Oxidative Coupling of Methane: The Role of Solid State Chemistry

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Oxidative coupling of methane by a mixed manganese–magnesium oxide is governed in part by the solid state structure and chemistry.
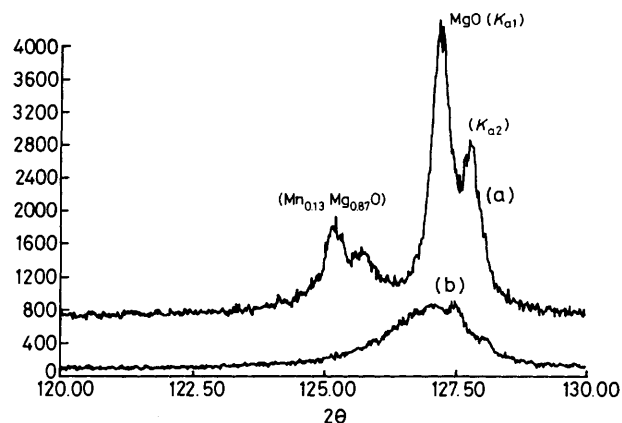
Oxidative coupling of methane to form higher hydrocarbons has been explored as a potential route for methane conversion.[1] This reaction has been achieved both by passing a mixture of methane and air over a suitable catalyst,[2] and by treating methane with a reducible metal oxide which can subsequently be reoxidized by air.[3] For a catalyst which follows the common Mars–van Krevelen mechanism for oxidation,[4] the nature of the interaction of methane with the surface and subsequent reactions may well be closely similar in these two cases. However, this scheme requires a facile solid state migration process if the amount of methane to be converted per cycle is to exceed the oxidizing capacity initially present on the surface of the metal oxide particles. We report here preliminary data on this process, which we have obtained from kinetics and solid state characterization studies on one such metal oxide system.

Catalysts employed in this work were prepared by impregnating MgO (Dart Industries) with aqueous solutions of NaMnO₄, drying, and calcining at 800 °C.[5] This procedure yields powdery solids with low surface areas, $\leqslant 1$ m² g⁻¹.

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Under typical methane reaction conditions (825 °C, 1 g CH₄ per g solid per h flow rate, 1 min run time) *ca.* 25% of the methane is converted, with a product split of roughly 75% hydrocarbons (mostly ethane and ethylene, with smaller amounts of heavier unsaturated species up to toluene) and 25% CO_2. The extent of catalyst reduction is calculated by summing gaseous products; in such a run about 5×10^{-4} equiv. [O]/g solid is consumed, whereas only *ca.* 2×10^{-6} equiv. [O]/g is present on the surface.

Powder-pattern X-ray diffraction (x.r.d.) identifies the predominant Mn-containing species as Mg_6MnO_8,[6] as long as the Mn loading does not exceed the stoicheiometry for this compound. This corresponds to a Mn oxidation state of +4, in agreement with the following observations. (i) Exhaustive reduction with methane or hydrogen gives a total yield of products requiring 1 equivalent of [O] per Mn. (ii) X.r.d. of a sample reduced as in (i) exhibits peaks assigned to the solid solution (Mn,Mg)O.[7] (iii) Iodometric titration of a fully oxidized sample dissolved in HCl indicates an oxidation state of +4. Characterization studies were performed on a sample containing 5% by weight Mn. By stoicheiometry, the oxidized form should consist of about 26% Mg_6MnO_8 and 74% MgO, which was indeed observed by x.r.d. (Na is present in the form of Na_2MgSiO_4, as the commercial MgO utilized contains

Figure 1. High-angle region of x.r.d. traces for H_2 reduced samples. (a) Physical mixture of 26% Mg_6MnO_8 and 74% MgO. (b) 5% Mn/MgO, prepared as in ref. 5.

Figure 2. Relative methane conversion rate vs. methane pressure. (a) Data for 5% Mn/MgO, line calculated from double reciprocal plot. (b) Data for 15% Mn/MgO; line calculated from 5% Mn/MgO data as discussed in text. All data at 825 °C and f = 90%.

about 2 wt% SiO_2 added as binder.) However, the following show that the solid is not simply a mixture of crystallites of these two substances. (iv) Electron microprobe analysis shows a rather uniform Mn and Mg distribution throughout the sample. (v) Scanning transmission electron microscopy (s.t.e.m.) reveals only one type of particle (aside from the Na_2MgSiO_4 mentioned above). These all have the approximate *bulk* Mn/Mg ratio and all exhibit electron diffraction patterns characteristic of Mg_6MnO_8 in the oxidized form. (vi) The composition of (Mn,Mg)O solid solution can be estimated by x.r.d. from the lattice expansion.[7] Reduction of a physical mixture of Mg_6MnO_8 and MgO gives two species, 'Mg_6MnO_7' and MgO, by x.r.d.; however, reduction of the mixed metal oxide prepared as described above gives instead a single broad x.r.d. peak corresponding to the average overall composition (Figure 1).

