Korean J. Chem. Eng., **16**(5), 595-601 (1999)

Oxidative Coupling of Methane over Promoted Strontium Chlorapatite

Yoon Kyung Bae, Jin Hyuk Jun and Ki June Yoon†

Department of Chemical Engineering, Sung Kyun Kwan University, Suwon 440-746, Korea

(*Received 31 May 1999 • accepted 12 July 1999*)

Abstract–Strontium zirconium phosphate, unpromoted strontium chlorapatite and strontium hydroxyapatite showed low C_2 selectivity for the oxidative coupling of methane, but promoted strontium chlorapatite catalysts showed markedly increased activity and selectivity and also exhibited stable behavior. $SrCl_2$ was the primary promoter and strontium zirconium oxides were considered to be acting as other promoters, but strontium zirconium phosphate and strontium carbonate seemed to be acting adversely. A promoted strontium chlorapatite catalyst which contained a slightly larger amount of $SrCl_2$ than needed to form the chlorapatite showed the best performance and was stable up to 50 h at 1,023 K, and the highest C_{2+} selectivity and yield were 52% and 13.8%, respectively. Although $SrCl_2$ was more stable than NaCl it decomposed slowly during the reaction, leaving strontium oxide or strontium carbonate behind, which is considered to result in slow deactivation of the catalyst.

Key words : Methane, Oxidative Coupling, Strontium Chloride, Strontium Chlorapatite, Strontium Zirconium Phosphate

INTRODUCTION

Direct catalytic conversion of methane to C_2 and higher hydrocarbons (C_{2+}) by oxidative coupling of methane (OCM) is considered a potential route for the production of useful chemicals and fuels from abundant natural gas. A large number of materials, such as alkali-promoted alkaline earth metal oxides, transition metal oxides and rare earth metal oxides, have so far been found to be effective in catalyzing the OCM, but more effective catalysts are still being sought [Amenomiya et al., 1990; Baeck et al., 1998; Cho et al., 1998; Guo et al., 1998; Hutchings and Scurrell, 1992; Kim et al., 1997; Kim and Lee, 1993; Kim et al., 1990; Kim and Yu, 1990; Lee and Oyama, 1988; Lee and Oyama, 1989; Maitra, 1993].

Recently, NaCl-promoted sodium zirconium phosphates and lead-substituted calcium hydroxyapatite, both being based on the phosphate compounds instead of oxides, have been reported to show good catalytic performance for the OCM [Yoon and Seo, 1997; Lee et al., 1998; Matsumura et al., 1995]. While the latter catalyst showed very stable performance, the former deactivated relatively fast. The main cause of the deactivation is the disappearance of chlorine because chlorine in NaCl is relatively unstable at such a high reaction temperature. Since chlorine is known to enhance the activity and selectivity [Maitra, 1993], more stable chlorine-containing catalyst can be expected to exhibit better catalytic performance. In this work, promoted strontium chlorapatite ($Sr_{10}Cl_2(PO_4)_6$) as the OCM catalyst was investigated, because the chlorine in the chlorapatite, or that in $SrCl_2$ which was used as a starting material for the catalyst preparation and was considered to act as a promoter, was anticipated to be more stable than that in NaCl. The idea that $SrCl_2$ will be thermally more stable than NaCl may be deduced by comparing the melting point which may be used as a rough measure for the stability of inorganic chlorides. The melting point of $SrCl_2$ is 1,146 K and that of NaCl is 1073.6 K. Since unpromoted (or pure) strontium chlorapatite as well as strontium hydroxyapatite ($Sr_{10}(OH)_2(PO_4)_6$) and calcium hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$) showed poor catalytic performance [Sugiyama et al., 1996; Matsumura et al., 1995; Lee et al., 1998], a zirconium compound and excess $SrCl_2$ were added to promote the catalyst performance. Besides the chlorapatite catalyst, sodium zirconium phosphate was also investigated because it was observed to be present in the prepared chlorapatite catalyst system and it was needed to see its effect. The main purpose of this work is, first, to investigate the promoter effects and second, to test the stability of the catalysts.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

Strontium zirconium phosphate catalysts were prepared from strontium hydroxide ($Sr(OH)_2\cdot 8H_2O$, Aldrich Chemical), zirconyl chloride ($ZrOCl_2\cdot 8H_2O$, Junsei Chemical) and phosphoric acid (Yakuri Pure Chemicals). A 0.5 M aqueous solution of zirconyl chloride was added to a 1 M solution of phosphoric acid with vigorous stirring and the resulting mixture was aged for 12 h at room temperature and for additional 12 h at 363 K with gentle stirring, and then dried in air at 333 K for 50 h. The resulting solid was highly hydrated gel containing various zirconium phosphate compounds [Chang et al., 1989; Clearfield et al., 1973; Kong et al., 1999], but containing virtually no chlorine since it was vaporized as HCl during aging and drying. A nearly saturated $Sr(OH)_2$ solution was mixed with the gel and then dried at 333 K for 50 h. The resulting solid was heat-treated at 1,073 K for 2 h, to obtain the strontium zirconium phosphate catalyst. Varying ratios of Sr : Zr : PO_4 were employed and the catalyst was designated as SrZrP(a/b), where a

---

†To whom correspondence should be addressed.
E-mail : kijyoon@yurim.skku.ac.kr

and b are the number of moles of Sr and Zr per 6 moles of PO_4.

