Cation effects in the oxidative coupling of methane on phosphate catalysts

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The conversion of methane and the selectivities to the various products have been measured at 700 and 775°C on a variety of phosphates of La(III), Zr(IV), V(V), Cr(III), Mn(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Al(III), B(III), Pb(II), Bi(III) and Sm(III) in the presence and absence of carbon tetrachloride. The conversions reach as high as 30 and 49% at 700 and 775°C, respectively, with methane and oxygen at partial pressures of 200 and 25 Torr, respectively. The highest C_{2+} selectivities (61 and 82%, respectively) were obtained for lead(II) phosphate at 700 and 775°C, respectively. In general the conversions and C_{2+} selectivities are enhanced on addition of carbon tetrachloride (1.1 Torr) to the feedstream, although there are notable exceptions. Significantly high selectivities to formaldehyde are observed with a number of the catalysts, in particular 32% with boron(III)phosphate.

Keywords: Phosphate catalysts; cation effects; oxidative coupling of methane

1. Introduction

Optimization of the utilization of supplies of natural gas is a topic of great interest currently [1]. The partial oxidation of methane to oxygenates [2] and the oxidative dehydrogenation to ethane and ethylene [3] are undoubtedly the most studied processes.

A wide variety of catalysts has been examined for the oxidative coupling process with oxides undoubtedly receiving the greatest attention [3]. While the effect of changing the cation of the oxide has been extensively studied, relatively little work has been concerned with the use of a larger anion such as phosphate.

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In earlier work from this laboratory a number of phosphates with alkali metals and alkaline earths as cations were tested for their activity and selectivity in the oxidative coupling process for methane [4]. Certain of these phosphates, in particular that of strontium, were found to be highly selective for the formation of C_{2+} hydrocarbons at 700°C, but, unfortunately, with low conversions under these conditions.

Recent work in this laboratory has been concerned with the effect on the methane conversion process of the introduction of chlorinated species, such as tetrachloromethane (TCM), into the reactant stream (see, for example ref. [4] and references therein). In the partial oxidation of methane on 12-molybdophosphoric and 12-tungstophosphoric acids supported on silica, the addition of a small partial pressure of TCM in the feedstream alters not only the conversion but also the nature of the products, with methyl chloride in selectivities up to 80% being produced over the latter catalyst [5]. In contrast, with a variety of supported oxides, particularly those of the alkali metals and alkaline earths, doped and undoped, both the conversion of methane and the selectivities to C_{2+} hydrocarbons are enhanced but, in particular substantial selectivities to ethylene are observed [6–9]. However, the introduction of TCM into the feed is found to poison a silica supported thallium catalyst [10]. Although the mechanism for the effect of TCM is not yet known there is evidence that the chlorinated methane operates through interaction with the catalyst [6] and thus may alter the acidic and/or basic nature of the sites or even generate new sites which are active in the C–H bond scission process.

In the present work a series of phosphates with cations from Groups III–VIII of the Periodic Table are examined under identical conditions for their activities and selectivities in the methane conversion process at 700 and 775°C and in the presence and absence of TCM.

2. Experimental

Most phosphate catalysts were prepared by the addition of appropriate amounts of aqueous solutions of metal acetates or nitrates to an aqueous solution of diammonium-hydrogen phosphate. For B–P–O and Al–P–O tri-*n*-propylborate and aluminum tri-sec-butoxide were used, respectively, and orthophosphoric acid replaced diammonium-hydrogen phosphate. V–P–O was prepared from ammonium metavanadate and orthophosphoric acid [11]. The precipitates from the reaction mixtures were washed with small amounts of distilled water several times followed by drying in air or under vacuum at 110°C for 3 h. The catalysts were finally calcined in air at 450–775°C for 2–18 h before charging to the reactor. Prior to reaction the temperature of the catalyst was raised to 775°C in the flow of helium followed by calcination in situ in an oxygen flow ($\approx$ 26 ml/min) at the same temperature for 1 h.

