Oxidative coupling of methane over doped Li/MgO catalysts

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Abstract

A series of zirconia doped Li/MgO catalysts with a fixed amount of zirconia and varying concentrations of lithium was used for the oxidative coupling of methane. It was found that an increase in lithium concentration resulted in a decrease in initial activity, while the selectivity was not affected. The life-time of Zr doped Li/MgO catalysts with a fixed concentration of ZrO_2 is a function of the lithium concentration. Previous results have shown that $Li_2Mg_3ZrO_6$ is active and selective but it is now shown to be instable under reaction conditions.

1. Introduction

Previous work from our laboratory showed that Li/Sn/MgO catalysts are active and selective for the oxidative coupling of methane (OCM) reaction [1]. A $Li_2Mg_3SnO_6$ phase was assumed to be responsible for the good properties of this type of material [2]. Because Zr can form a similar compound with lithium and magnesium, an investigation into Li/Zr/MgO catalysts was started. It was shown that zirconia doped Li/MgO catalysts are relatively good catalysts for the oxidative coupling of methane. For a series of catalysts with a fixed amount of lithium and varying amounts of zirconia, it was found that zirconia improves the activity, while a high selectivity was maintained. However, from this study it was not clear what the role of each of the phases present in these Li/Zr/MgO materials were. The objective of this paper is to find out more about the relative importance of the various phases present.

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2. Experimental

Li/MgO (3.2 wt.-% Li) was prepared according to a standard procedure described elsewhere [1]. Zr/MgO was prepared by adding 1 mmol ZrO_2 per 1 g of dried MgO. Li/ZrO_2 was prepared by wet impregnation of ZrO_2 with LiOH. A series of catalysts with a constant Mg-to-Zr ratio and varying amounts of lithium was prepared. First, a large batch of ZrO_2 and $Mg(OH)_2$ was prepared by wet mixing. After drying, varying amounts of Li_2CO_3 were added to four portions of this mixture. The resulting catalyst precursors were pressed isostatically at 2000 bar for five minutes and calcined in static air at 850°C. The preparation procedure for Li/Zr/MgO-a and b is given in [3]. The standard set-up for catalyst testing is described elsewhere [1]. The total flow-rate was 100 ml/min, with a CH_4:O_2 ratio of ca. 10.

3. Results

3.1. Li/MgO, Zr/MgO and Li/ZrO₂ catalysts

Three catalysts containing only two metals were prepared and tested. Their compositions are given in Table 1. Fig. 1 shows the methane conversion and C_{2+} selectivity for Li/MgO, Zr/MgO and Li/ZrO_2 as a function of temperature. Both Li/MgO and Zr/MgO reached total oxygen conversion around 775°C. Li/ZrO_2 never reached more than 50% oxygen conversion.

Fig. 1 shows that Li/MgO shows the highest methane conversion. However, assuming that methane activation takes place at the catalyst surface, it should be noted that Li/ZrO_2 has a lower surface area than Li/MgO. Therefore, it can not be concluded if Li/MgO is more active that Li/ZrO_2. Zr/MgO is active but its activity per square meter is not very high. Li/MgO and Li/ZrO_2 show the same high C_{2+} selectivity. The high selectivity may be the result of the low-surface area of Li/MgO and Li/ZrO_2. It has been shown that a high-surface area is detrimental with respect to selectivity [4]. However, the low selectivity of Zr/MgO is ascribed to the ZrO_2 phase. Pure ZrO_2 was also tested (not shown) and produced mainly CO, CO_2, H_2 and H_2O.

Table 1
Characterisation data for Li/ZrO_2, Li/MgO and Zr/MgO

Catalysts	Li (wt.-%)	S_{BET} (m^2/g)[a]	Phases detected by XRD
Li/ZrO_2	8.6	0.4	Li_2ZrO_3 (cubic, monoclinic)
Li/MgO	3.2	1	Li_2CO_3, MgO
Zr/MgO	–	44	ZrO_2 (monoclinic), MgO

[a] Determined after calcination.

