

The oxidation of ethane in the presence and absence of tetrachloromethane on calcium hydroxyapatites with incorporated lead

Shigeru Sugiyama ^{a,*}, Keiichi Abe ^a, Takashi Miyamoto ^a, Hiromu Hayashi ^a,
John B. Moffat ^b

^a Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima, Tokushima 770, Japan

^b Department of Chemistry and the Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

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Abstract

The oxidative dehydrogenation of ethane has been investigated on various lead-added calcium hydroxyapatites and the effect of the addition of tetrachloromethane (TCM) into the feedstream has been examined. The catalysts are stable up to 873 K but are converted to the corresponding phosphates at approximately 973 K. The conversions of ethane and the selectivities to C₁ and C₂ compounds were found to be dependent on the lead contents of the catalysts, both the pretreatment and reaction temperatures, the presence of TCM and the times-on-stream as well as the structural forms of the catalysts. In the absence of TCM the conversion of ethane and the various selectivities show a dependence on the lead content of the catalysts which is similar at 773 and 873 K, but dissimilar at 973 K due, at least in part to the formation of the phosphates at the latter temperature. With TCM in the process feedstream the influence of the chlorapatites which are formed overrides that of the added lead. © 1998 Elsevier Science B.V.

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1. Introduction

The oxidative dehydrogenation of ethane to ethylene is a process of both fundamental and practical importance [1]. Studies of this reaction provide valuable comparative information in relation to the conversion of methane as well as data which may be useful in optimizing the process under industrial conditions. Earlier work

from our laboratories has shown that the addition of small quantities (< 1 mol%) of tetrachloromethane (TCM) to the methane oxidative coupling feedstream has advantageous effects, with a variety of catalysts, in increasing the conversion of methane and/or the selectivity to C₂ hydrocarbons, particularly ethylene [2]. The oxidative dehydrogenation of ethane has also been investigated in our laboratories with several catalysts both with and without TCM [3–9]. With 12-molybdophosphoric acid supported on silica the conversion of ethane is increased upon

* Corresponding author. Tel.: +81-886-567432; fax: +81-886-557025; e-mail: sugiyama@chem.tokushima-u.ac.jp

the addition of TCM while the selectivity to ethylene is relatively unaltered [3,4]. In the oxidation of ethane on magnesium salts the effects produced by the addition of TCM on the conversion and selectivity appear to be dependent on the nature and composition of the anion and evidence for the formation of magnesium chloride has been found [5–7]. Although the introduction of TCM produced no significant changes with rare earth oxides such as La_2O_3 , Sm_2O_3 and Pr_6O_{11} the conversion of ethane and the selectivity to ethylene on CeO_2 were significantly increased and the corresponding oxychloride forms on each of the four oxides [8,9].

Calcium hydroxyapatites are bifunctional catalysts with acidic and basic properties depending on their compositions ($\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$, $0 \leq x \leq 1$) [10–15]. The hydroxyapatites retain their structure during exchange of calcium by lead [16,17] although the size of the unit cell increases [18,19]. On stoichiometric ($x = 0$) and nonstoichiometric ($0 < x \leq 1$) calcium hydroxyapatites methane is predominantly converted to carbon oxides [20–24]. On the same solids the selectivity to carbon monoxide, but not to C_2 compounds, was increased upon addition of TCM to the methane conversion feedstream [22–24]. The addition of lead to calcium hydroxyapatite, either by ion exchange or in the preparation process, transforms the catalyst into one which produces a high conversion of methane and high selectivities to C_2 compounds [25–27]. Both the lead content of the catalysts and their pretreatment temperatures have been shown to be important variables in the process [28]. Particularly important in this context is the ability of the aforementioned hydroxyapatites to retain the lead during the coupling process with methane [25–27] in contrast with other highly active catalysts which have been reported to suffer depletion of lead during the methane oxidation process [29–38].

With strontium hydroxyapatite high selectivities to carbon monoxide are produced either with or without TCM [39–41] while with ion-

exchanged lead selectivities to methyl chloride of 70% or higher were obtained from methane in the presence of TCM [42,43].

To provide comparative information the present study investigates the effect of the introduction of TCM and both pretreatment and reaction temperatures on the oxidation of ethane on calcium hydroxyapatites with and without incorporated lead. In addition to the usual characterization methods, X-ray diffraction and X-ray photoelectron spectroscopic analyses are applied to both new and used catalysts to provide further information on the role of TCM in the oxidation process.

2. Experimental

Calcium and lead–calcium hydroxyapatites were prepared from $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Wako Pure Chemicals, Osaka), $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (Wako) and $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (Wako) according to the procedure reported by Bigi et al. [19]. An aqueous solution of lead and calcium acetates was added dropwise with stirring to an aqueous solution of sodium monohydrogen phosphate held at 353 K. The resulting two phase system, after storing overnight, was filtered and the solid was washed with distilled water. The resulting solids were dried in air at 373 K overnight followed by calcination at 773 K for 3 h (denoted as ‘fresh catalyst’). All catalysts were sieved to the particle sizes of 1.70–0.85 mm. The concentrations of Ca, Pb and P in each catalyst were measured in an aqueous HNO_3 solution with inductively coupled plasma (ICP) spectrometry (SPS-1700, Seiko). The calcium and lead–calcium hydroxyapatites are denoted as HAp and Pb_{xx}HAp , respectively, with xx equal to $100\text{Pb}/(\text{Pb} + \text{Ca})$ (atomic ratio). The BET surface areas, measured with a conventional nitrogen adsorption apparatus (Shibata P-700), apparent densities and the atomic ratios of Ca/P and Pb/P are summarized in Table 1. A portion of each catalyst preparation was further calcined at 873 or 973

Table 1
Surface areas, apparent densities and composition of fresh catalysts

	Catalyst					
	HAp	Pb0.85HAp	Pb5.7HAp	Pb12HAp	Pb20HAp	Pb35HAp
Area ^a	72.8	69.1	74.7	65.6	51.0	51.5
Density ^b	0.37	0.30	0.33	0.36	0.40	0.59
Ca/P ^c	1.65	1.76	1.58	1.66	1.36	0.98
Pb/P ^c	0	0.02	0.10	0.23	0.34	0.53

^aBET surface area (m²/g).

^bApparent density (g/cm³).

^cAtomic ratio.

K for 8 h in order to investigate the thermal stability.

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 [22]. Prior to reaction the catalyst was calcined in situ in an oxygen flow (12.5 ml/min) at a given temperature for 1 h. Except as noted reaction conditions were: $W = 0.5$ g, $F = 15$ ml/min, $T = 973$, 873 or 773 K, $P(\text{C}_2\text{H}_6) = 27.1$ kPa, $P(\text{O}_2) = 6.7$ kPa and $P(\text{TCM}) = 0$ or 0.17 kPa; balance to atmospheric pressure was provided by helium.

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 [5,8].

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X diffractometer, using monochromatized Cu-K α radiation. Patterns were recorded over the range $2\theta = 5\text{--}60^\circ$. X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-1000AX) used monochromatized Mg K α 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 SiO₂. The concentrations of Cl were mea-

sured in an aqueous HNO₃ solution with ion-chromatography (Shimadzu PIA-1000).

