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Ba Doped Cerium Oxides Active for Oxidative Coupling of Methane

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Among the alkali or alkaline earth metal doped CeO_2 catalysts examined, Ba doped CeO_2 (Ba/CeO_2) was the most active catalyst for oxidative coupling of CH_4. C_2-STY for the Ba/CeO_2 reached 0.95 mol g^{-1} h^{-1}, under the reaction conditions; T=1023 K, $P(CH_4)$=73 kPa, $P(O_2)$=28 kPa, and $W/F=6.1\times10^{-4}$ g h l^{-1}. A compound oxide, $BaCeO_3$, formed in the Ba/CeO_2 is the active species for the reaction.

Currently, natural gas is used principally as a fuel. Industry is now searching for new or novel ways to enhance the use and value of this methane-containing natural resouces. One of the most probable ways, oxidative coupling of methane into C_2H_6 and C_2H_4 (C_2-compounds) has attracted much attention in recent years.[1-11] We have reported that most of the rare earth metal oxides are active and selective catalysts for this reaction.[11a] It has been demonstrated that Sm_2O_3 is the most active compared with other metal oxides reported so far.[11e] From the industrial point of view, however, Sm_2O_3 is rather expensive because its amount of mining production is not so large.

We turn our attention to CeO_2, which is the most abundant of the rare earth metal oxides. The catalytic activity of CeO_2 for deep oxidation of CH_4 was fairly high, but that for C_2-formation was negligible.[11a] In the case of some transition metal oxides which were also active for the deep oxidation, the addition of alkali salts to the oxides retarded the deep oxidation but promoted the formation of C_2-compounds.[11b] Therefore, it seems possible to endow CeO_2 with the catalytic activity to produce C_2-compounds by the similar modification with basic additives. In this communication, we report the catalytic activity of the alkali or alkaline earth metal doped CeO_2 for the oxidative coupling of CH_4, and discuss the active species in the most active catalyst to be found.

The experiments were carried out using a conventional gas-flow system under atmospheric pressure. A reactant mixture of CH_4 and O_2 was introduced to a fixed bed reactor with He as a carrier gas. The selectivity and yield of the products were calculated on the basis of carbon number of CH_4 reacted. The alkali or alkaline earth metal doped CeO_2 catalysts were prepared by the usual impregnation method with alkali carbonates, alkaline earth (Be, Mg) nitrates or alkaline earth (Ca, Sr, Ba) hydroxides. They were calcined at 1073 K for 2 h in air before the

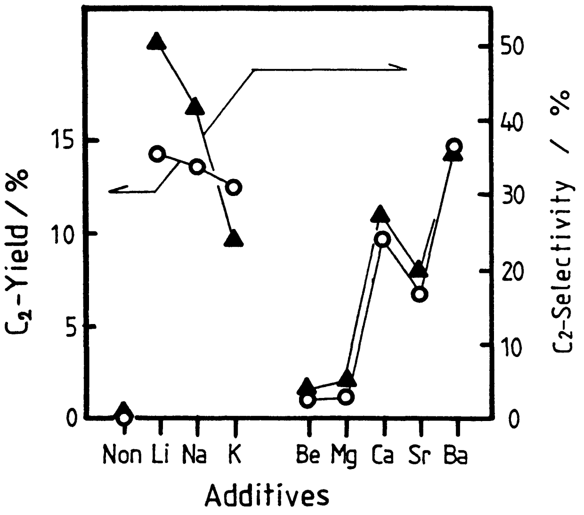

Fig. 1. Effect of alkali or alkaline earth metal additives on C_2-yields (○) and C_2-selectivties (▲).

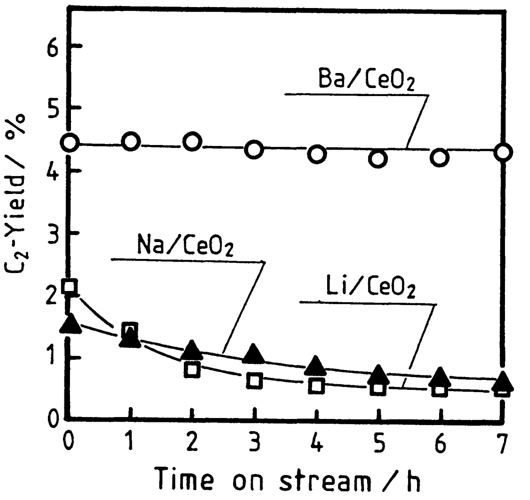

Fig. 2. Change in C_2-yields with time on stream.

○ Ba/CeO_2
□ Li/CeO_2
▲ Na/CeO_2

experiments. The amounts of additives were 20 mol%.

Figure 1 shows the results of CH_4-conversion observed at a time on stream of 30 min for various alkali or alkaline earth metal doped CeO_2 catalysts. The reaction conditions were as follows; T=1023 K, $P(CH_4)$=20 kPa, $P(O_2)$=10 kPa, and W/F=0.56 g h l^{-1}. No C_2-compounds were formed over the parent CeO_2 (Non), while in any case, addition of the alkali or alkaline earth metal generated the catalytic activity for C_2-formation. Among the catalysts tested, Li, Na, and Ba doped CeO_2 showed higher selectivities and yields of C_2-compounds.

