

THE KINETIC AND MECHANISTIC ASPECTS OF THE OXIDATIVE DEHYDROGENATION OF ETHANE OVER LI/Na/MgO CATALYSTS

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SUMMARY

Kinetic and mechanistic aspects of the oxidative dehydrogenation of ethane catalysed by Li/MgO and Li/Na/MgO have been investigated. Initial rate measurements at 600°C revealed that the Li/MgO catalyst produced C₂H₄, CO₂, CO and H₂ by parallel reactions whereas the sodium-promoted catalyst produced only C₂H₄ and CO₂, again by parallel reactions. Experiments were also carried out in which water and carbon dioxide were added to the feed, these being designed to study the mechanism of hydrogen production. The results indicate that the hydrogen and carbon monoxide are unlikely to have been produced by steam reforming or carbon dioxide reforming of ethane or by the water-gas shift reaction; they are possibly formed directly from the ethane via surface ethoxy species.

INTRODUCTION

It has been shown by Koits [1] and by Morales and Lunsford [2] that Li/MgO is a suitable catalyst for both the methane coupling reaction and for the oxidative dehydrogenation (ODH) of ethane. We have shown previously [3,4] that the performance of a Li/MgO catalyst could be improved when used for the coupling reaction by the addition of several promoters. We also showed that the ODH of ethane occurred as a consecutive step in the methane coupling reaction and that the combustion products were formed predominantly from C₂ products. We therefore tested for the ODH of ethane those promoted catalysts which had the most promising properties [5] and showed that the addition of sodium to a Li/MgO catalyst decreased its activity but increased its selectivity to ethylene; we also found that the modified catalyst produced only small amounts of hydrogen and carbon monoxide.

We have now carried out further work to examine how the addition of sodium affects the mechanism of the ODH of ethane, paying particular attention to the mode of formation of hydrogen and carbon monoxide. Theoretically, these molecules can be produced during the oxidative dehydrogenation reaction in two ways: (i) by the decomposition of an intermediate which may give rise to either ethylene or carbon monoxide, or (ii) as a product in side-reactions such as steam reforming or the water-gas shift reaction. In order to attempt to distinguish between such routes, two sets of experiments were thus performed for the Li/MgO catalyst and the sodium-promoted Li/MgO catalyst: firstly, the product distribution was analyzed as a function of W/F to identify those compounds produced at short contact times (≈ 0.1 s) and low conversions, the aim being to see how carbon monoxide and hydrogen were

produced; secondly, either water or carbon dioxide was added to the feed, the aim being to determine whether or not secondary reactions give rise to the production of carbon monoxide and hydrogen. Preliminary experiments were also carried out on the reaction of ethanol over the two catalysts to examine the possibility that surface ethoxy species might be responsible for the formation of carbon monoxide and hydrogen

EXPERIMENTAL

Catalyst Preparation

The Li/MgO catalyst used as reference material was made according to the method described by Korf et al. [3]. Lithium hydroxide (Merck P.A.) was dissolved in demineralised water at 80°C. Magnesium hydroxide was then added to this solution to form a slurry and carbon dioxide was bubbled through this slurry while stirring, the mixture being kept at 80°C. The water of the slurry was then evaporated until a thick paste was obtained and the remaining water was then removed by drying for 16 hours at 140°C. The resulting solid material was crushed and sieved and a sieve fraction of 0.3-0.6 mm was collected and calcined in air at 725°C for 6 hours. This resulted in a material containing 3 wt% Li and 11 wt% CO₃ and having a surface area of 1.2 m²g⁻¹. The sodium-doped material (Li/Na/MgO) was prepared in a similar way: the sodium was added as sodium hydroxide prior to the evaporation step and this results in a material containing 2.8 wt% Li, 5.0 wt% Na and 16 wt% CO₃ and having a surface area of 1.8 m²g⁻¹.

