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The effects of the introduction of tetrachloromethane into the feedstream for the partial oxidation and oxidative coupling of methane

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Abstract

The addition of small quantities of tetrachloromethane (TCM) into the feedstream of the partial oxidation and oxidative coupling of methane produces, with a wide variety of catalysts, advantageous effects. In general, both the conversion and selectivities to the desired products, in the latter reaction hydrocarbons containing two or more carbon atoms, are increased. Experiments in which the catalysts are pretreated with TCM and subsequently employed in the absence of feedstream TCM, together with XPS and XRD analyses show that the beneficial effects of the addition of TCM predominantly arise from the presence of chloride ions in the interfacial regions of the catalysts. Since the distribution of chloride ions within the surface is undoubtedly nonuniform, unambiguous identification of the stoichiometry is difficult, but the relatively low quantities of these ions in the surface suggest that stoichiometries similar to those of oxychlorides may be formed. Although the surface chloride ions may be participating directly or indirectly in the methane conversion process, it appears that the former is more probable.

Keywords: Methane; Oxidative coupling; Partial oxidation; Chlorine

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1. Introduction

The last decade has seen great interest in the catalytic conversion of alkanes, particularly methane, in large part as a result of the desire to transform natural gas to value-added products [1–3]. Much of the published results have focused on two processes, the partial oxidation and the oxidative coupling of methane with the desired products from the former reaction being formaldehyde and methane, while ethylene and/or ethane are preferred from the latter process. Although the work has undoubtedly increased the body of knowledge available on processes involving methane, unfortunately the yields of the desired products have been less than the minimum necessary to render either of the aforementioned processes economically viable for large-scale implementation. At least in part the unattractive yields result from the tendency of the desired products to be further oxidized to less desirable compounds such as carbon oxides.

Our understanding of partial oxidation and oxidative coupling processes has been enhanced from both the fundamental and practical research studies. Information on free radical processes, chain mechanisms, dissociation of C–H bonds, the nature of the participation of heterogeneous catalysts and the active sites for

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both the dissociation and oxidation steps, and the relative importance of gaseous and surface processes has been generated.

Work on this topic in this laboratory has been concerned with, among other things, the influence of gas phase additives on the oxidation and coupling processes. The present contribution is intended to provide a brief review of the effects of the addition of CCl_4 to the feedstream in the methane conversion process.

The homogeneous reaction between hydrogen and the halogen, Br_2, may well be the best known example of a chain mechanism. Benson, in his book published in 1960, suggests that the reactions of the halogens with CH_4 should be at least approximately parallel to those with H_2, although, as he notes, relatively little evidence was available at that time [4]. Several decades later Benson [5] obtained a patent for a process in which ethylene and ethane are produced in a flame of mixtures of methane and chlorine.

$$CH_4 + Cl_2 \rightarrow \frac{1}{2}C_2H_4 + 2HCl \tag{1}$$

Benson indicates that the primary product is methyl chloride but this is unstable at high temperatures (>1000°C) in the flame and thus, both C_2 species and HCl are formed.

In the meantime, the results were reported of studies of the effects of gaseous additives on the oxidation of methane on palladium catalysts prepared by coating alumina with a mixture of palladium and thoria [6]. The four chloromethanes as well as dibromo- and diiodomethane were examined. The introduction of the halogen compounds was found to reduce the rate of oxidation of methane and increase the selectivity to formaldehyde, possibly by modifying the catalyst surface and inhibiting the further oxidation of the initial products from the methane conversion process.

The aforementioned work, extended to include platinum catalysts, showed that the deactivating effect of the halogen compounds depends markedly on the temperature with bromine, a more effective inhibitor than chlorine, and platinum being more resistant to poisoning than palladium [7]. The results of studies of the gas phase pyrolysis of methyl chloride, the primary product in the Cl_2 and CH_4 reaction, were published at approximately the same time [8]. The pyrolysis of methyl chloride (<1260 K) produced C_2H_4 and C_2H_2 as intermediates. Methyl chloride does not decompose at a rapid rate ($t_{1/2} < 5$ s) at temperature much below 1073 K [9].

