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Nitrous oxide as oxidant for the oxidation of methane on barium hydroxyapatites in the presence and absence of tetrachloromethane

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Abstract

The oxidation of methane with nitrous oxide on PO₄-deficient barium hydroxyapatite (BaHAp) has been investigated in the presence and absence of tetrachloromethane (TCM) and compared to that with oxygen in order to obtain possible activities for the partial oxidation of methane using hydroxyapatite catalysts. In the absence of an external oxidant, the addition of TCM suppressed the formation of oxidation products with the essential elimination of CO and CO₂, in favor of an increased selectivity to C₂H₆ while that to C₂H₄ changed relatively little, indicating that TCM directly contributes to an activation of structural oxygen of the catalyst. In the absence of TCM and with nitrous oxide as the oxidant, the maximum selectivity to the coupling products reached approximately 80% at a conversion of methane of 4.5% at 0.5 h on-stream although calcium hydroxyapatites mainly afforded CO_x under the corresponding conditions. However, carbon oxides, primarily CO₂, were the predominant products with oxygen. With nitrous oxide and in the presence of TCM with increasing time-on-stream carbon monoxide became the only significant product. The formation of barium chlorapatite is demonstrated and the relative effects of nitrous oxide and TCM are compared. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methane oxidation; Barium hydroxyapatite; Tetrachloromethane; N₂O

1. Introduction

The conversion of methane to value-added products continues to attract the attention of catalyst researchers, in spite of the realization that practical solutions are more complex than originally anticipated [1–9]. While work continues on the oxidative coupling [1–4] and partial oxidation [5] processes in-

creased attention has been directed to the production of synthesis gas [6–8] as well as the application of oxidants other than oxygen [9]. Work on this subject in our laboratories has recently focused on the application of calcium and strontium hydroxyapatites, both stoichiometric and nonstoichiometric [10]. The effects on the conversion and selectivities to the various products of the addition of small quantities of tetrachloromethane (TCM) to the methane feedstream have also been investigated [11]. Since it has been already reported that the oxidative coupling of methane appears to be related to the electronegativity of the cation of the salts of alkaline earth metals [12,13],

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most recently the hydroxyapatite with barium (BaHAp) as cation has been prepared employed for the oxidation of methane [14]. It has been shown to form CO₂ as the principal products from the oxidation of methane with O₂ in the absence of TCM while, with a small partial pressure of TCM and at higher times-on-stream, the formation of CO₂ was virtually eliminated in favor of CO and C₂ hydrocarbons [14].

As is well known, many of the earlier studies of the partial oxidation of methane made use of nitrous oxide as the oxidant. The partial oxidation of methane to methanol and formaldehyde with N₂O was investigated on silica-supported molybdenum oxide [15] and vanadium oxide [16]. Nitrous oxide has also employed for the oxidative coupling of methane on rare earth oxides [17,18] and on magnesium-based catalysts [19,20]. Atomic oxygen species as O⁻ ion produced from the decomposition of N₂O have been proposed as the active species [18,19,21]. Therefore, the employment of N₂O for O₂ in the presence and absence of TCM appeared both interesting and useful for the facile conversion of methane to the partial oxidation products on BaHAp.

2. Experimental

Three separate samples (identified as BaHAp-*X* where *X* is the sample number) of BaHAp were prepared from Ba(OH)₂·8H₂O and H₃PO₄ [14,22,23]. The calcined BaHAp was pressed, crushed and sieved to particle size of 1.70–0.85 mm and referred to as the “fresh catalyst”. 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 [10]. 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 reaction conditions were as follows: $W = 0.25, 0.5$ or 0.75 g, $F = 30$ ml min⁻¹, $T = 973$ K, $P(\text{CH}_4) = 28.7$ kPa, $P(\text{N}_2\text{O}) = 3.1, 6.2$ or 12.3 kPa [$P(\text{O}_2) = 12.3$ kPa for O₂ oxidation] and $P(\text{TCM}) = 0, 0.085, 0.17$ or 0.34 kPa; balanced 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). Three columns, Porapak

Q (6 m × 3 mm), molecular sieve 5A (0.2 m × 3 mm) and molecular sieve 13× (1 m × 3 mm) were employed. In the present study, oxygen produced from the decomposition of N₂O under various reaction conditions was almost completely consumed in the oxidation process. 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 balance 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 Mg Kα radiation and 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. The atomic ratios of Ba/P were determined with ICP (Shimadzu ICPS-5000). The surface area of the samples were calculated from adsorption isotherms obtained with a conventional BET nitrogen adsorption apparatus (Shibata P-700).

