Catalysis Letters 68 (2000) 191–196

New efficient catalysts for the oxidative coupling of methane

Alejandra Palermo, Juan Pedro Holgado Vazquez * and Richard M. Lambert **
Chemistry Department, Cambridge University, Cambridge CB2 1EW, UK
E-mail: rml1@cam.ac.uk

Received 27 June 2000; accepted 30 June 2000

During calcination of OCM catalyst precursors, Li. . .Cs spectacularly lower the amorphous silica → α-cristobalite phase transition temperature, shown here to be a critically important requirement for production of effective catalysts. Incorporation of W switches on OCM activity and newly discovered K/W and Rb/W formulations exhibit unsurpassed ethylene selectivity at high methane conversion. Addition of Mn significantly improves the performance of the former. An alkali-stabilised tungsten oxo species is thought to be the OCM active site.

Keywords: oxidative coupling of methane, OCM, silica phase transition, alkalis, ethylene selectivity

1. Introduction

The oxidative coupling of methane (OCM) to higher hydrocarbons in order to generate either chemical feedstocks or fuels continues to attract considerable interest. In the last three years alone over 200 papers have appeared in which a range of catalysts and reactor strategies have been explored. In a recent paper Pak et al. [1] provide a concise review of recycle reactor and dual reactor strategies. They also describe their own encouraging results achieved with an OCM/H-ZSM-5 dual bed reactor with which they achieved 100% methane conversion with good selectivity towards C_{4+} products. The OCM catalyst they employed was an efficient trimetallic $Mn/Na_2WO_4/SiO_2$ formulation – which belongs to the class of materials that is the subject of the present paper. Whatever the implementation of OCM, selectivity towards *ethylene* (as opposed to ethylene + ethane) is of paramount importance. Leaving aside the issue of long term stability, ethylene selectivity at high methane conversion provides the most important single figure of merit for an OCM catalyst. Here, among other things, we report on a new bimetallic formulation and a new trimetallic formulation which, on the above basis, outperform all other catalysts described thus far.

In 1992 Fang et al. [2] identified a very promising OCM catalyst with the formulation 1.9 wt% Mn, 5% Na_2WO_4 supported on SiO_2. In a subsequent paper [3] they proposed tetrahedral WO_4 surface as the OCM active site, with manganese oxide enhancing the exchange between gaseous and lattice oxygen. The model was then elaborated to include a redox mechanism involving lattice oxygen ions and the W^{6+}/W^{5+} couple [4] The same catalyst was studied by Lunsford et al. [5] who took a somewhat different view as to the roles of the various chemical components in the full trimetallic system. They suggested that a Na–O–Mn species is responsible for the activation of methane, and from a later kinetic study they concluded [6] that the catalyst was unreactive towards methyl radicals even at 790 °C. It was inferred that this property could be responsible for its good performance as an OCM catalyst. We too investigated this Na/W/Mn OCM catalyst by means of XRD, XPS/XAES, TPR analysis and microreactor testing [7]. We also studied similar formulations without one or more of Na, Mn and W.

A clear correlation emerged between catalyst performance and support structure in the final calcined material. Amorphous silica gave active but very unselective catalysts. Crystalline SiO_2 (α-cristobalite) generated active and highly selective catalysts – especially with respect to the formation of ethylene. We showed that the presence of Na was essential for the anomalous low temperature silica → cristobalite support phase transition to occur, and that the occurrence of this process is critically important in the genesis of high performance catalysts. The strategy of progressively "taking apart" the trimetallic system also enabled us to demonstrate that the presence of Mn is not crucial for obtaining high ethylene yields, and the structural, catalytic and spectroscopic results indicated that Na plays a dual role as both structural and chemical promoter. Given the key role played by Na in this catalytic system, it is of interest to investigate the consequences of replacing Na with other alkalis or alkaline earths. Here we report the structural and reactive properties of a series of OCM catalysts incorporating Li, K, Rb, Cs, Mg, or Ca/WO_4 supported on silica and (in certain cases) in the presence of Mn. It is found that K- and Rb-based catalysts are best of all. The K/WO_4 catalysts exceed the performance of the corresponding Na system while the Rb analogue is even better. Addition of Mn somewhat improves the K-based catalyst but degrades the Rb-based system.