3.2. Activity and selectivity of catalysts containing Li₂MgZrO₄

Table 2 compiles data on the chemical composition and the phases detected by XRD (detection limit 5 wt.-%) for the series of catalysts with varying weight percentages lithium. The zirconia content was chosen high enough to make the formed mixed oxides detectable with XRD. Earlier work has shown that more zirconia (incorporated in Li_2MgZrO_4) is detrimental to the selectivity [3].

The catalysts names indicate the weight percentage of lithium present in the materials. The phases detected with XRD are shown in order of decreasing concentration. The XRD pattern of Li-9 did not show clear evidence of a Li_2MgZrO_4 phase due to interference of the large (overlapping) Li_2CO_3 and MgO peaks. It was assumed to be present in minute quantities.

Fig. 2 shows the C_2+ yield as a function of temperature for the first cycle in a series of three temperature cycles between 600 and 825°C, in comparison with a Li/MgO catalyst containing 4 wt.-% Li. All catalysts showed a similar behaviour. In comparison with Li/MgO, Li-1, 2 and 4 gave considerably higher yields at temperatures below 740°C. Li-7 gave almost the same yield as Li/MgO at temperatures up to 750°C but Li/MgO reached a higher yield above that temperature. Li-
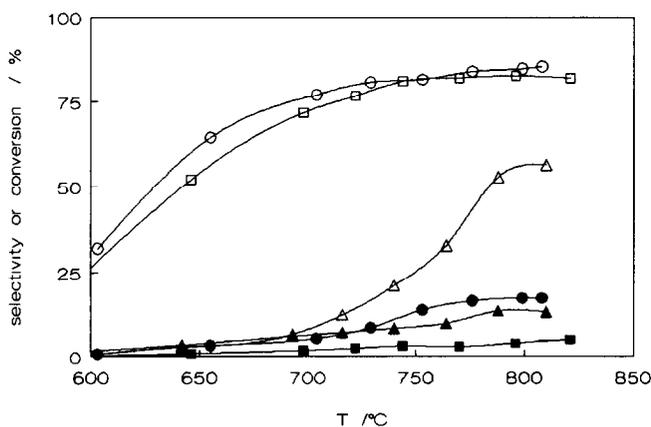

Fig. 1. CH_4 conversion (closed symbols) and C_{2+} selectivity (open symbols) vs. temperature for Li/MgO (O), Zr/MgO (△) and Li/ZrO₂ (□).

Table 2
Catalyst characterisation for a series of catalysts with varying concentrations of lithium

Catalysts	Li (wt.-%)	Zr (wt.-%)	Phases detected by XRD
Li-1	0.8	2.4	MgO, Li_2MgZrO_4 [a]
Li-2	1.8	n.d	MgO, Li_2MgZrO_4, Li_2CO_3
Li-4	4.1	2.1	MgO, Li_2CO_3, Li_2MgZrO_4
Li-7	7.2	n.d	MgO, Li_2CO_3, Li_2MgZrO_4
Li-9	9.0	1.6	MgO, Li_2CO_3, Li_2MgZrO_4

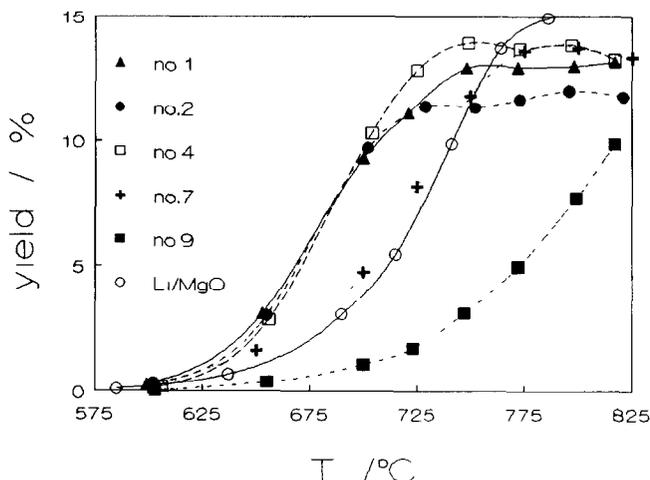[a] Other minor peaks were observed: possibly ZrO_2.

Fig 2. C_2+ yield vs. temperature for Li/Zr/MgO catalysts in comparison with Li/MgO (first cycle).

