Effect of the introduction of tetrachloromethane into the feedstream for methane oxidation with oxygen and nitrous oxide on thermally stable strontium hydroxyapatites

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Received 29 June 1998; accepted 19 September 1998

Thermally stable strontium hydroxyapatite (SrHAp) was prepared with a variety of stoichiometries and employed as catalysts for the oxidation of methane with oxygen and nitrous oxide in the presence and absence of tetrachloromethane (TCM) as a gas-phase additive. In contrast to the oxidation of methane on thermally unstable SrHAp, non-selective oxidation to CO and CO_2 at 873 K proceeded with oxygen while the selectivity to CO increased with increasing time-on-stream in the presence of TCM and was higher than 90% at 6 h on-stream, regardless of the Sr/P ratios in the catalysts. However, with nitrous oxide the selectivity to CO in the presence of TCM was strongly influenced by the Sr/P ratio with smaller values producing higher CO selectivity. In the presence of TCM, the catalyst consists of a complex mixture of the hydroxyapatite, the corresponding chlorapatite, phosphate, chloride and oxychloride, each of which contributes dissimilarly to the catalytic process.

Keywords: strontium hydroxyapatite, methane oxidation, tetrachloromethane, thermal stability

1. Introduction

Selectivities to carbon monoxide higher than 90% for conversions of methane greater than 10% have been obtained from the partial oxidation of methane on strontium hydroxyapatites (SrHAp) at 873 K during 6 h on-stream [1]. However, the activities decreased gradually with increasing time-on-stream due to the transformation of the apatite to $Sr_3(PO_4)_2$.

The cations of strontium hydroxyapatite (stoichiometric form $Sr_{10}(PO_4)_6(OH)_2$) and the isomorphous calcium hydroxyapatite (CaHAp, stoichiometric form $Ca_{10}(PO_4)_6(OH)_2$) may be exchanged by other metal ions [2–7]. The surface properties of SrHAp and CaHAp [8–11] and the dehydration of butanol on non-stoichiometric SrHAp ($Sr_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, $0 < x \leqslant 1$) have been examined [12,13]. The catalytic properties of SrHAp and its lead ion-exchanged analogue have been evaluated in hydrocarbon oxidation processes, particularly in the presence of small quantities of tetrachloromethene (TCM) introduced as a gas-phase additive, which contributes mainly to the enhancement of the partial oxidation of alkanes to carbon monoxide or methyl chloride [1,14–19]. Unfortunately, however, there is a paucity of information on the surface and bulk properties of SrHAp.

The present paper reports on studies of the oxidation of methane with oxygen and dinitrogen oxide on thermally stable SrHAp in the presence and absence of TCM.

2. Experimental

2.1. Catalyst preparation

All chemicals were of high purity and were used as supplied. Strontium hydroxyapatites ($SrHAp_{1.52}$, $SrHAp_{1.56}$, $SrHAp_{1.64}$ and $SrHAp_{1.67}$, where the subscripts represent the Sr/P atomic ratio of each apatite as determined by ICP) were prepared from $Sr(OH)_2 \cdot 8H_2O$ (Wako Pure Chemicals, Osaka) and H_3PO_4 (Wako) according to the procedure of Ishikawa et al. [11]. The resulting solids were calcined at 773 K for 3 h after drying in air at 373 K overnight and are herein described as "fresh catalysts". Particle sizes of 1.70–0.85 mm have been employed. The concentrations of Sr and P were measured in an aqueous HNO_3 solution with inductively coupled plasma (ICP) spectrometry (Shimadzu, ICPS5000).

2.2. 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 catalyst packing procedure have been described elsewhere [19]. Prior

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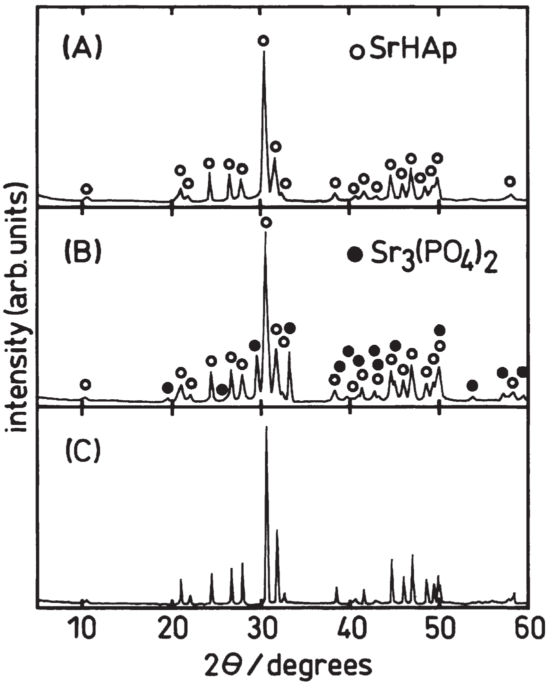

Figure 1. XRD patterns of fresh $SrHAp_{1.64}$ prepared from $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ followed by calcination at 873 (A) and 973 K (B) for 3 h and that prepared from $Sr(OH)_2$ and H_3PO_4 followed by calcination at 1473 K for 3 h (C).

to use, the catalyst was calcined *in situ* in an oxygen flow (25 ml/min) at the reaction temperature for 1 h unless otherwise stated. The typical reaction conditions were as follows: $W = 0.5$ g, $F = 30$ ml/min, $T = 873$ or 973 K for the oxidation with O_2 and N_2O, respectively, $P(CH_4) = 28.7$ kPa, $P(O_2) = 4.1$ kPa or $P(N_2O) = 12.3$ kPa and $P(TCM) = 0$ or 0.17 kPa; balance to atmospheric pressure was provided by helium.

