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Oxidative coupling of methane over (Ca^{+2}+Zr^{+4}) modified with Na^+

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ABSTRACT

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^+.

KEYWORDS

OCM;
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. There for, 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 washed with water and mixed thoroughly with an aqueous solution of Na^+. The Na^+ added sample was dried up at 373K and calcined at 1073K for 5h in air. The catalyst thus prepared is denoted as [(ZrO_2+CaO_2) Na^+].

The catalyst was pressed into pellets and the pellets were crushed and sieved to 30/35 mesh size. The catalyst (0.2g) packed in the reactor was heated to 1053K in a flow of oxygen, prior to the reaction.

Reactions

The oxidation of methane was performed with a fixed-bed flow reactor made of a quartz tube (i.e. of 4mm, length of 65mm) 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 thermo well and at a center of the catalyst bed. Methane and oxygen were fed with a nitrogen 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), using Cu radiation at 40kV and 40mA. 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 (PDF) data of particles was based on Scherrer's equation:

RESULTS AND DISCUSSION

Oxidative coupling of methane over NaOH added metal oxide catalysts

Figure 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 $X_{Zr}\approx0.19$ 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) at1048K over all 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.

M_{NaOH}	yield	selectivity	conversion
0%	17%	42%	40%
2%	21%	48%	44%
5%	20%	43%	47%
9%	20%	42%	48%

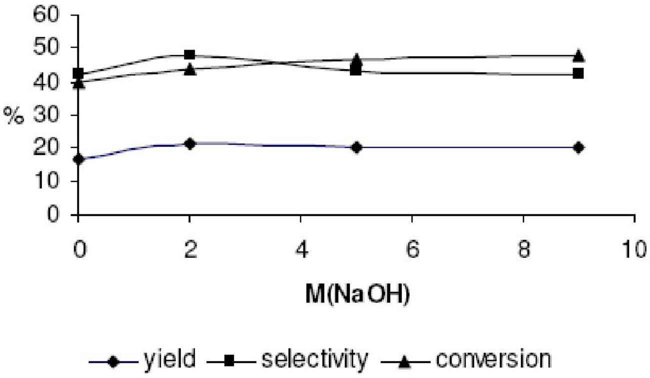

Figure 1 : Effect of the amount of NaOH added on the oxidation of methane at 1048K over the (CaO+ZrO$_2$), X_{Zr}0.19 catalysts. Catalysts: 2g; CH_4:N_2:O_2=2:2:1 flow rate: 100 ml min

M_{NaCl}	yield	selectivity	conversion
5%	12%	25%	47%
9%	20%	41%	48%
16%	17%	36%	48%
23%	13%	29%	43%

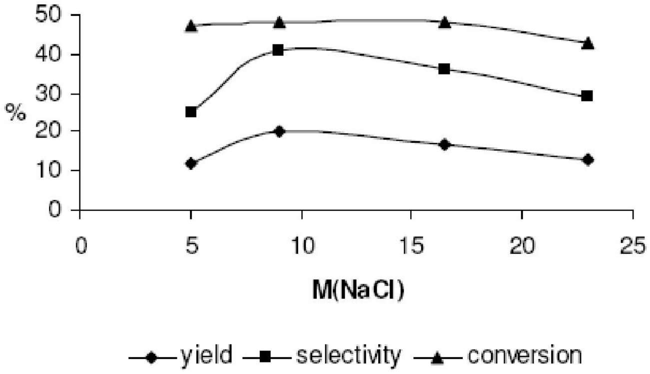

Figure 2 : Effect of the amount of NaCl added on the oxidation of methane at 1048K over the (CaO+ZrO$_2$), $X_{Zr}\approx0.09$ catalysts. Catalysts: 2g; CH_4:N_2:O_2=2:2:1 flow rate: 100 ml/min

Oxidative coupling of methane over NaCl added metal oxide catalysts

Figure 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

M_{NaCl}	yield	selectivity	conversion
9%	20%	41%	48%
16%	17%	37%	45%
23%	14%	35%	40%

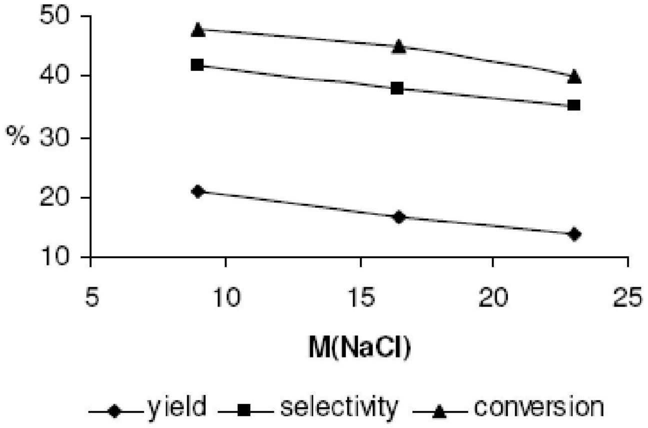

Figure 3 : Effect of the amount of NaCl added on the oxidation of methane at 1048K over the ($CaO+ZrO_2$), ($X_{Na}=X_{Zr}$) catalysts. Catalysts: 2g; CH_4:N_2:O_2=2:2:1 flow rate: 100 ml/min