3. Results

3.1. Properties of the catalyst

XRD patterns of all BaHAp prepared are essentially identical and in agreement with reference patterns for Ba₁₀(PO₄)₆(OH)₂ (JCPDS 36-0272) (not shown). The binding energies from XPS for Ba 3d_{5/2}, O 1s and P 2s both before and after argon-ion etching were as expected and showed no significant differences from sample to sample of BaHAp (Table 1). Although the three samples of BaHAp were prepared in a similar manner with identical quantities of the reactants, the surface compositions vary substantially from sample to sample, although the bulk Ba/P ratios and surface areas are identical, within experimental error. This, at least in part, reflects the well-known difficulty in reproducible preparation of many of the hydroxyapatites. Since the samples of BaHAp were not identical in surface compositions, activities on BaHAp-1, BaHAp-2 and BaHAp-3 under the same reaction conditions were not strictly identical as described below.

Table 1
Bulk and surface properties of fresh BaHAp

Catalysis	Ba/P ^a	S.A. (m ² /g) ^b	A.D. (g/cm ³) ^c	Binding energy (eV)			Atomic ratio ^d	
				Ba 3d _{5/2}	O 1s	P 2s	Ba/P	O/P
BaHAp-1	1.96	17	0.90	780.1 (780.8) ^e	530.6 (531.4)	190.2 (190.4)	0.97 (1.24)	2.52 (2.64)
BaHAp-2	2.02	21	1.02	779.8 (780.4)	530.4 (530.9)	189.6 (190.1)	0.65 (0.78)	1.90 (2.08)
BaHAp-3	1.96	20	1.07	780.2 (780.9)	531.0 (531.4)	190.3 (190.8)	0.85 (1.24)	2.02 (2.43)

^a Atomic ratio determined with ICP.

^b Surface area.

^c Apparent density.

^d As determined from XPS.

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

3.2. Effects of oxidant and partial pressure of TCM

In the absence of TCM the oxidation of methane with O₂ produced carbon oxides, in particular CO₂, as principal products, while with N₂O selectivities to C₂ compounds (C₂H₄ and C₂H₆) of approximately 40% and CH₄ conversion of approximately 11% were observed on BaHAp-1 (Fig. 1). Increases in the time-on-stream produced relatively little changes in the conversions and selectivities. It is of interest to note that the conversion of both CH₄ and the oxidant

decreased by a factor of approximately two when oxygen was replaced by N₂O, probably indicating that the decomposition of N₂O is the rate-limiting step.

In the presence of TCM the conversion of CH₄ with N₂O and the selectivities to C₂ compounds decreased while the selectivity to CO increased with increasing time-on-stream to the detriment of that to C₂ compounds, regardless of the partial pressure of TCM (*P*(TCM)). Additionally, CH₃Cl formed at higher values of *P*(TCM). The effect of the introduction of TCM is similar to that observed with O₂

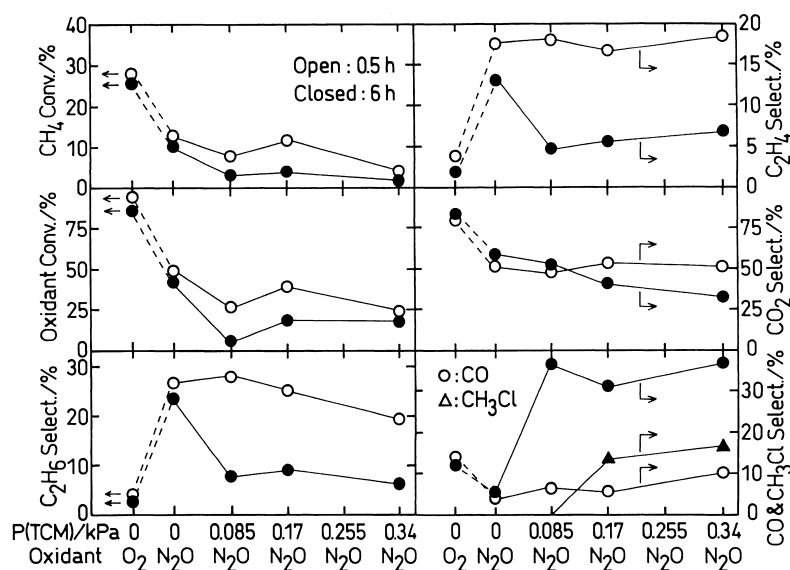


Fig. 1. Effect of oxidant and partial pressure of TCM on methane oxidation over BaHAp-1 at 973 K. Reaction conditions: $W = 0.5$ g, $F = 30$ ml min⁻¹, $P(\text{CH}_4) = 28.7$ kPa, $P(\text{O}_2 \text{ or } \text{N}_2\text{O}) = 12.3$ kPa and $P(\text{TCM}) = 0, 0.085, 0.17$ or 0.34 kPa; balance to atmospheric pressure was provided by He.

