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Partial oxidation of methane to methyl chloride with tetrachloromethane on strontium hydroxyapatites ion-exchanged with lead

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The partial oxidation of methane has been investigated in the presence and absence of tetrachloromethane (TCM) on strontium hydroxyapatites ion-exchanged with lead (SrPbHAp) at 773 K, at which temperature the apatites exist stably and do not convert to the corresponding phosphates. In the absence of TCM, the conversion of methane increased and the selectivity to carbon dioxide approached 100% as the lead content was increased. With a small quantity of TCM in the feedstream and at longer times-on-stream the selectivities to carbon dioxide decreased, those to carbon monoxide increased. Methyl chloride was formed at the higher times-on-stream on all catalyst compositions, but reached selectivities of 73% with those catalysts of Pb/Sr equal to or greater than 0.26. In contrast the conversion of methane decreased with increasing times-on-stream with the latter compositions. XRD and XPS measurements provide evidence for the introduction of Cl into the surface of PbSrAp, apparently forming the corresponding chlorapatite, although not precluding the existence of chlorine in additional configurations. Concomitantly a portion of the cationic lead is reduced to the metallic state. While TCM is evidently required for the production of methyl chloride, the presence of ion-exchanged lead appears to be required to achieve the highest selectivities for the aforementioned chloride.

Keywords: methane, partial oxidation, methyl chloride, strontium hydroxyapatite, tetrachloromethane, lead

1. Introduction

Earlier work from our laboratories investigated the effect of the addition of chloromethanes to the feedstream for the partial oxidation of methane with metal–oxygen cluster compounds (heteropoly oxometalates) as catalysts [1–3]. With 12-molybdophosphoric acid the conversion of methane was markedly increased with the introduction of TCM and a small selectivity to methyl chloride was observed while that to formaldehyde remained largely unchanged. In contrast, with 12-tungstophosphoric acid the introduction of TCM resulted in the formation of methyl chloride with selectivities as high as 80%. Subsequent work with a variety of catalysts has shown that the introduction of TCM in the oxidative coupling of methane produces significant increases in the selectivity to ethane and ethylene, particularly the latter, whereas, in the partial oxidation of methane the selectivity to CO is enhanced to the detriment of CO_2 [4]. Such observations appear to result, at least partially, from the suppression of secondary oxidation processes [5,6].

Studies of catalytic processes on hydroxyapatite ($Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}$ $(0 \leqslant z \leqslant 1)$) offer a number of advantages. The acid/base properties of these materials have been shown to be dependent on the composition, in particular the Ca/P ratio, with those of stoichiometric hydroxyapatite ($z = 0$, $Ca/P = 1.67$) showing activity in the dehydrogenation of alcohols while dehydrogenation and dehydration are observed on nonstoichiometric hydroxyapatites ($0 < z \leqslant 1$, $1.67 > Ca/P \geqslant 1.50$) [7,8]. Further, the crystallographic structures are invariant under changes in the Ca/P ratio, as well as being thermally stable and permitting cation substitutions through ion-exchange procedures [9,10].

Recent work in our laboratories has examined the structural, surface, ion-exchange and catalytic properties of stoichiometric and nonstoichiometric calcium hydroxyapatites as well as those ion-exchanged with strontium and lead [11–23]. With the calcium and strontium hydroxyapatites methane conversion yields the partial oxidation products, carbon monoxide and dioxide, the selectivity to the former being increased on addition of TCM [12,13,17–19,21–23]. The introduction of lead into the calcium hydroxyapatites results in the generation, from methane, of oxidative coupling products, ethane and ethylene with significantly high selectivities [11,14–16].

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The present work reports on studies of strontium hydroxyapatites and the corresponding structures ion-exchanged with lead, their thermal stabilities and their catalytic properties in the oxidation of methane in the presence of TCM.