2.3. 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). Three columns, Porapak Q (6 m × 3 mm), Molecular Sieve 5A (0.2 m × 3 mm), and Molecular Sieve 13X (1 m × 3 mm) were employed in the analyses, the latter to separate N_2 and O_2. 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 ± 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 catalyst was carried out at 2 kV for 1 min with a sputtering rate estimated as ca. 2 nm/min for SiO_2. Infrared spectra of the fresh catalysts and SrHAp prepared from $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ were recorded with a Shimadzu FTIR-8200 PC immediately after the calcination at 773 K.

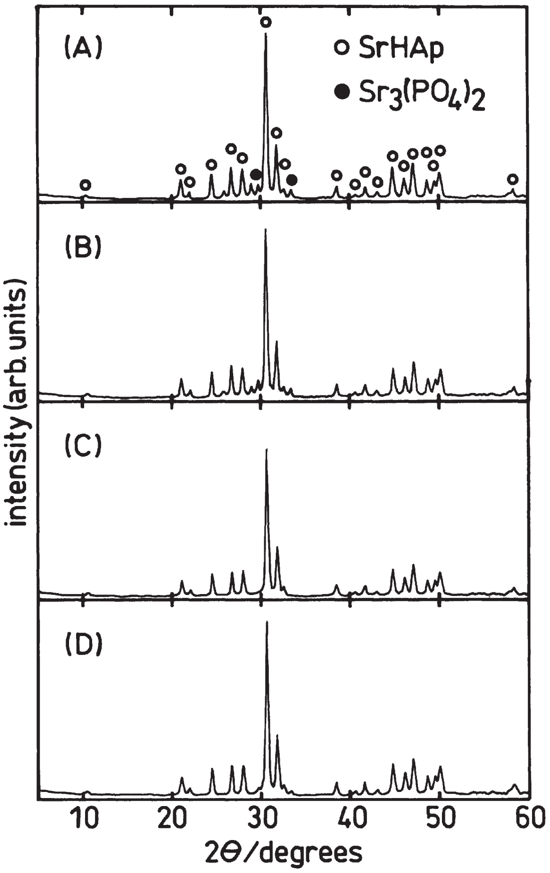

Figure 2. XRD patterns of fresh SrHAp prepared from $Sr(OH)_2$ and H_3PO_4 followed by calcination at 973 K for 3 h. (A) $SrHAp_{1.52}$, (B) $SrHAp_{1.56}$, (C) $SrHAp_{1.64}$, (D) $SrHAp_{1.67}$.

3. Results and discussion

3.1. Properties of catalyst

In view of the dissimilar preparative reagents used previously ($Sr(NO_3)_2$ and $(NH_4)_2HPO_4$) [6,14–19] and in the present work for the preparation of SrHAp the thermal stabilities of $SrHAp_{1.64}$ prepared by the two methods are compared in figure 1. The XRD pattern of $SrHAp_{1.64}$ prepared previously showed only one component at 873 K, but evidence of the conversion of SrHAp to $Sr_3(PO_4)_2$ was found at temperatures as low as 973 K (figure 1 (A) and (B)), respectively. In contrast, the XRD pattern of SrHAp prepared in the present work shows no evidence for a second component up to 1473 K (figure 1(C)). XRD patterns of the catalysts prepared by the earlier method after calcination at 973 K show that extensive conversion to the corresponding phosphate has occurred (figure 2) [15]. Although with some stoichiometries of SrHAp a trace amount of $Sr_3(PO_4)_2$ was observed, the thermal stabilities of the solids prepared as described in the present work were significantly improved as compared with those previously prepared. The BET surface

Table 1
Surface area, apparent density and XPS analysis of SrHAp.

Sr/P	SA[a]	AD[b]	Sr $2p_{3/2}$[c]	O 1s[c]	P 2s[c]	Sr/P[d]	O/P[d]
1.52	37	0.64	269.1 (269.8)	531.2 (531.7)	190.5 (191.0)	1.89 (1.83)	3.48 (3.34)
1.56	38	0.56	268.9 (269.5)	531.0 (531.4)	190.1 (190.9)	1.80 (1.80)	3.23 (3.24)
1.64	41	0.62	269.0 (269.9)	531.1 (531.7)	190.4 (191.1)	1.69 (1.87)	3.89 (3.98)
1.67	34	0.62	269.0 (269.5)	531.0 (531.5)	190.3 (190.7)	2.01 (2.06)	3.02 (3.31)

[a] BET surface area (m^2/g).
[b] Apparent density (g/cm^3).
[c] Binding energy (eV). Values in parentheses: after argon-ion etching for 1 min.
[d] Atomic ratio (XPS). Values in parentheses: after argon-ion etching for 1 min.

areas, apparent densities and XPS results of the SrHAp are summarized in table 1. The surface areas of SrHAp as prepared for the present work were smaller by approximately 30 m^2/g than those prepared previously [15]. The IR spectra of SrHAp prepared by the two methods were essentially identical for all stoichiometries of the apatites. $\nu_3(PO_4)$, $\nu_1(PO_4)$, $\nu_4(PO_4)_2$ and OH libration modes were detected at 1075 and 1018, 949, 592 and 562, and 534 cm^{-1}, respectively, as reported by Fowler [20], although a peak due to the OH stretching mode, expected at 3590 cm^{-1}, overlapped with those due to air. The remainder of this report is concerned with the thermally stable SrHAp.