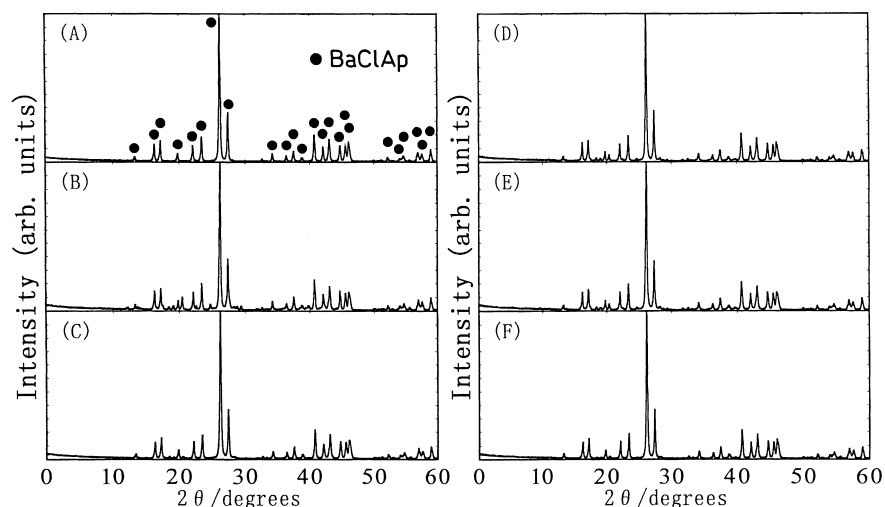


Fig. 2. XRD patterns of BaHAp previously employed in obtaining the results reported in each figure but after 6 h on-stream. (A) Fig. 1 but $P(\text{TCM}) = 0.085 \text{ kPa}$; (B) Fig. 1 but $P(\text{TCM}) = 0.34 \text{ kPa}$; (C) Fig. 3B but $P(\text{N}_2\text{O}) = 3.1 \text{ kPa}$; (D) Fig. 3B but $P(\text{N}_2\text{O}) = 12.3 \text{ kPa}$; (E) Fig. 4B but $10^3 W/F = 8.3 \text{ g min ml}^{-1}$; (F) Fig. 4B but $10^3 W/F = 25.0 \text{ g min ml}^{-1}$.

on various hydroxyapatites [10,11] but dissimilar to that found on BaHAp with O_2 and TCM present [14] where the selectivity to C_2 compounds increased with time-on-stream. In contrast to the present observations, with calcium hydroxyapatites the selectivities to C_2 compounds in the oxidation of CH_4 with N_2O increased with time-on-stream [24]. While the present results show that the selectivity to CO_2 varies relatively little with time-on-stream, previous studies with a variety of hydroxyapatites have shown that the selectivity to CO_2 are substantially suppressed particularly with increase in the time-on-stream, on addition of TCM, regardless of the oxidant [11].

As seen from the XRD patterns of BaHAp-1 obtained after use for 6 h on-stream in the oxidation with added TCM, the corresponding barium chlorapatite [BaClAp ; JCPDS 16-0686 for $\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2$] is formed from BaHAp at all $P(\text{TCM})$ and no other phases were detected [Fig. 2A and B (not shown for $P(\text{TCM}) = 0.17 \text{ kPa}$)]. As suggested in previous reports [11], the aforementioned effects of the introduction of TCM may be attributed to the formation of this chlorinated species and/or non-structural chloride.

X-ray photoelectron spectra of BaHAp-1 previously employed in the oxidation of methane with N_2O in the presence of TCM contained peaks attributed to Ba $3d_{5/2}$, O $1s$, P $2s$ and Cl $2p$ at approximately 780.5,

531.5, 190.0 and 199.0 eV, respectively, either before and after argon-ion etching (not shown). The atomic ratios of Ba/P and O/P in the used catalyst varied to some extent from those in the fresh sample while those of Cl/P were similar to the expected value (0.33) for the stoichiometric chlorapatite and showed no dependence on $P(\text{TCM})$ (Table 2, columns 1–3).

