Catalysis Letters 21 (1993) 123–131

Redox properties of molten salts for methane activation

J.B. Claridge, M.L.H. Green, R.M. Lago, S.C. Tsang and A.P.E. York

*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road,
Oxford, OX1 3QR, UK*

Received 26 November 1992; accepted 4 June 1993

Molten salt mixtures have been tested in a redox mode as catalysts for the activation of methane at 750°C. It is found that after pre-treatment with dioxygen a transition metal halide/sodium vanadate melt can convert methane selectively to C_{2+} products in the absence of molecular oxygen. The melt can be reactivated by passing dioxygen. Electron paramagnetic resonance studies of the quenched samples showed that the transition metal ions are reduced by methane and can be reoxidised by dioxygen. It is also found that higher C_{2+} selectivity, C_{2+} yield and C_2H_4/C_2H_6 ratio are promoted by added transition metal chlorides and, surprisingly, also by the corresponding metal bromides. It supports the suggestion that surface modification by halogen is more important than gas radical reactions. Comparison of the molten mixtures under redox and cofeed conditions showed that the former gave a higher C_{2+} selectivity, but no oxygenated products whereas formaldehyde was only detected in the cofeed conditions.

Keywords: Molten salts; redox mode; oxidative coupling of methane; transition metal halides / sodium metavanadate mixtures

1. Introduction

Selective functionalization of methane using molecular oxygen to give useful products, i.e. methanol, formaldehyde and ethene, has been extensively investigated [1–8]. However, much of the attention has been concentrated on using solid heterogeneous catalysts. It has been shown that many different oxygen species are present in molten salt mixtures [9–12], some of which may activate methane selectively. Recently, only a few studies have been carried out using molten salts as catalysts [13–18]. For example, ternary eutectic mixtures of Li_2CO_3, K_2CO_3, and Na_2CO_3 have been reported in the patent literature to give 20% methane conversion with 24% C_2 selectivity [18]. Lunsford et al. [15] have also reported 43% methane conversion with 40% C_2 selectivity over lithium carbonate melts. However, the catalytic performance of molten salt mixtures under redox conditions has not been reported. The absence of molecular oxygen under redox conditions would be expected to reduce further oxidation of products and, therefore, high selectivity to useful products might be obtained. Also, the addition of chloride to catalyst systems can lead to higher C_2 selectivity and C_2H_4/C_2H_6 ratio [19–24]. Therefore, we have also investigated the redox properties of molten mixtures containing halides.

2. Experimental

2.1. CATALYST PREPARATION

The molten salt catalysts were all prepared from high purity reagents without further purification. The components were mixed, ground, and melted in a furnace at 800°C for 2 h (see tables 1–3 for individual catalyst). 2 g of the resulting mixture was then transferred to the reaction vessel.

2.2. CATALYST REACTIONS

The catalyst testing apparatus is shown in fig. 1. The catalytic experiments were carried out in a silica tube reactor of 120 mm in length and 8 mm i.d. Salt mixtures were melted in the reactor tube using a programmed temperature controlled tube furnace. Reactant gases were bubbled to the molten salts via a thin stainless steel tube. In order to reduce the extent of gas phase reactions, the dead volume above the melt was minimized. The product gases were monitored by either a quadrupole mass spectrometer HP5971A or a UNICAM-PYE gas chromatograph. All the exit tubes were heated to 120°C to avoid any product vapour condensation.

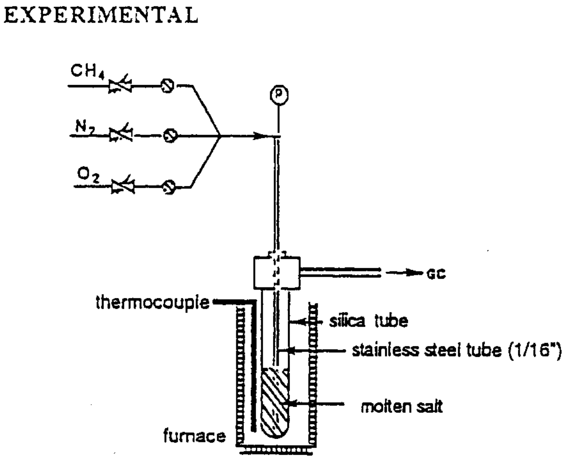

Fig. 1. Diagram of the reactor used for the catalytic experiments.

