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SHORT COMMUNICATION

OXIDATIVE COUPLING OF METHANE OVER Na^+-ZrO_2-Cl^-/Al_2O_3 CATALYSTS

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Abstract – Oxidative coupling of methane (OCM) was carried out over Na^+-ZrO_2-Cl /Al_2O_3 catalysts in a temperature range from 1023 to 1123 K. The catalysts were prepared by impregnating the α- or γ-Al_2O_3 supports with sodium carbonate and/or zirconyl chloride. The OCM activity was examined using the catalysts prepared by three different preparation procedures. The best catalyst was the one prepared by subsequent impregnation of sodium carbonate-preimpregnated γ-Al_2O_3 with a mixed solution of sodium carbonate and zirconyl chloride. It was found that preimpregnated sodium played an important role in reducing the combustion activity of the γ-Al_2O_3. The catalyst with an optimal composition showed the highest C_2 selectivity and yield of 40.8% and 15.1%, respectively. From the X-ray diffraction analysis it was found that tetragonal ZrO_2 was formed and that NaCl existed in the catalysts with relatively high sodium contents.

Key words: *Alumina-Supported, Methane, Oxidative Coupling, Sodium Chloride, Zirconia*

INTRODUCTION

Direct conversion of methane into petrochemical feedstocks has been the focus of a number of research efforts because the conversion can provide significant advantages of storage and transportation of natural gas. One of the promising direct conversions to C_2 (ethane and ethylene) is oxidative coupling of methane (OCM). Since the pioneering work of Keller and Bhasin [1982] opened a possibility of this reaction over metal oxide catalysts, a vast number of different catalysts have been put to a test for the OCM, and many investigators have found that promotion of various oxides with alkali metal compounds gives considerable improvements of the activity and product selectivity [Lee and Oyama, 1988; Amenomiya et al., 1990; Hutchings and Scurrell, 1992].

ZrO_2 has been reported to be almost inactive for the oxidative coupling [Keller and Bhasin, 1982], but recently several studies have shown that ZrO_2 promoted with alkali metal compounds exhibits noticeable activity and selectivity for the OCM. Matsuhashi et al. [1989] reported that C_3 hydrocarbons were predominantly produced over sodium-doped ZrO_2 catalysts. Their best result was that the conversion of methane was 18.2% and selectivity for C_{2+} was 59% at the temperature of 878 K using a 4.3 mol% sodium-doped catalyst. Khan and Ruckenstein [1992, 1993] reported that Na^+-ZrO_2-Cl catalysts which were prepared by a sol-gel method exhibited good performance. They obtained the highest C_2 yield of 14.1% with the C_2 selectivity of 43% and the highest C_2 selectivity of 77% with the C_2 yield of 10.6%. Our previous study [Yoon and Seo, 1996] also showed that unsupported Na^+-ZrO_2-Cl catalysts, which were prepared from a mixed solution of zirconyl chloride and sodium carbonate, gave the highest C_{2+} yield of 16.6% with the C_{2+} selectivity of 64% at 1023 K. It was also found from the characterization that the catalyst prepared from zirconyl chloride and sodium carbonate as the precursors could more properly be designated as Na^+-ZrO_2-Cl^-.

Support materials have been used in the catalysts for the OCM and existence of strong support effects has been reported by several investigators. Hinsen et al. [1984] have reported that for PbO catalysts supported on various oxides the C_2 selectivity increases as the basicity of the support increases, and Chang and Park [1992] have reported similar results. Park and Chang [1992] have also suggested that a strong support interaction may exist in alumina-supported PbO catalysts or lead aluminate formed by the reaction between PbO and the support may be the active species for the OCM.