The decomposition of chlorine and chloromethanes has also been studied by modulated beam mass spectrometry in a low-pressure flow reactor over pyrolytic carbon surfaces between 850 and 1280 K [10]. Methyl chloride was shown to be stable at these temperatures in contrast to molecular chlorine which readily dissociated.

The reaction of alkanes with CCl_4 proceeds through a free-radical chain mechanism

$$R^\bullet + CCl_4 \rightarrow RCl + {}^\bullet CCl_3$$

$$RH + {}^\bullet CCl_3 \rightarrow R^\bullet + HCCl_3$$

in both the gas and solution phases [11–17].

2. Experimental

The preparation and procedures have been described earlier [18–51].

3. Results and discussion

The partial oxidation of methane has been investigated with metal–oxygen cluster compounds (MOCC) (also known as heteropoly oxometalates) as heterogeneous catalysts [18–29]. Although these are of various chemical composition and structures, those originally identified by Keggin have been employed more frequently as catalysts [30]. These are ionic solids with discrete cations and anions, the latter being large, approximately spherical species containing a minimum of three elements: one central atom such as phosphorus, twelve peripheral metal atoms such as tungsten or molybdenum, and forty oxygen atoms. The cations can be one or more of any of the elements of the Periodic Table with stable +1 oxidation states.

With 12-molybdophosphoric ($H_3PMo_{12}O_{40}$, abbreviated as HPMo) and 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated as HPW) supported (20 wt%) on silica, the introduction of less than 0.5 mol% tetrachloromethane (TCM) produces an approximate doubling of the conversions of methane at 723 K (Fig. 1) [22,27,29]. The selectivity to formaldehyde remains relatively unchanged on HPMo

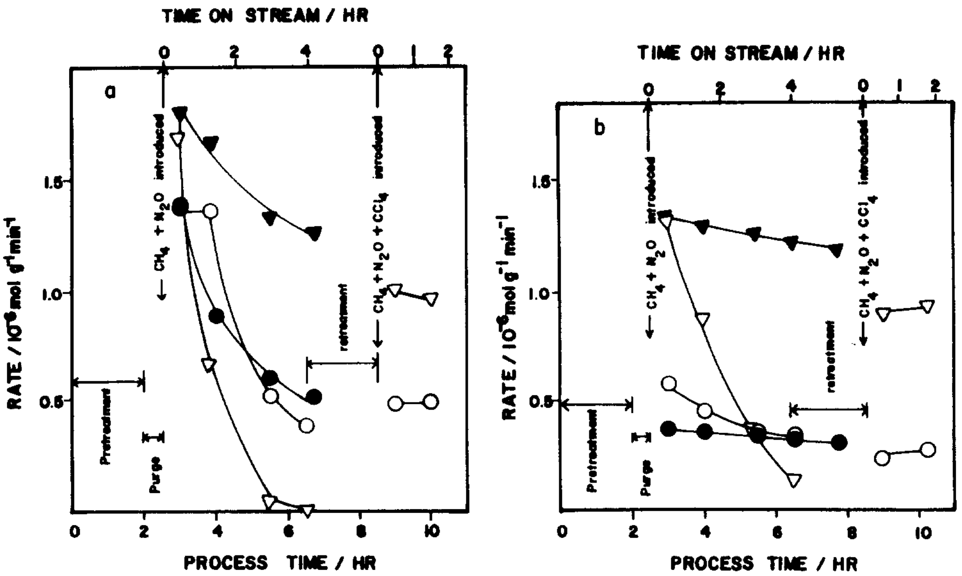

Fig. 1. Conversion and selectivity as a function of residence time (W/F) in the presence and absence of CCl_4 in the feed ($T = 723$ K, W = 0.25–4.0 g): (a) – HPMo/SiO_2, $[CCl_4]_{fed} = 0.17\%$ (by mole), $F = 60$ ml min^{-1}, $CH_4/N_2O \approx 4$; and (b) –HPW/SiO_2, $[CCl_4]_{fed} = 0.38\%$ (by mole), $F = 11$ ml min^{-1}, $CH_4/N_2O \approx 1$. Filled symbols: CCl_4 present; open symbols: CCl_4 absent ◇, ◆ conversion [(products/methane fed)(×100)]; ▲ CH_3Cl; ○. ● H_2CO (balance CO + CO_2 omitted for clarity).

but decreases on HPW. However, with the latter catalyst and at low residence times methyl chloride is produced with selectivities as high as 80%. With both catalysts the changes in conversion and selectivity are most pronounced for feedstream concentrations of TCM up to ~0.1 mol%, remaining relatively unchanged for larger amounts of TCM, particularly with HPW [22].