The GC was equipped with a gas sampling valve and flame ionization detector. In order to detect carbon oxides a methanator containing a commercial nickel catalyst was incorporated. The response factors for the different gases were determined and taken into account in our results.

Experiments in the redox mode were performed as follows: Pure dioxygen at 5 ml min^{-1} was bubbled through the melt for 10 min, and then the system was flushed with dinitrogen at 10 ml min^{-1} for 10 min (until no residual oxygen could be detected by the mass spectrometer). Finally methane was bubbled through the melt at 10 ml min^{-1}. The initial product gases were sampled for gas chromatographic analysis 2 min after methane was introduced. The mass spectrometer was used to monitor the product gases continuously.

Experiments in the cofeed mode were performed as follows: The methane and dioxygen were premixed and bubbled through the melt. The total flow rate was 15 ml min^{-1} with a methane to oxygen ratio of 2 : 1.

2.3. CATALYST CHARACTERIZATION

The melt was quenched from the reaction temperature and a sample was transferred under inert atmosphere for electron paramagnetic resonance studies. The spectrometer was a Varian E-line Century Series and was calibrated by DPPH (α,α-diphenyl-β-picrylhydrazyl radicals) for which the *g* value is 2.0036.

3. Results and discussion

We have found that sodium metavanadate can form apparently homogeneous molten mixtures with many transition metal compounds. The sodium metavanadate melts at 630°C and gases are readily bubbled through the melt at the reaction temperature. Analysis of the products 2 min after the methane had been introduced to the pure melt showed that less than 2% of methane had been activated. It is also found that more about 50% total C_{2+} (surprisingly high C_{3+} selectivity of $\sim$ 20%) was obtained over molten sodium metavanadate. The preferable formation of C_{3+} products over some types of oxide catalyst from methane and oxygen reactions have been reported before [25], however, the mechanism is still not yet known.

The data in fig. 2 show that addition of $CoCl_2$ to the molten metavanadate, increased the methane conversion and the total C_{2+} selectivity dramatically (C_{3+} decreased). For example, the methane conversion was 9.6% giving 68.9% total C_{2+} selectivity (4% C_{3+}) when $CoCl_2$ was present in 0.33 molar in sodium metavanadate. It is also interesting to note that higher concentrations of $CoCl_2$ enhanced selectivity to ethene at the expense of ethane. The results suggest that molten mixtures of $CoCl_2$ in sodium metavanadate are very active for hydrocarbons activation.

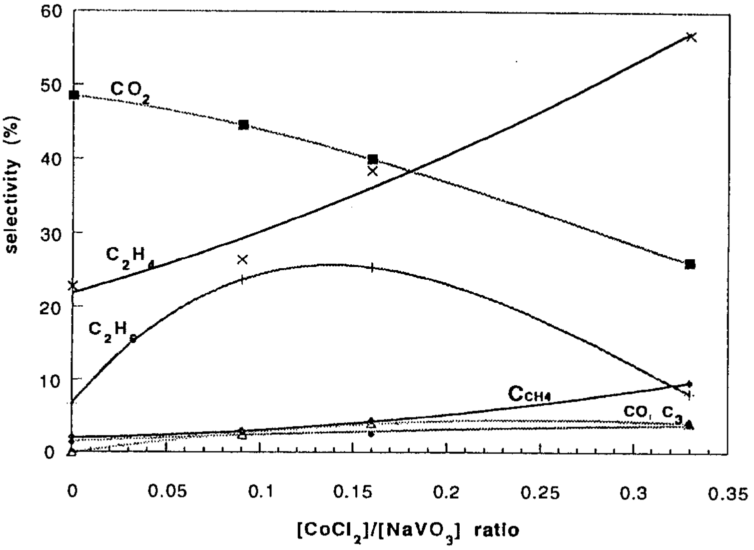

Fig. 2. Effect of the $CoCl_2$ concentration in the oxidative coupling of methane in $CoCl_2/NaVO_3$ melts at 750°C in redox mode. Initial methane conversion C_{CH_4} (◇) and product selectivities, CO (△), CO_2 (■), C_2H_4 (×), C_2H_6 (+), and C_3 (◆).

