Molten Salts in a Bubble Column Reactor as Catalysts for the Oxidative Coupling of Methane

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Liquid lithium carbonate is a catalyst for the oxidative coupling of methane and the catalysis is promoted by addition of solid magnesium oxide particles.

Oxidative coupling of methane is a very promising new route for the production of ethylene from natural gas.[1] Many materials have been reported to be catalytically active for this process,[2—8] especially lithium doped magnesium oxide.[7—11] This catalyst system was first reported by Lunsford and coworkers and is still among the best performing catalysts.[9,10] In earlier reported work[14] it appeared possible to use pure Li_2CO_3 supported on ZrO_2 as a catalyst with similar behaviour to Li/MgO, albeit that its stability appeared very limited. It was proposed that Li_2CO_3 is an active catalyst or catalyst precursor in Li/MgO. As for the Li/MgO catalyst, the C_2 selectivity has an optimum with respect to the amount of lithium loading as shown in Figure 1. This optimum shifts to higher loadings when the reaction temperature is increased. It is of interest to know if this trend continues. Therefore, the catalytic activities of lithium carbonate, pure and doped with minor amounts of magnesium oxide, have been tested.

Lithium carbonate melts at 723 °C, which makes it impossible to investigate the catalytic activity of pure lithium carbonate or heavily doped Li/MgO catalysts in a fixed-bed reactor at higher temperatures. The lithium carbonate would just melt and trickle downwards in the reactor. Therefore, a bubble column reactor was developed in our laboratory in order to investigate liquid catalyst systems.

The reactions were carried out in a micro-flow reactor system operated at atmospheric pressure, as described elsewhere,[11] in which the fixed bed reactor is replaced by a bubble column reactor. The reactor, made of quartz, had an inner diameter of 0.016 m and a column length of 0.2 m. Methane, oxygen, helium, and carbon dioxide were fed to the reactor through a central dip pipe (outer diam. 0.004 m) at feed rates of 19.5, 4.4, 13.0, and 0.43 $cm^3\ min^{-1}$ at STP, respectively. The methane/oxygen ratio was 4.4 and the dilution with helium ensured that the reaction heat produced did not influence the reactor temperature. This temperature was kept uniform over the whole bubble column by inserting it in an air fluidised sand bed which was electrically heated. The carbon dioxide partial pressure inside the reactor was kept at 0.01 bar (1 bar = 10^5 Pa) by addition of CO_2 to the feed. This was sufficiently high to keep the lithium in its carbonate form, in

Table 1. The influences of temperature on the catalytic performance of pure lithium carbonate. *P* 1 bar; feed $CH_4:O_2:He:CO_2$, 1:0.23:0.67:0.022 (flow rate ratios).

T/	Conv./%		Selectivity/%			
°C	CH_4	O_2	C_2H_6	C_2H_4	CO	CO_2
700	16.9	82.6	19.4	35.2	5.9	39.4
750	12.6	97.9	2.1	5.5	24.9	67.6
800	12.2	98.5	0.0	2.4	28.4	69.3

Table 2. The influences of temperature and wt% MgO in the liquid phase on the catalytic performance, *P* 1 bar; feed $CH_4:O_2:He:CO_2$, 1:0.23:0.67:0.022 (flow rate ratios).

MgO/	*T*/	Conv./%		Selectivity/%			
wt%	°C	CH_4	O_2	C_2H_6	C_2H_4	CO	CO_2
2	750	12.7	96.5	2.4	2.9	40.7	54.0
	800	14.0	96.9	3.8	17.9	19.8	58.5
50	750	17.2	99.6	9.9	33.2	4.3	52.6
	800	16.7	99.6	5.3	36.2	4.3	54.2

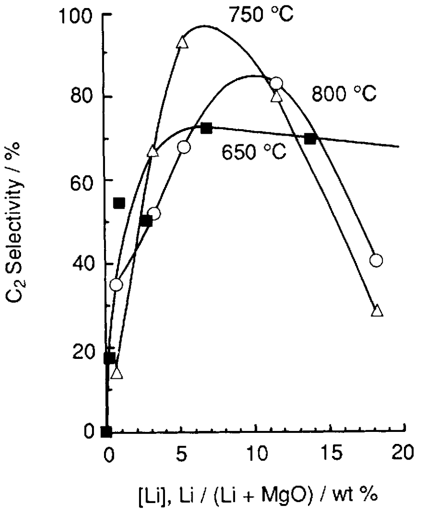

Figure 1. C_2 hydrocarbon selectivity *vs.* lithium concentration and temperature. *P* 1 bar, CH_4/O_2 10, *W/F* 0.5 g s cm^{-3} at STP; data at 650 °C see ref. 10.

