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OXIDATIVE COUPLING OF METHANE OVER CaO-MgO MIXED OXIDE

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Mixed oxide catalyst prepared by co-precipitating magnesium oxide and calcium oxide showed an excellent activity for the oxidative coupling of methane. The high performances were presumed to arise from the high basicity of the mixed oxide.

1. Introduction

Alkaline earth metal oxides, especially MgO have been known to be active catalysts for the title reaction. The catalytic performances are greatly promoted by incorporating additives such as Li_2CO_3 [1], $NaNO_3$, $RbNO_3$ [2], BaOH [3], $La(NO_3)_3$ [4] and $CaCl_2$ [5]. In the present study mixed oxide of magnesium (MgO) and calcium (CaO) have been found to show an excellent catalytic activity for the reaction.

2. Experimental

Catalysts were prepared by precipitating the hydroxides from aqueous solutions of magnesium nitrate and calcium nitrate with the addition of 1 N sodium hydroxide at 50 ° C. After repeated washing with water the precursors were dried in air at 120 ° C for 12 h and were activated in air at 750 ° C for 30 min before reaction or CO_2 TPD measurement. The size of the catalyst particles was 20–40 mesh. Reactions were conducted in a fixed-bed, flow type reactor made of quartz. The details of the reaction apparatus have been described in a previous paper [5]. The reaction conditions were: 750 ° C, atmospheric pressure, $CH_4:O_2:N_2 = 13:1.4:85.6$ $W/F = 1$ g-cat · h/mol, $W = 0.3$ g. Temperature-programmed-desorption (TPD) of CO_2 was carried to investigated surface basicity. The catalyst on which CO_2 had been already adsorbed was heated in flowing helium at a constant rate (10 ° C/min).

3. Result and discussion

The conversion of methane and the selectivity for C2 hydrocarbons at 750 ° C are illustrated in fig. 1. The composition of MgO ranges from 0 mol% to 100 mol%. Methane conversion to C2 hydrocarbons was only 0.5% or less without catalyst. Both the activity and the selectivity for C2 hydrocarbons were the highest at 85 mol% MgO, giving the methane conversion of 9.2% and the C2 selectivity of 67.1%. The methane conversion to CO and CO_2 (CO*x*) is not affected by the catalyst composition in contrast to the case of the C2 hydrocarbons.

In fig. 2 are shown the effects of temperature on the reaction for the 85 mol% MgO catalyst, which showed the highest performance at 750 ° C. The selectivity for C2 hydrocarbons increased with the rise in reaction temperature because the formation rate of C2 increased while that of CO*x* was constant. Methane conversion leveled out at around 800 ° C because of the complete oxygen conversion. The conversion was 16.9% and the C2 selectivity was 71.8 carbon-mol% at 800 ° C.

We found that the halide ion in the CaO or MgO catalyst suppressed the formation of CO*x* [5]. The $CaCl_2$/MgO catalyst showed lower methane conversion (11.6%) and higher selectivity for C2 hydrocarbons (77.0 C-mol%) under the same reaction conditions. A small amount of halide compound supplied with feed gas also showed the similar effects for the halogen-free catalyst [5,6]. Mixed oxide catalyst (MgO-CaO) is superior to the halogen-containing catalysts in the catalytic activity.

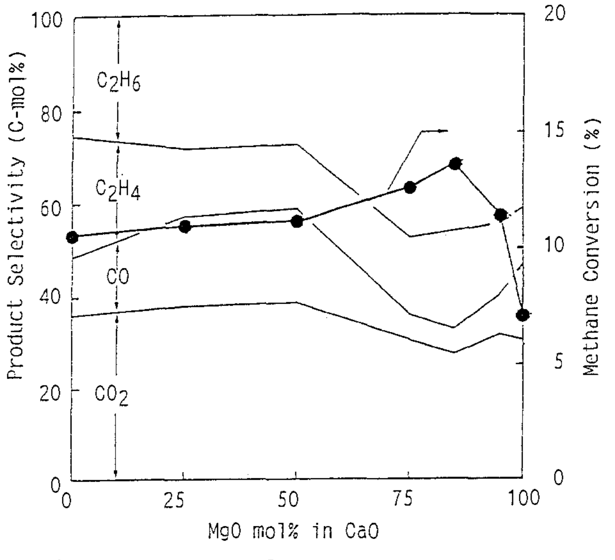

Fig. 1. Catalytic activity of mixed oxide at 750 ° C, atmospheric pressure, CH_4:O_2:N_2 = 13:1.4:85.6, W/F = 1 g-cat·h/mol.