These apparent anomalies can be understood in terms of the structure of Mg_6MnO_8, which is derived from that of MgO by replacing, in every cation layer, Mg^{2+} alternately by Mn^{4+} and vacancy, with only a small change in lattice parameter. This is completely analogous to the structure of the Suzuki phases, in which small domains of composition Na_6DCl_8 form upon doping NaCl with divalent ions D^{2+}; such phases exhibit high ionic mobility.[8] We therefore propose that the active metal oxide species here is composed of ordered domains of Mg_6MnO_8 in MgO. Methane reacts with surface Mg_6MnO_8 sites to give gas-phase CH_3·[9] and surface –OH, the latter eventually departing as water and leaving a reduced surface site. Regeneration of an active surface site is achieved by cation migration to a bulk defect, which both propagates surface reduction to the interior and effects the complete (Mn,Mg) scrambling implied by the x.r.d. results [(vi) above]. This process would just be reversed in reoxidation of a reduced catalyst.
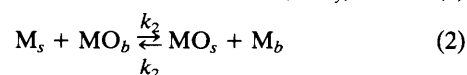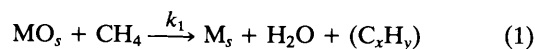
This model implies two consequences which have been tested. First, since transport of oxidizing equivalents from bulk to surface is achieved by cation, not anion, migration, O atoms utilized in the reaction with methane should be (mostly) the same as those added during reoxidation. On fully reducing a catalyst sample, reoxidizing with $^{18}O_2$, and treating with methane, the CO_2 produced contains 70—80% ^{18}O even though the oxidized sample, by stoicheiometry, is only 3.6% ^{18}O. Hence O atoms must be added to and removed from the outer shell of oxide particles, with very little redistribution under the reaction conditions.

Secondly, the kinetics of reaction with methane should become limited by solid state migration at some point.
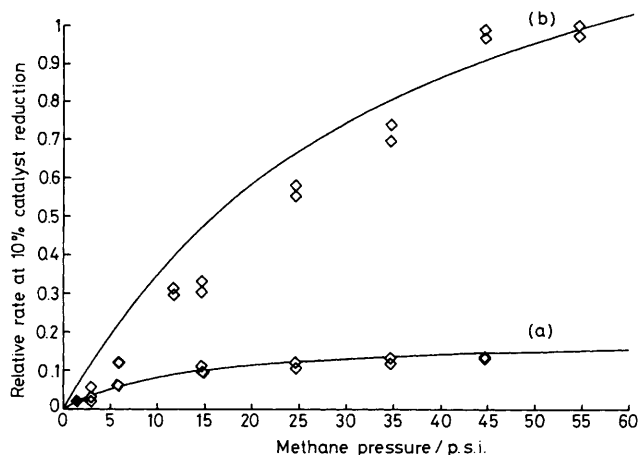
Equations (1) and (2) represent a simplified mechanism which describes the resupply of surface O where MO and M are oxidized and reduced sites, respectively, and subscripts s and b refer to surface and bulk. Defining M = total sites (surface plus bulk), S = fraction of sites on surface, and f = fraction oxidized, then $MO_b \approx fM$ (since S is very small), $M_b \approx (1-f)M$, and $M_s = SM-MO_s$. Solving for MO_s in the steady-state approximation and substituting gives equations (3) and (4), where $a = k_2fSM^2$, $b = M[k_2f + k_{-2}(1-f)]/k_1$, and P = methane pressure. Plots of rate^{-1} vs. P^{-1} are indeed linear. More importantly, curves for samples of different Mn loadings are related. Assuming k values and S are fairly independent of loading, and by taking data at constant f (90%), the rate–pressure curve for a sample 15% by weight Mn should be calculable from that determined for the 5% sample by multiplying values for a and b (obtained from the above double reciprocal plots) by 9 and 3 respectively. As shown in Figure 2, the curve thus calculated agrees quite well with experimental results. The ability to thus quantitatively predict the reactivity of one solid from data obtained on another is a much-desired goal in catalytic studies.

$$MO_s + CH_4 \xrightarrow{k_1} M_s + H_2O + (C_xH_y) \qquad (1)$$

$$M_s + MO_b \underset{k_2}{\overset{k_2}{\rightleftharpoons}} MO_s + M_b \qquad (2)$$

$$\text{Rate} = k_1(MO_s)P \qquad (3)$$

$$\text{Rate} = aP/(P + b) \qquad (4)$$

This catalyst is superior in activity and selectivity to most of those reported previously, where conversions <10% and selectivities <70% have been typical,[2,3] and it is tempting to ascribe this fact to the special structural features present. However, it should be noted that there are several quite different materials that exhibit similarly exceptional performance.[5,10] Detailed structural characterization has not been carried out for these materials, but it seems probable that many of the same principles will apply.

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