OXIDATIVE COUPLING OF METHANE: AN INHERENT LIMIT TO SELECTIVITY?

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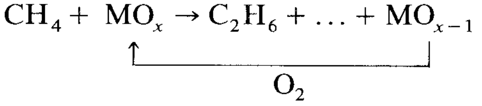
Mechanistic considerations show that pressure must be taken into account in evaluating oxidative coupling catalyst performance, and predict an upper limit of around 30% yield of higher hydrocarbons at one atmosphere.

The oxidative coupling of methane (eq. (1)) has received intense interest over the last few years as a potentially practical alternative to syngas-based routes for conversion of natural gas to liquids [1]. The goal, obviously, is to achieve high selectivity for C_{2+} hydrocarbon products. As is typically the case for partial oxidation there is a strong inverse correlation between selectivity and conversion, whether the reaction is carried out in "normal" catalytic fashion or by the cyclic "redox" modification (eq. (2)).

$$CH_4 + O_2 \rightarrow C_2H_6 + C_2H_4 + C_{3+}H_x + CO + CO_2 + H_2O \qquad (1)$$



$$CH_4 + MO_x \rightarrow C_2H_6 + \ldots + MO_{x-1} \qquad (2)$$

While indisputable forecasts of the engineering feasibility of this approach and its economic competitiveness with current technology are not yet available, it has been estimated that around 20–25% per pass yield (conversion times selectivity) of higher hydrocarbon products would be the *minimum* requirement for a viable process [2]. In fact, there are a number of literature reports with quite different catalysts that appear to meet or surpass this target, suggesting that even substantially better yields might be achieved with the right catalyst. Mechanistic considerations, however suggest that this picture may be much too optimistic. First, there is a pronounced pressure effect which makes many of the published results appear better than they will be under practical conditions; second, mechanistic constraints seem to place an upper bound on yield, *independent of catalyst*, which is not far above the target values. This latter presents arguments in support of these claims.

SCHEME

$$CH_4 \xrightarrow{MO} CH_3\cdot \tag{3}$$

$$2\ CH_3\cdot \longrightarrow C_2H_6 \tag{4}$$

$$CH_3\cdot \xrightarrow{MO} CO_2 \tag{5}$$

$$C_2H_6 \xrightarrow{MO} C_2H_4 \tag{6}$$

$$C_2H_6 \xrightarrow{\Delta} C_2H_4 \tag{7}$$

$$C_2H_6 + CH_3\cdot \longrightarrow CH_4 + (C_2H_5\cdot \xrightarrow{fast} C_2H_4) \tag{8}$$

$$C_2H_4 \xrightarrow{MO} 2\ CO_2 \tag{9}$$

$$C_2H_4 \xrightarrow{MO} 2/3\ C_{3+} \tag{10}$$

$$C_2H_4 \xrightarrow{\Delta} 2/3\ C_{3+} \tag{11}$$

$$C_2H_4 + CH_3\cdot \longrightarrow CH_4 + (C_2H_3\cdot \xrightarrow{fast} C_2H_2 \xrightarrow{MO/fast} 2\ CO_2) \tag{12}$$

$$C_2H_4 + CH_3\cdot \longrightarrow (C_3H_7\cdot \xrightarrow{fast} C_{3+}) \tag{13}$$

$$C_{3+} \xrightarrow{MO} 3\ CO_2 \tag{14}$$

We have reported studies which led to a complete kinetic model for the oxidative coupling of methane by a mixed Mn-Mg oxide, following eq. (2) [3]. The reaction network deduced is shown in the Scheme, with the following key points:

1. CO_2 is produced by two paths: a *primary* one, directly from $CH_3\cdot$ (eq. (5)), and a *secondary* one, via ethylene. The latter is the main source of CO_2 at higher (> 15%) conversions.