---

* Instituto de Ciencia de Materiales de Sevilla, CSIC, Américo Vespucio S/N, Isla de la Cartuja, 41092 Seville, Spain.
** To whom correspondence should be addressed.

2. Experimental

2.1. Catalyst preparation

Monometallic, bimetallic and trimetallic formulations supported on silica were prepared by incipient wetness impregnation of the amorphous support (Aldrich Davisil^{TM} 23,684-5) with the appropriate aqueous solutions. For the monometallic samples we used the relevant alkali or alkaline earth hydroxide. In every case the total molar quantity of alkali or alkaline earth was the same as in the bimetallic and trimetallic samples described below. Trimetallic catalyst precursors were made using solutions containing $Mn_2(NO_3)$ and X_2WO_4 or YWO_4, where X = alkali (Li, Na, K, Rb and Cs) and Y = alkaline earth (Ca and Mg). Bimetallic precursors were prepared by using the relevant tungstate salt. In the case of the Rb_2WO_4/SiO_2 and Cs_2WO_4/SiO_2 formulations for which the tungstate salts were not commercially available, appropriate amounts of $Rb(OH)_2$ and $Cs(OH)_2$ were mixed with the correct volume of an aqueous solution of $(NH_4)_2WO_4$ and the resultant liquid impregnated onto the SiO_2 support. Our earlier experience [7] with $Na(OH)_2$ and $(NH_4)_2WO_4$ showed that this preparation method gave better results than a two-stage impregnation.

The loadings used correspond to a fixed molar amount of alkali or alkali tungstate, 3.03×10^{-4} mol per gram of SiO_2 support and, when present, 3.7×10^{-4} mol Mn per gram of support. This procedure was adopted because it corresponds to the optimum Na/W/Mn loading reported by Jiang et al. [3], a finding confirmed by more recent combinatorial studies [8]. It is thought that this loading corresponds to formation of a close-packed dispersed monolayer of the catalytically active phase; at higher loadings, excess of Na_2WO_4 crystallises as a separate phase [3]. Samples were dried in air for 8 h at 120 °C and then calcined in flowing oxygen for 8 h at 750 °C. If crystallisation did not take place at this temperature, the samples were calcined at successively higher temperatures up to a maximum of 900 °C. The resulting information is summarised in table 1. In the case of the Rb precursor which generated a particularly promising catalyst, we also investigated the effect of varying the molar amounts of alkali as follows: 0.75×10^{-4}, 1.5×10^{-4}, 3×10^{-4}, 6×10^{-4} and 12×10^{-4} mol Rb per gram of silica. For the Rb/W precursor, we also varied the Rb : tungstate ratio from $x = 1$ to 16, where $x = 2$ corresponds to stoichiometric Rb_2WO_4.

2.2. XRD analysis

X-ray diffraction patterns of fresh and used catalysts were obtained with a Philips PW 1710 diffractometer using Cu K_α radiation. Diffractograms were recorded from $2\theta = 10$–$70°$ with the detector moving in $\Delta 2\theta = 0.05°$ steps to achieve good angular resolution.

2.3. Microreactor testing

Measurements were carried out using a single-pass, plug-flow microreactor, equipped with on-line gas chromatographic sampling using a 60–80 Carboxen-1000 column. The reactor consisted of a down-flow alumina tube (DEGUSSIT AL23 6 × 3 × 400 mm) with 0.4 g of catalyst and alumina wool above and below the catalyst bed to retain the sample. Blank runs with the alumina tube and alumina wool and without catalyst showed negligible reaction up to 900 °C. A K-type thermocouple was attached to the outside wall of the reactor. Reactant gases (10% CH_4 in He (99.95%) and 20% O_2 in He (99.996%)) were used without further purification. He was used as a balance gas, and gas flow rates were regulated by mass flow controllers (Brooks

Table 1
Catalyst structure after calcination of a range of precursors.

