An apparent ensemble effect in the oxidative coupling of methane on hydroxyapatites with incorporated lead

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The introduction of small quantities of lead into calcium hydroxyapatite catalysts produces marked increases in the selectivity to C_{2+} hydrocarbons, while the conversion of methane remains relatively constant. Small surface concentrations of lead are sufficient to achieve C_{2+} selectivities of 80 and 90%, with oxygen and nitrous oxide, respectively, in contrast with 18 and 46%, respectively, obtained in the absence of lead. Since surface concentration of lead species sufficient to stabilize pairs of methyl radicals in close proximity to each other would be expected to facilitate the formation of C_2 hydrocarbons, an ensemble effect appears to be extant.

Keywords: oxidative coupling; methane; ensemble effect; hydroxyapatites; lead

1. Introduction

The last decade has witnessed great efforts by scientists from many countries to convert methane to value added products [1]. While the yields of ethylene and ethane from the oxidative coupling process have been considered as less than sufficient for large scale operation of this process [2], considerable advances have been achieved in understanding the mechanism of the process and the principal source of the relatively low yields [3], that is, the degradation of the desirable products. Although the earlier focus is shifting to the problem of reducing the further oxidation of ethane and ethylene [3], the mechanistic aspects of the process and particu-

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larly the participation and relevant properties of active and selective catalysts continue to be active area of research.

The advantages of the study of catalysts capable of structure retention during changes in composition are well known. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is an inorganic solid for which a number of elemental substitutions are possible [4–9] while retaining the semiquantitative nature of the structure. Although the substitution of calcium by lead in the structure of hydroxyapatite produces an increase in the size of the unit cell [8,9], for compositions of less than 50% lead atoms, the latter atoms apparently occupy only one of two types of sites available in the solid.

The present work examines the effect on the oxidative coupling of methane of changes in the relative amounts of calcium and lead in the hydroxyapatite structure. Since lead–calcium hydroxyapatite can be synthesized from aqueous solutions of calcium, lead and phosphate [9] with retention of the hydroxyapatite structure and with both lead and calcium ions as intrinsic units of the crystallographic structure, the lead ions can be taken as well dispersed within the sample. In the present report results are presented which provide evidence for the existence of an ensemble effect in the oxidative coupling of methane. Although structure sensitivity has been demonstrated in the oxidation of methanol on MoO_3, for example in ref. [10], and ensemble effects are clearly evident in the dehydrogenation of cyclohexane and the hydrogenolysis of ethane on copper–nickel surfaces [11], the present authors are not aware of work suggesting the possibility of an ensemble effect in the oxidative coupling of methane.

2. Experimental

Calcium and lead–calcium hydroxyapatites were prepared from $NaHPO_4 \cdot 12H_2O$ (BDH, AnalaR), $Ca(CH_3COO)_2 \cdot H_2O$ (Baker, Analyzed), and $Pb(CH_3COO)_2 \cdot 3H_2O$ (BDH, ACS) according to the method described in ref. [9]. The resulting solids were heated in air at 500°C for 3 h. The chemical compositions of the prepared samples were determined by atomic absorption spectrometry for cations and by ion chromatography for anions. Formation of the hydroxyapatite structure was confirmed by recording the X-ray diffraction (XRD) patterns for these samples [12]. No peaks other than those of hydroxyapatite were observed.

Methane conversion was performed in a conventional fixed-bed continuous flow reactor operated under atmospheric pressure. The reactor consisted of a quartz tube of 8 mm i.d. and 35 mm in length sealed at each end to 4 mm i.d. quartz tubes. The catalyst was sandwiched with quartz wool plugs, whose contribution to the reaction was negligible. The reactants were diluted with helium gas and the total flow rate was 0.9 $dm^3\ h^{-1}$. Catalysts (0.05–0.30 g) were preheated in the flow of oxygen (6 kPa) diluted with helium (total flow rate, 0.6 $dm^3\ h^{-1}$) at 700°C for 1 h. The reactants and products were analyzed with an on-stream gas chromatograph equipped with a TCD. Two columns, one Porapak T (5.4 m) or HeySep Dip

(5.4 m), the other Molecular Sieve 5A (0.4 m) were employed in the analyses. The conversion and selectivities were calculated from the amounts of reaction products formed (carbon atom basis) as determined by the GC analysis.

