

The Effect of Addition of a Third Component on the Behaviour of the Lithium Doped Magnesium Catalysts for the Oxidative Dehydrogenation of Ethane

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Summary

The oxidative dehydrogenation of ethane was studied with the use of promoted Li/MgO catalysts at temperatures of 600-650°C. The addition of known promoters, cobalt and tin, gave a slight increase in activity but a strong decrease in selectivity to ethylene under the conditions used. The addition of sodium improved the selectivity to ethylene and suppressed the formation of carbon monoxide. Using a feed of 12 vol% ethane and 6 vol% oxygen, the Li/Na/MgO catalyst with 3.2wt% sodium showed a selectivity of 86 % to ethylene at 38 % conversion of ethane; the Li/MgO catalyst showed a selectivity of 80 % at similar conversions. Thermal investigations of the Li/Na/MgO catalyst showed that an eutectic melt of LiNaCO₃ is formed at 490°C; the existence of this molten phase is probably the cause of the increased selectivity.

INTRODUCTION

The use of a Lithium-doped magnesium oxide catalyst (Li/MgO) is well established for the Oxidative Coupling of Methane (OCM) [1]. We have recently shown that the performance of this catalyst can be improved by the addition of dopants [2]. The oxidative dehydrogenation of ethane (ODHE) is the second step for the formation of ethylene during the methane coupling process and has been studied by several researchers [3-7]. For example, it has been shown that Li/MgO is also a good catalyst for the ODHE reaction [8,9]. Using a Li/MgO catalyst, the highest selectivity for ethylene has been reported to be attained at 700 °C [10]. However, the gas phase reaction occurs to a significant extent at this temperature. We have found that the catalytic reaction is predominant at 600 °C and so the use of such a low temperature permits us to investigate in more detail the role of the catalyst. In this study of the ODH of ethane at temperatures from 550°C to 650°C, the effect of the addition of a third compound to a Li/MgO catalyst has been investigated. We have tried two ways of modifying the catalyst; firstly by adding promoters which are known to have positive influence on the methane coupling reaction, i.e. the oxides of Sn, Co [2] and Ce [11]; secondly, by the addition of various alkali carbonates. Addition of a second alkali is expected to give eutectic melts with the lithium carbonate and consequently change the melting point of the carbonate phase, this melt should be able to cover the most active sites of the catalyst and the effect the catalytic behaviour.

EXPERIMENTAL

Preparation of the Catalysts. The catalysts, shown in Table 1, were made according to the wet mixing method described by Korf and coworkers [2], with the exception that a calcination temperature of 725°C was used instead of 850°C. The promoted Li/MgO catalysts were also prepared by means of wet mixing. The third component (0.2 mmol/g cat) was added during the impregnation stage. When this compound was an oxide, it was milled and added as a slurry to the solution of lithium hydroxide; when the precursor of the third component was a hydroxide or nitrate, the compound was dissolved in water before addition to the lithium hydroxide solution. The unpromoted catalyst contained 3-4 wt% lithium, 10 wt % carbonate and had a surface area of 1 m²/g; generally, the promoted catalysts had slightly higher surface areas

and higher carbonate contents.

Catalyst Characterisation. The surface area of the catalyst was determined using a Micromeritics ASAP 2400 system, using nitrogen adsorption at 78 K. The melting behaviour of the phases was analyzed by means of a differential scanning calorimeter/thermogravimetric analysis instrument; PL Thermal Sciences (DSC-TG 1500.)

Table 1 Catalysts used for ODHE reaction
(Initial concentrations)

Catalyst	Li Content [wt%]	Additive [wt%]	CO ₃ content [wt%]	Surface Area /m ² g ⁻¹
Li/MgO	3.5	-	11	0.8
Li/Ce/MgO	3.78	8.4	10.4	2.0
Li/Co/MgO	3.16	1.56	10.9	2.1
Li/Sn/MgO	4.13	0.28	12	3.8
Li/Na/MgO	3.72	3.18	16.8	1.7
Li/Cu/MgO	3.6	1.38	9.7	1.2
Li/Na/Co/MgO	3.04	3.08/1.12	8.7	3.4
Li/Nb/MgO	3.7	2.6	9	4.0
Li/Ti/MgO	4.55	1.35	14.3	1.2
Li/Zr/MgO	4.35	2.24	14.6	2.3
Li/La/MgO	3.90	4.40	13.5	1.5
Li/Pb/MgO	4.66	4.99	13	1.6
Li/B/MgO	3.5	6	12	1.8
Li/P/MgO	4.8	4.82	9	0.9

