Effects of incorporated lead and chlorine on the oxidation of ethane on strontium hydroxyapatites

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The oxidation of ethane in the presence and absence of tetrachloromethane (TCM) has been examined at 773 K on strontium hydroxyapatite (SrHAp). Introduction of lead in strontium hydroxyapatite resulted in the enhancement of the formation of the deep oxidation product CO_2 in the absence of TCM. On addition of TCM to the ethane conversion feedstream, the conversion of ethane and the selectivity to CO_2 decreased with increasing time-on-stream while the selectivity to ethene markedly increased. Although chlorides together with chlorapatites formed from the corresponding hydroxyapatites during the oxidation are believed to be responsible for the effects produced by the addition of TCM, the participation of non-structural chlorine cannot be excluded.

Calcium hydroxyapatites are bifunctional catalysts with acidic or basic properties depending on their compositions $[Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}, 0\leqslant x\leqslant 1]$.[1–6] On stoichiometric ($x=0$) and non-stoichiometric ($0\leqslant x\leqslant 1$) calcium hydroxyapatites, methane is predominantly converted to carbon oxides under oxidation conditions.[7,8] On the same solids the selectivity to carbon monoxide was increased while that to carbon dioxide decreased upon addition of TCM to the methane conversion feedstream although deactivation with increasing time-on-stream is also observed.[9–11] Strontium hydroxyapatites (SrHAp), regardless of their stoichiometry, also produce carbon oxides[12] and selectivities to carbon monoxide as high as 80% in the absence of TCM in the feedstream.[13,14] The selectivity to carbon monoxide is further enhanced with increasing time-on-stream by the introduction of TCM while concomitantly the conversion of methane decreases.[13,14] In contrast to the aforementioned, calcium hydroxyapatites which have been doped with lead yield coupling products such as ethene and ethane from methane in the absence of TCM,[15–17] as reported on many lead-containing solid catalysts.[18–26] The selectivities to C_2 compounds on the leaded hydroxyapatites are not influenced by the addition of TCM into the feedstream, in contrast to the effects of TCM on the oxidative coupling of methane on other solid catalysts.[27] The selectivity to carbon monoxide and that to carbon dioxide increase and decrease, respectively, under the latter conditions.[28] However, over strontium hydroxyapatites ion-exchanged with lead (SrPbHAp), selectivities to methyl chloride as high as 70% are observed with TCM in the methane conversion feedstream at 773 K while on SrPbHAp in the absence of TCM, carbon dioxide is the favoured product.[29,30] Evidently the catalytic properties of the hydroxyapatites in the methane conversion process, particularly in the presence of TCM, are strongly influenced by the nature of the cation(s) contained therein, although there is considerable evidence to suggest that the hydroxyapatites are converted to corresponding chlorapatites during oxidation in the presence of TCM.[9,11,28–30]

To determine the dependence of the aforementioned effects produced by TCM on the hydrocarbon under oxidation, the present study reports on the oxidation of ethane on strontium hydroxyapatite as such and ion-exchanged with lead for which comparative information for methane oxidation in the presence of TCM is available.[29–36]

Experimental

Catalyst preparation

Strontium hydroxyapatite was prepared from $Sr(NO_3)_2$ (Wako Pure Chemicals, Osaka) and $(NH_4)_2HPO_4$ (Wako) according to the procedure reported previously.[12] The resulting solid was calcined at 773 K for 3 h after drying in air at 373 K overnight. Lead cation was ion-exchanged into the hydroxyapatite by stirring the apatite sample (20 g) in 150 or 200 ml of aqueous solution of $Pb(NO_3)_2$ (Wako) at room temperature (Table 1). The samples were washed with water, dried at 323 K overnight, and calcined at 773 K for 3 h (denoted as fresh catalyst). All catalysts were sieved to particle sizes of 1.70–0.85 mm. The concentrations of Sr, Pb and P in each catalyst were measured in aqueous HNO_3 solution with inductively coupled plasma (ICP) spectrometry. The ion-exchanged catalysts are denoted as SrPb*xx*HAp, with *xx* equal to 100Pb/Sr (atomic ratio) and strontium hydroxyapatite as SrHAp. The BET surface areas, apparent densities and the atomic ratios of Sr/P and Pb/P of each catalyst are summarized in Table 1.

