OXIDATIVE COUPLING OF METHANE OVER SODIUM-CHLORIDE-ADDED SODIUM ZIRCONIUM PHOSPHATES

Sang Jun Kong, Yoon Kyung Bae and Ki June Yoon†

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

Abstract—Monosodium zirconium phosphate or disodium zirconium phosphate by itself did not catalyze the oxidative coupling of methane and also the deep oxidation of methane. However, NaCl-added sodium zirconium phosphates showed markedly increased activity and high C_{2+} selectivity in the oxidative coupling of methane, which indicates that chlorine species or NaCl plays an essential role in the catalytic action. The catalytic performance became more stable with increasing content of NaCl. The primary reason for the catalyst deactivation is the loss of chlorine, and a possible secondary reason is the transformation of catalytic substance to the sodium zirconium phosphates having higher Na/Zr ratios or decomposition of sodium zirconium phosphates to zirconium oxide and sodium phosphate. Two kinds of surface chlorine species were observed, and the lower-binding-energy species is considered to be much more active than the higher-binding-energy species in methane activation, although the latter is present in a larger amount than the former.

Key words : Chlorine, Methane, Oxidative Coupling, Sodium Chloride, Sodium Pyrophosphate, Sodium Zirconium Phosphates

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 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., 1990, 1997; Kim and Lee, 1993; 1990; Kim and Yu, 1990; Lee and Oyama, 1988; Lee and Oyama, 1989; Maitra, 1993]. We recently reported that the catalyst prepared from a mixture of zirconyl chloride and sodium pyrophosphate exhibited high activity and selectivity (up to about 30 % C_{2+} yield) for the OCM and suggested that NaCl-promoted sodium zirconium phosphates were likely to be the catalytically active substance [Yoon and Seo, 1997]. However, this catalyst contained several compounds such as monosodium zirconium phosphate [NaZr$_2$(PO$_4$)$_3$], disodium zirconium phosphate [Na$_2$Zr(PO$_4$)$_2$], zirconium oxide and excess sodium pyrophosphate together with sodium chloride. Except that the presence of sodium chloride was observed to be crucial for the catalyst to be effective for the OCM, the role of each compound, the interaction between the compounds, and the stability of the catalyst were not satisfactorily investigated. In this work, a more systematic study was carried out to investigate such characteristics of the catalyst. Instead of using sodium pyrophosphate, we prepared the catalysts in this work by adding sodium chloride and/or so-

dium hydroxide to zirconium phosphate gel which was obtained from zirconyl chloride and phosphoric acid. The catalysts were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) analyses.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

Zirconium phosphate gel (abbreviated as ZrP gel) was obtained by following the procedure in the literature [Chang et al., 1989; Clearfield et al., 1973; Segawa et al., 1985a, b]. A 0.5 M aqueous solution of zirconyl chloride (ZrOCl$_2$·8H$_2$O, Junsei Chemical) was added to an excess amount of 1 M phosphoric acid solution (PO$_4$/Zr mole ratio of 4), and the mixture was stirred overnight and then the precipitate was filtered off. The precipitate was washed and filtered twice with a 5 wt% solution of phosphoric acid and then washed and filtered repeatedly with distilled water until the effluent attained a pH of slightly higher than 3. The solid was then dried at 333 K for 50 h to obtain amorphous, highly-hydrated gelatinous ZrP gel. The gel was mixed with a 20 wt% of NaCl solution and/or a 25 wt% NaOH solution. The mixture was dried and then treated in air at 1,073 K for 2 h to obtain the catalyst sample.

The catalysts were designated as NaZP(*ab*), where *a* and *b* are the nominal mole ratios of NaOH/Zr and NaCl/Zr, respectively. Although the PO$_4$/Zr ratio in the ZrP gel is not certain and may vary depending on the preparation procedure [Clearfield et al., 1973; Segawa et al., 1985a, b], it was assumed from the XRD analysis that the gel after high-temperature treatment was pure ZrP$_2$O$_7$, and then *a* and *b* were calculated from the amounts employed in the preparation.

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

The fresh (before reaction) and used (after reaction, usually 8 h on-stream) catalysts were characterized by XRD (NAC Science), EDS (Tracor Northern, JSM-35CF), and XPS (SPECS, LHS-10) analyses. For the XPS analysis, binding energies of Zr 3d, Na 1s, Cl 2p, O 1s and P 2p were obtained with the reference of C (graphite) 1s at 284.5 eV.