2. Experimental

Strontium hydroxyapatites (SrHAp) were prepared from $Sr(NO_3)_2$ (Wako Pure Chemical, Osaka) and $(NH_4)_2HPO_4$ (Wako) according to the procedure described in ref. [22]. Lead cations were ion-exchanged into the hydroxyapatites by stirring the apatite sample (20 g) in 150 or 250 ml of aqueous solution of $Pb(NO_3)_2$ (Wako) at room temperature under the conditions given in table 1. After washing with water and drying at 373 K overnight, the sample was calcined at 773 K for 3 h. All catalysts were sieved to the particle size of 1.70–0.85 mm. The concentrations of Sr, Pb and P in each catalyst were determined in aqueous HNO_3 solutions by inductively coupled plasma (ICP) spectrometry (SPS-1700, Seiko). The catalysts are denoted as SrPb*xx*HAp, in which *xx* refers to 100Pb/Sr (atomic ratio). The BET surface areas, apparent density and the atomic ratio of Sr/P and Pb/P in each catalyst are summarized in table 1. The catalytic reactions were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design and procedures have been described elsewhere [17]. The reaction was monitored with an on-stream Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, one Porapak N (6 m × 3 mm) and the other Molecular Sieve 5A (0.2 mm × 3 mm), were employed in the analyses. The methane conversion was calculated from the products and the methane introduced into the feed. The selectivities were calculated from the conversion of methane to each product on a carbon base. The carbon mass balances were $100 \pm 5\%$. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X, using monochromatized Cu Kα radiation. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used monochromatized Mg Kα radiation. The binding energies were corrected using 285 eV for C 1s as an internal standard. Argon-ion etching of the catalysts was carried out at 2 kV for 1 min with a sputtering rate estimated as ca. 2 nm/min for SiO_2.

3. Results and discussion

3.1. Thermal stability of strontium hydroxyapatites ion-exchanged with lead

Recent studies have shown that both stoichiometric and nonstoichiometric strontium hydroxyapatites are thermally converted to $Sr_3(PO_4)_2$ at temperatures as low as 973 K [21,22]. XRD patterns of the catalysts employed in the present work as obtained after calcination at 773 K for 3 h correspond to those for $Sr_{10}(PO_4)_6(OH)_2$ (JCPDS 33-1348) and $Pb_{10}(PO_4)_6(OH)_2$ (JCPDS 8-0259), with the exception of that for SrPb33HAp in which traces of the corresponding phosphates, $Sr_3(PO_4)_2$ (JCPDS 24-1008) and $Pb_3(PO_4)_2$ (JCPDS 22-0668) are also present (figure 1). Peaks attributed to Sr $3p_{1/2}$, Sr $3p_{3/2}$, O 1s and P 2s were found in the XPS spectra of the aforementioned catalysts at approximately 280, 270, 532 and 191 eV either before or after argon-ion etching, regardless of the content in ion-exchanged lead. XPS spectra for SrPb26HAp and SrPb33HAp after the etching show the presence of both metallic and cationic lead as well as the dissimilarity of the compositions of the bulk and surface regions (table 2). Since, after calcination at 873 K for 3 h XRD of the catalysts, with the exception of SrHAp and SrPb26HAp, showed the presence of strontium and lead phosphates (not shown), ion exchange with lead apparently reduces the thermal stability of the catalysts. Since the thermal properties of SrHAp ion-exchanged with lead are apparently dependent upon both the stoichiometry and the lead content 773 K was selected as the pretreatment and reaction temperature to preclude the presence of phosphate.

Table 1
Composition and surface areas of hydroxyapatites

Catalyst	Pb conc. [a]	Time [b] (h)	Sr/P [c]	Pb/P [c]	SA [d]	AD [e]
SrHAp	0 mmol/150 ml	24	1.62	0	65.6	0.31
SrPb11HAp	13.5 mmol/150 ml	68	1.42	0.16	55.2	0.41
SrPb26HAp	101 mmol/250 ml	24	1.50	0.40	22.3	0.60
SrPb33HAp	33.8 mmol/150 ml	24	1.21	0.40	46.7	0.37
SrPb71HAp	67.6 mmol/150 ml	68	1.09	0.78	17.3	0.64

[a] Initial concentration of lead ion in ion-exchange solution.

[b] Duration of ion-exchange at room temperature.

[c] Atomic ratio.

[d] BET surface area ($m^2\ g^{-1}$).

[e] Apparent density ($g\ cm^{-3}$).

