OXIDATIVE COUPLING OF METHANE ON CALCIUM-LEAD AND BARIUM-LEAD HYDROXYAPATITES

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Abstract Oxidative coupling of methane to ethylene and ethane has been investigated on binary hydroxyapatite catalysts; calcium-lead hydroxyapatite (CaHAp-PbHAp) and barium-lead hydroxyapatite (BaHAp-PbHAp) at 973 K. Although BaHAp, CaHAp and PbHAp were inactive for the oxidative coupling of methane, those binary hydroxyapatites afforded C₂ compounds rather selectively. During the oxidation on CaHAp-PbHAp catalysts, those catalysts were mainly converted to Ca_{5.5}Pb_{4.5}(PO₄)₆(OH)₂ to afford great activities while an unfavorable conversion of CaHAp to Ca₃(PO₄)₂, which was inactive for the oxidation of alkanes, was rather suppressed. In contrast, BaHAp in the BaHAp-PbHAp catalysts was extensively converted to inactive Ba₃(PO₄)₂, resulted in the complete deactivation on BaHAp-PbHAp, particularly on PbHAp-rich catalysts.

INTRODUCTION

Our laboratory has extensively investigated the catalytic activities of various hydroxyapatites for the oxidation of methane.¹ Strontium hydroxyapatite (SrHAp: Sr₁₀(PO₄)₆(OH)₂) afforded carbon monoxide selectively from the partial oxidation of methane.² However the addition of lead hydroxyapatite (PbHAp: Pb₁₀(PO₄)₆(OH)₂) into SrHAp resulted in the great enhancement of the activities for the oxidative coupling of methane.³ It has been suggested that hydrogen-abstraction from methane to methyl

radical proceeds on SrHAp, followed by the stabilization of the radical on PbHAp.^{3,4} Since, on various catalysts consisting of alkaline earth metal cations, the activities for the oxidation of methane are strongly influenced by those divalent cations,⁵ the effect of the introduction of PbHAp into calcium and barium hydroxyapatites (CaHAp: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and BaHAp: $\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$, respectively) seems to be attractive. The present work provides further information on the effect of the addition of PbHAp into hydroxyapatite consisting of Ca^{2+} and Ba^{2+} on the oxidation of methane. It has been already reported that CaHAp⁶ and BaHAp⁷ afforded CO and CO_2 nonselectively from the oxidation of methane.

EXPERIMENTAL

All chemicals were high purity and were used as supplied. Calcium hydroxyapatite (CaHAp) was prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Wako Pure Chemicals, Osaka) and $(\text{NH}_4)_2\text{HPO}_4$ (Wako).⁸ Barium hydroxyapatite (BaHAp) was prepared from $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Wako) and H_3PO_4 (Wako).^{8,9} Lead hydroxyapatite (PbHAp) was prepared from H_3PO_4 and $\text{Pb}(\text{NO}_3)_2 \cdot 5\text{PbO}$,^{8,10} while facile preparation procedure of PbHAp was recently reported.¹¹ Those hydroxyapatites thus obtained were calcined at 773 K for 3 h after drying in air at 373 K overnight. XRD patterns of CaHAp, BaHAp and PbHAp agreed with the reference patterns for the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (JCPDS 9-0432), $\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$ (JCPDS 36-0272) and $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ (JCPDS 8-0259), respectively. Binary hydroxyapatites, CaHAp-PbHAp and BaHAp-PbHAp, were prepared by kneading the component hydroxyapatites with small quantities of water. The resultant paste was spread over a glass plate, dried overnight at 373 K, crushed, sieved to the particle size of 0.85-1.70 mm and calcined at 773 K for 3 h in air. Each pure

hydroxyapatite, CaHAp, BaHAp and PbHAp, was also treated in the same manner. The re-calcined catalysts were referred to as the “fresh catalyst”. The surface areas and apparent densities of all fresh catalysts are summarized in Table 1. 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.² Prior to the reaction, the catalyst was calcined *in situ* in an oxygen flow (25 ml/min) at 973 K for 1 h. The reaction conditions were as follows: W = 0.5 g, F = 30 ml/min, T= 973 K, P(CH₄)=28.7 kPa, and P(O₂)=4.1 kPa; balance to atmospheric pressure was provided by helium. The reaction was monitored with an on-stream gas chromatograph (Shimadzu GC-8APT) equipped with a TC detector (Shimadzu C-R6A). Two columns, Porapak N (6 m x 3 mm) and Molecular Sieve 5A (0.2 m x 3 mm), were employed in the analyses. The conversion of methane was calculated from the products and the methane introduced into the feed. The selectivities to the products were calculated from the conversion of methane to each product on a carbon base. The carbon mass balances were 100±5 %. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500X, using monochromatized Cu K α radiation.

TABLE 1 Surface areas and apparent densities of fresh catalysts.

		MHAp-PbHAp (M=Ca or Ba)								
Weight % of PbHAp		0	5	10	25	30	50	70	75	100
Surface area ^a	M=Ca	70	64	56	-	44	33	27	-	4
	M=Ba	19	17	18	17	-	12	-	8	4
Apparent density ^b	M=Ca	0.51	0.53	0.48	-	0.48	0.61	0.88	-	1.43
	M=Ba	0.67	0.71	0.73	0.71	-	0.74	-	0.80	1.43

^a m²/g. ^b g/cm³.

