Catalytic oxidative coupling of methane over hydroxyapatite modified with lead

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Hydroxyapatite modified with lead catalyzes the oxidative dehydrogenation of methane with high selectivity to C_2 compounds at reaction temperatures as low as 700°C. The activity is stabilized after reduction in the surface area of the catalyst during the reaction.

Keywords: Methane; conversion; oxidative dehydrogenation; oxidative coupling; hydroxyapatite

1. Introduction

Although a considerable amount of research has been concerned with the oxidative coupling of methane to ethane and ethylene, the conversions and selectivities so far obtained are lower than desirable [1]. Lead oxide supported on basic materials such as alumina and magnesia has been shown to be an effective catalyst for the reaction [2–12]. For example, 71.9% selectivity to C_2 compounds with 13.2% methane conversion was obtained with PbO/MgO at 750°C from 13 kPa of methane and 1.4 kPa of oxygen [10]. However, under reaction conditions the catalyst has been shown to lose lead [13]. Nonvolatile lead salts such as lead phosphate and lead sulfate catalyze the oxidative coupling process reasonably well, but selectivity to the C_2 compounds is relatively low, i.e. 51 and 63% with 9 and 8% conversion of methane, respectively at 740°C from 66 kPa of methane and 8 kPa of oxygen [14].

Hydroxyapatites ($Ca_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}$; $0 \leqslant z \leqslant 1$), especially the stoichiometric form ($z = 0$), often function as base catalysts [15–20] and have a cation exchanging capacity [21,22]. Calcium ions may be replaced with lead ions in the solids [22,23] and are expected to be implanted in the structure [23].

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Hence, this material should be a suitable support for the lead catalyst employed in the oxidative coupling of methane.

In this work it will be shown that hydroxyapatite modified with lead catalyzes the oxidative coupling of methane with high selectivity to C_2 compounds at reaction temperatures as low as 700°C. The activity is stabilized after reduction in the surface area of the catalyst during the reaction.

2. Experimental

Stoichiometric and nonstoichiometric 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. [24]. The resulting solid was heated in air at 500°C for 3 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 remaining solution from the synthesis by ion chromatography. The values for the samples ($Ap_{1.65}$ and $Ap_{1.51}$) are given in table 1. Formation of hydroxyapatite was confirmed by recording the X-ray diffraction (XRD) patterns for these samples [25]. Lead cation was doped on the hydroxyapatite by stirring the apatite sample (2.0 g) in 0.20 dm^3 of aqueous solution of lead nitrate (BDH AnalaR) at room temperature, usually for 2 h. After washing with water, the sample was heated at 500°C for 1 h. The chemical composition of the sample was determined by analyzing the concentrations of Pb^{2+} and Ca^{2+} ions in the filtrate by atomic absorption spectrometry (see table 1). No dissolving of PO_4^{3-} was observed in this process. The sample, $Pb_{15}Ap_{1.65}$, was prepared from $Ap_{1.65}$ with 50 mM solution of lead nitrate while $Pb_{24}Ap_{1.51}$ and $Pb_{25}Ap_{1.51}$ were from $Ap_{1.51}$ with 50 and 75 mM solutions, respectively. The samples, $Pb_{29}Ap_{1.51}$ and $Pb_{45}Ap_{1.51}$ were prepared from $Ap_{1.51}$ with 50 mM solution by stirring for 5 and 17 h, respectively. Surface areas for the samples were calculated by the BET method from nitrogen adsorption isotherms (table 1). The sample of β-tricalcium phosphate (TCP) was prepared from $Ap_{1.51}$ by heating at 1000°C for 2 h.

Table 1
Composition and surface area of hydroxyapatites

Sample	Atomic ratio		Content of Pb (wt%)	BET surface area (m^2 g^{-1})
	Ca/P	Pb/P		
$Ap_{1.65}$	1.65			53.6
$Ap_{1.51}$	1.51			71.7
$Pb_{15}Ap_{1.65}$	1.52	0.14	15	49.0
$Pb_{24}Ap_{1.51}$	1.32	0.23	24	54.7
$Pb_{25}Ap_{1.51}$	1.32	0.25	25	51.4
$Pb_{29}Ap_{1.51}$	1.26	0.30	29	48.4
$Pb_{45}Ap_{1.51}$	1.05	0.56	45	37.5

By recording its XRD pattern, it was confirmed that the apatite structure of $Ap_{1.51}$ was almost perfectly transformed into that of β-tricalcium phosphate. Lead oxide supported on magnesium oxide (20 wt% PbO/MgO) or on β-tricalcium phosphate (20 wt% PbO/TCP) was prepared by impregnation of lead nitrate on magnesium oxide (Fisher Scientific Company) or TCP, respectively. Both samples were heated in air at 500°C for 5 h after the impregnation.