Catalyst Testing. The reactor used had a length of 10 cm and an internal diameter of 10 mm. The gases were led in the reactor via capillary tubes to ensure that there was a minimum empty volume in order that the gas-phase reactions were minimised. The internal diameter of the capillary tubes was 1 mm. It was filled from the top with 6.2 g of catalyst (particle size 0.3-0.6 mm) and the remaining empty space was filled with quartz pellets (0.3-0.6 mm). The feed consisted of 12 vol % ethane (>99% (UCAR), 6 vol% oxygen (99% Hoekloos), 82 vol% helium (H.P., Ucar). The products were analyzed with a Varian 3300 G.C. equipped with a Carbosieve SII column (3m, particle size 80 mesh). In order to test the catalyst, the reactor was heated to 640 °C for 5 hours in the feed stream and then cooled down to 500 °C. The reactor temperature was increased in steps to 640 °C. At each temperature, two samples were taken; when the catalyst was promoted with sodium, the catalyst required 3 hours to reach a stable performance at 600°C.

RESULTS AND DISCUSSION

Blank experiments. An empty reactor and a reactor completely filled with quartz chips were tested, under the reaction conditions given above, to examine the contributions from gas phase reactions. With the empty reactor, in which the gases had a residence time of 0.86 second, ethylene was formed at temperatures as low as 560°C. At 600°C, at which temperature there was 86% oxygen conversion and 51 % ethane conversion, the ethylene selectivity was about 60 %; the balance was mainly carbon monoxide. An activation energy of around 300 kJ.mol⁻¹ for the disappearance of ethane was determined in this case. A reactor filled with silica particles (diameter: 0.3-0.6 mm), in which the gases had residence time of 0.35 second, showed no activity up to 600°C. From 600 to 640°C the concentrations of ethylene and carbon monoxide increased slowly (with an approximate activation energy of 161 kJ/mol). The decrease in activity upon packing the reactor was more than would have been expected because of a

decrease in residence time; we must conclude that the surface of the quartz particles quenched the ethyl radicals formed under these conditions. The results for the blank reactor are in good agreement with those reported by Morales et al. [8].

Promoted Li/MgO catalysts. The behaviour of the various Li/X/MgO catalysts are shown in Table 2. The results of the Li/MgO catalyst are included for comparison. In order to compare the behaviour of the catalysts, an arbitrary reference point of 50 % oxygen conversion was chosen; the temperature, necessary to reach this reference point, is given for each, as is the selectivity to the different products. It can be seen that with the addition of cobalt oxide gives an improvement in activity. The selectivity, however, is lower in this case because of more carbon dioxide production. The addition of both sodium and cobalt oxide to Li/MgO gave a catalyst with a lower activity compared to the Li/MgO catalyst, the selectivity to ethene was 83%. The Li/Nb/MgO catalyst gave a lower selectivity to ethylene, the formation of the combustion products (carbon monoxide and carbon dioxide) was 50 % higher. The addition of cerium and lanthanum had no effect upon the catalysts performance. The addition titanium, zirconium and tin increased both the carbon monoxide and carbon dioxide production, while the addition of lead gave mainly combustion to carbon dioxide. The addition of boron and phosphorus gave a sharp decrease in activity and some improvement in the selectivity to ethylene.

Table 2. The Performances of Various Li/X/MgO Catalysts at 50 % Conversion of O₂.

Catalyst ^a	Conversion (%) C ₂ H ₆	Product Selectivity (%)					Temp (°C)
		H ₂ ^{**}	CO	CH ₄	CO ₂	C ₂ H ₄	
Li/MgO	38	34	4.2	0	15	79.7	581
Li/Ce/MgO	35	27	3.5	0.1	14.2	81.0	583
Li/Co/MgO	20	27	1.2	0.2	28.4	70.5	550
Li/Sn/MgO	35	57	6.8	0.2	25.7	67	565
Li/Na/MgO	38	0	1.4	0.2	11.7	86.4	625
Li/Cu/MgO	23	13	3.8	0.4	36.8	60.1	595
Li/Co/Na/MgO	38	3.6	1.3	0	10	83	612
Li/Nb/MgO	28	49	6.2	0	21	71.5	583
Li/Ti/MgO	24	67	11.6	0.3	30.5	56.8	580
Li/Zr/MgO	12	110	28	0.4	46	24.3	550
Li/La/MgO	38.9	034	4.5	0.2	14.7	80.0	580
Li/Pb/MgO	7	0	0	0	90	10.1	530
Li/B/MgO	34	24	2.2	0.5	11.3	84	630
Li/P/MgO	35	25	3.2	0.7	12.3	83	645

^a) all results at 50% oxygen conversion.