A number of mixed melts of transition metal chlorides/sodium metavanadate (molar ratio of about 0.33) were tested under redox conditions. The data is shown in table 1. Generally methane conversion was higher when transition metal chlorides were present in the sodium metavanadate melt. The best result was obtained using $MnCl_2$ which gave 12% methane conversion with 75% C_{2+} selectivity. Further, $CuCl_2$ gave a high initial methane conversion of 25.3% but the C_{2+} selectivity was poor.

Table 1
Transition metal halide/sodium vanadate mixture tested for the oxidative coupling of methane in redox mode at 750°C

System[a]	Conv. CH_4	Product selectivities (%)				
		CO	CO_2	C_2H_4	C_2H_6	others[b]
$NaVO_3$	2.0	1.3	48.4	22.8	6.7	10.7 (C_4)
$CoCl_2/NaVO_3$	9.6	3.8	26.1	56.8	8.1	4.0 (C_3)
$MnCl_2/NaVO_3$	12.0	5.0	20.0	55.6	9.5	9.8 (C_3 and C_4)
$NiCl_2/NaVO_3$	4.9	3.3	33.5	47.3	11.5	4.2 (C_3)
$MoCl_4/NaVO_3$	6.7	5.4	45.0	40.8	6.2	2.6
$CuCl_2/NaVO_3$	25.3	4.1	54.9	30.6	2.4	8.4 (C_3 and C_4)

[a] The mixtures were pre-melted in a furnace at 800°C for 2 h. Amount used for the reaction 2 g. Transition metal halide/sodium vanadate molar ratio approximately 0.33.

[b] Others: C_3 and C_4.

It was found that the quenched samples from $MnCl_2/NaVO_3$ melts gave after exposure to oxygen a broad signal at $g = 2.0705$. This signal increased in intensity about four times with samples which had been exposed to methane at the reaction temperature and it reverted to the weaker signal when these reduced samples had been retreated with oxygen gas. These observations suggest the more intense signal is indicative of Mn(II) (d^5) which is oxidised by added oxygen to a higher oxidation state which gives rise to the weaker signal [26]. It is not clear whether Mn(III) or other higher oxidation species have been formed in the oxidation, however, it is beyond any doubt that molten $MnCl_2/NaVO_3$ can activate methane under the given redox conditions.

Table 2 shows the methane conversions and product selectivities of melts formed using different cobalt halides dissolved in molten sodium metavanadate. Higher C_2 yield and especially higher C_2H_4/C_2H_6 (ca. 7.0) associated with the addition of chloride anions was detected. The chloride effect has been extensively studied in methane activation over solid state catalysts, and is normally observed for chloride only [19–24]. However, it is surprising to find that the C_2H_4/C_2H_6 ratio found for melts containing bromide (ca. 6.3) is almost as high as for the chloride melts. Continuously monitoring of the reaction products showed that small amounts of HCl and methyl chloride were detected over the molten chloride catalysts but only traces of methyl bromide and no HBr were detected over the bromide rich molten salts. No enhancement of the ethene/ethane ratio (about 1.2) was observed using catalyst melts containing added fluoride or iodide.

The molten halide catalysts have also been investigated under cofeed conditions. The data in fig. 3 indicate that both chloride and bromide have a pronounced effect on the ratio even under steady state cofeed conditions.

