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LiCl DOPED COBALT OXIDE IS AN ACTIVE CATALYST FOR THE FORMATION OF ETHYLENE IN THE OXIDATIVE COUPLING OF METHANE

Takayuki KOMATSU *, Toru AMAYA and Kiyoshi OTSUKA

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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The title compound was found to be an active and selective catalyst for oxidative coupling of methane at temperatures even lower than 900 K, where the selectivity for the formation of ethylene exceeded that of ethane.

1. Introduction

Oxidative coupling of methane into ethane and ethylene has attracted much attention of researchers in chemistry and chemical industry from the viewpoint of the chemical utilization of natural gas. Many kinds of catalysts have been reported to be active and selective for the reaction [1]. This reaction involves the activation of methane molecules by breaking their stable C-H bonds. Therefore, higher yield of C_2-hydrocarbons (ethane and ethylene) could be obtained only at high temperatures (> 950 K). In the case of catalytic combustion of methane, however, some catalysts convert methane into carbon oxides at lower temperatures (< 700 K). The oxides of transition metals such as Cr, Fe, Co, Ni or Cu have generally high ability for the combustion of methane at temperatures higher than 700 K. We intended to apply such active transition metal oxides to oxidative coupling of methane at lower temperatures than 900 K. It is reported that the addition of alkali elements into metal oxides of Ni [2], Mn [3,4], Ti [3], Zn [5], Sm [6], Mg [7,8], improves their catalytic activity for oxidative coupling of methane. Especially, alkali halides are effective additives for the formation of ethylene [2–6]. In this study, we expect that the modification of the transition metal oxides by adding alkali salts might generate active and selective catalysts for oxidative coupling of methane into ethylene at lower temperatures than 900 K.

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* Author to whom correspondence should be addressed.

2. Experimental

The experiments were carried out using a conventional gasflow system under atmospheric pressure. A reactant mixture of CH_4 and O_2 was introduced to a fixed bed reactor (i.d. = 6 mm) with He as a carrier gas. Products were analyzed by gas chromatography. The selectivity and the yield of the products were calculated on the basis of the carbon number of CH_4 reacted. The alkali doped transition metal oxides were prepared by the usual impregnation method with alkali salts and the oxides. For example, in the case of LiCl doped cobalt oxides. LiCl and Co_3O_4 were used typically with the ratio of $Li/(Li + Co) = 0.17$ (17 atom%). The impregnated oxides were calcined at 973 K for 2 h in air.

3. Results and discussion

First we have tested the catalytic activity of some alkali doped transition metal oxides for oxidative coupling of methane at 873 K. It was found that LiCl doped cobalt oxide ($LiCl/Co_3O_4$) gave the highest yield of C_2-hydrocarbons. We have already reported that alkali halide doped transition metal oxides, such as LiCl/NiO [2], $LiCl/MnO_2$ [3], $NaCl/MnO_2$ [4], etc., are active and selective for the formation of ethylene in oxidative coupling of methane at a high temperature of 1023 K. Therefore, we compared the catalytic performance of the $LiCl/Co_3O_4$ with those of the LiCl/NiO and $NaCl/MnO_2$ under the same reaction conditions. Figure 1 shows the yields of C_2-hydrocarbons as a function of the reaction temperature for LiCl(17 atom%)/Co_3O_4, LiCl(20 atom%)/NiO and NaCl (20 atom%)/MnO_2, together with the yield for Li(30 atom%)/MgO. The last catalyst has also been reported to be active for oxidative coupling of methane [7]. LiCl/NiO [2], $NaCl/MnO_2$ [4] and Li/MgO [7] were prepared in the same

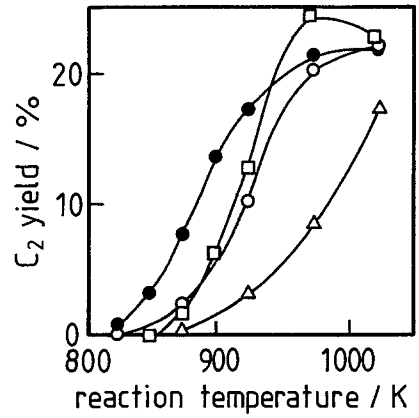

Fig. 1. Comparison of the yields of C_2-hydrocarbons over LiCl(17 atom%)/Co_3O_4 (●), LiCl(20 atom%)/NiO (○), NaCl(20 atom%)/MnO_2 (□), and Li(30 atom%)/MgO (△).