The catalytic experiments were performed in a fixed-bed continuous flow reaction system operated at atmospheric pressure. The reactor was a quartz tube (9 mm i.d. × 35 mm) which was sealed on two ends with 4 mm i.d. quartz tubing (the total length of the reactor was ≈ 200 mm). The catalyst was placed in the 9 mm i.d. portion of the reactor and packed between two layers of quartz wool. 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 (1.0 g for Bi(III)–P–O), $F = 30$–33 ml/min, $W/F = 0.02$ g min/ml; $T = 700$ or 775°C, $P(CH_4) = 200$ Torr, $P(O_2) = 25$ Torr, $P(CCl_4) = 0$ or 1.1 Torr. The balance to the atmospheric pressure was provided by helium. The results collected after 15 min of on-stream time are reported. Although the stabilities of the catalysts varied with the cation present deactivation was, of course, inevitably observed, but was generally smaller in the presence of TCM.

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 conversion of methane was calculated from the carbon-containing products formed. The selectivities were calculated from the quantities of products formed. These values were expressed as mole percent. The details of the apparatus and the procedures have been described previously [7].

3. Results

The main products of the reaction were CO, CO_2, C_2H_4, C_2H_6, CH_2O and H_2O. Acetylene, C_3 hydrocarbons and hydrogen were produced in small quantities. When TCM was introduced into the system, CH_3Cl and Cl_2 were also formed, usually in trace quantities. A considerable amount of water was produced on all catalysts but is not reported. Some evidence for the occurrence of steam reforming and/or the water–gas shift processes can be deduced from the detection of small amounts of hydrogen with some of the alkali metal and alkaline earth phosphates.

Tables 1 and 2 and figs. 1 and 2 summarize the results in terms of conversion, selectivities and yields of C_{2+} hydrocarbons at 700 and 775°C, respectively. The figures display the results for those catalysts where either the conversion and/or the selectivity to C_{2+} hydrocarbons are relatively high. The results given in fig. 1 show that these catalysts are selective for the formation of deep oxidation products at 700°C. It is interesting to note that the addition of TCM to the feedstream with the Mn(III) catalyst increases both the conversion and the selectivity to C_{2+} hydrocarbons whereas, with the Bi(III) catalyst the additive

