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Methane oxidative coupling over bismuth oxychloride-lithium carbonate-magnesia systems

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The conversion of methane, the selectivity to C_2 hydrocarbons, and, particularly, the ethene-to-ethane ratio are much higher over BiOCl-Li_2CO_3-MgO than those over pure BiOCl and BiOCl-MgO. In addition, they remain almost the same over a period of 5 h for the former system, but decline significantly for the other two systems (BiOCl and 10% BiOCl-MgO). The XPS investigations provide some insight about the processes responsible for this behavior, indicating that not only Cl but also Bi is likely to play a role.

Keywords: Methane oxidative coupling; bismuth oxychloride; lithium carbonate; magnesia; XPS

1. Introduction

The fundamental requirement of the oxidative coupling of methane, which occurs over an ever increasing number of oxide catalysts [1], is to inhibit the thermodynamically favorable complete oxidation to carbon oxides and enhance the selectivity to C_2 hydrocarbons. It has been reported that this selectivity, particularly to ethene, can be enhanced in the presence of chloride-containing catalysts [2–10], or if a chlorine-containing gaseous compound is passed over the catalyst bed [11–14]. Burch et al. [9] observed high ethene-to-ethane ratios over several chloride catalysts, but in the approach to the steady state this ratio decreased to less than 1:1. Thomas et al. [10] have found that a number of bismuth oxychloride-containing catalysts with different structures exhibit good C_2 selectivities with very high ethene-to-ethane ratios. However, it was also found that both the selectivity and the ratio decreased significantly in time.

In this communication, we report on the methane oxidative coupling activity and selectivity over pure bismuth oxychloride, and in combination with lithium

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carbonate and/or magnesia. We show that the presence of the lithium carbonate enhances both the activity and the selectivity to C_2 hydrocarbons and maintains them for 5 h at almost their initial high levels.

2. Experimental

The catalysts were prepared by introducing MgO powder (Aldrich, 99.99%) into boiling water under vigorous stirring, followed by the addition of an appropriate amount of BiOCl powder (Aldrich, 99.99%) and Li_2CO_3 powder (Aldrich, 99.99%), when required, also under stirring. This was followed by drying, calcination in air at 750°C for 15 h, powdering, pressing and crushing to 80 mesh particle sizes.

The methane coupling reactions were performed at 700–800°C under atmospheric pressure by co-feeding the reaction gases ($He:CH_4:O_2 = 15:4:1$) into a quartz reactor (6 mm i.d., 30 cm long) packed with 200 mg of catalyst sandwiched between quartz wool and heated by a specially constructed small electric furnace (Lindberg 54 S-42) fitted with a K-type thermocouple. An inconel sheathed thermocouple measured the temperature of the catalyst bed. The gases were of high purity (Union Carbide, 99.99%) grade and the flow of each gas was controlled by a variable constant differential flow controller (Porter VCD 1000), the total flow rate being 50 ml/min (NTP). Under these conditions the purely homogeneous gas phase reactions produced less than 0.5% conversion of methane.

The reaction products after passing through a heptanol-liquid nitrogen bath (−40°C) were sampled on-line using an automatic 10-port sampling valve (Valco) and analyzed simultaneously by a dual detector (TCD and FID) Perkin-Elmer Sigma 2000 GC fitted with three different columns: a molecular sieve 5A, a Porapak T and a Chromosorb 102. The response factors for the reactants and products were determined using certified calibration gases (Cryogenic Supply).

The XPS spectra of the calcined and post-catalysis samples were recorded with a PHI 500 spectrophotometer, using MgK_α radiation, according to [15]. The temperature-programmed thermal desorption of chlorine was studied with a conventional TCD, using helium both as a reference and a carrier gas.

