Oxidative coupling of methane over BaF_2–TiO_2 catalysts

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The addition of F^- to Ba–Ti mixed oxide catalysts significantly improves the catalytic performances for the oxidative coupling of methane (MOC), which can achieve high C_2 yields at wide feed composition range and high GHSV. The effect is particularly marked for the BaF_2–TiO_2 catalysts containing more than 50 mol% BaF_2. The C_2 yield of 17% and the C_2 selectivity of $> 60\%$ were achieved over these catalysts at 700°C. After being on stream for 31 h, the $\geqslant 50$ mol% BaF_2–TiO_2 catalysts showed only a 1–1.5% decrease in the C_2 yields. Results obtained by XRD show that various Ba–Ti oxyfluoride phases were formed due to the substitution of F^- to O^{2-}.

Keywords: Methane oxidative coupling; barium– titanium oxides; oxyfluorides

1. Introduction

Most of the active catalysts for MOC are reducible metal oxides, rare earth metal oxides, or the oxides of alkali and alkaline earth metals [1–3]. Comparatively, the modification of anions in catalysts has not been studied widely. Lunsford et al. [4] pay particular attention to the Li–MgO catalysts promoted with Cl^-, which exhibited good activity and selectivity for MOC. Due to the volatilization loss of alkali metal and chloride ions at high temperature, such catalysts suffer from deactivation in time. To overcome these disadvantages, it is significant to develop stable, active and selective catalysts for MOC at lower temperatures. Considering the similarity in size of F^- and O^{2-}, the stronger electronegativity of F compared to O and the virtually isolating effect of F^- dispersed on the surface of catalysts for oxygen species, we select fluorides as anion modifier of the oxide catalysts for MOC. A series of alkaline earth oxides, rare earth oxides, transition metal oxide catalysts modified by fluorides have been developed in our laboratory, which showed good properties (activity, selectivity and stability) for MOC at lower temperature. The objective of the present work is to study the effect of fluoride promoter on the Ba–Ti mixed oxides and the relation of catalytic performances with the catalyst structure, and to examine the influences of reaction conditions.

2. Experimental

Catalysts were prepared by mechanical mixing BaF_2 or BaO with TiO_2 with a small amount of water. The catalyst paste was dried for 4 h at 120°C and calcined in air for 6 h at 900°C. The material was then crushed and sieved to 40–60 mesh.

The catalytic reactions were carried out in a fixed bed quartz reactor 5 mm i.d. with heated length of 20 cm. A typical set of operating conditions was as follows: atmospheric pressure, 0.2 ml catalyst loading, methane/oxygen ratio of 4, no inert gas for dilution, and flow rate of 50 ml/min. Effluent gases were analyzed by gas chromatograph (5A carbosieve column for O_2, CO and GDX 502 column for CH_4, C_2H_4, C_2H_6 and CO_2) at room temperature.

XRD were recorded with a Rigaku D/max-RC diffractometer using Cu K_α radiation (40 kV, 30 mA).

3. Results and discussion

3.1. EFFECT OF FLUORIDE ON THE Ba–Ti MIXED OXIDES

Table 1 shows the catalytic performances of BaO–TiO_2 and BaF_2–TiO_2 catalysts for MOC. The substitution of part of F^- for O^{2-} resulted in a drastic increase of the methane conversion and C_2 selectivity. For the case of barium/titanium mole ratios of 1, 2 and 3, C_2 yields of 11.1, 17.1 and 16.6% were achieved over the BaF_2–TiO_2 system at 650, 700 and 720°C, respectively. Correspondingly, the BaO–TiO_2 mixed oxides only gained C_2 yields of 1.8 and 4.6% at identical conditions. All the data in tables 1 and 2 of BaF_2–TiO_2 catalysts were obtained over 20–40 h time-on-stream, but the data of BaO–TiO_2 catalysts were obtained over 3–9 h time-on-stream. The $\geqslant 50$ mol% BaF_2–TiO_2 catalysts showed only a 1–1.5% decrease of C_2 yields after 31 h on stream.