3.2. Methane oxidation with O_2 on thermally stable SrHAp

The conversion of methane decreased with increasing atomic ratio of Sr/P in the catalysts in both the absence and presence of TCM (figure 3 (A) and (B)). In contrast to the oxidation of methane on thermally unstable SrHAp [1], the present SrHAp generate CO and CO_2 unselectively. Upon addition of TCM (figure 3(B)), however, the selectivity to CO increased with increasing time-on-stream. Although the selectivities to carbon oxides varied with the Sr/P ratio, those to C_2 compounds were virtually independent of this ratio. With the addition of TCM to the feedstream, the conversion of methane and the selectivity to CO decreased and increased, respectively, with increasing time-on-stream, irrespective of the Sr/P ratio in the catalysts and the partial pressure of TCM (figure 4 (B)–(D)). The conversion of methane at 0.5 h on-stream and the selectivities to carbon oxides at 0.5 and 6 h on-stream were evidently influenced by the Sr/P ratio, while the conversion at 6 h on-stream and the selectivities to C_2 compounds were not dependent on the stoichiometry. It should be noted that the deep oxidation to CO_2 was strongly suppressed on $SrHAp_{1.52}$ and $SrHAp_{1.56}$ by the addition of TCM, while significant selectivities to CO_2 remained at 6 h on-stream on $SrHAp_{1.64}$ and $SrHAp_{1.67}$. In all runs, O_2 obtained from the decomposition of N_2O was completely consumed. The XRD patterns of SrHAp previously employed in the oxidation in the absence of TCM show that the conversion to $Sr_3(PO_4)_2$ proceeded extensively on $SrHAp_{1.52}$ and $SrHAp_{1.56}$, while no conversion was observed on $SrHAp_{1.64}$ and $SrHAp_{1.67}$ (figure 5), indicating that the catalysts can be classified into two groups. However, the process of chlorination of SrHAp was relatively complex and independent of the Sr/P ratio. Upon addition of 0.085 kPa of TCM into the feedstream on $SrHAp_{1.52}$, the XRD pattern of the used catalyst showed that $SrHAp_{1.52}$ converted to $Sr_3(PO_4)_2$ and strontium chlorapatite and further increase of the partial pressure of TCM resulted in the formation of chlorapatite together with a trace amount of $SrCl_2 \cdot 6H_2O$ (not shown). The XRD patterns of $SrHAp_{1.67}$ used in the methane conversion process with 0.085 kPa of TCM showed the presence of chlorapatite only although a small proportion of $SrCl_2 \cdot 6H_2O$ was detected in the catalyst previously employed at a higher partial pressure of TCM (not shown). However, in the XRD patterns of $SrHAp_{1.56}$ and $SrHAp_{1.64}$,

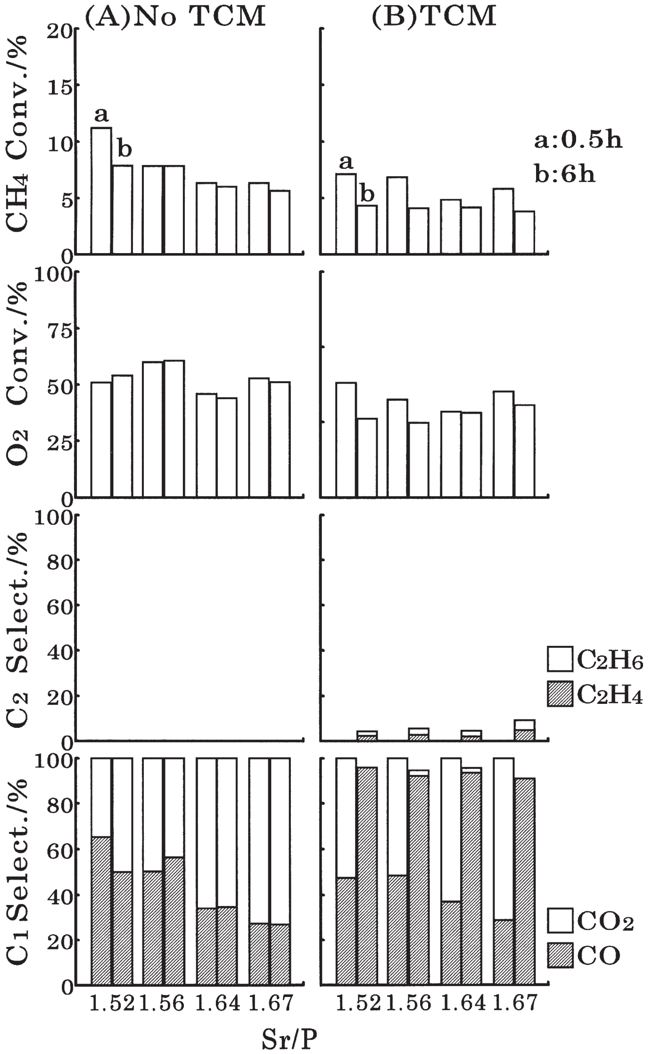

Figure 3. Methane oxidation with O_2 on SrHAp in the absence (A) and presence (B) of TCM at 873 K. Reaction conditions: $W = 0.5$ g, $P(CH_4) = 28.7$ kPa, $P(O_2) = 4.1$ kPa and $P(TCM) = 0.17$ kPa (when present) diluted with He. $F = 30$ ml/min. Catalysts were pretreated with O_2 (25 ml/min) at 873 K for 1 h.