3. Results and discussion

The methane coupling reactions were carried out over a wide number of catalysts at 700, 750 and 800°C. The results obtained for MgO, BiOCl and varying compositions of BiOCl-MgO and BiOCl-Li_2CO_3-MgO at 750°C are reported in table 1. For the pure MgO the conversion is quite low, the main products being ethane and carbon dioxide. The ethene-to-ethane ratio is as low

Table 1
Conversion and selectivity data for the methane oxidative coupling reaction over various catalysts at 750°C

Sample No.	Catalyst [a]	CH_4 Conv. (%) [b]	O_2 Conv. (%) [b]	Selectivity (%)				C_2H_4/C_2H_6 ratio
				C_2H_4	C_2H_6	CO_2	CO	
1	MgO	4.5	43.2	8.3	39.5	41.5	4.7	0.2
2	BiOCl	5.0	43.8	15.0	37.0	44.8	3.2	0.4
3	10% BiOCl-MgO	9.5	79.7	28.2	25.0	44.8	2.0	1.1
4	20% BiOCl-MgO	10.4	82.1	32.5	26.8	36.2	4.5	1.2
5	30% BiOCl-MgO	14.7	82.3	36.8	18.0	41.2	4.0	2.0
6	40% BiOCl-MgO	14.5	81.5	37.5	25.0	31.1	6.4	1.5
7	10% BiOCl-10% Li_2CO_3-MgO	18.4	62.0	62.0	21.4	26.0	0	2.9
8	40% BiOCl-10% Li_2CO_3-MgO	22.8	80.5	60.0	16.0	24.0	0	3.8
9	10% BiOCl-40% Li_2CO_3-MgO	20.7	73.6	58.6	16.3	20.0	5.1	3.6
10	40% BiOCl-40% Li_2CO_3-MgO	20.2	82.5	56.4	14.0	29.6	0	3.6
11	10% Li_2CO_3-MgO	9.4	56.9	16.8	21.5	51.1	10.6	0.8
12	20% Li_2CO_3-MgO	10.5	59.8	18.0	25.7	47.5	8.8	0.7
13	30% Li_2CO_3-MgO	14.7	51.4	18.1	36.3	37.6	8.0	0.5
14	40% Li_2CO_3-MgO	12.4	50.5	17.2	53.7	20.3	8.8	0.3
15 [c]	6% LiCl-MgO	11.8	48.2	10.1	30.3	51.4	8.2	0.3
16 [c]	7% LiCl-8% Li_2CO_3-MgO	13.6	52.4	16.1	27.2	48.8	8.0	0.6

[a] Composition is on mol% basis.

[b] Measured after 30 min of reaction.

[c] As Cl and Li are concerned, the compositions of samples 15 and 16 are comparable to those of samples 3 and 7, respectively.

as 0.2. For the pure BiOCl a similar low activity is observed with a slight improvement in the ethene-to-ethane ratio. Thomas et al. [10] have reported a much higher selectivity and ethene-to-ethane ratio over pure BiOCl, which is due to different reactions conditions than ours. As suggested by Baldwin et al. [9], the large volume of the empty space after the catalyst bed in ref. [10] contributes significantly to a homogeneous gas phase reaction. In contrast, in the present study the use of a very small reaction zone where the catalyst is located (1.66 cm^3) followed by a space where the temperature is much lower (200–300°C) ensures that the reaction is mostly heterogeneous.

When BiOCl is supported on MgO, some increases in the conversion of methane and selectivity to C_2 hydrocarbons are observed. In addition, the ethene-to-ethane ratio becomes higher than unity. However, upon increasing the BiOCl content from 10 to 40 mol%, no significant change either in the methane conversion or in the selectivity to C_2 hydrocarbons is observed. The ethene-to-ethane ratios vary between 1.1 to 2.0.

When Li_2CO_3 is introduced into BiOCl-MgO, the methane conversion increases up to 23 mol% and the selectivity to C_2 hydrocarbons up to 83 mol% compared to 5% and 52%, respectively, for the unsupported BiOCl. Thus, for

10% BiOCl-10% Li_2CO_3-MgO (the composition is in mol%) the methane conversion and the selectivity to C_2 hydrocarbons reach 18.4 and 83 mol%, respectively, the ethene-to-ethane molar ratio being 2.9. Increasing the BiOCl content up to 40 mol% increases, mainly, the ethene-to-ethane ratio to 3.8. However, for the system with maximum BiOCl and Li_2CO_3 contents (40% BiOCl-40% Li_2CO_3-MgO) there is no significant change in conversion, selectivity and ethene-to-ethane ratio compared to the system with 10% BiOCl-10% Li_2CO_3-MgO.

