Methane–water redox reaction on A_2SnO_4 (A = Mg, Ca, Sr, Ba) oxide to produce C_2 hydrocarbons

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A_2BO_4 type oxides consisting of an alkali earth metal and tin showed high selectivity (> 99%) and activity for the oxidative coupling of methane at 1023 K in a methane–water redox system where active oxygen species were regenerated by water. The products were C_2 hydrocarbons and hydrogen. Repeated reaction–oxidation cycles showed that the oxide is stable under both oxidative and reductive atmosphere. Doping of Bi to the oxide was found to enhance the activity for the oxidative coupling of methane.

Keywords: oxidative coupling of methane, perovskite oxide, K_2NiF_4 oxide, water as oxidant, hydrogen production

1. Introduction

Natural gas has potential as a source of fossil energy and as a huge reservoir of carbon. The oxidative coupling of methane (OCM) to higher hydrocarbons is one of the attractive processes to utilize natural gas as chemical resource [1–5]. A serious problem of this reaction is the non-selective oxidation of methyl radicals by oxygen molecules to produce CO_x. To avoid this side reaction, CO_2 was used as an alternative oxidant [6].

Another approach to reduce the side reaction is to use water as additive or as alternative oxidant. In some cases the activity and/or selectivity for C_2 hydrocarbons were promoted by water in both catalytic and non-catalytic processes [7–9]. For example, water stabilizes the surface active site on Ca–Ni–K oxide to show high activity at extremely low temperature [8]. Recently, Li et al. have proposed the utilization of water as the main oxidant under co-feeding of methane and water with perovskite oxide to avoid non-selective oxidation by oxygen [10].

From an industrial point of view, the methane–water co-feed reaction has some advantages over the conventional OCM reaction. In the conventional OCM reaction, hydrogen of the methane is usually removed as water because usually air/oxygen is supplied as oxidant:

$$2CH_4 + O_2 \rightarrow C_2H_6 + 2H_2O \tag{1}$$

In the methane–water reaction, on the other hand, hydrogen molecules are produced instead of water because the stoichiometric reactions of methane and oxide surface for ethane formation are

$$2CH_4 + \frac{1}{\alpha}MO \rightarrow C_2H_6 + \frac{1}{\alpha}MO_{1-\alpha} + H_2O \tag{2}$$

$$\frac{1}{\alpha}MO_{1-\alpha} + H_2O \rightarrow \frac{1}{\alpha}MO + H_2 \tag{3}$$

and so, the overall reaction is

$$2CH_4 \rightarrow C_2H_6 + H_2 \tag{4}$$

where MO is the original oxide surface and $MO_{1-\alpha}$ is the partially reduced oxide surface. Water can be applied in the OCM reaction as oxidant both to reduce side reactions and to produce hydrogen.

The problems of this methane–water co-feed reaction are that overall reaction (4) is not thermodynamically favored at high temperature and steam reforming of CH_4 occurs as follows [10]:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{5}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6}$$

In the present study the methane–water reaction was carried out in redox manner to shift the equilibrium of reaction (4) and to avoid the steam reforming reactions (5) and (6). From thermodynamical considerations, when the oxide is in low oxidation state, only few oxides, such as those of Ce, V, Ti, Fe and Sn, are available to reduce water as $MO_{1-\alpha}$ in reaction (3). Among SnO_2, CeO_2, and V_2O_5 supported on γ-alumina (10 wt% as metal), only SnO_2/Al_2O_3 showed C_2 formation activity in reaction (2), as shown later. Therefore, we focused our attention on tin oxides. About the catalysis of tin oxide it is known that the activity of SnO_2 for OCM reaction in redox manner is low [1] and that SnO_2 shows a promoter effect when supported on MgO [11–13]. Recently, pyrochlore structure [14,15] or K_2NiF_4 structure [16] oxides containing Sn have been reported as effective catalysts for the conventional OCM reaction. In the present work the activities of mixed oxides consisting of SnO_2 and an alkali earth metal oxide were tested by cycling redox