Apparatus and procedure

The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design and operating procedure have been described elsewhere.[9] Prior to reaction the catalyst was calcined *in situ* in an oxygen flow (12.5 ml min^{-1}) at 773 K for 1 h. Except as noted reaction conditions were: $W=0.5$ g, $F=15$ ml min^{-1}, $T=773$ K, $P(C_2H_6)=27.1$ kPa, $P(O_2)=6.7$ kPa

Table 1 Ion-exchange conditions, composition, surface area and apparent density of fresh catalysts

catalyst	Pb concentration[a]	time[b]	Sr/P[c]	Pb/P[c]	S.A.[d]	A.D.[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 (h). [c]Atomic ratio. [d]BET surface area (m^2 g^{-1}). [e]Apparent density (g cm^{-3}).

and $P(\mathrm{TCM}) = 0$ or 0.17 kPa; balance to atmospheric pressure was provided by helium.

Analysis and characterization

The reactants and products were analyzed with an on-stream gas-chromatograph (Shimadzu GC-8APT) equipped with a TC detector and integrator (Shimadzu C-R6A). The column systems used in the present study and the procedures employed in the calculation of conversions and selectivities have been described previously.[9,31]

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X diffractometer, using monochromated Cu-Kα radiation. Patterns were recorded over the 2θ range 5–60°. X-Ray photoelectron spectrometry (XPS; Shimadzu ESCA-1000AX) used monochromated Mg-Kα radiation. Binding energies were corrected using 285 eV for C 1 s as an internal standard. Argon-ion etching of the catalyst was carried out at 2 kV for 1 min with a sputtering rate estimated as *ca.* 2 nm min^{-1} for SiO_2.

Results and Discussion

Since the strontium lead hydroxyapatites employed in the present study are stable at 773 K but convert to the corresponding phosphates at temperatures higher than 873,[28] 773 K was employed for pretreatment and reaction in the present work. Earlier work has shown that this temperature is also appropriate to minimize the gas phase ethane oxidation process.

In the absence of TCM [Fig. 1(A)], the conversion of ethane decreases on addition of the smallest quantity of lead but increases with further addition of lead, passing through a maximum for SrPb33HAp. This contrasts with the results obtained for the oxidation of methane for which the conversion increased as the concentration of lead in the catalysts increased. Under similar reaction conditions the conversions of ethane found in the present work exceed those reported for the alkaline earth salts[31–33] and rare earth oxides.[34,35] The selectivity to ethene remained small and relatively unchanged as the Pb/Sr ratio increased while that to CO_2 increased significantly to the detriment of that to CO, the observations with CO_x being similar to those reported previously for the oxidation of methane on these catalysts.[29,30]

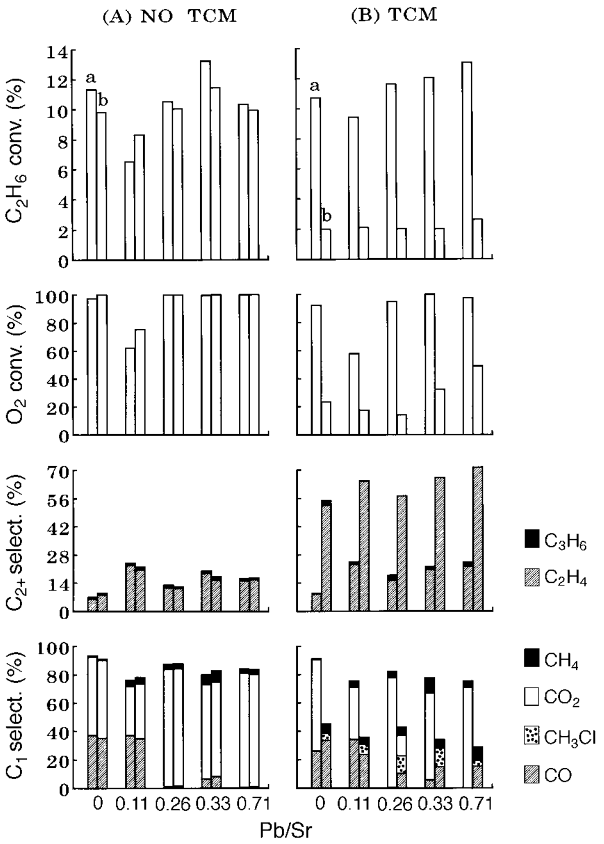

Fig. 1 Oxidation of ethane on SrHAp and SrPbHAp in the absence (A) and presence (B) of TCM at 773 K. Conditions: $W = 0.5$ g, $F = 15$ ml min^{-1}, $P(C_2H_6) = 27.1$ kPa, $P(O_2) = 6.7$ kPa and $P(\mathrm{TCM}) = 0.17$ kPa (when present) diluted with He. Symbols: a, 0.5 h on-stream; b, 6 h on-stream.

