Approaches to catalytic methane conversion in academic and industrial research: comparison, competition, collaboration*[1]

JAY A. LABINGER*[2]

Efficient and economic conversion of methane to more valuable products has immense potential for many applications, both for fuel and chemicals. A major target is the transformation of methane to a liquid product, in order to circumvent the cost of transporting methane from "remote" locations where there is insufficient local demand. Two routes are currently available in established technology. One, developed by Mobil, is practiced in New Zealand; it proceeds in three steps from methane to gasoline, via steam reformation to synthesis gas, methanol synthesis, and conversion to gasoline over the zeolite ZMS-5; stopping at methanol might be a viable alternative, particularly if methanol-powered automobiles become more important.

$$CH_4 + H_2O \rightarrow H_2 + CO \rightarrow CH_3OH \rightarrow C_nH_m + H_2O$$

The second also begins with steam reformation, but then utilizes the Fischer-Tropsch synthesis to yield hydrocarbons directly. A version of this process is being commercialized by Shell for Malaysia.

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These routes appear intuitively inefficient, in that they start by breaking four C-H bonds per molecule and making a C-O bond, afterwards putting back some of the four H's and removing the oxygen. Indeed, it has been estimated that processes that avoid the energy- and capital-intensive steam reformation step **could** be economically much superior. However, in trying to conceive a more direct pathway from methane to methanol or higher hydrocarbons, we encounter a fundamental problem: methane is usually **considerably** much less reactive than products derived therefrom. this means that a process based on such a reaction may be carried out under conditions where **either** conversion or selectivity is optimized, but achieving **both** good selectivity and conversion is extremely difficult. There is thus a major scientific challenge as well as the practical issue: how can methane, a relatively highly inert molecule, be activated under conditions that do not lead to complete degradation to valueless products?

Possible direct routes for methane conversion might include:

- Dehydrogenative coupling

$$n\,CH_4 \rightarrow C_nH_m + \frac{(4n-m)}{2}\,H_2$$

The disadvantages are that the reaction is thermodynamically disfavored below ≈1000°C; hence it is energy-intensive and unselective. It has been used for acetylene production.

- Oxidative variant

$$n\,CH_4 + (4n-m)/4\,O_2 \rightarrow C_nH_m + \frac{4n-m}{2}\,H_2O$$

Incorporating oxidation removes the thermodynamic barrier, but introduces a severe problem of selectivity – how are we to stop short of CO_2?

- Methane to methanol

$$CH_4 + 1/2\,O_2 \rightarrow CH_3OH$$

Again there is a selectivity problem, and the best literature yields reported are only ≈5%, using traditional catalytic methods. However, there are efficient bacterial enzymes, called methane monooxygenases (MMO), that can carry out this reaction.

Approaches to achieving these conversions may be very broadly grouped into three classes:

i) "Traditional" heterogeneous catalysis, utilizing solid metal or metal oxide catalysts.

ii) Homogeneous catalysis, generally involving organometallic species.

iii) Biological and "biomimetic" catalysis, based on actual enzymes or synthetic catalysts thought to mimic enzymatic action.

The vast majority of industrial research in catalysis in general has followed the first approach, and methane conversion has been no exception, with particular emphasis on the so-called oxidative coupling reactions shown hown above. The second and third approaches have been almost exclusively the province of academic laboratories, as they are perceived as having promise only over a much longer term, as well as being suited to a more mechanistic program fo study.

Based on this background, the history of oxidative coupling research over the last 5-10 years is somewhat surprising. Since the initial reports around 1982-1983, several hundred papers and patents have issued from at least 50 groups in all types of labs –