The data in table 3 show the comparison of the methane activation under redox and cofeed conditions. Generally methane conversion was higher in our cofeed mode than in redox mode (at the initial time of 2 min), presumably it is due to the presence of very active, weakly adsorbed oxygen which existed only in the presence

Table 2
Molten cobalt halide/sodium vanadate mixtures tested for the oxidative coupling of methane in redox mode at 750°C

System [a]	Conv. CH_4	Product selectivities (%)					
		CO	CO_2	C_2H_4	C_2H_6	others [b]	C_2H_4/C_2H_6
$CoCl_2/NaVO_3$	9.6	3.8	26.1	56.8	8.1	4.0	7.0
$CoBr_2/NaVO_3$	9.5	7.8	17.9	62.1	9.9	2.3	6.3
$CoI_2/NaVO_3$	4.9	7.3	27.7	40.1	29.9	4.0	1.3
$CoF_2/NaVO_3$	1.9	0.8	50.8	26.4	22.8	–	1.2
$Co(OH)_2/NaVO_3$	2.3	7.0	49.4	19.8	20.8	2.7	1.0

[a] Molar ratio approximately $[CoX_2]/[NaVO_3] = 0.33$. The mixtures were pre-melted in a furnace at 800°C for 2 h. Amount used for the reaction 2 g.

[b] Others: C_3 and C_4.

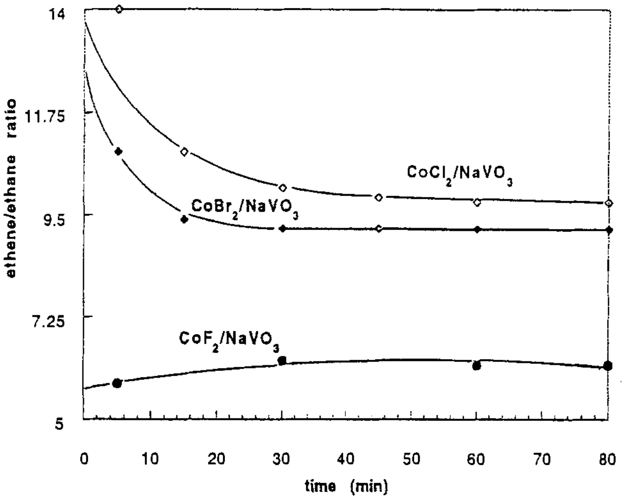

Fig. 3. Ethene/ethane ratio in the oxidative coupling of methane in $CoCl_2/NaVO_3$ (◇), $CoBr_2/NaVO_3$ (◆), and $CoF_2/NaVO_3$ (●) molten mixtures at 750°C in cofeed mode. ($CH_4/O_2 = 2$, flow rate = 15 ml/min.)

of dioxygen. Pure gas phase methane and oxygen reactions have also contributed to increase methane conversions in the cofeed mode. It should be noted that two effects can be clearly observed. Firstly, the selectivity to products other than carbon oxides under the redox conditions was higher than under cofeed conditions

Table 3
Molten mixtures tested for the activation of methane in redox and cofeeding mode at 750°C

System[a]	Mode[b]	Conv. CH_4	Product selectivities (%)						Yield HCHO (%)
			CO	CO_2	C_2H_4	C_2H_6	C_{3+}	HCHO	
gas phase[c]	RO	0.3	11.2	36.2	30.8	13.3	5.2	–	–
	CF	2.5	35.1	5.9	19.5	21.3	8.8	7.6	0.19
B_2O_3	RO	0.6	9.0	2.8	52.8	8.9	9.0	–	–
	CF	5.8	42.5	1.3	14.5	27.3	6.5	6.0	0.31
CuO/B_2O_3	RO	1.3	11.2	36.2	30.8	13.3	5.2	–	–
	CF	9.8	50.9	10.8	11.0	16.7	5.8	4.6	0.45
$CoBr_2/$	RO	9.5	7.8	17.9	62.1	9.9	2.3	–	–
$NaVO_3$	CF	33.4	42.9	22.0	29.8	3.3	2.0	traces	traces

[a] The mixtures were pre-melted in a furnace at 800°C for 2 h. Amount used for the reaction 2 g. [transition metal compound]/[oxide] molar ratio = 0.3.

[b] Mode: RO = redox and CF = cofeed mode (CH_4/O_2 ratio = 2/1, flow rate 15 ml/min).