2. Catalytic Performance Testing

The oxidative coupling reaction was carried out in an 8-mm inside diameter quartz tube under atmospheric pressure by co-feeding methane, air and nitrogen as a diluent. The reactor was mounted vertically and heated with an electric furnace. 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 ($CH_4/O_2=2$) with the total gas flow rate of 100 cm^3/min, and the catalyst loading was 1.0 g, giving the space time of 0.6 g·s/cm^3. The product effluent was analyzed by two on-line TCD-equipped gas chromatographs, one fitted with a Chromosorb 102 column to analyze carbon dioxide, methane and higher hydrocarbons, and the other with a Carbosieve S-II (Supelco) column to analyze oxygen, carbon monoxide, methane and carbon dioxide.

RESULTS AND DISCUSSION

1. Weight Loss during Drying and High-Temperature Treatment

The ZrP gel obtained after drying at 333 K for 50 h was highly hydrated and most of the water in it could be liberated near 373 K. The weight loss from the gel after drying at 373 K for 1 h amounted to 83-88 %, and the total weight loss after treating at 1,073 K for 2 h amounted to 85-90 %. If based on the weight of the sample dried at 373 K, the percent weight loss which occurred from 373 K to 450 K was about 3 %, and that from 450 K to 1,073 K was about 6 %. The percent weight loss which occurred from 450 K to 1,073 K is certainly due to the condensation of phosphate groups, that is, from $Zr(HPO_4)_2$ to ZrP_2O_7, which is similar to the observation from the temperature-programmed decomposition in earlier works by other investigators [Segawa et al., 1985a, b].

2. XRD Analysis

The crystalline phases identified by XRD are presented in Table 1, and their abbreviations are listed in Table 2. It was found that the ZrP gel after the treatment at 1,073 K contained well-developed cubic zirconium pyrophosphate (ZrPP : ZrP_2O_7) and no other crystalline phases were obviously observed. The d and intensity ratio (I/I_0) values for the cubic ZrPP were in excellent agreement with those reported in JCPDS (file no. 29-1399). Although it cannot be ruled out that some other amorphous substances may be present, it is certain that the heat-treated gel is mostly composed of ZrP_2O_7.

In NaZP(20), which was prepared by adding NaOH only, monosodium zirconium phosphate [MSZP : $NaZr_2(PO_4)_3$] and disodium zirconium phosphate [DSZP-A : $Na_2Zr(PO_4)_2$, phase A] were observed, but ZrPP and other crystalline phases were

Table 1. Crystalline phases identified by XRD

Catalyst		Crystalline phases[a] and relative intensity
ZrP gel	heated	ZrPP
NaZP(20)[b]	Fresh	MSZP ≈ DSZP-A
NaZP(02)	Fresh	MSZP
	Used	MSZP > DSZP-A
NaZP(04)	Fresh	NaCl > MSZP >> PSZP ≈ UI
	Used	m-ZrO_2 > DSZP-N ≈ PSZP ≈ UI
NaZP(06)	Fresh	NaCl > MSZP >> PSZP
	Used	NaCl > MSZP ≈ PSZP
NaZP(21)	Fresh	NaCl > MSZP ≈ DSZP-A ≈ UI(c-Na_3PO_4, $NaPO_3$) > DSZP-N ≈ PSZP
	Used	MSZP ≈ PSZP ≈ UI(c-Na_3PO_4, $NaPO_3$) > DSZP-A ≈ DSZP-N
NaZP(22)	Fresh	NaCl >> DSZP-A ≈ UI(c-Na_3PO_4) > MSZP
	Used	m-ZrO_2 > DSZP-N ≈ PSZP > DSZP-A
NaZP(24)	Fresh	NaCl >> DSZP-A ≈ DSZP-N ≈ UI(c-Na_3PO_4)
	Used	m-ZrO_2 ≈ UI(c-Na_3PO_4) > UI($NaPO_3$) > PSZP ≈ t-ZrO_2
NaZP(26)	Fresh	NaCl >> PSZP ≈ UI(c-Na_3PO_4)
	Used	NaCl ≈ m-ZrO_2 ≈ c-NaZP >> DSZP-N ≈ UI($NaPO_3$)

[a]The abbreviations are listed in Table 2, and possible phases are given in parentheses.
[b]The first and second digits in parentheses denote the nominal mole ratios of NaOH/Zr and NaCl/Zr, respectively.