In this study, as a continued study of our previous work to investigate the effects of support materials, we investigated the OCM over Na^+-ZrO_2-Cl^- catalysts supported on α or γ-Al_2O_3. It is expected that there might be a trade-off for the two types of Al_2O_3 supports, in a sense that α-Al_2O_3 has smaller surface area but lower acidity and higher stability at high temperature while γ-Al_2O_3 has larger surface area but stronger acidity and lower stability at high temperature. Presence of the sodium compound may alter the acidity and surface area of the supports. With those catalysts the activity and selectivity of C_2 production for the oxidative coupling reaction were investigated using an atmospheric presssure cofeed mode fixed-bed reactor. Catalytic and structural characteristics of the catalysts used in this study were examined by reaction experiments, XRD and BET measurements.

EXPERIMENTAL

The supported Na^+-ZrO_2-Cl^- catalysts used in this experiment were prepared with both α- and γ-Al_2O_3 supports. Commercial

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α-Al_2O_3 (Johnson Matthey; pore volume=0.23 cm^3/g) and γ-Al_2O_3 (Harshaw, Al-3996R; surface area=188 m^2/g, pore volume=0.71 cm^3/g) supports were used after crushing it to the particle sizes of −40/+80 mesh.

The catalysts were prepared by impregnating the supports with zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, Junsei Chemical, >99% purity) and/or sodium carbonate ($Na_2CO_3 \cdot 10H_2O$, Shinyo Pure Chemical, >99% purity) solutions. The catalysts were dried at 673 K for 2 h and calcined at 1073 K for 2 h. Since the amount of the catalytic materials impregnated per impregnation cycle was limited, repeated impregnation was performed to have a certain catalyst composition. For the impregnation, the salt solutions were used either separately or as a premixed solution. As a mixed solution, the Na/Zr molar ratio of 1.2 was selected, which had been reported to be an optimum for the oxidative coupling reaction [Yoon and Seo, 1996]. Three types of the Na^+-ZrO_2-Cl^- catalysts were prepared for the experiment, which were

(1) catalysts impregnated with sodium carbonate and zirconyl chloride, separately in series,

(2) catalysts impregnated with a premixed solution only,

(3) catalysts impregnated with sodium carbonate and a premixed solution in series.

Througout this study the catalysts are designated as *-*/*(*). The first alphabet is used as a classification of different supports, that is to say, A for α-Al_2O_3, C for γ-Al_2O_3. The next two numbers mean the atomic ratios of (Na/Al)×100 and (Zr/Al)×100, respectively. The last number in the parenthesis means the different preparation procedure of catalysts.

The oxidative coupling reaction was carried out in a fixed-bed tubular reactor operated at atmospheric pressure. Reactants were methane and air, and the diluent gas was nitrogen. The reaction experiments were carried out with a cofeed mode in which both reactants enter the reactor simultaneously with higher CH_4/O_2 ratio above the explosion limit. The reaction was carried out in the temperature range from 1023 to 1123 K with the partial pressures of methane and oxygen of 0.16 and 0.08 atm, respectively, and with the total flow rate of reactants of 100 cm^3/min. The amount of catalyst used in a run was 2 g.

The product analyses were performed by temperature-programmed gas chromatography using a Carbosieve S-II column to detect H_2, O_2, CH_4, CO_2 and CO, and a Chromosorb 102 column for CH_4, CO_2, C_2H_6, C_2H_4, C_3H_8, and C_3H_6. Structural properties of the catalysts before and after a reaction run were characterized by X-ray diffraction ($20° < 2\theta < 80°$, Cu-Kα line) and BET measurements.

RESULTS AND DISCUSSION

1. OCM Reaction with Al_2O_3 and Na_2CO_3/Al_2O_3

As a result of the reaction with Al_2O_3 supports only, the reaction products were mostly CO_2 and no C_2 products were observed as shown in Table 1. The Al_2O_3 itself does not have OCM activity, but high activity for direct combustion of methane. This high activity for combustion is considered to be due to high acidity or lattice oxygens of Al_2O_3. The γ-Al_2O_3 exhibited much higher methane conversion than α-Al_2O_3, which is probably due to larger surface area and higher acidity of γ-Al_2O_3.