The promoted strontium chlorapatite catalyst was prepared by the same procedure as described above, except for further addition of strontium chloride ($SrCl_2 \cdot 6H_2O$, Junsei Chemical) together with $Sr(OH)_2$. The ratio of $Sr(OH)_2$: Zr : PO_4 was fixed at 1 : 4 : 6 and the amount of $SrCl_2$ added was varied. The catalyst was designated as SrClZrP(a/4), where a denotes the total moles of Sr per 6 moles of PO_4.

Unpromoted strontium chlorapatite ($Sr_{10}Cl_2(PO_4)_6$) and strontium hydroxyapatite ($Sr_{10}(OH)_2(PO_4)_6$) were also similarly prepared from stoichiometric quantities of $SrCl_2$ and $(NH_4)_2HPO_4$ for the former and $Sr(NO_3)_2$ and $(NH_4)_2HPO_4$ with addition of aqueous ammonia for the latter as reported in the literature [Lee et al., 1998]. These catalysts were designated as SrClAp and SrHyAp.

The fresh (before reaction) and used (after reaction) catalysts were characterized by X-ray diffraction (XRD : Mao Science, M18xHF-SRA) with the Cu Kα line to observe the crystalline phases and energy dispersive X-ray spectroscopy (EDS : Tracor Northern, JSM-35 CF) with 15 kV of applied voltage to observe the mole ratios of the elements. In EDS analysis, several particles were taken and the average value was used for the analysis.

2. Catalyst Performance Testing

The catalyst performance was tested by a conventional procedure. The OCM reaction was carried out in an 8-mm inside diameter quartz tube under atmospheric pressure by feeding methane, oxygen and helium as a diluent. The reactor was mounted vertically and heated with an electric furnace, and the feed gas flowed downward. The reaction temperature was measured with a thermocouple which was inserted into the catalyst bed from the top of the reactor. The following reaction conditions were employed unless otherwise specified. The reaction temperature was 1,023 K; the partial pressures of methane and oxygen (p_{CH_4} and p_{O_2}) were 16.5 and 8.3 kPa (0.16 and 0.08 atm) with the total gas flow rate of 100 cm^3/min and the catalyst loading of 1.0 g, giving the space time of 0.6 g·s/cm^3. The product effluent was passed through a $CaCl_2$ trap to remove water and then analyzed by two on-line TCD-equipped gas chromatographs, one fitted with a Carboxen 1004 column (Supelco) to analyze O_2, CO and CH_4, and the other with a Hayesep Q column (Supelco) to analyze O_2+CO, CO_2, CH_4 and higher hydrocarbons.

RESULTS AND DISCUSSION

As is generally used, the selectivity to a product in this work is also defined as (the number of moles of C in that product)/(the number of moles of CH_4 consumed) ; the yield is defined as (the number of moles C in that product)/(the number of moles of CH_4 fed) and is equal to (the CH_4 conversion)×(the selectivity). The C_{2+} selectivity and yield mean the sum of selectivities and yields of C_2 (ethane and ethene) and higher hydrocarbons. If the terms are used without specifying any product, they mean the C_{2+} selectivity and yield. The observed higher hydrocarbons in this work were propane and propene, and these were usually (but not always) obtained within a few percent of selectivity when the conversion was higher than about 20% and the selectivity was higher than about 40%. For brevity's sake, the propane and propene selectivities were not presented in the following data.

Table 1. Crystalline phases in strontium zirconium phosphate catalysts

Catalyst	Status	Crystalline phases and relative peak intensity	Possible other major compounds[b]
SrZrP(1/4)[a]	Fresh	$SrZr_4(PO_4)_6$	-
	Used	$SrZr_4(PO_4)_6$	-
SrZrP(2/4)	Fresh	$SrZr_4(PO_4)_6$>>$SrZrO_3$	-
	Used	$SrZr_4(PO_4)_6$	$SrCO_3$
SrZrP(3/4)	Fresh	$SrZr_4(PO_4)_6$>$Sr_{10}(OH)_2(PO_4)_6$>> $Sr_3Zr_2O_7$	-
	Used	$SrZr_4(PO_4)_6$ >> $Sr_{10}(OH)_2(PO_4)_6$	$Sr_xZr_yO_z$[c]
SrZrP(3/3)	Fresh	ZrP_2O_7 >> $SrZr_4(PO_4)_6$	-
	Used	ZrP_2O_7>>$SrZr_4(PO_4)_6$	$SrCO_3$

[a] The numbers of moles of Sr/Zr per 6 moles of PO_4 used in the preparation.

[b] Not observed by XRD ; see text.

[c] Various strontium zirconium oxides.