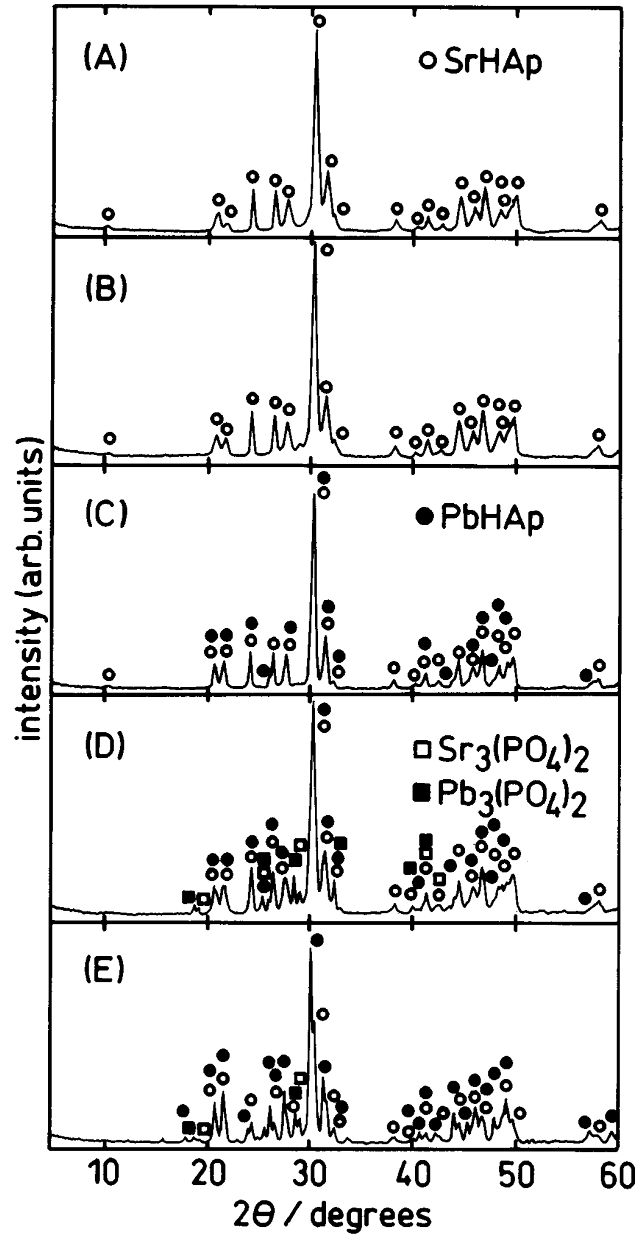

Figure 1. XRD patterns of fresh catalysts calcined at 773 K for 3 h. (A) SrHAp; (B) SrPb11HAp; (C) SrPb26HAp; (D) SrPb33HAp; (E) SrPb71HAp.

Table 2
XPS analyses of the fresh catalysts

Catalyst	Time[a]	Pb $4f_{5/2}$[b]	Sr/P[c]	Pb/P[c]	O/P[c]	Pb^0/Pb^{2+}[c]
SrHAp	0	–	1.64	–	3.62	–
	1	–	1.92	–	3.64	–
SrPb11HAp	0	143.8	1.46	0.21	3.71	–
	1	143.8	1.78	0.04	3.95	–
SrPb26HAp	0	142.8	1.11	0.70	3.67	–
	1	142.8 (140.8)[d]	1.38	0.28	3.45	0.10
SrPb33HAp	0	143.0	1.34	0.51	3.93	–
	1	142.9 (141.0)[d]	1.47	0.21	3.47	0.16
SrPb71HAp	0	143.4	1.08	0.66	3.49	–
	1	143.7	1.39	0.19	3.60	–

[a] Etching time (min).
[b] Binding energy (eV).
[c] Atomic ratio.
[d] Binding energy due to metallic Pb (Pb^0).

3.2. Effect of TCM on the oxidation of methane on SrHAp ion-exchanged with lead

In the absence of TCM, the conversion of methane and the selectivity to CO_2 at 773 K on SrHAp pretreated with O_2 (25 ml/min, 773 K, 1 h) increased with the lead content, indicating a lead-induced enhancement of the deep oxidation of methane (figure 2). In the presence of feedstream TCM the conversion of methane increased with lead content for times-on-stream of 0.5 h, while passing through a maximum for 6 h on-stream.

The formation of methyl chloride was observed after 6 h on-stream with both the lead-free and the SrHAp ion-exchanged with lead. The selectivity to CH_3Cl increased to 73% for SrHAp with Pb/Sr equal to 0.26 and remained relatively unchanged for higher lead contents. Upon stopping the supply of TCM after 6 h on-stream, CH_3Cl and CO were no longer observed in the product stream. It is noteworthy that the introduction of TCM with calcium and strontium hydroxyapatites has been shown to result in an enhanced selectivity to CO [12,13,17–19,22,23]. In view of the attainment of the highest selectivity to lead with the catalyst of Pb/Sr equal to 0.26, which has been shown to be the most thermally stable of those catalysts studied in the present work, further experiments have been carried out on SrPb26HAp.