Table 1. Results of the reaction over Al_2O_3 and Na_2CO_3/Al_2O_3
(Flow rate=100 cm^3/min, $CH_4/O_2=2$, $P_{CH4}=0.16$ atm, Temp. =1023 K)

Catalyst	CH_4 conversion (%)	Selectivity (%)				C_2 yield (%)	C_2H_4/C_2H_6
		CO_2	CO	C_2H_4	C_2H_6		
α-Al_2O_3	18.1	100	-	-	-	-	-
γ-Al_2O_3	26.5	100	-	-	-	-	-
A-3.3/0	25.1	74.6	-	9.9	15.5	6.4	0.64
A-8.6/0	28.5	61.4	-	18.3	20.3	11.0	0.90
C-17.0/0	26.8	82.0	13.4	2.3	2.3	1.2	1.00
C-34.5/0	27.0	83.1	13.4	1.3	2.3	1.0	0.57

Table 2. Results of the reaction over Na^+-ZrO_2-Cl /α-Al_2O_3
(Flow rate=100 cm^3/min, $CH_4/O_2=2$, $P_{CH4}=0.16$ atm, Temp. =1023 K)

Catalyst	CH_4 conversion (%)	Selectivity (%)				C_2 yield (%)	C_2H_4/C_2H_6
		CO_2	CO	C_2H_4	C_2H_6		
A-5.0/6.9 (1)	29.8	67.7	-	17.2	15.0	9.6	1.1
A-3.6/3.0 (2)	28.3	71.9	-	12.7	15.4	8.0	0.82
A-6.1/5.0 (2)	30.0	61.0	-	25.1	13.9	11.7	1.8
A-9.3/7.8 (2)	31.1	68.9	-	17.2	13.9	8.6	1.2
A-17.2/4.8 (3)	23.7	73.0	-	9.8	17.2	6.4	0.57

The catalysts impregnated with Na_2CO_3 showed the OCM activity, which is thought to be originated from sodium aluminate produced by the reaction of sodium carbonate with Al_2O_3. The γ-Al_2O_3 supported catalysts have much lower C_2 selectivity than α-Al_2O_3 supported catalysts. This might be due to the fact that the γ-Al_2O_3 has higher acidity and larger pore volume to cause subsequent combustion of C_2 products after they have been produced.

2. OCM Reaction with Na^+-ZrO_2-Cl^-/α-Al_2O_3 Catalysts

The OCM activity of the Na^+-ZrO_2-Cl^-/α-Al_2O_3 catalysts prepared by three different procedures are shown in Table 2. All the catalysts showed similar OCM activity and no noticeable differences were observed between the differently prepared catalysts. In view of showing the similar activity to those of Na_2CO_3/α-Al_2O_3, the zirconium oxide by itself is considered to contribute little on the OCM activity. While the highest C_2 yield was obtained with A-6.1/5.0 (2), the catalysts prepared by the procedure (3) showed the lowest yield. Due to the small pore volume of α-Al_2O_3, the preparation of catalysts with higher impregnation was not possible.

3. OCM Reaction with Na^+-ZrO_2-Cl /γ-Al_2O_3 Catalysts

As listed in Table 3, C-13.5/11.5 (2) showed lower C_2 selectivity and yield than those of the α-Al_2O_3 supported catalysts although it had higher Na/Al and Zr/Al atomic ratios. This result could be explained by the stronger acidity and higher surface area of γ-Al_2O_3 which might have helped undesirable combustion reactions to take place. For this reason, the catalysts with higher contents of Na were prepared by the procedure (3), in order to suppress the combustion reactions by the preimpregnated Na. In this regard, it is worthwhile to note that the preparation

Table. 3. Results of the reaction over Na$^+$-ZrO$_2$-Cl$^-$/γ-Al$_2$O$_3$: Effect of increasing impregnation of the Na-preimpregnated alumina with the mixed solution