3.3. Effect of partial pressure of N_2O

In the absence of TCM the effects on the selectivities of changes in the partial pressure of N_2O [$P(\text{N}_2\text{O})$] after 6 h on-stream on BaHAp-2 were relatively small but at 0.5 h on-stream the selectivities to C_2 compounds, which reached approximately 80% at a $P(\text{N}_2\text{O})$ of 3.1 kPa were lower at the higher values of $P(\text{N}_2\text{O})$ (Fig. 3A). The high selectivity (ca. 80%) to C_2 compounds has not been reported for the oxidative coupling of methane on calcium and strontium hydroxyapatites. The carbon oxides produced were predominantly CO_2 at all $P(\text{N}_2\text{O})$ and times-on-stream. Samples used for the study of the effect of $P(\text{N}_2\text{O})$ in the absence of TCM were found, from XRD analysis, to have been partially converted to $\text{Ba}_3(\text{PO}_4)_2$ (not shown), the formation of which may be at least partially responsible for the decline in conversion and C_2 selectivities under these conditions.

Table 2

Near-surface composition^a of BaHAp previously employed in methane oxidation in the presence of TCM under various conditions^b

Catalysis	BaHAp-1			BaHAp-2			BaHAp-3		
	1	2	3	4	5	6	7	8	9
$P(\text{TCM})^c$	0.085	0.17	0.34	0.17	0.17	0.17	0.17	0.17	0.17
$P(\text{N}_2\text{O})^c$	12.3	12.3	12.3	3.1	6.2	12.3	3.1	3.1	3.1
W^d	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.5	0.75
$10^3 W/F^e$	16.7	16.7	16.7	16.7	16.7	16.7	8.3	16.7	25.0
Ba/P ^f	0.54 (0.66) ^g	0.68 (0.73)	0.92 (1.06)	0.82 (0.97)	0.73 (0.97)	0.27 (0.29)	0.41 (0.65)	0.85 (0.90)	0.63 (0.75)
O/P ^f	1.62 (1.70)	1.94 (1.74)	1.97 (1.87)	1.81 (1.75)	1.89 (1.99)	1.66 (1.54)	1.26 (1.77)	2.00 (1.66)	1.66 (1.61)
Cl/P ^f	0.29 (0.25)	0.32 (0.27)	0.31 (0.18)	0.35 (0.21)	0.31 (0.26)	0.36 (0.31)	0.38 (0.24)	0.66 (0.44)	0.40 (0.26)

^a From XPS.^b After 6 h on-stream.^c Partial pressure (kPa).^d Weight of catalyst (g).^e Space time (g min ml^{-1}).^f Atomic ratio by XPS.^g Values in parentheses: after argon-ion etching for 1 min.

In the presence of TCM and at 0.5 h on-stream CO_2 is the principal oxide produced, regardless of $P(\text{N}_2\text{O})$ (Fig. 3B). However, at 6 h on-stream and $P(\text{N}_2\text{O})$ equal to 3.1 kPa the only significant product was CO while at the higher values of $P(\text{N}_2\text{O})$ both CO and CO_2 were formed and at the highest $P(\text{N}_2\text{O})$ of 12.3 kPa methyl chloride was also formed. XRD of the samples showed that essentially complete conversion to the chlorapatite had taken place (Fig. 2C and D). While the catalyst previously used in the presence of TCM and at a $P(\text{N}_2\text{O})$ of 3.1 kPa was completely converted to the corresponding chlorapatite (Fig. 2C), the XRD patterns of that used at a $P(\text{N}_2\text{O})$ of 12.3 kPa (Fig. 2D) were essentially identical to those used under other reaction conditions (Fig. 2A–C). However, the XPS results are substantially different after the experiment at the highest $P(\text{N}_2\text{O})$, with both Ba/P and O/P significantly smaller than those observed at the lower two partial pressures while the value obtained for Cl/P remains essentially unchanged. It is of interest to note that methyl chloride is found in the products at 12.3 kPa of N_2O .