Table 1
Methane oxidative coupling on phosphate catalysts at 700°C

Metal (valence)	CCl_4 [a]	Conv. (%)	Selectivity (mol%) [b]								C_{2+} total select. (mol%)	C_{2+} total yield (mol%)
		CH_4	Co	CO_2	C_2H_4	C_2H_6	C_2H_2 $+C_3$	CH_2O	CH_3OH	CH_3Cl		
La(III)	A	7.9	71.2	27.7	≈ 0	0.1	n.d.	1.0	n.d.	–	0.1	0.01
	P	5.2	73.9	13.2	3.3	2.5	n.d.	6.7	n.d.	0.4	5.8	0.3
Zr(IV)	A	6.5	92.9	5.5	≈ 0	≈ 0	n.d.	1.5	n.d.	–	≈ 0	≈ 0
	P	10.8	90.7	6.9	1.0	0.2	n.d.	n.d.	n.d.	1.1	1.2	0.13
V(V)	A	0.9	46.5	26.7	≈ 0	≈ 0	n.d.	26.7	n.d.	–	≈ 0	≈ 0
	P	7.4	85.3	7.0	3.9	1.4	n.d.	u.	n.d.	2.4	5.3	0.39
Cr(III)	A	9.5	84.8	13.2	≈ 0	≈ 0	n.d.	2.0	n.d.	–	≈ 0	≈ 0
	P	10.3	79.4	19.0	1.1	0.5	n.d.	u.	n.d.	u.	1.6	0.16
Mn(III)	A	4.7	54.9	6.6	8.9	18.7	n.d.	6.6	n.d.	–	27.6	1.29
	P	13.5	40.7	2.8	41.4	8.9	2.6	3.2	n.d.	0.4	52.9	7.15
Mn(II)	A	5.3	70.7	19.2	1.0	3.1	n.d.	6.0	n.d.	–	4.1	0.21
	P	12.6	66.1	4.5	22.3	6.8	n.d.	u.	n.d.	0.2	29.1	3.65
Fe(III)	A	11.6	88.8	3.9	≈ 0	≈ 0	n.d.	5.1	2.2	–	≈ 0	≈ 0
	P	20.4	81.6	2.3	0.6	tr.	1.4	4.5	7.9	1.8	≈ 2	1.2
Co(II)	A	3.7	23.8	76.2	≈ 0	≈ 0	n.d.	n.d.	n.d.	–	≈ 0	≈ 0
	P	30.2	14.0	74.6	9.1	2.0	0.4	n.d.	n.d.	0.1	11.5	3.5
Ni(II)	A	7.6	33.6	65.0	≈ 0	0.1	n.d.	1.3	n.d.	–	0.1	0.01
	P	13.6	85.6	14.4	≈ 0	≈ 0	n.d.	0.5	n.d.	n.d.	≈ 0	≈ 0
Cu(II)	A	5.7	3.5	91.4	0	5.1	n.d.	5.1	n.d.	–	5.1	0.29
	P	7.2	15.9	45.7	1.2	1.5	n.d.	16.6	n.d.	19.1	2.7	0.2
Zn(II)	A	0.4	29.7	29.7	≈ 0	10.8	n.d.	29.7	n.d.	–	10.8	0.04
	P	1.2	34.6	25.8	9.7	12.1	tr.	17.7	n.d.	tr.	21.8	0.27
Al(III)	A	0.4	81.6	18.4	≈ 0	≈ 0	n.d.	n.d.	n.d.	–	≈ 0	≈ 0
	P	1.6	60.6	12.5	6.3	6.3	n.d.	u.	n.d.	14.4	12.6	0.2
B(III)	A	1.1	65.8	0.5	0.5	1.3	n.d.	32.0	n.d.	–	1.8	≈ 0.02
	P	2.1	64.7	7.4	7.9	20.0	n.d.	u.	n.d.	u.	27.9	0.6
Pb(II)	A	0.06	≈ 0	38.7	≈ 0	61.3	tr.	tr.	n.d.	–	61.3	≈ 0.04
	P	0.9	17.6	22.0	9.9	36.3	tr.	12.1	n.d.	2.2	46.2	0.42
Bi(III)	A	10.0	21.0	60.1	1.7	13.0	0.4	3.7	n.d.	–	15.1	≈ 1.5
	P	9.6	30.2	57.3	3.0	2.0	n.d.	2.6	n.d.	4.9	5.0	0.48
Sm(III)	A	3.2	93.2	3.4	≈ 0	tr.	n.d.	3.4	n.d.	–	≈ 0	≈ 0
	P	5.6	80.8	9.2	3.1	0.5	0.4	5.7	n.d.	0.4	4.0	0.22

[a] A: without TCM, P: With TCM.

[b] n.d. = none detected, u. = unknown, tr. = trace.

has little or no effect on the conversion and a disadvantageous effect on the C_{2+} selectivity.

In contrast with these observations, at a reaction temperature of 775°C the conversion with the Mn(III) catalyst is improved by the additive while the selectivity remains unchanged (fig. 2). At this temperature the Pb(II) catalyst is effective in producing C_{2+} hydrocarbons but the conversion is very small. On

