The Role of Tin in Li/Sn/MgO Catalysts for the Oxidative Coupling of Methane

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The addition of SnO_2 to the Li/MgO catalyst system has been found to stabilize its catalytic activity for the oxidative coupling of methane, and, when a large amount of SnO_2 is added, a new phase, $Li_2Mg_3SnO_6$ is identified; pure $Li_2Mg_3SnO_6$ is also an active and selective catalyst for the oxidative coupling of methane, and in contrast with Li/MgO, it retains lithium under reaction conditions, thereby suppressing deactivation.

The conversion of methane into useful products has recently attracted a great deal of interest. Oxidative coupling, in which methane is converted into ethane and ethylene, has received particular attention. The best known catalytic system for this reaction is Li/MgO,[1,2] which is one of the most active and selective catalyst types reported to date. However, its stability is poor owing to loss of the lithium under reaction conditions. Korf *et al.*[3] found that the addition of reducible metal oxides (*e.g.* SnO_2, CoO, TiO_2 or Dy_2O_3) to the Li/MgO system prolonged the lifetime of these catalysts; this improved stability apparently being caused by the fact that the oxides prevented the loss of lithium from the catalytic material. This communication presents an explanation of how tin prevents this lithium loss in the Li/Sn/MgO system.

Three different catalysts were prepared. The first was an unpromoted Li/MgO sample, prepared by wet impregnation of $Mg(OH)_2$ with LiOH in the presence of a stream of CO_2; after drying at 130 °C, the material was calcined at 850 °C for 6 h.[2,3] The second, denoted as Li/Sn/MgO(**a**), was prepared by physically mixing 100 g of the dried Li/MgO material with 3.0 g of SnO_2, followed by calcination at 850 °C for 6 h.[3,4] The third, denoted as Li/Sn/MgO(**b**), was prepared by wet impregnation of 6.90 g of SnO_2 and 50.8 g of $Mg(OH)_2$ with 12.10 g of LiOH in the presence of a stream of CO_2. The resultant slurry was dried at 130 °C, and then calcined at 850 °C for 6 h. After calcination, all the catalysts were crushed and sieved to a particle diameter of 0.3–0.6 mm.[4]

The weight percentages of lithium and tin for these catalysts are given in Table 1. The weight percentages of lithium were measured with atomic absorption spectroscopy and tin with X-ray fluorescence spectroscopy. From Table 1, it is clear that the Li/Sn/MgO(**b**) sample contains more Sn than does Li/Sn/MgO(**a**). It can also be seen that addition of tin to Li/MgO brings about the retention of lithium in the material during calcination, which is in accordance with the results of Korf *et al.*[3] Table 1 also gives the Brunauer-Emmett-Teller (BET) surface areas, measured with a Micromeritics ASAP 2400 instrument; the surface area appears to increase with increasing Sn content.

Catalytic screening tests[4] showed that both of the Li/Sn/MgO catalysts behaved identically to the Li/Sn/MgO catalysts as prepared by Korf *et al.*[3] However, X-ray diffraction (XRD) examination of the sample with high Sn content, Li/Sn/MgO(**b**), showed that all the peaks belonging to MgO were split (Fig. 1). This splitting appears to be due to the existence of a second phase, $Li_2Mg_3SnO_6$.[5,6] This phase, like MgO, has a face-centred-cubic structure, with the Li-, Mg- and Sn-ions randomly distributed over the Mg^{2+} sites. The lattice parameter of the mixed oxide is somewhat larger than that of MgO: 4.246 instead of 4.213 Å. This causes the $Li_2Mg_3SnO_6$ reflections to appear at slightly lower values of 2θ than the MgO reflections, thereby seemingly splitting each reflection.

Table 1 Weight percentages of Li and Sn, together with the BET surface areas of the catalysts; (l.t. = lifetime test, the error in the wt% is ±2%)

Catalyst	Li	Sn	BET
Li/MgO	2.1	—	0.5
Li/Sn/MgO(**a**)	4.2	2.8	1.9
Li/Sn/MgO(**b**)	3.5	11.1	4.0
$Li_2Mg_3SnO_6$ before l.t.	4.9	39.6	0.1
after l.t.	4.5	40.3	0.02
pure compound	4.6	39.4	—

Since it seemed that the appearance of the $Li_2Mg_3SnO_6$ phase could be stabilizing the lithium, an attempt was made to prepare the pure mixed oxide. A total of 12.10 g of LiOH, 34.0 g of $Mg(OH)_2$ and 30.15 g of SnO_2 were slurried in water in the presence of a stream of CO_2. The slurry was then evaporated to dryness and the remaining paste was dried overnight at 130 °C. Subsequently the material was calcined at 900 °C for 22 h, after which it was crushed, mixed and pressed at 150 kg m^{-2}, followed by further calcination at 950 °C for 20 h. Finally, it was crushed and sieved to a particle diameter of 0.3–0.6 mm. It should be noted that an excess of lithium over that required for the stochiometric compound, was added purposely so that the solid state reaction would be facilitated. Furthermore, past experience[3,7] had shown that the excess of lithium would evaporate.