3. Results and discussion

3.1. Properties of catalysts

XRD patterns of HAp, Pb0.85HAp and Pb5.7HAp after calcination at 873 K for 3 h in air are essentially identical and in agreement with reference patterns Ca₁₀(PO₄)₆(OH)₂ (JCPDS 9-0432), although those of the remaining three lead-containing catalysts are dissimilar to those of either calcium hydroxyapatite or lead hydroxyapatite (Pb₁₀(PO₄)₆(OH)₂, JCPDS 8-0259) (Fig. 1). Although reference XRD data are not available for the hydroxyapatites containing lead, since the strongest XRD peak of the remaining three catalysts shifted to lower diffraction angles with increasing lead content, an observation previously reported by Bigi et al. for various Pb–HAp [18,19], Pb12HAp, Pb20HAp and Pb35HAp evidently also possess the crystallographic structures of the corresponding hydroxyapatites. XRD patterns of fresh catalysts were similar to those calcined at 873 K (not shown) [28]. On calcining at 973 K, all the catalysts were converted to the corresponding phosphates (not shown). Although calcium hydroxyapatite is believed to be stable up to 1273 K [44] the HAp prepared in the present work is converted to Ca₃(PO₄)₂ at 973 K. Since calcium hydroxyapatites employed in our previous

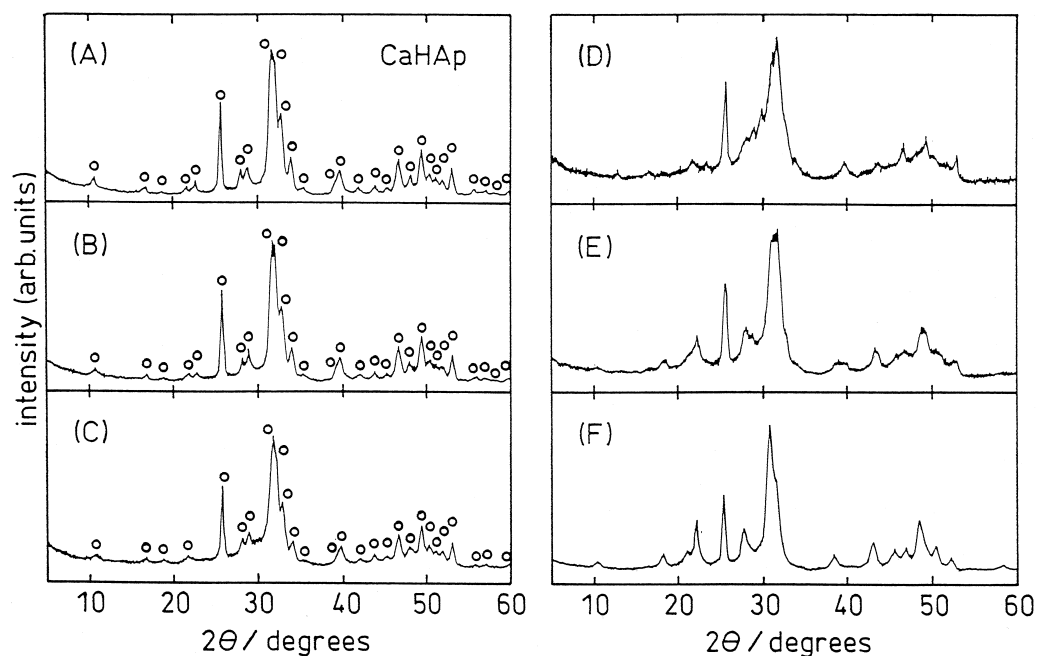


Fig. 1. XRD patterns of HAp and PbHAp calcined with the fresh samples at 873 K for 3 h in air. (A) HAp, (B) Pb0.85HAp, (C) Pb5.7HAp, (D) Pb12HAp, (E) Pb20HAp and (F) Pb35HAp. 'CaHAp' refers to calcium hydroxyapatite.

study, prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$, were stable at 1048 K [22–24], the temperature at which the conversion of the

hydroxyapatite to the corresponding phosphate occurs appears to be strongly influenced by the preparative reagents.

Table 2
XPS analyses of fresh catalysts

	Catalyst						
	T ^a	HAp	Pb0.58HAp	Pb5.7HAp	Pb12HAp	Pb20HAp	Pb35HAp
Ca2p _{1/2} ^b	0	350.8	351.0	350.3	350.0	350.8	351.0
	1	351.4	351.3	350.7	350.5	351.8	351.3
O 1s ^b	0	531.3	531.3	530.8	530.8	531.2	531.3
	1	531.9	531.7	531.4	531.0	532.4	531.8
P 2p ^b	0	133.2	133.2	132.8	132.6	133.0	133.4
	1	134.2	133.8	133.2	133.1	133.9	133.7
Pb 4f _{5/2} ^b	0		143.9	143.3	143.2	143.6	143.8
	1		144.1	143.5	143.2	144.2 (142.3) ^c	143.8 (141.6) ^c
Ca/P ^d	0	1.15	1.15	1.08	0.96	1.01	1.00
	1	1.24	1.31	1.47	1.73	1.86	1.70
Pb/P ^d	0		0.01	0.08	0.19	0.37	0.65
	1		0.004	0.03	0.10	0.23	0.51
O/P ^d	0	2.90	2.81	3.09	2.65	2.88	3.68
	1	2.90	3.03	3.69	4.06	4.30	5.04
Pb ⁰ /Pb ²⁺ ^d	1			—		0.30	0.31

^a Etching time (min).

^b Binding energy (eV).

^c Binding energy due to metal Pb.

^d Atomic ratio.

The surface analyses by XPS of the fresh catalysts show no significant differences in the binding energies of Ca 2p_{1/2}, O 1s, P 2p and Pb 4f_{5/2} either before or after argon-ion etching (Table 2). No significant shoulders were observed in the spectra except those of Pd 4f_{5/2} due to the formation of Pb⁰ on Pb20HAp and Pb35HAp after the etching. The atomic ratios of Ca/P on the surface of the catalysts (etching time = 0) were, except for Pb35HAp, smaller than those in the bulk phase (Table 1) but increased with argon-ion etching while those of Pb/P on the surface were essentially identical to those in the bulk phase and decreased with etching. The atomic ratios of O/P on the surface also increased with etching. Since the effects of etching were more pronounced on the catalysts with higher lead contents the introduction of lead apparently resulted in changes in the mobility of the cations, oxygen and electrons as well as the composition.

