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A Comparison of the Catalytic Performance of the Lithium and Sodium Analogues of Bismuth Oxyhalides in the Oxidative Dimerization of Methane

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The lithium and sodium salts of four distinct types of complex bismuth oxychlorides having different structural layer units within the Sillenite family of solids have been employed as catalysts for the selective oxidation of methane. The catalytic performance strongly depends on the environment of chloride ion in the structure; and it is likely that a radical mechanism operates.

Many kinds of catalysts which are active for the oxidation of methane to higher hydrocarbons have already been reported in the patent and open literature.[1-7] Most of them are based on alkali, alkaline earth, or rare earth metal oxides, and are either promoted by metal ion or combined with other metal oxides. The structures of these catalysts are rather complicated and derived from one or other of the rock salt, perovskite or spinel families. It is no coincidence that these structural types are prominent since it is well known that they have the properties desired in present contexts: an ability to accommodate point defects, high thermal stability and the right degree of acid-base character.

The catalysts employed by us are complex layered oxyhalides based on or derived from the phases first identified by Sillen.[8] We have previously reported[9-12] that the layered bismuth oxyhalides constitute a new family of heterogeneous solid catalysts for the selective oxidation of methane to C_2 and higher hydrocarbons.

The bismuth oxyhalides constitute a large family of layered compounds,[8,12] all of which crystallize into structures consisting of cation-oxygen (anion) layers associated with the tetragonal PbO structure, alternating with single or multiple sheets of halide ions. The halide layers may also accommodate additional cations in their interstices. Large cations such as Na^+ and Ca^{2+} often occur in place of Bi^{3+} and play the same structural role as that ion.

The materials tested in this study are classified into four types, which are designated as the X_1, X_3, X_1X_3, and $X_1X_1X_3$ types(Fig. 1). Polycrystalline layered bismuth oxychlorides were prepared by heating the mixture of appropriate metal chlorides, metal oxides, and oxychlorides to the given temperature in an

Table 1. Preparative conditions and structural data

Reactant	Temp[a)] K	Formula	Type	c_0[b)] Å	%-age[c)] triple Cl layer
$1Bi_2O_3$ + 1BiOCl + 1LiCl	1073	$LiBi_3O_4Cl_2$	X_1	12.03	0
$1Bi_2O_3$ + 1BiOCl + 1LiCl + $2CaCl_2$[d)]	1173	$Li_3Ca_2Bi_9O_{12}Cl_{10}$	$X_1X_1X_3$	45.56	22.3
$1Bi_2O_3$ + 1BiOCl + 1LiCl + $2CaCl_2$[d)]	1073	$LiCaBi_3O_4Cl_4$	X_1X_3	16.64	50
$1Bi_2O_3$ + 1BiOCl + 1LiCl + $2CaCl_2$	873	$LiCa_2Bi_3O_4Cl_6$	X_3	21.29	100
$1Bi_2O_3$ + 1BiOCl + 1NaCl	1073	$NaBi_3O_4Cl_2$	X_1	12.13	0
$1Bi_2O_3$ + 1BiOCl + 1NaCl + $2CaCl_2$[d)]	1173	$Na_3Ca_2Bi_9O_{12}Cl_{10}$	$X_1X_1X_3$	46.60	22.3
$1Bi_2O_3$ + 1BiOCl + 1NaCl + $2CaCl_2$[d)]	1073	$NaCaBi_3O_4Cl_4$	X_1X_3	16.88	50
$1Bi_2O_3$ + 1BiOCl + 1NaCl + $2CaCl_2$	873	$NaCa_2Bi_3O_4Cl_6$	X_3	21.66	100

a) Soaking duration is 20 hours for all cases. b) The structure of every compound is tetragonal (space group ; I4/mmm, a_0= 3.90 Å). c) Number of triple Cl layer in unit cell/(number of triple + single Cl layer)x100.
d) Excess metal chlorides were washed out with a mixed solvent of acetone and water(10:1).

alumina crucible. The preparation conditions are listed in Table 1. All materials were sintered(surface area, less than 1 m^2/g, by BET) and well-crystallized(as ascertained by XRD analysis).

In the simplest layered bismuth oxychloride, the X_1 type, there are alternate stacking of cation and oxygen anion layer and single layers of chloride. In the X_3 type, the cation-oxygen sheets alternate with triple chlorine layers which contain Ca^{2+} ion in their interstices. X_1X_3 and $X_1X_1X_3$ types are new variants which we were the first to synthesize. Although the structures have not yet been completely solved, we know that they may be regarded as complex structure of X_1 and X_3 type, as shown in Fig. 1.

The catalytic activity and selectivity data pertaining to the solids reported here in the oxidation of methane are listed in Table 2. Activity tests were carried out using a fixed-bed reactor(quartz) with a conventional gas-flow system under atmospheric pressure. Products were analyzed by gas chromatography (Porapak T and Molecular sieve 13X) connected directly with the reaction flow system. The standard reaction conditions were as follows: reaction temperature, 993 K, partial pressure of methane, 20 kPa, CH_4/O_2=2, total flow rate, 50 $mL.min^{-1}$(nitrogen was used as a diluent), catalyst weight, 2 g.

All the various types of oxychlorides exhibit good performance for the formation of C_2-compounds in the oxidation of methane. Other products were CO and CO_2. But the X_3 type showed the highest activity in both sets (Table 2). The catalytic activity of this type of solid is, however, unstable, decaying quickly with reaction time. After prolonged reaction, the X_3 phase changes into $X_1X_1X_3$ and the resulting activity is the same as that of the $X_1X_1X_3$ type catalyst when freshly prepared. On the other hand, the other three types of catalyst showed highly stable activity for the conversion of methane (in contrast to the rather poor stability of the X_2 layer represented by BiOCl).