With TCM in the feedstream [Fig. 1(B)] the conversion and selectivities at 0.5 h on-stream were similar to those observed in the absence of the chlorinated additive. However, after 6 h on-stream both the conversion of ethane and the selectivity to CO_2 were substantially reduced, the latter to vanishingly small values as observed in the oxidation of methane on the same catalysts.[29,30] Concomitantly the selectivities to C_2H_4 are increased by factors of 3–4 while relatively small selectivities to CH_3Cl were also generated.

Although caution must be exercised in any generalization, evidence gathered to this date suggests that on those catalysts with which the enhancement of the selectivity to ethene resulting from the introduction of TCM occurs in methane oxidation similar observations are noted in ethane conversion. However, with the present catalysts and in the presence of TCM the selectivity to C_2H_4 from methane at 873 K decreases, C_2 compounds are not produced at 773 K, high selectivities to CH_3Cl are observed at 773 K and the catalysts are converted to the corresponding chlorapatites during the oxidation process.[29,30] Such differences in observations with the present catalysts as compared with those studied earlier suggest that a non-additive dependence may exist between the hydrocarbon being oxidized and the nature of the catalyst.

As shown in the XRD patterns of the catalysts after use in the oxidation of ethane with TCM present, and after 6 h on-stream, the hydroxyapatites are converted to the chlorapatite and no other compounds of chlorine were detected (Fig. 2).

Peaks in the XPS spectra of the fresh and used catalysts were found at approximately 280, 270, 532, 191 and 144 eV and have been attributed to Sr $3p_{1/2}$, Sr $3p_{3/2}$, O 1 s, P 2p and Pb $4f_{5/2}$ (when present). A peak at *ca.* 199 eV due to Cl 2p was also detected in the used samples. A peak at *ca.* 142 eV due to Pb^0 was found with some of the lead-containing catalysts, particularly after argon-ion etching. The Sr/P ratios of the samples changed relatively little after use in the oxidation process with TCM present (Table 2). In contrast the values of Pb/P found with the used samples show clearly evident decreases in comparison with those found on the corresponding fresh catalysts and those after argon-ion etching are smaller than those in the surface region, indicating loss of Pb from the surface region of the catalysts. Similar observations for Sr/P and Pb/P ratios have been reported on these catalysts after use in methane oxidation and contributions to the catalytic properties of oxygen species vicinal to lead have been inferred from EXAFS analyses.[30] Although no correlation of the Cl/P ratio in the near-surface region with the lead content of the catalysts is evident, the ratio was greater than that theoretically expected (0.33) for the corresponding chlorapatite, particularly with those catalysts containing lead, suggesting that additional chlorinated compounds or non-structural chlorine may form during the oxidation with TCM present.

SrPb33HAp showed the highest conversion in the absence of TCM; without TCM, the conversion of ethane increased with the partial pressure of O_2 [$P(O_2)$], while the selectivities were relatively unchanged [Fig. 3(A)]. Both of these observables remained approximately constant with time on stream.

On addition of TCM into the feedstream [Fig. 3(B)], the conversion and selectivities to C_1 and C_{2+} at the initial 0.5 h on-stream were similar to those found without TCM regardless of $P(O_2)$. The conversion of ethane decreased while the

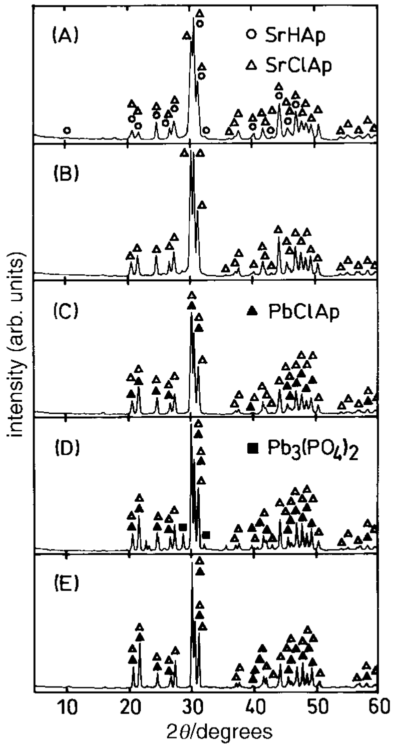

Fig. 2 XRD patterns of catalysts previously employed in obtaining the results shown in Fig. 1(B) but after 6 h on-stream. (A) SrHAp, (B) SrPb11HAp, (C) SrPb26HAp, (D) SrPb33HAp, (E) SrPb71HAp, SrHAp, SrClAp and PbClAp refer to strontium hydroxyapatite, strontium chlorapatite and lead chlorapatite, respectively.