3.2. Effects of the transformation of hydroxyapatites to the corresponding phosphates on the oxidation of ethane

For studies of the oxidation of ethane, the pretreatment and reaction temperatures were held at 773 K to eliminate conversion of the hydroxyapatites to the corresponding phosphates and to minimize the contribution of gas-phase processes (Table 3) [5,6]. Under these conditions the conversion of methane and the selectivity to ethylene in the absence of TCM increased with increasing lead content of the catalysts while with the highest lead content the selectivity to ethylene decreased (Fig. 2A). The conversion of oxygen passed through a minimum with lead content, indicating that the formation of hydrogen proceeds most favourably on Pb12HAp while that of H₂O more readily takes place on HAp or Pb35HAp. Therefore the reactivities of both the ethyl radicals and hydrogen atoms formed in the scission of ethane are apparently dependent upon the lead content while the latter is also influenced by the catalyst

Table 3

The oxidation of ethane in the empty reactor in the presence and absence of TCM

Temp. ^a	TCM ^b	Conv. (%)		Selectivity (%)				
		C ₂ H ₆	O ₂	CO	CO ₂	CH ₄	C ₂ H ₄	others
763	A	1.5	2	—	69.4	29.0	1.6	—
	P	0.5	17	—	—	0.5	99.4	—
773	A	0.6	6	—	83.3	15.1	1.5	—
	P	1.4	33	2.1	—	1.5	96.3	—
803	A	21	86	22.2	3.1	12.3	60.0	2.5
	P	14	86	9.3	—	4.5	81.8	4.4
823	A	21	88	18.4	—	12.5	61.1	8.0
	P	13	82	10.2	—	13.0	63.6	13.2
843	A	28	97	25.4	2.5	16.3	51.4	4.4
	P	37	96	27.7	1.1	17.8	47.1	6.4
898	A	40	96	23.7	2.9	16.9	53.4	3.2
	P	44	89	25.0	0.4	19.8	49.7	5.2
998	A	67	94	12.1	0.4	17.0	61.2	9.4
	P	64	92	20.9	1.1	18.0	58.4	1.6

The composition and flow rate of the reactant gas same as those described in Section 2.

^aReaction temperature (K).

^bA: absence of TCM, P: presence of TCM.

stoichiometry. With TCM in the feedstream, neither the conversions nor the selectivities showed significant variation with lead content. However the conversions of ethane and oxygen as well as the selectivity to CO₂ decreased with time-on-stream with all catalysts while the selectivity to ethylene increased. The XRD patterns of HAp, Pb0.85HAp and Pb5.7HAp previously employed in the oxidation in the presence of TCM were similar to those of calcium chlorapatite (Ca₁₀(PO₄)₆Cl₂; JCPDS 33-0271) (Fig. 3A–C). Since the XRD patterns of the remaining three catalysts (Fig. 3D–F) were dissimilar to those of the fresh catalyst or those calcined at 873 K (Fig. 1D–F) while the atomic ratios of Cl/P in the bulk phase of all samples were similar (Cl/P = 0.21, 0.22, 0.23, 0.25, 0.31 and 0.25 for HAp, Pb0.85HAp, Pb5.7HAp, Pb12HAp, Pb20HAp and Pb35HAp, respectively) and approximately equal to the theoretical value (0.33), the three catalysts with the highest lead contents are apparently also converted to the corresponding chlorapatites during the oxidation with TCM. The surface regions of the samples previously employed in the oxida-

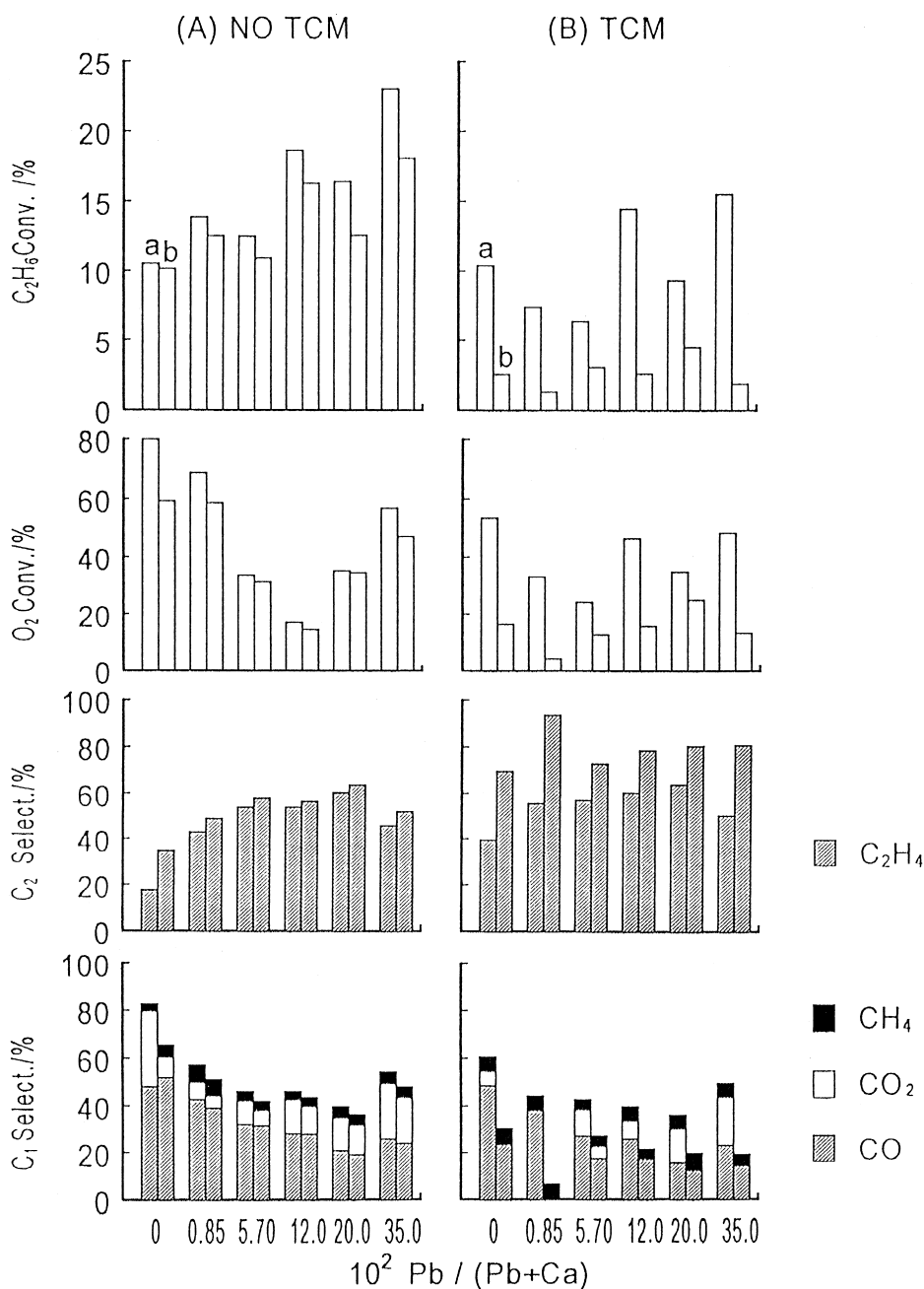


Fig. 2. Ethane oxidation on HAP and PbHAp pretreated at 773 K in the presence and absence of TCM at 773 K. Conditions: $W = 0.5$ g, $F = 15$ ml/min, $P(\text{C}_2\text{H}_6) = 27.1$ kPa, $P(\text{O}_2) = 6.7$ kPa and $P(\text{TCM}) = 0.17$ kPa (when present) diluted with He. Symbols: (a) 0.5 h on-stream and (b) 6 h on-stream.