(Flow rate=100 cm^3/min, CH$_4$/O$_2$=2, P_{CH4}=0.16 atm)

Catalyst	Temp. (K)	CH$_4$ conversion (%)	Selectivity (%)				C$_2$ yield (%)	C$_2$H$_4$/C$_2$H$_6$
			CO$_2$	CO	C$_2$H$_4$	C$_2$H$_6$		
C-13.5/11.5 (2)	1023	28.1	76.9	14.9	5.1	3.1	2.3	1.65
C-13.5/11.5 (2)	1073	29.4	76.9	15.1	3.7	4.4	2.4	0.84
C-80.6/29.3 (3)	1023	36.5	52.4	10.2	8.5	28.8	13.7	0.30
C-59.3/11.5 (3)	1073	35.8	58.4	5.1	16.2	20.3	13.1	0.80
C-72.7/22.5 (3)	1073	37.4	54.7	6.0	17.0	22.3	14.7	0.76
C-80.6/29.3 (3)	1073	37.0	52.9	6.3	16.0	24.8	15.1	0.65
C-59.3/11.5 (3)	1123	35.3	57.6	7.4	13.0	22.0	12.4	0.59
C-72.7/22.5 (3)	1123	35.5	59.2	7.5	11.3	22.0	11.8	0.51
C-80.6/29.3 (3)	1123	37.0	52.9	6.3	16.0	24.8	14.2	0.65

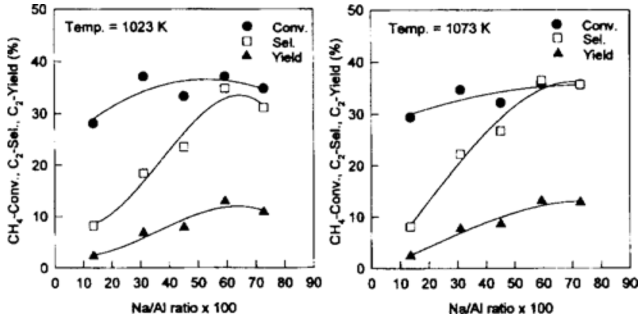

Fig. 1. Methane conversion, selectivity and yield to C$_2$ products over Na$^+$-ZrO$_2$-Cl$^-$/γ-Al$_2$O$_3$ (3) catalysts (Zr/Al=0.115).
(Reaction conditions: total flow rate=100 cm^3/min, CH$_4$/O$_2$=2, P_{CH4}=0.16 atm)

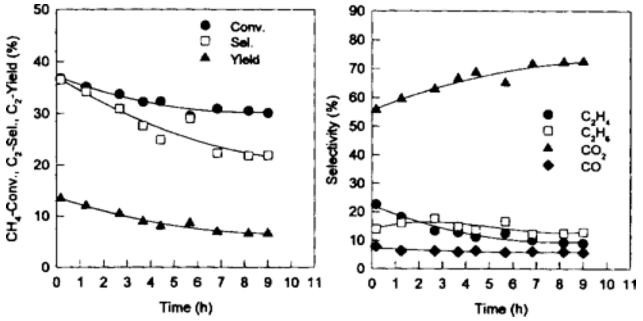

Fig. 2. Activity and product selectivity changes with reaction time for a Na$^+$-ZrO$_2$-Cl$^-$/γ-Al$_2$O$_3$ catalyst [C-72.7/22.5 (3)].
(Reaction conditions: total flow rate=100 cm^3/min, CH$_4$/O$_2$=2, P_{CH4}=0.16 atm, Temp.=1023 K)

procedure (3) gave the best result for the OCM reaction over SiO$_2$-supported Na$^+$-ZrO$_2$-Cl$^-$ catalysts and that the preimpregnated Na was found to greatly suppress the combustion activity of the support [Tung and Yoon, 1995].