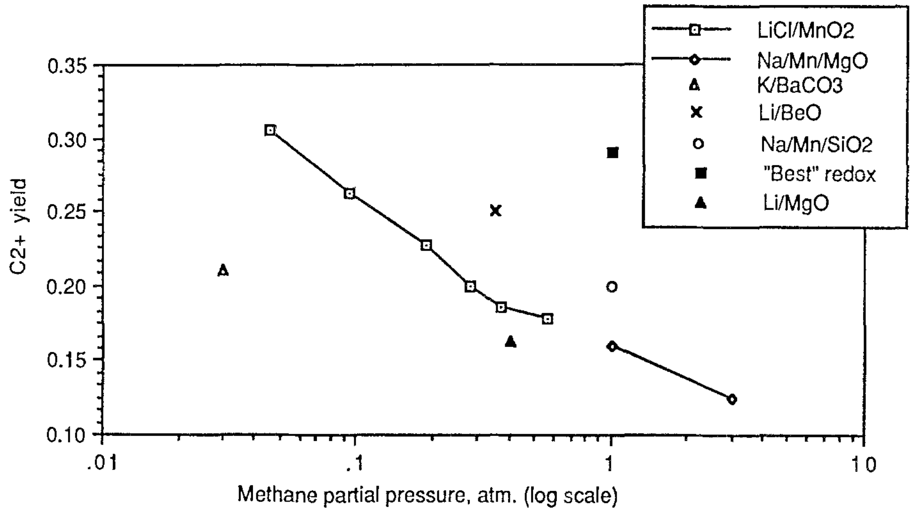


Fig. 1. Best reported oxidative coupling yields vs. methane partial pressure. $LiCl/MnO_2$, ref. [4]; Na/Mn/MgO, ref. [3]; $K/BaCO_3$, ref. [5]; Li/BeO, ref. [6]; $Na/Mn/SiO_2$, ref. [7]; “Best” redox, ref. [8]; Li/MgO, ref. [9].

2. Much of the ethylene forms by the *gas-phase* reaction of $CH_3\cdot$ with ethane (eq. (8)). Note that this is a second-order step, and ethylene is a major precursor to CO_2, by reaction with both the catalyst (eq. (9)) and (via acetylene) with $CH_3\cdot$ (eq. (12)), another second-order step.

3. The relative rates of reaction with the metal oxide for the various hydrocarbons-methane, ethane, ethylene, propene (eqs. (3, 6, 9, 10, 14)–are very similar to those for reactions of gas-phase radicals ($CH_3O\cdot$, $HO\cdot$), implying they are determined simply by C-H bond strengths.

Point 2 implies that at high conversion, where most of the CO_2 is produced sequentially from ethylene rather than directly from $CH_3\cdot$, selectivity will *decrease* as pressure increases. This is in fact the case [3]. The vast majority of published data are collected at low methane partial pressures, which inflates the apparent yield. Figure 1 shows some of the better published yields plotted against methane partial pressure, and includes a set of data which clearly demonstrate this pressure effect [4]. It can be seen that very few catalysts in the literature approach the target of 25% yield *at or above atmospheric pressure*, which will certainly be needed in a practical process.

Point 3 implies that the ability to control the *relative* reactivities of different species by changing the catalyst–a factor which is crucial in determining the conversion-selectivity relationship–may be strictly limited. If radical H · abstraction is the key step in these reactions, as several studies strongly indicate [3,7,9], then (absent some degree of shape-selectivity, which will be difficult to achieve at the high temperatures required) the best catalyst should be essentially *non-discriminating* between various types of C-H bonds [10]. Since the rates for the

