Catalysis Letters 8 (1991) 169–174

CATALYTIC CONVERSION OF METHANE TO SYNTHESIS GAS OVER EUROPIUM IRIDATE, $Eu_2Ir_2O_7$: AN *IN SITU* STUDY BY X-RAY DIFFRACTION AND MASS SPECTROMETRY

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Received 20 November 1990; accepted 11 December 1990

The selective partial oxidation of methane over the europium iridium pyrochlore, $Eu_2Ir_2O_7$, has been studied *in situ* by using powder X-ray diffraction and mass spectrometry. At a temperature of 873 K and 1 atmosphere pressure, with a $CH_4 : O_2$ ratio of 2 : 1 under argon dilution, high yields of synthesis gas are obtained. The pyrochlore structure of the iridate is modified during the initiation of the catalyst, giving an active solid that is shown to comprise particles of iridium metal, ~ 30 Å in diameter, supported on europium oxide, Eu_2O_3. The modification of the pyrochlore structure was monitored by X-ray diffraction, and the product gases were continuously analysed by mass spectrometry.

Keywords: Methane oxidation, synthesis gas, europium iridate, pyrochlore, iridium, in-situ

1. Introduction

Increasing concern about world dependence upon petroleum oil, in the light of dwindling supplies and the sensitive political situation in the Middle East, has provoked increased interest in the more efficient use of natural gas. Methane itself is a common fuel, but it may also be converted to synthesis gas (carbon monoxide and hydrogen), a highly versatile feedstock in, for example, methanol synthesis and Fischer-Tropsch conversions. Synthesis gas production is usually achieved by the steam reforming of methane [1] according to:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

or by partial oxidation at temperatures in excess of 1473 K [2]

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2. \tag{2}$$

The steam reforming reaction is highly endothermic, and substantial amounts of carbon dioxide and water are formed by side reactions, notably the shift reaction:

$$CO + H_2O = CO_2 + H_2. \tag{3}$$

By contrast, the partial oxidation reaction is mildly exothermic, more selective, and produces a more desirable H_2/CO ratio.

Very recently, impressive yields of synthesis gas have been obtained at much lower temperatures (~ 1050 K) over the ruthenium-containing rare-earth pyrochlores, $Ln_2Ru_2O_7$ [3], and over a range of transition metals, either supported on alumina or present in mixed-metal oxide precursors [4]. Initial studies on the ruthenium pyrochlores [3] suggested that they are partially reduced during catalysis, leading to the formation of ruthenium metal on the surface of a mixed rare-earth ruthenium oxide of the type $(Ln, Ru)O_{2-x}$. In the present work, the formation of synthesis gas over europium iridate, $Eu_2Ir_2O_7$, was recorded *in situ* by mass spectrometry, and the key components of the catalytically active solid identified simultaneously by X-ray diffraction. This was made possible by the combined rotating-anode X-ray and catalytic reactor facility located at the Royal Institution [5,6].

2. Experimental

The europium iridate was prepared from the appropriate stoichiometric ratios of europium oxide (Aldrich Chem. Co. Ltd.) and iridium oxide (Johnson Matthey, batch 051236A) which were intimately mixed, ground, pressed into pellets, and heated in air at 1323 K for 10 days, with frequent re-grinding to ensure sample homogeneity.

The catalyst was mixed with an approximately equal weight of amorphous silica and packed down smoothly into a porous silica frit, through which the reactant gas (BOC Ltd., 5.01% CH_4, 2.52% O_2, 92.47% Ar) could pass. A pre-calibrated heating coil was wound around the frit, and the entire catalytic cell was mounted on a Siemens D500 powder X-ray diffractometer with a Stoe rotating anode X-ray source. The product gases were continuously monitored by using a VG Micromass PC200 mass spectrometer and an AMS Model 91 gas chromatograph equipped with a thermal conductivity detector [5,6].

