Catalysis Letters 9 (1991) 23–34

THE OXIDATIVE COUPLING OF METHANE ON ALKALI- AND ALKALINE EARTH-PHOSPHATE CATALYSTS

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Received 15 January 1991; accepted 18 March 1991

The oxidative coupling of methane has been tested over alkali- and alkaline earth-phosphate catalysts at 700 and 775 ° C with and without the introduction of a small quantity of tetrachloromethane (TCM) to the feedstream. In general, the conversion of methane was enhanced by the addition of TCM but the effect on selectivity was dependent on the catalyst being examined. The selectivity to C_2 and higher hydrocarbons and that to oxidation products have been shown to have a dependence on the cation radius/charge ratio.

Keywords: Methane, phosphates

1. Introduction

Abundant supplies of natural gas in many countries of the world provide a continuing incentive for research on the conversion of methane to more advantageous chemical precursors. Subsequent to the pioneering work of Keller and Bhasin [1] in 1982 many reports have appeared on the oxidative coupling of methane to form ethane and ethylene [2–4]. While a wide variety of materials have been examined as heterogeneous catalysts for this process, much of the work has focussed on oxides of the alkali, alkaline earth and rare earth elements [2–4].

There is a growing body of evidence to support the contention that the catalytic efficiencies of a solid for the oxidative coupling process are related to the basicity of the solids [5]. However it is also clear that basicity is not a sufficient condition for such catalysts [2]. It is consequently of considerable interest to study a group of solids related by a common feature, whose acidities and basicities can be varied in a semicontinuous manner by a change in the elemental compositions. Inorganic phosphates appear to satisfy such requirements. Variations of the catalytic properties from those expected of bases to those

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found with acids can be achieved by changes of the cation present with the phosphate or by alterations of the cation/anion ratios [6,7].

Relatively few studies of phosphates as catalysts in the conversion of methane have appeared previously. Baerns and coworkers have examined a number of alkaline earth compound catalysts, including calcium phosphate [5]. Russian workers have reported briefly on the alkaline phosphates as catalysts in the oxidative coupling process [8] and a patent from Standard Oil under the names of Brazdil, Teller, Bartek and Grasselli describes the oxidative coupling of methane on Pb, Bi, Sb, Sn, Tl, In, Mn, Cd and Ge phosphates [9].

Solid phase doping of the catalyst has frequently been reported in studies of the oxidative coupling of methane [2–4]. Relatively few studies, however, have been concerned with the use of gaseous additives. Earlier reports from this laboratory have shown that substantial effects in methane processes on heteropoly oxometalates result from the addition of small quantities (less than 1 mole%) of a chloromethane (e.g. tetrachloromethane) [10–12]. With molybdenum-containing heteropoly oxometalates the yield to formaldehyde was increased by a factor of approximately two on addition of less than 0.4 mole% of tetrachloromethane (TCM) to the feedstream [12], while with a tungsten-containing catalyst the introduction of a similar quantity of TCM produced a selectivity as high as 80% to methyl chloride [11]. Subsequent work in this laboratory has demonstrated that the addition of similarly small quantities of TCM to the feedstream in the oxidative coupling of methane produces significant enhancement of the conversions and selectivities to C_2 hydrocarbons on some but not all of a variety of oxides [13–15].

The present work is concerned with the evaluation of a number of phosphate catalysts with and without the introduction of small quantities of TCM into the feedstream as catalysts for the oxidative coupling of methane.

2. Experimental

Most phosphate catalysts were prepared by the addition of appropriate amounts of aqueous solutions of the acetate of the desired cation of aqueous solution of diammonium-hydrogen phosphate. The precipitates from the reaction mixtures were washed with a small amount of distilled water several times followed by drying in air at 110 °C for 3 h. The catalysts were finally calcined in air at 500–775 °C for 2–18 h before charging to the reactor. Details of the preparation of the catalysts are summarized in table 1. Prior to reaction the samples were calcined in situ in an oxygen flow (ca. 26 ml/min) at 775 °C for 1 h. The BET surface areas for the samples fall between 1.0 and 4.0 m^2/g with the exception of those for the phosphates of magnesium and calcium which are 24.6 and 65.7 m^2/g, respectively.