Experiments in which HPW was pretreated with TCM prior to use in the methane conversion reaction have shown that the chloroadditive interacts with the surface of the solid with retention of the Cl (Fig. 2) [29]. The experiments employed the catalyst pretreated in a flow of He, N_2O and TCM at 723 K and subsequently employed in the methane conversion reaction with, and without, TCM in the feedstream. The figure shows that the rates of formation of CH_3Cl are similar at the commencement of these two experiments but decrease less markedly with time-on-stream, where TCM is present in the feedstream. At least initially, chlorine appearing in the product (CH_3Cl) is obtained almost entirely from that retained by the catalyst during the pretreatment with TCM. The rapid decline in the rates of production of CH_3Cl with time-on-stream when TCM was not subsequently present in the feed, approaching a negligible value within a few hours, is apparently due to the rapid depletion of Cl taken up by the catalyst during the pretreatment. When the catalyst was retreated with the additive at a later time-on-stream, a high rate of formation of CH_3Cl was re-established. With this catalyst the formation of oxygenated species (H_2CO and CO) from methane was little influenced by the presence of TCM, either in the pretreatment stage or in the methane conversion feedstream.

The advantageous effect of TCM in the methane partial oxidation process is not restricted to the MOCC. Preliminary work published in 1989 on silica-supported oxides of Ba, Bi, Ca, Co, Cs, K, Mn, Pb and Ti has shown that the conversions and selectivities in the oxidative coupling of methane are also influenced by the presence of TCM [31]. Table 1 summarizes some of the results with these catalysts at 1023 K with and without TCM in the feedstream. Notable increases in the selectivities to C_2 hydrocarbons are observed with Ba and Cs on addition of TCM and concomitantly, the selectivity to CO decreased by at least 50%. In contrast, little change in the C_2

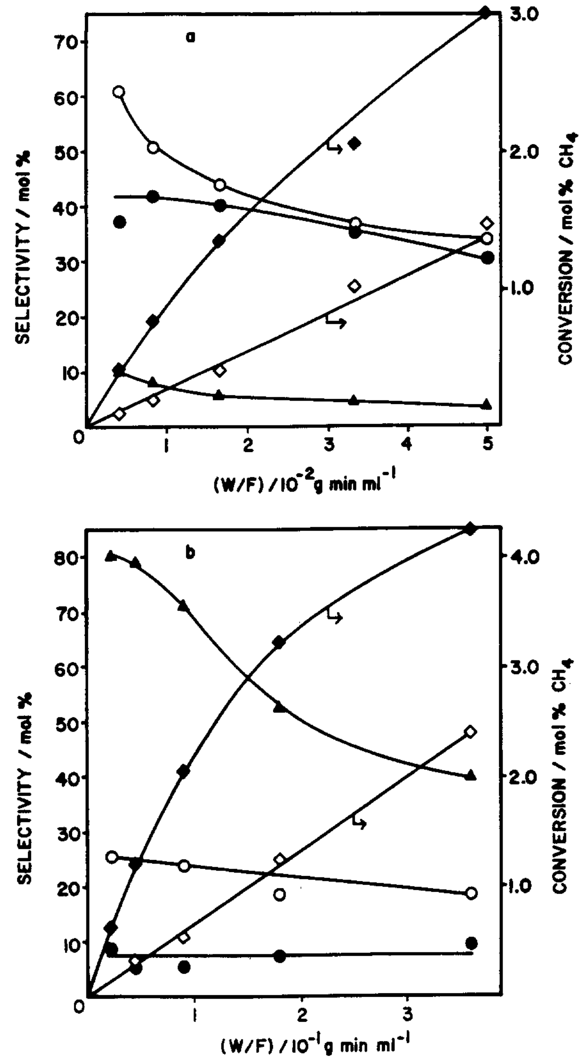

Fig. 2. Rates of production of CH_3Cl and CO with time on stream (a) 20% and (b) 10% HPW/SiO_2, respectively. △. ▼, CH_3Cl; ○, ●, CO. Open symbols: pretreatment, CCl_4; reactants, CH_4, N_2O. Solid symbols: pretreatment, CCl_4; reactants, CH_4, N_2O, CCl_4. W=2.0 g, F=11 ml min^{-1}, [CCl_4]=0.38 mol%, CH_4, $N_2O \approx 1$, T=723 K (pretreatment conditions as above except read He for CH_4).

selectivities occurred with Co but the selectivity to CO increased by a factor of three. The conversion increased on addition of TCM with the three catalysts.