Table 2
Methane oxidative coupling on phosphate catalysts at 775°C

Metal (valence)	CCl_4 [a]	Conv. (%)	Selectivity [b] (mol%)								C_{2+} total select. (mol%)	C_{2+} total yield (mol%)
		CH_4	CO	CO_2	C_2H_4	C_2H_6	C_2H_2 + C_3	CH_2O	CH_3OH	CH_3Cl		
La(III)	A	8.6	71.0	23.9	1.1	3.6	n.d.	0.8	n.d.	–	4.7	0.40
	P	5.2	69.9	16.6	7.9	3.3	0.3	1.4	n.d.	0.7	11.5	0.60
Zr(IV)	A	10.9	91.5	6.9	0.6	0.5	n.d.	0.6	n.d.	–	1.1	0.12
	P	13.2	86.8	8.2	3.9	0.8	0.2	u.	n.d.	0.2	4.9	0.63
V(V)	A	3.9	68.4	16.7	≈ 0	1.0	n.d.	13.9	n.d.	–	≈ 1	0.04
	P	12.3	87.8	3.6	5.0	2.0	0.4	u.	n.d.	1.3	7.4	0.9
Cr(III)	A	11.2	86.0	11.0	0.6	≈ 0	n.d.	u.	2.3	–	≈ 0.6	0.07
	P	12.3	84.1	10.5	4.5	1.0	n.d.	u.	n.d.	u.	5.5	0.67
Mn(III)	A	9.5	39.4	3.5	25.6	26.6	2.3	2.6	n.d.	–	54.5	5.17
	P	15.5	40.5	5.3	45.0	6.3	2.9	u.	n.d.	u.	54.2	8.42
Mn(II)	A	9.4	66.2	6.2	9.0	12.1	n.d.	6.4	n.d.	–	21.1	1.98
	P	10.1	45.1	4.5	40.1	9.3	0.9	u.	n.d.	u.	50.3	5.02
Fe(III)	A	10.6	89.6	3.0	≈ 0	0.5	n.d.	6.9	n.d.	–	≈ 0.5	0.05
	P	10.3	83.3	3.0	9.1	2.4	0.5	u.	n.d.	1.7	12.0	1.24
Co(II)	A	49.0	91.1	8.9	≈ 0	≈ 0	n.d.	n.d.	n.d.	–	≈ 0	≈ 0
	P	24.6	81.4	17.8	≈ 0	0.8	n.d.	u.	n.d.	u.	≈ 0.8	0.19
Ni(II)	A	47.2	89.7	9.9	≈ 0	≈ 0	n.d.	0.5	n.d.	–	≈ 0	≈ 0
	P	21.6	96.4	3.4	≈ 0	0.1	n.d.	u.	n.d.	u.	≈ 0.1	0.03
Cu(II)	A	7.3	10.3	78.3	≈ 0	0.7	n.d.	10.7	n.d.	–	≈ 0.7	0.05
	P	9.6	28.5	43.8	5.1	4.2	0.2	14.1	n.d.	4.0	9.5	0.91
Zn(II)	A	1.4	42.1	13.6	5.7	25.7	n.d.	12.9	n.d.	–	31.4	0.44
	P	3.1	46.3	19.6	21.9	11.3	tr.	n.d.	n.d.	tr.	33.2	1.03
Al(III)	A	1.3	68.9	10.6	1.5	6.8	n.d.	12.1	n.d.	–	8.3	0.11
	P	3.3	65.3	10.0	15.1	9.1	0.6	u.	n.d.	u.	24.8	0.82
B(III)	A	1.3	66.9	0.4	4.5	12.6	n.d.	15.6	n.d.	–	17.1	0.23
	P	2.7	55.2	7.8	24.1	11.5	1.5	u.	n.d.	u.	37.1	1.0
Pb(II)	A	≈ 0.5	tr.	12.0	8.0	74.0	tr.	6.0	n.d.	–	82.0	0.37
	P	2.6	16.3	9.3	24.5	39.3	2.3	6.6	n.d.	1.6	66.1	1.7
Bi(III)	A	10.5	14.3	63.1	3.6	15.3	0.2	3.4	n.d.	–	19.1	2.0
	P	12.9	69.5	11.6	13.9	4.6	n.d.	u.	n.d.	0.4	18.5	2.4
Sm(III)	A	8.1	88.7	5.2	2.8	2.2	n.d.	1.1	n.d.	–	5.0	0.41
	P	10.2	76.8	9.9	9.1	2.1	0.2	1.9	n.d.	0.1	11.4	1.16

[a] A: without TCM, P: With TCM.