^{**}) Selectivity to H₂ is defined as 100*[H₂ out]/[C₂H₆ converted]

However, the addition of sodium gave an increase in selectivity due to the suppression of carbon monoxide formation, while the activity decreased. All the catalysts showed an overall activation energy of 160 - 170 kJ/mol for the consumption of ethane, similar to that found for SiO₂.

In the case of the Li/Co/MgO catalyst, decrease of the residence time gave an increase in selectivity to carbon monoxide at lower residence times, indicating that the carbon dioxide was produced by the oxidation of carbon monoxide, which was therefore an intermediate product.

The sodium-promoted catalyst appeared to suppress hydrogen production, whereas the zirconium-promoted catalyst produced large amounts of hydrogen. The formation of hydrogen during the ODH of ethane has implications for the types of reactions taking place on the catalyst surface. Possible routes for the formation of hydrogen are the water-gas shift reaction and the steam-reforming reactions of

ethane and methane. Earlier studies in our group [13] have shown that these two types of reactions do not take place over Li/MgO and Li/Na/MgO catalysts under our conditions. It was however shown that the addition of carbon dioxide to the feed increases the selectivity to ethylene and strongly suppresses hydrogen formation. Hydrogen is possibly formed, together with carbon monoxide, via a different route.

Table 3. Comparison of promoted Li/MgO catalysts for the ODH of ethane and for the methane coupling reaction, at 90 % oxygen conversion.

Promoter X in Li/X/MgO	ODH of Ethane		Methane coupling [2,12]	
	T_r , /°C	ΔT_r , /°C	T_r , /°C	ΔT_r , /°C
-	610	-	760	-
Co	585	-25	690	-70
Sn	690	-20	680	-80
Nb	610	-	720	-40
Ti	590	-20	690	-70
Na	665	+55	840	+80
Co/Na	650	+40	800	+40

Various of the promoted lithium magnesium oxide catalysts have also been studied by our group [2,12], for the methane couplings reaction; the residence times were shorter than in the work presented here. Table 3 compares the results of these catalysts for the two reactions, for 90% oxygen conversions, showing the temperatures of reaction (T_r) and the temperature difference (ΔT_r) compared with the unpromoted LiMgO catalyst. For example, it was observed that the addition of 0.2 mmol of Sn or Co gave a decrease of temperature of almost 20 °C at similar oxygen conversions for the ODHE, whereas the temperature decrease was only 70 °C for the OCM reaction. In the case of sodium addition, both the ODHE and OCM reactions gave an increase of 40-50 °C in temperature needed, to reach the same oxygen conversion.

Results of Thermal Analysis of the Catalysts

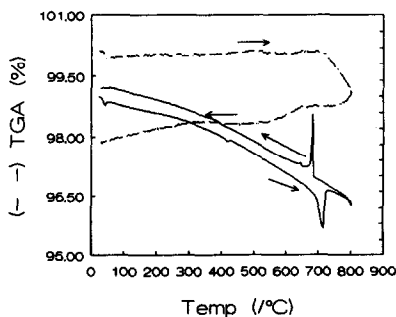


Figure 1 Thermal analysis of Li/MgO.
-, DSC; ---, TGA¹⁾

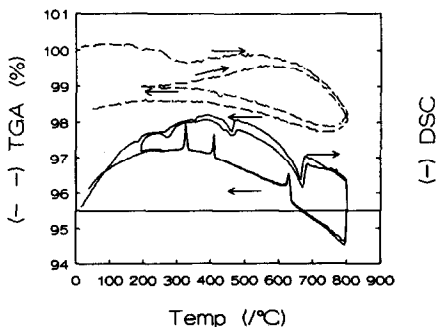


Figure 2 Thermal Analysis of Li/Na/MgO,
-, DSC; ---, TGA¹⁾

*)The lower curve represents the DSC signal and the upper curve represents the TGA signal. (The measurements are performed in air; a heating- and cooling rate of 4 °C was used.)