The beneficial effect of TCM is, however, not universal. Thallium oxide supported on silica produced conversions of 15% and C_2 selectivities of 74% at 1048 K in its presence and the catalyst was permanently poisoned [32]. The effect of residence times and of temperatures on the rates, conversions and selectivities suggests that C_2 hydrocarbons and C_1 oxides are produced on the thallium catalysts largely by independent and distinct mechanisms, and that C_2H_6 and CO are the primary products of reaction. Whereas the latter conclusion is not unexpected, the former observation may, at least in part, explain the unexpected effect of TCM.

Studies of the silica-supported alkaline earth oxides [33] and those with alkali metals added [34] showed semiquantitatively similar results with TCM in the feedstream. The LiBa/SiO_2 catalyst showed particu-

Table 1
The effect of the addition of TCM on the oxidative coupling of methane on silica-supported oxides [a]

Catalyst	CCl_4	Conversion (%)	Selectivity (mol%)			
			CO	CO_2	C_2H_4	C_2H_6
Ba/SiO_2	A	4.8	79.0	8.0	6.2	6.8
Ba/SiO_2	P	1.9	37.5	5.0	41.0	13.5
Cs/SiO_2	A	3.9	87.5	9.0	10.0	2.0
Cs/SiO_2	P	13.3	37.0	4.0	42.5	15.5
Co/SiO_2	A	5.9	31.0	57.0	3.5	8.5
Co/SiO_2	P	20.5	92.5	4.5	*t*	3.0

[a] CH_4 = 220 torr, O_2 = 25 torr, W = 1.5 g, F = 30 ml min^{-1}, T = 1048 K, TCM = 1.1 ± 0.1 torr when present; conversion and selectivities are at near steady state; A and P=absent and present, respectively.

larly strong effects due to the addition of TCM. With the catalyst containing 1.0 wt% Li and 5.0 wt% Ba at 1048 K the conversion increased from 5 to 21% on addition of a partial pressure of TCM equal to 1.2 torr, the CO and CO_2 selectivities decreased from 67 to 17% and 20 to 4%, respectively, and the C_{2+} selectivity increased from 14 to 80%.

Alkali metal oxides supported on silica show similar effects resulting from the addition of small quantities of TCM to the feedstream [35,36]. However, the most significant improvements in conversion and selectivity to C_2 hydrocarbons are found with the oxides of Li and Cs, particularly where the preparations of the former employ LiCl.

Silica-supported alkali-added manganese oxide catalysts are also promoted by TCM, particularly those with Na or K, with which 20–22% yield and 75–80% selectivities to C_2 hydrocarbons were obtained [36,37].

The effect of changing the cation while retaining the anion of the catalyst has been studied with the oxidative coupling of methane [38–40]. With phosphate catalysts a marked dependence on the nature of the cation is evident, both with and without TCM. However, with these catalysts the introduction of TCM is generally only marginally beneficial and, in some cases, even detrimental.

The conversions and selectivities obtained with sulfates can be related to the electronegativities of the cations which would be expected if the catalyst serves principally as a methane activator [41,42].

The results of studies of the oxidative coupling of methane on the rare-earth oxides show some unexpected differences [43–45]. With the oxides of La, Pr and Sm, addition of a small quantity of TCM to the reactant stream improves the conversions and C_{2+} selectivities. In particular, with the oxide of Pr, which produces predominantly carbon oxides from methane, addition of TCM considerably enhances the selectivity to C_2H_4. However, with the oxide of Ce, C_{2+} selectivities are vanishingly small regardless of the presence of TCM.