Table 1

Preparation of alkali- and alkaline earth-phosphate catalysts

Metal	Preparative ratio metal/phosphorus	Preparative components	Calcination condition in air	
			Temp. (°C)	Time
Li	3/1	CH_3CO_2Li, $(NH_4)_2HPO_4$	500	15.5 h
Na	3/1	CH_3CO_2Na, $(NH_4)_2HPO_4$	500	14 h
K	3/1	KNO_3, $(NH_4)_2HPO_4$	500	6 h+775 °C, 1 h
Rb	3/1	RbCl, $(NH_4)_2HPO_4$	500	7.5 h
Cs	3/1	CH_3CO_2Cs, $(NH_4)_2HPO_4$	500	18 h
Be	3/2	$BeSO_4$, $(NH_4)_2HPO_4$	600	2 h+750 °C, 10 min
Mg	3/2	$(CH_3CO_2)_2Mg$, $(NH_4)_2HPO_4$	500	14.5 h
Ca	3/2	$(CH_3CO_2)_2Ca$. $(NH_4)_2HPO_4$	500	8 h
Sr	3/2	$SrCO_3$, $(NH_4)_2HPO_4$, HCl	500	8 h
Ba	3/2	$(CH_3CO_2)_2Ba$, $(NH_4)_2HPO_4$	500	8 h

The catalytic experiments were performed in a fixed-bed continuous flow reactor operated at atmospheric pressure. The catalyst was packed between two layers of quartz wool in the centre of the quartz tube reactor to minimize the reactor dead space with the aim of minimizing the contribution of non-catalytic homogeneous reactions. The additive, tetrachloromethane (TCM), was admitted to the main flow of reactants (methane, oxygen, and helium) by passing a separate stream of helium through a gas dispersion tube in a glass saturator containing the liquid at ice-water temperature. The reaction conditions were as follows unless otherwise stated: $W = 0.60$ g, $F = 30$–33 ml/min, $W/F = \sim 0.02$ g. min/ml: $T = 700$ or 775 °C, $P(CH_4) = \sim 200$ Torr, $P(O_2) = \sim 25$ Torr, $P(CCl_4) = 0$ or ~ 1.1 Torr, balance to the atmospheric pressure was provided by helium.

The reactants and products were analyzed with a Hewlett-Packard 5880A Gas Chromatograph (TCD) equipped with Molecular Sieve 5A (1.25 m) and Porapak T (5.5 m) column packings. The details of the apparatus and the procedures have been described elsewhere [14,15].

3. Results

The predominant products of reaction were CO, CO_2, C_2H_4, C_2H_6, H_2CO, C_3 hydrocarbons and H_2O. Acetylene and hydrogen were produced in small quantities. CH_3Cl and Cl_2 also were formed, usually in trace quantities, when TCM was introduced into the system. A considerable amount of water was generated on all catalysts but is not reported. No significant deactivation of any of the catalysts was observed at 700 °C after reaction for several hours. However, at 775 °C,