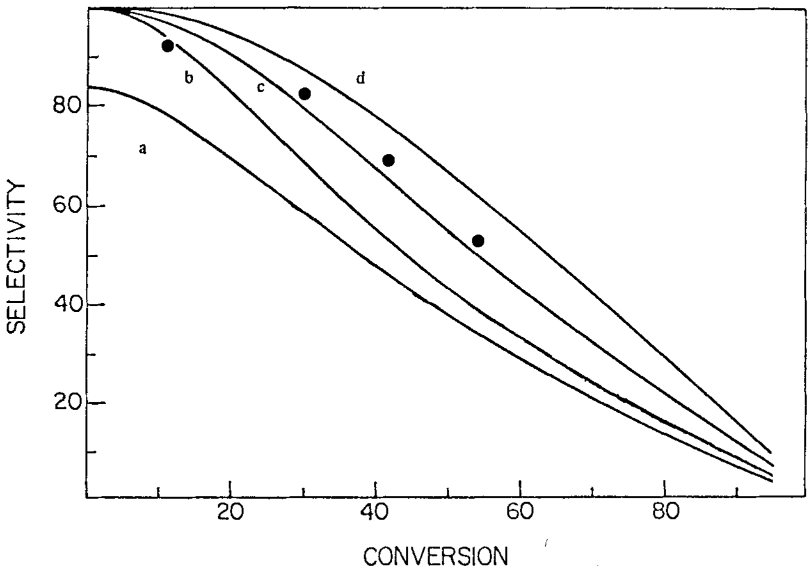


Fig. 2. Calculated "optimal" selectivity-conversion relationships and best experimental results; see text for details.

Mn-Mg catalyst used here closely parallel those of species like OH·, this has already been achieved.

What, then, *can* be done to improve performance? Conceptually, two things:

(i) Increase overall catalyst activity. This will reduce the relative importance of purely gas-phase reactions such as eqs. (8) and (12) that are CO_2 producers.

(ii) Decrease the relative rate for eq. (5). This would cut down on the contribution of direct conversion to CO_2.

The quantitative effects of these catalyst "modifications" can be estimated by making suitable adjustments in the model evolved in the earlier studies [3]. Based on examination of a very large number of materials, increases in activity over that baseline catalyst of 3–10 fold are achievable. As for the relative rate of eq. (5), it was determined to be 2700 times that of eq. (3) for the original study [3]. Using gas-phase studies on O atom reactions as the best available model [11], a value of 150 can be taken as a lower limit.

Figure 2 shows the effects of these modifications. Curve a is the baseline [3]; in the rest, k_5 is adjusted to 150 times k_1, while the set of rates k_3, k_6, k_9, k_{10} and k_{14} are all set at 1 (b), 3 (c), and 10 (d) times their baseline values. From the resulting curves, there appears to be a mechanistically imposed limit of around 30% yield at 1 atmosphere. *This limit has not been exceeded (or indeed often approached, as seen in fig. 1) by any published results.* The points in fig. 2 correspond to the "best redox" result of fig. 1 [8]; note that they agree well, both in top yield and in the shape of the selectivity-conversion relation, with the predicted behavior.

Of course, the mechanistic underpinning to these arguments derive from studies on a single catalyst in redox mode. However, there is considerable evidence that the mechanisms for other catalysts, even with cofed oxygen, are closely similar if not identical. This includes the pressure trends cited above; findings that ethylene is the crucial CO_x precursor [12], and very close resemblances between product distributions using the *same* catalyst in redox and cofeed mode [13]. It may thus be argued that these conclusions are general, with two main consequences: pressure must be taken into account in evaluating the relative merits of literature data; and investing in a major program in oxidative coupling predicated on the expectation that substantial improvements in performance may be achieved with enough work, might not be wise decision.

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[10] Lunsford has noted that the C-H bond in ethylene is *stronger* than that in methane, and suggested that a catalyst might be found for which the former is less reactive and hence the constraints discussed here need not apply (J.H. Lunsford, in: *Methane Conversion*, eds. D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak (Elsevier, New York, 1988) 359.). However, since ethylene is more reactive even for gas-phase reactions with OH· and related species, in spite of its stronger bond, it does not seem very likely that this could be achieved.

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