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Oxidative Coupling of Methane with Alkaline Earth Halide Catalysts Supported on Alkaline Earth Oxides

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Halides of alkaline earth metal oxides such as $MgCl_2$ or $CaCl_2$ on CaO or on MgO were found to be excellent catalysts for the oxidative coupling of methane. The selectivity of C_2 hydrocarbon reached 87% at 750 °C and $CH_4/O_2=9$.

Oxidative coupling of methane is now a current subject in the field of hydrocarbon oxidation. Many metal oxides have been claimed to be effective catalysts for the reaction.[1-6] Present authors have clarified that the lead oxide supported on magnesium oxide is an excellent catalyst[7,8] and that the bulk oxygen in the lead oxide is an active species for the reaction.[9] Recently, it was found that transition metal oxides which were doped with lithium halide exhibited high catalytic activities in making ethylene from methane.[10]

In the present work catalytic features of alkaline earth halides supported on alkaline earth oxides for the oxidative coupling of methane have been studied.

Catalysts were prepared by impregnating commercially available MgO or CaO with alkaline earth halides from their aqueous solutions. Fluoride catalysts were prepared by fluoriding the surface of calcium and magnesium oxides by treating them with hydrofluoric acid. The loading of each compound was 5 wt% as metal halide. The apparatuses and procedures of the reaction and product analysis have been described before.[7] The selectivities to C_2 hydrocarbon and ethylene on the alkaline earth catalysts decreased gradually with process time. This phenomenon might be attributed to the vaporization of halogen compounds. All the data shown in Tables 1-3 were taken at 15 min.

Table 1. Catalytic performances[a)]

Catalyst	Conversion /%		Selectivity /%	
	CH_4	O_2	C_2	(C_2H_4)
PbO/MgO	13.2	97.6	71.9	(15.6)
Li_2O/MgO	6.7	82.4	54.7	(13.9)
LiBr/MgO	10.5	93.6	72.2	(25.7)
NaF/MgO	2.7	12.7	77.6	(13.4)
$MgCl_2/TiO_2$	0.5	5.4	10.3	(0)
$MgCl_2/SiO_2$	0.1	1.4	26.5	(0)

a) Data at 15 min, Loading 5 wt%, Temp 750 °C, W/F=1.0 g·h/mol, $P(CH_4)=13$ kPa, $P(O_2)=1.4$ kPa.

In Table 1 are shown the catalytic performances of magnesia supported alkali oxides and alkali halides. As demonstrated by Ito et al.,[4)] the magnesium oxide doped with alkali oxide promoted its catalytic activity and selectivity. However, both levels of the activity and selectivity of C_2 hydrocarbons were lower than those of a PbO/MgO catalyst developed by the present authors.7) Also, alkali halides/MgO catalysts, especially a LiBr/MgO catalyst, showed a high activity and C_2 hydrocarbon selectivity (with a considerably high ethylene selectivity), as demonstrated by Otsuka et al.11) It should be noted that sodium fluoride, which has never been reported to have catalytic activity, exhibited a fairly high C_2 selectivity.

Table 2 shows the results obtained with a variety of alkaline earth halide catalysts supported on MgO. It is clear that MgF_2 is an negative catalyst for MgO. It inhibits either the formation of carbon oxides or the formation of C_2 hydrocarbons. However, a $MgCl_2$/MgO catalyst and a $CaCl_2$/MgO catalyst exhibit even superior performances to alkali halide catalysts. Especially, the $CaCl_2$/MgO catalyst give the highest selectivity of C_2 hydrocarbons (and also the highest ethylene selectivity). Although alkaline earth bromides are active for the reaction to some extent, their performances are inferior to those of alkaline earth chlorides.

Table 2. Catalytic performances of MgO-supported catalysts^a)

Catalyst	Conversion /%		Selectivity /%	
	CH_4	O_2	C_2	(C_2H_4)
MgF_2/MgO	0.4	0.9	12.7	(0)
$MgCl_2$/MgO	8.0	44.8	74.6	(18.3)
$MgBr_2$/MgO	2.5	24.8	47.6	(8.2)
$CaCl_2$/MgO	7.4	58.2	76.3	(27.8)
$CaBr_2$/MgO	9.0	97.9	61.0	(20.9)
MgO	0.8	12.9	48.1	(3.1)

a) Data at 15 min, Loading 5 wt%, Temp 750 °C, W/F=1.0 g·h/mol, $P(CH_4)$=13 kPa, $P(O_2)$=1.4 kPa.

In Table 3 are shown some of the catalytic properties of alkaline earth halides supported on calcium oxide. It should be noted that the CaO exhibits higher catalytic activity for methane conversion than any other doped CaO catalysts although its selectivity of C_2 hydrocarbons is not high. It is worth noting that $MgCl_2$ and $CaCl_2$ on the CaO exhibits extraordinary high selectivity for C_2 hydrocarbons and also that on the $MgCl_2$/CaO catalyst about 46% of C_2 hydrocarbon is ethylene. Similarly to the cases of the MgO supported catalyst, a fluoride catalyst CaF_2/CaO has low activity and bromide catalysts ($CaBr_2$ and $MgBr_2$) exhibit low selectivity of C_2 hydrocarbons.