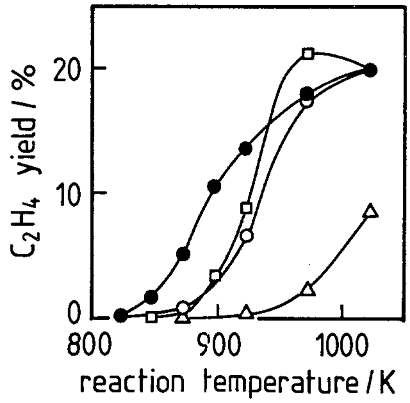

Fig. 2. Comparison of the yields of C_2H_4 over LiCl(17 atom%)/Co_3O_4 (●), LiCl(20 atom%)/NiO (○), NaCl(20 atom%)/MnO_2 (□), and Li(30 atom%)MgO (△).

methods reported in the literatures. The reaction conditions are as follows; catalyst weight = 2.0 g, $P(CH_4) = 10.1$ kPa, $P(O_2) = 5.1$ kPa, and the total flow rate = 50 ml STP min^{-1}. At 1023 K, LiCl/Co_3O_4, LiCl/NiO and NaCl/MnO_2 exhibited almost the same C_2 yield of about 20%, while Li/MgO gave lower C_2 yield. On decreasing the temperature, the C_2 yield for LiCl/Co_3O_4 decreased gradually, while those for other catalysts decreased steeply except for the maximum yield for NaCl/MnO_2 at 973 K. LiCl/Co_3O_4 gave the highest yield at any temperatures below 923 K and C_2-hydrocarbon formation occurred at as low as 823 K. The C_2 yield increased to 7.7% at 873 K and exceeded 13% at 898 K.

Figure 2 shows the yield of ethylene for each catalyst in the reaction described in fig. 1. At higher temperatures, LiCl/Co_3O_4, LiCl/NiO and NaCl/MnO_2 gave higher C_2H_4 yields compared with Li/MgO. We have already reported that alkali halide doped transition metal oxides give excellent selectivity for the formation of C_2H_4 in oxidative coupling of methane at higher temperatures around 1023 K [2–4]. At lower temperatures than 950 K, the C_2H_4 yield for LiCl/Co_3O_4 exceeded those for other catalysts. For example, C_2H_4 yields at 873 K were 5.0 (LiCl/Co_3O_4), 0.7 (LiCl/NiO), 0.5 (NaCl/MnO_2), and 0% (Li/MgO), respectively. The surface areas of the catalysts were 0.60 (LiCl/Co_3O_4), 0.51 (LiCl/NiO), 1.5 (NaCl/MnO_2), and 1.0 m^2 g^{-1} (Li/MgO), respectively. Accordingly, the specific rate of C_2H_4 formation per surface area of the LiCl/Co_3O_4 is also the highest among these catalysts.

It has been reported that the gas phase dehydrogenation of ethane may be significant when there is a certain amount of residual oxygen in the post-catalyst zone of LiCl doped Mn-oxide catalysts [9]. We examined the gas phase dehydrogenation with the vacant reactor (i.d. = 6 mm) under the following reaction conditions; $T = 873$ K, $P(C_2H_6) = 1.0$ kPa, $P(O_2) = 2.8$ kPa, and the total flow rate = 50 ml STP min^{-1}. These values of partial pressures are roughly equal to those in the post-catalyst zone of the run shown in fig. 2 for LiCl/Co_3O_4. It was

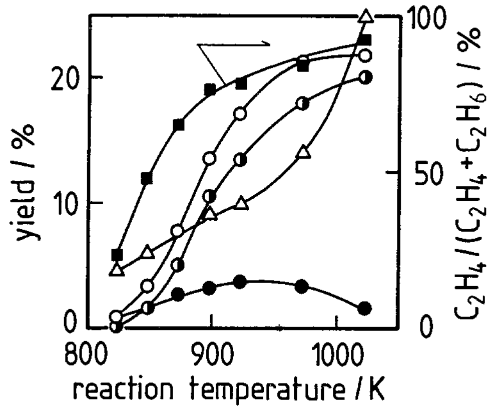

Fig. 3. Effect of reaction temperature on the yields of $CO+CO_2$ (△), C_2-hydrocarbons, (○), C_2H_4 (◑), and C_2H_6 (●) and on the $C_2H_4/(C_2H_4+C_2H_6)$ ratio (■) over LiCl(17 atom%)/Co_3O_4.

found that any products were not formed from C_2H_6. Therefore, the gas phase dehydrogenation of ethane into ethylene can be neglected at 873 K during the reaction of CH_4 over LiCl/Co_3O_4. We conclude that LiCl/Co_3O_4 is the highly active catalyst for the formation of C_2H_4 in oxidative coupling of methane even at lower temperatures than 900 K.