Table 1

Comparison of the oxidative coupling of methane over BaO–TiO_2 and BaF_2–TiO_2 catalysts

Ba/Ti	Catalyst	Temp. (C°)	CH_4 conv. (%)	Selectivity (%)					C_2 yield (%)
				C_2H_4	C_2H_6	CO	CO_2	C_2	
1	BaO–TiO_2	650	8.6	3.7	17.3	14.9	64.1	21.0	1.8
1	BaF_2–TiO_2	650	20.9	26.4	26.5	5.7	41.4	52.9	11.1
2	BaO–TiO_2	700	7.8	13.5	45.4	7.4	33.7	58.9	4.6
2	BaF_2–TiO_2	700	28.1	36.7	24.0	7.7	31.7	60.7	17.1
3	BaO–TiO_2	720	7.7	15.8	43.6	23.5	17.0	59.4	4.6
3	BaF_2–TiO_2	720	27.3	34.3	26.5	9.3	29.8	60.8	16.6

3.2. EFFECT OF BaF_2 CONCENTRATION ON OXIDATIVE COUPLING OF METHANE OVER BaF_2–TiO_2 CATALYSTS

To investigate the effect of BaF_2 concentration on catalytic performances, the BaF_2–TiO_2 catalysts containing 0–100 mol% BaF_2 were examined. The variation of catalytic performances at 700°C with different BaF_2 concentration is shown in table 2. Pure TiO_2 and BaF_2 are rather inactive for MOC. When BaF_2 content was lower than 50%, the conversion of CH_4 and C_2 selectivity increased slowly with the increase of BaF_2 content, and the BaF_2–TiO_2 catalysts did not show high C_2 yields. After the BaF_2 content reached 60%, the catalytic activity and selectivity increased dramatically. The catalysts containing 60–75% BaF_2 exhibited C_2 yields of about 17% and C_2 selectivity of $> 60\%$. Clearly, a new phase favorable to activating methane may be produced in these catalysts.

3.3. CATALYST STRUCTURE

The crystalline phases of the bulk of BaF_2–TiO_2 catalysts of various BaF_2 contents are shown in table 3. Due to the substitution of part of F^- for O^{2-}, all BaF_2–TiO_2 systems produced Ba–Ti oxyfluorides. At the meantime, various Ba–Ti complex oxides with different structures existed in all BaO–TiO_2 or BaF_2–TiO_2 systems. Apparently, these Ba–Ti complex oxides were not very active for the selective oxidation of methane. When the BaF_2 content reached 20–50%, $BaTiOF_4$ phase was observed, which is likely to promote the C_2 yields of MOC limitedly and lower the activation temperature of methane. When the BaF_2 content reached over 60%, the orthorhombic $Ba_3Ti_2O_2F_{10}$ was observed. In fact, it is a distorted cubic structure ($a = 10.32, b = 10.07, c = 9.70$). All Ti^{4+} coordinated with $5F^-$ and O^{2-} averagely form the octahedral sharing two vertices. The coordination environments of three Ba^{2+} are different, with coordination numbers of 10, $10 + 3$ and $11 + 2$, respectively [5]. This special structure might be favorable to the activation

Table 2

Catalytic performances of BaF_2–TiO_2 catalysts with different BaF_2 concentration at 700°C

Catalyst[a]	CH_4 conv. (%)	Selectivity (%)					C_2 yield (%)
		C_2H_4	C_2H_6	CO	CO_2	C_2	
TiO_2	1.9	0	13.7	49.5	36.8	13.7	0.3
20% BaF_2–TiO_2	2.9	8.8	35.1	13.9	42.2	43.9	1.3
50% BaF_2–TiO_2	21.3	25.4	23.8	7.0	43.8	49.2	10.5
60% BaF_2–TiO_2	28.5	38.0	22.2	4.6	35.2	60.2	17.2
66.7% BaF_2–TiO_2	28.1	36.7	24.0	7.7	31.7	60.7	17.1
75% BaF_2–TiO_2[b]	28.1	38.0	24.2	7.0	30.8	62.2	17.5
BaF_2	0	0	0	0	0	0	0

[a] Composition is on mol% basis.

[b] Temperature = 750°C.

