

Oxidation of methane with nitrous oxide on calcium hydroxyapatites in the presence and absence of tetrachloromethane

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Abstract

The reactions of N₂O and CH₄ have been studied on calcium hydroxyapatite with various stoichiometries at 973 and 1023 K, partial pressures of CH₄, 28.7 kPa and of N₂O, 4.1 and 12.3 kPa, 30 ml min⁻¹ and catalyst masses of 0.25, 0.5 and 0.75 g. On CaHAp with Ca/P from 1.59 to 1.72 the conversion of N₂O was 80 ± 5% while that of CH₄ was 4 ± 1%, regardless of Ca/P. The introduction of tetrachloromethane (TCM), with partial pressures: 0.085, 0.17 and 0.34 kPa, to the feedstream resulted in decreases in the conversions of both N₂O and CH₄ and increases in the selectivities to C₂ hydrocarbons and CO, apparently due to the formation of chlorapatite and/or nonstructural chlorine species in the catalysts. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interest in developing new techniques for the decomposition and/or reduction of nitrogen oxides by application of heterogeneous catalysts continues unabated [1]. Not surprisingly much of the work has centered on nitrogen monoxide/dioxide with the use of hydrocarbons as reductants as a recurrent theme. Less attention has been paid to nitrous oxide as an ozone

depleter and a greenhouse gas [2] although relatively large quantities of this oxide are produced in combustion, the production of adipic and nitric acids, as well as fertilizers, and in mobile and stationary NO_x reduction processes [3–7]. Much of the published reports on the removal of nitrous oxide are concerned with its catalyzed decomposition in contrast to the reduction emphasized with NO_x [6–9].

Methane has frequently been advocated, for practical purposes, as an appropriate reductant for NO_x, particularly in view of its convenience in comparison with ammonia [10]. It is therefore

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of interest to examine the application of CH_4 to the reduction of N_2O . The partial oxidation of methane has been studied in a number of laboratories [11]. What appears to be the earliest work employed silica-supported molybdenum oxide [12] and vanadium oxide [13] with N_2O as the oxidant to convert methane to methanol and formaldehyde at 733–853 K. Nitrous oxide has also been utilized in the oxidative coupling of methane on rare earth oxides [14,15] and on magnesia-based catalysts [16–18] at temperatures lower than 870 K. O^- ions produced from the decomposition of N_2O have been proposed as the active species [15,16,19]. Work in our laboratories has been concerned with the partial oxidation and oxidative coupling of methane with either oxygen or nitrous oxide on a variety of catalysts including heteropolyoxometalates, phosphates, sulfates, oxides and hydroxyapatites of various elemental compositions and stoichiometries [20]. In addition, the effects of the introduction of small partial pressures of tetrachloromethane (TCM) as a gas phase additive in these oxidative processes have been investigated, first on the heteropoly oxometalates in 1988 [21] and more recently on hydroxyapatites [20,22].

The present work employs N_2O as the oxidant for CH_4 with calcium hydroxyapatite of a number of stoichiometries as the catalyst with and without TCM as a feedstream additive. Although previous work has demonstrated that the further oxidation of products from methane is suppressed by the introduction of TCM [20,22], the effect of changes in the stoichiometry of the catalyst, in the present case calcium hydroxyapatite, with N_2O as oxidant and TCM as an additive has not been reported previously.

2. Experimental

2.1. Catalyst preparation

All chemicals were of high purity and were used as supplied. Calcium hydroxyapatites ($\text{CaHAp}_{1.59}$, $\text{CaHAp}_{1.63}$, $\text{CaHAp}_{1.66}$, and