Table 2

Methane oxidative coupling on phosphate catalysts at 700 °C

Catalyst	CCl_4	Conv. (mol%) CH_4	Selectivity (mol%)								C_{2+} total selectivity (mol%)	C_{2+} total yield (mol%)
			CO	CO_2	C_2H_4	C_2H_6	C_2H_2	C_3	HCHO	CH_3Cl		
Li-P-O	A	5.7	3.5	18.1	18.8	54.9	n.d.	2.8	1.9	–	76.5	4.3
	P	1.9	13.3	6.4	33.0	30.3	n.d.	2.1	u.	14.9	63.3	1.2
Na-P-O	A	~ 0.1	6.5	50.6	6.5	36.4	n.d.	n.d.	n.d.	–	42.9	0.03
	P	1.2	20.0	18.3	12.2	33.0	tr.	tr.	[13.9]	2.6	45.2	~ 0.5
K-P-O	A	~ 0.6	69.8	6.3	1.6	15.9	n.d.	n.d.	6.3	–	17.5	0.1
	P	1.3	38.9	17.5	4.8	27.0	n.d.	n.d.	11.9	n.d.	31.8	0.4
Rb-P-O	A	~ 0.7	18.9	10.8	10.8	48.6	n.d.	n.d.	10.8	–	59.4	0.4
	P	1.2	24.2	18.3	12.5	35.8	n.d.	0.8	8.3	2.2	49.1	0.6
Cs-P-O	A	~ 0.2	52.3	34.9	2.3	10.5	n.d.	n.d.	n.d.	–	12.8	0.02
	P	1.5	30.5	39.0	7.8	22.7	n.d.	tr.	n.d.	n.d.	30.5	0.5
Be-P-O *	A	~ 0.2	tr.	tr.	neg.	4.3	n.d.	tr.	95.7	–	4.3	~ 0.01
	P	0.8	26.9	20.5	20.5	30.8	n.d.	1.3	12.3	u.	52.6	~ 0.4
Mg-P-O	A	1.4	56.1	41.0	neg.	neg.	n.d.	n.d.	2.9	–	~ 0	~ 0
	P	2.9	54.8	27.1	7.9	5.5	n.d.	0.7	1.4	2.7	14.1	0.8
Ca-P-O	A	13.3	72.6	16.3	3.2	6.3	n.d.	0.5	1.1	–	10.0	1.3
	P	13.7	71.4	15.6	4.6	6.7	n.d.	0.4	1.4	n.d.	11.7	1.6
Sr-P-O	A	~ 0.2	tr.	tr.	17.6	82.4	n.d.	tr.	n.d.	–	~ 100	0.2
	P	~ 1.2	16.0	12.8	26.4	32.0	n.d.	tr.	n.d.	12.8	58.4	0.7
Ba-P-O	A	1.6	22.1	34.4	4.9	38.7	n.d.	tr.	n.d.	–	43.6	0.7
	P	3.5	13.1	38.5	9.1	35.3	n.d.	1.1	2.3	0.6	45.5	1.6

CH_4/O_2 = ~ 7.7, CH_4 = ~ 200 Torr, O_2 = ~ 25 Torr, CCl_4 = ~ 1.1 Torr, W = 0.6 g (*0.1 g), F = 30–33 ml/min, W/F = ~ 0.02 (*0.003) g.min/ml, Stream-on-time 15 min. [] = CH_3OH, A: Without TCM, P: With TCM, n.d. = no detective, u. = unknown, tr. = trace, neg. = negligible.

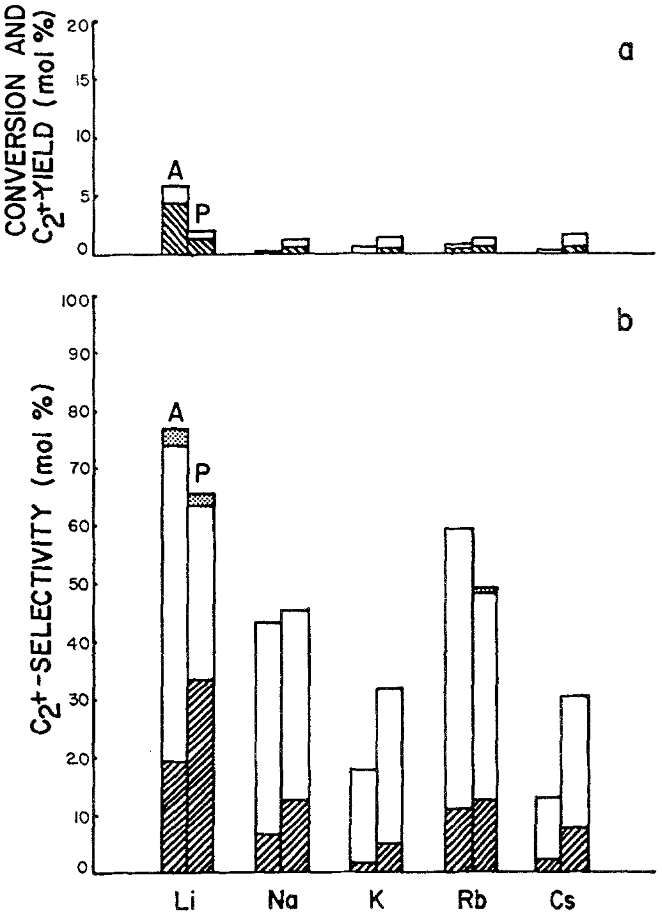

Fig. 1. Conversion, C_{2^+} selectivity and yield on alkali phosphate catalysts at 700 °C. A and P refer to TCM absent and present, respectively. a. ▤ conversion ▧ yield. b. Selectivity to C_2H_4 ▨, C_2H_6 □, C_3 ▦.