Nominal composition of catalyst	Precursor compound(s)	Structure	T (calcination) (°C)
Li/SiO_2	Li(OH)	Crystalline	900
Na/SiO_2	Na(OH)	α-cristobalite	800
K/SiO_2	K(OH)	α-cristobalite	850
Rb/SiO_2	Rb(OH)	α-cristobalite	900
Cs/SiO_2	Cs(OH)	Crystalline	900
Ca/SiO_2	$Ca(OH)_2$	Amorphous	900
Mg/SiO_2	$Mg(OH)_2$	Amorphous	900
Li_2WO_4/SiO_2	Li_2WO_4	Crystalline	850
Na_2WO_4/SiO_2	Na_2WO_4	α-cristobalite	750
K_2WO_4/SiO_2	K_2WO_4	α-cristobalite	800
Rb_2WO_4/SiO_2	$Rb(OH) + (NH_4)_2WO_4$	α-cristobalite	850
Cs_2WO_4/SiO_2	$Cs(OH) + (NH_4)_2WO_4$	Crystalline	900
$CaWO_4/SiO_2$	$CaWO_4$	Amorphous	900
$MgWO_4/SiO_2$	$MgWO_4$	Amorphous	900
$Mn/Na_2WO_4/SiO_2$	$Mn(NO_3)_2 + Na_2WO_4$	α-cristobalite	750
$Mn/K_2WO_4/SiO_2$	$Mn(NO_3)_2 + K_2WO_4$	α-cristobalite	800
$Mn/Rb_2WO_4/SiO_2$	$Mn(NO_3)_2 + Rb_2WO_4$	α-cristobalite	850

5890). Before admission of the reactant mixture, each catalyst sample was heated in flowing oxygen at 10 °C min^{-1} up to reaction temperature. Catalytic testing was carried out at 850 °C and 2000 h^{-1} space velocity with reactant composition methane : oxygen $= 4.5$ at a total pressure of 1 bar, except where stated otherwise. In the case of the Mn/K/W catalyst we also explored methane : oxygen ratios ranging from 0.5 to 9.0 and temperatures from 700 to 900 °C.

3. Results and discussion

Our previous work showed that good OCM catalysts are produced only when the preparation technique leads to conversion of the originally amorphous SiO_2 to highly crystalline α-cristobalite. It also showed that neither W or Mn alone could bring about this anomalous low-temperature phase transition whose occurrence depended critically on the presence of Na. The questions addressed here are (i) how dependent is this behaviour on the identity of the alkali (alkaline earth), and (ii) what is the catalytic merit, if any, of the resulting materials?

3.1. XRD analysis

As indicated in table 1 and illustrated in figure 1, monometallic precursors containing Ca or Mg were totally ineffective in inducing silica crystallisation, for calcination temperatures up to 900 °C (figure 1). Addition of W to the alkaline earth precursors made no difference. However, Li alone *did* induce some crystallisation of the initially amorphous silica, though much less effectively than Na, requiring a higher temperature, as illustrated in figure 2 (a) and (b) (900 °C versus 800 °C for Na [7]). The crystalline SiO_2 product is tridymite (closely related to α-cristobalite). Addition of W to the Li-based precursor facilitated silica crystallisation (figure 2(c)), but less so than in the case of W/Na [7] (850 °C versus 900 °C). In addition to tridymite, the resulting material contained α-cristobalite and lithium silicate.