tion in the presence of TCM were identical with those of the corresponding fresh catalysts from XPS analyses except for the existence of a peak due to Cl 2p at approximately 199 eV with all

samples and that of a peak due to metallic Pb on Pb5.7HAp and Pb12HAp (Table 4). Since the surface atomic ratios of Cl/P increase with increasing lead content and attain values ex-

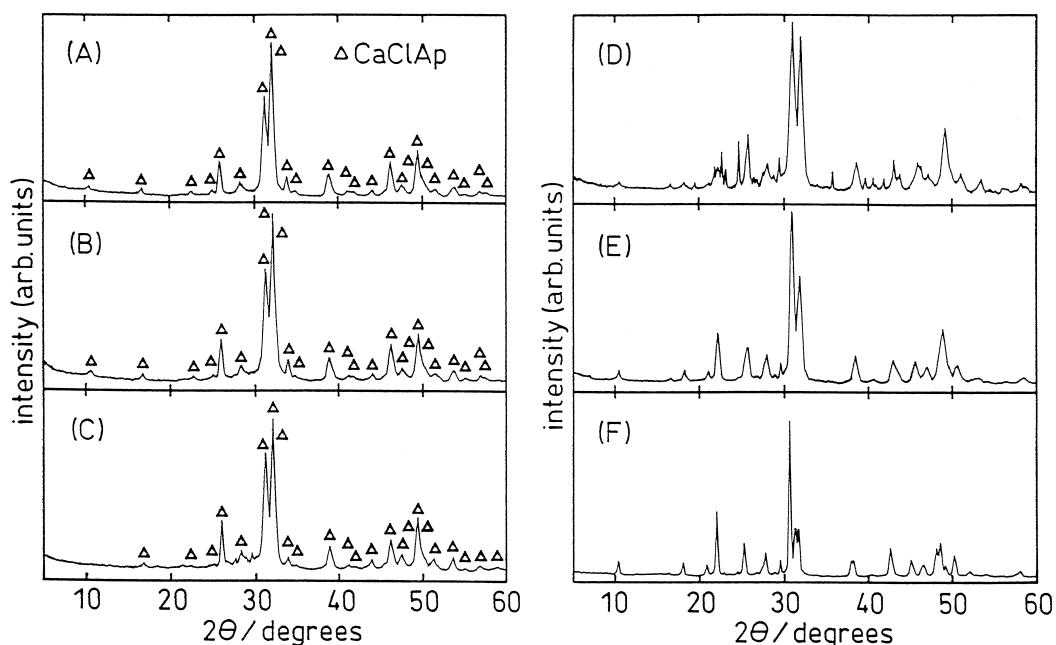


Fig. 3. XRD patterns of catalysts previously employed in obtaining the results shown in Fig. 2(B) but after 6 h on-stream. Symbols: same as those in Fig. 1. 'CaClAp' refers to calcium chlorapatite.

pected from the stoichiometry, chlorapatites probably also form on the surface. Since the reaction observables were not influenced by the lead contents in the presence of TCM, in contrast to those in the absence of TCM, the effects produced by TCM appear to be dominant.

Since the hydroxyapatite structure is retained at 773 K while the corresponding phosphates are formed at 973 K, the oxidation of ethane on the catalysts pretreated at 773 K was compared with that at 973 K and at a reaction temperature of 773 K (Fig. 4, cf. Fig. 2). The conversion of

Table 4

Atomic ratios of $\text{Pb}^0/\text{Pb}^{2+}$ and Cl/P in the near-surface region of catalysts previously employed in the oxidation in the presence of TCM

Catalyst	Time ^a	Reaction temp. (K), pretreatment temp. (K)							
		$\text{Pb}^0/\text{Pb}^{2+}$				Cl/P			
		773, 773	773, 973	873, 873	973, 973	773, 773	773, 973	873, 873	973, 973
HAp	0	—	—	—	—	0.14	0.02	0.20	0.06
	1	—	—	—	—	0.14	0.03	0.14	0.07
Pb0.85HAp	0	—	—	—	—	0.15	—	0.10	—
	1	—	—	—	—	0.13	—	0.07	—
Pb5.7HAp	0	—	—	—	—	0.17	0.08	0.35	0.06
	1	0.11	—	—	0.10	0.22	0.16	0.34	0.07
Pb12HAp	0	—	—	—	—	0.25	0.14	0.10	0.07
	1	0.21	0.17	0.11	0.12	0.28	0.16	0.14	0.08
Pb20HAp	0	—	—	—	—	0.46	—	0.35	—
	1	0.22	0.21	0.25	0.11	0.42	—	0.38	—
Pb35HAp	0	—	—	—	—	0.39	—	0.23	—
	1	0.22	0.25	0.25	0.14	0.43	—	0.28	—

^a Etching time (min).