9 gave a low yield. The behaviour of Li-9 indicates that a high wt.-% Li (>7%) initially does not result in high yields. However, the results for the second cycle, see Fig. 3, show that Li-9 increased in activity. Li-1, 2 and 4 showed a decrease in activity, while Li-7 showed a relatively stable behaviour. The third cycle (not shown) showed further change in the same direction for all catalysts. All materials gave similar selectivities as a function of temperature. From 600°C to 725°C the selectivity of all catalysts rose from ca. 20% to ca. 75%. The selectivity stayed at 75% from 725°C to 825°C. Therefore, it is clear that the differences in initial yield were caused mainly by differences in conversion.

Analysis of the lithium concentration with AAS after use indicated that all catalysts lost lithium. Catalysts initially containing high concentrations of lithium
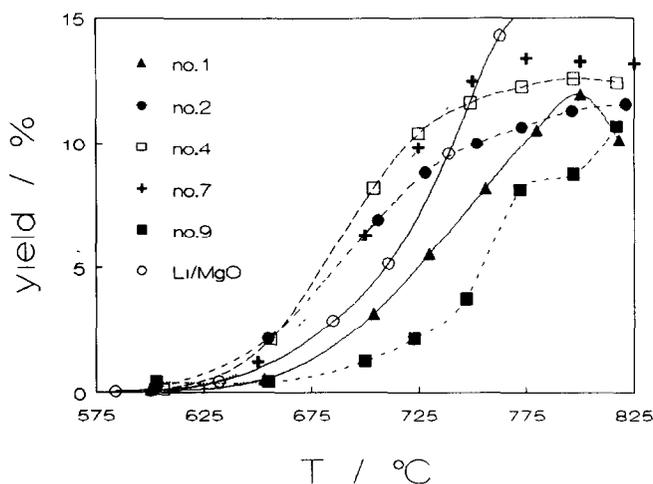
Fig. 3. C_2+ yield vs. temperature for Li/Zr/MgO catalysts in comparison with Li/MgO.

lost more than catalysts that initially contained little lithium. This is in agreement with the fact that most lithium in the low-concentration catalysts is incorporated in the Li_2MgZrO_4 phase. Li_2MgZrO_4 is more stable than Li_2CO_3. XRD after use showed that in all catalysts the Li_2MgZrO_4 phase was unchanged while the Li_2CO_3 reflections had decreased in intensity.

Previous results on a series of $Li/Zr/MgO$ catalysts with varying concentrations of zirconia and a fixed concentration of lithium (ca. 4 wt.-%), showed that an increase in Li_2MgZrO_4 resulted in increased initial activities while the selectivities did not vary significantly [3]. It was also shown that a catalyst containing mainly Li_2MgZrO_4 together with some MgO was less active and less selective. In combination with the results presented here it can be concluded that Li_2MgZrO_4 is not responsible for the high activity and selectivity in $Li/Zr/MgO$ catalysts. The results indicate that there is an optimum Li_2CO_3 content. A high Li_2CO_3 concentration results in an initially inactive catalyst, indicating that Li_2CO_3 itself is not very active. This is in agreement with the results of Ito et al. [4]. Under their conditions Ito et al. found that the optimum Li_2CO_3 content in Li/MgO catalysts lies between 1 and 3 wt.-% with respect to conversion.

For $Li/Zr/MgO$ catalysts, apparently no more than a certain amount of Li_2CO_3 can be present in order for the most active sites to appear. For catalysts with high lithium loadings this means a certain amount of Li_2CO_3 has to be lost before activity increases. But when too much Li_2CO_3 is lost the selectivity is affected. Possibly, a further increase in active sites rapidly causes total oxidation of C_2 products.

3.3. Stability of catalysts containing Li_2MgZrO_4

The activity and selectivity data obtained during the three temperature cycles indicated that catalysts with a low lithium concentration deactivated relatively fast in comparison with catalysts containing a high weight percentage lithium. The catalyst with the highest lithium concentration initially did not deactivate but gained activity.