$\text{CaHAp}_{1.72}$, where the subscripts represent the Ca/P atomic ratio of each apatite as determined by ICP) were prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Wako, Osaka) and $(\text{NH}_4)_2\text{HPO}_4$ (Wako) [23–25]. The resulting solid was 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 Ca 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 [22]. Prior to the reaction the catalyst was calcined in situ in an oxygen flow (25 ml min^{-1}) at 973 K for 1 h. The typical reaction conditions were as follows: $W = 0.5 \text{ g}$, $F = 30 \text{ ml min}^{-1}$, $T = 973$ or 1023 K , $P(\text{CH}_4) = 28.7 \text{ kPa}$, $P(\text{N}_2\text{O}) = 4.1$ or 12.3 kPa and $P(\text{TCM}) = 0, 0.085, 0.17$ or 0.34 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 ($6 \text{ m} \times 3 \text{ mm}$), Molecular Sieve 5A ($0.2 \text{ m} \times 3 \text{ mm}$) and Molecular Sieve 13X ($1 \text{ m} \times 3 \text{ mm}$), the latter to separate N_2 and O_2 , were employed. The methane conversion was calculated from the products formed 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 $\text{K}\alpha$ radiation. 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⁻¹ for SiO₂.

3. Results and discussion

3.1. Properties of fresh catalysts

The XRD patterns of fresh CaHAp_{1.59}, CaHAp_{1.63}, CaHAp_{1.66}, and CaHAp_{1.72}, were essentially identical as reported earlier [23–25] and were identified as Ca₁₀(PO₄)₆(OH)₂ [JCPDS 9-0432] (not shown). The BET surface areas, apparent densities and XPS results of the fresh CaHAp are summarized in Table 1. The bulk properties show no correlation with the Ca/P atomic ratios.

3.2. Comparison of methane oxidation with O₂ and N₂O

Fig. 1 shows the results of the oxidation of methane with N₂O (4.1 kPa) on CaHAp (0.5 g) at 973 K in the presence and absence of TCM the conditions of which were essentially identical to those employed with oxygen as the oxidant [23–25]. In the absence of TCM, the conversion and the selectivities were little influenced by the Ca/P ratio (Fig. 1A). In contrast, with O₂ as the oxidant the conversion of

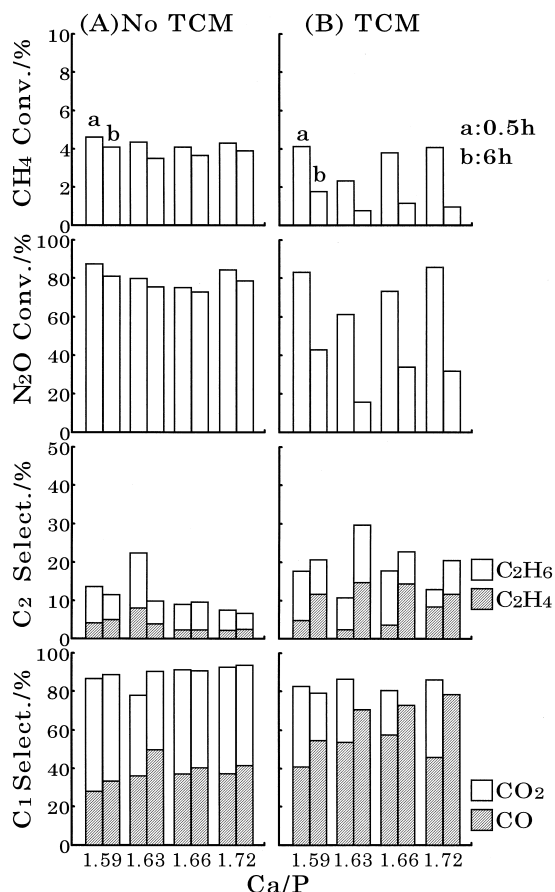


Fig. 1. Methane oxidation with N₂O on CaHAp in the absence (A) and presence (B) of TCM at 973 K. Reaction conditions: $W = 0.5$ g, $P(\text{CH}_4) = 28.7$ kPa, $P(\text{N}_2\text{O}) = 4.1$ kPa and $P(\text{TCM}) = 0.17$ kPa (when present) diluted with He. $F = 30$ ml min⁻¹. Catalysts were pretreated with O₂ (25 ml min⁻¹) at 973 K for 1 h.

methane was approximately twice that observed with N₂O under the same reaction reactions and significantly more dependent on the stoichiom-

