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Oxidative Coupling of Methane Over (CaO + ZrO_2) Modified with Sodium Ion

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Oxidative coupling of methane was carried out over various metal oxide catalysts (CaO + ZrO_4) modified with NaCl, NaI and NaOH and the catalytic performance of the catalysts was examined. These catalyst, which was prepared by sol-gel and then mixed of [$Zr(OH)_4 + Ca(OH)_2$] with an aqueous solution of NaCl and NaOH, was the most effective for the formation of ethene and ethane among all the catalysts tested in this study. The results shows that the surface concentration of Na^+ species on each series of catalysts are related to electronegativity of counter ion with Na^+.

Key Words: Methane, Oxidative coupling of methane, Catalysts, Ethane, Ethene.

INTRODUCTION

Direct catalytic conversion of methane to ethane and ethene by oxidative coupling is considered to be a promising route for the production of useful chemicals from abundant natural gas. It is well known that basic metal oxides such as MgO, Sm_2O_3, La_2O_3, *etc.* are effective catalysts for the oxidative coupling of methane[1-3]. The modification of the basic metal oxides with alkali ions (such as Li^+ and Na^+) improves the catalytic performance of the metal oxides for the oxidative coupling of methane, *i.e.*, the addition of alkali ions into the metal oxides brings about the suppression of total oxidation of methane and then the improvement of selectivities to ethane and ethene[4-8]. Although the Li^+ and Na^+ added metal oxide catalysts are often studied on the oxidative coupling of methane, the counter ions of Na^+ effect of the catalysts is one of the problems to be solved. Therefore, the counter ions effect of the Na^+ added catalyst is believed to be caused by the bond power between Na^+ and anion.

EXPERIMENTAL

Catalysts: [$Zr(OH)_4 + Ca(OH)_2$] was prepared by using an aqueous solution of $CaCO_3$ and $ZrOCl_2$ and NaOH or NaCl and or NaI solution. The precipitate was

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washed with water and mixed thoroughly with an aqueous solution of Na^+. The Na^+ added sample was dried up at 373 K and calcined at 1073 K for 5 h in air. The catalyst thus prepared is denoted as [(ZrO_2 + CaO) Na^+]. The catalyst was pressed into pellets and the pellets were crushed and sieved to 30/35 mesh size. The catalyst (0.2 g) packed in the reactor was heated to 1053 K in a flow of oxygen, prior to the reaction.

Reactions: The oxidation of methane was performed with a fixed-bed flow reactor made of an quartz tube (i.d. of 4 mm, length of 65 mm) at an atmospheric pressure. In order to minimize the contribution of the gas-phase chain reaction, quartz sands were filled in the space above and below the catalyst bed in the reactor. The temperature profile was measured by using a thermocouple, which was placed in an axial thermowell and at a center of the catalyst bed. Methane and oxygen were fed with a nitrogene carrier through the catalyst bed. The gas out of the catalyst bed was analyzed by gas chromatographs.

Phase composition of the catalysts were determined using X-ray diffraction (Philips Analytical) having Cu radiation at 40 kV and 40 mA. Scans were measured over a 2θ range from 10° to 70° using increments of 0.08° 2θ. The peak positions and relatively intensities of the powder pattern were identified by comparison with powder diffraction file data.

RESULTS AND DISCUSSION

Oxidative coupling of methane over NaOH added metal oxide catalysts: Fig. 1 shows results on methane oxidation over various NaOH added basic metal oxide catalysts. The amount of NaOH added into metal oxides ($CaO + ZrO_2$) was adjusted to be $(X_{Na}/X_{Ca} + X_{Zr})100 = M_{NaOH}$ in mole fraction ratio when $X_{Zr} \approx 0.19$ in all catalysts of this series. Over all the catalysts, ethane and ethene were produced mainly as partial oxidation products. Conversions of methane over $M_{NaOH} = 9$ was higher than those over other catalysts. However, for $M_{NaOH} = 2$ catalyst, selectivities to ethene and ethane were considerably high compared to those for other catalysts.The C^2 yields (ethene + ethane) at1048 K all over the catalysts except for the $M_{NaOH} = 0$ catalyst were almost the same. On the other hand, the C^2 selectivities were kept relatively high. Thus, the NaOH added ($CaO + ZrO_2$) catalyst showed the highest yield of ethene and ethane.

Oxidative coupling of methane over NaCl added metal oxide catalysts: Fig. 2 shows experimental results obtained over ($CaO + ZrO_2$) catalysts modified by different amounts of NaCl. The amount of NaOH added into metal oxides ($CaO + ZrO_2$) was adjusted to be $(X_{Na}/X_{Ca} + X_{Zr})\ 100 = M_{NaCl}$ in mole fraction ratio when $X_{Zr} \approx 0.09$ in all catalysts of this series. The reactions were carried out at 1048 K. Conversion of methane did not depend significantly on the amount of Na^+ added to ($CaO + ZrO_2$), in the range $5 \leq M_{NaCl} \leq 17$ and at $M_{NaCl} = 23$ the conversion decreased. On the other hand, product selectivities varied with the amount of M_{NaCl}. The C^2 yield showed a maximum (20.0 %) at $M_{NaCl} = 9$.

