Oxidative Coupling of Methane over Tin-containing Rare-earth Pyrochlores

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Rare-earth pyrochlores of general formula $Ln_2Sn_2O_7$ (Ln = rare-earth) are found to be active catalysts for the oxidative coupling of methane, with enhanced conversion to useful hydrocarbons, particularly ethene, being observed at 1150 K for those rare-earths that exhibit mixed valence behaviour (Ln = Pr, Sm, Eu, Tb, Tm, and Yb).

Since Keller and Bhasin[1] first demonstrated the possibility of oxidatively dimerising methane, many oxide systems have been investigated.[2—7] Attention has focused on the use of alkaline earth or rare-earth oxide catalysts, with and without promotors, but mixed metal oxides[8—11] and oxy-chlorides[12,13] have also been examined. In the present work, we describe the oxidative coupling of methane over a range of monophasic, tin-containing rare-earth pyrochlores of general formula $Ln_2Sn_2O_7$ (Ln = rare-earth). By examining a complete series of isostructural materials, we are able to identify some of the chemical factors that influence catalytic activity.

The samples were prepared at 1473 K by standard solid-state reaction techniques, as described in our previous studies of these materials by ^{119}Sn MAS NMR,[14,15] and their purity was confirmed by *X*-ray powder diffraction and NMR. No attempt was made to enhance the surface area of these high temperature reaction products. Catalytic measurements were performed as shown in the footnote to Table 1. *X*-Ray powder diffraction and analytical electron microscopy measurements on the used catalysts revealed no discernible changes relative to the starting materials.

Results obtained at 1000 K are given in Table 1 and some key trends are shown in Figure 1. At this temperature, all of the pyrochlores are catalytically active and produce low yields of useful hydrocarbons. There is an inverse relationship between their performance in oxidative coupling, on the one hand, and combustion, on the other. The most striking chemical feature, however, is that the most selective coupling catalysts are those oxides containing rare-earth elements that exhibit mixed valence behaviour; Sm, Eu, Tb, Tm, and Yb. Note, for example, the striking changes within the group Eu, Gd, and Tb (Figure 1). An interesting exception to this general trend is the case of praseodymium, which is a good combustion catalyst at 1000 K.

An important feature of our pyrochlore materials is their excellent thermal stability, which has enabled us to examine

Table 1. Results obtained at 1000 K for the pyrochlores $Ln_2Sn_2O_7$ with methane : oxygen = 2 : 1 and flow rate = 27 ml min^{-1}.[a] Data for Sm_2O_3, under the same conditions, are also given. Oxygen conversions were approx. 40% for the active catalysts (*i.e.* >20% conversion), but below 5% for the less active ones.

	Product selectivities as % of methane converted						
Ln	% CO	% CO_2	% C_2H_4	% C_2H_6	% Other C	% Conv.	% Yield C_2 + other C
Y	1.2	87.8	2.1	8.9	0.0	21.3	2.3
La	5.0	80.0	5.1	9.9	0.0	29.7	4.4
Pr	9.8	72.9	2.8	14.5	0.0	4.3	0.7
Nd	10.7	62.0	5.3	22.0	0.0	4.6	1.3
Sm	44.6	9.9	12.2	32.4	0.9	3.9	1.8
Eu	51.4	12.8	5.9	29.9	0.0	2.0	0.7
Gd	15.5	74.6	3.2	6.7	0.0	28.1	2.8
Tb	38.4	31.9	9.2	20.6	0.0	4.4	1.3
Dy	8.8	68.3	11.4	10.5	1.0	30.4	7.0
Ho	2.7	86.3	2.1	8.8	0.0	26.5	2.9
Er	6.6	81.8	2.7	8.8	0.0	24.9	2.9
Tm	29.5	41.5	5.0	23.9	0.0	2.1	0.6
Yb	43.8	11.7	7.5	35.5	1.5	2.0	0.9
Lu	19.9	49.2	8.9	22.0	0.0	5.8	1.8
Sm_2O_3	11.9	55.8	16.6	14.8	0.9	37.3	12.1

% Other C = % MeOH + % HCHO + % C_3 + % C_4 + % C_6

[a] Catalytic reactions were performed in a 4 mm internal diameter horizontal quartz tube placed in a Heraeus tube furnace. The tube contained 0.05 g of the catalyst, held in place by Multilab quartz wool (<0.3% carbon). Reaction temperatures were monitored by a thermocouple placed adjacent to the reaction tube. All reactants and products were analysed by using a Hewlett Packard 5890A Gas Chromatograph, equipped with an HP 5895A GC Workstation and containing Porapak Q and Molecular Sieve 5A columns from J.J.'s Chromatography. Samples were left under the reaction conditions for at least 30 min to allow a dynamic equilibrium to establish.

Table 2. Results obtained at 1150 K for the pyrochlores $Ln_2Sn_2O_7$ with methane : oxygen = 2 : 1 and flow rate = 75 ml min^{-1}. Data for Sm_2O_3, under the same conditions, are also given. Oxygen conversions were approx. 50%.