In the absence of TCM and at $P(O_2) = 2.0$ kPa small quantities of coupling products were formed, but these vanished with increase of the partial pressure of oxygen and only CO_2 resulted (figure 3). With TCM the conversion of CH_4 was again observed to decrease as the time-on-stream increased at all three partial pressures of oxygen and at 6 h was virtually independent of the partial pressure of oxygen. No evidence for coupling products was found and the selectivities to C_1 products were essentially independent of the partial pressure of oxygen. As before CH_3Cl did not appear at the shorter times-on-stream but at 6 h time-on-stream significant selectivities to both CO and CH_3Cl were observed, with little variation with $P(O_2)$.

With increase in the partial pressure of TCM the selectivity to CH_3Cl increased to a maximum at P(TCM) equal to 0.17 (figure 4). Although the conversions measured after 6 h on stream decreased on introduction of TCM, with increase in the partial pressure of the latter the aforementioned loss was largely recovered at P(TCM) equal to 0.51 kPa. In contrast, the selectivity to CO was virtually independent of the partial pressure of TCM.

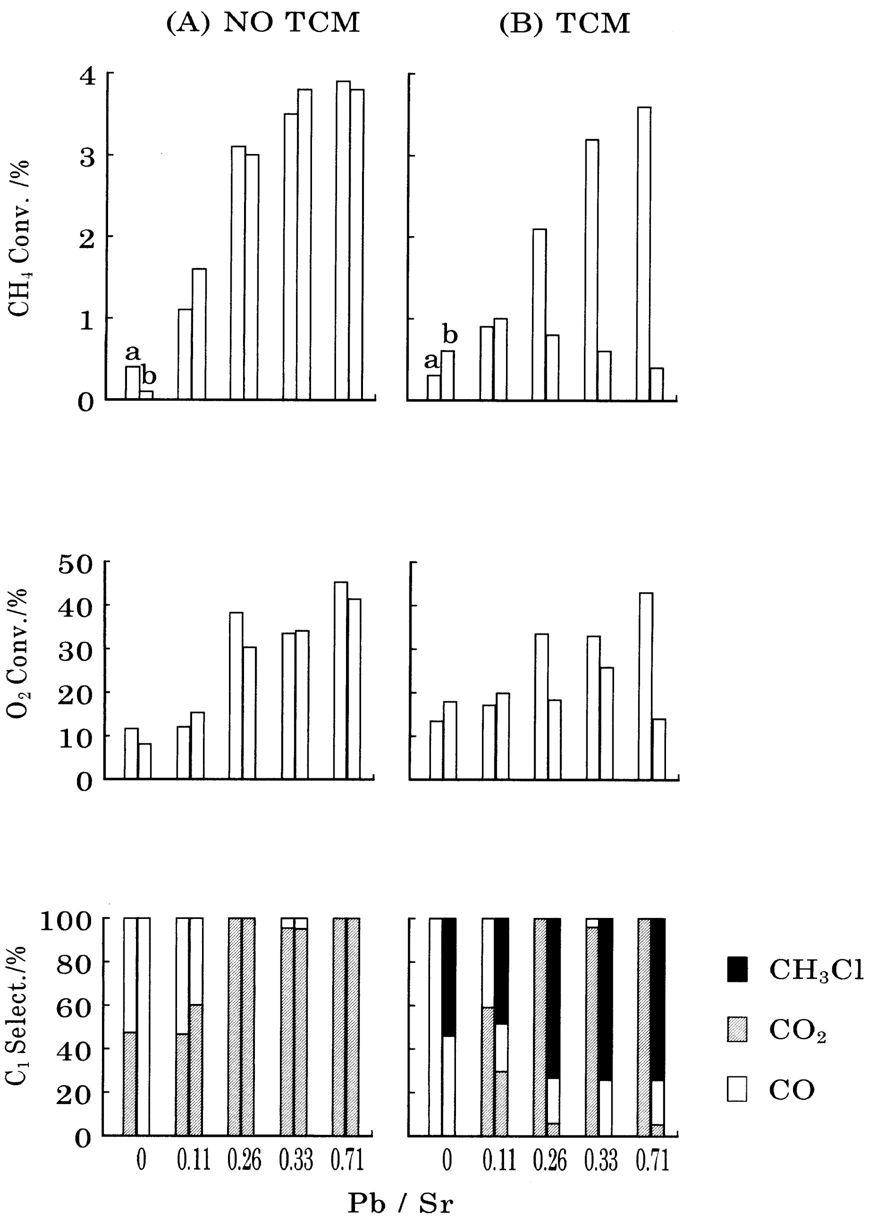

Figure 2. Methane oxidation on SrHAp and various SrPbHAp in the presence and absence of TCM at 773 K. Conditions: $W = 0.5$ g, $F = 30$ ml/min, $P(CH_4) = 28.7$ kPa, $P(O_2) = 4.1$ kPa, and P(TCM)= 0.17 kPa (when present) diluted with He. Catalysts were pretreated with O_2 (25 ml/min) at 773 K for 1 h. (a) 0.5 h on-stream; (b) 6 h on-stream.

3.3. XRD and XPS analyses of catalysts after the oxidation with TCM

A comparison of XRD patterns of catalysts previously employed in the oxidation process in the presence of TCM with those obtained prior to use shows that, regardless of the lead content, all of the catalysts were converted to the corresponding chlorapatites, $Sr_{10}(PO_4)_6Cl_2$ (JCPDS 16-0666) and $Pb_{10}(PO_4)_6Cl_2$ (JCPDS 19-0701) (not shown). The XPS spectra of the previously employed samples showed the peaks found for the catalysts prior to use together with that for Cl 2p at approximately 199 eV. No obvious correlation of the Cl/P ratio in the near-surface region with the lead content of the catalysts was found, but the surface-enhanced concentration of chlorine is evident (table 3). The values of Pb/P found with the used samples show clearly evident decreases in comparison with those found on the fresh catalysts (compare table 3 with table 2) and the values of this ratio in the bulk of the used samples are considerably smaller than those in the surface region, indicative of the conversion of Pb^{2+} to the metallic state of lead (Pb^0) (note column 8 of table 3), apparently resulting from the transfer of electrons from the surface region to the bulk during the oxidation process.