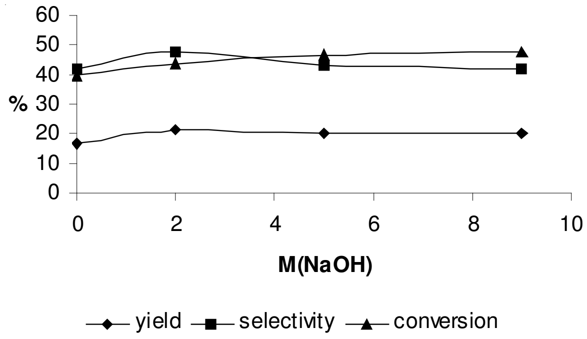

Fig. 1. Effect of the amount of NaOH added on the oxidation of methane at 1048 K over the (CaO + ZrO_2), $X_{Zr} \approx 0.19$ catalysts. Catalysts: 2 g; CH_4:N_2:O_2 = 2:2:1 flow rate: 100 mL/min

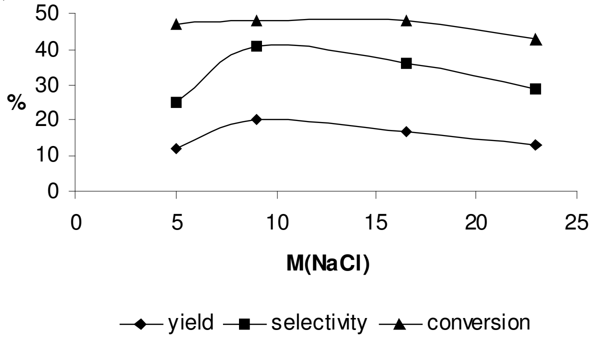

Fig. 2. Effect of the amount of NaCl added on the oxidation of methane at 1048 K over the (CaO + ZrO_2), $X_{Zr} \approx 0.09$ catalysts. Catalysts: 2 g; CH_4:N_2:O_2 = 2:2:1 flow rate: 100 mL/min

Fig. 3 shows changes in the conversion of methane, product selectivities and C^2 yield in the oxidative coupling of methane over the NaCl added (CaO + ZrO_2) catalyst ($X_{Na} = X_{Zr}$) at 1048 K. Conversion, selectivities and C^2 yield of oxidative coupling of methane decreased with M_{NaCl} addition.

Oxidative coupling of methane over NaI added metal oxide catalysts: Fig. 4 shows the results for the oxidation of methane over NaI added (CaO + ZrO_2) catalysts ($X_{Na} = X_{Zr}$) at 1048 K. Conversion of methane unchanged approximately with increasing the M_{NaI}. The changes in the selectivities and C^2 yield with M_{NaI} were very similar path.

Therefore, it would be natural to consider that the catalytic active site which activates methane and/or oxygen is the same on the two kinds [NaOH(CaO + ZrO_2)] and [NaCl(CaO + ZrO_2)] of catalysts series (O, Cl have the same electronegativity but I has different electronegativity). However, the highest C^2 yield was observed at different ($X_{Na}/X_{Ca} + X_{Zr}$) 100 ratios, *i.e.*, for the [NaOH(CaO + ZrO_2)] the highest

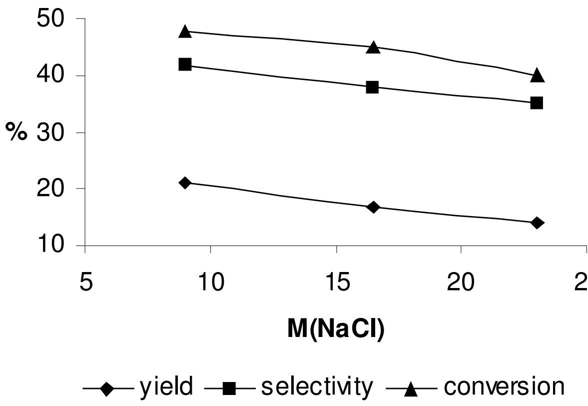

Fig. 3. Effect of the amount of NaCl added on the oxidation of methane at 1048 K over the (CaO + ZrO_2), ($X_{Na} = X_{Zr}$) catalysts. Catalysts: 2 g; CH_4:N_2:O_2 = 2:2:1 flow rate: 100 mL/min