1. Strontium Zirconium Phosphate Catalysts

1-1. XRD Analysis

The crystalline phases observed by XRD are presented in Table 1. In SrZrP(1/4), only the hexagonal $SrZr_4(PO_4)_6$, which has the same stoichiometric ratio of the elements and groups as the materials used in the preparation, was observed. In SrZrP(2/4), which had a larger amount of strontium, a small amount of cubic $SrZrO_3$ was observed in the fresh sample, but in the used sample it was not observed. Considering the larger amount of strontium added than needed to form $SrZr_4(PO_4)_6$, some strontium compounds which were not detected by the XRD should be present in SrZrP(2/4) as amorphous forms or in small amounts. When the amount of strontium added was further increased, as in SrZrP(3/4), the presence of hexagonal strontium hydroxyapatite ($Sr_{10}(OH)_2(PO_4)_6$) and tetragonal $Sr_3Zr_2O_7$ was observed in the fresh sample, but the latter was not observed in the used sample. Taking again into account the amounts of materials used in the preparation, some compounds which were not detected by the XRD should also be present in SrZrP(3/4). The compounds which were not observed by the XRD due to small amount or amorphousness are considered to be most probably strontium zirconium oxides, some of which were observed in the fresh samples, and amorphous $SrCO_3$ which was formed from strontium, moist and carbon dioxide in the reaction product gas and in air. In SrZrP(2/4), a relatively large amount of $SrCO_3$ is considered to be present, and the presence of a small amount of strontium hydroxyapatite may not be ruled out. In SrZrP(3/4), various strontium zirconium oxides ($Sr_xZr_yO_z$, which are poorly crystalline) are considered to be present in a relatively larger amount than $SrCO_3$ since formation of strontium hydroxyapatite was observed. When the ratio of Zr to PO_4 was decreased to 1 : 2, as in SrZrP(3/3), formation of

$SrZr_4(PO_4)_6$ was greatly depressed but crystalline zirconium pyrophosphate (cubic ZrP_2O_7) was well developed. Another strontium zirconium phosphate compound, $SrZr(PO_4)_2$, is known to exist, but this compound was not formed although the materials employed were stoichiometrically the same and treated at 1,273 K. This is probably due to the fact that the treatment temperature was not high enough for the formation of $SrZr(PO_4)_2$. Considering again the large amount of strontium added, a large amount of $SrCO_3$ is considered to be present.

1-2. Performance Test

The results of the OCM reaction over the strontium zirconium phosphate catalysts are presented in Table 2. These catalysts showed very stable (constant activity and selectivity) behavior for 8 h, and the data in Table 2 are the average values from 2 to 8 h on-stream. However, the C_2 selectivity and yield were quite low, which indicates that $SrZr_4(PO_4)_6$ is not a good catalyst for the OCM. SrZrP(3/3) showed almost inert behavior, and this is due to the zirconium pyrophosphate as the main component [Kong et al., 1999]. $SrCO_3$ also seems to be a poor catalyst. Since SrZrP(3/4) showed the highest yield among these catalysts, strontium hydroxyapatite and strontium zirconium oxides are considered to be more effective for the OCM than $SrZr_4(PO_4)_6$ and $SrCO_3$. In fact, strontium hydroxyapatite and strontium zirconium oxides have been investigated for the OCM [Sugiyama et al., 1996; Yang et al., 1995; Nagamoto et al., 1988], and the latter seems to be better than the former although they are not good catalysts compared with other effective catalysts reported. Therefore, no further study on the strontium zirconium phosphate catalysts was carried out.

Table 2. Results of the reaction[a] over strontium zirconium phosphate catalysts, unpromoted strontium chlorapatite and strontium hydroxyapatite

Catalyst	CH_4 conv. (%)	C_2 sel. (%)	C_2 yield (%)	C_2H_4/C_2H_6
SrZrP(1/4)	6.8	16.2	1.1	0.52
SrZrP(2/4)	9.8	17.5	1.7	0.33
SrZrP(3/4)	16.5	15.3	2.5	0.58
SrZrP(3/3)	2.9	0	0	-
SrClAp	21.4	6.7	1.4	0
SrHyAp	11.8	6.6	0.8	0

[a] Average values from 2 to 8 h on-stream at 1,023 K.

2. Promoted Strontium Chlorapatite Catalysts

2-1. XRD and EDS Analyses

The XRD analysis results are presented in Table 3. For the catalysts prepared with relatively small ratios of Sr/PO_4, strontium zirconium phosphate and strontium chlorapatite were observed in comparable amounts. When the Sr/PO_4 ratio approached 10, as in SrClZrP(9/4), the amount of strontium zirconium phosphate formed became significantly smaller than that of strontium chlorapatite. When the Sr/PO_4 ratio exceeded 10, as in SrClZrP(13-21/4), strontium zirconium phosphate could barely be seen. Therefore, it can be said that if chlorine is present strontium chlorapatite is easily formed and is more preferentially formed than strontium zirconium phosphate. On the other hand, excess $SrCl_2$ was found to be decomposed during the reaction, as observed for the used SrClZrP(13-21/4) catalysts. Therefore, similarly to the discussion in the above section, $SrCO_3$ and strontium zirconium oxides are considered to be present, as list-

Table 3. XRD and EDS analysis results for promoted strontium chlorapatite catalysts