We examined the stability of these effective catalysts at a low W/F (0.011 g h l^{-1}); the reaction temperature and the pressures of reactants were same as those of Fig. 1. The C_2-yield for each catalyst as a function of the time on stream is shown in Fig. 2. The activity for C_2-formation of Li/CeO_2 or Na/CeO_2 decreased markedly with the time on stream. On the other hand, the C_2-yield for Ba/CeO_2 was almost constant during this experiment. Moreover, it is to be noted that the initial C_2-yield of the Ba/CeO_2 is more than twice as larger as that of Li/CeO_2 or Na/CeO_2. Such large differences, which were not demonstrated in Fig. 1, resulted from the lower oxygen conversion (22%) for the Ba/CeO_2 under the reaction conditions in Fig. 2 compared with that in Fig. 1 (98%). Therefore, the initial C_2-yields in Fig. 2 indicate a better comparison for the catalytic activities among the Ba/CeO_2, Li/CeO_2 and Na/CeO_2. The highest catalytic activity and stability observed for the Ba/CeO_2 show that this is the best catalyst for the oxidative coupling of CH_4 among the alkali or alkaline earth metal doped CeO_2 catalysts tested in this work.

Aika et al. have reported that $BaCO_3$ is the active catalyst for oxidative coupling of CH_4.$^{5)}$ In the case of Ba/CeO_2, Ba species might be the active species. In order to clarify this possibility, we carried out the reaction over Ba/SiO_2 and Ba/Al_2O_3 which were prepared similarly to Ba/CeO_2. These two catalysts were inactive for the formation of C_2-compounds. The $BaCO_3$ without carriers catalyzed the reaction. However, the specific activity (per surface area) of the $BaCO_3$ was one order of magnitude less than that of Ba/CeO_2 as will be described later. These results indicate that the catalytic activity of Ba/CeO_2 for the oxidative coupling of CH_4 can not be attributed to the Ba species by themselves. Accordingly, the interaction between Ba and Ce may generate new active species.

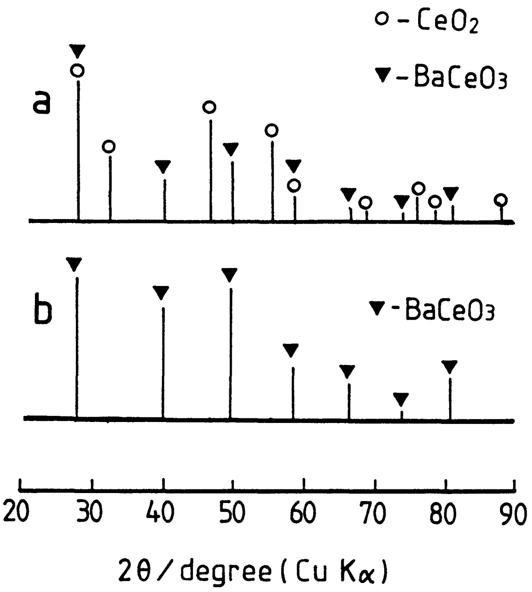

Fig. 3. XRD patterns
(a) Ba(20 mol%)/CeO_2
(b) Ba(50 mol%)/CeO_2.

If the consideration described above is true, the catalytic activity of Ba/CeO_2 should depend on its preparation method. We carried out the reaction over Ba/CeO_2 prepared by another method, that is, drying of the mixed aqueous solution of $Ba(OH)_2$ and $(NH_4)_2Ce(NO_3)_6$ following the calcination in air at 1073 K. C_2-yield for this Ba/CeO_2 was higher (5.8%) than that for the Ba/CeO_2 in Fig. 2 (4.4%) under the same reaction conditions. The catalytic activity per surface area for the former was 3.9 times greater than that of the latter. Therefore, we concentrate our discussion on the Ba/CeO_2 prepared from the aqueous solution of $Ba(OH)_2$ and $(NH_4)_2Ce(NO_3)_6$ hereafter. The separate experiment under higher pressures of reactants ($P(CH_4)$=73 kPa, $P(O_2)$=28 kPa) and a low W/F (6.1×10^{-4} g h l^{-1}) showed that C_2-STY (Space Time Yield) observed for this Ba/CeO_2 reached 0.95 mol g^{-1} h^{-1}, which corresponded to about one-third of the highest C_2-STY (2.98 mol g^{-1} h^{-1}) observed for Sm_2O_3.$^{11e)}$

X-Ray diffraction patterns of Ba/CeO_2 with different content of Ba are shown in Fig. 3. Ba(20 mol%)/CeO_2 (a) discussed above gave not only the diffraction peaks due to CeO_2 but also those due to a compound oxide, $BaCeO_3$.$^{12)}$ This $BaCeO_3$ may be the active catalyst for C_2-formation. Ba(50 mol%)/CeO_2 (b), whose bulk composition was the stoichiometric value of $BaCeO_3$, gave only the peaks due to $BaCeO_3$.

We have calculated the apparent activation energy for the conversion of CH_4 from the sum of the rates of C_2-formation and deep oxidation measured at the temperatures 823 - 1023 K. The results were as follows; Ba(20 mol%)/CeO_2 (142), $BaCeO_3$ (143), CeO_2 (142), and $BaCO_3$ (195 kJ mol^{-1}). The activation energy of

Ba/CeO_2 agreed well with that of $BaCeO_3$ or CeO_2, while $BaCO_3$ gave the higher activation energy. The total rate of CH_4-conversion per surface area observed for the $BaCO_3$ was one order of magnitude less than those for the other three catalysts. These results indicate that Ba species by themselves are not the active species in the Ba/CeO_2 for the activation of CH_4 under the reaction conditions taken in this work. The C-H bond breaking of CH_4 must be initiated on a common active site over the Ba/CeO_2, $BaCeO_3$, and CeO_2. We speculate that the activation of CH_4 occurs on Ce^{4+} cations commonly existing on the three catalysts. Ba must retard the subsequent deep oxidation, enhancing the C_2-production by forming the compound oxide, $BaCeO_3$.

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