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Low Temperature Oxidative Coupling of Methane by Perovskite Oxide

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Perovskite oxides, $SrTiO_3$ which was doped with MgO and contained oxygen defects, oxidized methane to C_2 coupled hydrocarbons at 425 ℃, with the selectivity over 90%. The used oxides could be regenerated by being treated in air at 425 ℃. Adsorbed oxide ion on the defect seemed to be responsible for their oxidation activity.

Numerous types of catalysts have been claimed to be effective for the catalytic oxidative coupling of methane (OCM).[1-3] These reactions have been usually operated at temperatures from 600 to 850 ℃. At these temperatures, methyl radical which is generated on the catalyst through the reaction of methane with either adsorbed oxygen[4] or lattice oxygen,[5,6] comes out into gas phase and is subjected to the gas phase reactions such as coupling or deep oxidation. A variety of perovskite type oxides such as M-Ti-O (M = Ca, Sr, Ba),[7] La-X-Mn-O (X = K, Na),[8] La-Sr-Y-O (Y = Cr, Mn, Co, Cu)[9] and Z-Ce-Gd-O (Z=Sr, Ba, Zn)[10] have been also tested as the catalyst for OCM. These catalysts have been used at temperatures around 700-800 ℃. It has been reported that the crystalline strontium titanate doped with magnesium oxide ($SrTi_{1-X}Mg_XO_{3-\delta}$) contains oxide ion defects because of its charge imbalance, and can adsorb oxygen reversibly from gas phase at around 500 ℃.[11] Otsuka *et al.* reported that superoxide of alkali or alkaline earth oxide oxidized methane to C_2 hydrocarbons as low as 400 ℃.[12] However, this oxide could not be regenerated by air oxidation. In this study we tried to utilize adsorbed oxygen on this defect-containing perovskite type oxide as the oxidant to convert methane to C_2 hydrocarbons.

$SrTi_{1-X}Mg_XO_{3-\delta}$ was prepared by calcining the powder of stoichiometric mixture of commercially available $SrCO_3$ (Koso Chemical Co., Inc. Tokyo, Japan. 99.9%), TiO_2 (Aerosil Co., Inc. Japan), and MgO (Kanto Chemical Co., Inc. 99.0%) at 1200 ℃ in air for 2 h. In this study, the oxide component was changed from x = 0 to x = 0.6. The structures of the oxides were determined by X-ray Diffraction (XRD) (CuK_α line, Rigaku RAD-1B). The samples loaded in the reactor were treated with air at 850 ℃ for 30 min before reaction. A fixed-bed reactor (made of quartz, inner diameter: 6 mm, length: 250 mm) was used under atmospheric pressure. 0.5 g of sample (40/60 mesh) was held in place by quartz wool, and a thermocouple in a quartz thermowell was located in the center of the bed. The reaction products were analyzed by on-line gas chromatographs with Porapak QS and MS-5A. Regeneration of

used oxide was conducted by introducing argon into the reactor for 20 min to blow methane off and then treating with flowing air for 30 min. Reaction and regeneration were repeated according to this procedure. Temperature programmed reaction (TPR) of methane was conducted over the temperature range 300-850 ℃ in the diluted methane flow (25 ml/min, CH_4/Ar = 1/4, with the heating rate of 6.25 ℃/min). Stoichiometric reactions of CH_4 with oxide samples at constant temperatures were also conducted in the same reactor with the same feed gas.

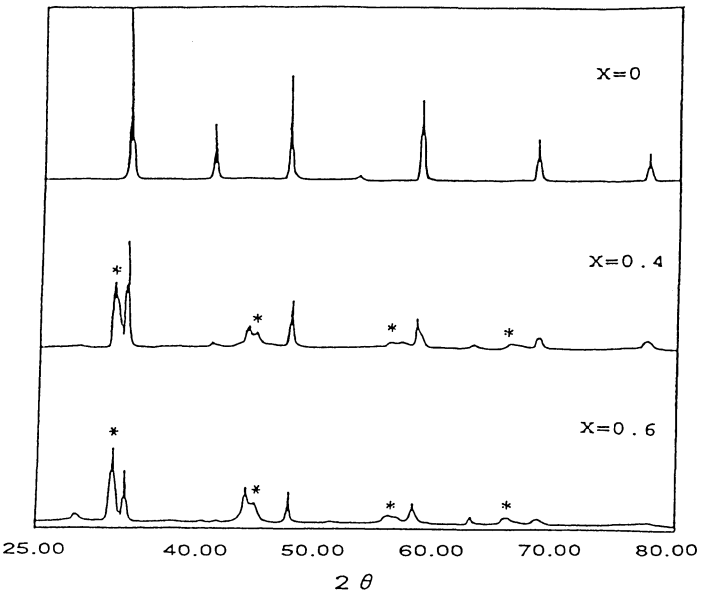

Fig.1. X-ray diffraction partten of $SrTi_{1-X}Mg_XO_{3-\delta}$. *new peak. Specific surface area (m^2/g): 2.15 (X = 0), 4.68 (X = 0.4), 4.15 (X = 0.6).