Figure 1 shows DSC results, obtained with the Li/MgO catalyst and Figure 2 shows equivalent results for the Li/Na/MgO catalyst (5 wt% Na) in each case heating and cooling results are given. The TGA signal of Li/MgO showed that there was a sharp weight loss above 700°C, while the DSC signal showed that the Li_2CO_3 melted at 720°C. During the cooling stage, a freezing point at was observed 675 °C as well as a small peak at 605 °C. The TGA signal of the Li/Na/MgO catalyst showed a gradual weight loss above 500°C, while the DSC signal showed two peaks: melting of the Li/Na carbonate phase at 500°C and melting of excess Li_2CO_3 at 470 °C. The first value has also been reported by Sanger and Pelton [14] for the melting point of LiNaCO_3 . The weight-increase of the sample during cooling of the catalyst sample is probably due to the adsorption of carbon dioxide from the air. Similar behaviour was observed for the Li/MgO catalyst, although this is not shown in the figure. The TGA curve of the Li/MgO catalyst showed a kink at 700 °C, during heating, whereas the Li/Na/MgO showed a gradual weight loss above 600 °C. The fact that the weight loss of the Li/Na/MgO catalyst proceeded more slowly than that of the Li/MgO catalyst may indicate that the carbonate bonding is stronger in the former case than in the latter.

Comparison of the catalysts

The performance of all the catalysts studied are compared in Figure 4. The x-axis represents the temperature at which the catalyst reached 50% oxygen conversion and the y axis represents the selectivity to ethylene at the reference point of 50% oxygen conversion. It can be seen that the addition of lanthanum or cerium oxide has hardly any influence on the performance of the Li/MgO catalyst. The addition of sodium gave a catalyst with the highest selectivity to ethene. The addition of cobalt gave a catalyst with a higher activity but a lower selectivity. In general, there seems to be a band from the lower left hand corner to the upper right corner. This figure is very similar to the one reported by Martin et al. [9], also for the ODH of ethane over an Li/MgO catalyst; they showed that the selectivity to ethylene increases with temperature. These authors suggested that, the life time of the radicals decreased with increasing temperature, the radicals can form peroxide species, which leads to combustion products. However, we have done experiments with a lower amount of a Li/MgO catalyst in order to compare it with the sodium-doped catalysts at similar ethane conversions and at the same temperature of 600 °C. The Li/Na/MgO catalyst still showed a higher selectivity to ethylene. With the Li/MgO catalyst, the selectivity to ethylene at 550 °C was lower than at 600 °C. However, with the Li/Na/MgO catalyst at 550°C, a selectivity to ethylene of 90% was observed; the selectivity in this case thus decreased with increasing temperature. It is therefore more likely that the molten phase formed covers those active sites, which are responsible for the production of the combustion products.

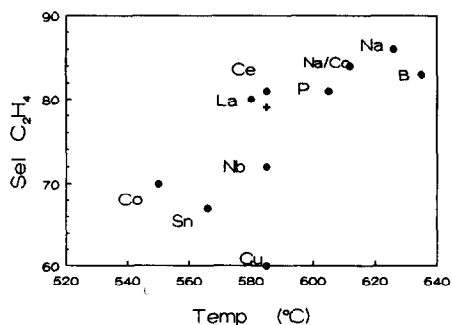


Figure 3 Selectivity to C_2H_4 at 50% O_2 conversion of the various Li/MgO promoted catalysts for the ODH of Ethane. The reference sample Li/MgO is noted as (+).

CONCLUSION

Dopants in the Li/MgO catalysts give similar effects for the OCM and the ODHE reactions. The addition of cobalt and tin increases the activity but decreases the selectivity to ethylene. The addition of sodium decreases the activity for the ODHE reaction and suppresses the formation of carbon monoxide and hydrogen. It is possible that an eutectic melt covers the most active but less selective sites on the sodium-doped catalysts.

Acknowledgements

We acknowledge with thanks the support of the European Commission (grant number JOUF-0044-C(TT), JOULE Programme) and our partners in this programme for useful discussions.

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