Li-P-O was significantly deactivated after 2 hours, while the remaining catalysts showed no differences between observations at 15 and 120 minutes of on-stream time. The conversion of methane was calculated from the carbon-containing products formed. The selectivities were calculated from the quantities of products formed.

Table 2 and figs. 1 and 2 summarize the results for the conversion to the various products obtained at 700 °C. At 700 °C the conversions of methane on alkali and alkaline earth-phosphate catalysts were low, except for that of Ca-P-O (figs. 1 and 2). However the selectivity to C_{2^+} hydrocarbons at 700 °C with Ca-P-O was only approximately 10%, one of the lower values for the phosphate catalysts. In contrast, with Sr-P-O the selectivity to C_{2^+} hydrocarbons was nearly 100% at 700 °C (in the absence of TCM) but unfortunately the conversion was only 0.2%.

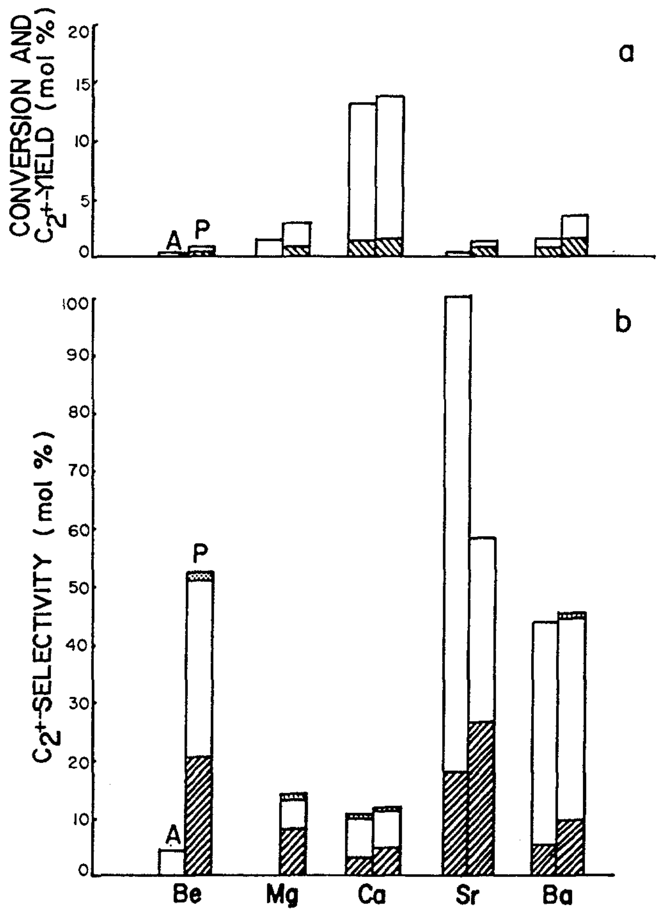

Fig. 2. Conversion, C_{2^+} selectivity and yield on alkaline earth phosphate catalysts at 700 °C. Symbols as in fig. 1.

It is of interest to note some particular features of the results given in table 2. It is evident that the presence of TCM in the feedstream promotes the conversion of methane on all the phosphate catalysts with the exception of Li-P-O, although the enhancement is relatively small on Ca-P-O. With all of the catalysts in table 2 the selectivity to ethylene is increased on addition to TCM to the feedstream, although as with the conversion, the enhancement of the selectivity to C_2H_4 on Ca-P-O is relatively small. In contrast the selectivities to ethane are decreased on addition of TCM, except with the phosphates of K, Cs, Be and Ca. Total selectivities to C_{2^+} are increased by this addition except for the catalysts with Li, Rb and Sr. With TCM in the feedstream, only Li-P-O and Sr-P-O generate appreciable quantities of CH_3Cl while with Na-P-O under the same conditions the selectivity to methanol is significant. However with K-P-O and Rb-P-O little or no quantities of CH_3Cl and methanol are produced in either the presence or absence of TCM, but quantities of formaldehyde were formed in either case. Perhaps most remarkable are the observations with Be-P-O. In the absence of