Table 1
Surface area, apparent density and XPS results for fresh CaHAp

| Catalyst | SA ^a | AD ^b | Ca 2p _{3/2} | O 1s ^c | P 2p ^c | Ca/P ^d | O/P ^d |
|-----------------------|-----------------|-----------------|----------------------|-------------------|-------------------|-------------------|------------------|
| CaHAp _{1.59} | 62 | 0.57 | 347.4 (347.4) | 531.3 (531.6) | 133.1 (133.5) | 1.31 (1.43) | 2.99 (3.01) |
| CaHAp _{1.63} | 75 | 0.57 | 347.0 (347.2) | 531.2 (531.4) | 132.9 (132.9) | 1.30 (1.38) | 3.07 (2.96) |
| CaHAp _{1.66} | 72 | 0.58 | 347.3 (347.5) | 531.3 (531.5) | 133.2 (133.6) | 1.28 (1.12) | 3.03 (3.00) |
| CaHAp _{1.72} | 61 | 0.63 | 347.1 (346.6) | 531.1 (531.5) | 132.9 (133.4) | 1.27 (1.34) | 2.94 (3.03) |

^aBET surface area (m² g⁻¹).

^bApparent density (g cm⁻³).

^cBinding energy (eV).

^dAtomic ratio.

Values in parentheses: after argon-ion etching for 1 min.

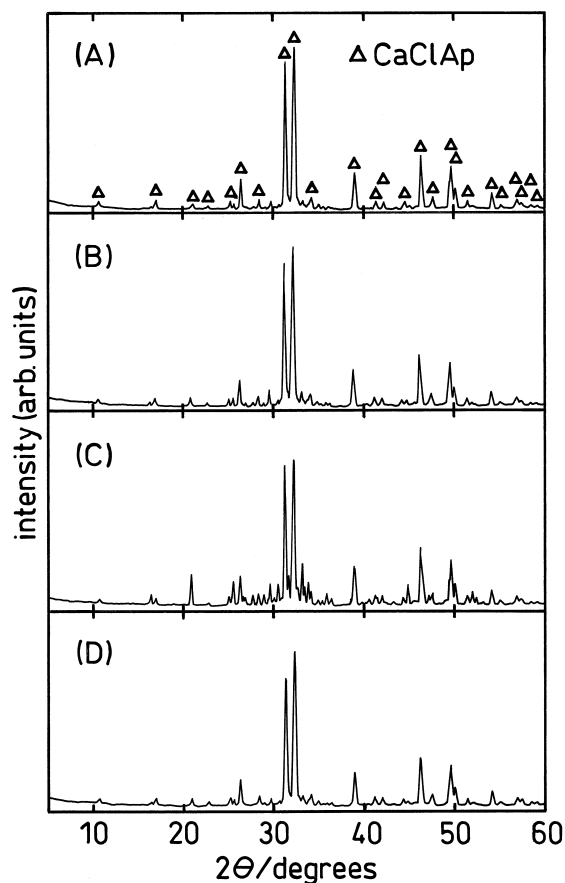


Fig. 2. XRD patterns of CaHAp previously employed in obtaining the results shown in Fig. 1 (B) but after 6 h on-stream. (A) CaHAp_{1.72} (B) CaHAp_{1.66} (C) CaHAp_{1.63} (D) CaHAp_{1.59}.

etry of the catalyst [23–25]. Oxygen molecules may be activated by the O²⁻ ions which are

produced from the dehydration of the hydroxyl groups in the structure of hydroxyapatite [26]. The dependence of the conversion on the stoichiometry of the catalyst may result from the variation of the numbers of these hydroxyl groups with the Ca/P ratio. In the presence of TCM (Fig. 1B), however, the conversion of CH₄ and N₂O at 0.5 h on-stream was at a minimum with CaHAp_{1.63} and decreased with increasing time-on-stream on all catalysts. With increasing time-on-stream to 6 h, the deep oxidation to CO₂ was depressed as observed in the oxidation of methane with O₂ [23–25], but somewhat surprisingly, the selectivity to ethylene increased particularly on CaHAp_{1.59}, CaHAp_{1.63}, and CaHAp_{1.66} in contrast to the observation with O₂ as oxidant [23–25]. The XRD patterns of the CaHAp after use in the presence of TCM (Fig. 2) provide evidence for the complete conversion to calcium chlorapatite [JCPDS 33-0271, Ca₁₀(PO₄)₆Cl₂, CaClAp], as observed with CaHAp previously employed in the oxidation with O₂ [23–25]. However, the atomic ratio of Cl/Ca in the near-surface region on CaHAp previously employed in obtaining the results shown in Fig. 1B but after 6 h on-stream (Table 2) was larger than expected (0.2) for the stoichiometric chlorapatite as well as relatively greater than that on CaHAp previously employed in the oxidation with O₂ [24], indicating that a deep chlorination of CaClAp