The presence of K alone resulted in crystallisation to pure α-cristobalite at 850 °C, which is far lower than the normal transition temperature (1500 °C [9]. In this respect, K was more effective than Li but less effective than Na [7]. The monometallic Rb and Cs precursor gave α-cristobalite upon calcination to 900 °C, although in the case of Cs the degree of crystallinity was less. With the K and Rb precursors, addition of W lowered the silica crystallisation temperature from 850 to 800 °C and from 900 to 850 °C, respectively. In the case of Cs no such effect was detectable. Figure 3 shows XRD data for the most interesting and important systems (K_2WO_4/SiO_2, Rb_2WO_4/SiO_2 and Cs_2WO_4/SiO_2) after calcination; the diffractogram for pure synthetic cristobalite is also shown for purposes of comparison. It is clear that in every case the amorphous silica has extensively crystallised to α-cristobalite and a trace of tridymite (shoulder at $\sim$21°). No bulk alkali tungstates are observed. Varying the amount of alkali in the monometallic Rb precursor showed that samples with Rb content <1.0 did not form α-cristobalite, whereas higher Rb loadings did induce crystallization. Addition of either W or W$+$Mn did not alter this pattern.

As we shall see, alkali-induced crystallisation of amorphous silica during precursor calcination is critically important to the production of effective OCM catalysts. Exactly how this process occurs is not known, although the very high mobility of alkalis in amorphous silica, even at low temperatures, may provide a clue [10].

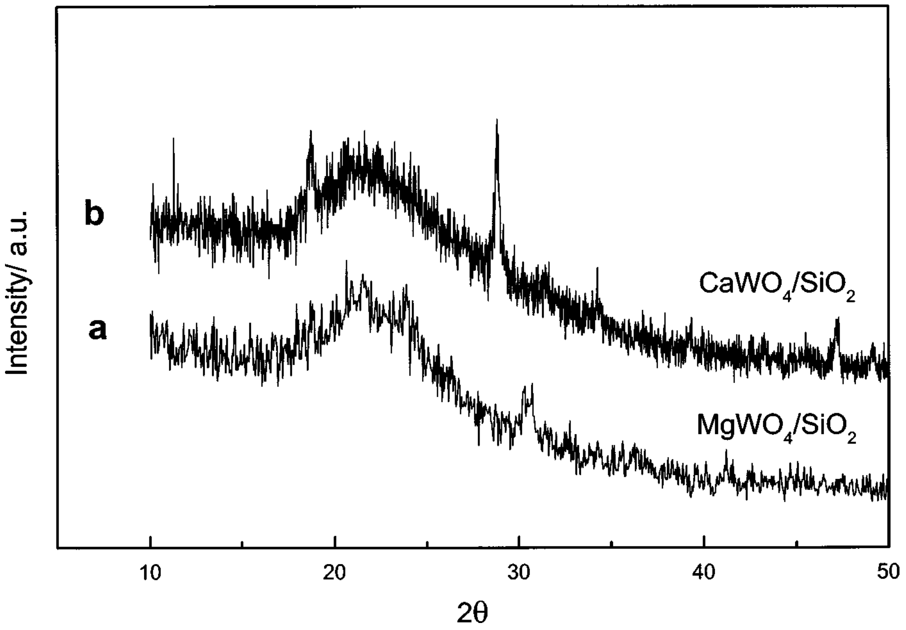

Figure 1. XRD patterns after calcination at 900 °C of (a) $MgWO_4/SiO_2$ and (b) $CaWO_4/SiO_2$.