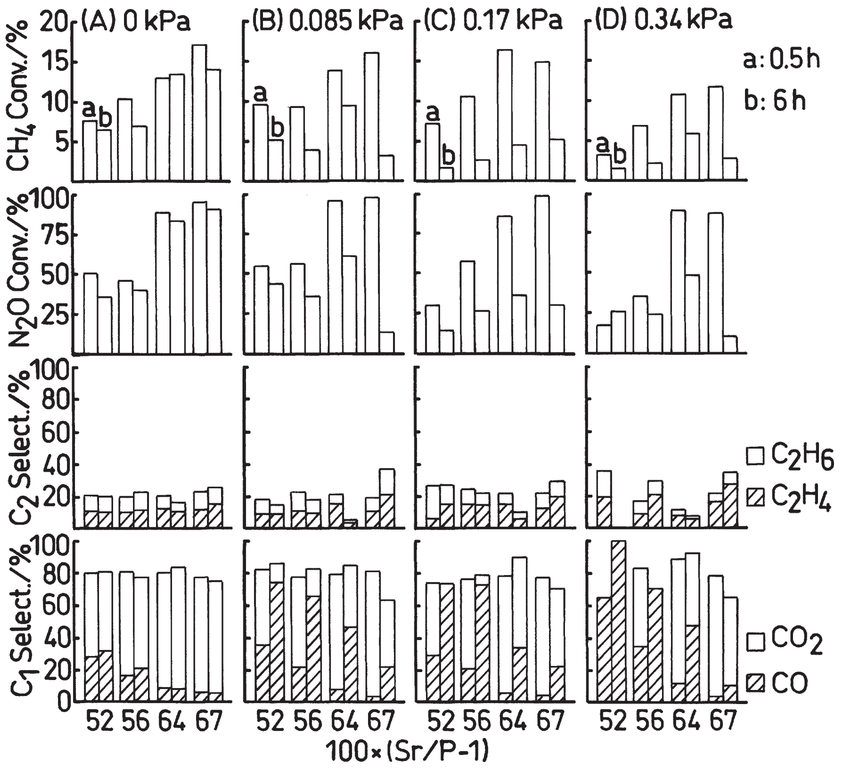

Figure 4. Effect of the partial pressure of TCM on methane oxidation with N_2O at 973 K. Reaction conditions: same as those in figure 3, except $P(N_2O) = 12.3$ kPa and P(TCM). Catalysts were pretreated with O_2 (25 ml/min) at 973 K for 1 h.

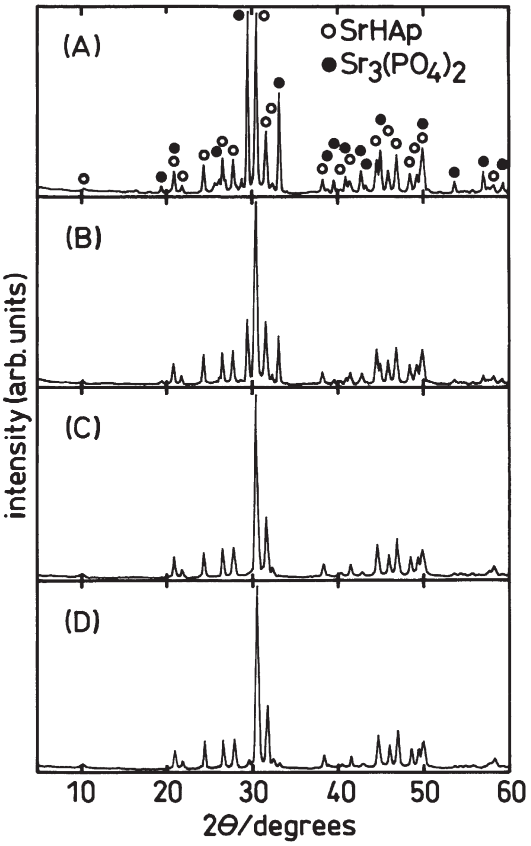

Figure 5. XRD patterns of SrHAp previously employed in obtaining the results shown in figure 4(A), but after 6 h on-stream. (A) $SrHAp_{1.52}$, (B) $SrHAp_{1.56}$, (C) $SrHAp_{1.64}$, (D) $SrHAp_{1.67}$.

the formation of $Sr(ClO_4)_2$ (JCPDS 37-0756) was also evident (figure 6). Since the oxychloride was not detected with SrHAp, prepared from $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$, which had previously been employed for the oxidation of methane [15,16,19] and ethane [17,18] in the presence of TCM, it appears that the OH groups on SrHAp as prepared in the present work may contribute to the formation of the oxychloride. The formation of $Sr(ClO_4)_2$ was dependent on the partial pressure of TCM as well as the stoichiometry of SrHAp and the formation of other chlorinated species (figure 6). XPS spectra of catalysts previously used in the oxidation process in the presence of TCM at various partial pressures contained a peak at approximately 199 eV due to Cl 2p together with peaks observed in the fresh catalysts (table 1). Irrespective of the argon-ion etching, the near-surface atomic ratios of Cl/P on SrHAp previously employed in obtaining the results shown in figure 4 (B)–(D) were generally greater than expected (0.33) for the stoichiometric chlorapatite but did not depend on the partial pressure of TCM in the feedstream (table 2).