Table 2
Cl/Ca from XPS of used^a CaHAp

| T (K) ^b | P(N ₂ O) ^c | P(TCM) ^c | 10 ³ W/F ^d | Ca/P | | | |
|--------------------|----------------------------------|---------------------|----------------------------------|-------------|-------------|-------------|-------------|
| | | | | 1.59 | 1.63 | 1.66 | 1.72 |
| 973 | 4.1 | 0.17 | 16.7 | 0.32 (0.29) | 0.34 (0.29) | 0.26 (0.25) | 0.26 (0.36) |
| 973 | 12.3 | 0.085 | 16.7 | 0.26 (0.24) | 0.16 (0.16) | 0.21 (0.20) | 0.23 (0.22) |
| 973 | 12.3 | 0.17 | 16.7 | 0.24 (0.19) | 0.29 (0.22) | 0.27 (0.23) | 0.23 (0.22) |
| 973 | 12.3 | 0.34 | 16.7 | 0.21 (0.18) | 0.41 (0.33) | 0.18 (0.17) | 0.19 (0.17) |
| 1023 | 12.3 | 0.34 | 8.3 | 0.46 (0.33) | 0.23 (0.23) | 0.52 (0.41) | 0.19 (0.19) |
| 1023 | 12.3 | 0.34 | 16.7 | 0.20 (0.18) | 0.27 (0.21) | 0.17 (0.17) | 0.42 (0.24) |
| 1023 | 12.3 | 0.34 | 25.0 | 0.22 (0.20) | 0.17 (0.17) | 0.18 (0.17) | 0.20 (0.20) |

^aPreviously employed for 6 h on-stream in the oxidation of methane with N₂O under various conditions.

^bReaction temperature (K).

^cPartial pressure (kPa).

^dSpace time (g min ml⁻¹)

Values in parentheses: after argon-ion etching for 1 min.

occurs in the oxidation with N_2O . Although the increased selectivity to C_2H_4 during the oxidation of methane in the presence of TCM may be attributed to the formation of the chloride or oxychloride, the extent of the contribution of nonstructural chlorine cannot be evaluated at this time [20]. Although XPS spectra of CaHAp previously employed in obtaining the results shown in Fig. 1B but after 6 h on-stream contained a peak at approximately 199 eV due to Cl 2p the surface chlorinated species cannot be definitively identified.

Earlier work has shown that the addition of alkali halides, particularly LiCl, to metal oxides suppressed the deep oxidation of CO to CO_2 , while increasing the selectivity to ethylene [27,28]. The addition of pulses of gaseous CH_2Cl_2 and $CHCl_3$ to the methane oxidation feedstream also produced an enhancement of the selectivity to ethylene from methane [29].

The introduction of HCl has also produced similar effects with a lithium/magnesium oxide catalyst [30].

3.3. Effect of partial pressure of TCM on methane oxidation

Since the introduction of a small partial pressure of TCM into the feedstream for the oxidation of methane with N_2O on CaHAp led to an unexpected increase in the selectivity to C_2H_4 , the effect of changes in the concentration of TCM was investigated at 973 K (Fig. 3). As observed at the lower partial pressure of N_2O , in the absence of TCM, the catalytic activities of all CaHAp were little influenced by changes in the atomic ratio of Ca/P (Fig. 3A). Regardless of the concentration of TCM (Fig. 3B–D), the conversion of methane at 0.5 h on-stream was at a minimum at a Ca/P ratio of 1.63. At