Table 2. Abbreviations of crystalline phases

Crystalline phases	JCPDS file no.	Abbreviation
ZrP_2O_7, cubic	29-1399	ZrPP
$NaZr_2(PO_4)_3$, hexagonal	33-1312	MSZP
$Na_2Zr(PO_4)_2$, phase A	35-124	DSZP-A
not specified	35-125	DSZP-N
$Na_5Zr(PO_4)_3$, rhombohedral	37-110	PSZP
$Na_{2.47}Zr_{0.13}PO_4$, cubic	37-333	c-NaZP
γ-Na_3PO_4, cubic	31-1318	c-Na_3PO_4
ZrO_2, monoclinic	37-1484	m-ZrO_2
tetragonal	17-923	t-ZrO_2
NaCl	5-0628	NaCl
Unidentified phase	-	UI(*)

*Possible phase, such as c-Na_3PO_4 and $NaPO_3$, are give in the parenthesis, when necessary.

not observed. This indicates that zirconium phosphate reacts relatively easily with NaOH to form monosodium and disodium zirconium phosphates.

In the fresh sample of NaZP(02) which was prepared by adding NaCl only with a relatively low amount, MSZP was the only crystalline phase observed but crystalline NaCl and ZrPP were not observed. In the fresh samples of NaZP(04) and NaZP(06) prepared with higher amounts of NaCl, NaCl and MSZP were observed together with small amounts of PSZP [pentasodium zirconium phosphate : $Na_5Zr(PO_4)_3$]. This means that NaCl can also react with zirconium phosphate relatively easily to form monosodium zirconium phosphate in the

first place with liberation of chlorine, and that about two moles of NaCl per Zr is readily consumed. However, the formation of crystalline disodium zirconium phosphate from NaCl does not seem to occur readily when compared with NaOH, and it is considered that poorly crystalline substances may exist to some extent. When the used samples were looked at, it was seen that decomposition of NaCl and subsequent solid state reactions of Na with MSZP occurred during the reaction of OCM to form DSZP and more PSZP.

In the fresh samples prepared by adding NaOH and NaCl together, the presence of NaCl was observed even if the added amount of NaCl was small, such as in NaZP(21) and NaZP (22). This means that zirconium phosphate reacts preferentially with NaOH rather than NaCl. In these fresh samples MSZP and DSZP were coexistent. In the fresh samples of NaZP(24) and NaZP(26), which were prepared with larger amounts of NaCl, however, the presence of MSZP was not observed but DSZP or PSZP was present. This is due to the larger amount of sodium ions which were freed from chlorine after decomposition of NaCl. Disappearance of NaCl was clearly seen in the used catalysts, and the amount of a sodium zirconium phosphate compound having a higher Na/Zr ratio appeared to become larger after the OCM reaction. Another aspect to be noted in the used samples is the presence of ZrO_2 with significantly large amounts, especially for the samples with high sodium content, which indicates that the sodium zirconium phosphates are not stable under the reaction conditions. Formation of ZrO_2 should accompany formation of other compounds such as sodium phosphates, but crystalline phases of such compounds were not clearly seen. However, it was observed that some unidentified phases were present, and they were considered to be partially crystallized Na_3PO_4 and/or $NaPO_3$ although the XRD peaks were in partial agreement with those in the JCPDS files, with one or two of the major peaks missing or somewhat shifted.

To summarize the results of XRD analysis, the heat-treated ZrP gel forms well-developed cubic ZrPP. The gel reacts with NaOH and NaCl relatively easily, the former reacting more readily than the latter, to form mostly MSZP and DSZP with formation of smaller amounts of PSZP in some cases. Decomposition of NaCl continues during the heat treatment and the OCM reaction, with subsequent conversion of MSZP to DSZP and then to PSZP and so on if a sufficient amount of sodium is present. The sodium zirconium phosphates are decomposed to ZrO_2 and sodium phosphates during the reaction of OCM, and it seems that a large amount of sodium may facilitate the decomposition.