[c] Empty silica tube. The methane conversion is very low and the formation of oxygenated products is presumably due to the presence of very small amount of residual oxygen in the system.

suggesting the over-oxidation of coupling products has been reduced. It can be understood that the hydrocarbon products are more susceptible for further activation in the presence of molecular oxygen. Therefore, it is advantageous to use redox conditions over cofeed conditions for obtaining a better hydrocarbon selectivity under the same reaction temperature. However, the other interesting observation is that formaldehyde can be only detected in the cofeed mode. The pure gas phase reactions and the molten boron oxide gave only 0.19 and 0.31% formaldehyde, respectively. CuO/B_2O_3 gave 0.45% yield (not optimised) only under cofeed conditions. The results agreed with the report of Otsuka et al. [27] that boric oxide-based catalysts could give good yields of oxygenates in cofeed mode. It should be noted that no oxygenates were detected in redox mode.

It is generally accepted that in heterogeneous catalysts, high temperature reactions of methane proceed by formation of gaseous methyl radicals. These are thought to arise by interaction of the methane with either adsorbed or lattice oxygen. Ethane is formed by recombination of the methyl radicals. In our case, there is no evidence to dispute the same mechanism which may have applied to our molten vanadate mixture, though other mechanisms may also be involved to account for the high selectivity of C_{3+} products. In addition, there is still unclear the mechanism for the formation of oxygenates over catalytic surfaces [2]. Gesser et al. have shown that pure has phase reactions of methane and oxygen can produce methanol via radical reactions at 50 bar [3]. Recently Sun Refining and Marketing Co. has shown that iron sodalite can catalyse the partial oxidation reaction of methane to give higher selectivity to methanol than determined for pure gas phase reactions under the same conditions [5]. Burch et al. [6,7] have demonstrated that formaldehyde can also be synthesised by the reaction of pure methane and oxygen at 1–5 bar. Other workers have reported selective formaldehyde formation over their various catalysts [2,4]. It should be noted that *all the above reports of giving significant amount of oxygenates are obtained under cofeed conditions*. In this work no oxygenates were observed over the molten mixtures under redox conditions. This conflicts with the expectation that higher selectivity of partial oxidation products should be obtained in redox mode, which indicates that structural or chemically bound oxygen does not act as the source of oxygen for the formation of oxygenates. Therefore, it is postulated that the observed formation of formaldehyde only under cofeed conditions may arise from the reaction between methyl radicals and short-lived and weakly bound surface oxygen [28], or, from gas phase methylperoxy radicals and their subsequent reactions on the catalysts surface [6,7].

We have described the improved methane conversions in the presence of added chloride. Previous studies of the chloride effect in oxidative coupling catalysis have considered a role for chloride radicals formed from CH_3Cl [23] or HCl. Burch et al. [19–21] and Lunsford et al. [24] argued that a surface reaction is more likely to account for the chloride effect [19]. In this work we have found that not only chloride but bromide has a beneficial effect on C_2H_4/C_2H_6 ratio. The rates of halogen radical gas phase reactions are significantly different for Cl and Br, for example, the rate constants of hydrogen abstraction from ethane by chlorine radical and bromine radical are 1.86×10^{-18} cm^3 molecule^{-1} s^{-1} [29] and 7.00×10^{-11} cm^3 molecule^{-1} s^{-1} [30] at 373 K, respectively. In consequence, it is not likely that the two halogen radicals will produce comparable effects. Therefore, we suggest that enhanced selectivity and higher ethene to ethane ratio observed in the Cl^- and Br^- rich melt reactions arise from surface reactions.

4. Conclusions

Molten salt mixtures have been tested for methane activation in redox conditions. The melts which include transition metal salts are reduced by methane and can be reoxidised. It is found that both chloride and bromide can enhance the ethene to ethane ratio to a similar extent in the cobalt halides/sodium metavanadate molten salt mixtures. It is concluded that surface modification by halogens to give a specific oxygen species in the melt that will dehydrogenate ethane to ethene accounts for the higher ethene/ethane ratio. In addition, formaldehyde has only been detected in cofeed conditions suggesting stable chemically bound oxygen (in the absence of dioxygen) is not the active oxygen species for oxygenate formation in boric oxide based molten salt systems.