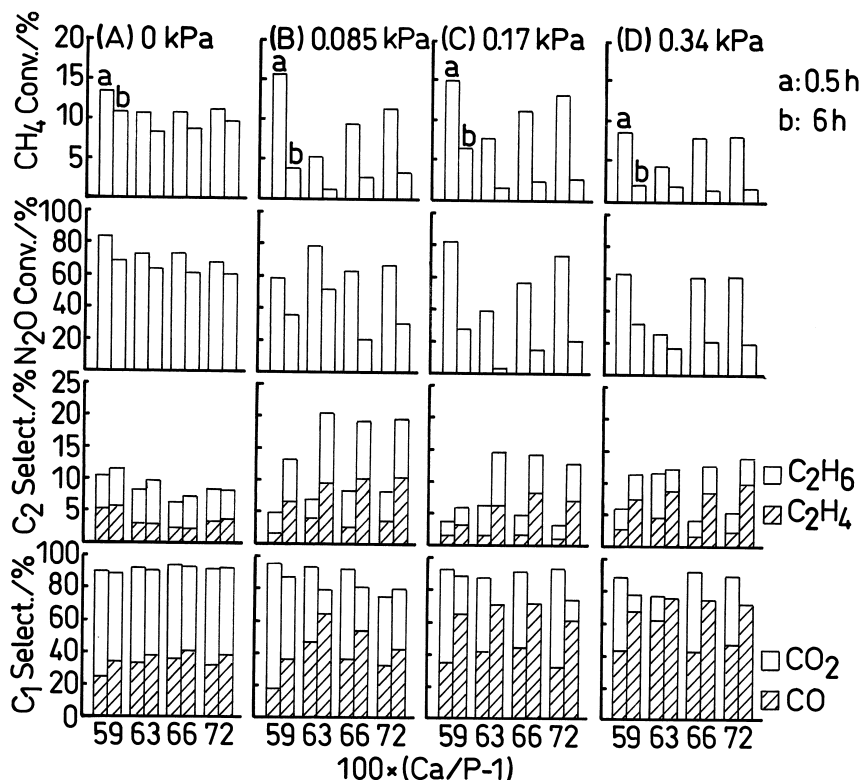


Fig. 3. Effect of the partial pressure of TCM on methane oxidation at 973 K. Reaction and pretreatment conditions: as in Fig. 1 except $P(N_2O) = 12.3$ kPa and $P(TCM)$.

6 h on-stream, the minimum was again observed at $P(\text{TCM}) = 0.085$ and 0.17 kPa but further increase of the partial pressure of TCM to 0.34 kPa resulted in an essentially identical conversion on each CaHAp. It should be noted that the selectivities to C_2H_6 and C_2H_4 increased substantially with increasing time-on-stream together with a slight decrease of the selectivity to CO_2 at the lowest partial pressure of TCM (0.085 kPa). The selectivity to C_2H_4 increased concomitantly with an almost complete disappearance of CO_2 from the product stream at 0.34 kPa of TCM. The XRD patterns of CaHAp_{1.59}, CaHAp_{1.66} and CaHAp_{1.72} previously employed in the oxidation of methane at various concentrations of TCM showed that the catalyst was completely converted to CaClAp and no other phases were present. CaClAp together with a relatively small proportion of unidentified species were detected in CaHAp_{1.63}

(not shown). The unidentified species is probably chlorinated since XPS analyses showed that the atomic ratio of Cl/Ca on CaHAp_{1.63} increased with increasing partial pressure of TCM while those on the remaining CaHAp were little influenced by the partial pressure (Table 2). Although the quantity of surface chlorinated species would be expected to increase with the partial pressure of TCM this was not observed from the XPS analyses (Table 2).

3.4. Effect of W/F on methane oxidation

Although chlorination of the catalyst is evidently responsible, directly or indirectly, for the enhancement of the selectivity to C_2H_4 , further information on the nature of the chlorinated species would be advantageous. For this purpose the effect of changes in contact time was examined at 1023 K, at which temperature a