M_{NaI}	yield	selectivity	conversion
5%	14%	32%	43%
9%	14%	32%	43%
13%	14%	33%	42%
16%	16%	38%	42%
23%	13%	30%	42%

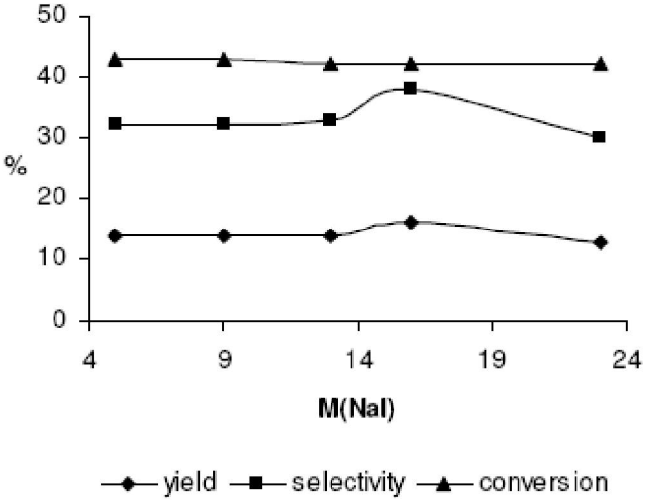

Figure 4 : Effect of the amount of NaI added on the oxidation of methane at 1048K over the ($CaO+ZrO_2$), ($X_{Na}=X_{Zr}$) catalysts. Catalysts: 2g; CH4:N_2:O_2=2:2:1 flow rate: 100 ml/min

X_{Zr}≈0.09 in all catalysts of this series. The reactions were carried out at 1048K. 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.

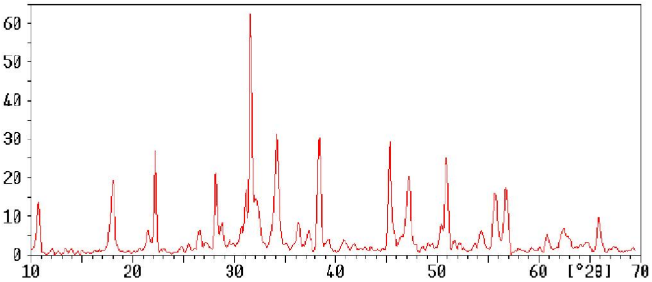

Figure 5: XRD pattern of the unused catalysts a[a=($CaO+ZrO_2$), X_{Zr}≈0.19 M_{NaOH}= 2%)]

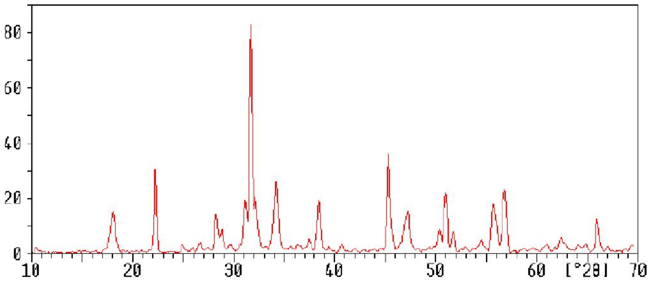

Figure 6 : XRD pattern of the unused catalysts a[a=($CaO+ZrO_2$), X_{Zr}≈0.19 M_{NaOH}= 2%)]

Figure 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 1048K. Conversion, selectivities and C^2 yield of Oxidative coupling of methane methane decreased with M_{NaCl} addition.

Oxidative coupling of methane over NaI added metal oxide catalysts

Figure 4 shows the results for the oxidation of methane over NaI added ($CaO+ZrO_2$) catalysts ($X_{Na}=X_{Zr}$) at 1048K. 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 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 catalystsare related to electronegativity of counter ion with Na^+.

XRD studies were also conducted to trace the conversion of unused and used catalysts. Figure 5 shows the XRD pattern of the unused catalysts a[a=($CaO+ZrO_2$), $XZ_r \approx 0.19$ M_{NaOH}= 2%)] while Figure 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.

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