

Bismuth-rich Layered Solids as Catalysts for the Oxidation of Methane to Higher Hydrocarbons

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Several complex layered oxyhalide structures based on, or derived from, the phases first identified by Sillén are shown to be good selective oxidation catalysts in the range 873 to 1023 K.

Bismuth molybdates, of which there are at least seven distinct phases,¹ are well known² as catalysts for the selective oxidation of propene to acraldehyde at moderate temperatures. It is also known³ that bismuth oxide, either alone or in the presence of other oxides, carbonates, or halides, shows modest activity, but generally poor stability, in the catalytic oxidative coupling of methane at rather higher temperatures. We here report the discovery that complex, layered bismuth oxyhalides of well-defined structure are promising catalysts for the conversion of methane into ethene, ethane, and higher hydrocarbons in the temperature range 873 to 1023 K.

We have tested the catalytic performance of over a dozen different solid compositions, all monophasic; and all these are

either examples of, or structurally related to, the so-called Sillén phases⁴ (Figure 1) which are derived from bismuth oxychloride.

Samples of polycrystalline complex layered bismuth oxyhalides were prepared by heating in sealed containers of platinum at 1023 to 1173 K, an appropriate stoichiometric mixture of the metal halide, metal oxide, and bismuth oxyhalide so as to yield the required phase. X-Ray powder diffraction (XRD) and analytical electron microscopy were used to identify the phases. Preparative details, unit-cell dimensions and space groups, as well as further information concerning catalyst testing and longevity, are given elsewhere.⁵ Briefly, a fixed-bed quartz reactor with a conventional gas flow system at atmospheric pressure was used and products were analysed chromatographically. Typical reaction conditions were: temperature, 873 to 1023 K; partial pressure of methane, 5 to 20 kPa; CH₄/O₂ ratio of 2; total flow rate, 50 ml m⁻¹ with N₂ as a

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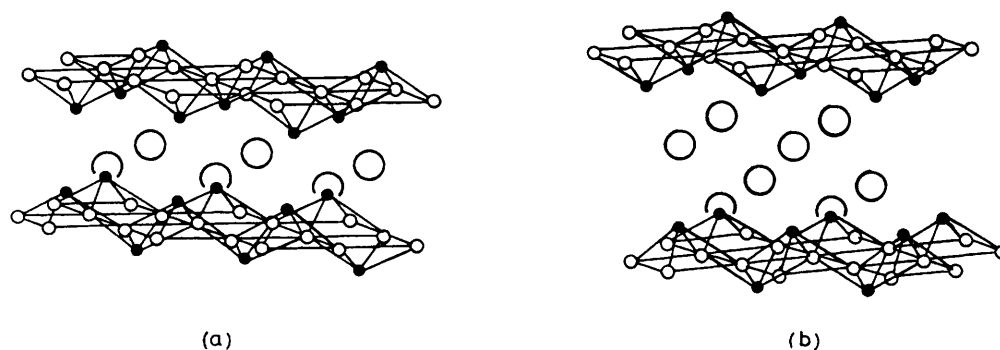


Figure 1. Schematic illustration of typical Sillén phases derived from BiOCl . In (a) there is a single, and (b) a double halogen layer, the separation of the sheets being, respectively, ca. 6.5 and 7.4 Å. The filled circles represent Bi, Na, Pb; the larger open circles represent chlorine, the smaller open circles oxygen.

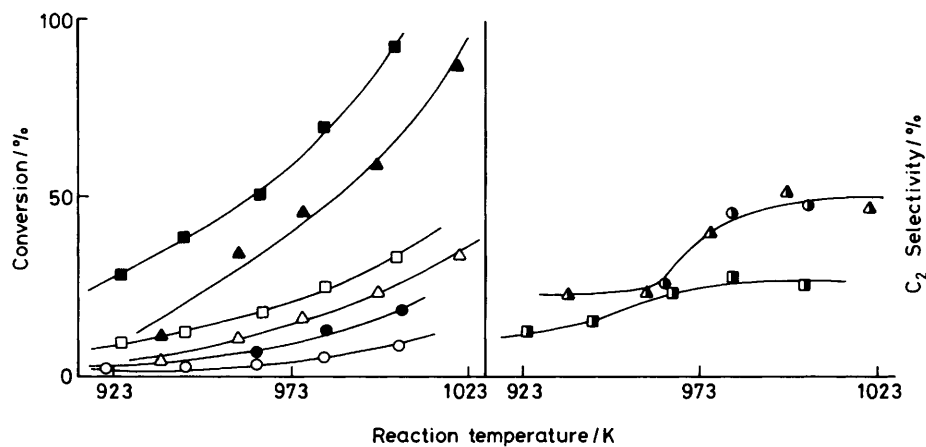


Figure 2. The catalytic performance (conversions and selectivities) of catalysts of composition $\text{NaBi}_3\text{O}_4\text{X}_2$ as a function of temperature, where $\text{X} = \text{F}$ (circles), Cl (triangles) and Br (squares). Conversion of methane denoted by open symbols, of oxygen by filled symbols. Half-filled symbols show selectivity to C_2 compounds. (Conditions: 2 g of sample, reactant flow rate of 50 ml m^{-1} partial pressures of CH_4 and O_2 20 and 10 kPa, respectively).

diluent. 2 g Samples of catalyst were used throughout. XRD runs carried out at the completion of the tests showed little change from the original; but there was some loss of halide during use.

A typical result, at a temperature of 998 K, for the monophasic catalyst of composition $\text{NaBi}_3\text{O}_4\text{Cl}_2$ was an oxygen conversion of 59.8 per cent with product selectivities (percentages) as follows: CO_2 , 38.4; C_2H_4 , 43.9; C_2H_6 , 8.4; C_3 , 1.9; C_4 , 1.0; and C_2^+ of 55.2 and a $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ ratio of 5.2. Figure 2 shows the comparative catalytic performance of $\text{NaBi}_3\text{O}_4\text{X}_2$ ($\text{X} = \text{F}$, Cl , and Br). Oxychlorides were found to be superior in stability and in all-round catalytic performance to the other analogue oxyhalides. Poorly crystalline preparations exhibited inferior catalytic properties.

Apart from the Sillén phases, we have found that generally comparable catalytic selectivity is also shown by two other types of solid. First, the so-called 'bipox' phases^{5,6} where a coherent, unit-cell-level intergrowth⁷ structure forms between an Aurivillius phase⁸ and a Sillén phase, yielding a layered sequence of $(\text{Bi}_2\text{O}_2)^{2+} \text{Cl}-(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{n-1}\text{M O}_{3n+1})$ where the A cation is 12-co-ordinated (often Bi^{3+}) and M cations are octahedrally co-ordinated as in perovskites AMO_3 . Second, a hitherto unknown complex, layered bismuth oxyhalide structure which is coherently intergrown at the unit-cell level with an alkali-metal halide layer. The structure of this new type of solid catalyst, exemplified by the formula $\text{Cs}_2\text{Bi}_{10}\text{Ca}_6\text{Cl}_{12}\text{O}_{16}$, where Ca^{2+} and Bi^{3+} ions are randomly distributed over the same sites, has recently been solved^{9,10} and will be described elsewhere. Mechanistically, it is not yet clear what occurs in

the crucial act of catalysis, but early indications,¹¹ recently elaborated,¹² leave little doubt that methyl radical production is favoured by the solid catalyst.

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