Catalyst	Status[a]	Crystalline phases and peak intensity	Possible other comp.	Cl/Sr (by EDS)
SrClZrP(3/4)	Fresh	$SrZr_4(PO_4)_6 \gg Sr_{10}Cl_2(PO_4)_6$	-	0.30
	Used	$SrZr_4(PO_4)_6 > Sr_{10}Cl_2(PO_4)_6$	$Sr_xZr_yO_z$	0.11
SrClZrP(5/4)	Fresh	$Sr_{10}Cl_2(PO_4)_6 > SrZr_4(PO_4)_6$	-	0.34
	Used	$Sr_{10}Cl_2(PO_4)_6 \approx SrZr_4(PO_4)_6 > SrZrO_3$	-	0.17
SrClZrP(9/4)	Fresh	$Sr_{10}Cl_2(PO_4)_6 > SrZr_4(PO_4)_6$	-	0.70
	Used	$Sr_{10}Cl_2(PO_4)_6 \gg SrZrO_3 \approx SrZr_4(PO_4)_6$	ZrO_2	0.57
SrClZrP(13/4)	Fresh	$Sr_{10}Cl_2(PO_4)_6 > SrCl_2$	-	1.07
	Used[b]	$Sr_{10}Cl_2(PO_4)_6 > SrZrO_3 \gg SrCl_2$	-	0.44
SrClZrP(17/4)	Fresh	$SrCl_2$[d] $> Sr_{10}Cl_2(PO_4)_6 \gg SrZr_4(PO_4)_6$	-	1.41
	Used[c]	$Sr_{10}Cl_2(PO_4)_6 \gg SrZrO_3 > SrZr_4(PO_4)_6$	$Sr_xZr_yO_z$, $SrCO_3$	0.21
SrClZrP(21/4)	Fresh	$SrCl_2$[d] $\gg Sr_{10}Cl_2(PO_4)_6$	-	1.97
	Used	$SrCl_2$[d] $> Sr_{10}Cl_2(PO_4)_6 \gg SrZr_4(PO_4)_6$	$Sr_xZr_yO_z$, $SrCO_3$	1.43
SrClAp	Fresh	$Sr_{10}Cl_2(PO_4)_6 \gg SrCl_2$[d]	-	0.30
	Used	$Sr_{10}Cl_2(PO_4)_6 \gg SrCl_2$[d]	-	0.24
SrHyAp	Fresh	$Sr_{10}(OH)_2(PO_4)_6$	-	-
	Used	$Sr_{10}(OH)_2(PO_4)_6$	-	-

[a] The used catalysts had usually been used for 8 h at 1,023 K and for 3-5 h at 1,073 K.

[b] Used for 50 h at 1,023 K.

[c] Used for 66 h at 1,023 K.

[d] Crystalline strontium chloride was observed as mixtures of anhydrous form and (di- and hexa-) hydrate form, and the latter would have been formed by the moisture in the reaction gas and air during cooling and storage. When the amount of strontium chloride remaining was large, the observed crystalline phase was mostly the hydrate form.

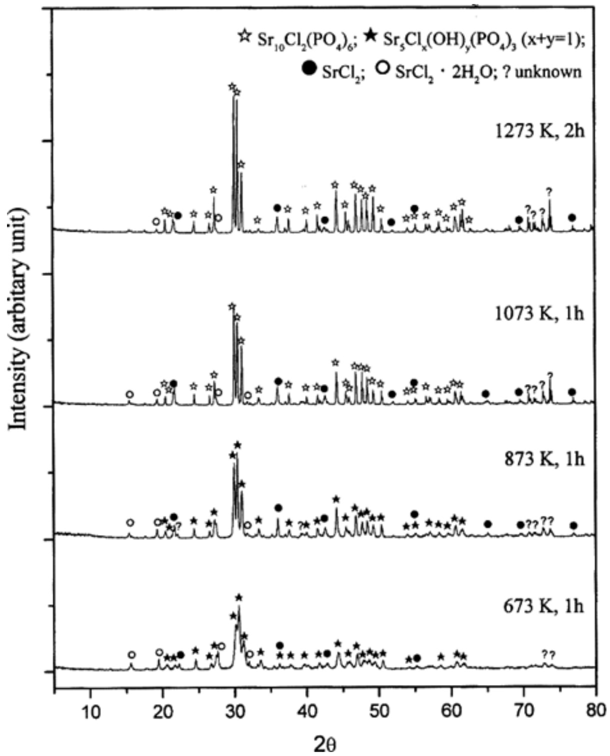

Fig. 1. X-ray diffractograms for SrClAp samples (Sr/PO_4=10/6) treated at different temperatures.

