Catalytic oxidative dimerization of methane to form C_2-compounds over Arppe's phase oxychlorides of Bi, La and Sm

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Received 8 April 1991; accepted 31 May 1991

Three distinct examples of Arppe's phase ($M_{24}O_{31}Cl_{10}$; M = Bi, La, Sm), which has a structure related to that of the layered oxychloride BiOCl, have been used as monophasic catalysts for the oxidative dehydrogenation of CH_4. The stability and performance of these rival those of the best catalysts previously reported.

1. Introduction

Previously [1.2] we have demonstrated that some twenty members of the monophasic bismuth oxychlorides exhibit high catalytic activity for the oxidation of methane and high selectivity to C_2-hydrocarbons. We have also shown [1,3] that there are some less attractive features of these catalysts. For example, many of them lack long-term stability, especially those which display high performance. BiOCl, for instance (see fig. 1), is rather unstable. The catalytic activity decreases rapidly with the progressive liberation of chlorine, whereas the selectivity increased. It is known that the so-called Arppe's phase ($Bi_{24}O_{31}O_{10}$) (fig. 2) is formed as the stable end-product after the chlorine ceases to be lost during prolonged thermal treatment. The same deactivation feature was observed on X_3 type bismuth oxychloride which has been found most active in the bismuth oxychloride catalyst group [4]. (For a resume of X_1, X_2, and X_3 structure types in this family of catalysts, see ref. [2].)

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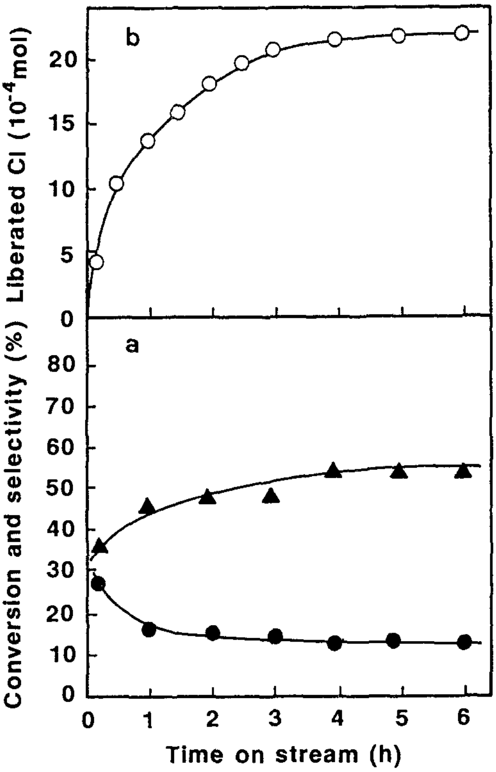

Fig. 1. Activity changes of BiOCl catalyst (a) evolution of HCl from the catalyst (b) as a function of reaction time in the oxidation of methane at 993 K. Reaction conditions; partial pressure of methane and oxygen, 20 and 10 kPa, remainder nitrogen, total flow rate 50 mL·min^{-1}, catalyst weight, 1 g. ●: conversion, ▲: selectivity to C_2-hydrocarbons.

Loss of chlorine from most of the bismuth oxychloride catalysts and chlorine-containing catalysts [1,3,5–7] is a potentially grave disadvantage since the release of chlorine into the gas phase complicates the subsequent chemical reactions and the performance of the catalyst itself falls off with time [8,9].

We have endeavoured to develop more stable catalysts, based on oxyhalide other than those hitherto reported. In this letter, we wish to report the catalytic performance of some highly stable metal oxychloride catalysts, and point the way to some possible improved catalysts for future investigation.

2. Experimental

The preparative conditions for each catalyst are summarized in table 1. All chemicals used for the preparation are commercially available reagent grade, some of which were used directly as catalysts. LaOCl was prepared by solid state reaction between La_2O_3 and $LaCl_3$ at 1123 K for 20 h in air. BiOCl was