Table 3. Catalytic performances of CaO-supported catalysts^a)

Catalyst	Conversion /%		Selectivity /%	
	CH_4	O_2	C_2	(C_2H_4)
$MgCl_2$/CaO	8.0	44.8	87.1	(40.4)
$MgBr_2$/CaO	8.3	64.9	74.6	(18.3)
CaF_2/CaO	5.9	62.2	51.0	(10.3)
$CaCl_2$/CaO	5.1	35.2	83.5	(33.7)
$CaBr_2$/CaO	9.5	98.0	50.5	(13.7)
CaO	10.5	79.7	46.3	(11.4)

a) Data at 15 min, Loading 5 wt%, Temp 750 °C, W/F=1.0 g·h/mol, $P(CH_4)$=13 kPa, $P(O_2)$=1.4 kPa.

Figure 1 shows the performances of the conversions of methane and oxygen of the $MgCl_2/CaO$ catalyst as a function of reaction temperature. Experimental data at 750 °C were measured after 4 h on stream, then those at 650, 700, and 800 °C were measured successively within 2 h. Therefore, the values were different from those shown in Tables 2 and 3. Both the

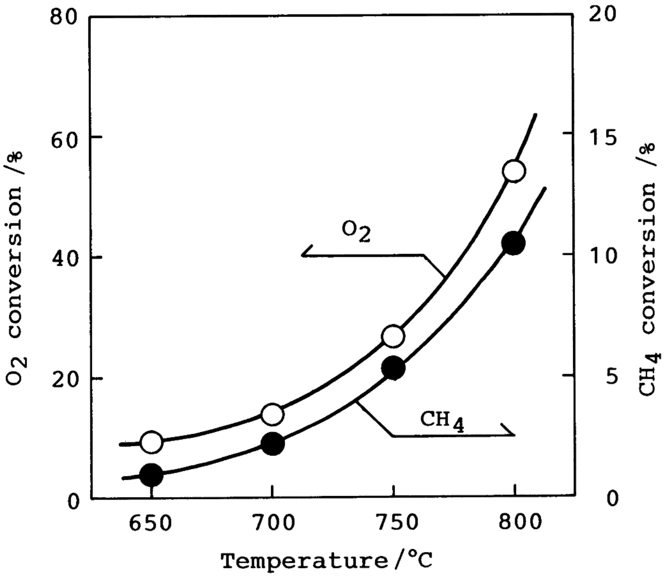

Fig. 1. Effect of reaction temperature on catalytic activity over $MgCl_2/CaO$.
Data at 4-6 h, Loading 5 wt%, W/F=1.0 g·h/mol, $P(CH_4)$=14 kPa, $P(O_2)$=1.6 kPa.

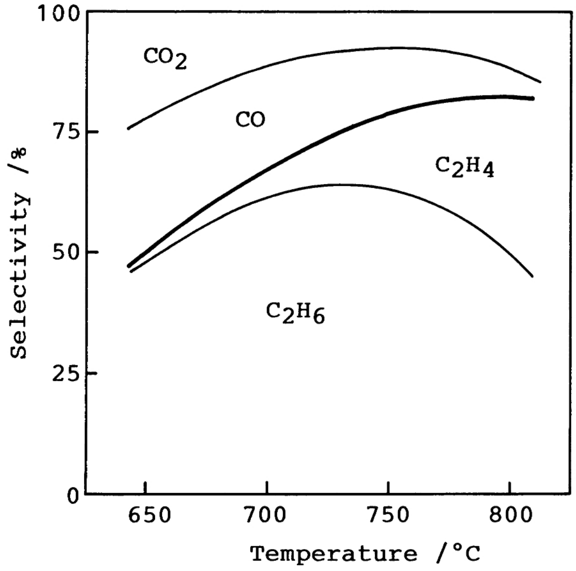

Fig. 2. Effect of reaction temperature on product selectivity over $MgCl_2/CaO$.
Data at 4-6 h, Loading 5 wt%, W/F=1.0 g·h/mol, $P(CH_4)$=14 kPa, $P(O_2)$=1.6 kPa.

conversions of methane and oxygen increased monotonically with the rise in reaction temperature. The selectivity of C_2 hydrocarbon increased with the increase in the temperature (Fig. 2) as was the case of the PbO/MgO catalyst.7) As for C_2 hydrocarbon the fraction of ethylene increased with rising reaction temperature.

Unsupported MgO exhibits poor catalytic properties for oxidative coupling of methane while CaO is highly active for the reaction. Both of them are comparably active and selective for the reaction when they are impregnated with chloride of magnesium or calcium. However, $MgCl_2$ on other supports, such as TiO_2 or SiO_2, exhibit much poorer catalytic functions than CaO or MgO supported ones (Table 1). In this alkaline earth halide/alkaline earth oxide catalyst system, since lattice oxygen of the catalyst is hard to react with methane, active oxygen species should be an adsorbed oxygen on the surface. The role of halogen is inferred to affect the reactivity of the adsorbed oxygen resulting in the suppression of deep oxidation of methane. The promoting effect of halide doping was $Cl>Br>F$ (Tables 2 and 3). Although the role of halide is not clear yet, the fact that alkaline earth oxides exhibits catalytic activity suggests that the high selectivity and activity of the title catalyst should be attributed to the combination of chloride and oxide of alkaline earth metals.

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