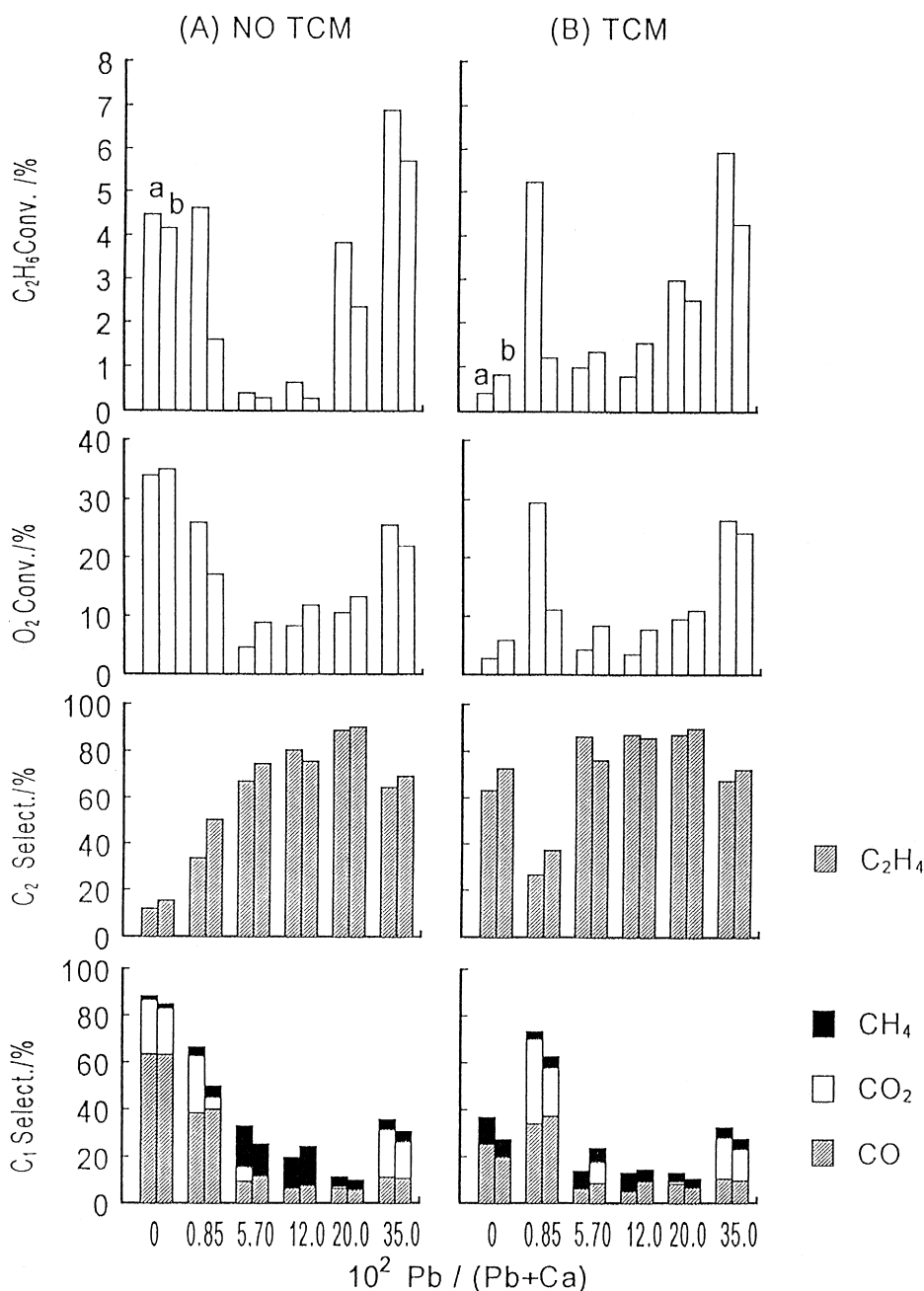


Fig. 4. Ethane oxidation on HAp and PbHAp pretreated at 973 K in the presence and absence of TCM at 773 K. Conditions and symbols: same as those in Fig. 2.

ethane in the absence of TCM passed through a minimum for the 5.7 and 12.0 catalysts (Fig. 4A) pretreated at 973 K and had maximum values for the 35.0 sample which were, however, approximately one-third of those for the

same catalyst pretreated at 773 K (Fig. 2A), suggesting that hydrogen abstraction from ethane on the hydroxyapatite is more facile than that on the corresponding phosphates. Similar results have recently been reported for the oxi-

duction of methane [24]. Although the selectivities to C_1 and C_2 compounds on the catalysts pretreated at 973 K were dependent upon the content of lead as observed on the catalysts pretreated at 773 K, the selectivities to ethylene were considerably higher with the former pretreatment temperature, reaching values as high as 90% with Pb20HAp. In the presence of TCM in the feedstream (Fig. 4B), the conversion of ethane and selectivity to ethylene decreased and increased substantially, respectively, on HAp while the catalysts containing lead did not display the TCM effects observed on the catalysts pretreated at 773 K. The XRD patterns of the catalysts after use in the oxidation process with TCM (Fig. 5) were significantly different from those of the fresh catalysts and the corresponding chlorapatites. Since the XRD of the used HAp, Pb0.85 HAp and Pb5.7HAp were similar to that of calcium phosphate (JCPDS 9-0169) it may be deduced that the XRD patterns of the catalysts with higher lead contents also correspond to those for the phosphates. The chlorine species in the near-surface region were detected

on HAp, Pb5.7HAp and Pb12HAp by XPS although the amounts were relatively small compared with those on the catalysts pretreated at 773 K (Table 4), while no chlorine species were detected on those with higher lead contents. It has been reported that the conversion of ethane and the selectivity to ethylene decreased and increased, respectively, on magnesium phosphate at 773 K on the addition of TCM and a small amount of chlorine species, apparently magnesium chloride, was detected on the surface [5]. Consequently the effects produced by TCM on HAp, which at 973 K has been converted to calcium phosphate, correspond to those observed with magnesium phosphate. Evidently the surface-retentive interaction with TCM is constrained on the phosphates and particularly those containing relatively large quantities of lead and thus the beneficial effects on the oxidation process of the addition of chlorine are minimized. Although evidence for the formation of chlorapatite was obtained with Pb12HAp, recent work has shown that the phosphates are converted to the corresponding chlorapatites in

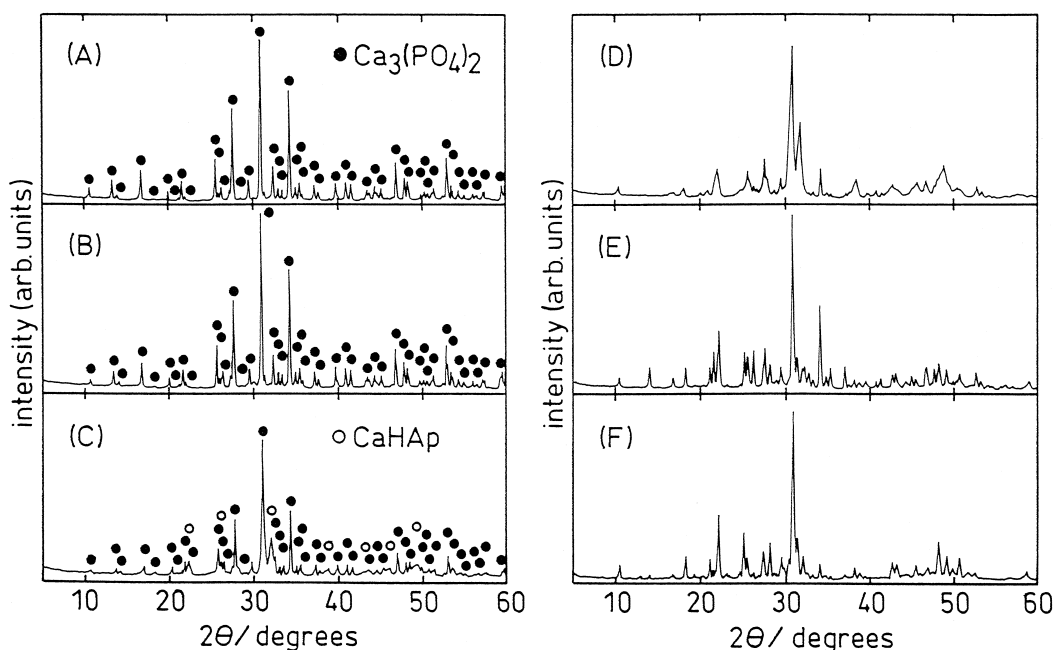


Fig. 5. XRD patterns of catalysts previously employed in obtaining the results shown in Fig. 4(B) but after 6 h on-stream. Symbols: same as those in Fig. 1.

the presence of TCM [24] and thus the chlorine species on Pb5.7HAp and Pb12HAp cannot be classified as constituents of any particular compound. Although some reduction of Pb^{2+} to its

metallic form has apparently occurred during the oxidation process it is not clear at this time if a direct coupling to form a redox process is extant (Table 4). It should be noted that the

