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Catalytic Activities of Layered Metal Chloride Oxides for the Dehydrohalogenation of *t*-Butyl Halides

Wataru UEDA,*,† Masato YAMAZAKI, and Yutaka MORIKAWA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227
† Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227

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Synopsis. Various metal chloride oxides having layered structures have been tested as catalysts for the dehydrohalogenation of *t*-butyl chloride and *t*-butyl bromide to form olefins and were found active for the reaction, depending on the metal constituents and the structure.

Metal chloride oxides construct a large family of layered compounds, all of which crystallize into structures consisiting of cation-oxygen layers having the tetragonal PbO structure alternating with single or multiple thickness sheets of halide ions. Numerous compounds of this family were synthesized by Sillen et al.,[1] and many more are reported by varing metal cation constituents, compositions, and stacking sequences of various thickness of halide layer and metal-oxygen layer.[2—7] In earlier papers we have shown that these layered compounds, all containing bismuth and all derived in one structural form or another from bismuth chloride oxides, are a potentially very large family of oxidative coupling catalysts of methane.[8—11]

It is supposed that layered halide oxides play key active phases in many more cases in catalysis involving the reactions of halogen-containing reactants and/or over halogen-containing catalysts. As in Fig. 1, where it is demonstrated by XRD measurements that a starting catalyst phase (La_2O_3) changes into a layered halide oxide (LaClO) during the catalytic dehydrohalogenation of alkyl halide, layered metal halide oxides, in fact, participate in catalysis. We, therefore, have been devoted to investigate the catalytic performance of monophasic layered halide oxides and the relationship between the structure and the catalytic performance.[10] In this paper we tested the catalytic performance of metal chloride oxides having various structures for the dehydrohalogenation of *t*-butyl chloride (TBC) or *t*-butyl bromide (TBB). Although many catalysts based on metal oxides and metal halides have been known active for the reaction,[12,13] none of these catalysts are structurally related to those described in this paper.

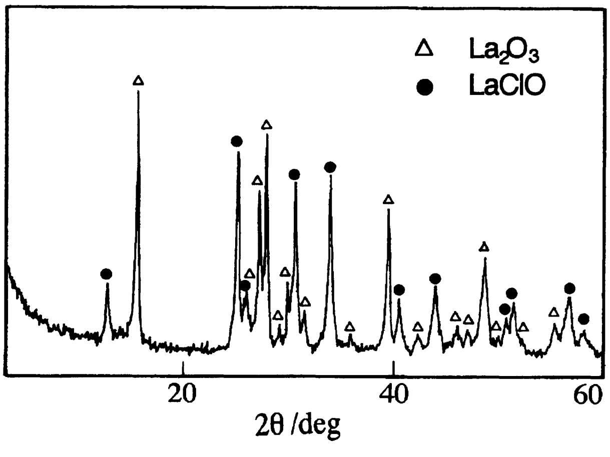

Fig. 1. Phase change of La_2O_3 catalyst during the dehydrochlorination of *s*-butyl chloride at 300°C under flow reaction conditions (chloride/N_2=1/4, total flow rate 75 ml min^{-1}). XRD pattern(Cu *K*α) was measured after the reaction for 2 h.

Experimental

Monophasic chloride oxides containing trivalent metal cation, MClO (M=Bi, Sb, V, Fe, and La), all of which are isostructural, were prepared as follows: In the preparations of VClO, FeClO, and LaClO, the desired mixtures of metal chlorides and metal oxides ($MCl_3+M_2O_3$, M=V, Fe, and La) were heated in sealed quartz tubes at 720, 370, and 800°C for 48, 60, and 20 h, respectively. BiClO was obtained by sintering commercial BiClO in a sealed quartz tube at 800°C for 20 h. SbClO was a commercial sample. Four alkali and alkaline earth cation-containing chloride oxides with different structures each other were prepared in the main by heating a stoichiometric mixture of the relevant halide (for example LiCl, NaCl, and $CaCl_2$), Bi_2O_3 and BiClO at temperatures generally in excess of 800°C in sealed platinum tubes or in alumina crucibles. Details have been given elsewhere for the preparations.[10] X-Ray powder diffractometry was used to ascertain phase purity and no phase change after use. All monophasic materials which were sintered and well crystallized were subjected to catalytic testing after being ground. The ground samples have surface area less than 1 m^2 g^{-1} except FeClO (2 m^2 g^{-1}).

Catalytic performance was assessed utilizing conventional

Table 1. Catalytic Activity of MClO (X_2-type) Catalysts for the Dehydrochlorination of TBC (100°C)

Catalyst	Conversion of TBC/%	Selectivity/%				
		C_4	C_5	C_6	C_7	C_8
BiClO	0.6	66	26	0	0	8
SbClO	1.4	93	0	5	0	2
VClO	1.5	96	0	0	0	4
FeClO	9.7	91	Tr	3	0	6
LaClO	3.6	93	0	6	0	1

Table 2. Catalytic Activities of MClO (X_2-type) Catalysts for the Dehydrobromination and the Halogen Exchange Reaction (100°C)

