Development of Catalyst-Membrane System for Oxidative Coupling of Methane by Water

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It has been reported that $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ catalyst showed good performance for the oxidative coupling of methane by using water as an oxidant ($2CH_4 + {*}H_2O \rightarrow C_2H_6 + {*}H_2 + H_2O$). But the yield of C_2 hydrocarbons in this reaction was almost constant at W/F= 5-20 gh/mol. $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ tube-type membrane was utilized to remove H_2 selectively in coupling of methane to C_2 hydrocarbons from CH_4 and water. When $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ catalyst was used in this catalyst-membrane system, the yield of C_2 hydrocarbons was drastically promoted.

Oxidative coupling of methane (OCM) to C_2 hydrocarbons is an important reaction from the viewpoint of effective use of natural gas. Though a lot of catalysts have been developed for this reaction, the common problem is that C_2 yield was limited at low level because of the oxidation of products and reaction intermediate to CO and CO_2. Therefore numerous studies have been attempted to solve this problem. Membrane reactor has been utilized for the supply of methane and oxidant separately. By using nonporous oxygen permeable membrane that consisted of modified PbO supported on porous SiO_2-Al_2O_3 tube, higher hydrocarbon was successfully synthesized with high selectivity.[1-3] In this system, oxygen permeation was rate-determining, but the promotion of this step was not so easy. The formation of C_2 hydrocarbon from CH_4 by using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ membrane reactor was reported.[4-6] It is reported that $SrZr_{0.95}Y_{0.05}O_{3-\alpha}$ films can be used as membrane for continuous hydrogen removal in the non-oxidative catalytic conversion of methane to higher hydrocarbons.[7] On the other hand, the oxidants other than oxygen have been developed. One case is to use CO_2 as an oxidant for OCM.[8] But catalytic activity of OCM with CO_2 was considerably low and CO_2 makes stable carbonate species on the catalyst, and this caused the catalyst deactivation. We reported the highly selective coupling of methane in the presence of water proceeded on $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$, as equations (1) and (2).[9] (3) and (4) are by-reactions.

$$2CH_4 + {*}H_2O \rightarrow C_2H_6 + {*}H_2 + H_2O \quad (1)$$
$$2CH_4 + 2{*}H_2O \rightarrow C_2H_4 + 2{*}H_2 + 2H_2O \quad (2)$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (3)$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (4)$$

It is suggested that the yield of C_2 hydrocarbons in this reaction did not become higher even at long W/F conditions. This is shown in Figure 2 (mentioned below). We investigate the effect of H_2 removal from the reaction system in the yield of C_2 hydrocarbons. Most famous method of hydrogen removal is to use hydrogen-permeable membrane reactor, especially Pd metal membrane. But in our case, Pd seems to be unfavorable in C_2 hydrocarbon formation from CH_4 and H_2O. This is because Pd is good catalyst for steam reforming reaction (eq.3) and also it is unstable under these conditions. In contrast, Perovskite-type oxides containing Ce, especially $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, has high and selective proton conductivity at high temperature.[10] This material has also been reported as mixed conductor when air was supplied to the cathode.[4]

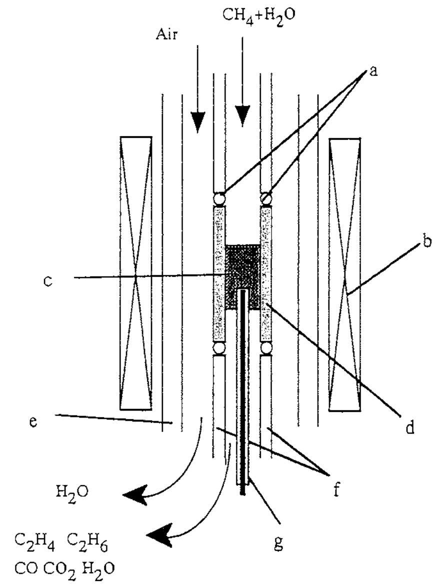

Figure 1. Catalyst-membrane system.
a: glass seal, b: heater, c: catalyst, d: membrane,
e: quartz tube, f: Al_2O_3 tube, g: thermocouple.

$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ tube was obtained by TYK. The size of this tube-type membrane was a thickness of 1 mm, outer diameter of 10 mmϕ, length of 40 mm. $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ was prepared by calcining a stoichiometric mixture of $SrCO_3$, TiO_2, MgO at 1473 K in air for 2h. This catalyst was pressed and broken into particles with 20-40 mesh. Catalyst particles were stuffed in membrane tube, and jointed to Al_2O_3 tube (10 mmϕ, 200 mm) with glass seal. The details of the reactor are shown in Figure 1. OCM by using water as an oxidant was carried out at 1173 K and atmospheric pressure. H_2O was introduced by microfeeder and vaporized by preheating at 393 K. Reaction was performed under $CH_4/H_2O=1/1$, catalyst weight 0.5 g, 1173 K, and W/F = 5 – 20 gh/mol (W=catalyst weight, F=total flow rate). Products were analyzed by gas chromatograph with on-line sampling after trapping residual water by iced bath. The leak of air from outside to inside of membrane was checked by monitoring N_2 using TCD gas chromatograph. As a reference, we investigated CH_4-H_2O reaction on $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ powder (BET surface area = 0.4 m^2 g^{-1}) which was prepared by crushing membrane tube into powder. All the reaction results shown in this letter were based on the data of *ca.* 1 h reaction time since the formaion rate was in the steady state at 1 h.