Comparison with the Li_2CO_3-MgO systems shows that the latter catalysts are much inferior to the BiOCl-Li_2CO_3-MgO systems, particularly, in terms of ethene-to-ethane ratio. However, increasing the Li_2CO_3 content from 10 to 40 mol% decreases the ethene-to-ethane ratio from 0.8 to 0.3, although the total C_2 selectivity for 40% Li_2CO_3-MgO is almost equal to those for the BiOCl-Li_2CO_3-MgO systems.

As the reaction proceeds for a period of 5 h, the differences in C_2 selectivities over pure BiOCl, BiOCl-MgO and BiOCl-Li_2CO_3-MgO become more prominent. Fig. 1 presents the variation of the total C_2 selectivity with time-on-stream over all these catalysts at 750°C. For the pure BiOCl, the selectivity to C_2 products declined from 40 to 5% after 5 h on-stream, while the ethene-to-ethane ratio changed from 0.4 to 0.3. For the 10 and 40% BiOCl-MgO a similar time decrease pattern is observed, although the final selectivities are somewhat higher. The decrease in C_2 selectivity with time was more pronounced for 40% BiOCl-MgO than for 10% BiOCl-MgO, with the final ethene-to-ethane ratio merging to almost the same value (0.9–1.0).

In contrast, when the MgO supported BiOCl is promoted with Li_2CO_3, the selectivity, after a slight initial decrease, is maintained at a high level after 5 h. The ethene-to-ethane ratio at the end of 5 h retains almost its high initial value (2.8–3.3).

The catalytic results presented show that promoting the MgO supported BiOCl with Li_2CO_3 a more stable system is obtained which is more selective than the other two systems. The decrease in performance of chloride and oxychloride catalysts was attributed to the loss of chlorine [9,10], although no quantitative estimations were provided. It is possible that the presence of the lithium carbonate in the system BiOCl-MgO decreases the loss of chlorine in the course of calcination and reaction. In an attempt to explore such a possibility, we have performed temperature-programmed desorption (TPD) of chlorine from both the uncalcined and calcined catalysts (calcined in air at 750°C for 15 h) by heating them from 300 to 900°C at a heating rate of 12°C/min. A significant amount (approximately 90%) of the initial chlorine is evolved from the samples during calcination, except for BiOCl-Li_2CO_3-MgO which releases less chlorine (approximately 70%) during the same pretreatment. These values are estimated on the basis of the TPD profiles of the uncalcined and calcined samples (fig. 2). In order to exclude any contribution from adsorbed CO_2 or that