Methane conversion was performed in a conventional flow quartz reactor (8 mm i.d.) at 700°C. The reactants (CH_4, 29 kPa; O_2, 2–6 kPa) were diluted with helium gas and the total flow rate was 0.9 $dm^3\ h^{-1}$. Catalysts were pretreated in the flow without methane (O_2, 6 kPa; 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 with two columns, one Porapak T (5.4 m) the other Molecular Sieve 5A (0.4 m).

3. Results and discussion

Over hydroxyapatite methane was mainly converted into carbon monoxide and carbon dioxide at 700°C (table 2) while the catalytic activities of the samples slightly decreased with time. Ethane, ethylene, C_3 compounds, formaldehyde, water and a small amount of hydrogen were also detected. Stoichiometric hydroxyapatite ($Ap_{1.65}$) produced higher methane conversion and selectivity to carbon dioxide than the nonstoichiometric form ($Ap_{1.51}$) while the C_{2+} yield was discernibly lower. The surface areas of $Ap_{1.65}$ and $Ap_{1.51}$ after the reaction were 31.4 and 16.9 $m^2\ g^{-1}$, respectively. In order to carry out the reaction at lower oxygen conversion, the amount of the catalyst was reduced. As can be seen in table 2, 0.05 g of $Ap_{1.65}$ produced nearly the same methane and oxygen conversions as found with 0.15 g of $Ap_{1.51}$. Since the surface areas of 0.05 g of $Ap_{1.65}$ and 0.15 g of $Ap_{1.51}$ are calculated as 1.6 and 2.5 m^2, respectively, the surface of the stoichiometric hydroxyapatite is highly active compared with the nonstoichiometric form. The XRD pattern of $Ap_{1.51}$ recorded after the reaction provided evidence for the partial formation of β-tricalcium phosphate ($Ca_3(PO_4)_2$), which is produced when the nonstoichiometric form is heated at high temperature [26,27]. In contrast, the crystalline structure of $Ap_{1.65}$ is preserved throughout the reaction. Since the intensity of the XRD peaks attributed to hydroxyapatite decreased to about 2/3 of that for $Ap_{1.51}$ as prepared, it is estimated that about 1/3 of the hydroxyapatite form in $Ap_{1.51}$ was transformed to β-tricalcium phosphate under the reaction conditions. To evaluate the contribution of β-tricalcium phosphate to the reaction, the methane oxidation with TCP was carried out (see table 2). After the reaction the surface area of TCP was 4.1 $m^2\ g^{-1}$, that is, 1.2 m^2 of TCP produced the methane conversion of 4.4% and selectivities similar to those observed with $Ap_{1.51}$.

Table 2
Methane oxidation over hydroxyapatites and other related compounds at 700°C after 3 h on-stream [a]

Catalyst	CH_4/O_2 ratio [b]	Conversion (%)		Selectivity (%)						C_{2+} yield (%)
		CH_4	O_2	CO	CO_2	H_2CO	C_2H_4	C_2H_6	C_3	
$Ap_{1.65}$	7.2	10.2	97	33.4	59.2	0.2	1.7	5.1	0.4	0.7
$Ap_{1.51}$	6.2	9.0	93	57.7	32.4	0.2	3.6	5.1	1.0	0.9
$Ap_{1.65}$ [c]	6.5	7.1	63	40.0	54.3	0.0	1.2	4.6	0.0	0.4
$Ap_{1.51}$ [d]	6.8	6.7	60	62.3	14.1	5.3	4.6	11.3	2.4	1.2
$Pb_{15}Ap_{1.65}$	6.8	15.6	96	0.1	33.2	0.1	25.3	39.3	2.1	10.4
$Pb_{24}Ap_{1.51}$	7.2	12.1	62	1.7	20.2	0.1	28.5	45.4	4.1	9.4
$Pb_{25}Ap_{1.51}$	6.3	13.8	67	1.6	20.7	0.1	30.9	44.3	2.5	10.7
$Pb_{25}Ap_{1.51}$	13.8	9.8	76	0.8	12.8	0.1	28.8	55.4	2.9	8.5
$Pb_{25}Ap_{1.51}$	4.3	17.1	63	2.6	26.1	0.1	31.3	37.8	2.2	12.2
$Pb_{29}Ap_{1.51}$	7.0	12.5	67	1.9	21.8	0.1	28.6	45.5	2.2	9.5
$Pb_{45}Ap_{1.51}$	7.1	14.2	87	0.4	32.1	0.1	24.5	40.9	2.0	9.6
TCP	6.7	4.4	41	66.0	23.0	3.7	1.3	6.0	0.0	0.3
20 wt% PbO/MgO [c]	6.9	6.7	72	1.1	66.7	0.0	4.9	26.2	1.1	2.2
20 wt% PbO/TCP [c]	7.0	4.5	42	2.6	55.4	0.0	5.7	34.7	1.6	1.9