3. Results and discussion

As the temperature was increased, no change was observed in the diffraction pattern of the sample below 873 K. Fig. 1 shows the collapse of the peaks due to the cubic pyrochlore structure with time at 873 K. It can be seen in fig. 2 that the new, broader peaks in the diffraction pattern correspond to those of iridium metal and an oxide with a fluorite-related structure. An *ex situ* experiment also revealed that some of the silica packing material had crystallised. The lattice parameter of the fluorite-related phase (5.47 Å) indicates that we are observing the sub-cell reflections of Eu_2O_3 in its C-type modification ($a = 10.866(5)$ Å [7]).

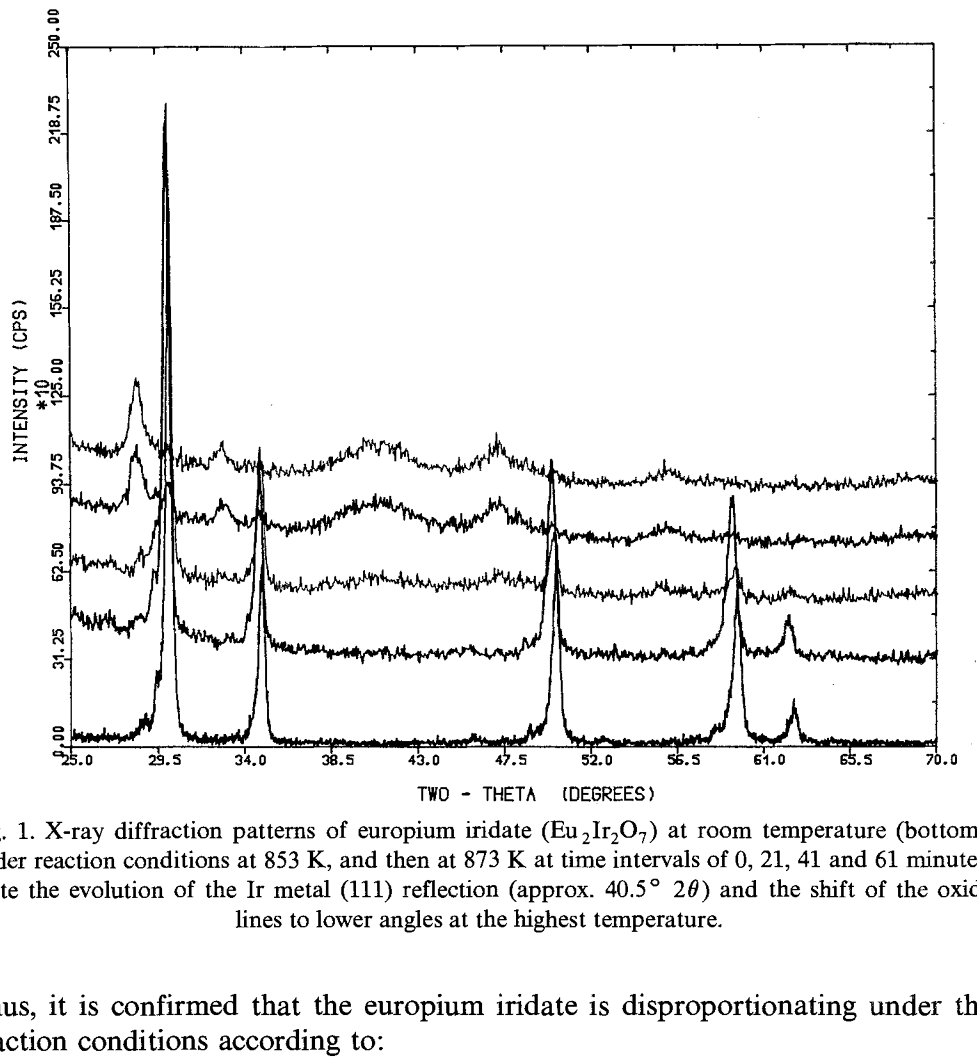

Fig. 1. X-ray diffraction patterns of europium iridate ($Eu_2Ir_2O_7$) at room temperature (bottom), under reaction conditions at 853 K, and then at 873 K at time intervals of 0, 21, 41 and 61 minutes. Note the evolution of the Ir metal (111) reflection (approx. 40.5° 2θ) and the shift of the oxide lines to lower angles at the highest temperature.