X-ray diffraction patterns of the rare-earth oxides after the CH_4 reaction with TCM present in the feedstream show that oxychlorides have formed in the La, Pr and Sm oxides but not with Ce [43–45]. The oxychlorides prepared by independent methods yield results in the methane reaction similar to those from the oxides in the presence of TCM.

Detailed studies of a series of binary alkali metal and alkaline earths supported on silica [46] showed the Na/Sr [47] and Li/Sr [48] catalysts to be superior to the remaining solids in the series. Additionally, the 10% Li/10% Sr/SiO_2 catalyst produced C_{2+} yields up to 29% and was stable for times on-stream up to at least 600 h. The superior properties were attributed to the formation of strontium and lithium silicates which are resistant to high temperatures and destructive gaseous environments.

Magnesium oxide, sulfate and phosphate show significant differences in the effects resulting from TCM, the changes with phosphate and sulfate being considerably larger than those with oxide [49–51]. Doping with alkali metals accentuated the effect of TCM on the phosphate and sulphate but these were also dependent on the nature of the alkali metal. That the magnitude of the changes produced on addition of TCM is dependent on the nature and composition of the catalyst has also been demonstrated with alkaline earth catalysts [50].

The effect of the introduction of TCM to the feedstream in the oxidative coupling of methane on alkaline earth catalysts supported on silica has been shown to be related to the ionic radius of the cation [52]. In the absence of TCM, silica-supported alkaline earth catalysts are relatively ineffective in the conversion of methane. The addition of TCM in the feedstream generally increases both conversion and selectivity with the latter, except for Mg, increasing as well with time-on-stream, demonstrating the cumulative effect of the addition of TCM and providing additional evidence for the retentive interaction between the catalyst and the feedstream halogen compound (Figs. 3 and 4).

It should be noted that regardless of the catalyst under investigation, the increase in selectivity to the C_2 hydrocarbons is gained primarily at the expense of decrease in the selectivity to CO, while that to CO_2 remains relatively unchanged.

The effect of changes in the alkaline earth can be seen in Figs. 3 and 4. As the radius of the cation increases, the enhancement of both the conversion and C_2 selectivities produced by the TCM increases. Such observations provide further evidence that the benefits derived from the addition of TCM arrive predominantly from the modification of the catalyst and its surface. Further, the aforementioned correlations suggest that the effectiveness of the added surface chloride is inversely related to the polarizing power of the alkaline earth cation. Magnesium ions with relatively high polarizing capabilities as compared with those of barium, for example, are less able to benefit from the introduction of the chloride than alkaline earth ions with lower polarizing abilities.

As noted earlier in this report, the catalytic properties of the oxides and sulphates in the conversion of methane with or without TCM are markedly different. In general, in the absence of TCM the conversion of methane is higher on the oxides than on the sulphates, possibly due to the basic sites on the former in contrast to the acid sites on the latter [41,49–51].

With magnesium as the cation, the conversion of methane increases on addition of TCM to the feedstream with the sulphate but not the oxide (Fig. 5) [53], while the selectivity increases with both catalysts. Studies of the oxidative coupling of methane with binary MgO–$MgSO_4$ catalysts of various compositions supplemented by data from XPS measurements show that the beneficial effects of TCM result, at least in this system, from two sources: the addition of chlorine to the surface (as seen from the XPS results) and the promotion (by TCM) of the conversion of sulphate to oxide.

The activation of methane has been attributed to basic sites which are present on many of the catalysts

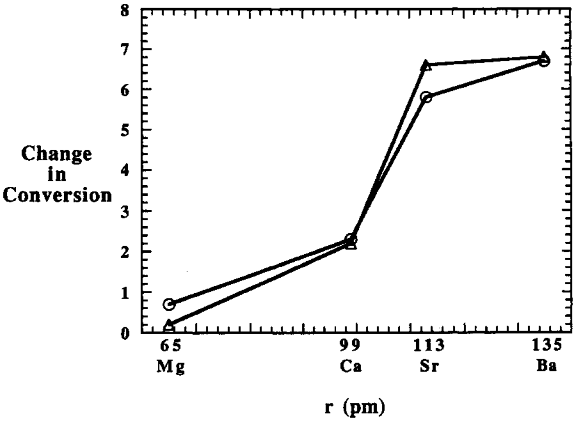

Fig. 3. Increases in conversion of methane on addition of TCM to the feedstream with alkaline earth/SiO_2 catalysts. Radius of alkaline earth cation=r. W=1.5 g, F=30 ml min^{-1}, T=1048 K, $P(CH_4)$=215 torr, $P(O_2)$=30–32 torr, remainder He. Catalyst prepared from acetate of the alkaline earth. (△) 0.5 h on-stream; (○) 3–3.5 h on-stream.