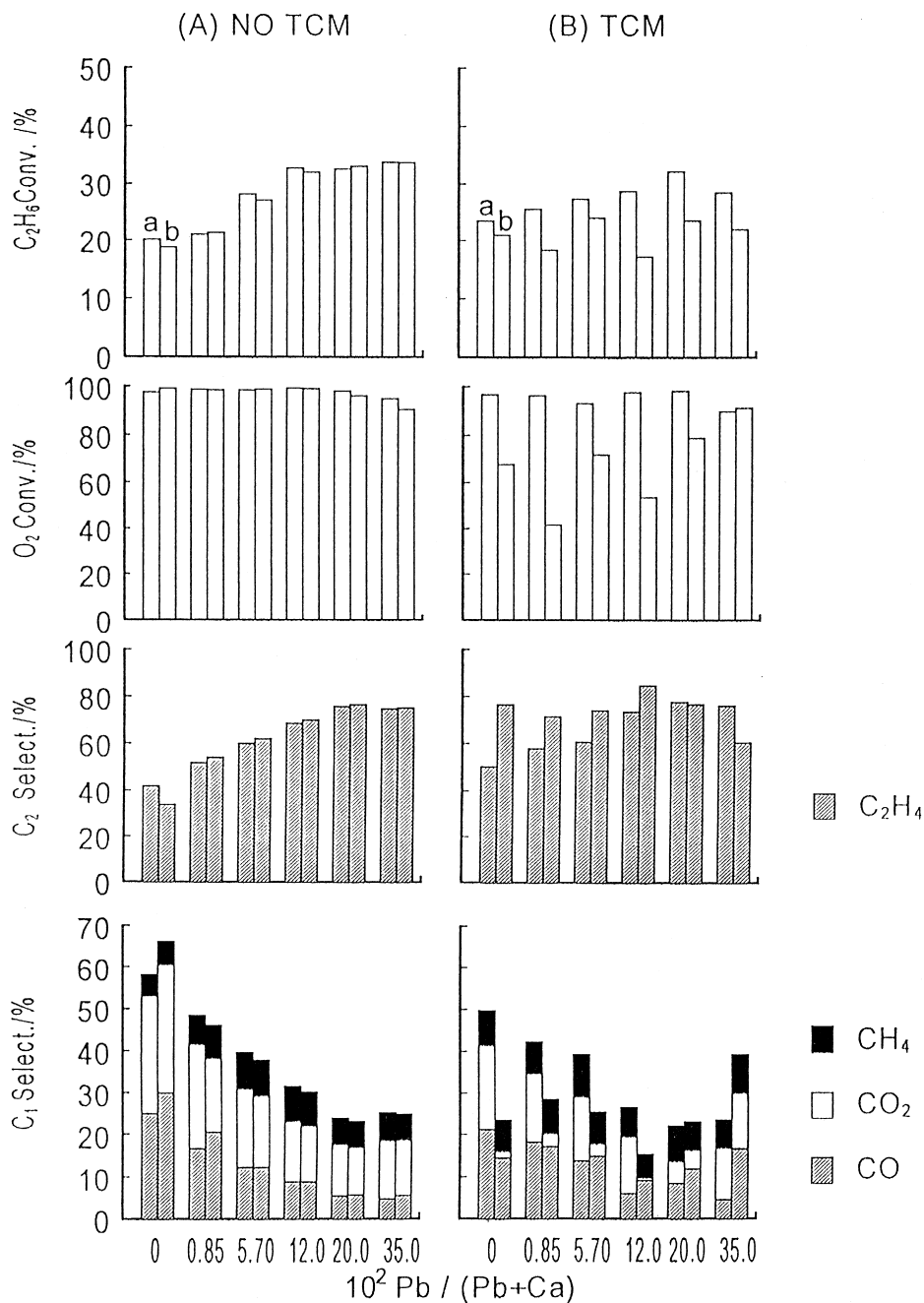


Fig. 6. Ethane oxidation on HAp and PbHAp pretreated at 873 K in the presence and absence of TCM at 873 K. Conditions and symbols: same as those in Fig. 2.

concentration of lead remained relatively unchanged following the oxidation process, in contrast to the depletion of lead frequently observed with other lead-containing catalysts during the methane oxidation process [29–38]. Thermal and structural properties of the present catalysts have been reported previously [28].

3.3. The homogeneous reaction and formation of phosphates

At 873 K the catalysts are relatively stable and retain the apatite structure. Although the homogeneous and heterogeneous reactions may not be additive the former is not dominant at 873 K (Table 3). At 873 K the conversion of ethane and the selectivity to ethylene without TCM increase with the lead content with CO , CO_2 and CH_4 appearing in the product stream, similar to the observations at 773 K. In contrast, with TCM present little or no dependence of either the conversion or C_2 selectivity on the composition of the catalyst was evident, al-

though significance decreases of the former were observed with time-on-stream again similar to the results at 773 K. With the catalysts containing the smaller concentrations of lead the selectivities to ethylene and CO_2 increased and decreased, respectively, with time-on-stream while with the Pb20HAp and Pb35HAp catalysts the selectivity to ethylene decreased, in contrast to the observations at 773 K. The XRD patterns of the used (with TCM) catalysts, with the exception of Pb0.85HAp provided evidence for the presence of phosphates as well as chlorapatite (Fig. 7, cf. Fig. 3). No correlation, with either the lead contents or temperature, of the surface concentrations of chlorine after use of the catalysts at 873 K is evident (Table 4).

At 973 K, at which temperature the catalysts are converted to the corresponding phosphates and the contribution of the homogeneous reaction is expected to be significant (Table 3), the conversion of ethane decreased on addition of lead to HAp but remained relatively unchanged for further increases in the lead content, while

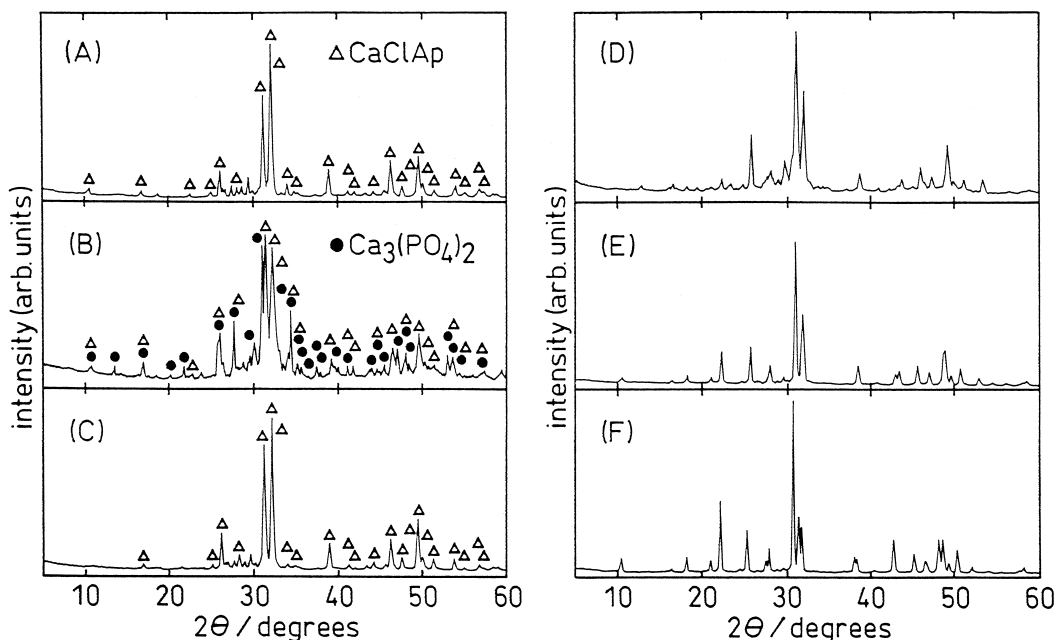


Fig. 7. XRD patterns of catalysts previously employed in obtaining the results shown in Fig. 6(B) but after 6 h on-stream. Symbols: same as those in Figs. 1 and 3.