[a] Reaction conditions: catalyst, 0.30 g; CH_4, 29 kPa; total flow rate, 0.9 $dm^3\ h^{-1}$.

[b] Molar ratio of CH_4/O_2 in the feedstream.

[c] Amount of catalyst, 0.05 g.

[d] Amount of catalyst, 0.15 g.

Hence, β-tricalcium phosphate in $Ap_{1.51}$ will contribute significantly to the reaction.

Modification with lead by ion-exchange produced a remarkable improvement in the catalytic activity of hydroxyapatite. In the case of $Pb_{15}Ap_{1.65}$, the methane conversion and selectivity to C_{2+} compounds were 15.6 and 66.6%, respectively (table 2). Hydrogen was not observed in the products of the reaction over the lead doped hydroxyapatites. The surface area of the catalyst after 3 h on-stream was 18.7 m^2 g^{-1}. In contrast, 0.05 g of 20 wt% PbO/MgO produced a relatively low C_{2+} selectivity (32.1%) at the reaction temperature of 700°C [4]. Since no peaks other than those attributed to hydroxyapatite were observed in the XRD pattern of $Pb_{15}Ap_{1.65}$ recorded after 3 h on-stream, the active sites producing higher selectivities than lead oxide are presumably incorporated in the structure of hydroxyapatite.

The cation-exchanging ability of $Ap_{1.65}$ was lower than that of $Ap_{1.51}$ (cf. $Pb_{15}Ap_{1.65}$ and $Pb_{24}Ap_{1.51}$ in table 1, which were prepared under the same conditions), and consequently the hydroxyapatites containing larger amounts of lead than that contained in $Pb_{15}Ap_{1.65}$ were prepared from $Ap_{1.51}$. Although β-tricalcium phosphate produces low selectivity to C_{2+} compounds, high C_{2+} selectivities (76–78%) were observed with $Pb_{24-29}Ap_{1.51}$ in which the partial formation of β-tricalcium phosphate was confirmed by recording XRD patterns after the reaction (see table 2). From the XRD patterns it is estimated that about 1/3 of apatite structure in $Pb_{24-29}Ap_{1.51}$ was transformed into β-tricalcium phosphate, suggesting that a considerable number of the latter species are on the surface. Thus, β-tricalcium phosphate would be one of the active species on the lead modified apatites while the presence of lead atoms on the surface would increase the selectivity to C_{2+} compounds. The conversion and selectivity depended on the CH_4/O_2 molar ratio of the reactants and somewhat surprisingly the selectivity to C_{2+} compounds was 86.3% at a value of 13.8 with $Pb_{25}Ap_{1.51}$ while the methane conversion was 9.8%. In the initial stages of the reaction the methane conversion increased slightly, then decreased with time up to about 30 h (fig. 1). Subsequently however, the activity became virtually constant. It is noteworthy that the selectivity to ethane increased with time on-stream while that to carbon oxides decreased. After the reaction, no deposit was observed on the walls of the reactor. The surface area of $Pb_{24}Ap_{1.51}$ after the pretreatment (heating at 700°C for 1 h) was 20.6 m^2 g^{-1} while after 3 h and 51 h on-stream the areas were 10.9 and 7.6 m^2 g^{-1}, respectively. Evidently the surface area of the catalyst was subjected to a rapid reduction during the initial stages of the reaction followed by a gradual decrease. This shows that the activity of the catalyst per unit surface area increases significantly during the initial stages while after 3 h on-stream the decrease in the methane conversion appears to be related to the reduction of the surface area. The XRD pattern of $Pb_{24}Ap_{1.51}$ just after the pretreatment showed partial formation of β-tricalcium phosphate in the apatite structure. The patterns of the samples after 3 h and 51