3.3. Effect of surface chlorinated species on methane oxidation

In order to examine the role of the chlorinated species over the surface of SrHAp in the presence of TCM, experiments were performed in which SrHAp was exposed to a gas mixture ($F = 30$ ml/min) of TCM (0.34 kPa) and N_2O (12.3 kPa) diluted He at 973 K for a given length of time prior to exposure to the reactant stream, not con-

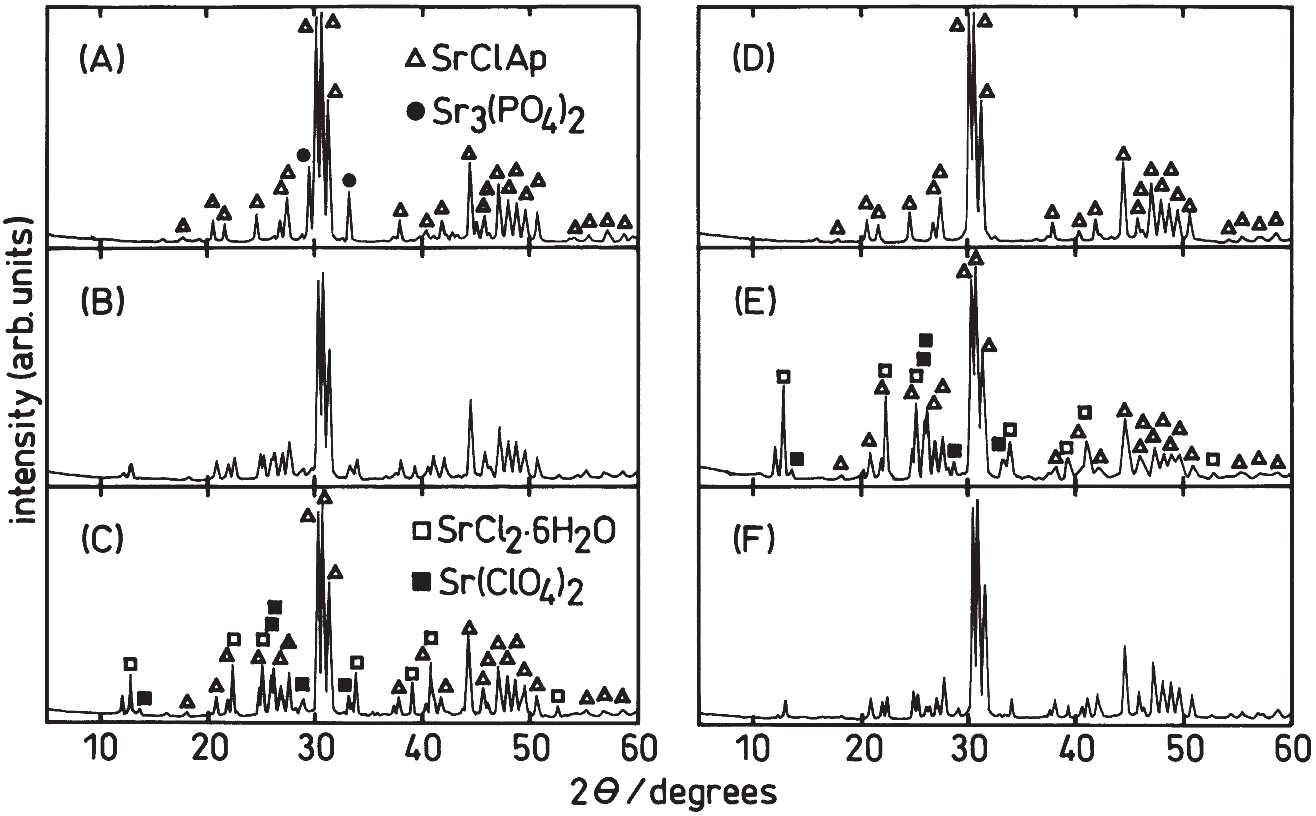

Figure 6. XRD patterns of $SrHAp_{1.56}$ and $SrHAp_{1.64}$ previously employed in obtaining the results shown in figure 4 (B)–(D), but after 6 h on-stream. (A) $SrHAp_{1.56}$, $P(TCM) = 0.085$ kPa; (B) $SrHAp_{1.56}$, $P(TCM) = 0.17$ kPa; (C) $SrHAp_{1.56}$, $P(TCM) = 0.34$ kPa; (D) $SrHAp_{1.64}$, $P(TCM) = 0.085$ kPa; (E) $SrHAp_{1.64}$, $P(TCM) = 0.17$ kPa; (F) $SrHAp_{1.64}$, $P(TCM) = 0.34$ kPa.

Table 2
Cl/P[a] of used[b] SrHAp.