the selectivity to ethylene increased, suggesting that the advantageous effects of lead remain extant at the higher temperature (Fig. 8). The aforementioned trends were also observed in the

presence of TCM. The catalysts with the smaller concentrations of lead showed evidence of larger proportions of chlorapatites than observed at the lower temperatures while those with higher lead

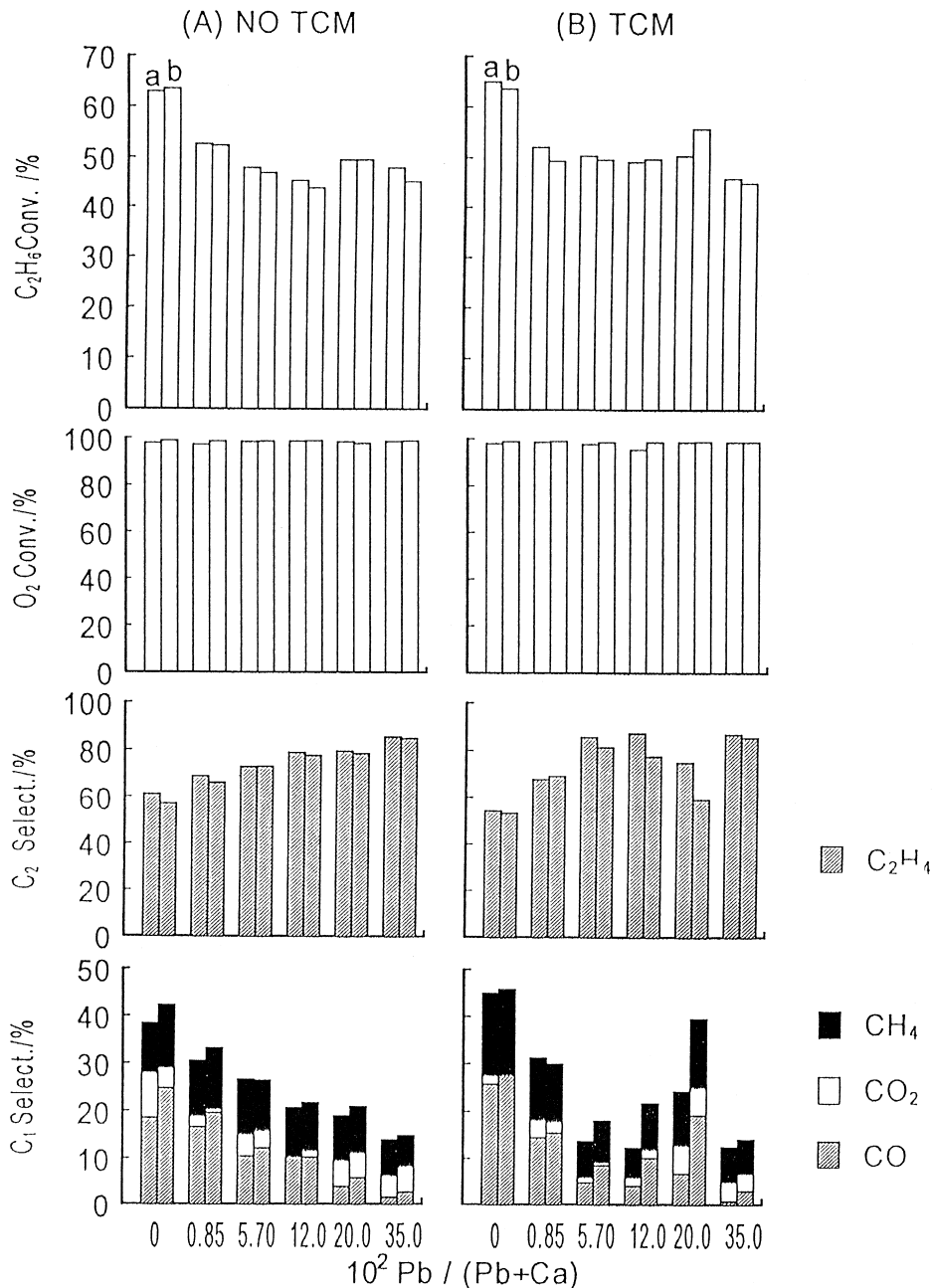


Fig. 8. Ethane oxidation of HAp and PbHAp pretreated at 973 K in the presence and absence of TCM at 973 K. Conditions and symbols: same as those in Fig. 2.

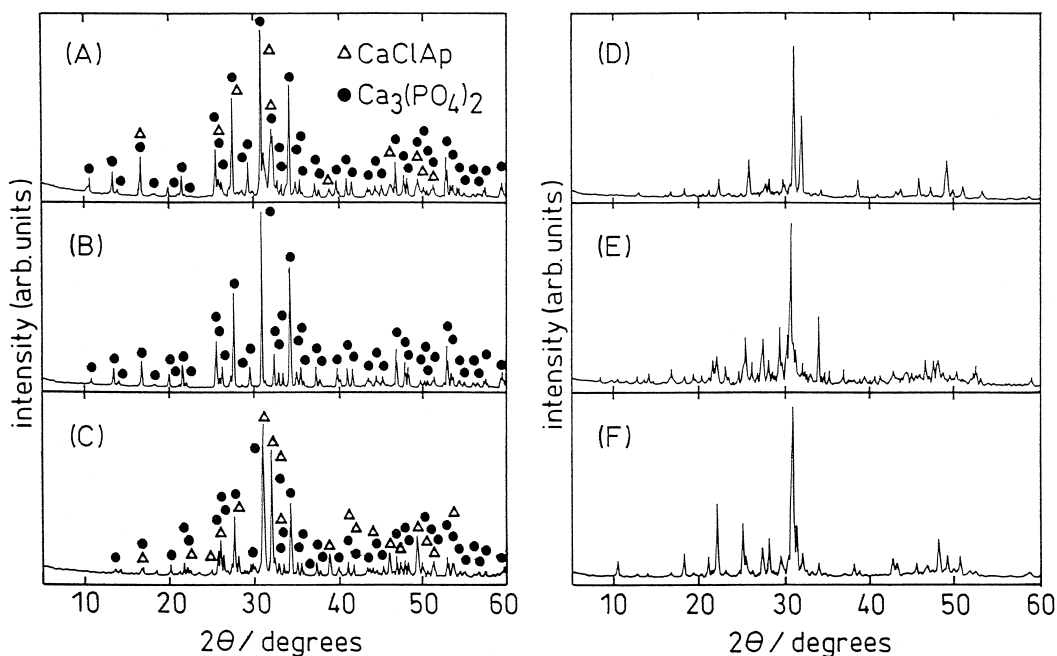


Fig. 9. XRD patterns of catalysts previously employed in obtaining the results shown in Fig. 8(B) but after 6 h on-stream. Symbols: same as those in Figs. 1 and 3.