Reactor System

The initial rate measurements were carried out using a constant flow of reactant, F, of 100 cm³(STP)min⁻¹, the composition of this being 12 vol% C₂H₆, 6 vol% O₂, and 82 vol% He. The catalyst under investigation was placed in a reactor of 5 mm internal diameter, the empty volume of the reactor tube being filled with silica to reduce undesired gas-phase reactions. The products (shown in the results given below in units of 10⁻⁹mol produced per second) were analyzed by means of a gas chromatograph (Varian 3300) equipped with a Carbosieve S-2 column and a thermal conductivity detector. The weight, W, of catalyst was varied between 0.15 g and 0.7g (particle size 0.3<d<0.6mm); in consequence, the residence time (W/F) varied from 0.05 to 0.6 g.s.mf⁻¹. Experiments were performed at different temperatures in the range 580 to 630°C for each value of W/F.

RESULTS AND DISCUSSION

Conversion as a Function of W/F

The results of measurements of product concentration versus W/F for the Li/MgO catalyst are shown in Figure 1 and the equivalent results for the Li/Na/MgO catalyst are shown in Figure 2; in both cases, the reaction temperature was 600°C and the conversions of both oxygen and ethane were lower

than 5%. Values of W/F less than $\approx 0.05 \text{ g.s.ml}^{-1}$ could not be measured accurately and so data at values lower than this are not given.

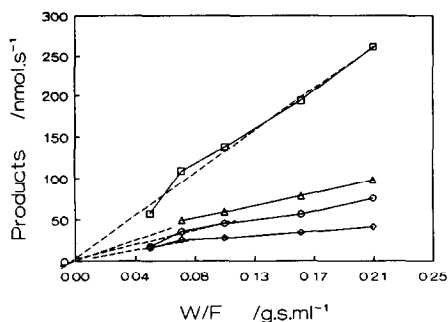


Fig. 1 Initial products for the ODH of Ethane over a Li/MgO catalyst at 600 °C (□, C₂H₄; ○, CO₂; △, CO; ◇, H₂)

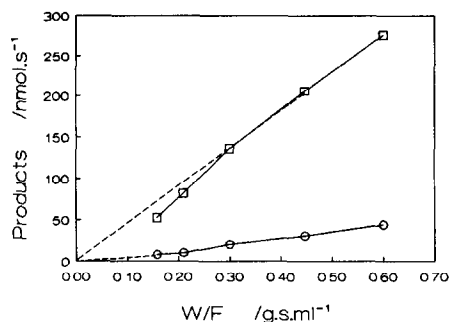


Fig. 2 Initial Products for the ODH of Ethane over a Li/Na/MgO catalyst at 600 °C (□, C₂H₄; ○, CO₂)

For the Li/MgO catalyst (Fig. 1), ethylene, carbon monoxide, carbon dioxide and hydrogen were all formed as initial products. This means that the combustion products (i.e. carbon monoxide and carbon dioxide) are probably produced in a route parallel to that giving rise to the formation of ethylene. The partial pressure of the ethylene increased essentially linearly with W/F while the partial pressures of carbon monoxide and carbon dioxide tended to level off at higher values of W/F.

With the Li/Na/MgO catalyst, ethylene and carbon dioxide were the only products formed at all these values of W/F; neither hydrogen nor carbon monoxide were detected. The Li/Na/MgO catalyst had a lower activity than had the Li/MgO material. This result is consistent with earlier work from our laboratory [4].

The reduction of the activity occurring on sodium addition to a Li/MgO catalyst reported here contrast with the results of Conway et al. [6] who studied the use of a mixture of molten lithium and sodium carbonates as catalyst for the methane coupling reaction; they reported that such a mixture gave a lower selectivity to C₂ products but a higher activity when compared to the behaviour of an unmodified lithium carbonate phase.

The initial rates of formation of all the products (i.e. at W/F tending to zero) at different temperatures were calculated for both catalysts from the tangents to curves such as those shown in Figs. 1 and 2. These values were then used to calculate the apparent activation energies for the production of the different molecules and the results are shown in Figures 3 and 4 and in Table 1.

In case of the un-doped Li/MgO catalyst (Fig.3), higher activation energies were found for the formation of ethylene (238 kJ.mol^{-1}) and for the formation of hydrogen (255 kJ.mol^{-1}) than for the formation of the combustion products, carbon dioxide (163 kJ.mol^{-1}) and carbon monoxide ($155 \pm 40 \text{ kJ.mol}^{-1}$).