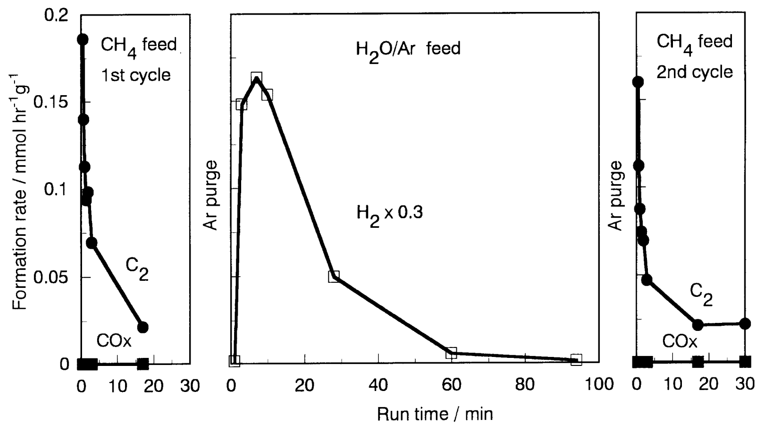

Figure 1. Transient response in cyclic activity test at 1023 K on mixed oxides of strontium and tin using [$SrSnO_3$].

mode in which methane and water were passed alternately over the oxide.

2. Experimental

Bulk oxides were prepared by a co-decomposition method in the following manner. After drying-up of the aqueous solution of acetates and/or nitrates of metals, the mixture was decomposed in air at 1223 K for 8 h to produce a mixed oxide. The oxides are denoted as [ABO_3] or A_2BO_4 according to the charged ratio of A to B, while the oxide [ABO_3] was found to be a mixture of SnO_2, perovskite (ABO_3) and K_2NiF_4/spinel type oxide (A_2BO_4) by XRD observation, as described later in detail. Specific surface areas were measured by nitrogen adsorption according to the BET method. The activities of the oxides were evaluated by periodic reaction in a flow-type fixed-bed reactor made of quartz. For the methane coupling reaction pure methane (99.99%, 37 ml/min) was introduced at 1023 K first from 90 s to 30 min, and then, after Ar purging, argon saturated with water vapor at r.t. was supplied to reoxidize the partially reduced oxide for 1.5 h. Methane and Ar were purified by passing over MnO/SiO_2 and molecular sieve 5A. The oxide granules (0.2 g) were placed in the annular space between the inner and outer tube with quartz granules (0.3 g) as diluent. Reaction temperature was monitored by a thermocouple placed inside the inner quartz tube. The products were analyzed by gas chromatographs. At methane conversion reaction, products were C_2 (C_2H_6 and C_2H_4), COx (CO and CO_2), and H_2. During reoxidation by steam, H_2 and a small amount of COx were observed, the latter should originate from carbon deposition during methane reaction.

3. Results and discussion

Figure 1 shows the typical activity change in methane–water redox cycles. As a transient response to the methane feed in the first cycle, [$SrSnO_3$] shows a high selectivity to C_2 hydrocarbons while hydrogen is observed as a response to the water/Ar feed. The activity and selectivity for methane conversion are reproduced after the feeding of water, as shown in the second cycle. It suggests that regeneration of the oxide by reaction (3) proceeds.

The maximum activities of the oxides supported on γ-alumina (10 wt% as metal) are compared in figure 2 for each cycle. Among SnO_2, CeO_2, and V_2O_5 supported on γ-alumina, only SnO_2/Al_2O_3 showed C_2 formation activity in reaction (2). In addition, the recovery of activity after reaction (3) was also observed. Figure 2 also shows the activity of supported and unsupported SnO_2. Both high selectivity for C_2 hydrocarbons and regeneration of activity are observed when SnO_2 was supported on MgO.

For higher C_2 selectivity and stable regeneration, we intended to synthesize mixed oxides of perovskite phase from alkali earth metal oxides and SnO_2. Surface area of [$MgSnO_3$], [$CaSnO_3$], [$SrSnO_3$] and [$BaSnO_3$] is 6.2, 7.3, 2.5 and 2.4 m^2/g, respectively. The maximum activities

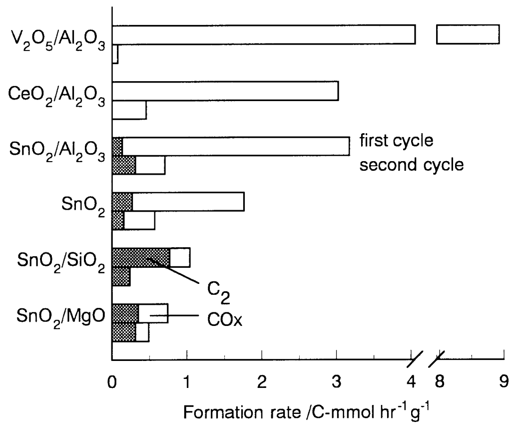

Figure 2. Methane conversion activity at 1023 K on supported oxides.