XRD patterns of the catalysts are shown in Fig. 1. The characteristic feature of the XRD patterns of the samples doped with MgO is that new peaks which located at slightly lower diffraction angle appeared and their peak height increased with increasing MgO content. These new peaks should be attributed to a new phase generated by added MgO. The lattice distance is larger than that of $SrTiO_3$. This new phase will be discussed later.

In Fig. 2 are shown the results of methane TPR on $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$. From the TPR data it is clear that a small amount of CO_2 is formed around 300 ℃ and that the formation of ethane and small amout of ethylene begins at 350 ℃, reaches maximum at 400 ℃ and then decreases. $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ showed similar TPR spectrum with smaller C_2 formation and no C_2 formation on pure $SrTiO_3$. Figure 3(a) shows the reaction behavior with reaction time for the fresh sample (calcined at 850 ℃). Figures 3(b) and 3(c) are the reaction behavior of the oxide regenerated at 500 ℃ and 425 ℃, respectively. It is clear that methane can be oxidized smoothly by $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ even at 425 ℃ and

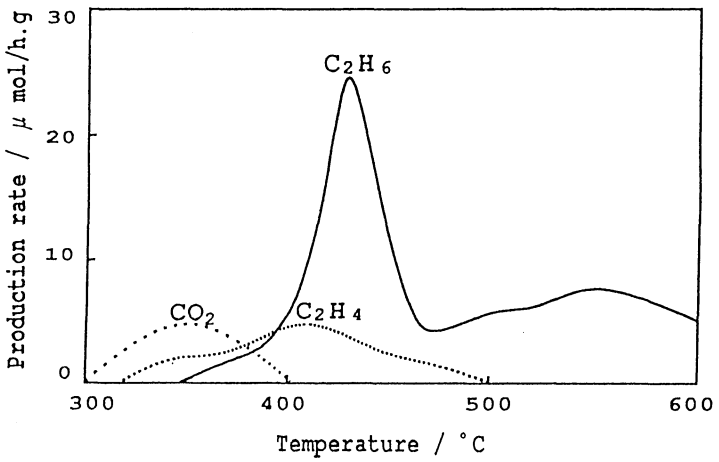

Fig.2. Spectra of temperature-programmed reaction of methane with: $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$, 0.5 g of sample, gas flow rate 25 ml/min, CH_4/Ar = 1/4, heating rate 6.25 ℃/min.

the oxidation rate decreases with reaction time, probably because of the consumption of the oxidizing species in the perovskite. Also it is obvious that the regeneration of the used sample by air proceeds completely at 425 ℃.

Figure 4, shows the total amounts of C_2 and CO_x, produced within 10 min from the start of the reaction on various perovskite samples at 425 ℃, demonstrating that the sample with x = 0.6 has the highest activity for C_2 formation. From the total amount of C_2 products and CO_x formed on the sample with x = 0.6, the amount of the oxidizing oxygen was calculated to be about 5.9 μmol/g. This value is close to that of oxygen adsorption on the perovskite at 300 ℃ (8.8 μmol/g). Other products than C_2 hydrocarbons which remained on the catalyst was proved to be only water by the high temperature desorption method. On the other hand, the pure $SrTiO_3$ (MgO free) showed neither C_2 formation at 425 ℃ nor oxygen adsorption at 300 ℃. The result suggests that the added MgO changes the conventional perovskite structure and makes adsorbed oxygen species which active for OCMat low temperature on air exposure.