selectivity to C_2H_4 increased with increasing time-on-stream, the latter of which was further enhanced with increasing $P(O_2)$. Increase of the time-on-stream resulted in the virtual elimination of CO_2 as a product while CH_3Cl was formed.

As noted, the introduction of TCM results in significant changes in the conversion and selectivities. However increases in the partial pressure of TCM [P(TCM)] had little or no effect, at either times-on-stream, on the conversions or selectivities observed at the lowest non-zero P(TCM), except for a P(TCM) of 0.08 at which no formation of CH_3Cl and vestiges of CO_2 were evident at 6 h on-stream (Fig. 4).

XRD patterns of SrPb33HAp previously employed in obtaining the results reported in Fig. 3 and 4 were essentially identical regardless of $P(O_2)$ and P(TCM) and demonstrated that the catalyst had been converted to the corresponding chlorapatite. XPS analyses show that Sr/P, Pb/P and Cl/P depend on the partial pressures of O_2 and of TCM but no trend is discernible (Table 3). As shown in Fig. 3, the selectivities on SrPb33HAp in the absence of TCM were relatively unaffected by $P(O_2)$ while in the presence of TCM and at 6 h on-stream significant differences in these were noted. The absence of a dependence of the selectivities on $P(O_2)$ can, at least tentatively be interpreted as suggesting that the surface remains relatively unaltered with the hydroxy groups playing a principal role in the oxidation process. However on substitution of these groups by chlorine, a process which is evidently time-dependent, the surface is less able to generate free radicals but more efficient in producing desirable products (C_2H_4) and in suppressing the formation of unwanted species (CO_2). XRD patterns of SrPb33HAp which had been employed in the oxidation of ethane under various conditions are relatively unchanged with either $P(O_2)$ or P(TCM) after 6 h time-on-stream, suggesting that the catalyst is fully chlorinated under these conditions and remains as such during the oxidation process (Fig. 5).

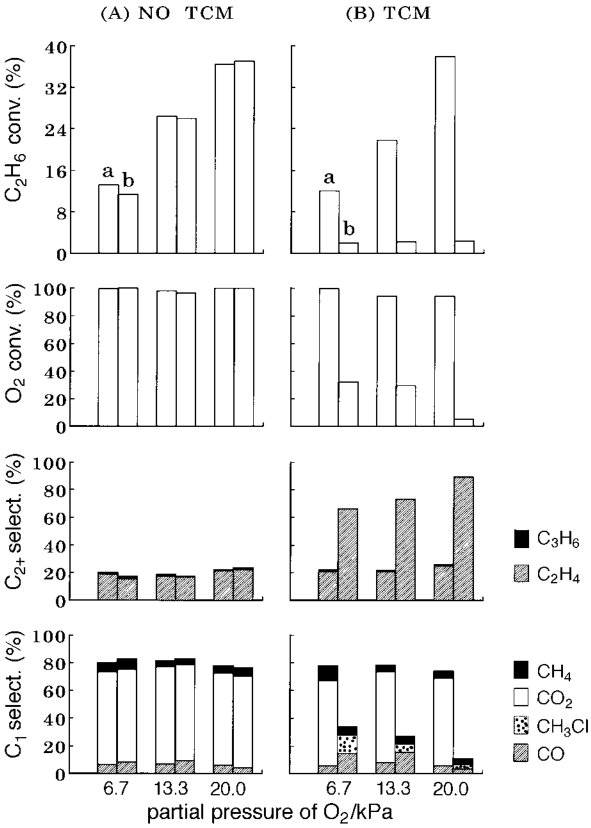

Fig. 3 Effects of the partial pressure of O_2 in the feedstream on ethane oxidation on SrPb33Hap in the absence (A) and presence (B) of TCM at 773 K. Symbols and reaction conditions: as in Fig. 1 except the partial pressure of O_2.