3. EDS and XPS Analyses

The results of EDS analysis are given in Table 3. The composition of each element could not be reliably determined because the Zr Lα and P Kα lines are so close that they could not be satisfactorily resolved by the spectrometer. Therefore, only the Cl/Na ratios are presented. The compositions of Zr plus P in the samples were estimated to be roughly 40-60 % when excluding oxygen. The EDS results are generally in agreement with the XRD results. Disappearance of chlorine during the heat treatment and during the reaction of OCM was

Table 3. Cl/Na atomic ratio analyzed by EDS

Catalyst	NaZP(02)	NaZP(04)	NaZP(06)	
Fresh	0.0	0.52	0.94	
Used	0.0	0.05	0.51	
Catalyst	NaZP(21)	NaZP(22)	NaZP(24)	NaZP(26)
Fresh	0.14	0.37	0.32	0.62
Used	0.0	0.10	0.19	0.31

clearly seen. The results also suggest that about two or more moles of sodium, whether originated from NaCl or NaOH, readily participate in the formation of sodium zirconium phosphates and that crystalline NaCl can hardly be observed by XRD if the Cl/Na ratio is smaller than about 0.2.

The XPS results for representative samples are presented in Tables 4 and 5. The binding energies of Zr $3d_{5/2}$, 182.5-182.8 eV, were almost the same for all the samples. These values are higher by about 0.5 eV than those reported for Zr^{4+} in ZrO_2 [Briggs and Seah, 1990; Wagner et al., 1979]. This difference might be due to the interaction between Zr^{4+} and the phosphate groups. This suggests that most of ZrO_2 which was observed by XRD was not present at the surface. For the binding energies of the other elements, the values were almost the same regardless of the sample except for the used NaZP(04) and the used NaZP(22). A common feature for these two samples is that the Cl/Na ratio is significantly low, or that the amount of NaCl remaining is small. The binding energy of near 198.0 eV for the chlorine indicates that most of the Cl⁻ is bound to Na⁺, when compared with the value reported in the literature [Briggs and Seah, 1990; Wagner et al., 1979]. The binding energy of around 199.0 eV for the chlorine in the

Table 4. XPS results for binding energies

Catalyst		Binding energy (eV)				
		Zr $3d_{5/2}$	P 2p	O 1s	Na 1s	Cl 2p
NaZP(04)	Fresh	182.7	133.0	530.9	1071.6	198.9
	Used	182.8	132.4	530.2	1071.0	197.9
NaZP(06)	Fresh	182.5	132.8	530.6	1071.6	198.7
	Used	182.7	133.1	530.9	1071.6	199.2
NaZP(22)	Fresh	182.8	133.1	531.0	1071.7	199.2
	Used	182.8	132.2	530.7	1071.3	198.3
NaZP(26)	Fresh	182.6	132.8	530.7	1071.6	199.0

Table 5. XPS results for surface composition

Catalyst		Surface composition (%)					Atomic ratio		
		Zr	P	O	Na	Cl	P/Zr	O/P	Cl/Na
NaZP(04)	Fresh	2.3	18.5	55.2	12.9	11.1	8.0	3.0	0.86
	Used	6.4	16.2	55.9	21.0	0.7	2.5	3.5	0.03
NaZP(06)	Fresh	1.9	17.2	49.5	14.2	17.3	9.1	2.9	1.22
	Used	2.9	18.4	53.6	13.0	12.1	6.3	2.9	0.93
NaZP(22)	Fresh	4.2	17.3	57.8	10.7	10.0	4.1	3.3	0.93
	Used	4.2	18.9	63.6	12.0	1.2	4.5	3.4	0.10
NaZP(26)	Fresh	4.3	17.9	56.5	11.0	10.3	4.2	3.2	0.94

other samples having larger amount of chlorine suggests that the electron density of the chlorine is lower, probably by interaction with Zr^{4+} besides Na^+. This suggestion may be supported by the fact that the chlorine bound to a cation of a higher oxidation number, such as Ni^{2+}, Cu^{2+}, Zn^{2+} or Fe^{3+}, shows a higher binding energy by about 1 eV [Briggs and Seah, 1990; Wagner et al., 1979]. The presence of this kind of higher-binding-energy chlorine species has been reported for a NaCl-added ZrO_2 system in an earlier work, and this is considered to be in some fashion related with the catalytic activity in the OCM [Yoon and Seo, 1996]. Although the observed binding energy of the chlorine in the fresh catalysts and the used NaZP(06) which had significantly high content of chlorine were all around 199.0 eV, this does not mean that all the chlorine species in these samples is the higher-binding-energy species but a small portion of the chlorine can be present as the lower-binding-energy species. It is considered that the amount of the lower-binding-energy species in these samples is considerably smaller than that of the other species, presumably by smaller than 1/10, and thus the peak for the lower-binding-energy species was not clearly seen in the XPS analysis.

