Inhibition of CO oxidation on hydroxyapatite by tetrachloromethane

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The introduction of tetrachloromethane (TCM) into the feedstream of CO and O_2 inhibits the formation of CO_2 on hydroxyapatite. TCM interacts with the surface of hydroxyapatite to form its chlorinated analogue, chlorapatite, which suppresses the oxidation of CO to CO_2. Thus, in the oxidative coupling of methane the beneficial effects of the addition of TCM to the feedstream result, at least in part, from the suppression of the further oxidation of CO.

Keywords: oxidation; hydroxyapatite; carbon monoxide; inhibition; tetrachloromethane

1. Introduction

In 1988 what is believed to be the first report of the effects of the introduction of tetrachloromethane (TCM) into the feedstream for the partial oxidation of methane was published [1–3]. Subsequently, the oxidative coupling of methane (OCM) in the presence and absence of TCM has been studied on a wide variety of supported and unsupported catalysts [4]. In the OCM process the introduction of TCM generally has the effect of increasing the selectivity to the desired products, C_2H_6 and C_2H_4, but particularly to C_2H_4, as well as increasing the conversion. Perhaps less important from a practical viewpoint, but equally interesting, is the observation that concomitantly with the aforementioned, the selectivities to CO are increased while those to CO_2 are decreased with many of the catalysts.

Calcium hydroxyapatite $[Ca_{10-z}(PO_4)_{6-z}(HPO_4)_z(OH)_{2-z}, 0 \leqslant z \leqslant 1]$ is an inorganic solid of hexagonal crystalline structure which is found in bone tissue. The space group and unit cell dimensions are P6 3/m and $a = b = 9.432$, $c = 6.881$, respectively [5]. The hydroxyl groups are surrounded and stabilized by the calcium ions and the O–H bonds are parallel with the C axes [6]. The hydroxyl groups can be substituted by halogens while transition metal cations can be introduced by ion exchange [7–11]. Hydroxyapatites of various elemental compositions have been shown to be active in a variety of catalytic processes [12–20].

In view of the aforementioned observations it appeared useful to examine the oxidation of CO in the presence and absence of TCM on hydroxyapatite of various stoichiometries which have been examined in this laboratory for their catalytic properties in the partial oxidation of methane to carbon monoxide and hydrogen [20].

2. Experimental

Calcium hydroxyapatites were prepared from $Ca(NO_3)_2 \cdot 4H_2O$ (BDH, AnalaR) and $(NH_4)_2HPO_4$ (BDH, AnalaR) according to the method described in ref. [21]. The resulting solids were heated in air at 500°C for 3 h after drying at 120°C for 18 h. The Ca/P molar ratio of the prepared hydroxyapatite was determined by analyzing the concentrations of Ca^{2+} and PO_4^{3-} ions in the solution remaining from the synthesis by ion chromatography (Dionex 4500i). The reaction was performed in a conventional fixed-bed continuous flow reactor operated under atmospheric pressure. The sample (0.2 g) was sandwiched with quartz wool plugs in a quartz-tube reactor. The reactants (CO, 22 kPa; O_2, 11 kPa; CCl_4, 0.2 kPa if present) were diluted with helium gas and the total flow rate was 1.8 $dm^3\ h^{-1}$. After the sample was pretreated under helium flow (1 $dm^3\ h^{-1}$) at 600°C for 1 h, the reaction was carried out at 600°C. The reactants and products were analyzed with an on-stream gas chromatograph (HP5880) equipped with a TCD. Two columns, one a Porapak T (3.0 m), the other a

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Molecular Sieve 5A (0.4 m) were employed in the analyses.

Powder X-ray diffraction patterns (XRD) for the samples were recorded on a Rigaku Rotaflex 20 diffractometer using nickel-filtered Cu Kα radiation. Patterns were recorded over the range $2\theta = 5$–$60°$.

XPS analyses were carried out using a Shimadzu ESCA-750 spectrometer, followed by argon-ion etching of the sample at 2 kV and re-analysis. Charge correction of the XPS data was accomplished by assuming that the binding energy of the C 1s peak was at 284.6 eV.

Table 1
Surface areas of hydroxyapatite samples

Sample	Surface area (m^2/g)		
	after pretreatment	after reaction [a]	
		TCM absent	TCM present
Ap-1.51	59.2	55.1	42.9
Ap-1.65	49.4	38.2	33.2

[a] 4 h time-on-stream.

