Oxidative coupling of methane by water as the oxidant on perovskite oxide catalysts

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Received 20 July 1995; accepted 21 September 1995

We found that methane was selectively oxidized by water to give C_2 hydrocarbons and hydrogen on $ATi_{1-x}B_xO_{3-\delta}$ (A = Sr, Ba, B = Mg, Ca). The coupling activity and selectivity on $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ in the presence of steam was ~ 95%, which was much higher than that on pure $SrTiO_3$. This suggests that the selective oxidative coupling of methane by water was catalyzed by the oxide ion defects on $ATi_{1-x}B_xO_{3-\delta}$ (A = Sr, Ba, B = Mg, Ca).

Keywords: oxidative coupling of methane; oxide ion defect; perovskite oxide; steam as oxidant

1. Introduction

Numerous catalysts, including perovskite oxides, have been reported to be effective for the oxidative coupling of methane (OCM) by oxygen, but their selectivity to C_2 hydrocarbons is not high enough because of the non-selective oxidation of methyl radical with oxygen in the gas phase [1,2], especially when the concentration of oxygen is high [3]. In order to avoid non-selective oxidation by oxygen, the oxidation of methane by metal oxide, either in the form of an oxide ion carrier [4,5] or a membrane [6,7], has been developed. Another approach to reduce non-selective oxidation is to use CO_2 as an oxidant which has weak interaction with methyl radicals in the gas phase [8]. However, CO_2 showed low reactivity for OCM and also it makes stable carbonate species on the catalyst at reaction temperature causing the catalyst deactivation. Some studies on the effects of steam on the oxidative coupling of methane have been investigated. The effect of water was different on each catalyst. In the case of Li/MgO catalyst, water reacted with Li_2CO_3 to form LiOH and promoted the catalytic activity of C_2 hydrocarbon formation [9]. On $Mg_{0.8}Sr_{0.2}O$ catalyst, steam promoted the selectivity to C_2H_4 and CO_2 but suppressed that to C_2H_6 and CO, while suppressing the reaction rate. In this case, water suppressed the consecutive reaction of methyl radicals or hydrocarbon products with oxygen [10]. On Ca-Ni-K oxides which have high activity at low temperature, water stabilized surface hydroxyl species on the Ca-Ni-K oxide to realize high activity at low temperature [11]. In these investigations, since the catalytic reactions were conducted under co-feeding of methane, oxygen and water, the main oxidant should be oxygen. In contrast, we propose the utilization of water as the oxidant in the oxidative coupling of methane.

When water is used as the oxidant, the reaction stoichiometry of ethane formation is given by

$$2CH_4 + MO \rightarrow C_2H_6 + H_2O + M \quad (1)$$

$$M + H_2O \rightarrow H_2 + MO \quad (2)$$

and ethene is formed by the oxidative dehydrogenation of ethane. Therefore, the reaction stoichiometry is substantially the same as that of simple dehydrogenative coupling. However, if some oxygen species are formed by water molecules on the catalyst the reaction should be promoted by H-atom abstraction from methane by those species. At the same time, steam reforming reactions of methane are other possible side reactions yielding CO or CO_2:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (3)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (4)$$

The steam reforming reactions (3) and (4) are thermodynamically more favorable than the reactions (1) and (2). Therefore, it is very important to activate the methane molecule suitably to the reactions (1) and (2). We report the results of oxidative coupling of methane by water on $ATi_{1-x}B_xO_{3-\delta}$ ($A = Sr^{2+}$, Ba^{2+}, $B = Mg^{2+}$, Ca^{2+}) catalysts. It has been reported that oxygen can be adsorbed on $SrTi_{1-x}Mg_xO_{3-\delta}$ catalysts and the adsorption site is suggested to be a surface oxide ion defect formed by the substitution of Ti^{4+} by Mg^{2+} [12]. In addition, we found that the oxidative coupling of methane proceeded selectively by the adsorbed oxygen species on $SrTi_{1-x}Mg_xO_{3-\delta}$ catalysts at much lower temperature than under usual catalytic reaction conditions [13]. Then under catalytic reaction conditions, when methane and water were cofed at 973–1073 K, $SrTi_{1-x}Mg_xO_{3-\delta}$ catalysts have higher activity and selectivity to C_2 hydrocarbon formation than $SrTiO_3$ catalyst; this suggested that the oxide ion defect is the main active site for the OCM reaction [14]. In this letter we report the selective synthesis of C_2 hydrocarbons from methane and water on $ATi_{1-x}B_xO_{3-\delta}$ ($A = Sr^{2+}, Ba^{2+}, B = Mg^{2+}, Ca^{2+}$).

