Oxidative Coupling of Methane over $Ba_2Sb(La_{0.5}Bi_{0.5})O_6$ and other Perovskite Oxide Catalysts

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Novel perovskite-type oxides $Ba_2M^{III}M'^{V}O_6$ containing high oxidation-state post-transition elements have been shown to catalyse the oxidative coupling of methane; yields of up to ca. 17% are obtained at 1023 K when the catalyst contains antimony(v).

Keller and Bhasin[1] first demonstrated the possibility of oxidatively dimerising methane over oxide catalysts, particularly those containing a metal that can exist in two different oxidation states, N and $N - 2$. Since then considerable progress has been made in the direct oxidative coupling of methane using oxide catalysts. Hinsen and Baerns[2] were the first to report catalytic methane coupling using a simultaneous cofeed of methane and air into a fixed bed of supported metal oxides and we have now made similar measurements on some new mixed metal oxides having the perovskite structure. To date most studies of catalytic methane coupling over perovskites appear to have focussed on rare-earth manganates, often doped with sodium.[3–7] However, Inoue *et al.*[8] have had some success with a $BaPb_{1-x}Bi_xO_3$ catalyst. Catalytic activity has also been reported for the Sillen phases $NaBi_3O_4X_2$ (X = F,Cl,Br),[9] synthetic kentrolite ($Pb_2Mn_2Si_2O_9$)[10] and the rare-earth pyrochlores $Ln_2Sn_2O_7$.[11] These latter compounds all contain post-transition metals, as did many of the oxides originally studied by Keller and Bhasin. We therefore reasoned that it may be possible to optimise the performance of oxide catalysts by introducing a number of post-transition metals into the perovskite structure.

Polycrystalline samples of the compounds to be evaluated were prepared by standard solid state techniques. The appropriate stoichiometric quantities of $BaCO_3$, La_2O_3, Bi_2O_3, Sb_2O_3 and RuO_2 were ground together and fired in an alumina crucible, initially at temperatures of 600–800 °C and finally at 1100–1300 °C. The purity of the final products was verified by X-ray powder diffraction; no attempt was made to enhance their surface area which was shown by Brunauer–Emmett–Teller (BET) measurements to be *ca.* 2 $m^2\ g^{-1}$. The diffraction patterns indicated that all the compounds to be discussed below have face-centred pseudo-cubic structures (a_0 *ca.* 8.60 Å) similar to that of Ba_2LaRuO_6[12] with the exception of $Ba_3NiSbTaO_9$ and $Ba_3NiSbNbO_9$ which apparently adopt the hexagonal 6H-$BaTiO_3$ structure (a_0 *ca.* 5.79, c_0 *ca.* 14.26 Å). The adoption, by the majority of the compounds, of a unit cell which is twice the size of the primitive cubic perovskite unit cell suggests that the six-coordinate cations (M and M′ in $Ba_2MM'O_6$) order in a 1 : 1 pattern, as seen in many other perovskites.[12] The detailed solid state chemistry of these materials will be discussed elsewhere. The catalytic activity of the compounds was evaluated using 4 mm internal diameter vertical quartz tubes placed in an SSL tube furnace. A catalyst loading of 0.05 g was held in place by Multilab quartz wool (<0.3% carbon). Reaction temperatures were monitored by a K-type thermocouple adjacent to the quartz reaction tube. All reactants and products were analysed using a Perkin-Elmer 8600 series gas chromatograph containing a 2 m Poropak QS column. Samples were left under reaction conditions for at least 30 min to allow equilibrium to be reached. The results of experiments carried out at 1023 K are presented in Table 1.