[b] n.d. = none detected, u. = unknown, tr. = trace.

almost all catalysts except for La–P–O, Cu–P–O and Bi–P–O at 700°C and La–P–O, Co–P–O and Ni–P–O at 775°C the conversion of methane together with the yield of C_{2+} hydrocarbon were enhanced by the introduction of TCM into the feed stream. In contrast, with Bi–P–O and Cu–P–O at 700°C the selectivity to C_{2+} hydrocarbons together with the yield of C_{2+} hydrocarbon was

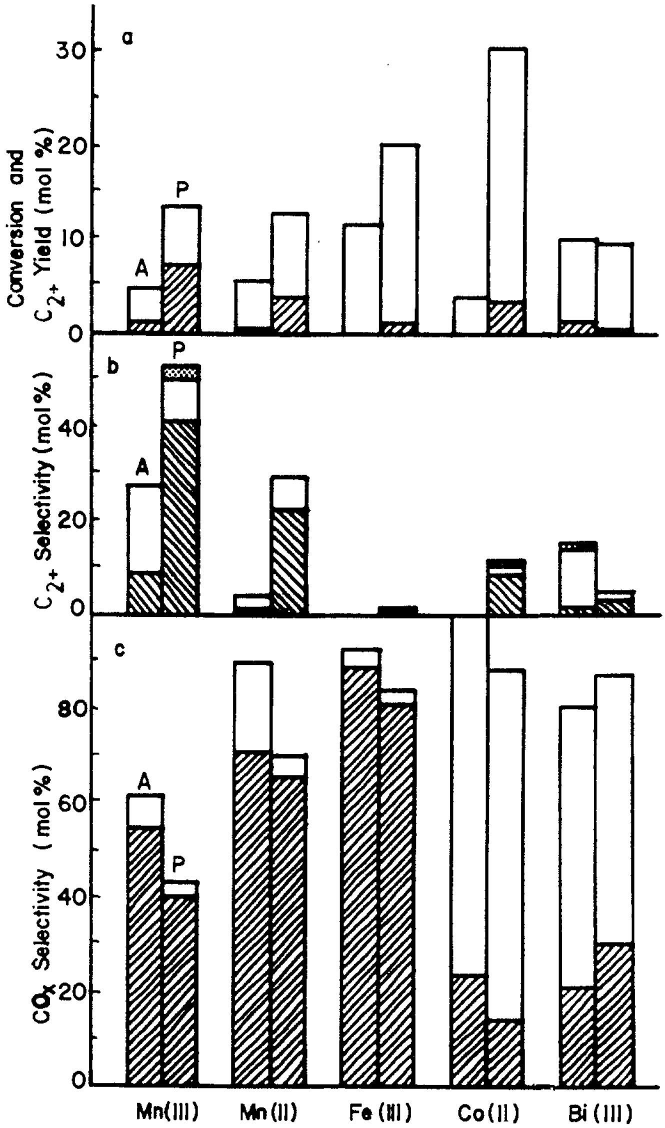

Fig. 1. Conversion, C_{2+} selectivity and C_{2+} yield on phosphate catalysts at 700°C. (a) CH_4 conversion (▤), C_{2+} yield (▨). (b) C_2H_6 (□), C_2H_4 (▧), $C_2H_2+C_{3+}$ (▦). (c) CO (▨), CO_2 (□). A and P indicate TCM absent and present, respectively.

reduced significantly by the introduction of TCM. For La–P–O at both reaction temperatures and Co–P–O and Ni–P–O at 775°C, the conversion of methane decreased while the selectivity to C_{2+} hydrocarbons as well as the yield of C_{2+} hydrocarbons increased by the introduction of TCM. The highest selectivity to C_{2+} hydrocarbons was 82% on Pb–P–O at 775°C. However, the conversion on Pb–P–O at 775°C was only 0.5%, the lowest value among those catalysts examined at the same temperature. Mn(III)–P–O was one of the best catalysts