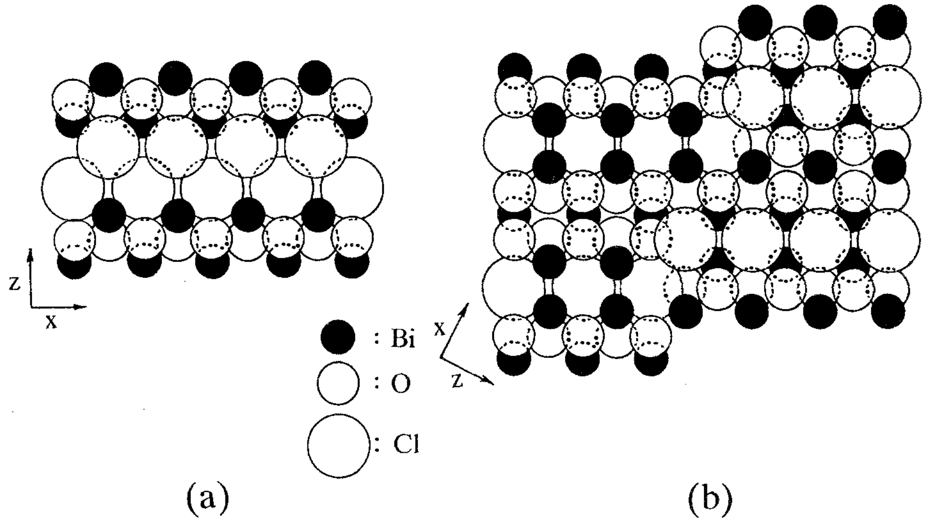

Fig. 2. Structures of BiOCl (X_2 type) (a) and Arppe's phase ($Bi_{24}O_{31}Cl_{10}$) (b). In the X_2 type structure, the oxide layer charged positively, like $[Bi_2O_2]^{2+}$, are separated with double thickness sheets of chloride ions. The Arppe's phase [12] is regarded as chlorine deficient and oxygen sufficient analogue of X_2. In the proposed structure, a part of chloride ion sheet originally presented in the X_2 type is replaced with oxide layer, forming zigzag stacking sheets.

prepared by heat-treatment of $BiCl_3$ in air at 923 K for 20 h, followed by re-heating at 1123 K for 20 h in sealed silica tube. Arppe's phase samples, $M_{24}O_{31}Cl_{10}$ (M: Bi, La, and Sm), were synthesized with the mixture (1:1) of corresponding MOCl and metal oxide at 1073 K for 5 h in sealed silica tube. The starting mixture consists of metal oxide in slightly higher amount than the ideal composition required of Arppe's phase. The resulting samples normally contain small amount of free metal oxides, although most of excess metal oxide reacted with silica tube during the preparation. All synthesized materials were sintered and well-crystallized: They were ground in an agate motor before use as catalysts. X-ray powder diffraction patterns (CuK_α radiation) were collected before and after use.

Measurement of the catalytic performance of the oxychlorides in the selective oxidative dimerization of methane were carried out using a fixed-bed reactor

Table 1
Preparative conditions for oxychloride catalysts

Catalyst	Group	Reactant	Condition (crucible)
LaOCl	X_2	La_2O_3, $LaCl_3$	1123 K, 20 h (alumina)
BiOCl	X_2	$BiCl_3$	923 K, 20 h (alumina)-1123 K, 20 h (sealed quartz)
$Bi_{24}O_{31}Cl_{10}$	Arppe	Bi_2O_3, BiOCl	1073 K, 5 h (sealed quartz)
$La_{24}O_{31}Cl_{10}$	Arppe	La_2O_3, LaOCl	1073 K, 5 h (sealed quartz)
$Sm_{24}O_{31}Cl_{10}$	Arppe	Sm_2O_3, SmOCl	1073 K, 5 h (sealed quartz)

with a conventional gas flow system under atmospheric pressure. A reactant mixture of CH_4(20 kPa) and O_2(10 kPa) was introduced to the reactor (993 K) with N_2 as a diluent (total flow rate; 50 $mL.min^{-1}$). The reaction products were analysed using a gas sampling valve connected directly with the reaction flow system, separated with Porapak T and Molecular sieve 13X in a gas chromatograph. The selectivity and yield of the products were calculated on the basis of the carbon number of methane reacted.

3. Results and discussion

Table 2 summarizes the catalytic activity, selectivity to C_2 hydrocarbons, structure, and stability of Bi-, La-, and Sm-based catalysts which have oxide, oxychloride (X_2-type), and Arppe's phase, respectively. Tabulated results show both the initial stage (after 10 min reaction) and steady state performances, so that the performance rating of the various catalysts may be compared with that of BiOCl.

Each of the three La-based catalysts show high catalytic activity for methane conversion, but rather poor performance for C_2 hydrocarbon production regardless of the catalyst structure. Since most of the oxygen fed into the reactor was consumed during passage through these catalysts, it it not relevant to compare the intrinsic activity. It is, however, reasonable to assume that the chloride ion in the lattice of the La-based catalysts has no positive effect on the activity because there is no appreciable difference among their catalytic performance. La-oxychloride catalysts were particularly stable. No deactivation was observed within the reaction time tested and no phase change was detected by XRD analysis before and after the reaction.