agreement with thermodynamic calculations. Lithium carbonate (Merck extra pure) and MgO (Merck p.a.) were used as the starting materials for the catalysts, which were made by slurrying the solids in water followed by evaporation, drying, and grinding.[11] No calcination took place before reaction. Conversions and selectivities were calculated on carbon bases.

In an empty apparatus the main product is carbon monoxide. Its selectivity is about 60%. The oxygen conversion amounts to 45% at the same flow rates as applied in the experiments (Tables 1 and 2) and at 700 °C. When the flow rate is increased by a factor of only 1.27, the oxygen conversion drops to 25%. However, the residence time in the bubble column reactor can roughly be estimated, by using a correlation of Hughmark,[12] to be 1/30 of that of the empty reactor. Thus, we do not expect any serious gas phase activation where the reactor is filled with catalyst; see also Figure 3 of ref. 13, which shows the dependence of residence time for homogeneous gas phase reactions.

Table 1 shows the catalytic performance of solid and liquid lithium carbonate (18 g) as a function of temperature. The methane conversion decreases slightly, but the oxygen conversion increases with temperature, which is accompanied by a dramatic loss of hydrocarbon selectivity. Although the experimental conditions have been kept the same, it is clear that the gas contact of solid and liquid lithium carbonate is different. However, it is acceptable to compare their selectivities, for the conversion levels are almost the same. From 700 to 800 °C the C_2 selectivity drops from 55 to only 2.4%. Qualitatively this is in agreement with the reaction mechanism proposed,[11] which is based on experiments with a 7 wt% Li/MgO catalyst. At higher temperatures, consecutive reactions, *i.e.*, the oxidation of C_2 hydrocarbons, become more important and cause the selectivity drop. Despite the decrease in specific surface when Li_2CO_3 melts, the activity, in terms of oxygen conversion, increases.

To investigate the influence of magnesium oxide on the catalytic behaviour of lithium carbonate, catalysts with different MgO/Li_2CO_3 ratios were prepared. Under the reaction conditions, magnesium oxide is present as a solid powder, suspended in the liquid. The presence of magnesium oxide has a significant effect on the selectivity, particularly at the high concentration level (compare Tables 2 and 1). This proves that the Li/MgO catalyst is not just a carrier covered with a molten Li_2CO_3/Li_2O phase, but that magnesium oxide plays an essential role. Former investigations[13] have shown that deactivation of the lithium doped magnesium oxide catalysts occurred in a fixed-bed reactor, but deactivation was not observed here. This can be explained by two facts. Firstly, there is no loss of Li or possible segregation of Li and MgO in the slurry system, in which there is an abundance of liquid Li_2CO_3. Therefore the composition is not changing. Secondly, the co-feed of CO_2 might also be important, as Korf *et al.*[14] have shown that it stabilizes these catalysts.

In conclusion, it can be said that minor amounts of higher hydrocarbons were obtained from molten lithium carbonate. However, addition of magnesium oxide to lithium carbonate is very beneficial for the production of ethane and ethylene and opens the possibility for the creation of (new) active centres. These centres could be mainly responsible for the catalytic coupling activity, as it is known that only a small part of the total Li content in Li/MgO causes the high activity observed during methane coupling.[15] In this respect, it can be said that the interaction of Li with Mg is essential for a high C_2 yield. Addition of other components to molten Li_2CO_3, as recently reported by Conway *et al.*,[16] is believed to result in improved catalysts. For reasons of heat removal, a bubble column reactor might be a suitable reactor for a methane oxidative coupling process. However, further research in order to develop improved catalysts has to be done.

We thank the European Communities in the framework of the Non-Nuclear Energy R&D programme, subprogramme 'Hydrocarbons,' under contract no. EN3C-0038-NL (GDF), and the Netherlands Organization of Scientific Research (NWO) for financial support. We also thank J. Crèvecoeur, E. Geelen, H. P. C. Hopstaken, and H. L. P. Poels for their contributions to this article.

Received, 13th December 1989; Com. 9/05321B

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