The binding energy of Na 1s in the samples having high Cl/Na ratios (1071.6-1071.7 eV) is in good agreement with that in NaCl [Briggs and Seah, 1990; Wagner et al., 1979], while that used in NaZP(04) and NaZP(22) having low Cl/Na ratios was somewhat lower. This may be explained by the fact that the former is mostly due to the sodium bound to chlorine while the latter is mainly due to the sodium bound to the phosphate group. The relatively lower binding energies of P 2p and O 1s as well as Na 1s in used NaZP(04) and NaZP(22) are considered due to the presence of a large amount of Na_3PO_4 on the surface in addition to the sodium zirconium phosphates, and those binding energies were in good agreement with those in Na_3PO_4 reported in the literature [Briggs and Seah, 1990; Morgan et al., 1973; Wagner et al., 1979]. The binding energies of P 2p and O 1s in the other samples may be ascribed to those in sodium zirconium phosphates.

The Cl/Na ratios obtained by XPS which were near unity except for used NaZP(04) and NaZP(22) were significantly higher than those obtained by EDS, and the Cl/Na ratios for used NaZP(04) and NaZP(22) were about the same as those obtained by EDS. This indicates that the chlorine whether bound to Zr^{4+} or to Na^+ is preferentially present at the surface rather than imbedded in the bulk, and so is NaCl. The surface compositions of zirconium were relatively low as indicated by the P/Zr ratios for all the samples, when compared with the stoichiometric ratios in the sodium zirconium phosphates. This may be explained by the presence of large amounts of NaCl or Na_3PO_4 on the surface.

4. Catalytic Performance Testing

The OCM was carried out with the empty tube, heat-treated ZrP gel and NaZP(20), and the results at 1,023 K are presented in Table 6. Although a small amount of ethane was obtained over the heat-treated gel, it is trifling. Since all the methane conversions were significantly low, it can be said that quartz, zirconium pyrophosphate and sodium zirconium phosphates by themselves do not practically catalyze the OCM as well as

Table 6. Activity test for the OCM at 1,023 K with empty tube, heat-treated ZrP gel and NaZP(20)

Catalyst	CH_4 conv. (%)	Selectivity (%)			C_2 yield (%)
		CO_2	C_2H_4	C_2H_6	
None	0.53	100	-	-	-
Heat-treated ZrP gel	0.81	46	-	54	0.44
NaZP(20)	0.14	100	-	-	-

the combustion reaction. In other words, the phosphate groups are inert for methane activation and combustion and the presence of sodium also has little effect on them.

Results of the OCM reaction with time on-stream over the catalysts added with NaCl are shown in Figs. 1-5. These catalysts showed markedly increased activity and high C_{2+} selectivity compared with heat-treated ZrP gel and NaZP(20). This indicates that the presence of chlorine is essential for the catalyst system to be effective. The product distribution at a given time for each catalyst is given in Table 7. In most cases, the selectivity to CO_2 was considerably low or the selectivity to CO was much higher than that to CO_2. This is considered to result from the low combustion activity of sodium zirconium phosphates.