3. Results and discussion

Carbon monoxide is converted to carbon dioxide on both the stoichiometric and nonstoichiometric calcium hydroxyapatite (fig. 1). In the absence of TCM the conversion on Ap-1.65 is substantially higher than that on Ap-1.51, but the conversion remains relatively constant with time-on-stream on the latter, in contrast with the decrease from approximately 18 to 14% in 4 h, with the former catalyst.

On addition of TCM (0.2 kPa) to the CO/O_2 reactant stream the conversion of CO on Ap-1.65 decreased while the rate of decrease of the conversion with time-on-stream increased. Initially, on Ap-1.51, the addition of TCM had little or no effect on the conversion of CO, but with increasing time-on-stream the conversion decreased somewhat.

The BET surface area of the Ap-1.51 sample was approximately 20% higher than that of Ap-1.65 (table 1). After 4 h time-on-stream in the absence of TCM the area of the former sample decreased by approximately 7% while the latter fell by more than 20%. In the presence of TCM the corresponding decreases were approximately 27 and 32%, respectively. It is of interest to note that, in the presence of TCM the losses in surface areas were 16.3 and 16.2 m^2/g, respectively. Although the source of the decreases in surface area is not known, the decreases in conversion with time-on-stream can presumably be attributed, at least in part, to the reduction in surface area during the reaction.

XRD patterns for the two samples after use in the CO oxidation reaction without TCM show similar patterns (fig. 2). After use in the presence of TCM the two samples again show similar patterns but features which are dissimilar to those obtained after use in the absence of TCM. The patterns of the former samples show evidence of the structural change of a portion of the hydroxyapatite to the corresponding chlorinated form, chlorapatite, although peaks attributable to hydroxyapatite remain [22,23].

To investigate the interaction of TCM with the catalyst in the CO oxidation process, the two hydroxyapatite samples were each subjected to a flow of oxygen (11 kPa) and TCM (0.1 kPa) in helium (total flow rate, 1.8 $dm^3\ h^{-1}$) at 600°C for 4 h. A quantity of carbon diox-

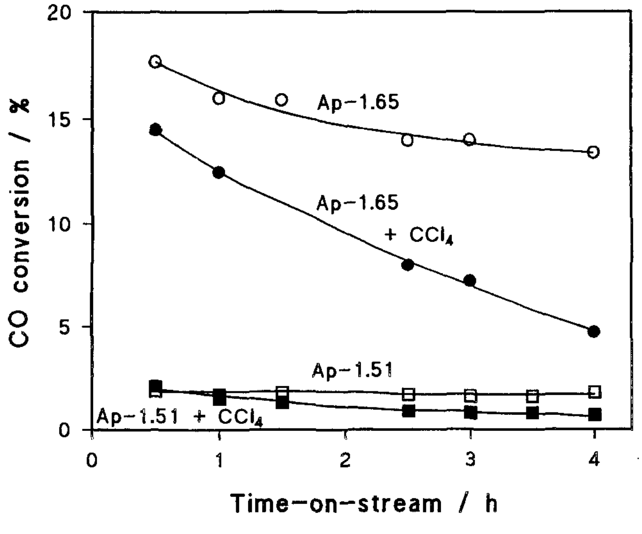

Fig. 1. Oxidation of carbon monoxide with and without carbon tetrachloride over hydroxyapatites at 600°C.

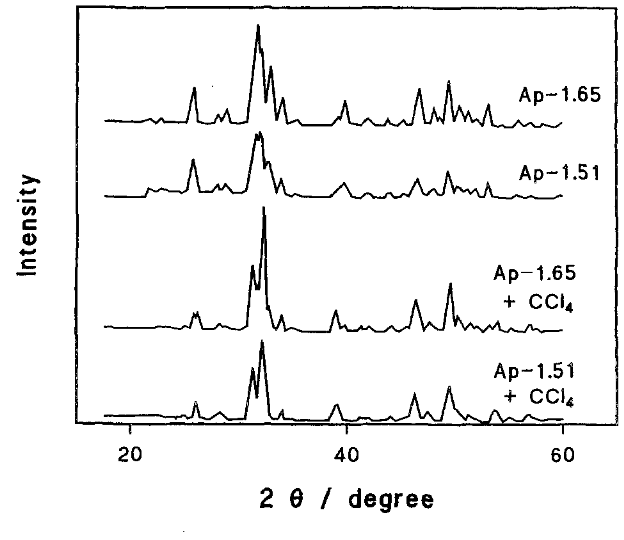

Fig. 2. XRD patterns for hydroxyapatite samples taken from reactor after the reactions with and without carbon tetrachloride.