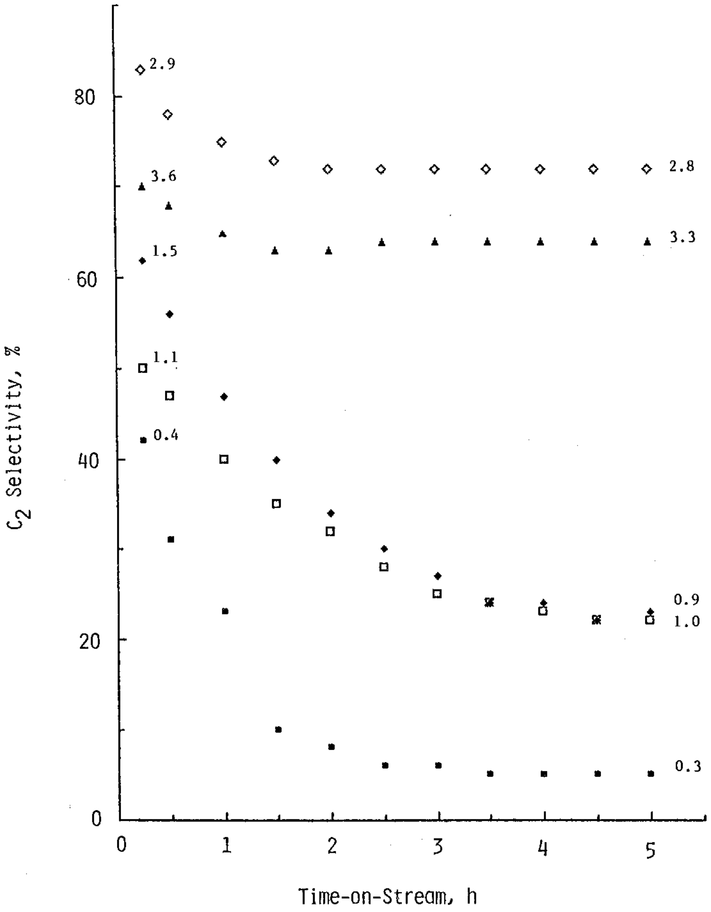

Fig. 1. Variation of the selectivity to C_2 hydrocarbons with time-on-stream for various catalysts at 750°C. Numbers in parentheses represent ethene-to-ethane ratio. (■) BiOCl, (□) 10% BiOCl-MgO, (♦) 40% BiOCl-MgO, (▲) 10% BiOCl-10% Li_2CO_3-MgO, (◇) 40% BiOCl-40% Li_2CO_3-MgO.

evolved from Li_2CO_3, the product effluent was passed through a molecular sieve 5A column which traps all CO_2 and moisture (as verified also chromatographically). The desorption of chlorine from the unsupported BiOCl takes place at 600–620°C, from 10% BiOCl-MgO at 680–700°C, and from 10% BiOCl-10% Li_2CO_3-MgO at 740–760°C (fig. 2), the latter being the reaction temperature. This shift in the desorption temperature is, apparently, due to strong interactions between the support and catalyst in the presence of the promoter. An estimation of the residual chlorine showed that on going from the calcined, unsupported BiOCl to calcined 10% BiOCl-10% Li_2CO_3-MgO the amount increased 4 times (fig. 2). This may suggest that the Li_2CO_3 dopant stabilizes, to some extent, chlorine in the catalyst and that chlorine may be

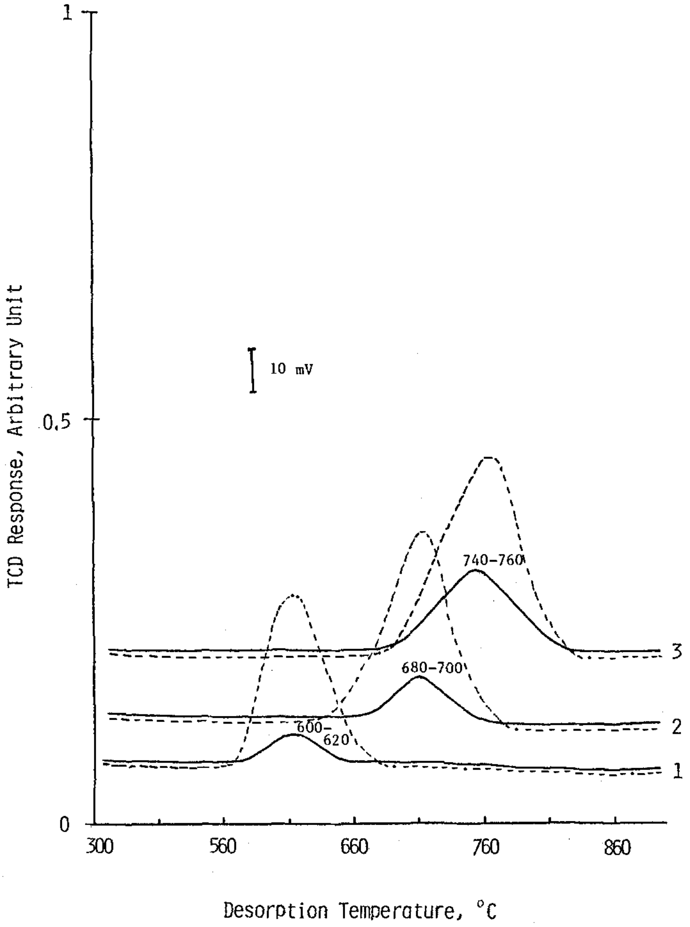

Fig. 2. Temperature-programmed desorption of chlorine from the uncalcined (— — —) and calcined (———) samples. Heating rate 12°C/min. 1. BiOCl; 2. 10% BiOCl-MgO; 3. 10% BiOCl-10% Li_2CO_3-MgO.

responsible for the enhanced C_2 selectivity. To further explore this, XPS investigations have been carried out and the results are presented in table 2.