Table 3

Methane oxidative coupling on phosphate catalysts at 775°C

Catalyst	CCl_4	Conv. (mol%) CH_4	Selectivity (mol%)								C_{2^+} total selectivity (mol%)	C_{2^+} total yield (mol%)
			CO	CO_2	C_2H_4	C_2H_6	C_2H_2	C_3	HCHO	CH_3Cl		
Blank	A	~ 0.1	neg.	neg.	~ 8	~ 62	n.d.	n.d.	~ 30	–	~ 70	0.1
	P	~ 2.5	~ 29	~ 5	~ 34	~ 17	tr.	~ 2	u.	~ 14	~ 53	1.3
Li-P-O	A	15.8	3.6	21.3	34.2	35.6	n.d.	4.8	0.5	–	74.6	11.8
	P	2.8	9.2	7.1	20.6	13.8	n.d.	1.4	u.	47.9	35.8	1.0
Na-P-O	A	0.6	36.7	10.0	6.7	46.7	n.d.	n.d.	n.d.	–	53.4	0.3
	P	2.7	20.1	11.9	24.6	35.8	tr.	2.2	4.9	0.4	62.6	1.7
K-P-O	A	1.5	49.0	6.8	6.8	34.0	n.d.	n.d.	3.4	–	40.8	0.6
	P	3.5	19.9	22.3	15.6	36.4	n.d.	2.3	3.5	n.d.	54.3	1.9
Rb-P-O	A	2.7	22.0	10.6	29.7	31.9	n.d.	2.6	3.3	–	64.2	1.8
	P	3.2	23.0	17.3	33.3	24.2	tr.	2.2	u.	u.	59.7	1.9
Cs-P-O	A	1.2	41.1	19.4	4.8	34.7	n.d.	n.d.	n.d.	–	39.5	0.5
	P	3.0	18.9	43.2	12.6	23.6	n.d.	1.7	n.d.	n.d.	37.9	1.1
Be-P-O *	A	~ 0.3	36.9	1.5	9.2	36.9	n.d.	3.1	12.3	–	49.2	0.2
	P	1.8	33.1	11.8	30.9	21.3	tr.	2.8	u.	u.	55.0	1.0
Mg-P-O	A	2.8	48.9	35.6	4.6	9.5	n.d.	n.d.	1.4	–	14.1	0.4
	P	3.2	45.3	24.8	18.0	8.9	tr.	0.9	1.5	0.6	27.8	0.9
Ca-P-O	A	17.4	44.1	14.6	22.2	14.6	2.0	1.6	0.9	–	40.4	7.0
	P	16.6	46.7	17.5	19.2	12.9	1.7	1.1	0.7	n.d.	34.9	5.8
Sr-P-O	A	~ 0.8	tr.	1.3	26.7	66.7	n.d.	tr.	5.3	–	93.4	0.7
	P	2.5	20.3	8.1	38.2	25.2	n.d.	2.4	n.d.	5.7	65.8	1.6
Ba-P-O	A	9.2	8.6	21.7	25.5	39.8	n.d.	3.4	1.0	–	68.7	6.3
	P	12.4	7.9	23.6	29.5	34.0	n.d.	4.3	0.7	n.d.	67.8	8.4

$CH_4/O_2 = \sim 7.7$, $CH_4 = \sim 200$ Torr, $O_2 = \sim 25$ Torr, $CCl_4 = \sim 1.1$ Torr, $W = 0.6$ g(*0.1 g), $F = 30$–33 ml/min, $W/F = \sim 0.02$(*0.003) g.min/ml, Stream-on-time 15 min, A: Without TCM, P: With TCM, n.d. = no detective, u. = unknown, tr. = trace, neg. = negligible.