Further information on the nature of the chlorinated species additionally formed with chlorapatite can be obtained from XRD analyses of SrHAp previously subjected to various treatments (Fig. 6). SrHAp is employed in order to simplify the rather complex XRD patterns of the lead-containing catalysts. As shown in Fig. 6(A) and (B), on treatment with a high concentration of TCM diluted with air, SrHAp is converted to hydrates of $SrCl_2$, rather than strontium chlorapatite. A lower concentration of TCM produced no discernible quantity

Table 2 XPS analyses of fresh and used catalysts[a]

catalyst	T^b	SrHAp		SrPb11HAp		SrPb26HAp		SrPb33HAp		SrPb71HAp	
Sr/P[c]	0	1.64	(1.56)	1.46	(1.43)	1.11	(1.22)	1.34	(1.21)	1.08	(1.14)
	1	1.92	(1.95)	1.78	(1.65)	1.38	(1.55)	1.47	(1.55)	1.39	(1.27)
Pb/P[c]	0	—	—	0.21	(0.12)	0.70	(0.38)	0.51	(0.32)	0.66	(0.48)
	1	—	—	0.04	(0.08)	0.28	(0.23)	0.21	(0.20)	0.19	(0.30)
Cl/P[c]	0	—	(0.36)	—	(0.38)	—	(0.48)	—	(0.43)	—	(0.48)
	1	—	(0.36)	—	(0.35)	—	(0.37)	—	(0.46)	—	(0.42)
Pb^0/Pb^{2+c}	1	—	(—)	—	(—)	0.10	(0.20)	0.16	(0.22)	—	(0.25)

[a] Previously employed in obtaining the results reported in Fig. 1(B) but after 6 h on-stream. Values in parentheses refer to previously employed catalysts. [b] Etching time (min). [c] Atomic ratio.

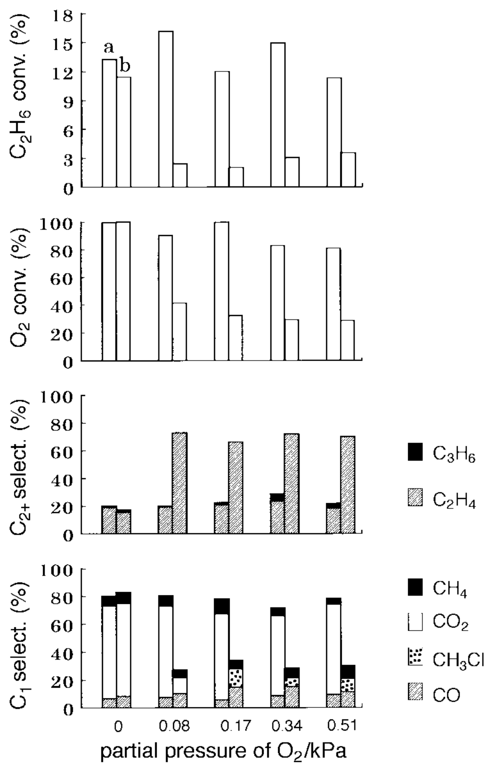

Fig. 4 Effects of the partial pressure of TCM in the feedstream on ethane oxidation on SrPb33HAp in the absence (A) and presence (B) of TCM at 773 K. Symbols and reaction conditions: as in Fig. 1 except the partial pressure of TCM.

Table 3 XPS analyses of used SrPb33HAp[a]

	T^b	$P(O_2)$/kPa: P(TCM)/kPa:	13.3 0.17	20.0 0.17	6.7 0.08	6.7 0.34	6.7 0.51
Sr/P[c]	0		1.28	1.24	1.50	1.31	1.63
	1		1.53	1.42	1.52	1.37	1.64
Pb/P[c]	0		0.33	0.39	0.37	0.40	0.19
	1		0.08	0.10	0.12	0.12	0.05
Cl/P[c]	0		0.52	0.51	0.58	0.50	0.54
	1		0.34	0.32	0.43	0.34	0.39

[a]Previously employed in obtaining the results reported in Fig. 3 and 4 but after 6 h on-stream. [b]Etching time (min). [c]Atomic ratio.

of either the chloride or chlorapatite [Fig. 6(C)], although helium was employed as a diluent to minimize the effect of water. A somewhat higher concentration of TCM with helium as diluent yielded chlorapatite and the chlorided six-hydrate [Fig. 6(D)], while the chlorapatite was detected together with a small quantity of unconverted SrHAp at 0.51 kPa of TCM [Fig. 6(E)]. Although both the chloride and the chlorapatite form during the oxidation of C_2H_6 in the presence of TCM, the existence of nonstructural chloride ions cannot be precluded.