2. Experimental

$ATi_{1-x}B_xO_{3-\delta}$ (A = Ba, Sr, B = Mg, Ca) was prepared by calcining the powder of a stoichiometric mixture of commercially available $SrCO_3$ (Koso Chemical Co., Inc. Tokyo, Japan, 99.9%). TiO_2 (Aerosil Co., Inc. Japan), MgO (Kanto Chemical Co., Inc 99.0%), $CaCO_3$ (Kanto Chemical Co., Inc over 99%) and $BaCO_3$ (Kanto Chemical Co., Inc over 99%) at 1473 K in air for 2 h. In this study, the oxide component was $x = 0$ and $x = 0.6$. The structure of the oxides was determined by X-ray diffraction (XRD) (Cu K_α line, Rigaku RAD-IB). The XRD pattern showed that a new phase, assigned as the oxide ion defect phase, appeared in the $x = 0.6$ sample [13]. Other perovskite oxides were prepared by a method similar to that of $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$.

A fixed-bed reactor (made of quartz, inner diameter: 6 mm, length: 250 mm) was used under 0.1 MPa. 500 mg of the catalyst sample (40/60 mesh) was held in place by packed quartz wool, a thermocouple in a quartz thermowell was set at the center of the bed, and the catalyst was pretreated at 1123 K in air flow for 0.5 h. After the treatment the reactor was purged with Ar and then reactant gas (CH_4 and H_2O) was introduced. The mole ratio of CH_4/H_2O in the feed was 1/1. Reaction temperature was in the range of 1023–1123 K. Reaction products were analyzed by on-line gaschromatographs with Porapak QS and MS-5A columns. The surface area was measured by the BET method. The results were: $SrTiO_3$ (2.0 m^2/g), $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ (2.3 m^2/g), $BaTiO_3$ (1.1 m^2/g), $BaTi_{0.4}Mg_{0.6}O_{3-\delta}$ (1.5 m^2/g), $CaTiO_3$ (3.8 m^2/g), $SrTi_{0.4}Ca_{0.6}O_{3-\delta}$ (1.6 m^2/g), Al_2O_3 (2.8 m^2/g).

3. Results and discussion

Fig. 1 shows the results of the CH_4–H_2O reaction as a function of reaction time under different reaction conditions. It is clear from the data that, although the catalytic functions of $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ were stable under CH_4–H_2O reaction conditions when the feed of H_2O was substituted by argon, the formation of C_2 hydrocarbons decreased gradually while that of CO increased quickly (pannel (2)). As described in eqs. (1) and (2), the oxidative coupling of methane (OCM) by H_2O as the oxidant yielded H_2O and H_2 as co-products with C_2 hydrocarbons. Therefore, there should be no apparent differences in products between the OCM by H_2O and the dehydrogenative coupling,

$$2CH_4 \rightarrow CH_3{-}CH_3 + H_2 \tag{5}$$

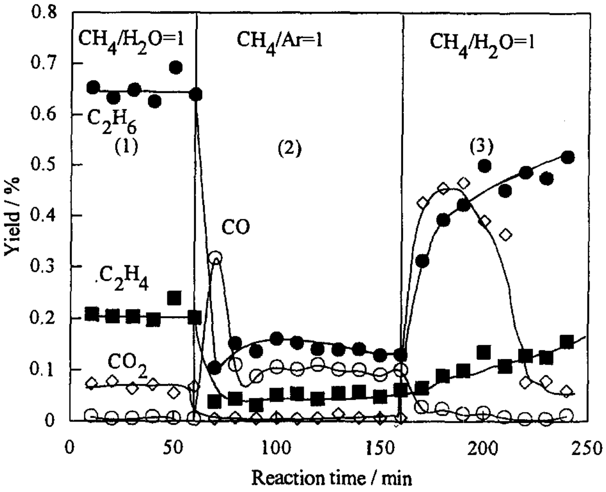

Fig. 1. Results of CH_4–H_2O reaction as a function of reaction time under the changed reaction conditions with $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ at 1123 K. Reaction conditions: $W/F = 5$ h g/mol, $CH_4/H_2O=1$, total pressure 0.1 MPa.

