Evidence of Carbene Formation in Oxidative Coupling of Methane over Lithium-promoted Magnesium Oxide

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The presence of carbene in oxidative coupling of methane over Li–Mg oxide is revealed by introducing ethylene, which is transformed into cyclopropane.

The selective oxidation of methane to C_2 hydrocarbons is of great interest. Since the pioneering work of Keller and Bhasin[1] various systems such as Pb, Bi, Sn, Mg, and Sm oxides, supported or not, generally associated with alkali metals, have been shown to be active.[2—5] Ito *et al.*[6] have suggested that the reaction over lithium-promoted magnesium oxide proceeds *via* hydrogen abstraction from CH_4 to form $CH_3^{\bullet}$ radicals, which recombine to give ethane molecules in the gas phase. This model is based on the direct observation by e.p.r. of methyl radicals in the gas phase and of Li^+O^- centres in the solid, which are believed to be responsible for initiating the reaction by abstracting atomic hydrogen.

The concentration of methyl radicals detected by e.p.r., however, is very small. Moreover, solids such as La_2O_3, where O^- is not observed, are very active.[7] The mechanism of this reaction still needs further investigation, and we have examined to what extent other intermediates such as carbene species might be involved in the coupling process.

$$CH_2{=}CH_2 + CH_2 \rightarrow [CH_2]_3 \qquad (1)$$

Carbene in the gas phase can be detected by taking advantage of its easy addition to double bonds to form cyclopropane derivatives, *e.g.* with ethylene [reaction (1)].

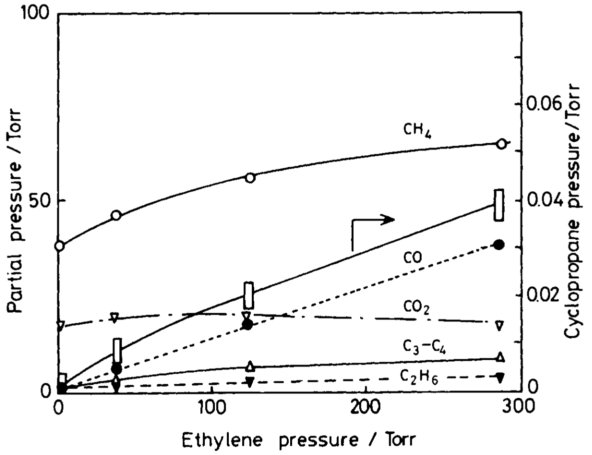

Figure 1. Influence of ethylene pressure on conversion of methane in the presence of oxygen over Li–Mg oxide at 907 K into carbon oxides and C_2 and C_3 hydrocarbons, including cyclopropane.

The formation of cyclopropane by the reaction of olefins with carbene ligands bonded to a metallic centre ($M{=}CH_2$) has also been established for the Fischer-type carbene complexes[8] with electrophilic carbon. In that case, a metallacyclobutane intermediate has been postulated [reaction (2)]

$$\begin{array}{c} CH_2 \\ \| \\ M \end{array} + \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} \rightarrow \begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ M & — & CH_2 \end{array} \rightarrow M + [CH_2]_3 \qquad (2)$$