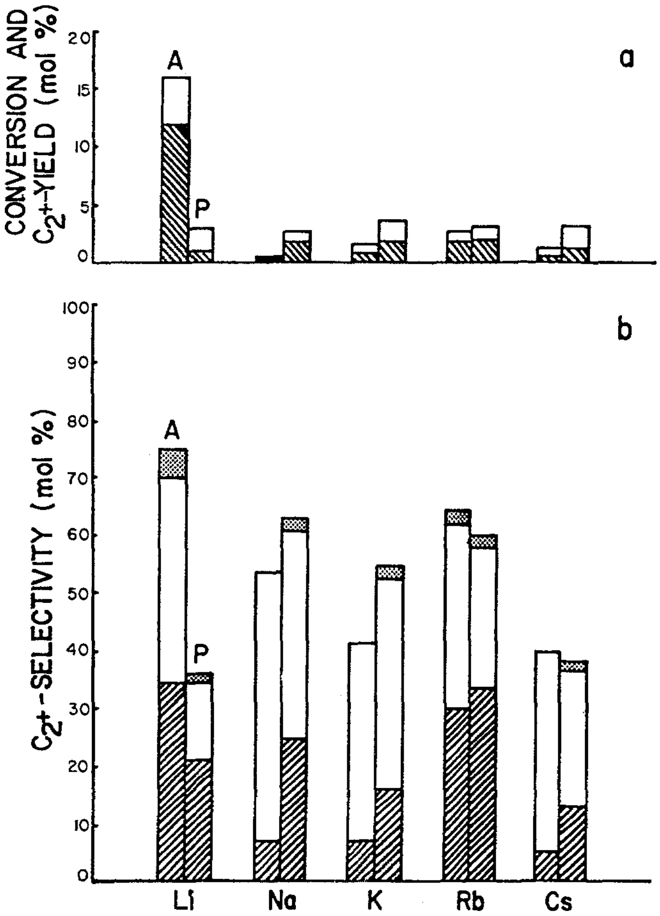

Fig. 3. Conversion C_{2+} selectivity and yield on alkali phosphate catalysts at 775 °C. Symbols as in fig. 1.

TCM, methane is converted to formaldehyde with a selectivity exceeding 95%, but a conversion less than 1%. In contrast with the same catalyst and TCM in the feedstream the predominant products are C_2 hydrocarbons but the conversion, although higher, remains at less than 1%.

At a reaction temperature of 775 °C (table 3 and figs. 3 and 4) the conversion of methane is less than 3% on all alkali phosphates except Li, on which the conversion is approximately 16%, in the absence of TCM. In contrast, the conversions on the phosphates of Ba and Ca are 9.2 and 17.4%, respectively. As noted with Sr at the reaction temperature of 700 °C, the selectivity to C_{2+} hydrocarbons at 775 °C is again high (93.4%) but the conversion is less than 1%.

With TCM in the feedstream, the observations are qualitatively similar at 775 °C to those at 700 °C. The conversion of methane increases with all catalysts except those of Li and Ca, and the selectivities of C_2H_4 similarly increase with the exception of those of the same two cations. The selectivities to ethane are decreased on addition of TCM to the feedstream except for catalysts of K.

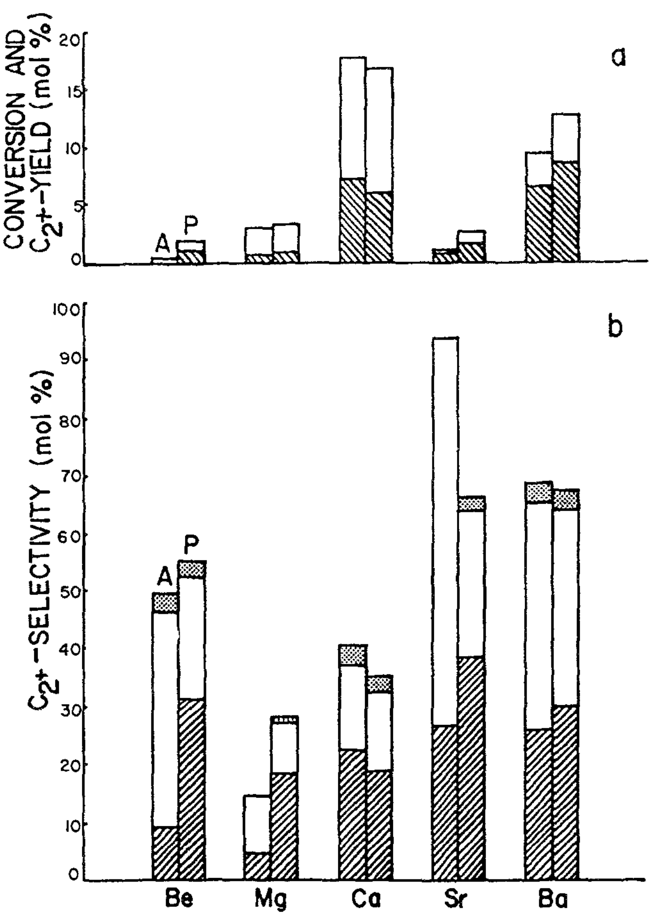

Fig. 4. Conversion C_{2+} selectivity and yield on alkaline earth phosphate catalysts at 775 °C. Symbols as in fig. 1.