The surface areas of the catalysts were measured by the conventional BET nitrogen adsorption method.

Surface analyses by XPS were carried out using a Shimadzu ESCA-1000AX spectrometer (table 1). The samples were mounted on a sample holder in air and set into the spectrometer. After measurement argon-ion etching of the sample was carried out (2 kV, 1 min), and the spectra were measured again after etching. Charge correction of the XPS data was accomplished by assuming that the binding energy of the C 1s peak was at 284.6 eV.

3. Results and discussion

With either nitrous oxide or oxygen as oxidant the principal products are ethane, ethylene, carbon dioxide and carbon monoxide. In the absence of lead, that is with calcium hydroxyapatite, and nitrous oxide as oxidant the conversion of methane is only 3% and the selectivities to C_{2+}, CO and CO_2 are 35, 25 and 40%, respectively (fig. 1). As lead is introduced to the catalyst and the surface concentration as obtained from the XPS data increases, the C_{2+} selectivities increase sharply while the conversion of methane remains almost constant up to a surface lead concentration of approximately 2% and increases to 9–10% for larger surface concentrations of lead. Concomitantly the selectivities to CO and CO_2 show precipitous decreases. The selectivity to C_{2+} hydrocarbons has reached a virtually constant value of approximately 90% for surface concentrations of lead as small as 3%, although both the conversions of N_2O and of CH_4 decrease for values of the surface concentrations of lead higher than 5%.

Somewhat different results are obtained with calcium hydroxyapatite and oxygen as the oxidant (fig. 2). The conversion of CH_4 is significantly higher, at 8%, than observed with N_2O. The selectivities to C_{2+}, CO and CO_2 are 45, 57 and 10%, the first two being significantly higher than found with N_2O. On addition of lead

Table 1
Bulk and surface concentrations of lead

Sample	Bulk molar ratio Pb/(Pb + Ca)	Surface concentration Pb (mol%)
1	0	0
2	0.010	2
3	0.022	3
4	0.063	5
5	0.106	6
6	0.300	8

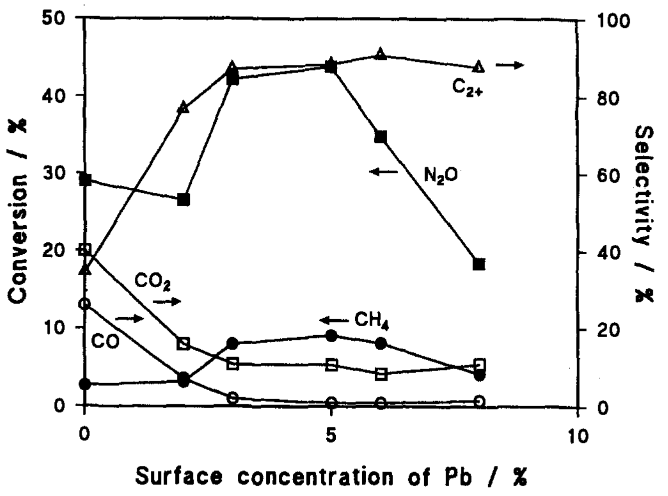

Fig. 1. Oxidative coupling of methane with nitrous oxide over lead–calcium hydroxyapatite. Reaction conditions: reaction temperature, 700°C; catalyst, 0.30 g; partial pressure of methane, 29 kPa; nitrous oxide, 7 kPa; total flow rate, 0.9 dm^3 h^{-1}; time-on-stream, 3 h.

the selectivity to C_{2+} hydrocarbons, as with N_2O, rises sharply, although the maximum value is lower than observed with N_2O, while the conversion of CH_4 shows a small increase. Although the selectivity to CO falls on addition of lead that to CO_2 increases. However, as with N_2O nearly constant values of the C_{2+} selectivity and conversion of CH_4 are achieved for approximately 5% of lead in the surface region.