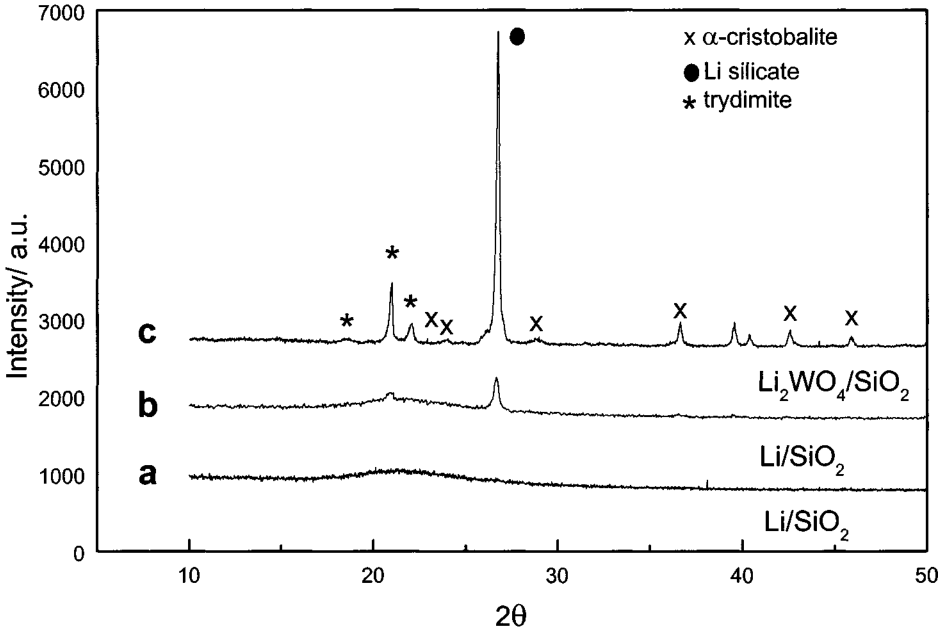

Figure 2. XRD patterns of various Li formulations after calcination: (a) $Li/SiO_2/800\,^{\circ}C$, (b) $Li/SiO_2/900\,^{\circ}C$ and (c) $Li_2WO_4/SiO_2/850\,^{\circ}C$.

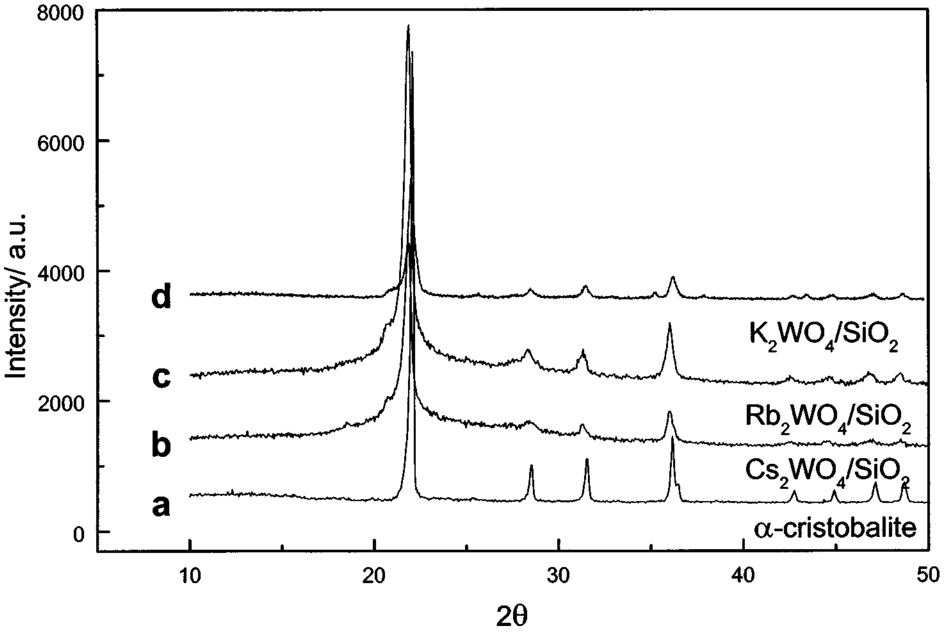

Figure 3. XRD patterns of alkali/W formulations after calcination: (a) synthetic α-cristobalite, (b) $Cs_2WO_4/SiO_2/900\,^{\circ}C$, (c) $Rb_2WO_4/SiO_2/850\,^{\circ}C$ and (d) $K_2WO_4/SiO_2/800\,^{\circ}C$.