Sr/P	Cl/P					
	0.085[c]		0.17[c]		0.34[c]	
1.52	0.38	(0.33)	0.34	(0.50)	0.66	(0.47)
1.56	0.38	(0.33)	0.46	(0.36)	0.69	(0.57)
1.64	0.45	(0.35)	0.73	(0.59)	0.74	(0.50)
1.67	0.59	(0.46)	0.76	(0.40)	0.74	(0.55)

[a] XPS analysis.

[b] Previously employed in obtaining results shown in figure 4 (B)–(D) but after 6 h on-stream.

[c] P(TCM) (kPa). Values in parentheses: after argon-ion etching for 1 min.

taining TCM (figure 7). For all catalysts, the conversion of CH_4 and N_2O decreased with increasing pretreatment time, but the effect of the pretreatment time on the selectivity to each product depended on the Sr/P ratio in SrHAp. On $SrHAp_{1.52}$, the selectivities to C_1 and C_2 products were little influenced by the pretreatment time (figure 7(A)). As expected from the results of the effect of the TCM on methane and ethane oxidation on various hydroxyapatites [1,15–19,21], the selectivity to CO increased with increasing pretreatment time on $SrHAp_{1.56}$ and $SrHAp_{1.64}$ (figure 7 (B) and (C)). It is of interest to note that with $SrHAp_{1.67}$ the longer pretreatment time resulted in the enhancement of the selectivity to C_2 compounds but not to that of CO (figure 7(D)). The XRD patterns of SrHAp previously employed in obtaining the results shown in figure 7 at pretreatment times of 0.5, 3 and 6 h are described in figures 8–10, respectively. At a shorter pretreatment time of 0.5 h, in all SrHAp, the hydroxyapatite was still present together with the corresponding chlorapatite and phosphate but the proportions of each species were dependent on the Sr/P ratio (figure 8). At the shorter pretreatment time, the conversions and selectivities obtained with each stoichiometry were similar to those on the non-pretreated catalyst, that is, where the pretreatment time was 0 h (figure 7). After 3 h of pretreatment, the XRD patterns of $SrHAp_{1.52}$, $SrHAp_{1.56}$ and $SrHAp_{1.64}$, although not identical, show evidence for the presence of strontium chloride and oxychloride together with the chlorapatite (figure 9 (A)–(C)). However, $SrCl_2$ and strontium chlorapatite, but not $Sr(ClO_4)_2$, were observed with $SrHAp_{1.67}$ (figure 9(D)). On further pretreatment of the various SrHAp compositions strontium chlorapatite was detected without exception (figure 10). In XRD patterns of $SrHAp_{1.52}$ and $SrHAp_{1.67}$, the corresponding oxychloride and chloride, respectively, were also detected (figure 10 (A) and (D)) but with the 1.56 and 1.64 compositions the XRD patterns are essentially identical (figure 10 (B) and (C)). These XRD results reveal that the chlorination behaviors might be classified with three catalyst groups, that is, $SrHAp_{1.52}$, $SrHAp_{1.56}$ and $SrHAp_{1.64}$, and $SrHAp_{1.67}$. It is of interest to note that the effect of pretreatment on methane oxidation (figure 7) could also be classified in a similar manner. Therefore, it might be sug-

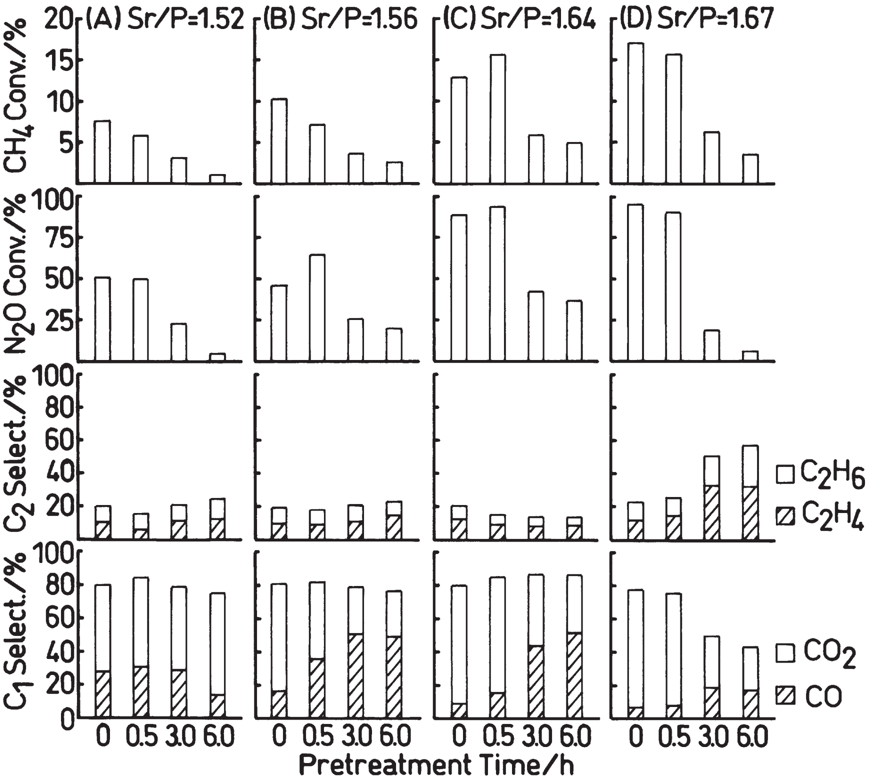

Figure 7. Effect of the pretreatment time prior to methane oxidation with N_2O in the absence of TCM at 973 K. Pretreatment gas: $P(\text{TCM}) = 0.34$ kPa and $P(N_2O) = 12.3$ kPa diluted with He ($F = 20$ ml/min). Catalyst (0.5 g) was pretreated with the gas at 973 K for a given time. Data were collected after 0.5 h on-stream. Reaction conditions: same as those in figure 4, but in the absence of TCM.