ide, stoichiometrically equivalent to that of TCM fed, was produced, implying that TCM is oxidized by the catalyst. Subsequent to the aforementioned pretreatment in the absence of CO, the oxidation of carbon monoxide under the previously noted conditions was carried out in the absence of TCM. The conversions of carbon monoxide were 0.5 and 2.7% for Ap-1.51 and Ap-1.65, respectively (time-on-stream, 0.5 h). The XRD patterns for the two samples, pretreated in O_2 and TCM prior to their use in a reaction, were identical with that of the chlorinated apatite [$Ca_{10}(PO_4)_6Cl_2$] [23]. Thus, pretreatment in O_2 and TCM converts hydroxyapatite to chlorapatite and the extent of this conversion and the consequent activity of hydroxyapatite in oxidation processes can be monitored by measurement of the loss of CO or the production of CO_2.

XPS analyses of the hydroxyapatite and (O_2 + TCM) pretreated samples produced binding energies for the latter (table 2) in agreement with those obtained for the former, except for Cl. The atomic ratios of the surface elements were calculated from the peak areas of the bands using atomic sensitivity factors [24] (table 2). The relatively small values for OH/P obtained from the stoichiometry of hydroxyapatite as shown in table 2 suggest that most of the OH groups in the pretreated hydroxyapatites have been exchanged by chlorine atoms. Since argon ion etching of the Ap-1.65 sample after the (O_2 + TCM) pretreatment produced relatively little changes in the atomic ratios (fig. 3) migration of chlorine from the surface into the bulk is apparently as rapid, if not more so, than the surface deposition process.

The introduction of TCM into the feedstream in the CO oxidation process evidently converts, at least partially, the hydroxyapatite into its chlorinated analogue, chlorapatite, which suppresses the oxidation of CO to CO_2. Thus, in the oxidative coupling of methane the beneficial addition of TCM results, at least in part, from the suppression of the further oxidation of CO and, by extrapolation, that of the desired primary products ethylene and ethane.

Table 2

Results of XPS analyses of hydroxyapatite samples pretreated in O_2 + TCM

	Binding energy (eV)			
P_{2p}	132.9 [a]			
Cl_{2p}	198.7 [b]			
$Ca_{2p_{3/2}}$	347.3 [c]			
O_{1s}	531.3 [b]			
Sample	Atomic ratio			
	Ca/P	Cl/P	O/P	OH/P [a]
Ap-1.51	1.6	0.2	3.0	0.18
Ap-1.65	1.8	0.3	3.0	0.32

[a] ±0.3 eV.

[b] ±0.2 eV.

[c] ±0.1 eV.

[d] Calculated from stoichiometric formula of hydroxyapatite.

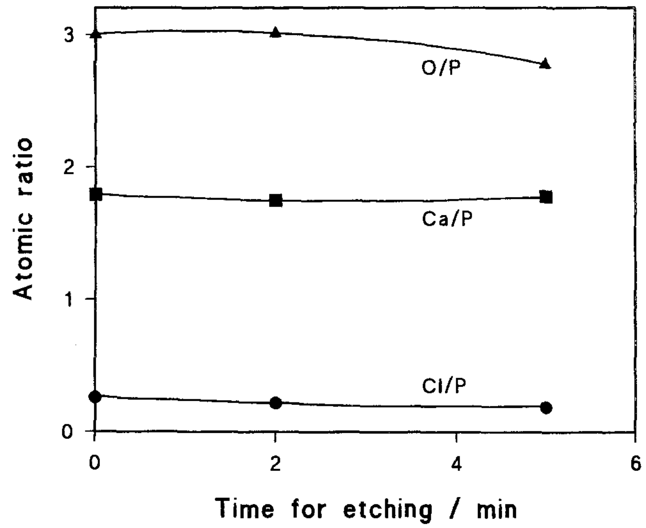

Fig. 3. Atomic ratios of the components in chlorinated apatite (Ap-1.65) determined from XPS.

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