3.2. Microreactor testing

All the catalysts were tested under the same experimental conditions ($T = 850\,^{\circ}C$, $CH_4 : O_2 = 4.5 : 1$, $p = 1$ bar) and the key results are summarised in table 2 which, for purposes of comparison, also shows results for Na formulations. The basis for choosing these standard conditions is given below. Catalytic performance is specified in terms of methane conversion, total selectivity towards C_2 products, ethylene selectivity, and ethylene yield expressed as moles of ethylene obtained per mole of methane reacted.

After calcination, the Ca- and Mg-containing precursors produced materials that behaved like unmodified amorphous SiO_2 itself: extensive burning of methane to CO_2 was the dominant reaction ($\sim$15% CH_4 conversion). On the other hand, the single-phase α-cristobalite product generated by the monometallic K, Rb and Cs precursors was catalytically inert within our detection limits. Almost the same was true for the crystalline tridymite/Li silicate material generated by Li alone: a small amount of methane burning was detectable. Taken together, these observations convincingly confirm the importance of one role played by

Table 2
Catalyst performance as a function of structure and composition.[a]

Catalyst	Structure	X_{CH_4} (%)	Selectivity[b] (mol%) Total C_2	C_2H_4	$\eta_{C_2H_4}$ yield
SiO_2	Amorphous	17	23	15	2.5
Li/SiO_2	Crystalline	<6	n.d.	n.d.	n.d.
Na/SiO_2	α-cristobalite	<2	n.d.	n.d.	n.d.
K/SiO_2	α-cristobalite	<2	n.d.	n.d.	n.d.
Rb/SiO_2	α-cristobalite	<2	~8	n.d.	n.d.
Cs/SiO_2	α-cristobalite	<5	~10	n.d.	n.d.
Mg/SiO_2	Amorphous	15	~20	n.d.	n.d.
Ca/SiO_2	Amorphous	15	~21	n.d.	n.d.
Na_2WO_4/SiO_2	α-cristobalite	44	52	42	~19
K_2WO_4/SiO_2	α-cristobalite	30	67	52	~16
Rb_2WO_4/SiO_2	α-cristobalite	32	78	59	~19
Cs_2WO_4/SiO_2	Crystalline	33	55	39	~13
Li_2WO_4/SiO_2	Crystalline	36	27	26	9.5
$CaWO_4/SiO_2$	Amorphous	16	25	20	3
$MgWO_4/SiO_2$	Amorphous	20	20	15	3

[a] Conditions: $T = 850\,^{\circ}C$, GHSV = 2000, $CH_4 : O_2 = 4.5$.
[b] n.d. = not detectable.

the alkalis: conversion of high surface area amorphous silica (which is very active for methane burning) [7] into low surface area α-cristobalite or tridymite (which are inactive for methane burning) [7].

Addition of W to *all* the alkali-containg precursors gave catalysts that exhibited pronounced activity and varying degrees of selectivity towards OCM. In this connection, recall that the W/silica system (derived from $(NH_4)_2WO_4$/silica) gave a bad catalyst yielding only methane burning under these test conditions [7]. We may therefore infer that there is an interaction between alkali and a W-containing surface species that results in formation of the OCM active site. The second key role played by alkali is therefore confirmed. Specifically, we propose that the OCM active site is a tetrahedrally co-ordinated WO_4 surface species stabilised by interaction with alkali. We suggest that in the absence of alkali, calcination leads to formation of octahedrally co-ordinated WO_3 surface species which are unselective towards OCM. These proposals are consistent with the well known oxidation properties of oxo-tungsten species in solution.