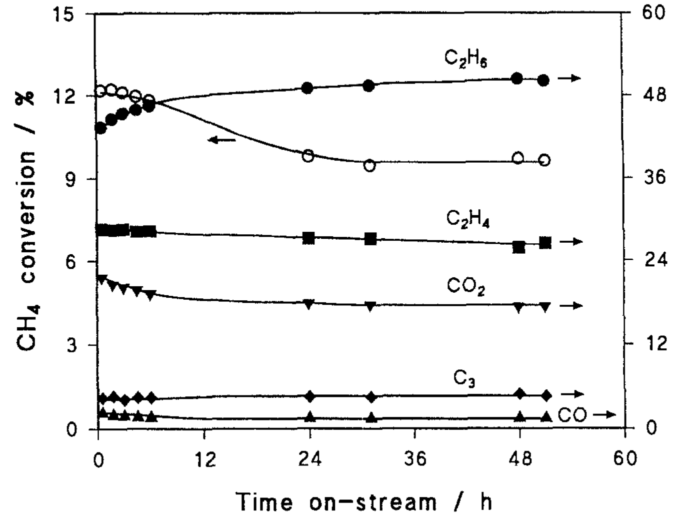

Fig. 1. Time course of oxidative methane coupling over $Pb_{24}Ap_{1.51}$ at 700°C. Reaction conditions: catalyst, 0.30 g; CH_4, 29 kPa; O_2, 4kPa; total flow rate, 0.9 dm^3 h^{-1}.

h on-stream were almost the same as that recorded just after the pretreatment. Hence, the partial formation of β-tricalcium phosphate apparently is not responsible for the decrease in catalytic activity.

It is noteworthy that the number of lead ions in the nonstoichiometric apatite samples is larger than that of the calcium ion exchanged with lead ion. For example, the molar ratio of (Ca + Pb)/P in $Pb_{45}Ap_{1.51}$ is 1.61 and the ratio is apparently larger than that of the original hydroxyapatite ($Ap_{1.51}$) by 0.10. The ratios for other samples are 1.55 for $Pb_{24}Ap_{1.51}$, 1.57 for $Pb_{25}Ap_{1.51}$, and 1.56 for $Pb_{29}Ap_{1.51}$. Since no peaks other than those of hydroxyapatite were observed in the XRD patterns for these three samples, it is apparent that a small number of lead ions are fixed at the calcium-deficient sites in nonstoichiometric hydroxyapatite. The presence of lead oxide phosphate ($5PbO \cdot Pb_3(PO_4)_2$) in the apatite structure was confirmed by recording the XRD pattern of $Pb_{45}Ap_{1.51}$ just after the preparation but new peaks attributed to β-tricalcium phosphate also appeared in the XRD pattern of the sample taken from the reactor while the catalyst produced higher oxygen conversion and lower C_{2+} selectivity compared with $Pb_{24-29}Ap_{1.51}$ (see table 2). Thus the large number of lead ions in these sites presumably result in the formation of lead oxide phosphate. The selectivity to C_{2+} compounds produced over 20 wt% PbO/TCP was higher than that for 20 wt% PbO/MgO (see table 2). Hence for the methane coupling process, β-tricalcium phosphate appears to be more appropriate support than magnesium oxide. However, the selectivity to C_{2+} compounds was significantly lower than that with lead modified apatites. The catalytic activity of 20 wt% PbO/TCP was considerably larger than that of TCP (see table 2, comparable oxygen conversions were obtained with 0.05 g of 20 wt% PbO/TCP and 0.30 g of TCP), suggesting that lead oxide is very active in methane oxidation. On the other hand, the addition of lead to hydroxyapatite did not increase the conversion of oxygen while $Pb_{45}Pa_{1.51}$ which includes lead oxide produced the highest oxygen conversion and lowest C_{2+} selectivity in $Pb_xAp_{1.51}$. Thus, the presence of lead oxide on $Pb_{45}Ap_{1.51}$ is estimated to be responsible for the low C_{2+} selectivity and high oxygen conversion while lead cations in the apatite structure enhance the formation of C_{2+} compounds.

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