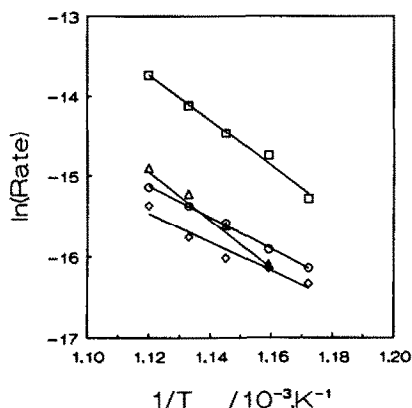


Fig. 3 Arrhenius Plot of Initial rates with a Li/MgO catalyst (\square , C₂H₄; \circ , CO₂; \triangle , CO; \diamond , H₂)

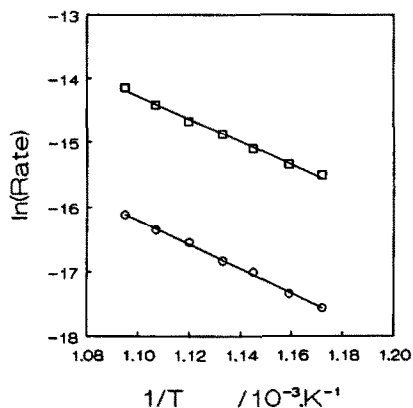


Fig.4 Arrhenius plot of Initial rates with a Li/Na/MgO catalyst (\square , C₂H₄; \circ , CO₂)

For carbon monoxide, the Arrhenius plot was slightly curved and so the uncertainty of the value given reflects the highest and lowest possible values. The difference in activation energies for the formation of the different products is consistent with the observation that there is an increase in selectivity to ethylene with increase in temperature.

TABLE 1. Overall activation energies and pre-exponential factors determined from initial rates.

| Product | Li/MgO Catalyst | | Li/Na/MgO Catalyst | |
|-------------------------------|--------------------------------------|--|--------------------------------------|--|
| | E _a /kJ.mol ⁻¹ | k ₀ /mol.s ⁻¹ .g ⁻¹ cat | E _a /kJ.mol ⁻¹ | k ₀ /mol.s ⁻¹ .g ⁻¹ cat |
| C ₂ H ₄ | 238 | 18.0 | 148 | 4.4 |
| CO ₂ | 163 | 6.9 | 155 | 4.3 |
| CO | 155 +/- 40 | 6.9 | - | - |
| H ₂ | 255 | 19.6 | - | - |

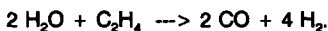
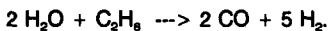
In the case of the Li/Na/MgO catalyst (see Fig. 4), the activation energy for the formation of ethylene (148 kJ.mol^{-1}) was almost the same as that for the formation of carbon dioxide (155 kJ.mol^{-1}). Thus, an increase of the temperature in this case gives a slight decrease in the selectivity to ethylene.

The results showing the effect on product concentrations of W/F for the Li/MgO catalyst presented above (Fig. 1) showed that all the products, ethylene, hydrogen, carbon monoxide and carbon dioxide, were formed as primary products of the reaction. We can therefore conclude that a consecutive step involving the oxidation of the product ethylene is unlikely to be an important route to carbon monoxide and carbon dioxide over this catalyst under the conditions used in these experiments. If all the products were produced from a common intermediate surface species and the formation of that species were rate determining, then one would expect that the activation energies for the formation of all of the products would be the same.

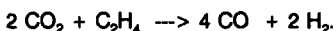
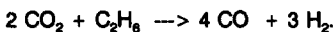
For the formation of ethylene and hydrogen on the Li/MgO catalyst, this is the case, but the carbon monoxide and carbon dioxide are apparently formed via a different route over this catalyst. In contrast to the results for the Li/MgO material, only ethylene and carbon dioxide were formed as products over the Li/Na/MgO material (Fig.2). As the activation energies for the formation of ethylene and carbon dioxide over the Li/Na/MgO were approximately the same, it would thus seem likely that both molecules are formed in this case from a common intermediate and that the formation of the intermediates is likely to be rate determining.

Effect of Addition of Water and Carbon Dioxide to the Feed.