Thus, it is confirmed that the europium iridate is disproportionating under the reaction conditions according to:

$$2Eu_2Ir_2O_7 \rightarrow 2Eu_2O_3 + 4Ir + 4O_2. \tag{4}$$

The experimental data from the X-ray diffraction pattern of the resultant iridium metal can be fitted to a pseudo-voigt function (fig. 3), with a line-width corresponding to particles of approximately 30 Å in diameter. This provides confirmation that the active catalytic species is indeed iridium metal particles on a rare-earth oxide support.

The profiles of the product gases shown in fig. 4 are instructive. They show little change below 573 K, but, that at this temperature, small increases occur in the pressures of H_2O, H_2, CO and CO_2, with a concomitant small decrease in that of O_2. Presumably, this is due to limited catalysis of the following reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{5}$$

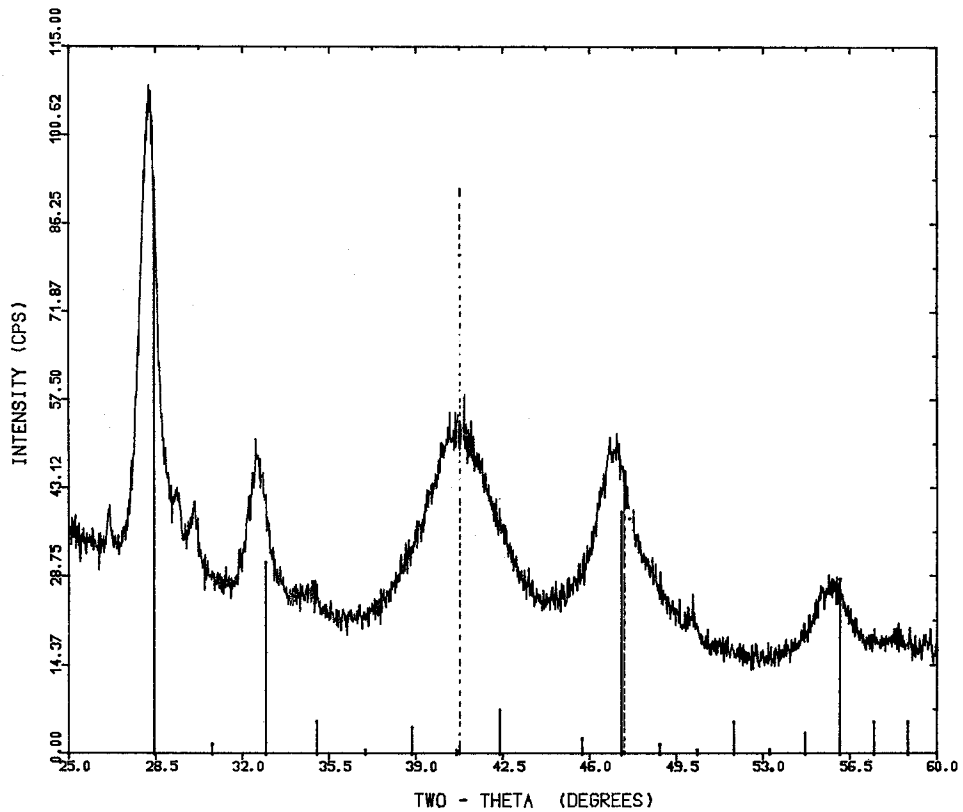

Fig. 2. *Ex situ* X-ray diffraction pattern of the decomposed pyrochlore at room temperature, with Eu_2O_3 (solid) and iridium metal (dashed) reflection markers.