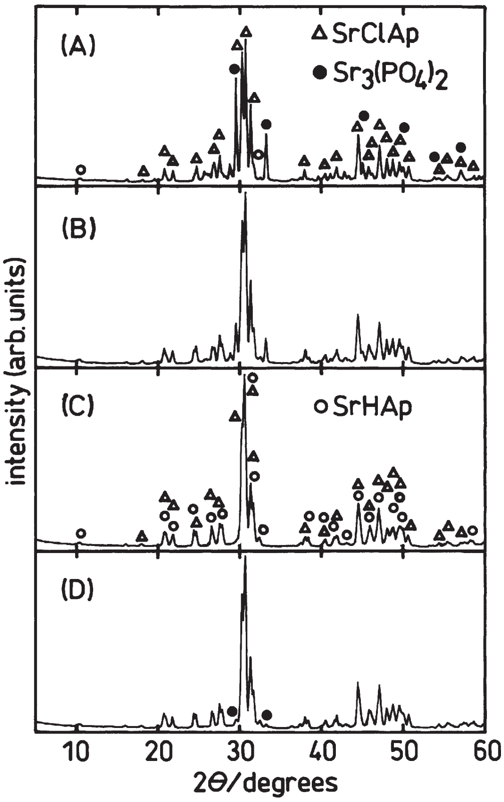

Figure 8. XRD patterns of SrHAp previously employed in obtaining the results shown in figure 7, but pretreated for 0.5 h. (A) $\text{SrHAp}_{1.52}$, (B) $\text{SrHAp}_{1.56}$, (C) $\text{SrHAp}_{1.64}$, (D) $\text{SrHAp}_{1.67}$.

gested that an excess of the oxychloride together with the chlorapatite produced little or no effect on the pretreatment on $\text{SrHAp}_{1.52}$ and an excess of the chloride on $\text{SrHAp}_{1.67}$ together with the chlorapatite resulted in an enhancement of the selectivity to C_2 compounds. Earlier work has demonstrated the beneficial effects of the chloride on the selectivity to C_2 compounds with a variety of catalysts [22]. However, in the present work a combination of the oxychloride and chloride together with the chlorapatite appears to lead to the enhancement of the selectivity to CO. With the previously employed catalysts, binding energies from XPS spectra of Sr 2p, O 1s and P 2s were essentially identical to those of the fresh catalysts and the Cl 2p signal appeared at approximately 199 eV. Quantitative analyses of the atomic ratio of Sr/P and O/P did not correlate with the XRD patterns described in figures 8–10 (not shown). At 0.5 h pretreatment, the Cl/P ratios of all samples were smaller than expected (0.33) for the stoichiometric chlorapatite (table 3) and quantitatively reflect the results of XRD patterns (figure 8). On increase of the pretreatment time to 3 h, the Cl/P ratio increased significantly, consistent with the formation of chlorinated species and/or the elimination of PO_4 groups. Further extension of the pretreatment time to 6 h resulted in further increases of Cl/P ratios on $\text{SrHAp}_{1.56}$ and $\text{SrHAp}_{1.67}$ and decrease of that on $\text{SrHAp}_{1.52}$ and $\text{SrHAp}_{1.64}$. Although the nature of surface chlorinated species cannot be established by XPS Cl/P ratios reveal that the chlorination in the near-surface region

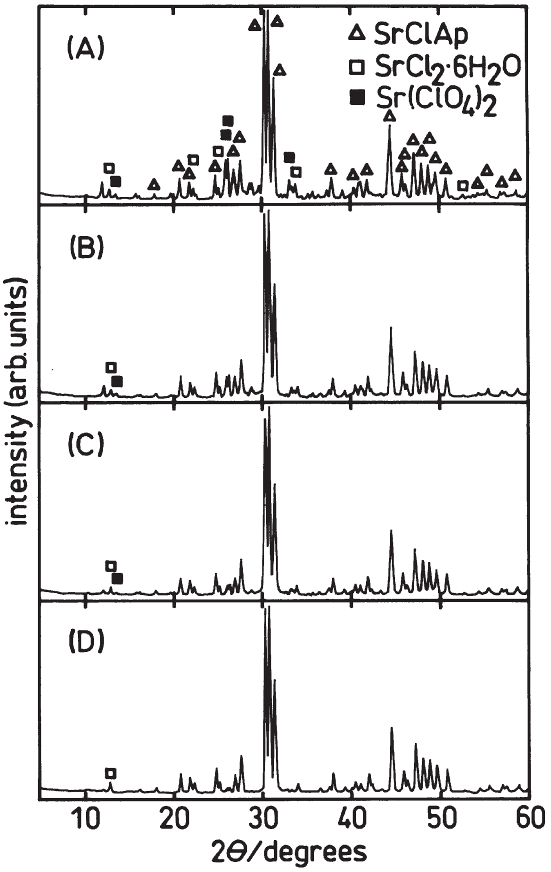

Figure 9. XRD patterns of SrHAp previously employed in obtaining the results shown in figure 7, but pretreated for 3 h. (A)–(D) as in figure 8.