Inspection of table 2 reveals that the K/W catalyst is superior to the previously reported [7] Na/W system: 52% ethylene at 30% methane conversion versus 42% ethylene at 44% methane conversion. The Rb/W formulation is best of all: 59% ethylene at 32% methane conversion with total C_2 selctivity of 78%. Cs is approximately as good as Na and substantially better than Li. Why is Li least effective of the alkalis? It should be recalled that this catalyst is a three-phase system and its relatively poor performance is almost certainly connected with extensive formation of Li silicate during calcination. It seems reasonable to suggest that the Li/tridymite Li/α-cristobalite components of this catalyst behave like Na, K, Rb, Cs/α-cristobalite and are effective for OCM, whereas the Li silicate component acts to burn methane.

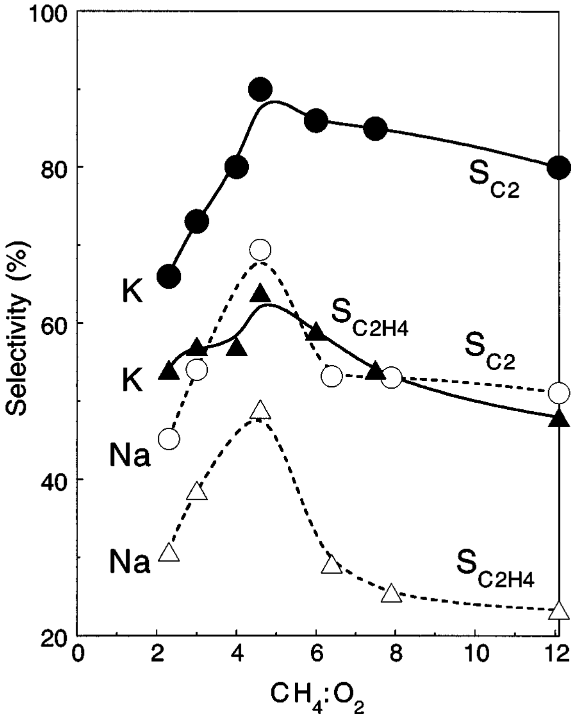

Figure 4. Effect of $CH_4 : O_2$ partial pressure ratio on total C_2 selectivity and C_2H_4 selectivity for $Mn/Na_2WO_4/SiO_2$ (●, ▲) and $Mn/K_2WO_4/SiO_2$ (○ △). Conditions: $T = 850\,^{\circ}C$, GHSV = 200.

Because the K/W catalyst showed even better ethylene selectivity than its Na counterpart *under reaction conditions that were optimised for the latter* we carried out a study of the effects of $CH_4 : O_2$ ratio and reaction temperature on catalyst performance. Figure 4 shows the result of varying the methane to oxygen ratio on the ethylene selectivity and methane conversion delivered by the K_2WO_4/SiO_2-derived catalyst. At 850 °C the best ethylene selectivity occurs at $CH_4 : O_2 = 4.5$, i.e., exactly the same as for the Na/W catalyst [7] for which the corresponding results are also shown. This is the basis on which the standard conditions for testing all the catalysts were chosen. The effect of varying the alkali/W ratio in the best (Rb/W) bimetallic formulation was also studied. It was found that $x = 2$ (equivalent to stoichiometric Rb_2WO_4) produced the most active and selective catalyst, namely that listed in table 2. This is at least consistent with our earlier view that the OCM active phase consists of monolayer-thick W-oxo species bonded to the cristobalite surface and stabilised by interaction with neighbouring alkali ions.

Finally, we investigated the consequences of adding Mn to the most promising bimetallic (K or Rb)/W formulations. Our earlier work showed that adding Mn to Na/W catalysts significantly enhanced selectivity at the cost of a ~25% decrease in conversion. Addition of the same amount of Mn to the K/W catalyst substantially boosted the performance to *64% ethylene selectivity* (90% C_2 selectivity at 29% CH_4 conversion) whereas it actually slightly degraded the Rb/W system (63% C_2 selectivity at 31% CH_4 conversion).