Among the catalysts added with NaCl only, NaZP(02) exhibited the lowest activity and this is due to the low content of chlorine remaining even in the fresh catalyst. NaZP(04) exhibited higher activity but deactivated more rapidly than NaZP(06). The rapid deactivation of NaZP(04) is certainly due to disappearance of chlorine, as shown by the EDS and XPS analyses (Tables 3 and 5). The lower activity of NaZP(06) may be explained by the larger amount of NaCl which covers a larger number of active surface sites during the early time on-stream, while the more stable behavior of NaZP(06) can be attributed to the content of NaCl maintaining higher for a longer time. Although the experiment for NaZP(04) was stopp-
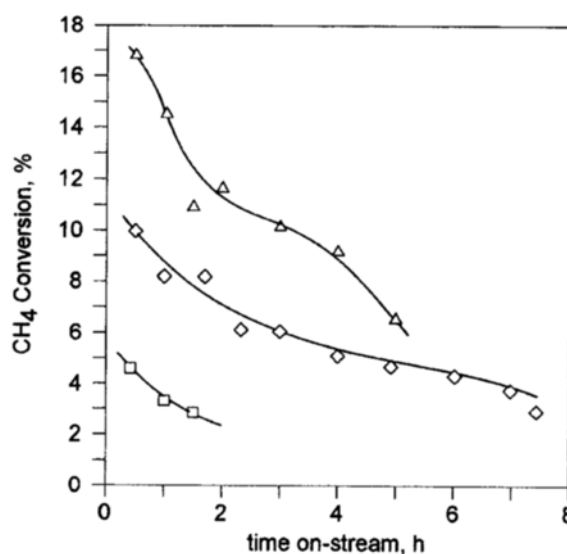
Fig. 1. CH_4 conversion vs. time on-stream at 1,023 K over NaCl-added catalysts.
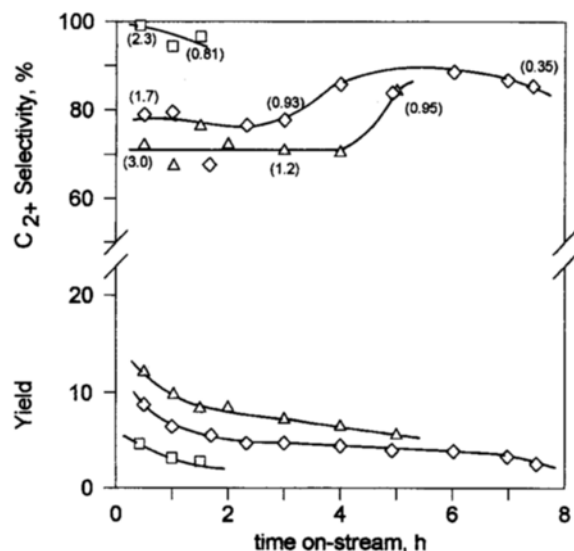□ : NaZP(02) ; △ : NaZP(04) ; ◇ : NaZP(06)

Fig. 2. C₂₊ selectivity and yield vs. time on-stream at 1,023 K over NaCl-added catalysts.

□: NaZP(02); △: NaZP(04); ◇: NaZP(06). The number in parentheses is the ethene/ethane ratio.
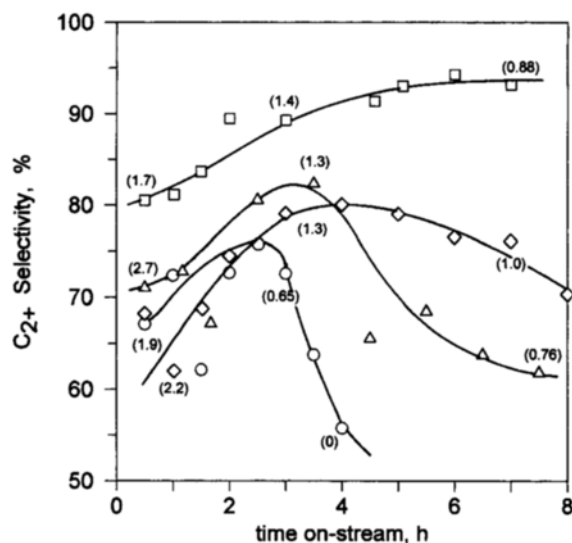

Fig. 4. C₂₊ selectivity vs. time on-stream at 1,023 K over (NaOH+ NaCl)-added catalysts.

○: NaZp(21); □: NaZP(22); △: NaZP(24); ◇: NaZP(26). The number in parentheses is the ethene/ethane ratio.
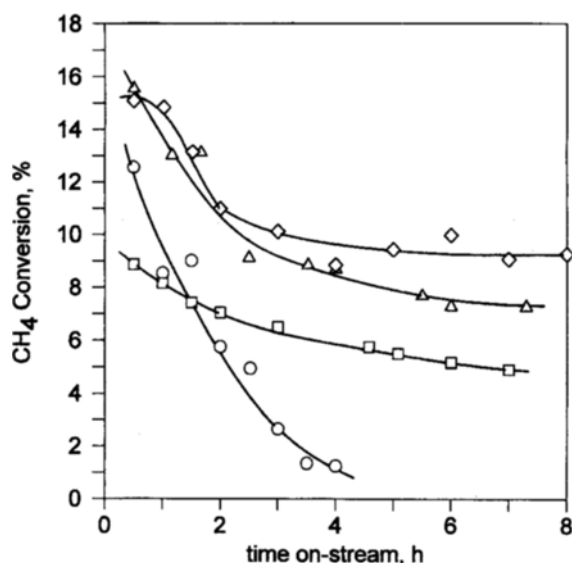