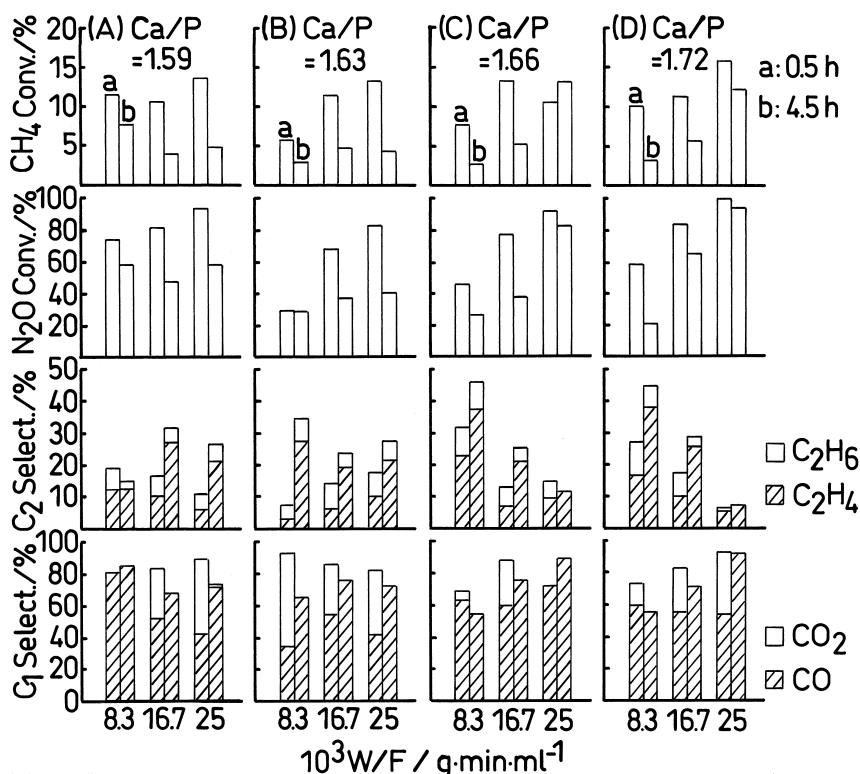


Fig. 4. Effect of W/F on methane oxidation at 1023 K. Reaction and pretreatment conditions: as in Fig. 1 except $P(\text{N}_2\text{O}) = 12.3$ kPa, $P(\text{TCM}) = 0.34$ kPa and weight of catalyst.

larger quantity of the unidentified chlorinated species could be expected. It should be noted that the contact times were altered by changing the mass of the catalyst while holding the flow rate fixed. The oxidation was allowed to occur for 4.5 h on-stream, followed by an in situ re-exposure to O_2 (25 ml min^{-1}) without CH_4 and TCM for 1 h at 1023 K and finally a repetition of the oxidation for a further 1.5 h. The results obtained before and after the reactivation process were sufficiently similar to show that little or no deactivation occurs in the oxidation with O_2 and TCM.

A number of general observations can be made from the results (Fig. 4). In general, increase of the contact time led to increases in the conversions of both CH_4 and N_2O , except for the 1.59 and 1.63 catalysts and 6 h on-stream. With the 1.66 and 1.72 samples the C_2 selectivities decreased with contact time in favour of increases in the selectivities to CO, particularly at 6 h on-stream.

Although there are quite evidently a number of factors contributing to these observations those related to the composition of the catalyst appear to be of particular importance. As the Ca/P ratio increases the relative number of hydroxyl groups also increases and consequently the number of chlorine atoms required for the complete substitution of the former. Therefore, it would be expected that the conversion of CaHAp to the corresponding chlorapatite would increase with decreasing Ca/P so that the chlorine available for the formation of species other than CaClAp or for nonstructural purposes would be higher with the catalysts of lower Ca/P.

The aforementioned deductions appear to be supported by XRD patterns for the four catalysts after use in the presence of TCM at contact times of 25.0×10^{-3} (Fig. 5) and $8.3 \times 10^{-3} \text{ g min ml}^{-1}$ (Fig. 6). At the higher contact time (Fig. 5) virtually complete conversion of CaHAp to CaClAp has occurred with all compositions whereas at the lower contact time (Fig. 6) either nonstructural chlorine or one or more