Table 3
Chemical species identified by XRD of series of catalysts

Catalyst	Identified species[a]
raw material	cubic BaF_2; tetragonal anatase TiO_2
20% BaF_2–TiO_2	monoclinic $BaTi_5O_{11}$ (s), $BaTiO_4$ (m), $BaTi_2O_5$ (w); $BaTiOF_4$ (m); hexagonal $BaTiO_3$ (m)
50% BaF_2–TiO_2	$BaTiOF_4$ (s); hexagonal $BaTiO_3$ (w)
60–75% BaF_2–TiO_2	cubic BaF_2 (s); orthorhombic $Ba_3Ti_2O_2F_{10}$ (m); tetragonal $BaTiO_3$ (m)
50% BaO–TiO_2	tetragonal $BaTiO_3$ (s)
66.7% BaO–TiO_2	orthorhombic Ba_2TiO_4 (s); monoclinic Ba_2TiO_4 (m); tetragonal $BaTiO_3$ (m)
75% BaO–TiO_2	monoclinic Ba_2TiO_4 (s); orthorhombic Ba_2TiO_4 (s); tetragonal BaO (w)

[a] s: strong; m: medium; w: weak.

of methane, so the BaF_2–TiO_2 catalysts containing over 60% BaF_2 gained good C_2 selectivity and C_2 yields.

3.4. INFLUENCES OF REACTION FACTORS ON CATALYTIC PERFORMANCES

Table 4 gives the catalytic performances in methane/oxygen ratio of 1.8–7.9 over 75% BaF_2–TiO_2 catalyst. An increase in methane/oxygen ratio resulted in a decrease of the conversion of CH_4 (from 44.4 to 17.5%) and an increase of the C_2 selectivity (from 41.6 to 78%). The ratio of C_2H_4 to C_2H_6 also decreased with the increase of methane/oxygen ratio, indicating that there was a higher rate of oxidative dehydrogenation of C_2H_6 to C_2H_4 at higher oxygen concentration.

The effect of the variation of GHSV at 750°C is also given in table 4. When GHSV increased from 5000 to 10000 h^{-1}, both the conversion of CH_4 and the C_2 selectivity increased. At GHSV ranging from 10000 to 20000 h^{-1}, the conversion of

Table 4
Influence of reaction conditions on the catalytic performances over 75% BaF_2–TiO_2 catalyst at 750°C

CH_4/O_2	GHSV (h^{-1})	CH_4 conv. (%)	Selectivity (%)					C_2 yield (%)
			C_2H_4	C_2H_6	CO	CO_2	C_2	
1.8	15000	44.4	30.3	11.3	8.8	49.6	41.6	18.5
2.8	15000	33.8	36.7	16.6	6.3	40.3	53.3	18.0
3.9	15000	27.4	39.5	22.8	4.4	33.3	62.3	17.1
5.0	15000	23.4	40.4	27.8	3.7	28.0	68.2	16.0
7.9	15000	17.5	38.3	39.7	2.2	19.8	78.0	13.7
3.0	5000	30.3	31.6	14.2	11.8	42.4	45.8	13.9
3.0	10000	33.0	40.0	17.1	6.9	35.9	57.1	18.8
3.0	20000	33.7	39.2	16.5	8.4	35.9	55.7	18.8
3.0	30000	10.9	24.0	45.9	0	30.1	69.9	7.6

CH_4 and the C_2 selectivity are almost invariable and the best C_2 yield of 18.8% was obtained. When GHSV reached 30000 h^{-1}, the C_2 selectivity increased, but the conversion of CH_4 and C_2 yields decreased dramatically. Viewing the effect of GHSV as a whole, the 75% BaF_2–TiO_2 catalyst can convert CH_4 to C_2 hydrocarbon effectively at higher GHSV.

4. Conclusions

The improved catalytic performances of Ba–Ti mixed oxides for MOC can be achieved by addition of F^-. The promotion of fluorides for BaF_2–TiO_2 catalysts containing over 60 mol% BaF_2 is especially remarkable because the orthorhombic $Ba_3Ti_2O_2F_{10}$ phase is formed, which may be responsible for the good catalytic properties for MOC. These catalysts containing $Ba_3Ti_2O_2F_{10}$ can activate and convert methane to C_2 hydrocarbon effectively at wider range of methane/oxygen and higher GHSV.

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