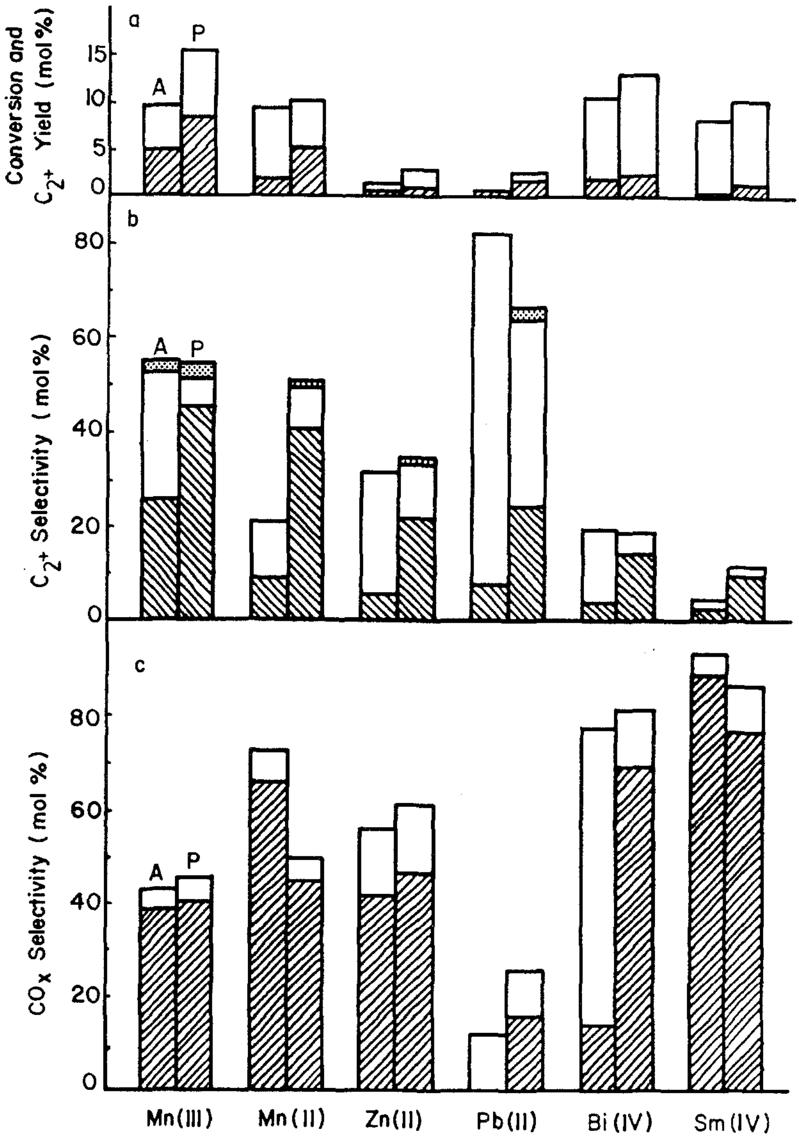

Fig. 2. Conversion, C_{2+} selectivity and C_{2+} yield on phosphate catalysts at 775°C. Symbols as in fig. 1.

in terms of yield of C_{2+} hydrocarbons and selectivity to these products at both reaction temperatures in the presence and absence of TCM in the feed stream. Although methane conversions of approximately 50% were obtained on Co–P–O and on Ni–P–O at 775°C, only total oxidation occurred and the presence of TCM seemed to suppress the total oxidation in both cases.

It is interesting to note some particular features of the results given in tables 1 and 2. Only Cu–P–O and Al–P–O produce appreciable amounts of CH_3Cl at 700°C in the presence of TCM. In addition, on Cu–P–O and Pb–P–O the formation of formaldehyde is enhanced significantly by the introduction of TCM at 700°C. Formaldehyde is a predominant partial oxidation product on most of the catalysts examined, with selectivities greater than 20% observed with V–P–O, Zn–P–O and B–P–O at 700°C. Small selectivities to methanol are observed with Fe–P–O at 700°C and Cr–P–O at 775°C, with the former increasing by approximately a factor of four on addition of TCM while vanishing with the latter on a decrease in reaction temperature to 700°C.

4. Discussion

The effect of varying the cation while retaining the anion is clearly evident from the results presented here. Conversions and C_2 selectivities ranging from insignificant to 50 and 80%, respectively, are observed.