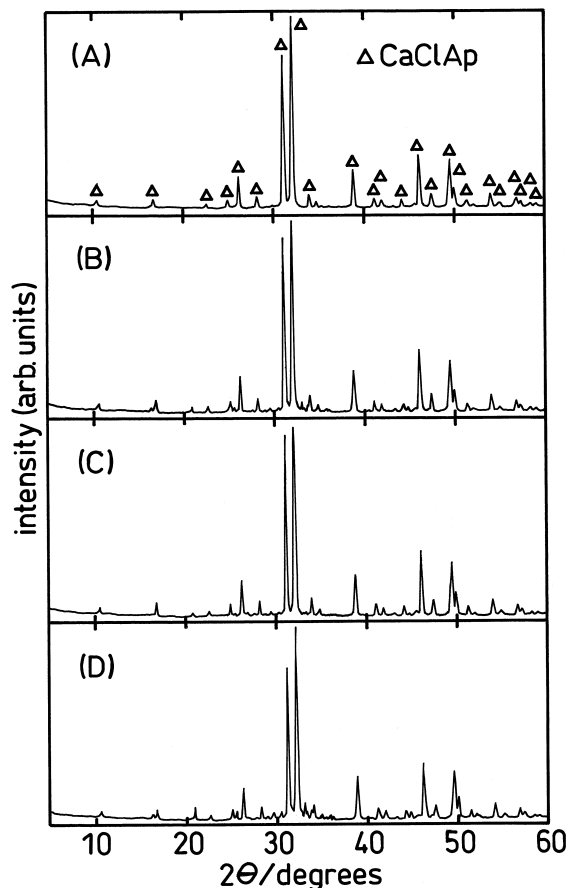


Fig. 5. XRD patterns of CaHAp previously employed in obtaining the results shown in Fig. 4 but after 6 h on-stream and $10^3 W/F = 25.0 \text{ g min ml}^{-1}$. (A) CaHAp_{1.72} (B) CaHAp_{1.66} (C) CaHAp_{1.63} (D) CaHAp_{1.59}

additional chlorinated species (whose XRD patterns could not be matched to any reference data for chlorides or oxychlorides) are also present on the two catalysts with lower Ca/P. Although the present results cannot be taken as definitive, these observations suggest that the chlorapatite is primarily responsible for the formation of C_2 hydrocarbons whereas the nonstructural chlorine may catalyze the formation of CO. Unfortunately, as noted earlier in the present report, the surface concentrations of chlorine (Table 2) do not show trends which correlate with the diffraction patterns.

Finally, further light can be shed on the role of TCM by experiments performed in the ab-

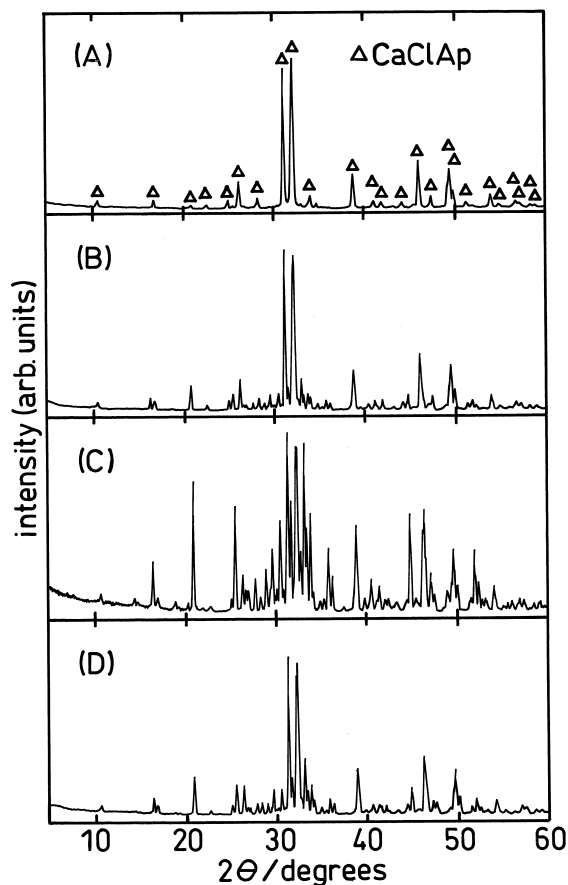


Fig. 6. XRD patterns of CaHAp previously employed in obtaining the results shown in Fig. 4 but after 6 h on-stream and $10^3 W/F = 8.3 \text{ g min ml}^{-1}$. (A) CaHAp_{1.72} (B) CaHAp_{1.66} (C) CaHAp_{1.63} (D) CaHAp_{1.59}