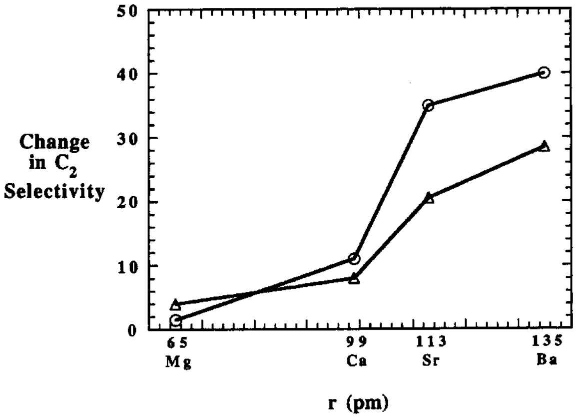

Fig. 4. Increases in selectivity to C_2 hydrocarbons on addition of TCM to the feedstream with alkaline earth/SiO_2 catalysts. Radius of alkaline earth cation=r. Conditions as in Fig. 3 but with P(TCM)=1.1 torr, remainder He.

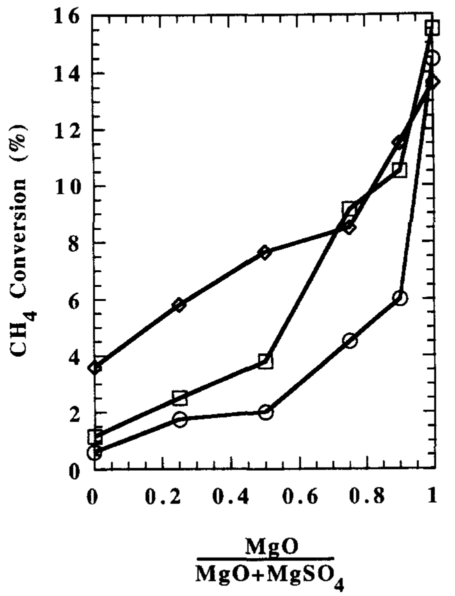

Fig. 5. The effect of CCl_4 on the conversion of methane on MgO–$MgSO_4$ catalysts at 1048 K. Reaction conditions: CH_4=28.7 kPa, O_2=4.1 kPa, and CCl_4=0, 0.17 or 0.34 kPa diluted with He. Total flow rate=30 ml min^{-1}. Weight of catalyst=0.7 g. (○) P(TCM)=0 kPa; (□) P(TCM)=0.17 kPa; (◇) P(TCM)=0.34 kPa.

which are active in the methane conversion process [1–3]. Hydroxyapatites [$Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}$ ($0 \leq z \leq 1$)] are bifunctional catalysts capable of displaying acid or basic properties, depending on their composition [54–59]. On the stoichiometric apatite ($z = 0$) methane is oxidized primarily to CO_2, while on the nonstoichiometric form ($z \neq 0$) partial oxidation to CO is observed [60–64].

The introduction of TCM to the methane feedstream has been shown, with the stoichiometric hydroxyapatite, to produce an increased selectivity to CO and a decreased conversion of methane with increasing time-on-stream, while the C_2 selectivity changed relatively little on addition of TCM [65–67]. For example, in the presence of 0.17 kPa TCM, the selectivity to CO increased, after 6 h, to 71% as compared with 37% in the absence of TCM. XPS analyses show that the surface is chlorided in the presence of TCM with the Cl/Ca ratio increasing from 0.15 after 0.5 h time-on-stream to 0.35 after 6 h, while the bulk Cl/Ca composition concomitantly increased from 0.007 to 0.143. In the bulk phase, the composition of the chlorided species corresponds to chlorapatite [$Ca_{10}(PO_4)_6Cl_2$] as shown from XRD analysis. These observations suggest that the introduction of chlorine suppresses the further oxidation of CO to CO_2.