Changes in the partial pressures of O_2 and of TCM

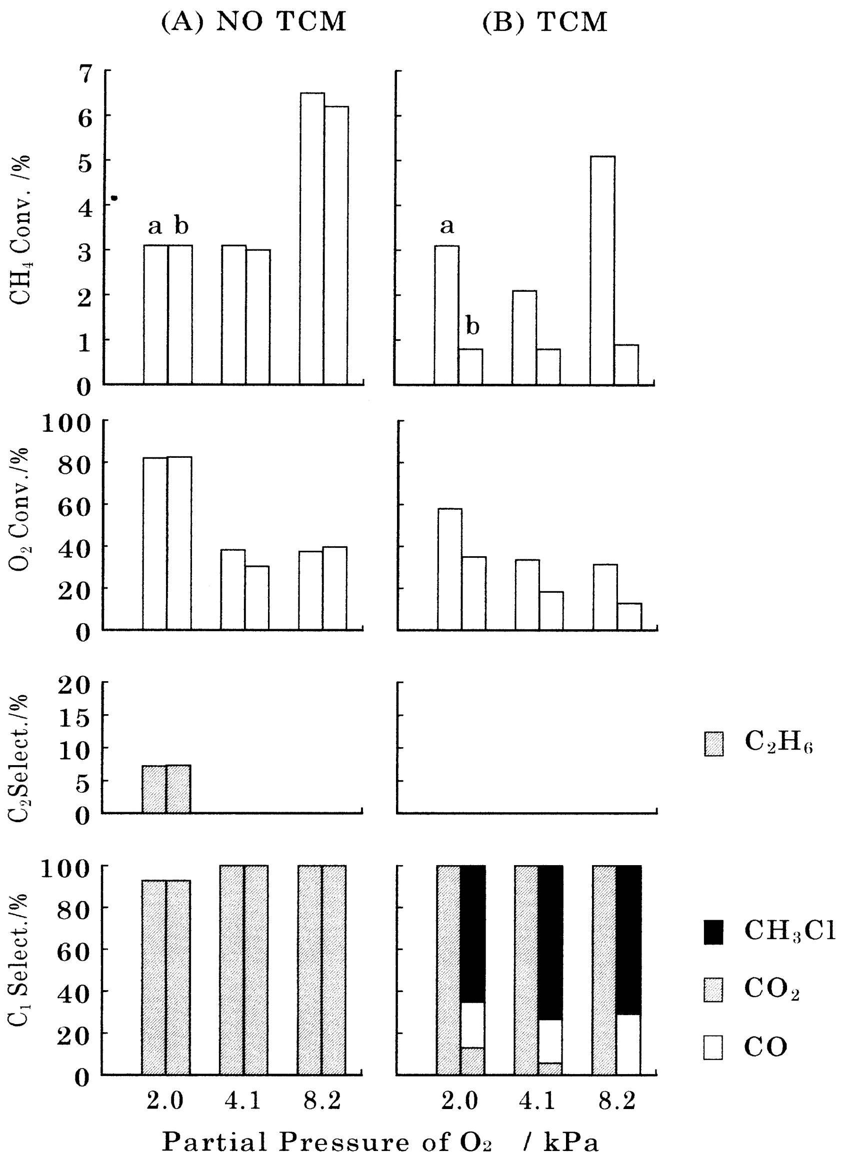

Figure 3. The effects of the partial pressure of O_2 on methane oxidation in the presence and absence of TCM on SrPb26HAp at 773 K. Symbols and reaction conditions: same as those in figure 3 except the partial pressure of O_2.

have substantial effects on the nature of lead and its contents in SrPb26HAp (not shown). The Pb/P ratio increases with increasing $P(O_2)$ but decreases with P(TCM), while the Pb^0/Pb^{2+} ratio decreases with increasing $P(O_2)$, indicating that the reduction of the lead cation was inhibited by the oxidant. For values of P(TCM) larger than 0.17 kPa, the effect of this variable on Pb^0/Pb^{2+} is insignificant.

3.4. Role of TCM in the oxidation of CH_4 on SrHAp ion-exchanged with lead

Earlier work on a variety of catalysts found that the introduction of TCM to the feedstream for the partial oxidation of methane produced enhanced selectivities to CO while with oxidative coupling the selectivities to C_{2+} hydrocarbons, particularly ethylene, were increased [4]. As shown in the present work the catalytic properties of strontium hydroxyapatite with and without ion-exchanged lead are markedly different from those of the aforementioned catalysts when employed in the presence of TCM.

The formation of CH_3Cl at longer times-on-stream but its absence at 0.5 h time-on-stream on strontium hydroxyapatite either with or without ion-exchanged lead indicates that the process through which CH_3Cl is formed involves the catalytic surface and in particular that which contains some critical concentration of chloride. Although the XRD patterns demonstrate that at least a substantial portion of the chlorided catalyst exists as the chlorapatite it is nevertheless possible that the surface, and indeed the bulk as well, contains chlorine in

