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THE CATALYSTS ACTIVE AND SELECTIVE IN OXIDATIVE COUPLING OF METHANE. ALKALI-DOPED SAMARIUM OXIDES

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Conversion of methane to C_2-hydrocarbons was tested on alkali-doped samarium oxides under the reaction conditions(T=1023K, $P(CH_4)$ =5.1 kPa, $P(CH_4)/P(O_2)$=5/2, W/F=600 g l^{-1}s). Among the catalysts tested, Li-doped samarium oxide was the most active and selective catalyst in the formation of C_2-compounds (C_2-yield 21%).

Partial oxidation of methane into more reactive chemicals such as ethylene and methanol is of great significance in heterogeneous catalysis. The proposed process in C_1 chemistry for the production of aliphatics or alcohols from natural gas (essentially methane) involves the intermediate formation of synthesis gas. This process suffers from the requirement of complicated engineering steps and also from the relative inefficiency of carrying out extensive oxidation of methane to carbon monoxide and then reduction of carbon monoxide to aliphatics or alcohols. Thus, a single step conversion process of methane to ethylene or to methanol, both are important raw chemicals, can have far reaching economic implications.

We have reported that rare earth metal oxides show very high catalytic selectivity for the production of C_2-hydrocarbons (C_2H_4 + C_2H_6) in the oxidative dehydrogenation and coupling of methane[1,2]($CH_4 + O_2 \rightarrow C_2H_6, C_2H_4, H_2O$). Among the rare earth oxides tested, Sm_2O_3 was the most active and selective catalyst in the formation of C_2-hydrocarbons.[1,2] However, the yield of C_2-hydrocarbons was less than 12%.[2] In this communication, we report the results of alkali-doped samarium oxides which show better catalytic activity and selectivity in the direct oxidative conversion of methane to C_2-hydrocarbons.

Powder catalysts of alkali/Sm_2O_3 , containing 5 to 40 mol% alkali, were prepared from alkali metal carbonates and Sm_2O_3 and then activated at 973 K in an oxygen flow. The experiments were carried out using a conventional gas-flow system at atmospheric pressure. A reacting gas mixture of CH_4, O_2 and He (a diluent) was introduced to the fixed bed reactor. The selectivity to the C_2-hydrocarbons is defined as the percentage of converted methane reacted to C_2H_4 and C_2H_6.

Figure 1 shows the effects of different alkali elements (20 mol%) added to Sm_2O_3 on the conversion of methane, selectivity to C_2-hydrocarbons and C_2-yield. The experimental conditions were as follows ; T=1023 K, $P(CH_4)$=5.1 kPa, $P(CH_4)/P(O_2)$=5/2, and W/F=600 g l^{-1}s. The Li_2CO_3 supported on SiO_2 did not show

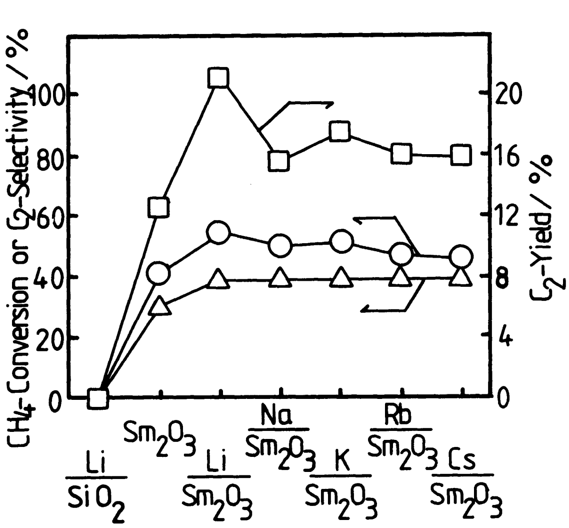

Fig. 1. Effects of alkali elements on the conversion of CH_4 (△), C_2-selectivity (○), and C_2-yield (□).

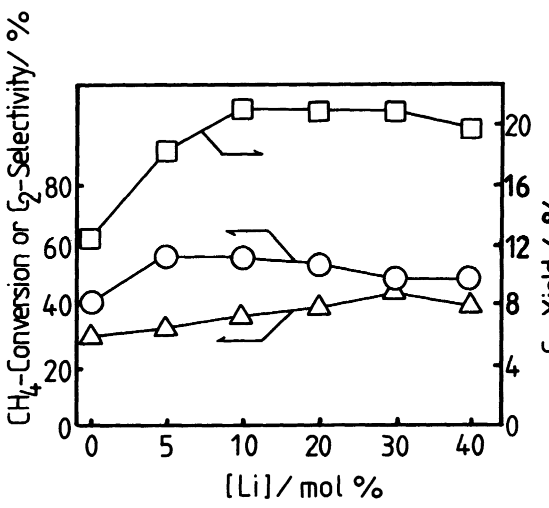

Fig. 2. Effect of the amount of Li added on the conversion of CH_4 (△), C_2-selectivity (○), and C_2-yield (□).

any catalytic activity. All the alkali-doped samarium oxides showed improved catalytic activities and C_2-selectivities compared to the samarium oxide alone. Besides C_2H_4, C_2H_6, CO_2, CO and H_2O, C_3H_6 and C_3H_8 also were produced, but in only trace amounts. The oxygen conversion were 100% for all the alkali/Sm_2O_3 catalysts. Among the alkali-doped oxides tested, the Li-doped samarium oxide showed the best C_2-selectivity and C_2-yield(21%).

Figure 2 shows the effect of the amount of Li added to samarium oxide on the results of reaction. The experimental conditions were same as those in Fig. 1. C_2-yield shows the maximum (21%) at the content of Li 10 to 20 mol%. C_2-selectivity shows the maximum (57%) at 5 to 10 mol% Li. The conversion of methane increases linearly with the content of Li in the range less than 30 mol%.

In conclusion, the addition of alkali carbonates to samarium oxide improved the catalytic activity and selectivity in the formation of C_2-hydrocarbons. The Li-doped samarium oxide showed the highest C_2-yield (21%) among the alkali-doped samarium oxides tested in this work.

References

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