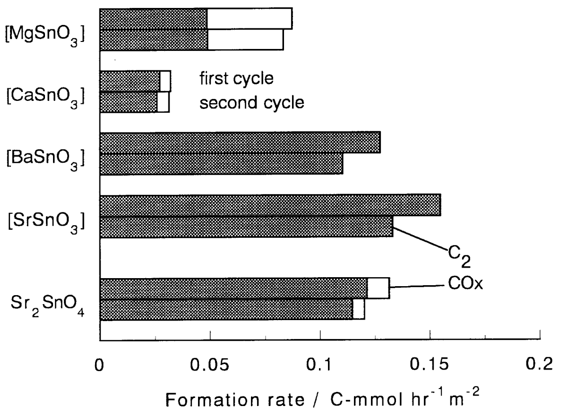

Figure 3. Methane conversion activity at 1023 K on mixed oxides of alkali earth metal and tin.

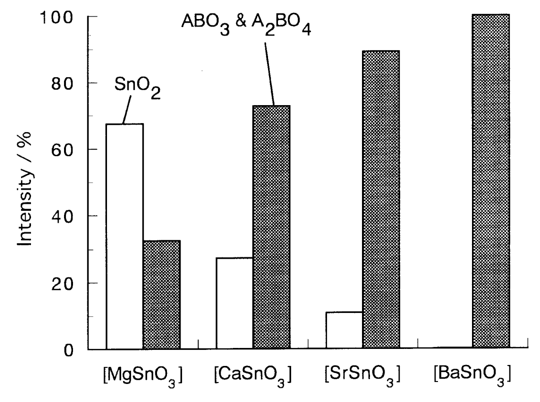

Figure 5. Peak intensities on the diffractograms of mixed oxides of alkali earth metal and tin.

of the mixed oxides in each cycle are compared in figure 3. Every oxide shows C_2 formation activity and the activity is almost recovered by feeding water/Ar. Among the [ABO_3] oxides, the activity, selectivity and activity-recovery of [$SrSnO_3$] are most remarkable.

The bulk phases of these oxides were characterized by XRD (figure 4). The presence of ABO_3 (perovskite oxide), A_2BO_4 (K_2NiF_4 or spinel type oxide) and SnO_2 was observed. Therefore, the activities in figure 3 are originated from every phase. The relative peak heights of these peaks are shown in figure 5 to clarify the relationship between the oxide phase and its activity. A relation between the intensity of SnO_2 and COx formation is suggested. The result suggests that SnO_2 is active for COx formation [11] but it is not clear if the A_2BO_4 and ABO_3 phases are active for C_2 formation or if the amorphous phase, which is not observed in diffractograms of mixed oxides, is active. To identify the activity of Sr_2SnO_4 phase, single Sr_2SnO_4 phase oxide was successfully prepared by calcination of its precursor at 1223 K. Single phase of ABO_3 was not obtained at that calcination temperature. The surface area of Sr_2SnO_4 was 3.8 m^3/g. The activity per unit surface area is also shown in figure 3. The C_2 activity of Sr_2SnO_4, almost the same as that of [$SrSnO_3$], suggests that the C_2 activity of [ABO_3] in figure 3 depends on ABO_3 or A_2BO_4 oxide phase.