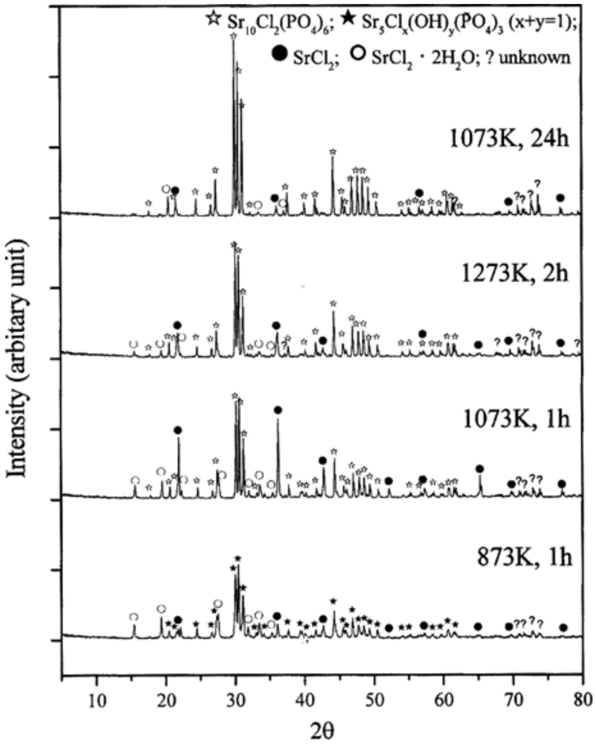

Fig. 2. X-ray diffractograms for SrClAp samples with excess $SrCl_2$ (Sr/PO_4=12/6) treated with different temperatures and times.

ed in Table 3, although they were not observed by XRD.

Fig. 1 shows the X-ray diffractograms for the SrClAp samples which were prepared by using stoichiometric amounts of Sr and PO_4 and treated at different temperatures. For the samples treated at 1,073 and 1,273 K, well-developed crystalline strontium chlorapatite was observed and the amount of $SrCl_2$ remaining was quite small. The samples treated at 673 and 873 K appeared to contain mixtures of strontium chlorapatite and strontium hydroxyapatite; and the strontium hydroxyapatite would be progressively converted to strontium chlorapatite at higher temperatures by the reaction with remaining $SrCl_2$. In fact, it has been reported that hydroxyapatite can easily be converted to chlorapatite in the presence of chlorine [Sugiyama et al., 1999]. Fig. 2 shows the X-ray diffractograms for the SrClAp samples which were prepared by using excess $SrCl_2$ (Sr/PO_4=12/6) and treated at different temperatures for different hours. The results were similar to those in Fig. 1, except for the peak intensity of $SrCl_2$. For the sample treated at 873 K, the $SrCl_2$ peaks were relatively small. This does not mean that the amount of $SrCl_2$ is small, but only a small portion of $SrCl_2$ is in the crystalline form due to poor crystallization. The crystallization seemed to proceed to a greater extent with increasing temperature, and the amount of crystalline $SrCl_2$ in the sample treated at 1,073 K was observed to be quite large, but it was significantly decreased after treatment at 1,273 K for 2 h. For the sample treated at 1,073 K for 24 h, the amount of $SrCl_2$ was very small, and it was approximately the same as that in the sample prepared by using stoichiometric amounts of Sr and PO_4 and treated at 1,273 K for 2 h. The results in Figs. 1 and 2 show that strontium chlorapatite is relatively easily formed and is stable under the reaction conditions for OCM, while excess $SrCl_2$ is continuously decomposed, probably leaving SrO and then $SrCO_3$ behind.

The EDS results are also shown in Table 3. The composition of each element could not reliably be determined because the Zr Lα and P Kα lines (2.03 and 2.01 keV, respectively) are so close that they could not satisfactorily be resolved. For Cl and Sr, Cl Kα (2.62 keV) and Sr Lα (1.81 keV) lines were used. Therefore, only the Cl/Sr ratios are presented. By comparing the Cl/Sr ratio for the fresh sample with that for the used sample, disappearance of chlorine during the OCM reaction was again confirmed. For the used samples of SrClZrP(9/4) and SrClZrP(13/4), which were observed from the XRD analysis to contain very small amounts of $SrCl_2$ and to be composed mostly of strontium chlorapatite, the Cl/Sr ratios were considerably greater than 0.2, which is the theoretical ratio for pure $Sr_{10}Cl_2(PO_4)_6$. For the used sample of SrClZrP(17/4), the ratio was slightly greater than 0.2, even though a large excess of Sr was employed for the preparation and used for a long period. This indicates that for these samples considerable amounts of $SrCl_2$ are still present near the catalyst surface, though crystalline $SrCl_2$ was not observed by the XRD.

2-2. Performance Test

Fig. 3 compares the performances of the promoted strontium chlorapatite catalysts. Since the catalysts showed stable behavior (nearly constant or slowly increasing conversion and selectivity for some catalysts), the average values of the data from 2 h to 8 h on-stream were presented in the figure. Unpromoted