Sm-based catalysts also, as expected by analogy with the work of Williams et al. [3], showed high catalytic activity and low selectivity toward C_2 hydrocarbons. Samarium oxide catalyst was rather less selective, whereas the oxychloride catalysts showed selectivities twice as high as that of the oxide catalyst. The molar ratio of ethene to ethane was also improved more than twice in the oxychloride catalysts. These results show that in the case of Sm-based catalysts the presence of chloride ions in the lattice enhances the catalytic performance. But SmOCl was slightly less stable under the reaction conditions than analogue oxychlorides, revealing a slow deactivation (methane conversion of 38 to 35% within 4 h reaction). Arppe's type oxychloride, $Sm_{24}O_{31}Cl_{10}$, was highly stable rivaling that of the corresponding oxide catalyst.

The catalytic performance of Bi-based compounds was quite different from that of La- or Sm-based compounds in terms of the effects of chlorine on the activity and of structural stability. First, the improvement of catalytic performance of Bi-based catalyst by changing the oxide phase to oxychlorides was striking, compared with other catalysts containing trivalent metal element.

Table 2

Structure and catalytic performance of various Bi-, La-, and Sm-based oxychlorides [a]

Catalyst				Conversion conversion		C_2 selec-tivity(%)	C_2 yield (%)	C_2H_4/C_2H_6	Stability [b]
Metal	Composition	Structure		of CH_4 (%)	of O_2 (%)				
Bi	Bi_2O_3	fluorite	I [c]	6.7	20.4	18.4	1.2	0.4	
			S [c]	6.5	20.6	15.8	1.0	0.1	+
	BiOCl	layer	I	29.8	53.7	35.3	10.6	13.2	
			S	12.4	24.0	50.8	6.3	1.5	−
	$Bi_{24}O_{31}Cl_{10}$	Arppe's phase	I	8.6	17.9	45.6	3.9	1.2	
			S	8.6	18.1	45.1	3.9	1.1	+
La	La_2O_3	M_2O_3	I	34.6	95.8	26.5	9.1	1.2	
			S	34.8	98.6	24.7	8.6	1.3	+
	LaOCl	layer	I	38.1	96.8	28.6	10.9	1.5	
			S	38.7	98.5	27.6	10.7	1.5	+
	$La_{24}O_{31}Cl_{10}$	Arppe's phase	I	36.1	94.0	22.8	8.2	1.4	
			S	36.1	94.0	24.5	8.8	1.2	+
Sm	Sm_2O_3	M_2O_3	I	34.5	99.0	16.5	5.7	1.4	
			S	33.0	99.7	17.6	5.8	1.2	+
	SmOCl	layer	I	36.4	78.0	31.3	11.4	3.5	
			S	34.9	77.2	27.6	9.6	2.9	−
	$Sm_{24}O_{31}Cl_{10}$	Arppe's phase	I	35.5	89.3	28.1	10.0	3.0	
			S	34.5	91.0	24.8	8.6	2.6	+

[a] Catalyst weight 1 g.

[b] +; highly stable, −; deactivation with phase transformation.

[c] I; initial stage (10 min) of the reaction, S; steady state.

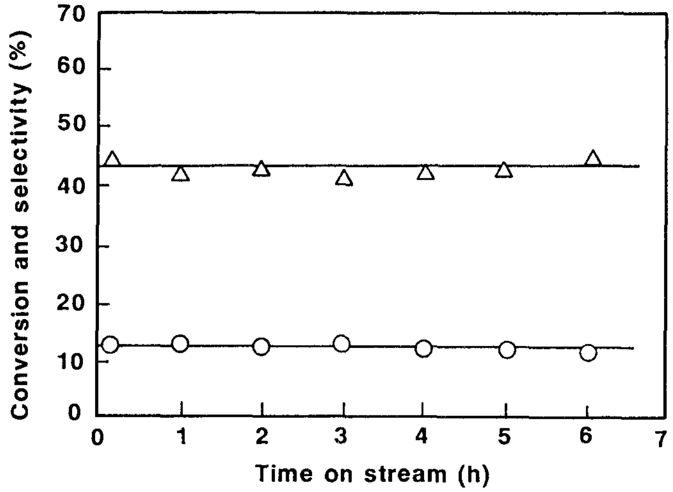

Fig. 3. Activity changes of $Bi_{24}O_{31}Cl_{10}$ catalyst (Arppe's phase) as a function reaction time in the oxidation of methane at 993 K. Catalyst weight; 2 g. ○; conversion, △; selectivity to C_2 hydrocarbons.