In order to investigate the OCM activity of various Na$^+$-ZrO$_2$-Cl$^-$/γ-Al$_2$O$_3$ catalysts prepared by the procedure (3), the sodium contents of the catalysts were increased by changing the preimpregnation, maintaining the zirconium content constant. As a result of the experiment, it was found that the preimpregnation of Na played an important role in the catalyst system. As shown in Fig. 1, the C$_2$ selectivity and yield increased with the preimpregnated Na contents (Na$_{pre}$), although the methane conversion did not change appreciably. With further increase of Na$_{pre}$, the C$_2$ selectivity and yield passed through a maximum or were flattened at the Na$_{pre}$/Al ratio of about 0.46 (in Fig. 1, Na$_{pre}$/Al=Na/Al-0.135). Considering high combustion activity and low OCM activity of Na$_2$CO$_3$/γ-Al$_2$O$_3$ catalysts due to the high acidity and surface area of γ-Al$_2$O$_3$, an increased amount of preimpregnated sodium is thought to compensate acidic sites of γ-Al$_2$O$_3$ or to cover the alumina surface to reduce the combustion activity. It is considered that preimpregnated sodium could also prevent further interaction or reaction of sodium in the mixed solution with the alumina support. Therefore, further addition of sodium and zirconium by mixed-solution impregnation might help to create active sites for the OCM due to an intimate interaction between ZrO$_2$ and Na$^+$Cl$^-$, as in the case for the unsupported as well as SiO$_2$-supported Na$^+$-ZrO$_2$-Cl$^-$ [Yoon and Seo, 1996; Tung and Yoon, 1995; Khan and Ruckenstein, 1992, 1993].

As the sodium and zirconium contents were increased by the repeated impregnation with the mixed solution after the optimal sodium preimpregnation of Na$_{pre}$/Al=0.46, the C$_2$ selectivity and yield were observed to increase, probably due to an increase in active sites of Na$^+$-ZrO$_2$-Cl$^-$. It is shown in Table 3. It was not possible to obtain catalysts with higher contents of sodium and zirconium because of limited pore volume of the γ-Al$_2$O$_3$. As a result of OCM reaction at three different temperatures of 1023, 1073 and 1123 K using the three different catalysts in the table, the highest C$_2$ yield was obtained at 1073 K with the C$_2$ selectivity of 40.8 %. At 1023 and 1123 K the methane conversion was comparable but the C$_2$ selectivity and yield were lower by 2-4 % and 1-3 %, respectively. These yields and selectivities are somewhat lower than those for the unsupported catalysts, probably due to the acidity and high surface area of the support.

4. Catalyst Deactivation

One of the problems in OCM catalysts is poor stability, which is more pronounced in the catalyst with additives particularly. The deactivation is caused by two main factors; one is the sintering effect at high reaction temperature, and the other is loss of additives which play an important role for the activity. It is expected that the coking could be ignored beacause of the existence of oxygen at the high reaction temperatures.

Typical catalyst deactivation with time is shown in Fig. 2 for the catalyst C-72.7/22.5(3). The methane conversion and C$_2$

Table 4. BET surface area of γ-alumina-supported catalysts

Catalyst	Surface area (m^2/g)	
	Before reaction	After reaction
γ-Al_2O_3	-	118
C-34.5/0	75	-
C-13.5/11.5 (3)	91	107
C-31.0/11.5 (3)	107	100
C-59.3/11.5 (3)	77	74
C-72.5/22.5 (3)	83	81

selectivity decreased with time relatively fast until 5 hours passed and the rate of decreases slowed down thereafter. After 9 hours the C_2 yield was reduced by half. At the early stage of the reaction, ethylene was produced more than ethane, but it was reversed as times went by. On the other hand, the CO selectivity was kept almost constant.