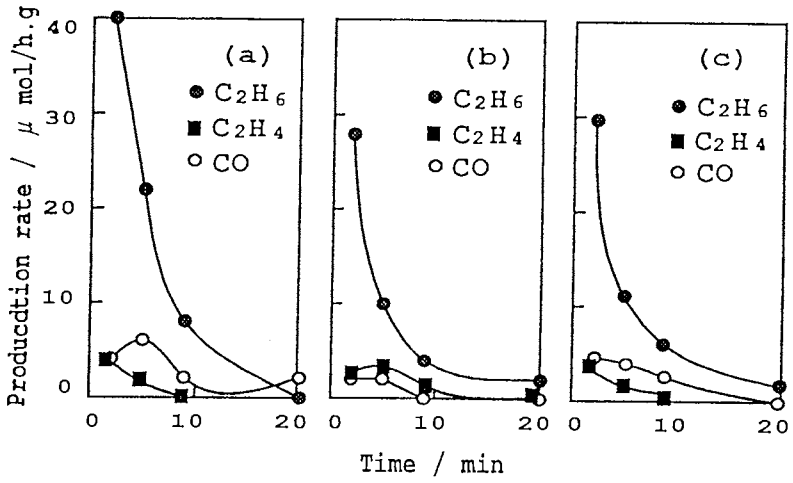

Fig.3. Effect of regeneration temperature for $SrTi_{0.4}Mg_{0.6}O_{3-\delta}$ on its reaction behavior with methane. (a) fresh. (b) at 500 ℃. (c) at 425 ℃. Sample 0.5 g, gas flow rate 25 ml/min, CH_4/Ar = 1/4 (mol ratio).

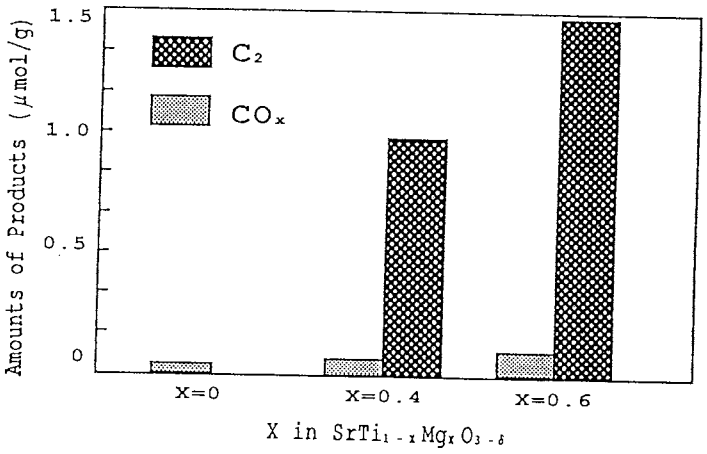

Fig.4. Oxidation of Methane by $SrMg_XTi_{1-X}O_{3-\delta}$ at 425℃, sample 0.5g, gas flow rate 25cc/min, CH4/Ar=1/4(mol ratio).

It has been pointed out that O_2^- [4] O^{2-} [5] and O_2^- [12] are important species as the oxidants for OCM and the reaction is regarded to proceed as shown below:[5]

$$2CH_4 + 1/yMO_x \cdot O_y = C_2H_6 + H_2O + 1/yMO_x \quad (1)$$

$$MO_x + y/2O_2 = MO_x \cdot O_y \quad (2)$$

(where O_y is active oxygen species)

It is clear from Fig. 1 that the structure of oxide containing no MgO (x = 0), is a typical perovskite crystal. When a part of TiO_2 is replaced by MgO, oxygen defect is formed due to the charge imbalance and the most compact structure of oxygen atom lattice is destroyed.[13] This destroyed perovskite structure forms larger lattice to show XRD peaks shifted to lower diffraction angle. Therefore, the addition of MgO into $SrTiO_3$ makes the mixture of the standard $SrTiO_3$ structure and the sturcture with oxygen defects.

It seems that the reversible desorption and adsorption of oxygen proceed in the oxygen-defected perovskite as follows:[11]

$$V_o^{\cdot\cdot} + 1/2O_2 = O_{o(ad)}^{-} + 2h^{+} \quad (3)$$

here $V_o^{\cdot\cdot}$ is an ion vacancy in oxide, $O_{o(ad)}^{-}$ is adsorbed oxygen and h^+ is positive hole. In this process, electron transfers from perovskite lattice to adsorbed species to form oxide ion (O^- or O_2^{2-}). Ding *et al.* have reported that even $SrTiO_3$ which was made by solid state reaction was rich in Sr^{2+} on surface, showed high basicity, adsorbed oxygen as O^- or O_2^{2-} and exhibited high C_2 selectivity in OCM.[14] The experimental results and the work of Ding *et al.* lead us to the conclusion that when the oxidized oxide is exposed to methane, the adsorbed oxide ion in the oxygen defect reacts directly with methane as low as 425 ℃ to form C_2 hydrocarbons selectively and that the exhausted oxygen defect is restored by air treatment at same temperature.

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