Table 1 shows the results of OCM by water using catalyst-membrane system. The formation rate of C_2 hydrocarbons and CO_X on $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ catalyst using the quartz reactor was very low. In this case, the formation rate of hydrogen almost the same as that of estimated by eqs. (1) - (4). In order to estimate the reaction rate on the wall of membrane reactor, we

Table 1. Results of oxidate coupling of methane by water on catalyst-membrane system

Catalyst	Reactor	Formation rate / mmol h^{-1} g^{-1} C_2	CO_x	H_2	H_2[a]	Conv. / % CH_4	Sel. / % C_2
$SrTi_{0.4}Mg_{0.6}O_{3-\alpha}$[b]	quartz tube	0.3	0.2	1.3	1.1	1.1	62
$SrCe_{0.95}Yb_{0.05}O_{3-\delta}$[c]	quartz tube	0.1	0.1	0.7	0.5	0.4	47
$SrTi_{0.4}Mg_{0.6}O_{3-\alpha}$	$SrCe_{0.95}Yb_{0.05}O_{3-\delta}$	1.1	0.8	1.2	4.2	3.9	58

Reaction condition : CH_4/H_2O = 1/2, 0.1 MPa, total flow rate 38 mmol/h, 1173 K.

[a] H_2 formation rate calculated from products on the basis of the stoichiometry of eqs.1-4,

[b] Catalyst weight : $SrTi_{0.4}Mg_{0.6}O_{3-\alpha}$ 0.5 g,

[c] $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ powder : membrane tube was crushed into particles, weight (3.8 g) was determined to be almost the same surface area as membrane wall.

performed the reaction over $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ powder. In this case, the main reaction was steam reforming and subsequent reverse water gas shift reaction. The formation rate of C_2 hydrocarbons and CO_X on membrane-catalyst system was much higher than other two systems. And hydrogen production rate in this system was much lower than the calculated amount based eq.(1) – eq.(4) . From these results, the membrane reactor was effective for the promotion in the yield of C_2 hydrocarbon formation by removing hydrogen from reaction system. In addition, the selectivity of C_2 hydrocarbon formation was decreased by the steam reforming reaction on membrane reactor wall.

Promoting effect of this membrane reactor on C_2 hydrocarbon formation can be explained as described below. OCM by water proceeds on the catalyst surface and forms C_2 hydrocarbons, H_2 and CO_X. H_2 reacts with two holes at the inner surface of the membrane to product two protons. These protons travel in membrane bulk from the inner to the outer surface, and react with oxygen in the air and to form H_2O and holes. These holes transfer from the outer to the inner surface of the membrane reactor. These are due to proton-hole mixed conductivity of membrane reactor.[4] In contrast, it has recently been claimed that this membrane applied to usual OCM exhibited both proton and oxide-ion conductivity and electron conductivity as well. In our experimental condition, the membrane reactor also have their properties. In this case, the partial pressure of H_2 decreased by the reaction with oxide ions transported. From both mechanisms, we think that the decrease of hydrogen in catalyst membrane system can promote C_2 hydrocarbon yield through the inhibition of the reaction of ethane and ethene with hydrogen to methane.

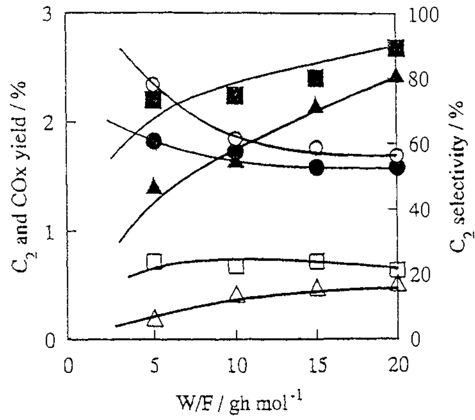

Figure 2. Dependence of yield of products and C_2 selectivity in oxidative coupling of methane by water.
■,▲,●: $SrTi_{0.4}Mg_{0.6}O_{3-\alpha}$+$SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ membrane.
□,△,○: $SrTi_{0.4}Mg_{0.6}O_{3-\alpha}$,quartz.
■,□: C_2 hydrocarbons yield. ▲,△: CO_X yield.
●,○: C_2 hydrocarbons selectivity.
Reaction condition : CH_4/H_2O= 1/1, 0.1MPa, 1173 K, total flow rate 25-100 mmol/h.

Figure 2 shows the formation rate of C_2 hydrocarbons and CO_X as a function of contact time over catalyst. Reaction rate was very stable in each case. In the case of $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ catalyst in quartz tube was used, C_2 hydrocarbon yield was saturated at very low level at very short contact time. On the contrary, the yield on our catalyst-membrane system was much higher than two other systems. But at high W/F region, the yield level was saturated even in this system. It is thought that this is probably due to the limitation of the removal rate of hydrogen. From the results, the combination of catalyst for OCM by water with hydrogen permeable membrane promoted drastically C_2 hydrocarbon yield. But the yield was not enough at present. In order to reach the much higher yield, we must enhance the removal rate of hydrogen by membrane reactor.

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