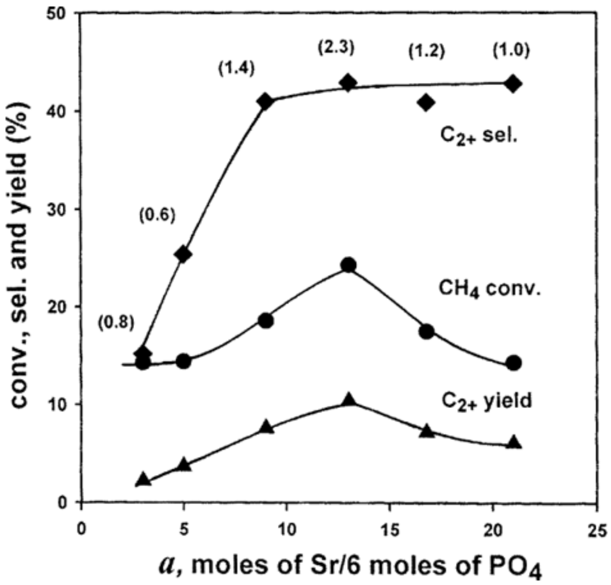

Fig. 3. Effect of the amount of $SrCl_2$ added on the catalytic performance at 1,023 K.
(The data are averaged values from 2 to 8 h on-stream; the number in the parenthesis denotes the C_2H_4/C_2H_6 ratio)

strontium chlorapatite and hydroxyapatite catalysts (SrClAp and SrHyAp) exhibited very low C_2 selectivities (Table 2), but promoted strontium chlorapatite catalysts (SrClZrP(a/4)) showed markedly higher selectivities. Therefore, it is certain that $SrCl_2$ is acting as a good promoter. As the ratio a increased, the selectivity increased up to 9 of a and then stayed almost constant. The maximum CH_4 conversion appeared at 13 of a, which indicates that the amount of $SrCl_2$, which is slightly larger than that needed for the formation of the chlorapatite, may be the optimum. The activity decrease with the larger amount of $SrCl_2$ is considered due to physical blocking of a larger area of the active surface by the inert $SrCl_2$. In addition, if the results of characterization and reaction are put together, strontium zirconium oxides seem to be acting as other promoters, while it is considered that strontium zirconium phosphate and strontium carbonate are not good promoters or they may act adversely.

Fig. 4 shows the activity and selectivity changes with time on-stream at 1,023 K over the SrClZrP(13/4) catalyst. The methane conversion increased during the initial several hours and then stayed almost constant up to 50 h. This initial increase is considered due to creation of more active sites, which results from ongoing reaction or interaction between $SrCl_2$ and other components such as strontium hydroxyapatite, strontium zirconium oxides and strontium chlorapatite. The selectivity also increased somewhat rapidly during the initial several hours and then increased slowly up to 50 h on-stream, where it came up to 52%. The C_2H_4/C_2H_6 ratio also remained almost constant. Fig. 5 shows the activity and selectivity changes with time on-stream at 1,023 K over the SrClZrP(17/4) catalyst. Up to 40 h on-stream the trend was similar to that for SrClZrP(13/4), but after that the selectivity began to decrease gradually. This decrease is considered due to the increasing amount of strontium oxide or strontium carbonate which was formed by slow decomposition of $SrCl_2$. Fig. 6 shows the changes with time on-stream at 1,073 K over the SrClZrP(9/4) catalyst. The activity, selectivity, yield and C_2H_4/C_2H_6 ratio were fairly high compared with those at 1,023 K. However, at this high temperature the stable behavior lasted only for 5 hours and then the performance deteriorated gradually. This deactivation is also considered due to decomposition of $SrCl_2$ occurring more rapidly at higher temperature. Therefore, the performance test at 1,073 K was not carried out intensively. From these stability tests, it can be summarized that the promoted strontium chlorapatite cata-

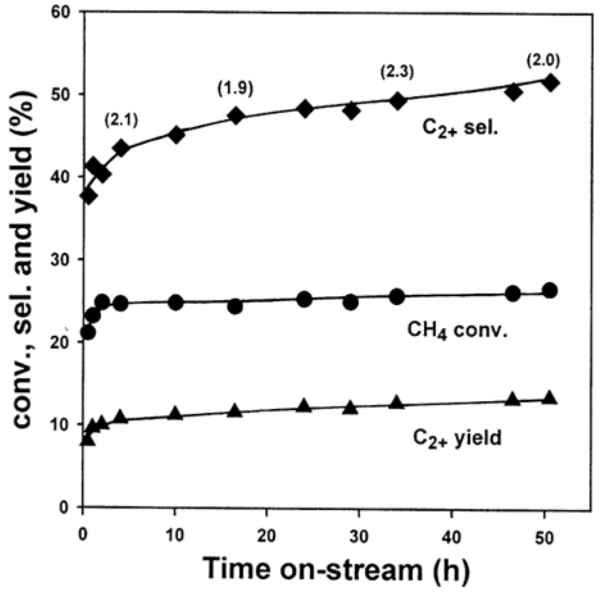

Fig. 4. Change of catalytic performance with time on-stream for SrClZrP(13/4) at 1,023 K.
(The number in the parenthesis denotes the C_2H_4/C_2H_6 ratio)