Clearly, the existence of the X_1 type layer unit in the oxychloride structure contributes to the high catalytic stability, even though the catalytic activity is

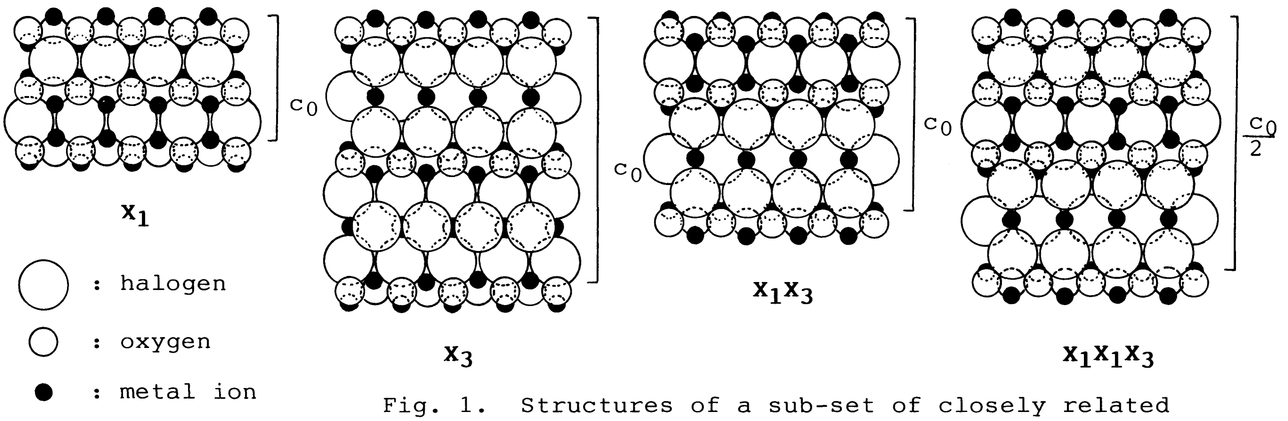

Fig. 1. Structures of a sub-set of closely related Sillen-type solids.

Table 2. Catalytic performance of the various structural types of bismuth oxychlorides in the oxidation of methane

Catalyst	Type	CH_4-conv. %	O_2-conv. %	C_2-sel. %	C_2-yield %	C_2H_4/C_2H_6
$LiBi_3O_4Cl_2$	X_1	15.6	35.5	62.9	9.8	2.1
$Li_3Ca_2Bi_9O_{12}Cl_{10}$	$X_1X_1X_3$	17.7	37.2	66.8	11.8	2.8
$LiCaBi_3O_4Cl_4$	X_1X_3	21.9	47.0	67.0	14.7	4.1
$LiCa_2Bi_3O_4Cl_6$	X_3	41.7	99.7	46.5	19.4	25.1
$NaBi_3O_4Cl_2$	X_1	13.2	24.2	56.6	7.2	2.0
$Na_3Ca_2Bi_9O_{12}Cl_{10}$	$X_1X_1X_3$	15.3	24.4	63.8	9.8	2.3
$NaCaBi_3O_4Cl_4$	X_1X_3	16.0	26.3	64.9	10.4	2.2
$NaCa_2Bi_3O_4Cl_6$	X_3	33.8	68.6	43.2	14.6	34.7

significantly impaired. The catalytic performance of the X_1X_3 and $X_1X_1X_3$ type of solid were superior among the various structural types. Their all-round catalytic performance seems to originate both from the activity endowed by the X_3 unit and from the intrinsic stability of the X_1 unit. The same trend is observed on the sub-set of both Li and Na-analogues. We find no prominent difference between the activities of these two sets, indicating that the influence of the chloride ion dominates over that of the alkali ion.

The above results reveal that the X_3 layer unit in the structure largely governs the catalytic activity, that the oxide layer is less influential, but that the state of chloride ion in the structure is also important. These conclusions are in line with the facts reported previously$^{9)}$ that Bi_2O_3 showed poor catalytic activity for both conversion and selectivity while BiOCl was highly active as a catalyst, and that, moreover, the catalytic performance of oxyhalides is strongly dependent upon the kind of halogen ion present in the structure. The indications recently elaborated leave little doubt that methyl radical production is favoured by the solid catalyst.$^{11-13)}$ In the case of oxychloride catalysts, chloride ion on the surface may play a role in the formation of methyl radical.

One possible preliminary step in the production of methyl redicals is the generation of neutral chlorine entities at the catalyst surface. This necessitates electron transfer from some of the chloride ions originally present there. On transition-metal halides, such transfer occurs at relatively low temperatures; but not, for obvious reasons, on alkali or alkaline earth chlorides. Ostensibly, the sodium and lithium salts of the bismuth oxyhalides, just like the LiCl/NiO catalysts reported by Otsuka,14) are capable of accommodating, in a manner that has yet to be clarified, electrons detached from surface halide ions. We know10,11) that some chlorine is lost to the gas phase from the bismuth oxychloride catalysts, and there is undoubtably some measure of homogeneous (gas phase) catalysis involved here.15) It is also possible, as Mims et al.16) have emphasized, that a surface oxygen is the key agent for the production of methyl radicals by abstraction of H from methane. It is conceivable that at the surfaces of the oxyhalides reported here, either an oxygen or chlorine atom, or both, could function in this way.

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