sence of an oxidant. As noted earlier in this report the effect of the introduction of TCM, namely the reduction in the conversion together with the decrease in selectivity to CO₂ and the increase in selectivities to CO and C₂ hydrocarbons, particularly C₂H₄, becomes more pronounced as the time-on-stream increases. This strongly suggests that the TCM is interacting with the catalyst on which the decomposition products, in particular the chlorine, are accumulating and thus the beneficial effect of TCM is largely related to the chlorine contained on and in the catalyst. The observation that excess of TCM is not beneficial and, in fact, may be detrimental suggests that structural chlorine (as

chlorapatite) rather than the nonstructural form is affecting the selectivities. Excess chlorine may participate further detrimentally in reducing the number of sites capable of activating methane, thus lowering the conversion.

The results obtained in the absence of any oxidant clearly show the effect of the addition of TCM (Fig. 7). In the absence of TCM selectivities to CO₂ of 7–13% are observed and no C₂H₄ is produced except with the catalyst for which Ca/P equals 1.59. Introduction of TCM eliminates all carbon oxides except for a small selectivity to CO₂ with the latter catalyst and generates selectivities to C₂ hydrocarbons of 97–100% although, not surprisingly, the con-

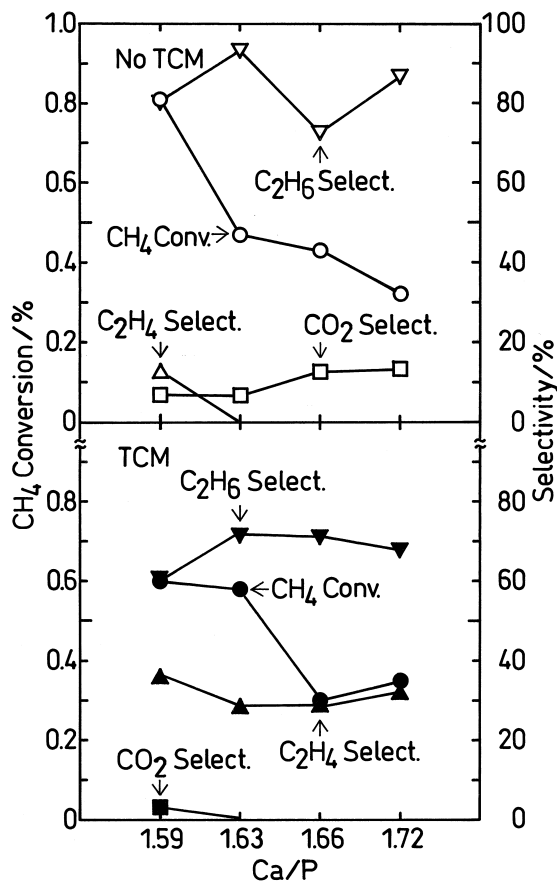


Fig. 7. Conversion of Methane on CaHAp of various Ca/P in the absence of N₂O. Reaction temperature, 1073 K. Catalysts (0.5 g) were pretreated with O₂ (25 ml/min) for 1 h at 973 K. $P(\text{CH}_4) = 28.7 \text{ kPa}$, $P(\text{TCM}) = 0$ or 0.17 kPa . Data collected after 0.5 h on-stream.

versions, either with or without TCM, are small. It is clear that a gas phase oxidant is not required for TCM to operate successfully.

4. Conclusions

1. In the absence of TCM the effect of changes in the stoichiometry of the catalyst is relatively small with N_2O as oxidant in contrast to that where O_2 is the oxidant.

2. With N_2O as oxidant and fieldstream TCM the conversion decreases with time-on-stream while the selectivities to C_2H_4 and CO increase with time-on-stream, the latter increasing also with increasing Ca/P.

3. The introduction of small partial pressures of TCM leads to the formation of chlorapatite while larger partial pressures produce nonstructural chlorine in the catalyst and are detrimental to both conversions and selectivities to desired products.

Acknowledgements

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