$$CH_4 + H_2O = CO + 3H_2 \tag{6}$$

$$CO_2 + H_2 = CO + H_2O \tag{7}$$

$$CH_4 + CO_2 = 2CO + 2H_2. \tag{8}$$

These reactions occur to such a limited extent between 573 K and 873 K that there is no observable decrease in the CH_4 trace. At 873 K, however, the thermodynamic equilibria and kinetic conditions are sufficiently favourable that significant amounts of synthesis gas are produced, even over the relatively poor catalyst, $Eu_2Ir_2O_7$. The hydrogen produced in these reactions triggers the reduction of the europium iridate, and a short burst of oxygen is observed as the pyrochlore decomposes (eq. (4)). The resultant material is an excellent catalyst for the partial oxidation reaction and there is a sharp increase in synthesis gas production. Indeed, analysis of the GC spectra reveals that some 64% of the methane has been converted, at a selectivity of 99% to synthesis gas; in separate microreactor studies [3,4], conversions of 94% were achieved.

4. Conclusion

By monitoring the onset of catalytic activity using a combination of X-ray diffraction and GC/mass spectrometry, we have demonstrated that the europium iridate itself is largely inactive; that, at 873 K, sufficient synthesis gas is produced to decompose the pyrochlore structure and yield a much more active phase; and that this active phase consists of 30 Å particles of iridium metal supported on europium oxide, Eu_2O_3.

Acknowledgements

We thank the S.E.R.C for general support, the Royal Society for a Warren Research Followship to RHJ, and British Gas for a studentship for ATA and for funding towards equipment. Johnson Matthey plc. are also thanked for the loan

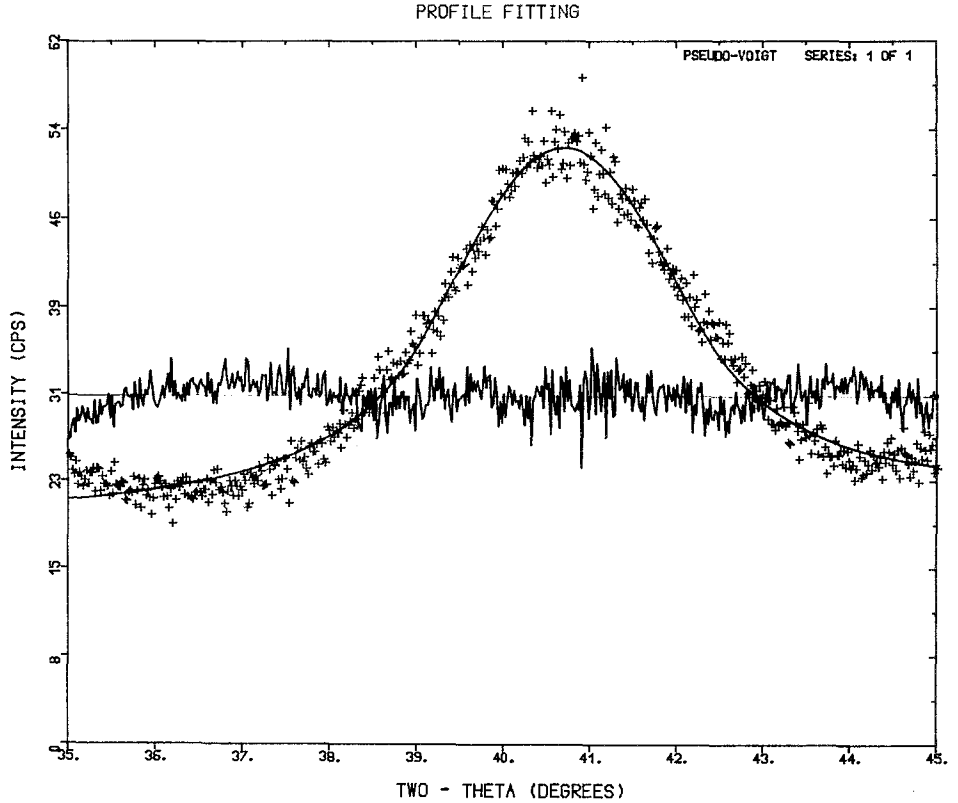

Fig. 3. A pseudo-Voigt function fitted to the (111) reflection of iridium metal; crosses show the experimental data and a smooth curve indicates the fitted function; a difference curve is also shown.