Fig. 3. CH₄ conversion vs. time on-stream at 1,023 K over (NaOH+NaCl)-added catalysts.
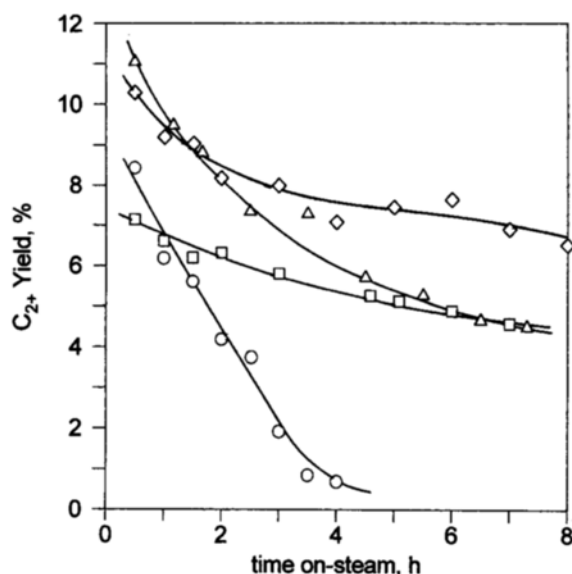
○: NaZp(21); □: NaZP(22); △: NaZP(24); ◇: NaZP(26)

Fig. 5. C₂₊ yield vs. time on-stream at 1,023 K over (NaOH+ NaCl)-added catalysts.

○: NaZp(21); □: NaZP(22); △: NaZP(24); ◇: NaZP(26)

ed at 5 h on-stream due to the rapid decrease of the conversion, the conversion over NaZP(04) after about 6 h is expected to become similar to that over NaZP(06). An observed trend is that the C₂₊ selectivity becomes higher with the decrease of the methane conversion, as is usually observed in the OCM studies. For example, as shown in Figs. 1 and 2, NaZP(04) showed higher conversion and lower selectivity compared with NaZP(06) during the early time on-stream, but at a later time the selectivity tended to become higher with the decrease of the conversion.

Among the catalysts added with NaOH and NaCl together, NaZP(21) rendered considerably high methane conversion at early time on-stream but deactivated very rapidly (Fig. 3). This

rapid deactivation is due to exhaustion of NaCl. For the other catalysts, the methane conversion became higher and the stability became better with increase of the amount of NaCl added. Although a catalyst with a higher amount of NaCl than NaZP(26) was not investigated, it is expected that the methane conversion will decrease if the amount of NaCl exceeds a certain value. The change of C₂₊ selectivity with time on-stream was rather complex (Fig. 4), and multiple factors seem to affect this. The increase of the selectivity during the initial 3-4 h may be considered in agreement with the general trend accompanying the decrease of methane conversion. One possible reason for the decrease after that is the change of catalytic substances such as transformation and decomposition of sodium

Table 7. Product distribution over the catalysts at a given time under standard conditions

Catalyst	Time (h)	Conv. (%)	Selectivity (%)					Yield (%)
			CO	CO$_2$	C$_2$H$_4$	C$_2$H$_6$	C$_3$	
NaZP(02)	1.5^a	2.9	-	3	42	52	3	0.8
NaZP(04)	4	9.2	25	5	32	30	9	6.5
NaZP(06)	4	5.1	-	14	33	53	-	4.4
NaZP(21)	4^a	1.2	-	44	-	56	-	0.7
NaZP(22)	6	5.2	4	2	40	54	-	4.9
NaZP(24)	6	7.3	32	4	29	35	-	4.6
NaZP(26)	6	10.0	20	3	39	31	6	7.6

^{a}Due to low conversion or rapid deactivation, the experiment was stopped at that time.

zirconium phosphates together with disappearance of NaCl. NaZP(22) showed relatively stable selectivity compared with NaZP(24) and NaZP(26), and this suggests that there is an optimum amount of sodium chloride for the selectivity to be stable ; if the sodium chloride is present too much, the change of catalytic substances seems to proceed to a greater extent. When the catalysts added with NaOH and NaCl are compared with those added with NaCl only, the overall catalytic performance of the former is better than that of the latter, specifically in activity and stability. This may be explained by the observed fact that the sodium zirconium phosphates are more readily formed by NaOH rather than by NaCl and thus the NaCl content can remain higher and longer, which rendering more active and stable catalytic substances.