Selectivities to C_2 and higher hydrocarbons increase except for the catalysts of Li, Rb, Cs, Ca, Sr and Ba. The selectivity to C_2 hydrocarbons on Li-P-O is approximately 75% without TCM but decreases to less than 40% when TCM is added to the reactant gases.

As with the lower reaction temperature, Li-P-O at 775 °C produces large quantities (selectivity $\approx$ 50%) of CH_3Cl with TCM in the feedstream. No other of the studied catalysts in the present work generated such large amounts of CH_3Cl. Be-P-O forms H_2CO in the absence of TCM but none in the presence of this chloromethane.

4. Discussion

Among the various phosphate catalysts examined in the present work, Li-P-O, Ca-P-O and Ba-P-O at 775 °C in the absence of TCM and Ca-P-O and Ba-P-O in the presence of TCM produce the highest yields of ethane and ethylene and compare favourably with many of those reported previously in the literature [2,4]. The remaining catalysts, while not inactive, generate considerably lower conversions of methane and selectivities to C_2 hydrocarbons. As is well known, alkali and alkaline earth metals, in particular lithium, or their oxides act as promoters in the oxidative coupling of methane [2] but a promoter metal or oxide is not always reactive itself in the corresponding reaction [13,16]. At 775 ° C on Li-P-O a C_{2^+} yield of approximately 12% and a selectivity of approximately 75% were obtained. These values may be compared with those reported on bare lithium oxide (yield 7.3%, selectivity 82.1% at 850 ° C) by DeBoy and Hicks [16] and on silica supported lithium oxide (yield 0.65%, selectivity 14.5% at 775 ° C) by Ahmed and Moffat [13]. The present values are also comparable to those obtained on lithium promoted oxide catalysts [2]. However, Li-P-O is signifi-

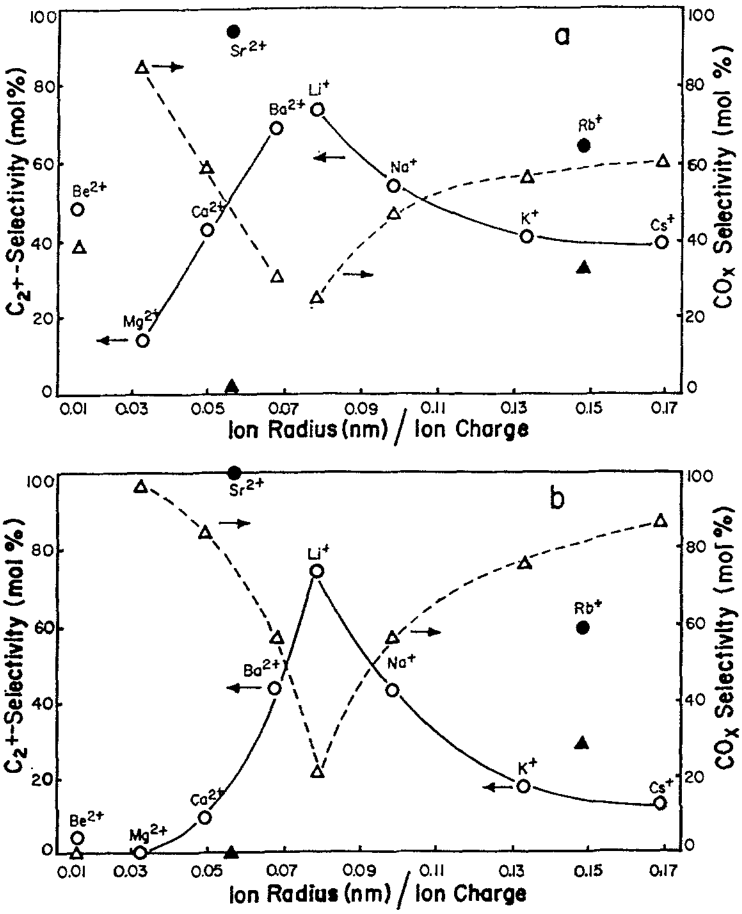

Fig. 5. C_{2^+} (o) and CO_x (Δ) selectivities versus cation radius per charge for phosphate catalysts at 775 (a) and 700 ° C (b). Filled symbols represent those catalysts prepared from chlorinated compounds.

