higher the thickness is, the lower the catalytic activity is. Naturally, the absolute content of chlorine in the catalyst must directly correlate with the activity in this case. This discussion does not exclude involvement of oxide sheet in the course of methane oxidation. There still exists a possibility that the lattice oxygen close to chlorine anion is active. However, since the selectivity decreased with increasing thickness of oxide sheet without apparent changes in the conversion ($Bi_3ClO_4 > Bi_{12}Cl_2O_{17} > Bi_2O_3$, as shown in Table 3), the oxide sheet is also active for methane oxidation but should be less selective, therefore diluting the effect of the selective oxidation site of the chlorine sheet.

Consequently, the catalytic methane oxidation can take place both over the metal oxygen sheet and over the chlorine sheet, the former mainly promoting nonselective oxidation and the latter effectively catalyzing the oxidative coupling of methane. Since gas-phase chlorine species, if any, which are liberated from the catalysts do not contribute for the reaction, the key to the effectiveness of the catalysts reported here may be linked to the formation of methyl radicals over the lattice chlorine anions which are supported by the coexistence of bismuth oxygen sheet in the structures. We believe that both sheets are interconnected by electron transfer at the reaction temperature.

Catalytic Performance of Lanthanum-Substituted Bismuth Chloride Oxides. In order to clarify the nonselective character of metal oxygen sheet more, we synthesized the lathanum-substituted bismuth chloride oxides having Bi_3ClO_4 structure. Since we knew that LaClO and La_2O_3 showed high activity and high stability but poor selectivity, the substituted catalysts are expected to be highly active but very poor in selectivity, if La in metal oxygen sheet is involved in the catalytic oxidation of methane. Moreover, to modify the catalytic performance of the lanthanum-substituted Bi_3ClO_4 type catalysts, we prepared NaCl-added catalysts. The catalytic performances of all the lanthanum-substituted bismuth chloride oxides are summarized in Table 4 in terms of the conversion of methane, selectivity to C_2-hydrocarbons, and ethylene/ethane ratio.

The lanthanum-substituted Bi_3ClO_4 type catalysts are proved by the XRD analyses to be a solid solution between Bi_3ClO_4 and La_3ClO_4,[15] possessing varied lattice parameters, although the lattice parameter varied randomly with the content of La (Table 2). As shown in Table 4, all the lanthanum-substituted Bi_3ClO_4 type catalysts containing various amounts of La were highly active for methane oxidation, but less selective, in spite of the existence of the chlorine sheets. This is due to that the catalytic performances of these systems are strongly dominated by the highly active, nonselective character of La. One would think that the result came from the fact that La may diminish or alter the selective character of the chlorine sheet. However, this can not explain the high oxidation activity without taking the intrinsic high oxidation ability of La into account. This result, accordingly, would be strong evidence for the involvement of the metal oxygen sheets as nonselective sites for the methane oxidation.

Before concluding the nonselective character of the metal oxygen sheets, we must consider the effect of exposed crystalline planes on the activity. All the catalyst samples tested here except Bi_2O_3 were plate-like crystalline, due to the crystal habit of the layered structure. Since the single chlorine sheet can not be formed on the (001) plane surface because of easy liberation of chlorine, chlorine can appear on the side plane only. On the other hand, oxygen can expose both on the (001) plane and its side plane. In order to investigate which plane mainly provides nonselective character, we added NaCl to the lanthanum-substituted Bi_3ClO_4 type catalysts, since we can expect that a thin film of NaCl can form on the (001) plane, in analogy with the structure of X_3 type bismuth chloride oxide, where a triple chlorine sheet containing Na^+ is one of the building units.[7] All thus prepared samples gave exactly the same XRD patterns as the simple lanthanum-substituted Bi_3ClO_4 samples. Although the XRD data can not prove the formation of a NaCl thin layer, no detection of any addition phase by XRD may support this positively. The NaCl added catalyst revealed half activity for methane conversion of the non-added catalysts (note that catalyst weight was different in each case) and interestingly their activities were quite similar to that of the simple Bi_3ClO_4 catalyst (Table 3). More important is that all the NaCl added catalysts showed high selectivity. These results might be explained by assuming that the (001) plane is a major nonselective surface and the thin layer of NaCl covering the nonselective surface can be another active and

Table 4. Catalytic Performance of Lanthanum-Substituted Bismuth Chloride Oxides in the Oxidative Coupling of Methane

Catalyst		Conversion/%		Selectivity to	Yield of	Ethylene
Composition	x	Methane	O_2	C_2-compounds/%	C_2-compounds/%	Ethane
$Bi_{3-x}La_xClO_4$[a]						
	0.75	15.7	37.8	25.1	3.9	0.9
	1.0	15.5	41.9	29.3	4.5	0.8
	1.5	20.0	50.9	32.9	6.6	0.9
	2.0	31.1	87.6	21.5	6.7	0.9
$Bi_{3-x}La_xClO_4$						
NaCl[b]	0.5	14.6	26.1	56.1	8.2	1.9
	1.0	17.4	30.8	56.8	9.9	2.4
	1.5	25.2	39.4	67.3	17.0	3.9
	2.0	24.5	46.8	47.8	11.7	2.0

a) Catalyst weight, 1 g. b) Catalyst weight, 2 g.

selective site for methane oxidation. Table 4 also shows an interesting result that the C_2 yield has a maximum at $x=1.5$. This result obviously relates with the state of NaCl in the catalyst as well as the effect of La but we need more information about it before full discussion.

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