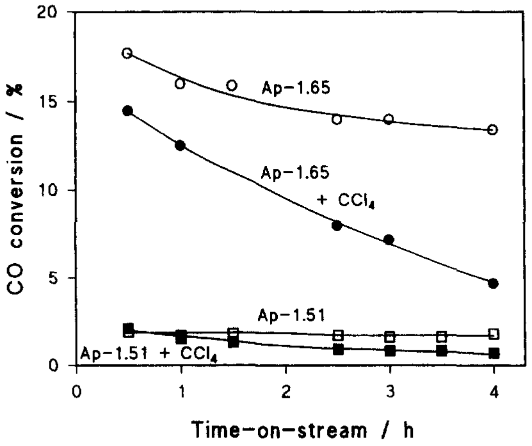

Fig. 6. Oxidation of CO with and without CCl_4 over hydroxyapatites of Ca/P 1.51 and 1.65 at 873 K.

Further evidence for the inhibition of oxidation processes in the presence of TCM can be obtained from studies of the oxidation of CO on hydroxyapatite [68]. CO is converted to CO_2 on both the stoichiometric ($Ca/P = 1.65$) and nonstoichiometric ($Ca/P = 1.51$) calcium hydroxyapatites, with the conversion on the former, in the absence of TCM, being a factor of 10 higher than that on the latter (Fig. 6). Addition of TCM to the feedstream resulted in a lower conversion with the 1.65 HAp and a continuing decrease with time-on-stream while little effect was evidenced by 1.51 HAp. The XPS data show that the surface of the catalyst is chlorinated in the presence of TCM, and XRD patterns demonstrate that at least a portion of HAp is converted to chlorapatite. Evidently, the chlorided catalyst suppresses the further oxidation of CO.

The aforementioned observations clearly demonstrate that the presence of TCM in the feedstream in either the partial oxidation or oxidative coupling of methane influences the process, generally in a beneficial manner. It is also evident from both XPS and XRD analyses, as well as from experiments in which catalysts were pretreated with TCM prior to use in the absence of methane, that TCM introduced to the gas phase initially interacts with the solid catalyst, not surprisingly, at its surface. At least at temperatures where the heterogeneous reaction is dominant, the effects of the introduction of TCM are predominantly produced at the chloride surface rather than the TCM in the gas phase.

The nature of the chlorine in the catalyst, particularly that at the surface, is ambiguous. That it exists as chloride ion appears certain. However, XPS analyses show that the quantities of Cl^- in the surface region are relatively small. It is possible that Cl^- is not uniformly distributed in the surface but exists in clusters from which diffusion into the bulk takes place, in some instances to form readily identifiable compounds such as the chlorapatite. Although stoichiometric compounds may be formed in the interface, the localized distribution of Cl^- renders the identification of these difficult, it not impossible, with the systems studied to date.

The results from both the partial oxidation and oxidative coupling experiments show that the further conversion of the primary products is suppressed by the chlorided surfaces. Thus, the selectivities to C_2H_4 and CO are increased, while those to C_2H_6 and CO_2 are decreased with the overall selectivity to species containing two or more carbon atoms generally increasing as does the conversion. Since it is widely held that the catalyst serves as a provider of sites at which methyl radicals are formed, it is tempting to assume that the presence of Cl^- in the interface alters this process. As has been suggested by others [1–3], methylperoxy species may form, exist in the gas phase, and serve as intermediates for both desirable and undesirable products.

The surface chloride ions may act directly or indirectly; in the former case serving as sites for the C–H bond dissociation, in the latter perturbing the electron densities of the surface oxygen atoms which themselves act as the sites. Since the XPS analyses suggest that relatively small numbers of chloride ions are implanted on the surface, the surface Cl^- may be acting indirectly. However, pretreatment experiments show that the surface Cl^- species are consumed during the methane conversion and must be continually replenished by TCM added to the feedstream. This strongly suggests the direct participation of the surface Cl^- in the process. The direct interaction of CH_4 and surface Cl^- may lead to the formation of CH_3Cl, which on decomposition produces an enhanced selectivity to C_2H_4 while methyl radicals remain in the gas phase to produce carbon oxides.

Acknowledgements

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