Dependence of the catalytic performance on the space time, W/F, is given in Fig. 6, where W is the catalyst weight and F is the volumetric gas flow rate. One thing to be mentioned here is that the NaZP(22) catalyst employed in this experiment was the one prepared from a batch different from that shown in previous tables and figures. This catalyst from a new batch showed somewhat higher activity and stability, and the data were collected between 2 and 6 h on stream during which the deactivation was slow. As is expected, the conversion increased with W/F while the selectivity decreased, and thus the yield stayed nearly constant above a certain value of W/F (about 1 g-cat·s/cm^3).

Although the presence of two kinds of surface chlorine species was observed, there is some uncertainty in the role of each species. It is hard to see any trend between the activity and the surface concentration of the higher-binding-energy chlorine species. The catalytic activities of NaZP(04) and NaZP (06) at about 6-h on stream are similar even though the chlorine species and the surface composition of chlorine for the used samples were observed to be quite different by XPS (Fig. 1, Tables 4 and 5). NaZP(22) still showed fairly high activity at 7-h on stream even though the used NaZP(22) had a significantly low surface composition of chlorine which is mostly composed of lower-binding-energy species. These suggest that the lower-binding-energy chlorine species is probably much more active than the higher-binding-energy species in methane activation and the contribution of the latter to methane activation is considerably small. Considering the fact that NaCl
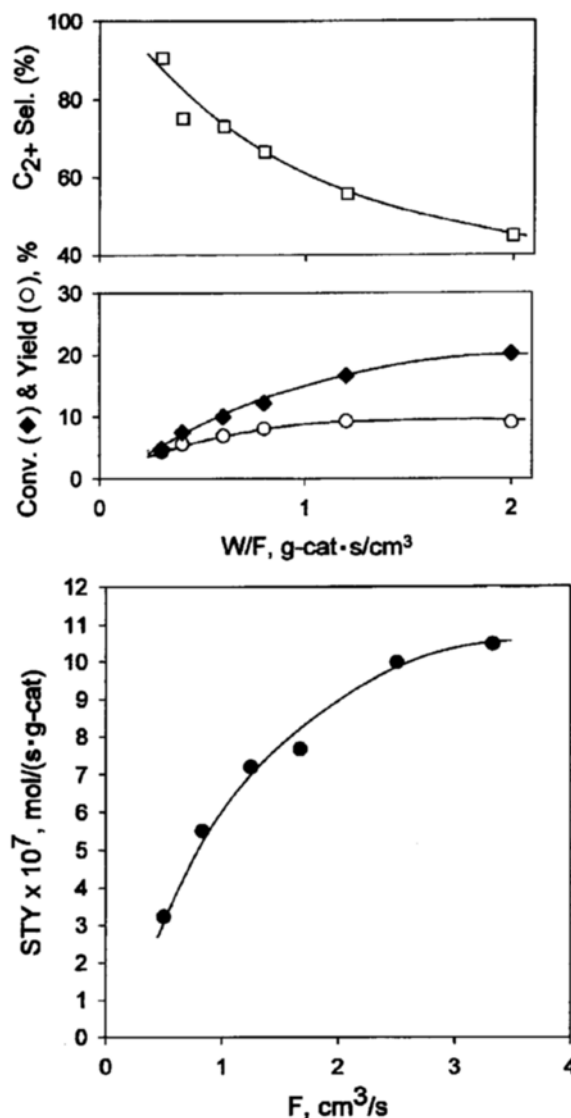
Fig. 6. Dependence of the catalytic performance on space time over NaZP(22) at 1,023 K (CH$_4$/O$_2$=2, STY=space time yield).

per se is ineffective for methane activation, it is considered that an aid of Zr^{4+} may be needed for the lower-binding-energy chlorine species to activate methane. In other words, it may be suggested that the active species for methane activation is the lower-binding-energy chlorine species which has an interaction to some (but not too high) extent with Zr^{4+}. The role of the higher-binding-energy chlorine species may be presumed to contribute as a reservoir for the lower-binding-energy chlorine species or only a very small part of it participates to activate methane. A similar suggestion has been made in an earlier work on NaCl-promoted ZrO$_2$ [Yoon and Seo, 1996].

A comparison of the catalysts investigated in this work with the catalyst prepared from a mixture of zirconium chloride and sodium pyrophosphate in a previous work [Yoon and Seo, 1997] indicates that the former showed comparable selectivity and stability but considerably lower activity and yield than the latter, even though the main active substances were considered to be the same. One possible reason to be consider-