Catalyst (MClO)	Conversion	Selectivity/%		Distribution of hydrocarbons/%					Enthalpy (298 K) of MCl_3
M=	of TBB/%	Hydrocarbons	TBC(Yield/%)	C_4	C_5	C_6	C_7	C_8	formation/kJ mol^{-1}
Bi	16.6	77	23 (3.8)	91	0	0	0	9	−377
Sb	38.5	58	42 (16.0)	89	Tr	0	0	11	−380
V	9.8	91	9 (0.9)	99	0	0	0	1	−577
Fe	9.3	61	39 (3.6)	91	0	0	0	9	−397
La	4.8	74	26 (1.2)	99	0	0	0	1	−1097

Table 3. Catalytic Activity of Alkali and Alkaline Earth Cation-Containing Bismuth Chloride Oxides for the Dehydrochlorination of TBC (200°C)

Catalyst				Conversion	Selectivity/%				
Composition	Type	c_0(Å)	% of oxide layer [a]	of TBC/%	C_4	C_5	C_6	C_7	C_8
$LiBi_3Cl_2O_4$	X_1	12.03	50	72	90	1	Tr	Tr	8
$NaBi_3Cl_2O_4$	X_1	12.16	50	41	97	Tr	0	0	3
$Li_3Ca_2Bi_9Cl_{10}O_{12}$	$X_1X_1X_3$	45.56	40	43	93	1	Tr	1	5
$LiCaBi_3Cl_4O_4$	X_1X_3	33.39	36	26	96	1	Tr	Tr	3

a) $\frac{n(\text{thicknesss of oxide sheet}[3.1\text{Å}])}{c_0(\text{Å})\text{ of unit cell}} \times 100$ (*n*: number of oxide layer unit in unit cell).

pulse technique. 0.5 µl of reagent grade alkyl halides, TBC and TBB, was injected in a helium stream as a carrier (70 ml min^{-1}) with aid of a microsyringe. Each catalyst (25 mg) was heat-treated in the helium stream for 2 h at 200°C, prior to the reaction at 100 or 200°C. It was ascertained that no reaction took place without catalysts under the present conditions. Products were analyzed by a gas chromatograph (Adsorb p-1) and GC-MS.

Results

The catalytic perfomance of the MClO (M=Bi, Sb, V, Fe, and La) samples in the dehydrohalogenation of TBC and TBB at 100°C are summarized in Tables 1 and 2, respectively. All data listed in the tables are average values of several pulses after a stable activity is attained. Products analyzed were hydrocarbons of carbon numbers from 4 to 8. The main product was 2-methylpropene and the others were mainly mixtures of iso-olefin isomers and trace amounts of praffins. No products of carbon numbers less than 3 were detected at all. Besides the dehydrohalogenation, a halogen-exchange reaction occurred to form TBC at the same time in the reaction of TBB over the MClO catalysts.

MClO such BiClO, designated as X_2 structural type according to Sillen's classification, has double layers of chloride ions which are stacked along [001] direction with cation-oxygen sheets ($[M_2O_2]^{2+}$) alternatively. As can seen from Tables 1 and 2, the X_2-type catalysts showed activities for both reactions and their catalytic performance differs from each other; the activity for the reaction of TBC increased in order of BiClO<SbClO<VClO<LaClO<FeClO, while LaClO<FeClO<VClO<BiClO<SbClO for the reaction of TBB, which is almost reversed. The observed difference in the catalytic performance may strongly reflect the catalytic properties of the metal cation site in MClO structure, since each catalyst is isostructural and the coordination circumstance surrounding metal cation in the lattice is also quite similar in each catalyst.

The yield of TBC in the halogen exchange reaction of TBB increased in order of VClO≤LaClO<FeClO≤BiClO<SbClO. The halogen exchange reaction is, on the other hand, related to the energy of metal-halogen bond formation (represented by enthalpies of MCl_3 formation in Table 2), since the reaction is accompanied a structural change, such as the replacement of chloride ion in MClO with bromide ion to form MBrO.

Table 3 shows the catalytic activities of four alkali and alkaline earth cation-containing bismuth chloride oxides for the dehydrochlorination of TBC. $LiBi_3Cl_2O_4$ and $NaBi_3Cl_2O_4$ are so-called X_1 structural type, where the cation-oxygen sheets alternate with single layer of chlorine. X_1X_3 and $X_1X_1X_3$ type samples having compositions of $LiCaBi_3Cl_4O_4$ and $Li_3Ca_2Bi_9Cl_{10}O_{12}$ are structural variants intergrown with X_1 and X_3 type at the sub-unit-cell level.[9,10] X_3 type structure consists of cation-oxygen layers alternating with triple thickness sheets of chlorine which contain additional cations such Ca^{2+} in their interstics. The occurence of such intergrowths is identified through the magnitude of the observed unit cell (*z*-direction) dimension.

Since these four bismuth chloride oxide catalysts were very less active than the X_2-type catalysts, the data listed in Table 3 were collected at 200°C. The product selectivities were quite similar to those of X_2-type catalysts. The most active catalyst was X_1-type sample among three layered bismuth chloride oxides having different structures, followed by $X_1X_1X_3$ and X_1X_3-

type sample. Interestingly, it can be seen that the catalytic activity decreases with decreasing the percentage occupancy of cation-oxygen layer in unit cell (*z*-direction), indicating here again the strong reflectance of the catalytic properties of metal cation site in the layer. $NaBi_3Cl_2O_4$ catalyst was less active than $LiBi_3Cl_2O_4$ catalyst. However, the reasons for this result as well as for the lower activities of the alkali and alkaline earth cation-containing catalysts than X_2-type are obscure at the present stage.

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