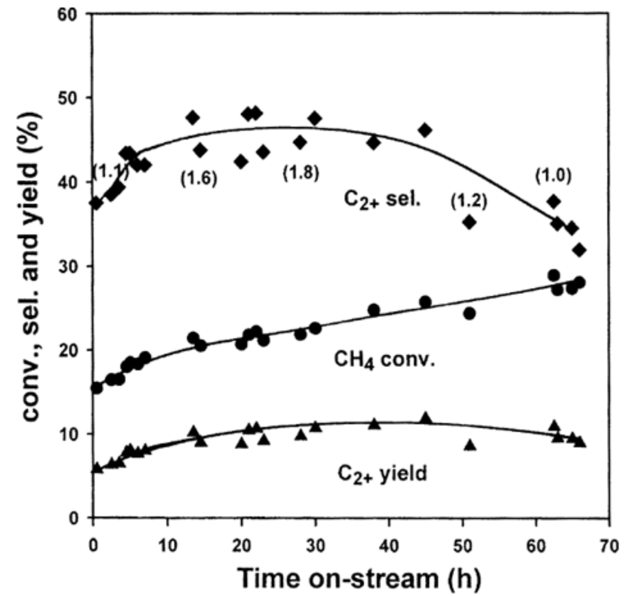

Fig. 5. Change of catalytic performance with time on-stream for SrClZrP(17/4) at 1023 K.
(The number in the parenthesis denotes the C_2H_4/C_2H_6 ratio)

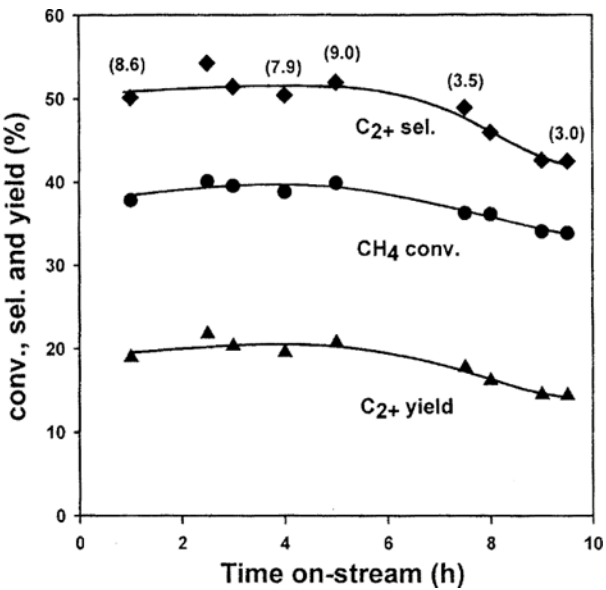

Fig. 6. Change of catalytic performance with time on-stream for SrClZrP(9/4) at 1,073 K.
(The number in the parenthesis denotes the C_2H_4/C_2H_6 ratio)

lysts exhibit fairly stable performance and $SrCl_2$ is much more stable than NaCl, but $SrCl_2$ decomposes slowly, resulting in slow deactivation in the long run.

CONCLUSIONS

Strontium zirconium phosphate, unpromoted strontium chlorapatite and strontium hydroxyapatite showed low C_2 selectivity for the oxidative coupling of methane, but promoted strontium chlorapatite catalysts showed markedly increased activity and selectivity and also exhibited stable behavior. $SrCl_2$ was the primary promoter and strontium zirconium oxides were considered to be acting as other promoters, but strontium zirconium phosphate and strontium carbonate seemed to be acting adversely. A promoted strontium chlorapatite catalyst, SrClZrP(13/4), which contained a slightly larger amount of $SrCl_2$ than needed to form the chlorapatite showed the best performance and was stable up to 50 h at 1,023 K, and the highest C_{2+} selectivity and yield were 52% and 13.8%, respectively. Although $SrCl_2$ was more stable than NaCl it decomposed slowly during the reaction, leaving SrO or $SrCO_3$ behind, which is considered to result in slow deactivation of the catalyst.

ACKNOWLEDGMENTS

This work was supported by Faculty Research Fund of Sungkyunkwan University (1977). The authors are also grateful to Mr. Soek-Ki Min for the assistance in the analysis of the XRD data.

REFERENCES

Amenomiya, Y., Birss, V. I., Goledzinowski, M., Galuszka, J. and Sanger, A. R., "Conversion of Methane Oxidative Coupling," *Catal. Rev.-Sci. Eng.*, **32**, 163 (1990).

Baeck, S. H., Chung, J. S. and Lee, W. Y., "Oxidative Coupling of Methane over BiOCl-Li_2CO_3-Sm_2O_3 Catalyst," *HWAHAK KONGHAK*, **36**, 429 (1998).

Chang, J.-S., Park, S.-E. and Lee, Y. K., "Characterization of Cobalt(II)-Exchanged Synthetic α-Zirconium Phosphate," *HWAHAK KONGHAK*, **27**, 323 (1989).

Cho, W., Baek, Y., Pang, H. and Kim, Y. C., "A Direct Catalytic Conversion of Natural Gas to C_{2+} Hydrocarbons by Microwave Plasma," *Korean J. Chem. Eng.*, **15**, 500 (1998).

Clearfield, A., Landis, A. L., Medina, A. S. and Troup, J. M., "More on Crystalline Zirconium Phosphates," *J. Inorg. Nucl. Chem.*, **35**, 1099 (1973).