To assess the relative importance of the oxidant and the catalyst the conversion of methane was investigated at 1073 K in the absence of N_2O (Table 3). As expected, the conversions with and without TCM were very low, and decreased slightly on its addition. However, most interestingly, the introduction of TCM completely eliminated the production of carbon oxides in

favor of the formation of C_2H_6 , thus demonstrating that the effect of TCM is primarily related to the enhancement of the C_2 selectivity of the catalyst, rather than the suppression of its activity. It should be noted that the present information on the effect of TCM is observed in the absence of oxidant in gas phase. When oxidant is present, it appears to be reasonable that C_2 compounds produced with the structural oxygen are deep oxidized to CO_x with gaseous oxygen species in the feed, as shown in Fig. 1. It is to be further emphasized that the principal impact of the addition of TCM is experienced by the catalyst although some gas phase effects cannot be ruled out. The results of the aforementioned experiment also provide evidence for the active participation of the structural oxygen of the catalyst.

3.4. Space time

In the absence of TCM on BaHAp-3 the conversion of CH_4 increased with contact time as expected, while the selectivity to C_2 compounds decreased slightly. Increases in the time-on-stream produced similar observations (Fig. 4A).

In the presence of TCM the conversion of CH_4 was significantly depressed, particularly after 6 h on-stream, and at the shorter time-on-stream C_2 selectivities of 60–70% were observed for all three contact times while at 6 h on-stream only CO was

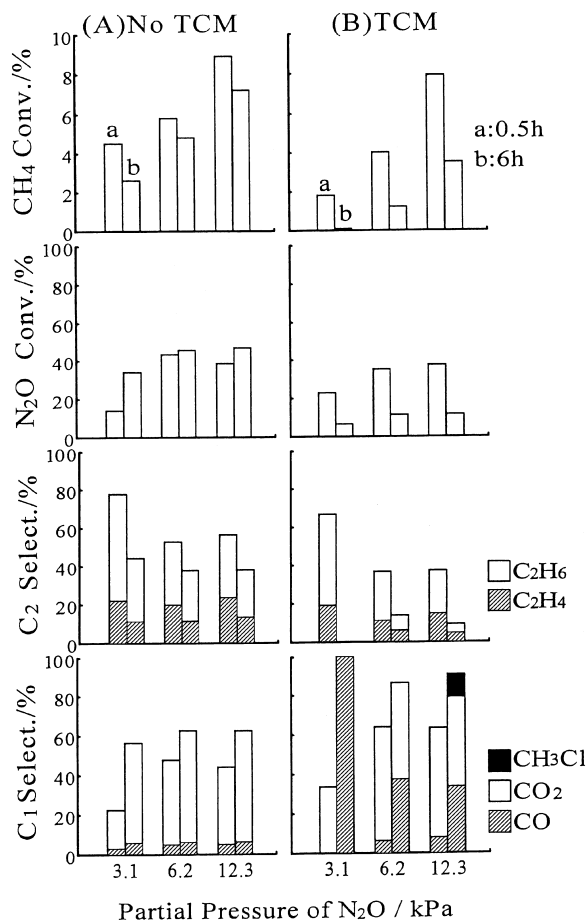


Fig. 3. Effect of partial pressure of N_2O on methane oxidation on BaHAp-2 at 973 K. Reaction conditions: as in Fig. 1 except $P(N_2O)$ and $P(TCM) = 0$ or 0.17 kPa.

found. Noteworthy differences in the surface compositions are evident. While after use at the lowest and highest contact time Ba/P and O/P (Table 2, Columns

Table 3
Conversion of CH_4 and selectivities to products on BaHAp-2 without external oxidant^a

	Conversion (%)		Selectivity (%)			
	CH_4		CO	CO ₂	C ₂ H ₄	C ₂ H ₆
No TCM	0.4		32.8	23.0	44.2	0
TCM	0.3		0	0	45.6	54.4

^a Reaction conditions: $W = 0.5$ g, $P(CH_4) = 28.7$ kPa and $P(TCM) = 0.17$ kPa diluted with He ($F = 30$ ml min⁻¹). $T = 1073$ K. Data were collected at 0.5 h on-stream.