SCHEME I

$$CH_4 \xrightarrow{MO} CH_3 \qquad 1$$

$$2\,CH_3 \overset{g}{\rightleftharpoons} C_2H_6 \qquad 2$$

$$CH_3 \xrightarrow{MO} CO_2 \qquad 3$$

$$C_2H_6 \xrightarrow{MO} C_2H_4 \qquad 4$$

$$C_2H_6 + CH_3 \xrightarrow{g} CH_4 + C_2H_4 \qquad 5$$

$$C_2H_4 \xrightarrow{MO} 2\,CO_2 \qquad 6$$

$$C_2H_4 \xrightarrow{MO,\,g} C_{3+} \qquad 7$$

$$C_2H_4 + CH_3 \xrightarrow{g} CH_4 + C_2H_2 \qquad 8$$

$$C_2H_2 \xrightarrow{MO} 2\,CO_2 \qquad 9$$

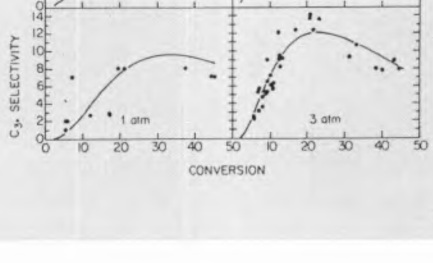
$$C_{3+} \xrightarrow{MO} 3\,CO_2 \qquad 10$$

industrial, academic, and government – in at least 20 countries worldwide. Furthermore, if we again broadly divide approaches to catalyst improvement into two – one Edisonian, testing as many types of materials as possible and trying to interpret trends, eventually converging on optimal performance; the other mechanistic, focusing on gaining understanding of the factors controlling performance and using the information to design improved catalysts – we find that the frequency of the two in academia and industry is about the same, contrary to what might have been expected.

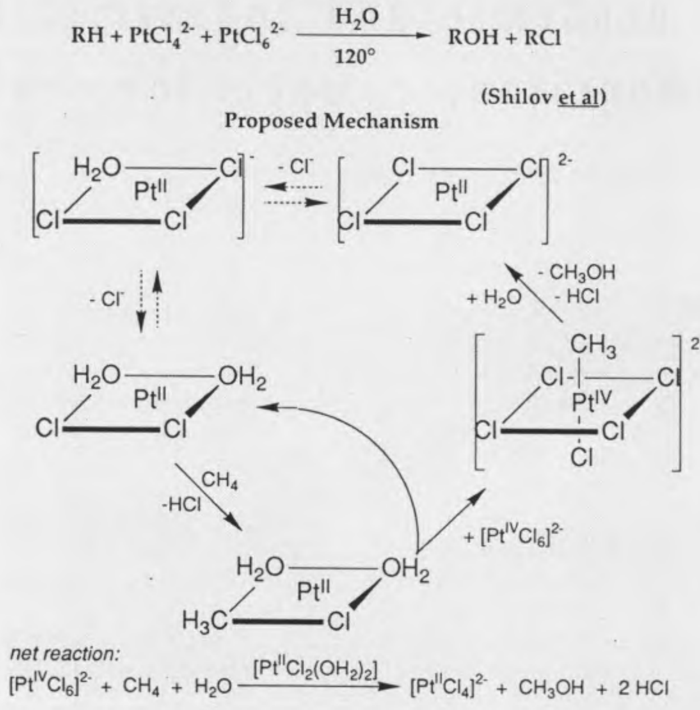
Our own work in this area has focused upon the mechanism of the oxidative coupling reaction, and the consequences of the mechanism for its viability. It has been estimated that catalyst performance in the vicinity of 25% yield (that is, conversion of methane times selectivity to higher hydrocarbon products) would be required. More than a few reports in the literature have met this requirement, leading many to conclude that the selectivity problem, at least, is one that **can** be overcome for this particular approach. This conclusion contains two inherent assumptions: that performance can be indefinitely improved by suitable catalyst optimization, and that results obtained under laboratory conditions will be reproducible in practically relevant conditions. We have attempted to check the validity of these assumptions through mechanistic investigation.