It is clear that under these conditions all of these perovskites are catalytically active, producing good yields of useful hydrocarbons. The selectivity did not decrease over a period of 72 h. However, $Ba_2Sb(La_{0.5}Bi_{0.5})O_6$ showed a particularly high activity and was therefore studied further at different

Table 1 Catalytic activity of perovskite oxides at 1023 K, methane : oxygen = 2 : 1, flow rate = 36 $cm^3\ min^{-1}$; data are also given for quartz wool under the same conditions

	Product selectivities as % of CH_4 converted						
Sample	%CO	%CO_2	%C_2H_4	%C_2H_6	% Other C[a]	% Conv.	Yield (%)[b]
$Ba_2Bi(Sb_{0.75}Ru_{0.25})O_6$	4.2	55.9	26.8	5.5	7.6	32.2	12.8
$Ba_2Bi(Sb_{0.5}Bi_{0.5})O_6$	30.2	38.1	23.7	4.4	3.6	32.4	10.3
$Ba_2Bi(Ru_{0.5}Bi_{0.5})O_6$	53.8	14.7	21.9	6.3	3.3	27.6	8.7
$Ba_2Sb(La_{0.5}Bi_{0.5})O_6$	1.1	51.3	25.1	17.5	5.0	35.9	17.1
$Ba_2(La_{0.5}Bi_{0.5})(Ru_{0.25}Sb_{0.75})O_6$	6.0	65.6	17.5	6.6	4.3	29.6	8.7
$Ba_2(La_{0.75}Bi_{0.25})(Ru_{0.5}Sb_{0.5})O_6$	3.0	62.1	20.6	6.9	7.4	30.7	10.7
$Ba_3NiSbBiO_9$	2.6	59.0	24.7	6.1	7.6	33.4	12.8
$Ba_3NiSbTaO_9$	10.0	54.9	23.1	5.8	6.2	31.6	11.1
$Ba_3NiSbNbO_9$	11.7	52.6	22.9	4.1	8.7	33.4	11.9
Quartz wool	12.2	68.4	14.9	4.3	0.2	0.6	0.1

[a] %Other C = %MeOH + %HCHO + %C_3 + %C_4 + %C_6. [b] Yield = Total amount of methane converted to C_2 + other C.

Table 2 Catalytic activity of $Ba_2Sb(La_{0.5}Bi_{0.5})O_6$ as a function of temperature, methane : oxygen = 2 : 1, flow rate = 36 $cm^3\ min^{-1}$

	Product selectivities as % of CH_4 converted						
Temperature /K	%CO	%CO_2	%C_2H_4	%C_2H_6	%Other C	%Conv.	Yield
973	1.1	50.5	24.1	19.4	6.0	36.3	18.1
1023	1.2	51.0	24.9	17.9	5.0	36.0	17.2
1073	1.7	52.6	25.3	13.4	7.0	35.7	16.3
1123	4.6	57.1	23.3	5.7	9.3	33.0	12.6
1173	44.0	32.8	17.4	1.1	4.7	38.7	9.0

operating temperatures. The results of these experiments, presented in Table 2, show that the yield of C_2 products decreases with increasing temperature and that the formation of CO and CO_2 increases. The decrease in the yield of C_2 products is due almost entirely to a decrease in the amount of ethane produced; the ethylene yield is virtually unchanged and the total methane conversion remains approximately constant at *ca.* 30%. The level of oxygen utilisation is 90–100% throughout the reaction. X-Ray diffraction patterns taken after catalytic testing showed that the material was structurally unchanged.

This work demonstrates that perovskites containing post-transition metals are among the best catalysts identified to date. The formulae of the compounds tested in this work are complex and it is therefore difficult at this stage to identify the features which are most important in producing a good catalyst. Our approach has been an empirical one in that we have tried to make and evaluate a large number of perovskites (only the successful reactions are reported above), the one constraint being that they should contain pentavalent antimony. The only compound tested that does not meet this condition, $Ba_2Bi(Bi_{0.5}Ru_{0.5})O_6$, is the least selective of our catalysts, and all the compounds which contain both bismuth and ruthenium are relatively inactive. However, it is important to recognise that most of these compounds are actually reasonable catalysts, but that many are made to look inactive by comparison with the exceptional activity of $Ba_2Sb(La_{0.5}Bi_{0.5})O_6$, which gives as good a yield of C_2 products as any other known oxide catalyst.[13,14] If we judge these materials not by the total C_2 yield, but by the ratio of ethylene to ethane in the product, then hexagonal $Ba_3NiNbSbO_9$ is the most effective catalyst at 1023 K, with $\%C_2H_4/\%C_2H_6 = 5.6$ at 11.9% yield. These two compounds clearly merit further study. Work is in progress to study the mechanism of the reaction and hence to understand whey these materials are such good catalysts.

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