It can be seen from this table that after calcination, there is little chlorine (0.74%) on the surface of 10% BiOCl-MgO which decreases further (to 0.56%) after the catalytic reaction. However, there is a four-fold decrease in Bi concentration after 6 h of reaction. The carbon C1s spectrum has two peaks: one at 285.0 (70%), and the other at 290.4 eV (30%), the latter indicating that a carbonate species representing 30% of the carbon is formed on the surface. This is, apparently, due to the adsorption of CO_2 during reaction and from the atmosphere by MgO.

For the calcined 10% BiOCl-10% Li_2CO_3-MgO, the surface chlorine concentration is higher (1.17%) than that for the undoped system and has a negligible

Table 2
Surface composition of various elements obtained by XPS

Sample	Pre-treatment	Atomic concentration C_x (%) [a]					
		Bi4f	Mg2p	Li1s	Cl2p	O1s	C1s
10% BiOCl-MgO	Calcined, 750°C, 15 h	2.98	25.67	–	0.74	50.65	19.96
10% BiOCl-MgO	Calcined + reaction with $CH_4/O_2/He$ at 700–800°C, 6 h	0.73	23.29	–	0.56	56.75	18.68
10% BiOCl-10% Li_2CO_3-MgO	Calcined, 750°C, 15 h	2.41	4.76	15.98	1.17	53.85	21.83
10% BiOCl-10% Li_2CO_3-MgO	Calcined + reaction with $CH_4/O_2/He$ at 700–800°C, 6 h	2.85	18.64	n.d.	1.10	54.60	22.83
10% BiOCl-40% Li_2CO_3-MgO	Calcined, 750°C, 15 h	2.78	17.96	n.d.	4.42	54.47	20.37
10% BiOCl-40% Li_2CO_3-MgO	Calcined + reaction with $CH_4/O_2/He$ at 700–800°C, 6 h	3.23	17.25	n.d.	2.26	55.78	21.47

[a] $C_x = \dfrac{I_x/S_x}{\sum_i I_i/S_i}$ where *I*-intensity of the peak, *S*-atomic sensitivity factor.

n.d. denotes not detectable.

decrease during reaction. Moreover, there was almost no decrease in the surface bismuth concentration during the reaction. The intensity of the carbonate species (290.4 eV) increases and constitutes 60% of the total carbon.

When the Li_2CO_3 content is increased to 40 mol%, the calcined 10% BiOCl-40% Li_2CO_3-MgO shows a quite high surface chlorine concentration (4.42%), which decreases during reaction to 2.26%. The latter value is still much higher than those for the other systems. However, the surface bismuth concentration shows some increase during the reaction (this increase is, however, in the limit of experimental errors which are, in general, for XPS between 10 and 20%).

It is clear from XPS measurements, that Li disappears from the surface during reaction. Presumably, the vacancies generated by this disappearance facilitate the formation of active sites. The relatively small amount of Mg on the surface of specimen 10% BiOCl-10% Li_2CO_3-MgO which is observed after calcination (table 2) is probably due to the higher surface activity of Li and to its high concentration. Since Li disappears during reaction, the surface concentration of Mg becomes much larger after reaction.

It appears that not only an appreciable amount of surface chlorine but also bismuth is necessary for the system to be selective. To verify if indeed bismuth plays a role, experiments have been carried out by employing LiCl-MgO as well as LiCl-Li_2CO_3-MgO (samples 15 and 16, table 1). The Cl content in sample 15 and the Cl and Li contents in sample 16 are comparable to those in BiOCl-MgO and BiOCl-LiCO$_3$-MgO systems, respectively. The selectivity to CO$_2$ was much higher than that to C$_2$ and the molar ethene to ethane ratio less than 1. This seems to indicate that the presence of Bi enhances the selectivity and the ethene to ethane ratio.

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