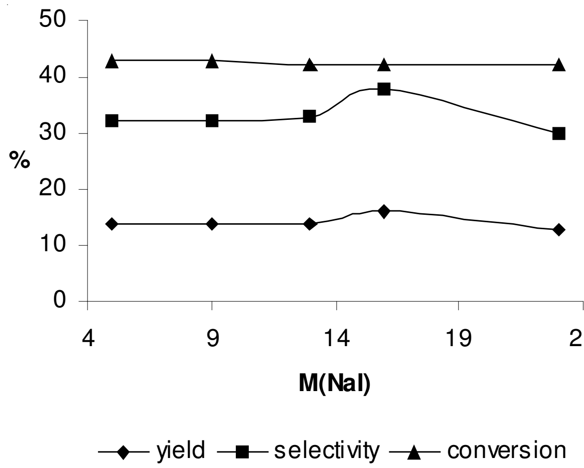

Fig. 4. Effect of the amount of NaI added on the oxidation of methane at 1048 K over the (CaO + ZrO_2), ($X_{Na} = X_{Zr}$) catalysts. Catalysts: 2 g; CH_4:N_2:O_2 = 2:2:1 flow rate: 100 mL/min

yield (21 %) appeared at the M_{NaOH} = 2, whereas the highest yield (20.0 %) for [NaCl(CaO + ZrO_2)] catalysts at M_{NaCl} = 2. These results might indicate that the surface concentration of Na^+ species on each series of catalysts are related to electronegativity of counter ion with Na^+.

XRD studies were also conducted to trace the conversion of unused and used catalysts. Fig. 5 shows the XRD pattern of the unused catalysts ‘a’ [a = (CaO + ZrO_2), $X_{Zr} \approx 0.19$ M_{NaOH} = 2 %)] while Fig. 6 shows the XRD pattern of the used catalysts ‘a’. It can be seen that phase calcium zirconium oxide, portlandite and baddeleyite were found in all case.

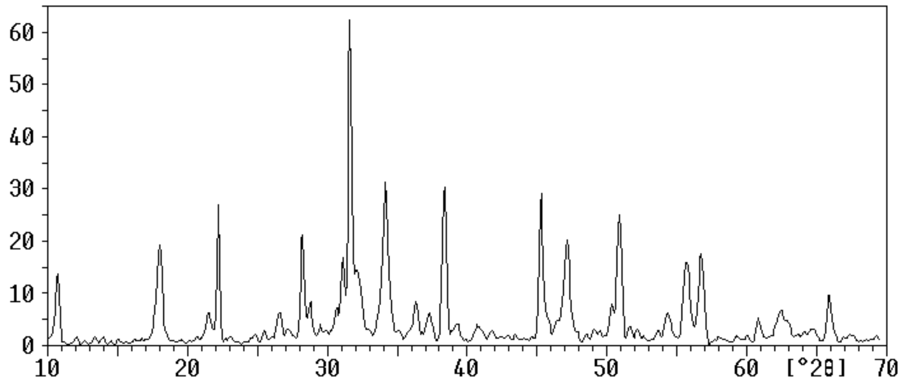

Fig. 5. XRD pattern of the unused catalysts 'a' [a = (CaO + ZrO_2), $X_{Zr} \approx 0.19$ $M_{NaOH} = 2$ %)]

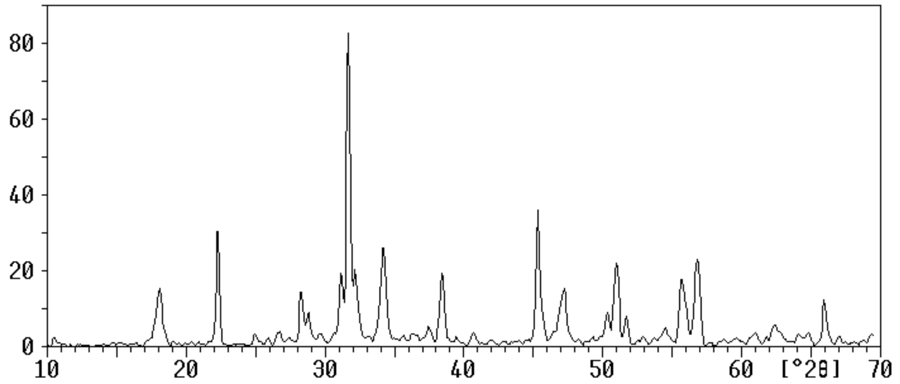

Fig. 6. XRD pattern of the used catalysts 'a' [a = (CaO + ZrO_2), $X_{Zr} \approx 0.19$ $M_{NaOH} = 2$ %)]

REFERENCES

1. K. Otsuka, K. Jinno and A. Morikawa, *Chem. Lett.*, 499 (1985).
2. C.-H. Lin, K.D. Campbell, J.-X. Wang and J.H. Lunsford, *J. Phys. Chem.*, **90**, 534 (1986).
3. R. Burch, A.A. Dost, D.A. Rice and G. Webb, *Catal. Lett.*, **3**, 331 (1989).
4. T. Ito and J.H. Lunsford, *Nature*, **314**, 721 (1985).
5. K. Otsuka, Q. Liu, M. Hatano and A. Morikawa, *Chem. Lett.*, 467 (1986).
6. M. Nakamura, S. Takenaka, I. Yamanaka and K. Otsuka, *Stud. Surf. Sci. Catal.*, **130**, 1781 (2000).
7. E.E. Wolf, Methane Conversion by Oxidative Processes, Van Nostrand Reinhold, New York (1992).
8. S. Takenaka, T. Tanaka and S. Yoshida, *J. Phys. Chem. B*, **102**, 2960 (1998).

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