XRD measurements of this material showed the presence of the mixed oxide only. Similarly, differential scanning calorimetry and thermogravimetric analysis experiments revealed that neither hydroxide nor carbonate phases were present, either before or after the lifetime test described below. These results indicate that the fresh catalysts consisted only of the mixed oxide, together with a small amount of Li_2O.

Using 4 g of the mixed oxide a lifetime test of 155 h was conducted in a quartz reactor with the feed consisting of 90 (±2) cm^3 min^{-1} CH_4 and 10(±0.2) cm^3 min^{-1} O_2. The temperature of the catalyst bed was 780(± 5) °C. The weight percentages of Li and Sn of the mixed oxide before and after operating for 155 h, together with the theoretical weight percentages are listed in Table 1. Before the lifetime test, the sample contained an excess of about 0.3 wt% of lithium over the theoretical value, while the amount of tin was the same, within the experimental error, as the theoretical value.

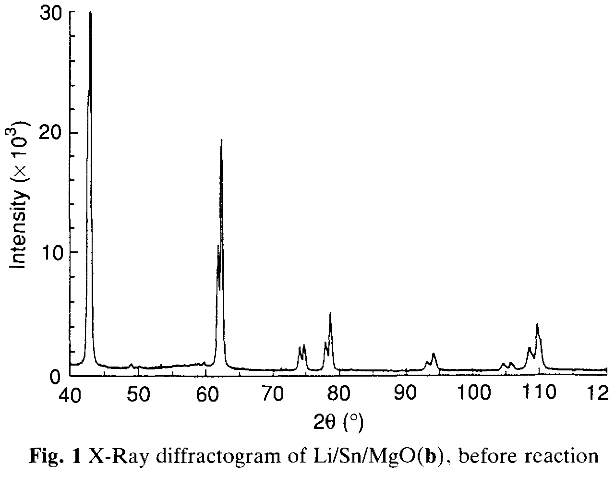

Fig. 1 X-Ray diffractogram of Li/Sn/MgO(**b**), before reaction

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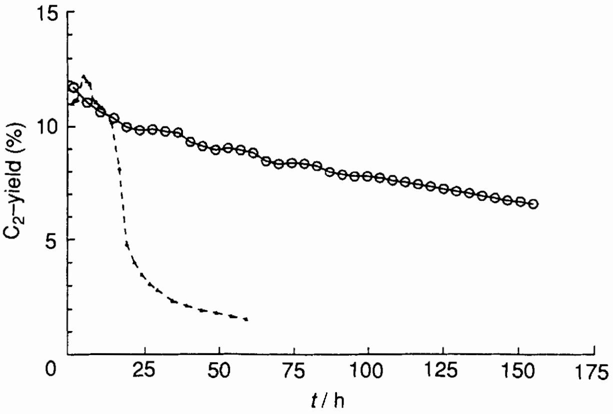

Fig. 2 C_2-yield *vs.* time for $Li_2Mg_3SnO_6$ ○ and Li/MgO ▲

However, after the lifetime test, the material still contained the quantity of lithium required for the pure mixed oxide. This result shows that the $Li_2Mg_3SnO_6$ is stable and does not lose lithium.

Fig. 2 shows the C_2-yield as a function of the time during the lifetime test. The yield fell quickly during the first 20 h on stream, from 11.7 after 2 h to 9.9% after 20 h. It then levelled off and the deactivation was much slower. After 155 h on stream the C_2-yield was 6.6%. During the experiment the C_2-selectivity increased slowly from 77 to 80%. For comparison, results for the activity of 0.38 g of Li/MgO, measured at 800 °C with a flow of 67 cm^3 min^{-1} CH_4, 7 cm^3 min^{-1} O_2 and 26 cm^3 min^{-1} He, as a function of time, are given as the dotted curve in Fig. 2. The $Li_2Mg_3SnO_6$ compound is much more stable than is the Li/MgO material.

The rapid deactivation at the beginning is believed to be caused by the loss of the excess lithium present. The slower deactivation, which starts after around 20 h, is thought to be caused by sintering. This seems probable since the surface area of the material had decreased after the lifetime test (Table 1). However, care must be taken with these values of surface area since they are too small to be measured accurately. On the other hand, scanning electron microscopy photos of the mixed oxide, before and after the lifetime test, indicated that the material had sintered extensively. Currently attempts are being made to find ways to stabilize the area of the $Li_2Mg_3SnO_6$ compound.

Tin improves the stability of Li/MgO through the formation of the mixed oxide $Li_2Mg_3SnO_6$. This mixed oxide does not lose lithium and its presence therefore slows down the deactivation. However, the material is still subject to deactivation due to sintering.

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