contents were structurally identical to phosphate (Fig. 9). As observed at a reaction temperature of 773 K and at a pretreatment temperature of 973 K surface chlorine was identified only on those samples containing the smaller concentrations of lead, in semiquantitative agreement with the results from XRD. Previous work has shown that significant quantities of chlorine appear on the surface of Pb_{0.85} HAp pretreated at 973 K during the oxidation of methane in the presence of TCM at 973 K [28], in contrast with the present results (Fig. 10). Since differences in the quantities of H₂O produced in the oxidation of methane and ethane would be expected the aforementioned chlorine-containing catalyst was exposed to H₂O (2.3 kPa) at 973 K for 2h. The XRD patterns show that the chlorapatite is converted to the corresponding phosphate, apparently resulting from its exposure to water vapour. The role of water is, however, ambiguous. Water molecules may be reducing the ability of the catalyst surface to accept the chlorine or alternatively the interaction with water may be strip-

ping the chlorine from the surface and thereby reducing its measured concentrations.

3.4. Role of lead in the hydroxyapatites

The dependence of the conversion of ethane and the various selectivities on the lead content, particularly in the absence of TCM, was semiquantitatively similar at 773 and 873 K (Figs. 2 and 6, respectively). At these reaction and pretreatment temperatures the catalysts are relatively stable and retain the apatite structure [28]. Since the Pb–O bond lengths in the present catalysts change monotonously with increasing lead content [28], the effect of the addition of lead may tentatively be attributed to a perturbation of the probable active site in the process. At the highest reaction and pretreatment temperature (973 K) and in the absence of TCM the hydroxyapatites have been converted to the corresponding phosphates whose catalytic properties (Figs. 4 and 8) are evidently altered dissimilarly from those of their precursor by the addi-

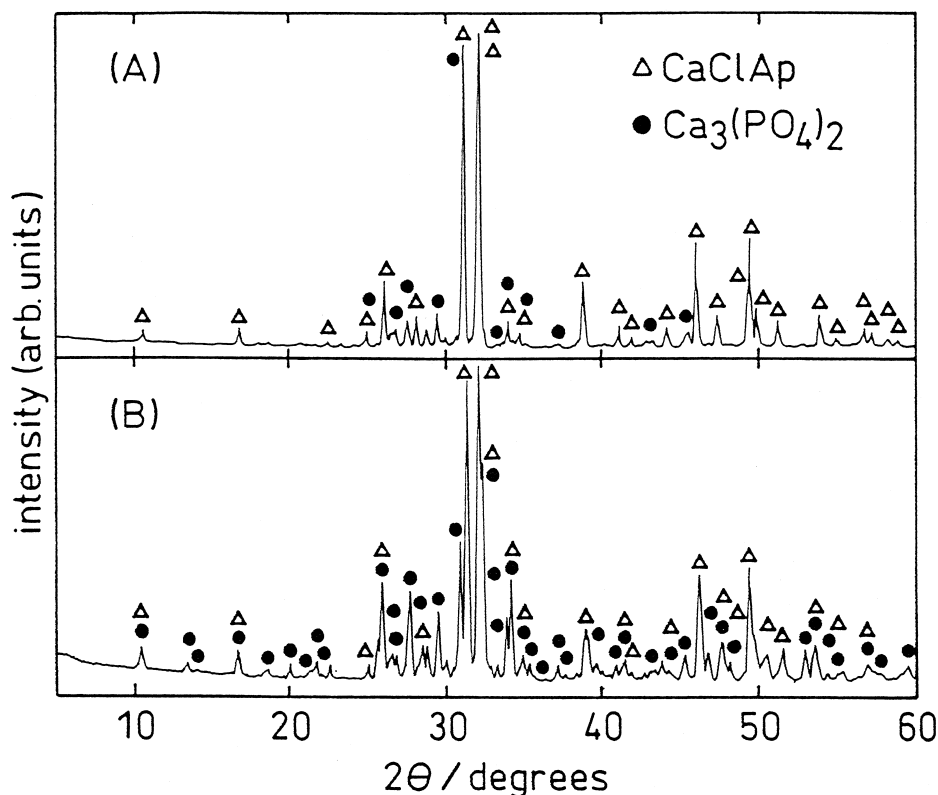


Fig. 10. XRD pattern of Pb_{0.85}HAp employed in the oxidation of methane in the presence of TCM at 973 K (A) [43] and those after calcination at 973 K for 2 h of the above Pb_{0.85}HAp with H₂O (2.3 kPa) diluted with air (B). Symbols: same as those in Fig. 3.

tion of lead (Figs. 2 and 6). In the presence of TCM, the properties of either of the aforementioned catalysts are strongly influenced by the formation of chlorapatites.

4. Conclusion

(1) The conversion of ethane in the absence of TCM at 773 K on HAp and various PbHAp pretreated at 773 K increased with increasing lead contents in the catalysts.

(2) On catalysts pretreated at 973 K the conversions at 773 K were smaller than the aforementioned and passed through a minimum at intermediate lead contents apparently due to the formation of the corresponding phosphates at the higher pretreatment temperature.

(3) The selectivities to C₂ compounds at 773 K and either pretreatment temperature increased with increasing lead content.

(4) The addition of TCM to the feedstream at 773 K resulted in increases of the conversion of ethane and the selectivity to ethylene together with decreases of the selectivity to CO₂ on the catalysts pretreated at 773 K due to the formation of the corresponding chlorapatites.

(5) With the catalysts pretreated at 973 K, the conversion of ethane and the selectivity to ethylene on HAp at 773 K were substantially suppressed and enhanced, respectively, on addition of TCM, probably due to the formation of calcium chloride.

(6) On lead-containing catalysts pretreated at 993 K the effect of TCM at 773 K was minimal and the incorporation of chlorine was found to

be strongly dependent on the catalyst compositions.

(7) At 873 K in the absence of TCM the reaction observables were dependent on the lead content of the catalysts. On addition of TCM the conversion of ethane decreased while evidence for the intrusion of homogeneous reactions was evident.

(8) At 973 K at which the catalysts were converted to the phosphates, the conversions of ethane in the absence of TCM showed little or dependence on lead content while, in contrast, the selectivities were markedly influenced by the composition of the catalyst. Since at this temperature the homogeneous reaction contributes significantly, the lead content appears to have considerable influence on the pathway followed by the ethyl radicals. This appears to be consistent with earlier hypothesis in which the ethyl radicals were postulated to be stabilized in ensembles on the surfaces of the catalysts.

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