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The catalytic activity of Ru and Ir supported on Eu_2O_3 for the reaction, $CO_2 + CH_4 \rightleftarrows 2\ H_2 + 2\ CO$: a viable solar-thermal energy system

J.S.H.Q. Perera *, J.W. Couves, G. Sankar and J.M. Thomas

Davy Faraday Research laboratory, The Royal Institution of Great Britain, 21 Albemarle Street,
London W1X 4BS, United Kingdom

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Methane and carbon dioxide which often co-exist in nature, constitute valuable potential resources both for the storage of solar (thermal) energy and the convenient production of synthesis gas. Ru and Ir supported on Eu_2O_3 are effective catalysts for the reforming of methane with carbon dioxide to produce synthesis gas with no significant coke formation even after prolonged activity. Ru catalysts show onset of activity around 673 K reaching a maximum at about 973 K. Loadings as low as 1% by weight of Ru are highly effective. Ir catalysts show onset around 823 K reaching a maximum conversion in excess of 94% with respect to CO_2 at 1023 K for a 1% loading of the metal. X-ray absorption studies on the spent Ru/Eu_2O_3 catalysts indicate the presence of the reduced metal, primarily in the form of large spherical particles (> 30 Å) of hexagonal structure. 5% Ir supported on Eu_2O_3 was found to transform an equimolar mixture of H_2 and CO to methane and carbon dioxide with a 42% conversion with respect to H_2 at around 848 K and atmospheric pressure. A 5% loading of Ru on Eu_2O_3 produced a 14% conversion with respect to H_2 at 973 K under similar conditions.

Keywords: Carbon dioxide; methane; 'syn gas'; ruthenium; iridium; europium oxide; supported noble metals; solar energy

1. Introduction

$CO_2 + CH_4 \rightleftarrows 2\ H_2 + 2\ CO$, is an industrially important reaction in that it produces "syn gas", a highly versatile feedstock in, for example, the synthesis of methanol and in Fischer-Tropsch conversions leading to the production of clean (benzene free) fuels. Moreover, the reverse reaction with an exothermicity of 247.3 kJ mol^{-1} may be used in chemical energy transmission systems suitable for

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* Commonwealth Academic Fellow on leave from University of Peradeniya, Peradeniya, Sri Lanka.

energy storage and transmission. Fossil-derived heat or solar energy drives the forward reaction homogeneously so that stored chemical energy (as a $CO + H_2$ mixture) may then be transported over large distances to a facility where the reverse reaction is effected by an appropriate heterogeneous catalyst to liberate the energy thus stored [1,2]. The cycle can be then repeated almost indefinitely, depending upon the effectiveness of the catalyst.

Rare-earth pyrochlores such as $Eu_2Ir_2O_7$ have been used to produce 'syn gas' by the partial oxidation of methane where the activation of the catalyst involves the breakdown of the pyrochlore to yield small particles of the noble metal supported on the rare earth oxide [3–5]. Reforming of carbon dioxide, $CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$, has been suggested as a constituent reaction in the many steps involved in the partial oxidation of methane [6], and hence, directly prepared active catalyst phases such as Ir/Eu_2O_3 and Ru/Eu_2O_3 are worthy of investigation. An efficient catalyst system determined for the forward reaction may then be tried out for carrying out the reverse reaction under appropriate thermodynamic conditions.

2. Experimental

Eu_2O_3 support for the catalysts was prepared by the slow thermal decomposition (ramped to 450°C at 5 K min^{-1} and held for 12 h) of a $Eu(OH)_3$ gel freshly prepared by the hydrolysis of $EuCl_3.6\ H_2O$ (Aldrich Chemical Co. Ltd.) with ammonia. Catalyst samples containing 1, 2, 3, and 5% by weight of Ru on Eu_2O_3 were prepared by supporting appropriate amounts of $RuCl_3.3\ H_2O$ (BDH Laboratory Supplies) on Eu_2O_3 using the incipient wetness method, followed by drying overnight at 110°C. Catalyst samples containing 1, 2, 3, and 5% Ir by weight on Eu_2O_3 were prepared similarly using $IrCl_4$ (Johnson Matthey) as the source of Ir.

The catalytic activity of the forward reaction was studied using 0.40 g of the pelletized (60–80 mesh) solid that had been reduced *in situ* in a flow of H_2 at 600°C for 5 hours in a single-pass microreactor prior to the introduction of the reactant gas feed consisting of an equimolar mixture of CH_4 and CO_2, (12.5% CO_2, 12.5% CH_4 and balance He (all gases supplied by BOC Ltd.)), at a flow rate of 70 $cm^3\ min^{-1}$ (space velocity $= 1.12 \times 10^4\ h^{-1}$) at atmospheric pressure. Reaction mixtures were analysed as a function of temperature using a mass spectrometer (VG Quadrupoles Micromass PC200) operating in the multiple ion monitoring mode. For the catalytic activity study of the reverse reaction the above procedure was repeated, using only the catalysts containing 5% by weight of Ru and Ir on Eu_2O_3, but replacing the reactant gas feed with an equimolar mixture of H_2 and CO (BOC Ltd.) diluted with He ($H_2:CO:He = 1:1:1.5$) at a flow rate of 70 $cm^3\ min^{-1}$ (space velocity $= 1.12 \times 10^4\ h^{-1}$) at atmospheric pressure.