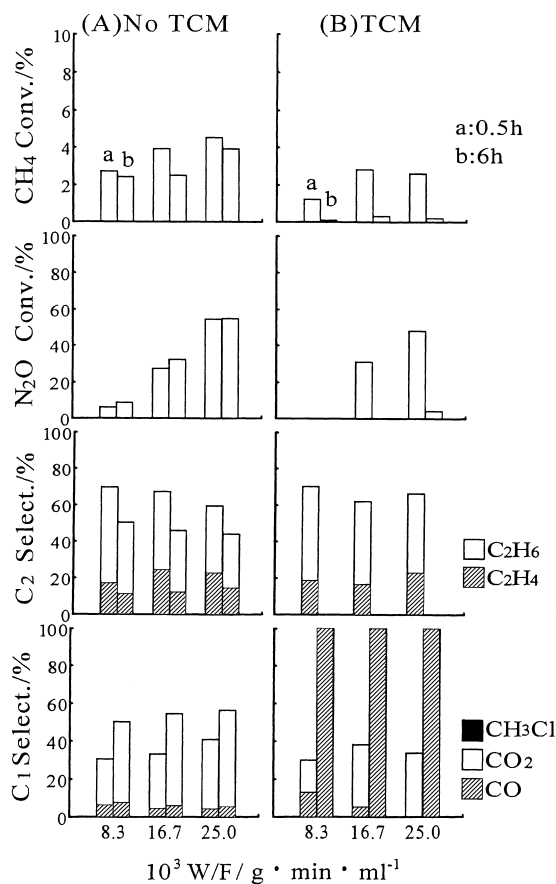


Fig. 4. Effect of space time on methane oxidation on BaHAp-3 at 973 K. Reaction conditions: as in Fig. 1 except W , $P(N_2O) = 3.1$ kPa and $P(TCM) = 0$ or 0.17 kPa.

7 and 9) have decreased to less than those for the fresh catalyst (Table 1) and Cl/P remains similar to that expected for chlorapatite, with the space time of 16.7×10^{-3} g min ml⁻¹ both Ba/P and O/P (Table 2, Column 8) are identical to those of the fresh catalyst but the value for Cl/P is approximately twice that for chlorapatite.

4. Discussion

In the absence of an oxidant, the addition of TCM to the methane feedstream suppressed the formation of oxidation products in favor of an increased selectivity to C₂H₆ while that to C₂H₄ changed relatively

little. Evidently both oxidation to carbon oxides and further oxidation of C_2H_6 , the primary oxidative coupling products, are discouraged by the introduction of TCM. Since no partial oxidation at the present reaction conditions is possible due to well-known thermodynamic limitations, these activities may be restricted to the structural removal oxygen species in the catalyst. It should be noted that OH groups of BaHAp is easily exchanged by Cl^- in a dilute HCl solution even at room temperature [25], indicating that OH groups of the catalysts is rather removable and oxygen species produced from OH groups might contribute to the activities in the absence of oxidant.

With N_2O as oxidant the addition of TCM to the feedstream suppresses the oxidative coupling process as well as the deep oxidation to CO_2 . That this is observed only after the longer time-on-stream (6 h) provides evidence for the interaction of TCM with the catalyst as further illustrated by the results obtained in the absence of an oxidant. With TCM in the feedstream and in the absence of an oxidant only coupling products are observed. However, as N_2O is introduced into the feedstream the selectivity to coupling products diminishes, with the formation of CO_2 , which at the lowest partial pressure of N_2O (3.1 kPa) and after 6 h on-stream has been completely eliminated in favor of CO. The present results suggest an interplay between the additive and the oxidant which was either less evident or absent where oxygen served as the oxidant [14]. With oxygen and in the absence of TCM predominantly C_1 products were formed on BaHAp while, on introduction of TCM, and after 6 h on-stream the selectivity to C_2 hydrocarbons increased to approximately 80%. It is noteworthy that Cl/P ratios obtained after use in the conversion of CH_4 with oxygen were larger, by a factor of two or greater than those found in the present work and as expected for barium chlorapatite. However, as with N_2O as oxidant the formation of CO_2 was significantly reduced.

It is clear that the introduction of TCM to the CH_4 conversion feedstream results in the sorption of chlorine into the surface of the catalyst. It is also evident that the surface chlorine which appears, in the present work, in the form of the chlorapatite, is capable of the suppression of deep oxidation processes, while N_2O produces CO_2 and C_2 hydrocarbons. Although a definitive mechanism cannot be proposed at this time a competitive process may be visualized in which N_2O

operates, in part, to replace oxygen lost from the catalyst during the CH_4 conversion process while hydroxyl groups are substituted by chloride through the interaction of TCM with the catalytic surface. Of course the gas phase reaction between TCM, N_2O and CH_4 undoubtedly occurs, although the present evidence suggests that the participation of TCM is largely related to the alteration of the composition of the catalyst. The formation of CH_3Cl and its subsequent conversion to C_2 hydrocarbons may also play a role in the present reaction.

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