Guo, X.-M., Hidaiat, K. and Ching, C.-B., "An Experimental Study of Oxidative Coupling of Methane in a Solid Oxide Fuel Cell with 1 wt% Sr/La_2O_3-Bi_2O_3-Ag-YSZ Membrane," *Korean J. Chem. Eng.*, **15**, 469 (1998).

Hutchings, G. J. and Scurrell, M. S., "Methane Conversion by Oxidative Processes: Fundamental and Engineering Aspects," Wolf, E. E., ed., Van Nostrand Reinhold, New York, 200 (1992).

Kim, C. S. and Lee, W. Y., "The Reaction Characteristics of Oxidative Coupling of Methane over Ba- and Sr-based Catalysts," *HWAHAK KONGHAK*, **31**, 62 (1993).

Kim, S.-C., Sunwoo, C.-S. and Yu, E.-Y., "The Effect of Alkali Promoters in Oxidative Coupling of Methane with Mn-Oxide Catalysts," *Korean J. Chem. Eng.*, **7**, 279 (1990).

Kim, S.-C. and Yu, E.-Y., "The Oxidative Coupling of Methane over Supported Zinc Oxide Catalyst with Alkali Promoters," *HWAHAK KONGHAK*, **28**, 536 (1990).

Kim, S. H., Cho, S. M. and Yoon, K. J., "Oxidative Coupling of Methane over Na^+-ZrO_2-Cl^-/Al_2O_3 Catalysts," *Korean J. Chem. Eng.*, **14**, 69 (1997).

Kong, S. J., Bae, Y. K. and Yoon, K. J., "Oxidative Coupling of Methane over Sodium-Chloride-Added Sodium Zirconium Phosphates," *Korean J. Chem. Eng.*, **16**, 234 (1999).

Lee, J. S. and Oyama, S. T., "Effect of Reaction Temperature on the Selectivity of Oxidative Coupling of Methane over Lead Oxide," *Korean J. Chem. Eng.*, **6**, 54 (1989).

Lee, J. S. and Oyama, S. T., "Oxidative Coupling of Methane to Higher Hydrocarbons," *Catal. Rev.-Sci. Eng.*, **30**, 249 (1988).

Lee, K.-Y., Han, Y.-C., Suh, D. J. and Park, T. J., "Pb-substituted Hydroxyapatite Catalysts Prepared by Coprecipitation Method for Oxidative Coupling of Methane," in "Natural Gas Conversion V," Parmaliana, A., Sanfilippo, D., Frusteri, F., Vaccari, A. and Arena, F., Eds., Elsevier, *Studies in Surf. Sci. Catal.*, **119**, 385 (1998).

Maitra, A. M., "Critical Performance Evaluation of Catalysts and Mechanistic Implications for Oxidative Coupling of Methane," *Applied Catalysis A : General*, **104**, 11 (1993).

Matsumura, Y., Sugiyama, S., Hayashi, H. and Moffat, J. B., "An Apparent Ensemble Effect in the Oxidative Coupling of Methane on Hydroxyapatite with Incorporated Lead," *Catal. Lett.*, **30**, 235 (1995).

Nagamoto, H., Amanuma, K., Nobutomo, H. and Inoue, H., "Methane Oxidation over Perovskite-type Oxide Containing Alkaline-earth Metal," *Chem, Lett.*, 237 (1988).

Segawa, K., Kurusu, Y. and Kinoshita, M., "Catalysis by Acids and Bases,"Imelik, B., ed., Elsevier, Amsterdam, B.V., 83 (1985a).

Segawa, K., Kurusu, Y., Nakajima, Y. and Kinoshita, M., "Characterization of Crystalline Zirconium Phosphates and Their Isomerization Activities,"*J. Catal.*, **94**, 491 (1985b).

Sugiyama, S., Matsumoto, H., Hayashi, H. and Moffat, J. B., "Decomposition of Tetrachloromethane on Calcium Hydroxyapatite under Methane Oxidation Conditions," *Appl. Catal. B*, **20**, 57 (1999).

Sugiyama, S., Minami, T., Hayashi, H., Tanaka, M. and Moffat, J. B., "Surface and Bulk Properties of Stoichiometric and Nonstoichiometric Strontium Hydroxyapatite and the Oxidation of Methane,"*J. Solid State Chem.*, **126**, 242 (1996).

Yang, W. M., Yan, Q. J. and Fu, X. C., "A Comparative Study of Catalytic Behaviours of Sr-Ti, Sr-Zr, Sr-Sn Perovskites and Corresponding Layered Perovskites for the Oxidative Coupling of Methane," in "Methane and Alkane Conversion Chemistry," Bhasin, M. M. and Slocum, D. W., Eds., Plenum, New York, 71 (1995).

Yoon, K. J. and Seo, S. W., "Oxidative Coupling of Methane over Sodium-salt-promoted Zirconia Catalysts Prepared by the Mixed Solution Method," *Applied Catalysis B*, **7**, 237 (1996).

Yoon, K. J. and Seo, S. W., "The Catalyst for Oxidative Coupling of Methane Prepared from Zirconyl Chloride and Sodium Pyrophosphate," *Applied Catalysis A*, **161**, L5 (1997).