X-ray diffraction patterns of the catalysts before and after reduction were obtained using a Siemens D500 powder X-ray diffractometer. X-ray absorption spectra (XAS) of the spent Ru/Eu_2O_3 catalysts were recorded *ex situ* (after catalysis). The samples (30–50 mg) were diluted in silica and held between two mylar sheets. Data were collected in the transmission geometry on station 9.2 at the Daresbury Synchrotron Radiation Source. This station has a Si(220) double crystal monochromator, which was held at 50% harmonic rejection using a servo mechanism. Data were collected on the Ru K-edge (at 22.122 keV). Pre and post edge background subtraction and edge normalization was performed using the EXBROOK programme. Curve fitting analysis was performed on the K^3-weighted data in the k-range $2 \rightarrow 14$ Å^{-1} using the EXCURV90 programme. Phase-shift corrections were determined from analysis of Ru metal powder data.

3. Results and discussion

Conversions of the reactant feed with respect to CO_2 and CH_4 at selected temperatures for the four Ru on Eu_2O_3 catalysts and the four Ir on Eu_2O_3 catalysts are given in tables 1 and 2, respectively. In all cases, H_2, CO and trace

Table 1
Temperature variation of conversion (w.r.t. CO_2) of Ru on Eu_2O_3 catalysts for $CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2$. (Conversions w.r.t. CH_4 given in parentheses)

Temperature (K)	Loading [a]	% conversion			
		1% Ru	2% Ru	3% Ru	5% Ru
673		5.5(2.6)	8.3(5.6)	9.1(6.1)	10.6(7.0)
773		29.6(17.5)	37.2(27.9)	41.4(29.7)	43.9(33.8)
873		65.6(49.9)	70.2(57.7)	73.7(57.6)	78.0(66.2)
973		86.3(73.3)	87.6(74.9)	87.9(75.7)	92.0(83.0)

[a] % by weight of Ru loaded on Eu_2O_3 support.

Table 2
Temperature variation of conversion (w.r.t. CO_2) of Ir on Eu_2O_3 catalysts for $CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2$. (Conversions w.r.t. CH_4 given in parentheses)

Temperature (K)	Loading [a]	% conversion			
		1% Ir	2% Ir	3% Ir	5% Ir
823		1.4(1.2)	9.7(4.3)	5.8(1.2)	10.5(4.4)
873		16.2(12.3)	30.8(18.6)	30.8(20.0)	29.8(16.5)
923		45.9(32.6)	54.9(41.4)	61.5(49.1)	65.8(54.4)
973		74.0(57.9)	80.4(64.8)	83.7(69.7)	86.0(72.8)
1023		94.6(84.0)	93.2(81.9)	93.2(80.6)	92.1(80.1)

[a] % by weight of Ir loaded on Eu_2O_3 support.

Table 3

Turnover numbers [a] for $CO_2(N_{CO_2})$ and $CH_4(N_{CH_4})$ estimated for the reaction, $CO_2+CH_4 \rightarrow 2\ CO+2\ H_2$, at selected temperatures

Catalyst	973 K		1023 K	
	N_{CO_2} (s^{-1})	N_{CH_4} (s^{-1})	N_{CO_2} (s^{-1})	N_{CH_4} (s^{-1})
1% Ru/Eu_2O_3	0.131	0.112	–	–
2% Ru/Eu_2O_3	0.067	0.058	–	–
3% Ru/Eu_2O_3	0.046	0.039	–	–
5% Ru/Eu_2O_3	0.029	0.026	–	–
1% Ir/Eu_2O_3	0.214	0.168	0.274	0.243
2% Ir/Eu_2O_3	0.117	0.095	0.136	0.120
3% Ir/Eu_2O_3	0.082	0.069	0.092	0.079
5% Ir/Eu_2O_3	0.052	0.044	0.055	0.048

[a] Estimated as the number of μmols of CO_2 and CH_4 converted per μmol of Ru or Ir per second.

amounts of H_2O were the only products detected by the mass spectrometer. Conversions with respect to CH_4 are consistently less than that with respect to CO_2 at all temperatures and for all catalysts studied. The fact that the degree of conversion of the CO_2 and CH_4 are not the same when the stoichiometry of the carbon dioxide reforming reaction would imply otherwise arises because other reactions, notably the reverse water-gas-shift process: $CO_2 + H_2 \rightleftarrows H_2O + CO$ also take place [7,8]. For the 5% Ru/Eu_2O_3, the percentage yield of H_2O at 973 K, estimated as, {[(amount of H_2O formed)/(amount of CO_2 reacted)] × 100}, was 9.0. For all samples, the catalytic activity remained constant for periods exceeding 8 hours at 973 K for Ru and at 1023 K for Ir. The catalysts showed no significant coke formation and could be used to carry out the reaction several times without any significant loss of activity. Increase in temperature beyond 973 K for Ru and 1023 K for Ir, decreased the activity of the catalysts. A control experiment carried out with pure Eu_2O_3 showed no reactivity.