The cyclopropane ring, however, is not very stable and therefore the reaction temperature should be both sufficiently low to avoid ring opening and high enough to ensure an acceptable rate of reaction. For the case of Mg-Li oxide prepared and activated according to the method proposed in ref. 6 a good compromise has been found at around 900 K. When C_2H_4 is progressively added to the reacting mixture (partial pressures of CH_4, O_2, and H_2 56, 33, and 671 Torr, respectively; flow rate 3.6 h^{-1}; catalyst weight 0.64 g; conversion 1%, selectivity towards C_2 hydrocarbons 56%), the amount of C_3 hydrocarbons increases, as shown in Figure 1. Interestingly, cyclopropane is detected in the C_3 fraction: the larger the partial pressure of ethylene, the larger the amount of cyclopropane. No cyclopropane is observed in the absence of catalyst, nor is it detected when a mixture of C_2H_4 and O_2, in the absence of CH_4, is introduced to the catalyst. It has been shown by adding cyclopropane in separate experiments to the $O_2/CH_4/He$ gas mixture that *ca.* 20% of the cyclic molecules remain unaltered. On this basis one can estimate the actual amount of carbene intermediate from that of cyclopropane detected at the reactor outlet. For example, when the partial pressure of ethylene is 300 Torr, the partial pressure of carbene (if it is formed in the gas phase) would be 0.2 Torr, corresponding to 0.04 Torr of cyclopropane. This figure compares well with the partial pressure of C_2 compounds observed when the O_2/CH_4 mixture reacts at this temperature, *i.e.* 0.3 Torr. This quantitative approach provides strong evidence that carbene, either unbound or on the surface, is involved in the oxidative dimerisation of methane, as a reactive intermediate or as a by-product. In the light of these data, the problem of the reaction mechanism can be reconsidered by examining the following two hypotheses.

(i) The carbene is formed in the gas phase. Basic O^{2-} sites would be capable of abstracting a proton from methane to give OH^- and CH_3^-, attached to a Lewis acid M^{n+} such as Mg^{2+} or Li^+ [reaction (3)]. Furthermore Li^+ could abstract a hydride ion from CH_3^- to form carbene [reaction (4)]. Carbene in the gas phase would insert into a C–H bond of methane to give ethane [reaction (5)]. The role of oxygen would be to restore the solid [reaction (6)].

$$CH_4 + M^{n+}, O^{2-} \rightarrow M^{n+}\ CH_3^- + OH^- \qquad (3)$$

$$Li^+\ CH_3^- \rightarrow Li^+\ H^- + :CH_2 \qquad (4)$$

$$:CH_2 + CH_4 \rightarrow C_2H_6 \qquad (5)$$

$$Li^+\ H^-, OH^- + 1/2\ O_2 \rightarrow Li^+, O^{2-} + H_2O \qquad (6)$$

The possibility of formation of carbene has been considered by the group of Lunsford[7] as an alternate explanation of the improvement in selectivity towards C_2H_4 as the temperature increases. This mechanism also accounts for the presence of methyl radicals, which were indeed observed in the gas phase by Ito *et al.*[6] at a concentration 10^4 or 10^3 times lower than we observed for carbene. Indeed, carbenes in the triplet state can abstract hydrogen to give free radicals [reaction (7)].

$$:CH_2 + RH \rightarrow CH_3^{\cdot} + R^{\cdot} \qquad (7)$$

It should be stressed that the hypothesis of gas-phase carbene formation is in keeping with the recent view expressed by Otsuka *et al.*,[9] according to which the active sites are O_2^{2-} ions; indeed it might be considered that these ions are capable of abstracting two H atoms from CH_4 to give $:CH_2$ and $2OH^-$.

(ii) The carbene is a ligand bonded to a metal centre. A methyl ligand (*e.g.* $MgCH_3$) could be formed, with subsequent dehydrogenation to a surface methylene species $Mg{=}CH_2$. The formation of the first C–C bond could result from the reaction of two $Mg{=}CH_2$ centres, giving ethylene. This path, however, is unlikely, since we know from contact time experiments that ethane is the primary C_2 product.

It is more reasonable, within the framework of this hypothesis, that $MgCH_3$ should undergo homolytic fission giving $CH_3^{\cdot}$, which would give ethane by reacting with another methyl radical. In the latter case, absorbed carbene would be a by-product which would not take part in oxidative coupling.

Further experiments aiming at discriminating between the gas-phase and adsorbed carbene hypotheses appear desirable. This work was supported by Gaz de France. We are grateful to the referees for suggestions.

Received, 27th March 1987; Com. 394

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