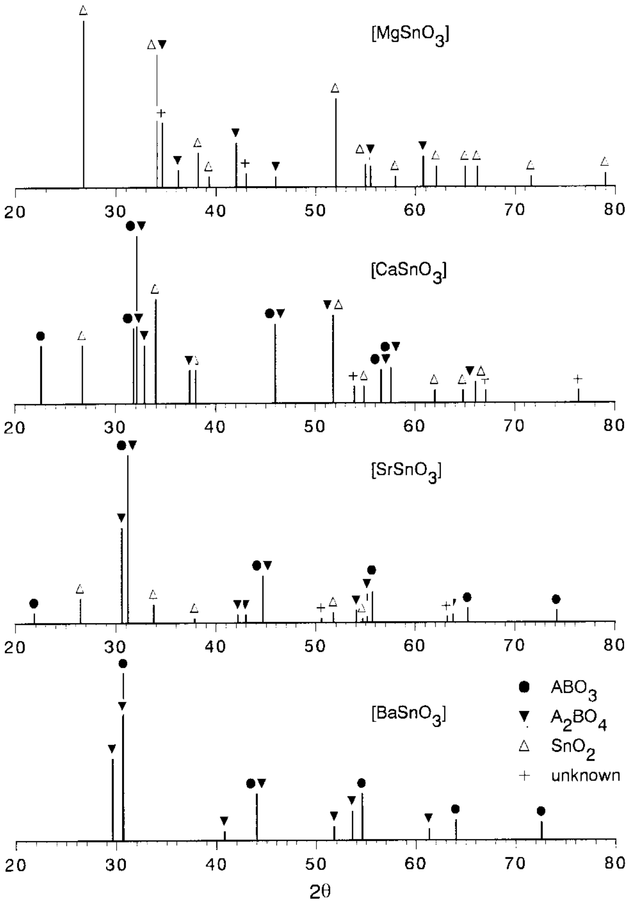

Figure 4. XRD pattern of mixed oxides of alkali earth metal and tin.

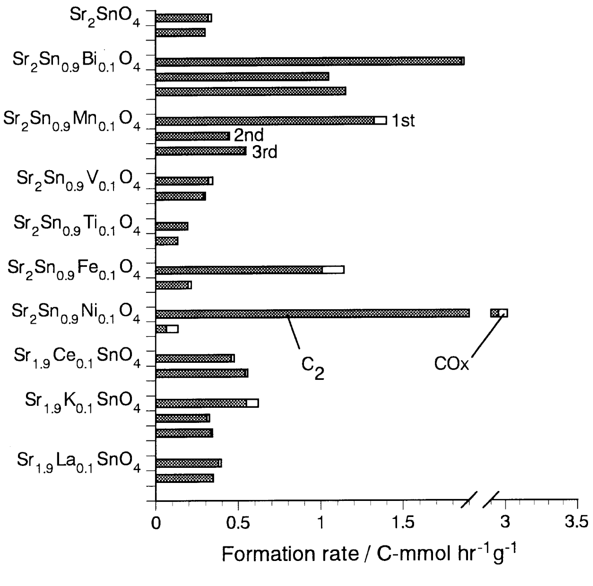

Figure 6. Effect of doping in Sr_2SnO_4.

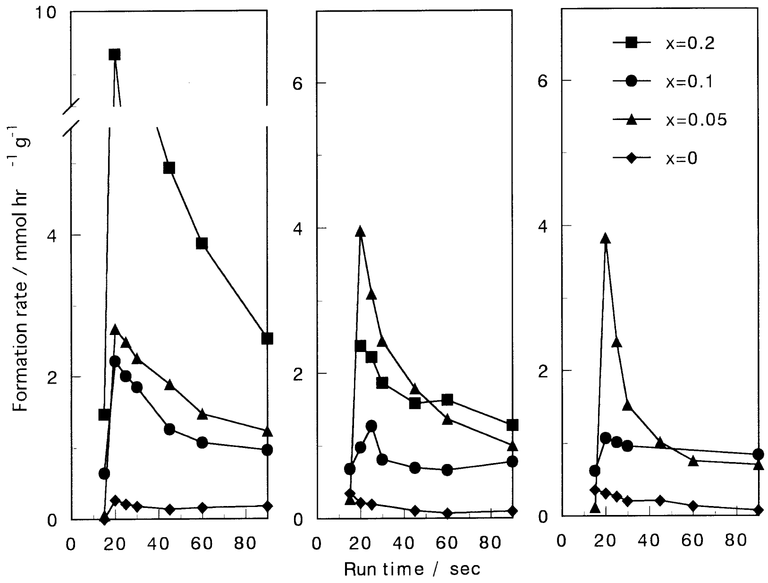

Figure 7. Effect of Bi doping in Sr_2SnO_4.

The effect of dopant on the catalytic activity of A_2BO_4 is shown in figure 6. Doping to B site Sn^{4+} cation is clearly effective while doping to A site cation results in almost the same activity. Ni^{2+}, Bi^{3+}, Mn^{4+} and Fe^{3+} enhanced the activity in the first cycle. Among them, however, only Bi^{3+} showed repeated activity-maxima. The effect of the amount of Bi doping is shown in figure 7. Activity-recovery after reoxidation by water is remarkable on $Sr_2Sn_{0.95}Bi_{0.05}O_4$ while the recovery on $Sr_2Sn_{0.9}Bi_{0.1}O_4$ and $Sr_2Sn_{0.8}Bi_{0.2}O_4$ is not so clear.