It is known that the stability of the $Li/Zr/MgO$ catalysts is very temperature dependent [3]. Li-4 and 1 were tested at relatively low temperatures (681 and 673°C respectively) because the data from three temperature cycles already showed they deactivated relatively fast. Li-9 was tested at 745°C, because it showed an increase in activity during the three cycles. The results are shown in Fig. 4. Li-1 deactivated fast. Both activity and selectivity decreased as a function of time. Li-1 after the life-time test contained 0.46 wt.-% Li. Li-4 gave a stable yield and selectivity for more than 150 hours and contained 0.98 wt.-% Li after reaction. The behaviour of $Li/Zr/MgO$-9 was quite remarkable. The selectivity stayed constant, but there was a major increase in yield, caused by an increase in conversion with time-on-stream. There was no measurable increase in temperature in the catalyst bed. This indicated that the increase in activity was not caused by an increase in
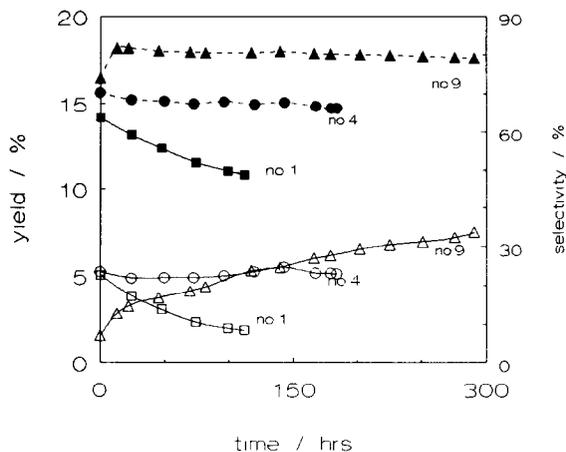
Fig. 4. C_2+ yield (open symbols) and selectivity (closed symbols) vs. time for Li-1 at 681°C, Li-4 at 673°C and Li-9 at 745°C. CH_4:O_2 = 10.

temperature. Apparently, the increase in time was associated with the number of active sites or the activity of the sites.

The increase in activity of Li-9 may be associated with the continuous loss of lithium. Li-9 contained 6.0 wt.-% Li after almost 300 h on stream. When the reaction was stopped, the C_{2+} yield was ca. 7.5% and the selectivity was almost 80%. This is in fairly good agreement with the initial yield for Li-7 at 745°C, which was 10%. On the basis of these observations, it was expected that the yield of Li-9 would increase further, reach a maximum and then decrease, as the lithium concentration keeps decreasing in time. This was tested, and the results are shown in Fig. 5. The conditions used were more severe than normally (CH_4:O_2 = 5 instead of 10), in order to increase the rate of lithium loss. It can be seen that the activity increased as a function of time-on-stream up to ca. 230 h. After 230 h on stream the activity
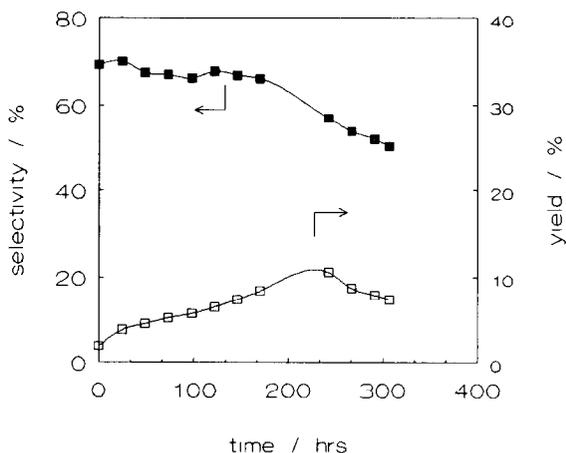