Table 3
Cl/P[a] of used[b] SrHAp.

Sr/P	Cl/P					
	0.5[c]		3[c]		6[c]	
1.52	0.25	(0.19)	0.80	(0.66)	0.38	(0.29)
1.56	0.25	(0.21)	0.46	(0.34)	0.66	(0.48)
1.64	0.28	(0.24)	0.74	(0.61)	0.42	(0.36)
1.67	0.24	(0.15)	0.70	(0.50)	0.71	(0.64)

[a] XPS analysis.
[b] Previously employed in obtaining the results shown in figure 7 but after 0.5 h on-stream.
[c] Pretreatment time (h). Values in parentheses: after argon-ion etching for 1 min.

is as complex as that in bulk phase and is undoubtedly dependent, in part, on the stoichiometry of the catalyst, as well as the OH groups formed in the present preparation procedure. The catalytic properties of solids in the methane oxidation process have frequently been attributed to the presence of basic sites [23]. The use of $Sr(OH)_2$ as the source of strontium in the present work, in contrast to $Sr(NO_3)_2$ in the previous studies, may lead to increased quantities of surface hydroxyl groups and further oxidation of CO to CO_2. Unfortunately, however, FTIR spectra were unable to distinguish between SrHAp prepared from $Sr(OH)_2$ and that from $Sr(NO_3)_2$. The relative intensities, $I_{\mathrm{OH}}/I_{\nu_4(\mathrm{PO}_4)}$, where I_{OH} and $I_{\nu_4(\mathrm{PO}_4)}$ represent the intensities at 534 and 592 cm^{-1}, were 0.06 ± 0.02 for the thermally stable samples of Sr/P from 1.52 to 1.67 and 0.07 ± 0.02 for the thermally unstable samples of Sr/P from 1.67 to 1.73, identical within experimental error. With TCM in the feedstream the hydroxyl groups, or at least a substantial portion of them, are probably converted to chloride. It should be noted that the oxidation of methane in the presence of TCM is also influenced by a gas-phase chlorine species as well as the chlorinated species found in the solid phase.

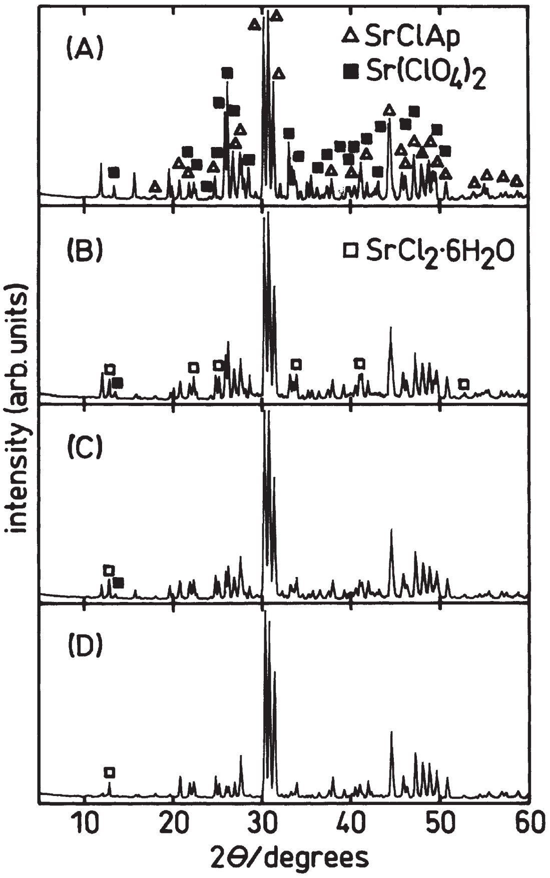

Figure 10. XRD patterns of SrHAp previously employed in obtaining the results shown in figure 7 but pretreated for 6 h. (A)–(D) as in figure 8.

4. Conclusions

(1) The thermal stability of SrHAp was improved by its preparation from $Sr(OH)_2$ and H_3PO_4.

(2) The thermally stable SrHAp produced CO and CO_2 non-selectively from the oxidation of methane, in contrast to thermally unstable SrHAp, prepared from $Sr(NO_2)_3$ and $(NH_4)_2HPO_4$ which produced CO selectively. It is suggested that increased concentrations of surface OH groups, as compared to that on thermally unstable SrHAp, contribute to the non-selective oxidation.

(3) In the oxidation of methane with N_2O in the presence of TCM, the conversion of methane and the selectivity to CO increased and decreased, respectively, with

increasing time-on-stream as observed in the oxidation with O_2. However, the increase of the selectivity to CO with time-on-stream was strongly influenced by the Sr/P ratio of the catalyst.

(4) $SrCl_2$, $Sr(ClO_4)_2$ and strontium chlorapatite, whose formation from TCM is dependent upon the Sr/P ratio, contribute to the oxidation in the presence of TCM.

Acknowledgement

This work was partially funded by the Natural Sciences and Engineering Research Council of Canada to JBM, to which our thanks are due.

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