	Product selectivities as % of methane converted						
Ln	% CO	% CO_2	% C_2H_4	% C_2H_6	% Other C	% Conv.	% Yield C_2 + other C
Pr	40.1	36.4	17.7	3.7	2.1	44.1	10.4
Sm	66.7	11.6	17.6	3.8	0.3	42.4	9.2
Eu	62.6	8.0	21.8	6.6	1.0	33.4	9.8
Tb	48.1	32.0	14.7	3.6	1.6	40.1	8.0
Tm	37.6	35.6	16.8	8.0	2.0	21.2	5.7
Yb	61.1	14.0	20.4	4.5	0.0	38.0	9.5
Sm_2O_3	57.2	33.4	7.0	2.4	0.0	44.1	4.1

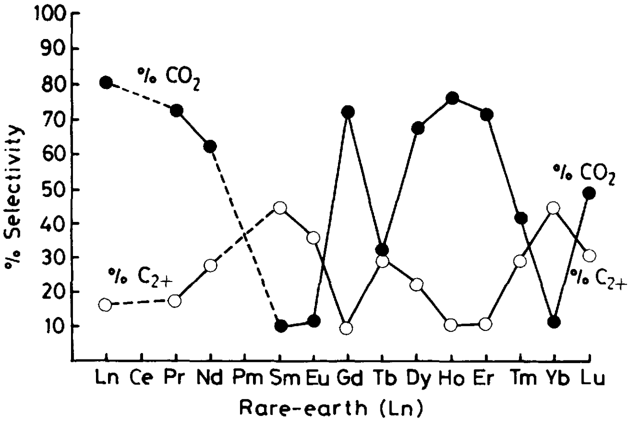

Figure 1. A comparison between combustion and oxidative coupling reactions of methane over the pyrochlores $Ln_2Sn_2O_7$ at 1000 K. % C_{2+} = % C_2H_4 + % C_2H_6 + % other C.

their performance at 1150 K without catalyst degradation. At the higher temperature, deep oxidation products become even more prevalent for the oxides with poor selectivity at 1000 K and, in many cases, all the oxygen is utilised. Indeed, for most of these compounds, the activity is too great to permit the required rate of flow through the tube to be maintained. By contrast, however, the more selective catalysts show improved yields (Table 2), and it is now clear that all of the mixed valence rare-earths, including Pr, are good coupling catalysts at 1150 K. Furthermore, the ratio of ethene to ethane is strikingly enhanced at the higher temperature, leading to sustainable ethene yields of up to 8%, and as high as 10% with optimisation. It seems likely that ethane is converted to ethene in the gas phase, either by steam cracking or by an oxidative dehydrogenation mechanism.[16] In addition, especially at higher temperatures, other products, including propene, but-1-ene and, in some cases, even benzene were detected. These presumably arise from further reactions of ethene.

Lunsford[17] and Otsuka[18] have discussed the possible role of different oxygen species in the dimerisation of methane and it is suggested that the O_2^{2-} and O_2^- species may be involved in methane activation. We have noted that the more selective catalysts have the common feature that in each case the rare-earth is able to exhibit mixed valence behaviour; for Sm, Eu, Tm, and Yb, both the +2 and +3 oxidation states are known, whereas for Pr and Tb, the +3 and +4 states are accessible. It is therefore possible that reactions of the general type shown in equations (1) or (2), followed by[19] equation (3), play an important role in methane conversion over pyrochlore catalysts. Alternatively, the role of the mixed valence cation may be to provide a facile mechanism for the reversible exchange of oxygen between the catalyst and the gas phase.

$$2Ln^{3+} + 2O^{2-} = 2Ln^{2+} + O_2^{2-} \tag{1}$$

$$2Ln^{4+} + 2O^{2-} = 2Ln^{3+} + O_2^{2-} \tag{2}$$

$$O_2 + O_2^{2-} = 2O_2^{-} \tag{3}$$

The activities observed at 1000 K are substantially less than those found for undoped samarium oxide (Table 1), but at the higher temperature the pyrochlores are more selective (Table 2). More significantly, the use of higher temperatures leads to a better yield of ethene with several of the pyrochlores than was obtainable with samarium oxide under any conditions in the present work. Nagamoto[8] has suggested a correlation between activity and lattice distortion for perovskite-type oxide catalysts. We find no such correlation between structural parameters and catalytic activity.

A particularly interesting feature of our results is that the order of reactivity of the rare-earth pyrochlores is different from that of the binary rare-earth oxides.[4,20,21] In particular, the behaviour of the dysprosium pyrochlore contrasts with the selective but unreactive sesquioxide, and the greater reactivity of the lanthanum and lutetium pyrochlores, compared with those of thulium and ytterbium at 1000 K, is the opposite of the situation encountered with the respective oxides. Also noticeable is the lack of selectivity of the pyrochlores containing holmium, erbium, gadolinium, yttrium, and lanthanum relative to those containing ytterbium, europium, and thulium; this is not a feature of the behaviour of the binary oxides. We note, however, that a very recent paper describes promising results for methane coupling with Pr_6O_{11}.[22] There is certainly no reason to suppose that the binary oxides possess the greatest potential for catalytic activity and the present work underlines the need for a careful scrutiny of appropriate mixed metal oxide systems, including other pyrochlores.

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