The role of Mn in these complex catalysts awaits clarification. It appears that there is no great synergy between Mn and either the alkalis or W. Since silica/manganese oxide is itself an active OCM catalyst [11] it seems possible that in the present case a Mn-oxide-catalysed process is simply running in parallel with an alkali-tungstate-catalysed reaction, a conclusion that is in line with our results for the best K- and Rb-containing materials. On the other hand, our results clearly do show that catalytic performance is strongly dependent on synergy between the alkali component and the W component. That is, in addition to the crucially important alkali-induced silica → α-cristobalite phase transition, alkalis must stabilise the WO_x OCM active site. Although direct comparisons with other work are not entirely straightforward, the high methane conversion per single pass combined with very high *ethylene* selectivity indicate that the bimetallic Rb/W catalyst and the trimetallic K/W/Mn catalyst deliver the best performances reported up to the present time. Why does Rb generate the best bimetallic system? We are unable to account for this on the basis of present knowledge: speculation about the relative stabilities of supported alkali/tungsten oxo species would not be justified. Further experimental and theoretical work is called for and this is in progress.

4. Conclusions

(1) Calcined materials containing amorphous silica are active for methane burning and almost totally ineffective catalysts for OCM. Calcined materials consisting of alkali tungstates suported on α-cristobalite are effective OCM catalysts.

(2) Alkalis play a key role as structural promoters, lowering the amorphous silica → α-cristobalite phase transition far below the normal value (1500 °C).

(3) There is a strong synergy between the alkali and W components in these catalysts, suggesting that the OCM active site consists of an alkali-stabilised W-oxo species.

(4) Li/W generates relatively poor OCM catalysts probably due to formation of Li silicate. K/W and, especially, Rb/W generate catalysts that are exceptionally selective, particularly with respect to ethylene production. Their performances are enhanced and degraded, respectively, by addition of Mn.

(5) In terms of methane conversion and ethylene selectivity, K/W/Mn and Rb/W formulations supported on α-cristobalite yield the best OCM catalysts reported thus far.

Acknowledgement

Support under European Union Grant No. JOE3CT 950010 is gratefully acknowledged. This work was also partly supported under Grant No. GR/M76706 awarded by the UK Engineering and Physical Sciences Research Council. JPHV thanks The Spanish Ministerio de Educación and the European Union for financial support.

References

[1] S. Pak, T. Rades, M.P. Rosynek and J.H. Lunsford, Catal. Lett. 66 (2000) 1.
[2] X.P. Fang, S.B. Li, J.Z. Lin, J.F. Gu and D.X. Yang, J. Mol. Catal. (China) 6 (1992) 427.
[3] Z.-C. Jiang, C.-J. Yu, X.-P. Fang, S.B. Li and H.-L. Wang, J. Phys. Chem. 97 (1993) 12870.
[4] J. Wu, S. Li, J. Niu and X. Fang, Appl. Catal. A 124 (1995) 9.
[5] D. Wang, M.P. Rosynek and J.H. Lunsford, J. Catal. 155 (1995) 390.
[6] S. Pak, P. Qui and J.H. Lunsford, J. Catal. 179 (1998) 222.
[7] A. Palermo, J.P. Holgado Vazquez, A.F. Lee, M.S. Tikhov and R.M. Lambert, J. Catal. 177 (1998) 259.
[8] U. Rodemerck, P. Ignaszewski, M. Lucas and P. Claus, Chem. Eng. Technol. 23 (2000) 413.
[9] A.F. Wells, *Structural Inorganic Chemistry* (Oxford Univ. Press, Oxford, 1987) ch. 23, p. 1004.
[10] C. Mazzara, J. Jupille, A.-M. Flank and P. Lagarde, J. Phys. Chem. B 104 (2000) 3438.
[11] C.A. Jones, J.J. Leonard and J.A. Sofranko, J. Catal. 103 (1987) 311.