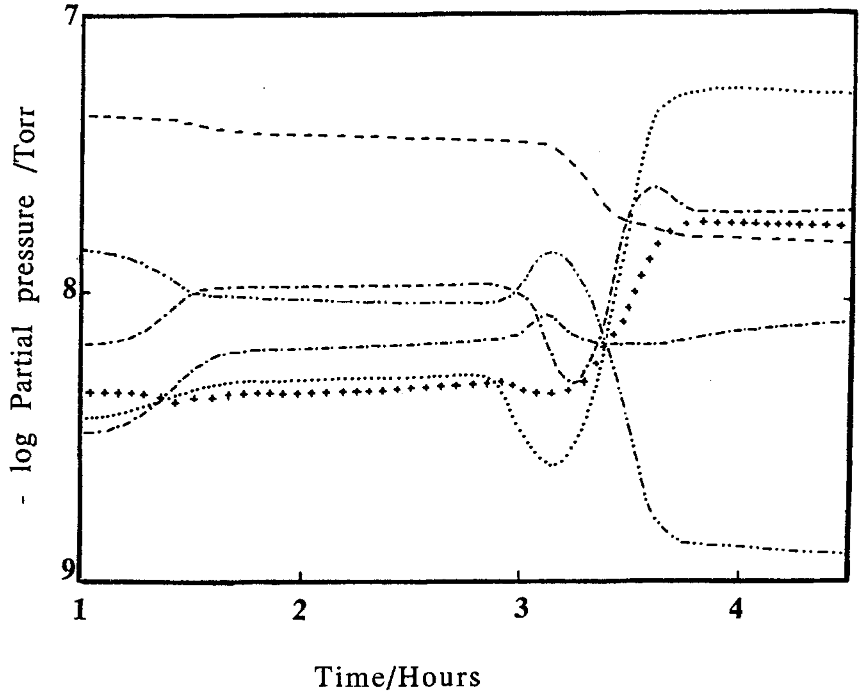

Fig. 4. Results of mass spectrometric analysis of the effluent gases as a function of time and temperature. The temperature was stepped up to 873 K over the first 3 hours, and then held at that temperature for a further 2 hours. The partial pressures of the gases are indicated as follows: CH_4(- - - - - -), O_2(· ·-· · ·-· ·), H_2O(- -·- - -·) CO(+ + + +), CO_2(-·-·-·), H_2(· · · · · ·).

of iridium oxide, and John Couves, Malcolm Green and Patrick Vernon for useful discussions.

References

[1] W. Keim (ed.), *Catalysis in C_1 Chemistry* (Reidel, Dordrecht, 1983).

[2] R.E. Kirk and D.F. Othmer, (eds.), *Encyclopedia of Chemical Technology*, 3rd edn., Vol. 12 (Wiley Interscience, New York, 1980) 952.

[3] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell and P.D.F. Vernon, Nature 344 (1990) 319.

[4] P.D.F. Vernon, M.L.H. Green, A.K. Cheetham and A.T. Ashcroft, Catal. Lett. 6 (1990) 181.

[5] P.J. Maddox, J. Stachurski and J.M. Thomas, Catal. Lett. 1 (1988) 191.

[6] J.W. Couves, R.H. Jones, J.M. Thomas and B.J. Smith, Advanced Materials 2 (1990) 181.

[7] D.H. Templeton and C.H. Dauben, J. Amer. Chem. Soc. 76 (1954) 5237.