All four Ir catalysts showed an onset of activity around 823 K, whereas the four Ru catalysts showed initial activity at a much lower temperature of around 673 K. The 'turnover numbers' for CO_2 and CH_4, N_{CO_2} and N_{CH_4}, on the Ru and Ir catalysts, estimated as the number of μmols of CO_2 and CH_4 converted per μmol of Ru or Ir per second are given in table 3. This shows that, although the percent conversion with respect to CO_2 and CH_4 show a general increase with the metal loading at lower temperatures (tables 1 and 2), the actual turnover rate clearly decreases with increased loading for both Ru and Ir.

The activation energy of the reaction, $CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$, for the four catalysts, 1%, 2%, 3% and 5% by weight of Ru on Eu_2O_3, was estimated to be 82.5 kJ mol^{-1}, 77.4 kJ mol^{-1}, 77.2 kJ mol^{-1} and 76.9 kJ mol^{-1}, respectively.

Table 4
The parameters derived from the best fits for the EXAFS first shell oscillations observed for Ru/Eu_2O_3 catalysts

Sample	N	R (Å)	σ^2 (Å^2)
1% Ru	7.4	2.676	0.006
2% Ru	10.1	2.675	0.009
3% Ru	10.8	2.677	0.008
5% Ru	10.3	2.672	0.009

N = Coordination number.
R = Ru-Ru distance.
σ^2 = Debye-Waller factor.

The corresponding values of activation energy estimated for 1%, 2%, 3% and 5% by weight of Ir on Eu_2O_3 are 185.4 kJ mol^{-1}, 149.6 kJ mol^{-1}, 162.1 kJ mol^{-1} and 172.9 kJ mol^{-1}, respectively.

X-ray diffraction patterns of the four Ru catalysts before and after reduction did not show any peaks due to $RuCl_3$ or ruthenium metal. Similarly, the X-ray diffraction patterns of the four Ir catalysts also did not show any peaks due to $IrCl_4$ or Ir metal.

In an earlier study at this laboratory we traced (by combined XRD and mass spectrometric gas analysis) the change in catalytic performance of $Eu_2Ru_2O_7$ as it decomposed in the presence of reacting gas to form an active metallic Ir catalyst supported on the rare-earth oxide [5]. In that study estimates, based on widths of X-ray diffraction peaks, were made of the particle size of the resulting noble metal catalyst. Here X-ray absorption spectroscopy has been used to pursue such investigations. The parameters used to obtain the best fits for the EXAFS oscillations recorded for the spent Ru/Eu_2O_3 catalysts are shown in table 4. The Fourier transforms (FT) of the EXAFS data are indicative of samples possessing the hcp structure of bulk Ru (fig. 1). The co-ordination numbers determined for the first shell, for the 2%, 3%, and 5% materials are all close to those expected for the bulk Ru, considering the approximate 6% error on co-ordination number [9]. The particle size of the noble metal catalyst is thus in excess of 30 Å (based on the average co-ordination number of the first shell). The outer shells are also consistent with large spherical particles.

The activity of the catalyst containing 5% Ru by weight supported on Eu_2O_3, for the reverse reaction, $2\ CO + 2\ H_2 \rightarrow CH_4 + 2\ CO$, studied as a function of temperature showed the onset of activity around 623 K with the concurrent appearance of the mass spectrometric signals for CO_2 and CH_4. The intensity of these signals increased with increasing temperature showing a maximum corresponding to a 14.4% conversion with respect to H_2 at 973 K. As in the case of the forward reaction there was no significant coke formation on the catalyst. CO_2 and CH_4 were the only products detected by the mass spectrometer. The