However, when the feed of water stopped, the formation of C_2 hydrocarbons decreased and that of CO increased drastically (fig. 1(2)). This indicated that C_2 hydrocarbons were formed only when methane and water coexisted, while CO was formed exclusively in the absence of water. Judging from the stoichiometry of these products, and the fact that the XRD pattern of the sample after the reaction shows the existence of a small amount of TiO phase, the reaction is described by

$$CH_4 + O^{2-} \rightarrow CO + 2H_2 + 2e^- \tag{6}$$

and e^- should reduce Ti^{4+} to Ti^{2+}. These phenomena strongly suggest that water is used as the oxidant for OCM. When the feed of water was re-started the formation of CO_2 increased drastically and then decreased while the formation of C_2 hydrocarbons increased gradually to reach the original level. This phenomenon suggests that the oxidation of the catalyst by water proceeds slowly. Therefore, the catalyst may be reduced by CH_4 even when methane and water are fed together, but in fact the catalytic activity was stable in time on stream longer than 10 h and the XRD pattern of the sample after the reaction agreed with that before the reaction. Though we have not proceeded the surface analysis of the sample after the reaction yet, these results strongly suggest that the catalyst is not reduced by CH_4 under the catalytic reaction conditions.

The yields of products are plotted in fig. 2 against the partial pressure of steam at 1123 K on $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$. The formation rate of C_2 hydrocarbons increased almost linearly with increasing steam partial pressure. These results suggest the formation of C_2 hydrocarbons from methane and water. The high partial pressure of H_2O promoted C_2 hydrocarbon formation. This tendency indicates that the C_2 hydrocarbons were not formed by the simple dehydrogenative coupling of methane, but

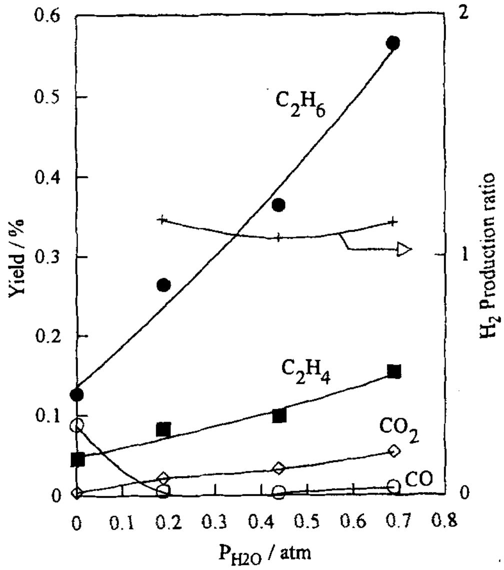

Fig. 2. Effect of partial pressure of steam on production yield over $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ catalyst. Reaction conditions: total pressure = 1 atm, temperature = 1123 K, $W/F = 2.5$ g h/mol, $P_{CH_4} = 0.31$ atm, balance gas: Ar and catalyst weight = 0.5 g. H_2 production ratio = $H_2/(4CO_2+3CO+C_2H_6+2C_2H_4)$. (For $P_{H_2O} = 0$, were showed the data under apparent steady state conditions.)

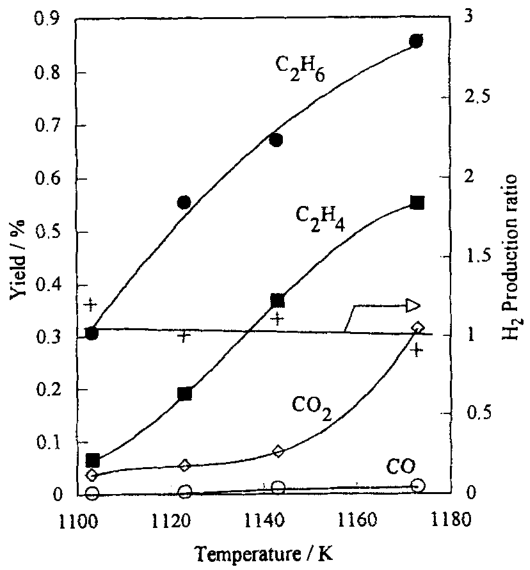

Fig. 3. Effect of the reaction temperature on product yields with 0.5 g $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$. Reaction conditions: $W/F = 2.5$ g h/mol, $CH_4/H_2O = 1$, total pressure 0.1 MPa. H_2 production ratio: $H_2/(4CO_2+3CO+C_2H_6+2C_2H_4)$.

they were formed catalytically on $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ catalyst by water as oxidant. The amount of H_2 production agreed with the estimation by assuming the stoichiometry of the reactions eqs. (1)–(4), which are defined as "H_2 production ratio", calculated as

$$H_2/(4CO_2 + 3CO + C_2H_6 + 2C_2H_4) \quad \text{(mole ratio)}. \tag{7}$$

CO_2 was the main product of COx because of the equilibrium of the water–gas shift reaction under high H_2O partial pressure.

