Oxidative coupling of methane over Pb-substituted chlorapatite

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Introduction

Although natural gas is an abundant resource, its utilization is limited due to the difficulties in storage/transportation and low chemical reactivity of its main component(CH_4) for useful conversion. OCM(Oxidative coupling of methane) is usually regarded as one of the promising routes for utilizing natural gas(CH_4) but the results are not satisfactory yet. Pb has been reported as a highly active catalytic component for OCM reaction[1]. High catalytic activity and thermal durability was reported when using Pb-substituted hydroxyapatites($Ca_{10-x}Pb_x(PO_4)_6(OH)_2$, $0 \leq X \leq 10$, which will be abbreviated by Pb-HAp)[2]. The character of Pb-substituted Chlorapatite($Ca_{10-x}Pb_x(PO_4)_6Cl_2$, $0 \leq X \leq 10$, which will be abbreviated by Pb-ClAp) is similar to Pb-HAp. It is widely accepted that chlorine activate CH_4. In this study, Pb-substituted chlorapatites were applied to OCM reaction, considering chlorine is effective for CH_4 activation.

Materials and Methods

The Pb-ClAp catalysts were prepared by coprecipitation method. Starting solution was obtained by dissolving $Ca(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, NH_4Cl and $(NH_4)_2HPO_4$ in distilled water. During the mixing, the pH of the mixure was adjusted 9 by addition of aqueous ammonia. After mixing, mixture was stirred at 90℃ for aging. Then the matured suspension was dried and calcined[2]. The measurements for activity of the catalysts performed with atmospheric pressure fixed bed reactor. Reactivity of the catalysts investigated with on-line GC.

Results and Discussion

Since OCM reaction is carried out usually at high temperature, the maintenance of Pb, which is highly volatile, is important as well as the activity of the catalyst. Therefore, it was necessary to investigate whether ClAp hold Pb effectively. PbO/Al_2O_3, used as catalyst for OCM by Roos et al.[3], was adopted for comparison. Table 1 showed that the change of atomic concentration in Pb-ClAp and PbO/Al_2O_3 by ICP-AES analysis. Unlike Pb in PbO/Al_2O_3, Pb in ClAp was maintained its initial concentration for 40 hours.

Table 1. ICP-AES analysis of Pb-ClAp and PbO/Al_2O_3

Catalyst	Ratio	Intended	Fresh	10 hr	20 hr	30 hr	40 hr
$Ca_{7.5}Pb_{2.5}(PO_4)_6Cl_2$	Ca/Pb	3.0	2.7	2.7	2.8	2.6	2.7
	Pb/P	0.4	0.5	0.5	0.4	0.5	0.4
PbO/Al_2O_3	Al_2/Pb	1.0	N.A	1.0	1.2	3.3	N.A

The C_2 yield of Pb-ClAps is shown in Fig. 1. At 800℃, $Ca_{8.0}Pb_{2.0}(PO_4)_6Cl_2$ showed 21.1% C_2 yield. As compared to $Ca_{9.4}Pb_{0.6}(PO_4)_6(OH)_2$ that prepared by coprecipitation[2], $Ca_{8.0}Pb_{2.0}(PO_4)_6Cl_2$ showed much higher C_2 yield.

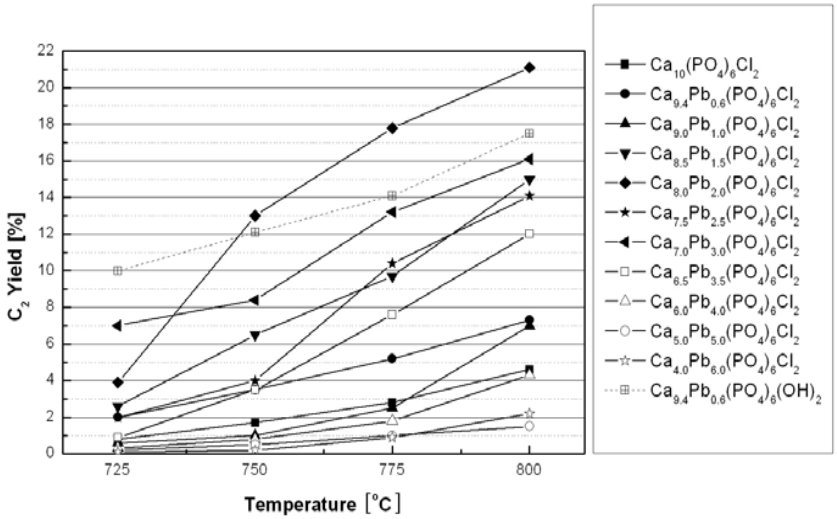

Figure 1. Catalytic activities of Pb-ClAp catalysts (catalyst 0.36g, total flow rate 37ml/min, CH_4:O_2:He=8:4:25, W/F=1.6× 10^{-4} g_{cat}·hr/ml)

Significance

As compared to Pb-HAp, Pb-ClAp showed much C_2 selectivity in OCM reaction.

Table 2. The comparison of Pb-HAp and Pb-ClAp in catalytic activity

Temp.(℃)	Catalyst	CH_4 Conv.(%)	C_2 Sel.(%)	C_2 Yield(%)
750	Ca8.5Pb1.5-HAp	15.3	26.2	4.0
	Ca8.5Pb1.5-ClAp	15.2	42.7	6.5
775	Ca8.5Pb1.5-HAp	19.8	24.7	4.9
	Ca8.5Pb1.5-ClAp	20.8	46.4	9.7
800	Ca8.5Pb1.5-HAp	23.7	26.5	6.3
	Ca8.5Pb1.5-ClAp	30.5	49.1	15.0

References

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