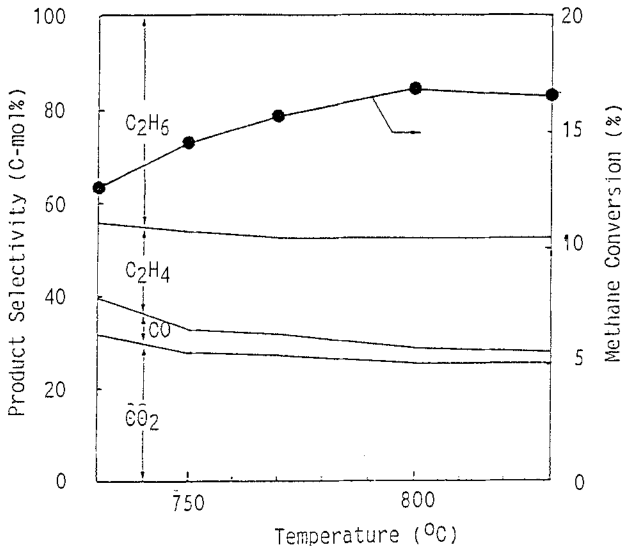

Fig. 2. Effect of temperature with MgO 85% catalyst at atmospheric pressure, CH_4:O_2:N_2 = 13:1.4:85.6, W/F = 1 g-cat·h/mol.

It has been pointed out that both the selectivity for C2 hydrocarbons and the basicity of alkaline earth metal oxides increases with the increase in atomic number [7,8]. It has been also reported that MgO shows higher basicity [9] and higher selectivity for C2 hydrocarbons [2] when sodium compounds such as $NaNO_3$ are doped. These facts suggest that the basicity of catalyst is essential for the high selectivity of C2 hydrocarbons.

The basicity of these oxides were investigated using a CO_2 TPD technique (fig. 3). The desorption peak of CO_2 at high temperature corresponds to high basicity

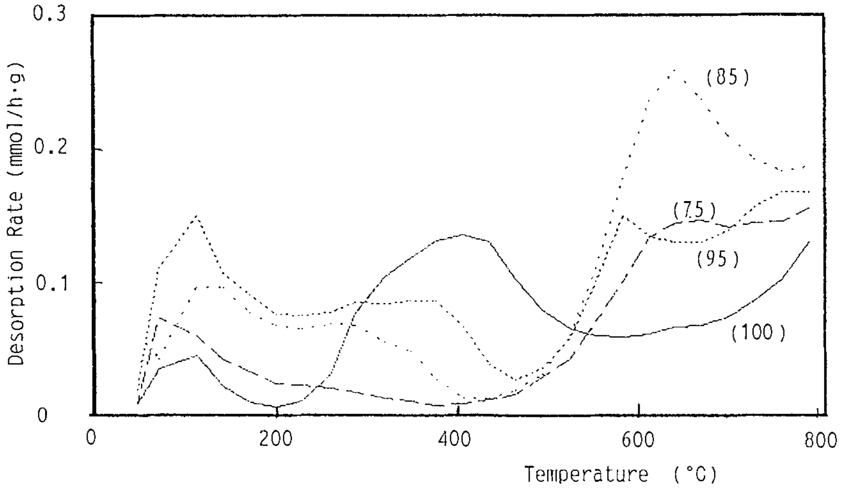

Fig. 3. Profile of CO_2 TPD, at 10 ° C/min. Figure in parenthesis presents mol% of MgO.

of the surface. The characteristic peak between 600 and 700 °C was most remarkable on 85% MgO among MgO-rich oxide catalyst. Recently, it has been shown that the oxygen anion of the MgO surface is displayed outward from the original (100) plane [10] when Ca^{2+} is doped and that Ca^{2+}/MgO shows higher basicity than pure MgO [11]. The observations mentioned above suggest that the high activity at 85% mol MgO arises from the high basicity originated from surface structure.

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