Fig. 5 CH_4 conversion and C_{2+} selectivity vs. time for Li-9 at 740°C. CH_4:O_2 = 4.6.
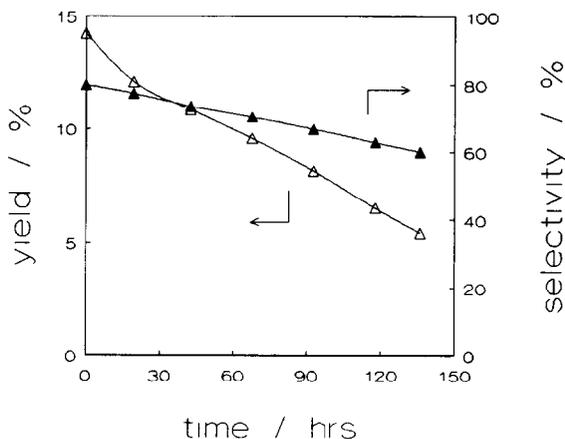
Fig. 6. C$_2$+ yield and selectivity as a function of time for Li/Zr/MgO-a at 745°C.

decreased. The selectivity stayed relatively constant for the first 130 h, but decreased with longer times on stream. After ca. 310 h on stream there was 3.9 wt.-% lithium left in the catalyst. The methane conversion of Li/Zr/MgO-9 after 310 h on stream was around 16%. This compares well to the initial methane conversion of Li-4 at 740°C, which was around 18%. However, it should be noted that the conversion of Li/Zr/MgO-9 from the experiment in Fig. 5 was obtained at a CH$_4$:O$_2$ ratio of 5. The selectivity of Li-9 at this ratio was remarkably high in comparison with the experiments at a CH$_4$:O$_2$ ratio of 10. Overall it can be concluded that for catalysts doped with a fixed amount of ZrO$_2$ there seems to be a direct correlation between the rate at which the yield decreases in time and the Li$_2$CO$_3$ content, as was indicated during the three temperature cycles (see Figs. 2 and 3). More Li$_2$CO$_3$ resulted in a slower decrease in yield. This was shown for a weight percentage of lithium up to 7%. A higher lithium concentration initially resulted in an increase in yield as a function of time.

4. Catalysts containing Li$_2$Mg$_3$ZrO$_6$

Previous results showed that a Li$_2$Mg$_3$ZrO$_6$ phase can be formed in zirconia doped Li/MgO catalysts after prolonged calcination at 850°C [2]. It was shown that Li/Zr/MgO-a (containing Li$_2$Mg$_3$ZrO$_6$, MgO and no detectable Li$_2$CO$_3$) was active and selective, while Li/Zr/MgO-b (containing Li$_2$MgZrO$_4$, MgO and no detectable Li$_2$CO$_3$) was catalytically active but not selective. These results showed that Li/Zr/MgO-a is a promising catalyst, possibly as good as Li$_2$Mg$_3$SnO$_6$. Therefore, a lifetime test of Li/Zr/MgO-a was performed at 745°C. The result is shown in Fig. 6. The behaviour of Li/Zr/MgO-a very much resembled the behaviour of a series of Li/Zr/MgO catalysts with varying weight percentages zirconia tested at a similar temperature: the yield was stable for a certain period of time, and then

decreased [3]. Analysis of Li/Zr/MgO-a with XRD after use showed that a transformation of $Li_2Mg_3ZrO_6$ into Li_2MgZrO_4 had taken place during this test. It is likely that this transformation occurred at the beginning of the life-time test, because the behaviour during the test closely resembled the behaviour of all Li/Zr/MgO catalysts that contained the Li_2MgZrO_4 phase [3]. The wt.-% lithium after use was 1.7. The Li:Zr ratio was 2.8, assuming no Zr was lost from the catalyst.

5. Conclusions

Based on the results for two-component catalysts it is concluded that ZrO_2 is very active for methane activation but it shows a poor C_2 selectivity. Lithium is essential to obtain a good selectivity. A high concentration of Li_2CO_3 at the surface of an Li/Zr/MgO catalysts results in a less active catalyst. In Li/Zr/MgO catalysts a high activity is obtained if a combination of Li and Zr or Li, Zr and Mg is present at the surface. The presence of Li_2MgZrO_4 in Li/Zr/MgO catalysts improves stability in comparison with Li/MgO catalysts. However, with increasing amounts of Li_2MgZrO_4, the rate of deactivation increases [3]. The time it takes for a Li/Zr/MgO catalysts to deactivate is a function of Li_2CO_3 content: more lithium delays deactivation. Previous results have shown that $Li_2Mg_3ZrO_6$ is active and selective but it is now shown to be instable under reaction conditions.

References

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