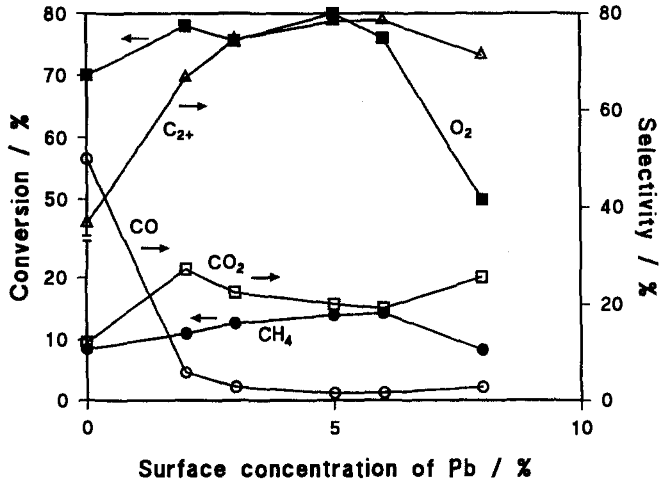

Fig. 2. Oxidative coupling of methane with dioxygen over lead–calcium hydroxyapatite. Reaction conditions: reaction temperature, 700°C; catalyst, 0.30 g; partial pressure of methane, 29 kPa; dioxygen, 4 kPa; total flow rate, 0.9 dm^3 h^{-1}; time-on-stream, 3 h.

A number of recent reports of the use of lead oxide in the conversion of methane have attributed the activity and selectivity to the lattice oxygen [13], the magnetoplumbite phase [14], isolated sites of PbO [15] and lead aluminate [16], the latter with a lead oxide/alumina catalyst. In the present work no peaks attributable to lead oxides were observed in the X-ray diffraction patterns.

The present work shows that the introduction of lead into calcium hydroxyapatite significantly improves the catalytic properties in the conversion of methane. However it is clear that the conversions and selectivities are dependent on both the oxidant and the presence of lead. The apparent absence of lead oxide from the present catalysts and the dissimilarity of the results with the two oxidants [13] suggest that the mechanism on the lead–calcium hydroxyapatites differs from that on the former catalysts.

The oxidative coupling of methane is generally believed to involve the formation of methyl radicals [1]. The relatively low conversions of methane obtained with calcium hydroxyapatite, where lead is absent, suggest that lead plays an active role in the production of these radicals. Further, the sharp increase in selectivity to C_{2+} hydrocarbons as the surface concentration of lead increases up to 2% suggests that lead is an important factor in the coupling of these radicals while the concomitant absence of change in the conversion of methane indicates that lead contained on the surface of the catalyst is not significantly contributing to the production of methyl radicals. With calcium hydroxyapatite, in the absence of lead, the relatively low C_{2+} selectivity may result from the reaction between methyl radicals and an oxidant, apparently in preference to the coupling process.

Although the mechanism of the conversion of methane is complex, two disparate processes can be visualized as important, one leading to the valued products, the other to undesirable species. The coupling of methyl radicals will produce the hydrocarbons while the oxidation of the methyl radicals will ultimately produce CO and CO_2. Presumably the former process will occur, in preference to the latter, only under those circumstances in which methyl radicals are in close proximity to each other. Since the stabilization of methyl radicals is expected to be facilitated by the lead present on the surface [17] of the hydroxyapatite catalysts, the presence of a sufficient concentration of lead to permit two stabilized methyl radicals to be found adjacent to each other should presumably facilitate the formation of ethane, rather than the oxygenated species which would result if either a gas phase or stabilized methyl radical encounters an oxidizing agent. The existence of stabilized free radicals in sufficiently close proximity to each other to permit coupling presumably is dependent on a minimum concentration of the stabilizing centres, in this case lead. This ensemble effect will achieve a maximum when the surface concentration of lead is sufficiently high to optimize the pairwise reaction of methyl radicals. Consequently the C_{2+} selectivities should remain constant for higher surface concentrations of lead while the sites for production of the methyl radicals will diminish as will the conversion of methane.

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