cantly deactivated at 775 ° C (not shown) owing to its relatively low melting point (837 ° C) and/or its reactivity with the quartz reactor or water vapour produced during the reaction.

In contrast to Li-P-O, virtually constant conversions of methane as well as selectivities to C_2 hydrocarbons are found with Ca-P-O at 775 ° C. The activity of calcium phosphate in the oxidative coupling of methane (C_2 selectivity 11% at 740 ° C) has been reported as less than that of calcium oxide [17]. Although, because of the differences in reaction conditions it is difficult to compare these results with those reported here, it is interesting to note that the Ca-P-O catalyst in the present work yields a conversion and selectivity to C_2 hydrocarbons of 17.4% and 36.8%, respectively to be compared with 6.3% and 20%, respectively, found with CaO/SiO_2 under similar reaction conditions [13].

For alkaline earth catalysts the rate of oxidative dimerization of methane has been reported to increase in the order $Mg < Ca < Sr < Ba$ corresponding with the increase of catalyst basicity [8]. While such behaviour is not observed in the present work, it is evident that the conditions of reaction, preparation and activation will have considerable effect on the results obtained.

The selectivities to ethane, ethylene, acetylene and any higher hydrocarbons are shown with the ion radius/ion charge (R/C) for the relevant cation in fig. 5. Although the conversions of CH_4 and of O_2 at which the selectivities have been compared in fig. 5 are not identical for all catalysts reported, they are generally sufficiently similar to justify the comparisons, provided that the curves in fig. 5 are interpreted as representing trends rather than absolute variations. The C_{2^+} selectivity increases with increasing R/C to a maximum for lithium phosphate. For further increases in R/C this selectivity decreases precipitously. The shapes of these curves for the two reaction temperatures bear some similarity although the decreases in C_{2^+} selectivity on either side of the maximum are not as substantial at 775 ° C.

The selectivities to oxidation products are also shown in fig. 5. At both reaction temperatures an approximately reciprocal relationship is evident between the C_{2^+} and CO_x selectivities.

As is evident from tables 2 and 3 and figures 1–4 the addition of a small quantity of TCM to the feedstream increases both the conversion of methane and the selectivity to ethylene at both reaction temperatures on all phosphate catalysts with the exception of Li-P-O and Ca-P-O. With many of the catalysts the selectivities to C_{2^+} hydrocarbons are relatively unchanged but at 700 ° C K and Cs and Be show a substantial increase while Sr produces a decrease.

Earlier work from this laboratory has shown that TCM does not participate in the methane conversion through a purely gas phase process [10–15]. Rather, the TCM is in some fashion, as yet unknown, incorporated into the catalyst. The present work also clearly demonstrates that the effect of the addition of TCM into the feedstream is dependent on the nature of the catalyst. It has been pointed out that chlorine is capable of both suppressing and enhancing radical formation

[11–15]. Although there have been a number of studies of chloride containing catalysts [2–4] relatively little work has been reported on the affects of addition of chlorinated compounds into the gas phase. However Burch and coworkers [18] have suggested that chlorine radicals in the gas phase may be generated from chlorine-containing catalysts.

It is of some interest to speculate on the correlations obtained between the selectivities and the ion radius/ion charge. The latter quantity may be viewed, at least approximately, as the one-dimensional space occupied per unit charge by the particular cation. Although the nature of the effect of the cation is not yet understood, there appears to be support for the contention that methane interacts with surface oxygen species of the catalyst and is converted, by loss of a hydrogen atom, into a methyl radical. It is possible that the cation enhances the ability of the surface oxygen atom to extract a hydrogen atom from methane through a polarization effect. Such an effect may be anticipated to be related to the charge density. However, it is not unreasonable to expect that too high a polarization could result in undesirable results.

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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