Conclusions

1. The conversion of ethane on SrPbHAp in the absence of TCM increases with the lead content to a maximum at a Pb/Sr ratio equal to 0.33, the selectivity to CO_2 is enhanced by the presence of lead and that to C_2H_4 was relatively independent of the lead content.

2. At short times-on-stream, the introduction of TCM has little effect on the oxidation of ethane. With increasing time-on-stream the selectivity to ethene increased substantially while that to CO_2 and the conversion decreased.

3. Only small selectivities to CH_3Cl were observed under

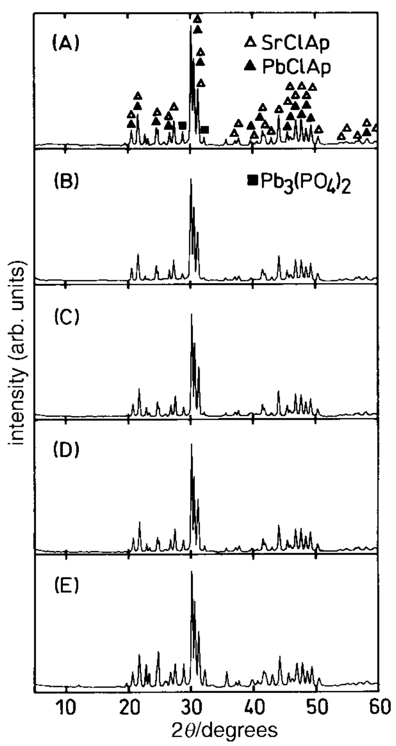

Fig. 5 XRD patterns of SrPb33HAp previously employed in obtaining the results shown in Fig. 3(B) and 4 but after 6 h on-stream. (A) $P(O_2)=13.3$ kPa in Fig. 3(B), (B) $P(O_2)=20.0$ kPa in Fig. 3(B), (C) $P(\text{TCM})=0.08$ kPa in Fig. 4, (D) $P(\text{TCM})=0.34$ kPa in Fig. 4, (E) $P(\text{TCM})=0.51$ kPa in Fig. 4.

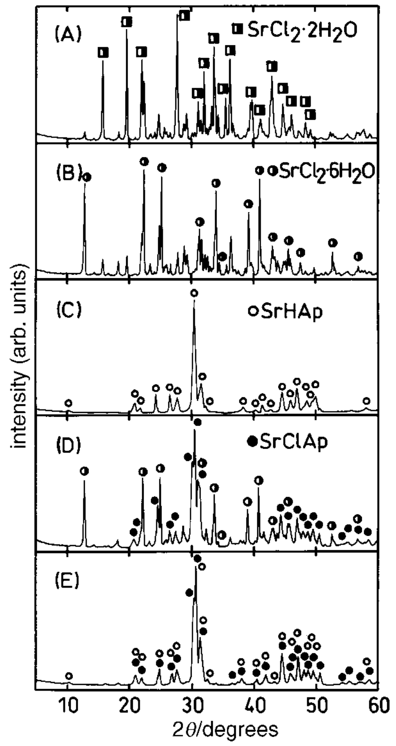

Fig. 6 XRD patterns of SrHAp pretreated with TCM at 773 K under various conditions. (A) SrHAp (12.5 g) pretreated with TCM (12 kPa) diluted with air for 3 h, (B) SrHAp (12.5 g) pretreated with TCM (12 kPa) diluted with air for 1.5 h, (C) SrHAp (5 g) pretreated with TCM (0.35 kPa) diluted with He for 1 h, (D) SrHAp (5 g) pretreated with TCM (1.0 kPa) diluted with He for 3 h, (E) SrHAp (3 g) pretreated with TCM (0.51 kPa) diluted with He for 2 h.

any conditions, in contrast with the observations with the same catalysts in the oxidation of methane.

4. Chlorapatites appear to be the dominant compounds formed from the hydroxyapatites in the oxidation of ethane in the presence of TCM but the chlorides and possibly non-structural chloride ions are also present and could play a significant role in the oxidation process.

This work was partially funded by a Grant for Natural Gas Research of The Japan Petroleum Institute to S.S. and the Natural Sciences and Engineering Research Council of Canada to J.B.M., to which our thanks are due.

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Paper 7/05467J; *Received* 28*th July*, 1997