Figure 3 shows the yields of the products and the $C_2H_4/(C_2H_4+C_2H_6)$ ratio as functions of the reaction temperature for the LiCl(17 atom%)/Co_3O_4 catalyst. The yield of carbon oxides increased gradually and that of C_2-hydrocarbons increased steeply with increasing temperatures below 950 K. This steep increase in the C_2 yield resulted from the increase in C_2H_4 yield. The yield of C_2H_6 increased a little and then decreased above 950 K. As a result, the $C_2H_4/(C_2H_4+C_2H_6)$ ratio increased with increasing temperatures and exceeded 50% at as low as 873 K. This result also indicates that the LiCl/Co_3O_4 is the effective catalyst for ethylene formation below 900 K. At 873 K, the formations of propane (yield of 1.0%) and C_4-hydrocarbons (yield of 0.2%) were also observed; the total selectivity of hydrocarbons ($> C_2$) amounted to 54%.

Figure 4 shows the effect of LiCl content on the activity and selectivity of the catalyst. The reaction conditions are as follows; catalyst weight = 1.0 g, reaction temperature = 873 K, $P(CH_4) = 10.1$ kPa, $P(O_2) = 5.1$ kPa, and the total flow rate = 100 ml STP min^{-1}. Without addition of LiCl, Co_3O_4 by itself catalyzed almost exclusively the deep oxidation of methane into carbon oxides. When a small amount of LiCl was added to Co_3O_4, CH_4 conversion decreased and C_2 selectivity increased. It is clear that the addition of LiCl retards the activity of the parent Co_3O_4 for deep oxidation. The addition of a larger amount of LiCl caused the increase in both CH_4 conversion and selectivity for C_2 formation. As a result, the yield of C_2-hydrocarbons increased with increasing the LiCl content. LiCl doped SiO_2 did not catalyze the oxidative coupling of methane although the

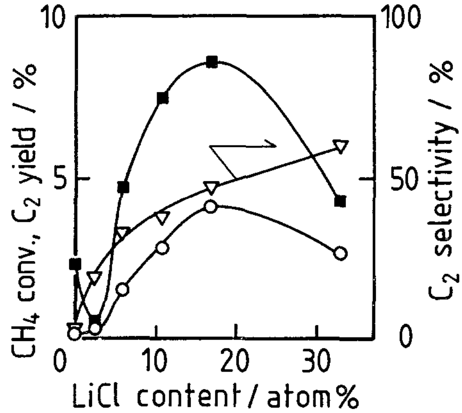

Fig. 4. Effect of LiCl content in $LiCl/Co_3O_4$ on CH_4 conversion (■) and yield (○) and selectivity (▽) of C_2-hydrocarbons.

dispersion of LiCl on SiO_2 may be higher than that on Co_3O_4. This result implies that LiCl by itself can not be the active species for C_2 formation and that new active species are formed in the $LiCl/Co_3O_4$ catalyst through a certain interaction between LiCl and Co_3O_4. At the Li content of 17 atom%, the C_2 yield reached its maximum. Further addition of LiCl caused the decrease in CH_4 conversion, which suggests that the excess amount of LiCl covers the active species on the catalyst.

Layered bismuth oxychlorides are also very active for the formation of ethylene in oxidative coupling of methane [10,11]. We have measured X-ray diffraction spectra of the $LiCl/Co_3O_4$ to clarify whether some bulk compound species which are active for the formation of ethylene are formed in the catalyst. The strong diffraction peaks attributed to the parent Co_3O_4 were observed. However, the existence of any compound species between LiCl and Co_3O_4 were not observed in the XRD pattern. Therefore, we speculate that the interaction between LiCl and Co_3O_4 described above may generate some active complexes only at the interface of LiCl and Co_3O_4. The XRD pattern did not change significantly before and after the reaction. The activity and selectivity of the $LiCl/Co_3O_4$ catalyst for C_2 formation slightly decreased at the initial stage of the reaction for about 3 h at 873 K. However, no change in the activity and selectivity was observed at least for 20 h after the initial decrease. It may be concluded that the active complexes between LiCl and Co_3O_4 are stable under the reaction conditions. It has been reported that Cl_2 reacts with CH_4 in the gas phase to form ethylene at higher temperatures [12]. In the case of the $LiCl/Co_3O_4$, however, the number of carbon atoms converted into C_2-hydrocarbons for 20 h of the reaction are more than 10 times as many as that of Cl^- in the catalyst. Accordingly, the reaction is not stoichiometric between CH_4 and Cl^- but probably catalytic between CH_4 and O_2. We may conclude that Cl^- contributes to the oxidative coupling of methane into ethylene only at the surface of the catalyst by forming the active compound species.

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