RESULTS AND DISCUSSION

To assess the contribution of PbHAp in binary hydroxyapatites, the oxidation of methane has been examined at 973 K on CaHAp-PbHAp, the former of which is generally known as a typical hydroxyapatite, at first. Figure 1 shows the conversion and selectivities on CaHAp-PbHAp at 0.5 h on-stream since the activities were kept stably at least for 6 h on-stream. With increasing additions of PbHAp to CaHAp, the conversion of methane increased up to 10 wt.% of PbHAp, showed plateau between 10 and 30 wt.% of PbHAp and then decreased since PbHAp was inactive for the oxidation of methane. The selectivity to C_2

FIGURE 1 Methane oxidation on CaHAp-PbHAp at 973 K and 0.5 h on-stream.

compounds was evidently improved by the addition of PbHAp to CaHAp. Although lead species has been pointed out to be an advantageous component in many catalysts for the oxidative coupling of methane to C_2 compounds, it is rather difficult to observe stable activities on those catalysts due to the volatility of lead compounds.¹² However rather stable and great activities were observed during 24 h on-stream on CaHAp-PbHAp containing 30 wt.% PbHAp (Fig. 2). XRD patterns of the catalysts previously

employed in obtaining the results shown in Fig. 1 but after 6 h on-stream showed that CaHAp and $\text{Ca}_3(\text{PO}_4)_2$ were mainly observed in the binary catalysts by 10 wt.% of PbHAp while a solid-solution-type apatite, $\text{Ca}_{5.5}\text{Pb}_{4.5}(\text{PO}_4)_6(\text{OH})_2$ (JCPDS 40-1496), was a principle component in the catalysts between 30 and 70 wt.% of PbHAp (Fig. 3). It should be noted that rather small quantity of $\text{Ca}_3(\text{PO}_4)_2$ was detected by XRD, compared with XRD patterns from BaHAp-PbHAp (see below). Since it is generally accepted that simple phosphate catalysts such as $\text{Ca}_3(\text{PO}_4)_2$ are acidic and unfavorable for the employment as a catalyst for oxidation of alkanes, the suppression of the conversion of CaHAp to $\text{Ca}_3(\text{PO}_4)_2$ directly contributed to the great activity on CaHAp-PbHAp. It is evident that PbHAp does not contribute to the hydrogen-abstraction from methane (Fig. 1). Therefore the synergistic combination of CaHAp, which directly contributes to the hydrogen-abstraction, and PbHAp, which stabilizes methyl radical formed from the hydrogen-abstraction of methane, is reflected on the activities on CaHAp-PbHAp. It is expected that the hydrogen abstraction followed by the stabilization of the radical simultaneously proceeded on $\text{Ca}_{5.5}\text{Pb}_{4.5}(\text{PO}_4)_6(\text{OH})_2$. As shown in Fig. 4, the effects of the addition of PbHAp into BaHAp on the oxidation of methane over BaHAp-PbHAp were dissimilar to those on CaHAp-PbHAp. Upon

FIGURE 2 Effects of the extended time-on-stream on methane oxidation at 973 K over CaHAp-PbHAp (30 wt. % of PbHAp).

FIGURE 3 XRD patterns of CaHAp-PbHAp after the employment for the oxidation of methane at 6 h on-stream at 973 K.

Value in each figure shows weight % of PbHAp in the catalysts.

addition of small quantities of PbHAp by 10 wt.%, the conversion of methane and the selectivity to C_2 compounds were evidently improved. However the further addition of PbHAp into BaHAp resulted in the complete deactivation (Fig. 4). It should be noted

FIGURE 4 Methane oxidation on BaHAp-PbHAp at 973 K and 0.5 h on-stream.

that PbHAp^{1,10} and BaHAp^{1,9} together with CaHAp¹ were thermally stable at the temperature higher than 973 K. However the conversion of BaHAp to Ba₃(PO₄)₂ was evidently enhanced by the addition of PbHAp and a principle compound detected in the catalysts containing PbHAp from 25 to 75 wt.% was Ba₃(PO₄)₂ (Fig. 5). Furthermore lead compound in BaHAp-PbHAp was converted to amorphous species after the reaction. It was reported that various binary hydroxyapatites containing PbHAp showed excellent activities for the oxidative coupling of methane when Pb²⁺ was fixed in the hydroxyapatite structure after the oxidation.¹ Therefore the conversion of BaHAp to Ba₃(PO₄)₂ and that of PbHAp to amorphous Pb species resulted in the deactivation on BaHAp-PbHAp.

FIGURE 5 XRD patterns of BaHAp-PbHAp after the employment of the oxidation of methane at 6 h on-stream at 973 K.

Values in each figure shows weight % of PbHAp in the catalysts.

In conclusion, it was found that activities for the oxidative coupling of methane on binary hydroxyapatites containing PbHAp were strongly dependent on the conversion of

another hydroxyapatite to the corresponding phosphate and that of lead species to the corresponding amorphous species.

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