Fig. 3 shows the results of catalytic reaction as a function of reaction temperature under steady state conditions. The products were C_2 hydrocarbons, carbon dioxides and hydrogen, while the formation of CO was negligibly small. Especially, the yield of ethylene increased markedly with the temperature, whereas that of ethane increased more moderately with temperature. The activation energy of the ethane and ethylene formation was 2.1×10^2 and 1.0×10^2 kJ mol^{-1}, respectively. It might be attributed to the successive dehydrogenation of ethane to ethylene and the reforming of C_2 hydrocarbon by water.

Fig. 4 shows the catalytic activities and the methane conversion rate normalized by the BET surface area on a variety of metal oxides and perovskite oxides. OCM by water did not proceed without catalyst and both alumina and titania showed little catalytic activity for this reaction. A relation between the catalytic properties and BET surface area was not observed. Perovskite oxides such as $SrTiO_3$, $BaTiO_3$ and $CaTiO_3$ showed some catalytic activities for OCM by water, but the main product on these catalysts was carbon dioxide. In contrast, when some part of the Ti^{4+} in these perovskite oxides were substituted by Mg^{2+} or Ca^{2+}, the formation of carbon dioxide in the CH_4–H_2O reaction was effectively suppressed and C_2 hydrocarbons were produced with high selectivity. These phenomena suggest strongly that oxide ion defects which are generated by substituting Ti^{4+} by Mg^{2+} or Ca^{2+} might be the main active sites for the activation of methane to methyl radical and the OCM reaction with water molecule as the oxidant. We imagine that the oxide ion defects are also the active sites

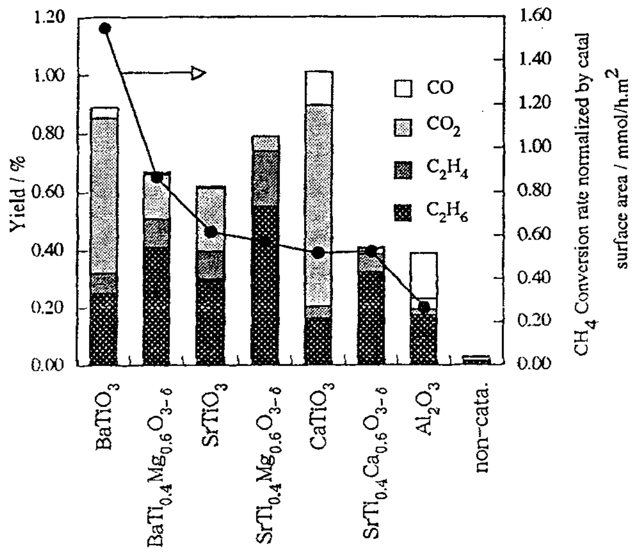

Fig. 4. Activity for methane conversion. Reaction conditions: total pressure = 1 atm, temperature = 1123 K, $W/F = 2.5$ g h/mol, $CH_4/H_2O = 1$ and catalysts weight = 0.5 g.

for the activation of H_2O molecules to the oxygen species for the methyl radical formation from methane. The activation process is described below:

$$O^{2-} + V_{\ddot{O}} + H_2O \rightarrow 2OH^- \tag{8}$$

In this equation, $V_{\ddot{O}}$ represents the oxide ion defects formed by substitution of Mg^{2+} to Ti^{4+}. OH^- species was thought to activate methane activation. On $SrTi_{1-x}B_xO_{3-\delta}$ ($B = Mg^{2+}, Ca^{2+}$) catalysts, the concentration of the oxide ion defects is higher than on $SrTiO_3$, and the conversion of methane is higher. This seems to be an important role of water as the oxidant. In addition, H_2O seemed to inhibit the reaction between methane and lattice oxide ion shown in eq. (6). This reaction produced mainly CO and its inhibition effectively contributed to the highly selective formation of C_2 hydrocarbons.

On this system, it is very important to elucidate the role of water, its interaction with the catalyst surface. Further investigation, especially of the characterization of the active site, is necessary.

4. Conclusion

We found that $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ showed excellent catalytic activity for the oxidative coupling of methane by water molecule as the oxidant. The catalytic reaction proceeded at temperatures higher than 800°C with high coupling selectivity. The catalysis of the oxidative coupling of methane by water is assumed to be closely related to the interaction between water and the oxide ion defects formed by the substitution of Ti^{4+} with Mg^{2+} in $SrTiO_3$.

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