Influence of CO_2 on the Oxidative Coupling of Methane over a Lithium Promoted Magnesium Oxide Catalyst

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Li/MgO catalysts used for the oxidative coupling of methane are found to deactivate relatively rapidly in use; this deactivation can be reversed by treating the the catalyst with CO_2 under the reaction conditions and the deactivation can be avoided completely if CO_2 is added in low concentrations to the reaction mixture.

The partial oxidation of methane to form C_2 hydrocarbons (oxidative coupling) is an interesting alternative to processes involving the conversion of methane into synthesis gas by steam reforming or partial oxidation and subsequent reaction of the synthesis gas as a means of producing useful chemicals. A number of reports on the oxidative coupling reaction have appeared recently.[1—5] For example, Ito *et al.*[1,2] have shown that lithium-doped magnesium oxide is an active and selective catalyst for the reaction; they proposed a mechanism in which Li^+O^- surface species were responsible for initiating the reaction by abstracting an H from CH_4. Otsuka and his colleagues[4] have reported on the use of rare-earth oxides as catalysts for the reaction. We have shown[3] that the behaviour of a Li/MgO type of material is more stable than that of the lead-based catalysts which have been studied by Baerns and his coworkers.[5] We have also shown that the behaviour of these catalysts depends markedly on the method used for their preparation, materials containing carbonates being more active than those which contain lower concentrations of carbonate species, *e.g.* those calcined at high temperature.[6] In this communication we report some results which appear to demonstrate clearly the importance in the oxidative coupling reaction of sites created by the decomposition of these surface carbonate species.

The lithium-doped MgO material (hereafter designated Li/MgO) used in these experiments was prepared by wet impregnation of an MgO sample (Merck) using $LiOH{\cdot}H_2O$. During impregnation, CO_2 was passed through the evaporating solution. After drying and calcination at 850 °C for 6 h in air, the catalyst was found, by atomic absorption spectroscopy, to contain 3.1 wt% Li and, by wet analysis, 8.24 wt% carbonate. *X*-Ray powder diffraction of the Li/MgO material indicated that two phases were present, MgO and Li_2CO_3.

The activity, selectivity, and stability of the sample were determined using a reaction system with a quartz fixed-bed reactor and gas analysis was carried out with g.c. The experiments were carried out with the catalyst maintained at 800 °C and with $P(CH_4) = 0.67$, $P(O_2) = 0.07$, $P(N_2) = 0.26$ bar, catalyst weight, $W = 0.744$ g and gas flow, $F = 3.33$ cm^3 s^{-1} (s.t.p.). The catalyst bed was diluted with the same weight of quartz particles. The values of the conversion of methane (α), the selectivity (S) towards C_2 products, and the yield (Y) of C_2 products ($\alpha \times S/100\%$) were measured as function of time for a period of 60 h and the results are shown in Figure 1. The conversion and the yield were both found to rise slightly for the first 2 h, the yield reaching a value of greater than 13%. Thereafter they both dropped continuously, levelling off to a relatively constant value after same 40 h. The selectivity remained virtually constant throughout at a value of *ca.* 83%. The constancy of the value of the selectivity indicates that the nature of the active site has not altered much but that the number of sites has decreased during the experiment. After the experiment, the carbonate content had fallen to 0.10 wt.% and the lithium content had also fallen to 0.1 wt.%. We therefore conclude that the carbonate and lithium contents of the catalyst at any time may have some bearing on the activity. We therefore repeated the experiment as described above, obtaining the same results; however, this time the experiment was stopped after it had been in progress for 60 h and the catalyst, maintained at 780 °C, was exposed to a flow of CO_2 [1.67 cm^3 s^{-1} (s.t.p.)] for 2 h. When the system was then returned to the reaction conditions given above, a methane conversion of 15.2% and a C_2 selectivity of 79% were obtained; *i.e.* the CO_2 treatment had thus restored the initial behaviour of the catalyst despite the fact that loss of Li must have occurred. However in this case the deactivation was much more rapid. We therefore conclude that the active sites are created on the surface by the gradual loss of CO_2 from surface lithium carbonate species and that the active sites, which are relatively unstable, can be recreated by first reforming and then decomposing the surface carbonate species.

Further evidence for this suggestion was obtained in an equivalent experiment to that described above but in which a partial pressure of 0.06 bar CO_2 was present.[b] The conversion under these conditions was 7.0% (which is relatively low) and the selectivity was 85%. After 20 h, during which time the behaviour remained constant, the CO_2 flow was stopped, and it was found that the conversion behaviour returned to that shown in Figure 1 for the fresh catalyst. It is therefore concluded that addition of CO_2 to the gas feed lowers the activity but improves the stability.of the catalyst. In this case the problem of low activity could be avoided by using a larger quantity of catalyst. It was also found that stable behaviour approaching that of the initial fresh catalyst could be obtained if the effluent from the reactor was recirculated, thus adding small quantities of CO_2 to the feed. Applying these principles and by carefully choosing the reaction conditions, it has been possible to achieve a yield of 18% for a period of some 13.5 h.[6]

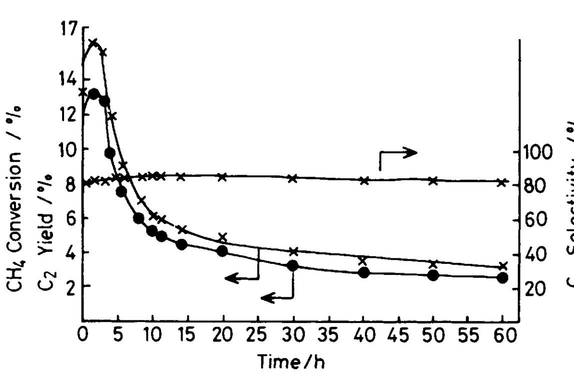

Figure 1. The change of catalytic behaviour with time for the reaction of CH_4 (0.67 bar) with O_2 (0.07 bar) over a Li/MgO catalyst at 800 °C; total pressure 1 bar (balance of gas mixture was He), total flow rate 3.33 cm^3 s^{-1} (s.t.p.). Left-hand axis: % CH_4 conversion (×), % C_2 yield (●); right-hand axis: % selectivity to C_2 products (×).

We conclude that the presence of CO_2 thus has two effects, namely to poison reversibly the active sites for the coupling reaction but also to stabilise them against deactivation. The lower yields and relative stability of similar catalysts which we reported previously,[3] in apparent contradiction with the above results, were probably due to two factors: (i) the lithium contents of the catalysts were higher, and (ii) the flow rates used were lower and thus back-mixing of the reaction products, including CO_2, could have occurred in the catalyst bed.[6,7]

It has also been found that dilution of the catalyst with quartz is detrimental to its stability. In another similar experiment carried out under the same reaction conditions without a quartz dilution, a C_2 yield of 12.0% was maintained over a period of 25 h when gradual deactivation started. The rapid deactivation in the case of quartz dilution may be caused by loss of lithium by diffusion into the quartz or by gradual coverage of the catalyst surface by silica.

From these results we conclude that the active sites created on the Li/MgO catalyst as a direct result of the loss of carbonate species are not stable in the reducing atmosphere of the oxidative coupling reaction. These sites can be regenerated by passing CO_2 over the catalyst at high temperature if lithium is still present in the catalyst. The presence of small quantities of CO_2 in the reaction mixture is sufficient to stop the deactivation process.

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