In order to attempt to understand better the difference in the behaviours of the two catalysts, we have carried out additional experiments to identify possible sources of the CO and hydrogen formed as products over the Li/MgO catalyst. In principle, hydrogen and carbon monoxide can be produced by the steam reforming reactions of ethane or ethene:



or by carbon dioxide reforming of one of these molecules:



In order to find out which of those reactions might be responsible for the carbon monoxide production, three types of experiments, the results of which are shown in Tables 2 and 3, were performed with the Li/MgO and Li/Na/MgO catalysts:

- (i) addition of carbon dioxide to the feed stream;
- (ii) addition of water to the feed stream; and
- (iii) addition of water to the a feed stream in the absence of oxygen.

Tables 2 and 3 also give the results of experiments carried out in the absence of the additives; the reaction conditions for all the experiments were chosen in such a way that the conversions in the absence of additives were about 60% for oxygen and 30% for ethane. With the Li/MgO catalyst (Table 2), the standard feed gave a product gas containing a mixture of ethylene (3.61 vol%, corresponding

to a selectivity of 77 vol%), carbon dioxide (1.71 vol%), carbon monoxide (0.46 vol%) and hydrogen (1.77 vol%). With the Li/Na/MgO catalyst (Table 3), less carbon monoxide and hydrogen were produced but the quantities of these products were now significant when compared with the results at lower conversions shown in Fig. 2; as was also the case in the results with lower conversions, the amount of carbon dioxide formed was lower than with the Li/MgO catalyst and the selectivity with the Li/Na/MgO catalyst was therefore significantly higher. When carbon dioxide was added to the feed over the two catalysts, the conversion of ethane was decreased strongly in both cases; the amounts of hydrogen and carbon monoxide formed both decreased and the selectivities to ethylene increased.

TABLE 2. Results for a Li/MgO catalyst (6.2 g) at 580 °C, showing product composition as a function of feed composition.

| Feed composition / vol % (total feed = 72 ml/min) | Composition of Products Stream /vol% | | | | Selectivity /% to C ₂ H ₄ |
|--|--------------------------------------|------|-----------------|----------------|--|
| | C ₂ H ₄ | CO | CO ₂ | H ₂ | |
| 12% C ₂ H ₆ ; 6% O ₂ [†] | 3.61 | 0.46 | 1.71 | 1.77 | 77 |
| 12% C ₂ H ₆ ; 6% O ₂ ; 20% CO ₂ [†] | 1.38 | 0.12 | 20.29 | 0.16 | 85 |
| 12% C ₂ H ₆ ; 6% O ₂ ; 5% H ₂ O [†] | 2.78 | 1.41 | 0.26 | 2.15 | 77 |
| 12% C ₂ H ₆ ; 8% H ₂ O [†] | 0.12 | 0 | 0.02 | 0.05 | |
| 12% C ₂ H ₄ ; 5% H ₂ O [†] | 11.9 | 0 | 0.11 | 10.03 | |

[†] Rest He

The product distribution for the Li/MgO catalyst (Table 2) was now similar to that obtained with the Li/Na/MgO catalyst without any addition of carbon dioxide. A possible explanation for this similarity is that more surface carbonates were present in both cases: the addition of carbon dioxide to the gas stream favoured the formation of lithium carbonate in the same way that the addition of sodium seemed to favour the retention, after calcination of the fresh catalyst, of larger concentrations of carbonate (see analyses given in the Experimental section). From the decrease in the production of carbon monoxide and hydrogen found in these experiments, we can conclude that carbon dioxide reforming does not take place over these catalysts.

TABLE 3 Results for a Li/Na/MgO catalyst (6.2 g) at 600 °C, Showing product compositions as a function of feed composition.

| Feed composition /vol% | Composition of Product stream /vol% | | | | Selectivity /% |
|--|-------------------------------------|-------|-----------------|----------------|----------------|
| | C ₂ H ₄ | CO | CO ₂ | H ₂ | |
| (total feed 72 ml/min) | | | | | |
| 12% C ₂ H ₆ ; 6% O ₂ [†] | 2.31 | 0.08 | 0.53 | 0.16 | 88 |
| 12% C ₂ H ₆ ; 6% O ₂ ; 20% CO ₂ [†] | 0.56 | 0.014 | 20.49 | 0 | 91 |
| 12% C ₂ H ₆ ; 6% O ₂ ; 5% H ₂ O [†] | 2.78 | 0.08 | 0.74 | 0.4 | 88 |
| 12% C ₂ H ₆ ; 8% H ₂ O [†] | 0.03 | 0 | 0.06 | 0 | |