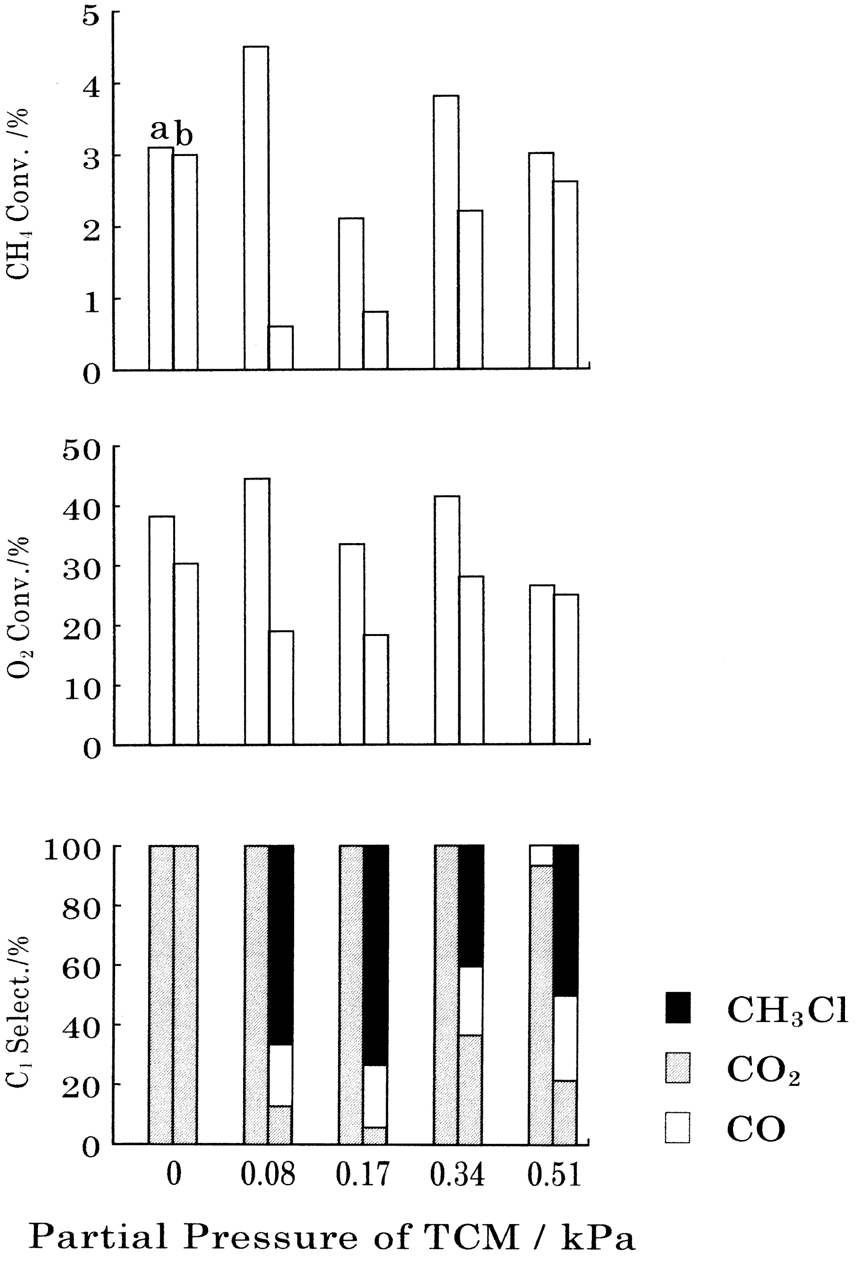

Figure 4. The effects of the partial pressure of TCM on methane oxidation on SrPb26HAp at 773 K. Symbols and reaction conditions; same as those in figure 3 except the partial pressure of TCM.

positions other than those previously occupied by hydroxyl groups of the apatite. While there is evidence for the participation of the lead in the ion-exchanged catalyst in the production of CH_3Cl it is, however, clear that the formation of the chloromethane does not require the presence of this element. Since CH_3Cl was not detected on the chlorinated catalyst in the absence of TCM, it is evident that methyl radicals react with Cl species generated from TCM to produce CH_3Cl. After the hydroxyapatites had been completely converted to the corresponding chlorapatites, the activity and selectivity were not sensitive to the lead contents, indicating that the role of lead in the catalysts on the formation of CH_3Cl is not strictly additive. The XPS data suggest that some reduction of the lead cation occurs during the oxidation process and there is evidence that the presence of TCM contributes to this reduction process. At least at this time the roles of ion-exchanged lead and TCM and their possible interactive participation in the production of CH_3Cl remain to be clarified.

Since the activities of the calcium [17–19], strontium [22,23] and the present strontium–lead hydroxyapatites decrease with increasing time-on-stream in the presence of TCM, apparently as a result of the formation of the corresponding chlorapatites, hydroxy groups must participate in the methane activation process.

Table 3
XPS analyses of the catalysts[a] used in the presence of TCM

Catalyst	Time[b]	Pb $4f_{5/2}$[c]	Sr/P[d]	Pb/P[d]	O/P[d]	Cl/P[d]	Pb^0/Pb^{2+}[d]
SrHAp	0	–	1.65	–	3.25	0.62	–
	1	–	1.80	–	3.54	0.57	–
SrPb11HAp	0	143.8	1.68	0.13	3.18	0.54	–
	1	143.7	1.77	0.07	3.24	0.40	–
SrPb26HAp	0	143.5	1.41	0.30	3.45	0.57	–
	1	143.9 (141.9)[e]	1.48	0.15	3.45	0.32	0.19
SrPb33HAp	0	143.5	1.25	0.36	2.81	0.49	–
	1	143.9 (141.7)[e]	1.43	0.09	3/10	0.36	0.21
SrPb71HAp	0	143.6	1.03	0.51	3.10	0.48	–
	1	143.9 (141.7)[e]	1.45	0.15	3.61	0.39	0.25

[a] Previously employed in obtaining the results reported in figure 3(B), but after 6 h on-stream.
[b] Etching time (min).
[c] Binding energy (eV).
[d] Atomic ratio.
[e] Binding energy due to metallic Pb (Pb^0).

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