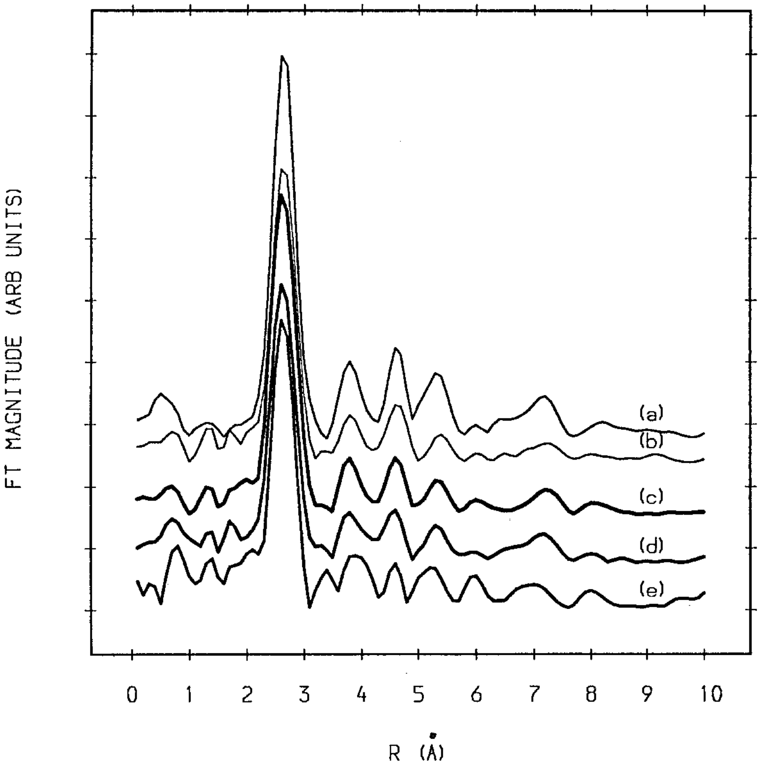

Fig. 1. Fourier transform magnitude of the Ru K-edge EXAFS for the spent Ru catalysts and Ru metal; (a) Ru metal; (b) 5% Ru/Eu_2O_3; (c) 3% Ru/Eu_2O_3; (d) 2% Ru/Eu_2O_3; (e) 1% Ru/Eu_2O_3.

onset of catalytic activity for 5% by weight Ir on Eu_2O_3 on the reverse reaction was observed around 723 K with the activity reaching a maximum at 848 K corresponding to a 42.5% conversion with respect to H_2. Thus, Ir supported on Eu_2O_3 clearly appeared to be the better catalyst for the reverse reaction under the conditions employed.

4. Conclusions

Both Ru and Ir supported on Eu_2O_3 are efficient catalysts in the conversion of an equimolar mixture of CH_4 and CO_2 to "syn gas". The catalysts did not show any significant coke formation even after prolonged usage, and could be used for several cycles without any noticeable loss of activity. Ru catalysts showed an onset of activity at a temperature as low as 673 K with the percentage conversion with respect to CO_2 reaching a maximum at about 973 K, with loadings as low as 1% Ru being highly effective. Although, the Ir catalysts showed the onset of activity at a temperature about 150 K higher than the Ru catalysts, at 1023 K the former showed a greater than 92% conversion with respect to CO_2, for all the different loadings of Ir on Eu_2O_3 studied in this work. The performance of these catalysts are not very different from that of Ir and Ru supported on Al_2O_3 [7] which indicates that the role of the nature of the support is more or less insignificant in the catalytic mechanism.

The XAS analysis of the spent Ru/Eu_2O_3 catalysts indicates the presence of the reduced noble metal, primarily in the form of large spherical particles (> 30 Å) of the hcp structure.

A catalyst containing 5% Ir by weight supported on Eu_2O_3 was found to catalyse the conversion of synthesis gas to CH_4 and CO_2 with the maximum efficiency observed around 848 K under ambient pressure conditions. Under these conditions, the percentage conversion with respect to H_2 was found to be 42.5. The 5% Ru by weight on Eu_2O_3 catalyst was found to produce a maximum conversion of 14.4% with respect to H_2 at 973 K under similar conditions. These catalysts may be expected to have a higher efficiency at elevated pressures, based on straight-forward thermodynamic considerations.

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References

[1] J.T. Richardson and S.A. Paripatyadar, Appl. Catal. 61 (1990) 293, and references therein.
[2] I. Dostrovsky, *Energy and the Missing Resource* (Cambridge University Press, Cambridge, 1988).
[3] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, G.P. Grey, A.J. Murrel 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] R.H. Jones, A.T. Ashcroft, D. Waller, A.K. Cheetham and J.M. Thomas, Catal. Lett. 8 (1991) 169.
[6] M. Prettre, C. Eichner and M. Perrin, Trans. Faraday Soc. 43 (1946) 335.
[7] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green and P.D.F. Vernon, Nature 352 (1991) 225.
[8] F. Solymosi and A. Erodohelyi, J. Mol. Catal. 8 (1980) 471.
[9] The 1% sample showed a significantly lower co-ordination number as might be expected for a less loaded, non-sintered, sample. However, since the measurements were made *ex situ*, the possibility of aerial oxidation of the metal after catalysis, which would cause a reduction in the effective co-ordination number, cannot be excluded.