The results in this report also clearly show that the introduction of a small amount of TCM in the feed stream increases the yields to C_{2+} hydrocarbons on almost all phosphate catalysts examined at 700 and 775°C except for Cu–P–O and Bi–P–O at 700°C. Usually the introduction of TCM onto the catalysts promotes both the conversions of methane and selectivities to hydrocarbons, especially ethylene, and consequently enhances the yields of C_{2+} hydrocarbons. However, for Co–P–O and Ni–P–O at 775°C and La–P–O at both reaction temperatures the conversion of methane as well as the yields of carbon oxides are reduced while the total yield and selectivity to C_{2+} hydrocarbons increased when a small partial pressure of TCM is added to the feed stream. This behaviour strongly suggests that the introduction of TCM in the feed stream not only enhances the coupling reaction but also suppresses the total oxidation on almost all phosphate catalysts examined. The possibility that the addition of TCM to the feedstream modifies the catalyst surface to facilitate the hydrogen abstraction step from methane has been suggested in earlier reports from this laboratory on the oxidative coupling of methane with a number of silica supported metal oxides [12]. Recently it has been reported [13] that in addition to the gas phase reactions involving chlorine radicals, a surface chloride phase plays an important role on the methane coupling reaction. It is reasonable that the way in which the nature of catalyst surface is affected by the presence of TCM depends strongly on the acidity and/or basicity of the phosphate used and on the reaction temperature.

Among the phosphate catalysts examined at 775°C Mn(II)–P–O in the presence of TCM and Mn(III)–P–O in the absence and presence of TCM produce good yields of C_{2+} hydrocarbon as well as reasonable selectivities to C_{2+} hydrocarbons. Even at 700°C Mn(III)–P–O yields high selectivities to C_{2+} hydrocarbons in the presence of TCM. These yields and selectivities are comparable with those reported previously [9] on silica supported manganese oxide and with those reported on various types of manganese oxides in the literature [14].

It is interesting to compare the results obtained on Pb–P–O and Bi–P–O with those obtained on Bi/SiO_2 and Pb/SiO_2 under similar reaction conditions [10]. In contrast to the enhancement in the yield of C_{2+} hydrocarbons resulting from the introduction of TCM with Bi/SiO_2, on Bi–P–O a substantial change in the selectivities to carbon oxides as well as hydrocarbons was obtained with TCM. The coupling reaction on Pb–P–O was favourably affected by the presence of TCM while that on Pb/SiO_2 was strongly inhibited by the addition of TCM. Such behaviour clearly reflects the differences in the surfaces of the phosphates and silica supported oxides. Although the nature of the active sites on the phosphate catalysts is unknown at the present time, the combination of bismuth and phosphorus in the Bi–P–O catalyst apparently weakens the effect of TCM on the coupling reaction while that of lead and phosphorus in Pb–P–O evidently augments the interaction of TCM.

While the significant effect of the cation in altering the methane conversion process may tentatively be attributing to changes in the electron distribution on the phosphate ions due to the electric fields produced by the cations, a number of caveats must be issued. The crystallographic structures of the various phosphate salts are not all identical and consequently the proximity of the cation–anion pairs as well as the number of nearest and next-nearest neighbours may introduce an additional factor. Further, the surface areas of the various phosphates undoubtedly will differ, although it is anticipated that many of these will be small.

Although the nature of the participation of chlorine species in the coupling process is not yet understood, nevertheless the present results together with unpublished information provides some clues to the mechanism. The sites of the methane activation process, in the absence of TCM, are undoubtedly the oxygen atoms of the phosphate group. The presence of chlorine, probably bonded to the surface oxygen species alters the electronic environment. The activation step may actually be a two-site process in which the methyl group becomes attached to the surface chlorine atom. Since experiments show that the chlorine contained on the catalyst must be replenished by the TCM it is possible that methyl chloride is formed as an intermediate in the process. The direct intersection of methane with surface chlorine species cannot, of course, be eliminated as a possible contributor to the activation process.

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