[†] Rest He

Addition of water to the feed stream over the Li/MgO catalyst (Table 2) gave a decrease of the

amount of ethylene produced relative to the experiment with only oxygen, as well as of the amount of carbon monoxide and carbon dioxide formed; the selectivity to ethylene remained the same. A feed gas consisting of only water and ethane gave rise to the formation of only small amounts of carbon dioxide, hydrogen and ethylene over the same catalyst, whereas water and ethylene as feed gave rise only to the formation of carbon dioxide and hydrogen. We can conclude in this case that water is only a slight poison for the oxidative dehydrogenation reaction; clearly, no steam reforming reaction occurred under these conditions.

Similar results were obtained for the addition of water to the feed with the Li/Na/MgO catalysts (Table 3). However, the conversion in the case of the ethane/oxygen/water mixture was higher than for the ethane/oxygen mixture; this may be a consequence of a slight shift caused by the water in the feed of the equilibrium between surface carbonate and surface hydroxide species. There was also a slight increase in the amounts of CO₂ and hydrogen formed, probably as a consequence of the occurrence of the water-gas shift reaction.

Possible Participation of Surface Ethoxy Species

From the above results, we can conclude that it is unlikely that hydrogen is produced via side reactions. We have previously postulated a scheme in which methoxy species are formed as intermediates in the oxidative coupling of methane over various different types of catalysts and that these species decompose to give carbon monoxide and hydrogen [7]. An alternative explanation for the present results is that the hydrogen and carbon monoxide are also produced from an oxygenated intermediate surface species.

In this case ethoxy groups can be formed directly from ethane. Tawezawa et al. [8] have shown that ethanol decomposes on a magnesium oxide surface to give either ethylene and water or acetaldehyde and hydrogen, as shown in Figure 5. It is possible that a similar series of steps can occur on our catalysts; rather than the desorption of acetaldehyde as product, this

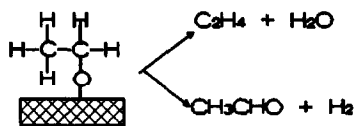


Fig. 5 Decomposition of Ethoxy Species

molecule might decompose further either to methane and carbon monoxide or to carbon, hydrogen and carbon monoxide. To investigate this possibility, preliminary experiments have been carried out in which an ethanol/helium mixture was added to both types of catalyst (feed composition: 12 vol% ethanol in He; flow of 190 cm³ min⁻¹; 0.5 g catalyst; 600 °C). Both catalysts converted the ethanol to ethylene (60 %) plus carbon monoxide and hydrogen. After use, the catalyst material and parts of the inlet and outlet capillary tubes of the reactor were black, indicating that soot had been formed, even prior to the catalyst bed. Consequently, addition of oxygen to the feed removed this soot completely. If our

supposition that ethoxy species are involved is correct, soot deposition is unlikely to be a major problem under normal reaction conditions due to the presence of the oxygen. Further work is in progress to attempt to quantify the contribution of surface reactions to the decomposition of ethanol under these conditions and to examine the effects of co-feeding ethanol to the ethane/oxygen mixture. Further evidence for the occurrence of surface ethoxy-type species as intermediates in the oxidative dehydrogenation of ethane has come from preliminary experiments using FTIR analysis of the gas leaving the catalyst bed; there is some evidence for the presence of bands in the spectra which are characteristic of alcohols or diols. Further work is therefore also in progress to confirm these results.

CONCLUSIONS

Measurements of initial product selectivities in the oxidative dehydrogenation of ethane show that a Li/MgO catalyst gives ethylene, carbon dioxide, carbon monoxide and hydrogen as initial products. This indicates that the combustion products are formed at the same time as the ethylene. In contrast, a Li/Na/MgO catalyst, which has a higher selectivity for ethylene, produced initially only ethylene and carbon dioxide. We conclude that the sodium addition suppresses a side reaction responsible for the production of hydrogen and carbon monoxide. Experiments in which carbon dioxide or water vapour were added to the reaction mixture over these two catalysts revealed that hydrogen is unlikely to be produced by either carbon dioxide reforming or steam reforming reactions. The decomposition of a surface ethoxy-type species formed directly from ethane seems to be the most likely source of hydrogen and of carbon monoxide.

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