5. Catalyst Characterization

The BET surface areas of the γ-Al_2O_3 supported catalysts are shown in Table 4. The surface area of unimpregnated γ-Al_2O_3 was somewhat reduced after impregnation, but still retained fairly high values. This is in agreement with an earlier observation that the sodium does not affect much to the reduction of the surface area of alumina [Perrichon and Durupty, 1988], but forms a contrast to the case of silica [Tung and Yoon, 1995]. The surface areas of the catalysts impregnated with sodium carbonate and zirconyl chloride were measured to the scattered values of about 74 to 107 m^2/g, not showing noticeable differences before and after the reaction. From the measurements it can be concluded that the surface area of the catalysts prepared in this study is thermally stable.

The X-ray diffraction was measured for the analysis of catalyst structural properties before and after the reaction. For the catalysts impregnated only with Na_2CO_3, no signs of the sodium species were detected, which means the species are present as thin layers or amorphous phases. On the other hand, the NaCl and tetragonal ZrO_2 peaks, although their intensities were relatively weak, were detected for the catalyst impregnated with both sodium carbonate and zirconyl chloride. In the previous study [Yoon and Seo, 1996], the unsupported Na^+-ZrO_2-Cl^- catalysts were reported to contain a monoclinic ZrO_2 phase. It has been reported by Sohn et al. [1989] that the tetragonal ZrO_2 phase changes to the monoclinic phase, starting from at 873 K and completing at above 1073 K. However, the γ-Al_2O_3 supported catalysts used in this study were found to contain tetragonal ZrO_2 even above 1073 K. This result can be explained by the fact that the phase transition could be deterred in the case of some multicomponent mixtures, as reported by Sohn et al. [1989].

The NaCl peaks were detected for the catalysts only with high sodium contents. The source of Cl^- was a precursor solution of $ZrOCl_2 \cdot 8H_2O$. Upon mixing Na_2CO_3 and $ZrOCl_2$ solutions, the NaCl could be formed without any excess if Na/Zr ratio is equal to 2. In the course of catalyst preparation, however, in order that all the Cl^- should participate in forming NaCl, a higher Na/Zr ratio than the stoichiometric ratio should be needed since a certain amount of Na^+ could be consumed by the reaction with γ-Al_2O_3. This was supported by the fact that the NaCl peaks have been consistently detected in the catalysts which have higher Na/Zr values than 2. The peaks of NaCl was carefully examined before and after the reaction, but any conceivable correlation was failed to bring in this present study.

The cause of deactivation was not clearly identified by the characterization in this study, which gave indirect information on the OCM over Na^+-ZrO_2-Cl^-/Al_2O_3 catalysts. However, it is considered that the loss of Na^+ and Cl^- would be a more plausible cause for the deactivation, in the light of the results in previous studies [Yoon and Seo, 1996; Khan and Ruckenstein, 1992, 1993].

CONCLUSIONS

The oxidative coupling reaction of methane was performed using α-Al_2O_3 and γ-Al_2O_3 supported catalysts impregnated with Na_2CO_3 and ZrO_2. While the reaction on the pure Al_2O_3 supports produced CO, CO_2, and H_2O, the addition of Na_2CO_3 and ZrO_2 initiated C_2 production. The α-Al_2O_3-supported catalysts which were prepared by impregnating the alumina with the mixed solution of Na_2CO_3 and $ZrOCl_2$ showed relatively good activity for the OCM. The γ-Al_2O_3-supported catalysts, which were prepared by impregnation of Na_2CO_3-preimpregnated alumina with the mixed solution of Na_2CO_3 and $ZrOCl_2$ and had proper compositions of the ingredients used in the preparation, showed the better C_2 selectivity and yield than α-Al_2O_3-supported ones. It is considered that preimpregnated sodium played an important role in suppressing the combustion activity of γ-Al_2O_3. The best C_2 selectivity and yield was 40.8 % and 15.1% at the temperature of 1073 K with the C-80.6/29.3(3) catalyst among all catalysts tested in this study.

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