Acknowledgement

We thank the Gas Research Institute for support (to SCT) and the Conselho Nacional de Ciencia e Tecnologia (CNPq-Brazil) for support (to RML).

References

[1] J.S. Lee and S.T. Oyama, Catal. Rev.-Sci. Eng. 30 (1988) 249.
[2] N.R. Foster, Appl. Catal. 19 (1985) 1.
[3] H.D. Gesser and N.R. Hunter, Chem. Rev. 85 (1985) 235.
[4] R. Pitchai and K. Klier, Catal. Rev.-Sci. Eng. 28 (1986) 13.
[5] V.A. Durante, D.W. Walker, S.M. Gussow and J.E. Lyons, US Patent 4 918 249.
[6] T.R. Baldwin, R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 74 (1991) 137.
[7] T.R. Baldwin, R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 75 (1991) 153.
[8] G. Mortiers, M. Cassir, C. Piolet and J. Devynck, Electrochim. Acta 36 (1991) 1063.
[9] A.J. Appleby and S. Micholson, J. Electroanal. Chem. 112 (1980) 71.
[10] P. Tilman, J.P. Wiaux, C. Dauby, J. Glibert and P. Claes, J. Electroanal. Chem. 167 (1984) 117.
[11] C. Moneuse, M. Cassir, G. Martin and J. Devynck, Appl. Catal. 85 (1992) 147.
[12] I.M. Dahl, K. Grande, K-J. Jens, E. Rytter and A. Slagtern, Appl. Catal. 63 (1991) 163.
[13] D.B. Fox and E.H. Lee, Chemtech. (1973) 186.
[14] C. Moneuse, M. Cassir, C. Piolet and J. Devynck, Appl. Catal. 63 (1990) 67.

[15] S.J. Conway, J. Szanyi and J.H. Lunsford, Appl. Catal. 56 (1989) 149.
[16] Y. Ohtsuka, M. Kuwabara and A. Tomita, Appl. Catal. 47 (1989) 307.
[17] J.A.S.P. Carreiro and M. Baerns, J. Catal. 117 (1989) 258.
[18] H. Mazurek, US Patent 4 665 2621.
[19] R. Burch, G.D. Squire and S.C. Tsang, Catal. Today 6 (1990) 503.
[20] T.R. Baldwin, R. Burch, E.M. Crabb, G.D. Squire and S.C. Tsang, Appl. Catal. 56 (1989) 219.
[21] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 46 (1989) 69.
[22] Kh.M. Minachev, N.Ya. Usachev, V.N. Udut and Yu.S. Khodakov, Russ. Chem. Rev. 57 (1988) 22.
[23] K. Otsuka, M. Hatano and T. Komatzu, in: *Methane Conversion*, eds. D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak (Elsevier, Amsterdam, 1988) p. 383.
[24] S.J. Conway and J.H. Lunsford, J. Catal. 131 (1991) 513.
[25] H. Matsuhashi, K. Sakurai and K. Arata, Chem. Lett. (1989) 585.
[26] P.B. Ayscough, *Electron Spin Resonance* (Methuen, London, 1967) p. 184.
[27] K. Otsuka, T. Komatsu, K. Jinno, Y. Uragami and A. Morikawa, *Proc. 9th Int. Congr. on Catalysis*, Vol. 2, Calgary 1988, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1985) p. 915.
[28] A. Brelanski and J. Haber, Catal. Rev.-Sci. Eng. 19 (1979) 1.
[29] D.L. Baulch, R.A. Cox, P.J. Crutzen, R.F. Hampson Jr., J.A. Kerr, J. Troe and R.T. Watson, J. Phys. Chem. Ref. Data 11 (1982) 329.
[30] G.C. Fettis, J.H. Knox and A.F.T. Dickenson, J. Chem. Soc. (1960) 4177.