There is a second feature concerning deactivation. BiOCl catalyst is specifically unstable; as the reaction time increased the methane conversion decreased to nearly one third of the initial value and selectivity to C_2 hydrocarbons increased whilst the concentration of ethene in C_2 hydrocarbons decreased significantly. After the steady state activity was attained, the catalyst consisted chiefly of the $Bi_{24}O_{31}Cl_{10}$ phase. $Bi_{24}O_{31}Cl_{10}$ synthesized by solid state reaction with Bi_2O_3 and BiOCl (see table 1) was active for selective oxidation of methane also, although the resulting conversion and selectivity were slightly lower than those

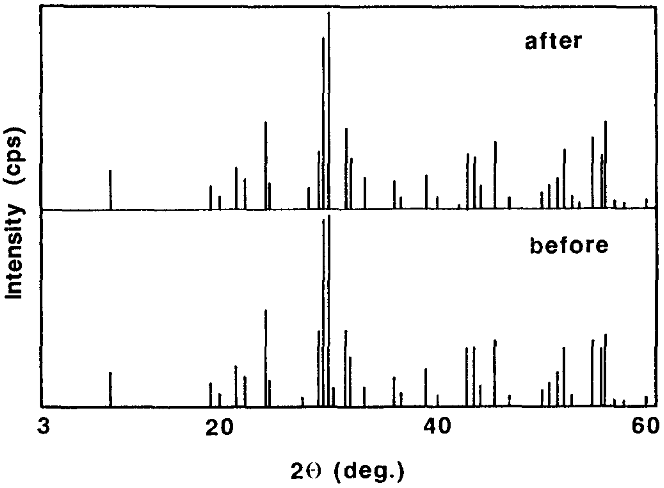

Fig. 4. X-ray diffractograms of $Bi_{24}O_{31}Cl_{10}$ before and after use for 6 h as a methane oxidation catalyst at 993 K.

for heat-treated BiOCl catalyst. This material was found to be extremely stable; no deactivation was observed within the test time and there was no detectable phase change before and after the reaction (figs. 3 and 4). Furthermore, evolution of HCl from the catalyst during the reaction was very small, 0.02 $\text{mmol} \cdot \text{g}^{-1} 6\text{h}^{-1}$ (note that BiOCl released 1.2 $\text{mmol} \cdot \text{g}^{-1}$ within 6 h reaction).

Although the role of chlorine in the selective oxidation of methane is not fully resolved, the fact that by combining with chlorine metal oxide can be highly selective catalyst for the reaction without showing any deactivation reveals that chlorine involves in the catalytic reaction directly or indirectly on the catalyst surface.

In summary, we have found that Arppe's bismuth oxychlorides are stable catalysts for the oxidative dehydrogenation of methane but their activity is somewhat impaired compared with other, less-stable bismuth containing solids. We are currently exploring whether improved catalysts, based on Arppe's phase may be produced by optimizing the Bi, La, and Sm contents.

Acknowledgment

J.M.T. thanks the S.E.R.C. for supporting part of this work.

References

[1] W. Ueda and J.M. Thomas, *Proc. 9th Intl. Congr. Catal.* 2 (1988) 960.

[2] J.M. Thomas, W. Ueda, J. Williams and K.D.M. Harris, Faraday Disc., Chem. Soc. 87 (1989) 33.

[3] J. Williams, R.H. Jones, J.M. Thomas and J. Kent, Catal. Lett. 3 (1989) 247.

[4] W. Ueda, T. Isozaki, Y. Morikawa and J.M. Thomas, Chem. Lett. (1989) 2103.

[5] K. Otsuka, Q. Lin and A. Morikawa, Inorg. Chim. Acta 118 (1986) L23.

[6] T. Komatsu, T. Amaya and K. Otsuka, Catal. Lett. 3 (1989) 317.

[7] A.N. Shigapov, M.A. Novozhilova, S.N. Vereshchagin, A.G. Anshits and V.D. Sokolovskii, React. Kinet. Catal. Lett. 37 (1988) 397.

[8] R. Burch, E.M. Crabb, G.D. Squire and S.C. Tsang, Catal. Lett. 2 (1989) 249.

[9] R. Burch, A.A. Dost, D.A. Rice, S.C. Tsang and G. Webb, Catal. Lett. 3 (1989) 331.

[10] L.G. Sillen, Z. Anorg. Allg. Chem. 242 (1939) 41.

[11] K.D.M. Harris, W. Ueda, J.M. Thomas and G.W. Smith, Angew. Chem. Intl. Edn. 27 (1988) 1364.

[12] A.F. Wells, *Structural Inorganic Chemistry*, 5th edn. (Clarendon Press, Cambridge, 1984).

[13] L.G. Sillen, Z. Kristallogr. 104 (1942) 178.

[14] H. Imai and T. Tagawa, J. Chem. Soc., Chem. Commun. (1986) 52.