Sr_2SnO_4 has been reported to be active for the conventional co-feed OCM reaction [16]. The active oxygen species is O_2^{2-}, which was observed by XPS. The mechanism of O_2^{2-} formation is decomposition of surface carbonate by vapor phase oxygen. A similar phenomenon was reported in the case of $BaPbO_3$ and $BaBiO_3$ [18,19] where barium peroxide is formed from barium carbonate. It is probable that O_2^{2-} is generally formed during OCM reaction (co-feed) at the surface of mixed oxides containing such alkali earth metal element as Ba and Sr. In the case of redox OCM reaction, however, vapor phase oxygen is lacking to decompose surface carbonate and so, the active surface center is not clear yet. Effect of Bi doping might be discussed in terms of p-type semiconductivity. When the B site cation of A_2BO_4, Sn^{4+}, is replaced by Bi^{3+} oxygen, a vacancy and hole are formed to attain electroneutrality. The generated hole promotes the formation of electron deficient oxygen species, such as O^-, O_2^{2-} and O_2^-, from lattice oxygen [20]. The result given in figure 7 could be explained by an increasing amount of such oxygen species. Further investigations about the characteristics of the Sr_2SnO_4 structure and the oxygen species which is generated by water are in progress.

References

[1] G.E. Keller and M.M. Bhasin, J. Catal. 73 (1982) 9.

[2] K. Otsuka, K. Jinno and A. Morikawa, Chem. Lett. (1985) 499.

[3] T. Ito, J.-X. Wang, C.-H. Lin and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 5062.

[4] J.A. Roos, A.G. Bakker, H. Bosch, J.G. van Ommen and J.R.H. Ross, Catal. Today 1 (1987) 133.

[5] K. Asami, S. Hashimoto, T. Shikada, K. Fujimoto and H. Tominaga, Ind. Eng. Chem. Res. 26 (1987) 1485.

[6] T. Nishiyama and K. Aika, J. Catal. 122 (1990) 348.

[7] J.B. Kimbles and J.H. Kolts, Energy Prog. 6 (1986) 226.

[8] P. Pereira, S.H. Lee, G.A. Somorjai and H. Heinemann, Catal. Lett. 6 (1990) 255;
J. Raskó, G.A. Somorjai and H. Heinemann, Appl. Catal. A 84 (1992) 57.

[9] V.R. Choudhary, S.T. Chaudhari and A.M. Rajput, AIChE J. 37 (1991) 915.

[10] X. Li, K. Tomishige and K. Fujimoto, Catal. Lett. 36 (1996) 21.

[11] S.K. Agarwal, R.A. Migone and G. Marcelin, J. Catal. 123 (1990) 228.

[12] S.J. Korf, J.A. Roos, J.A. Vreeman, J.W.H.C. Derksen, J.G. van Ommen and J.R.H. Ross, Catal. Today 6 (1990) 417.

[13] A.N.J. van Keulen, G.C. Hoogendam, K. Seshan, J.G. van Ommen and J.R.H. Ross, J. Chem. Soc. Chem. Commun. (1992) 1546.

[14] A.T. Ashcroft, A.K. Cheetham, M.L.H. Green, C.P. Grey and P.D.F. Vernon, J. Chem. Soc. Chem. Commun. (1989) 1667.

[15] C.A. Mims, A.J. Jacobson, R.B. Hall and J.T. Lewandowski Jr., J. Catal. 153 (1995) 197.

[16] W. Yang, Q. Yan and X. Fu, React. Kinet. Catal. Lett. 54 (1995) 21.

[17] W.H. Hall, Proc. Phys. Soc. A 62 (1949) 741.

[18] K.C.C. Kharas and J.H. Lunsford, J. Am. Chem. Soc. 111 (1989) 2336.

[19] D. Dissanayake, K.C.C. Kharas, J.H. Lunsford and M.P. Rosynek, J. Catal. 139 (1993) 652.

[20] C. Yu, W. Li, W. Feng, A. Qi and Y. Chen, in: *New Frontiers in Catalysis*, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 1119.