FIGURE 1

MODEL FIT TO EXPERIMENTAL DATA



SCHEME II



$$RH + PtCl_4^{2-} + PtCl_6^{2-} \xrightarrow[120^\circ]{H_2O} ROH + RCl$$

(Shilov et al)

Proposed Mechanism

net reaction:

$$[Pt^{IV}Cl_6]^{2-} + CH_4 + H_2O \xrightarrow{[Pt^{II}Cl_2(OH_2)_2]} [Pt^{II}Cl_4]^{2-} + CH_3OH + 2\,HCl$$

Studies were carried out on a Na/Mn/MgO catalyst prepared by impregnating MgO with a solution of $NaMnO_4$ and calcining. Reactions of methane, as well as of C_2 hydrocarbons, were followed by standard flow reactor methods, using quadrupole mass spectrometry for product analysis. A typical series of experiments consists of varying the gas flow rate, and hence the contact time, while keeping temperature and pressure constant; The relationship between conversion (which varies directly with contact time) and selectivity can thus be determined. (Selectivity is defined as total moles of carbon appearing in the desired C_{2+} products divided by the total moles of methane that have reacted). Further details are available in the literature.[1]

The basic results are as follows:

- Under all conditions, the selectivity decreases as conversion increases.
- At low conversions, the only products are ethane and CO_2. At constant conversion, the selectivity **increases** as pressure increases.
- At higher conversions, additional products, particularly ethylene and propylene, begin to appear. At constant conversion the selectivity **decreases** as pressure increases.

These trends may be qualitatively interpreted by means of the mechanism shown in Scheme I, where MO and g signify, respectively, reactions taking place at the catalyst surface and reactions in the gas phase. At very low conversions – that is, very short contact times – any stable product formed exits the reactor before it can react further, so the only steps that are significant are 1-3. Since the desired product ethane is produced by a second-order reaction, while CO_2 arises from a first-order step, the selectivity improves with pressure.

In contrast, as contact times lengthen reactions 4-10 become increasingly important, and the majority of the CO_2 is produced not by parallel reaction 3, but by consecutive reactions 6, 9 and 10. Of particular importance are the gas-phase reactions 5 and 8, yelding ethylene and acetylene, both of which are major percursors to CO_2. Since it is now the pathways leading to the undesired product that are second-order, the selectivity gets worse as pressure increases.

It is possible to obtain rate constants for all the steps in Scheme I. The values for steps 1, 4, 6, 7, 9 and 10 are found experimentally, by measuring the rate of conversion of various hydrocarbon reactants; rate constants for 2, 5 and 8 are in the literature; and that for 3 is calculated by fitting experimental selectivities in the low-conversion limit to the simple kinetic expression arising from treating reactions 1-3 in the steady-state approximation. These rate constants may then be used to predict the entire behavior of the system. Figure 1 shows the comparison between calculated and experimental overall selectivity, ethylene: ethane ratio, and C_{3+} selectivity as a function of conversion; as can be seen, the agreement is excellent.

Our analysis of the mechanism of the oxidative coupling reaction places an inherent limit on catalysis performance that in fact does **not** meet the above requirements under practical conditions of pressure. All of the earlier laboratory results that give 25% yield or better were obtained at or below – usually well below – one atmosphere of methane pressure. Any practical system will have to be run at a minimum of several atmospheres, and the mechanism implies that this will have severely detriment effects on selectivity. Figure 2 shows the predicted optimal performance of an oxidative coupling catalyst as a function of pressure, making every reasonable favorable assumption about individual rate constants consistent with the radical mechanism involved.[2] On the same graph are i) the best observed results at 1 atm, which agree well with the calculated limit; and ii) estimates of performance that would be required for a practical process, based on engineering and economic considerations. Clearly the requirements far exceed the best that is likely to be attainable.

In the face of this prediction, how should we proceed towards the target of methane conversion? As noted earlier, our problems stem primarily from the fact that methane is less reactive than the desired products we obtain from it. How could we overcome this obstacle? There are basically three strategies:

- Exploit separation techniques or advanced reactor design
- Control access or binding to active site (shape-selectivity, hydrophobicity)
- Find reaction mechanism where methane becomes **more** reactive

The first of these is certainly feasible, but bound to be highly expensive; in any case, it is largely outside the province of chemistry. The second is most probably the means by which MMO produces methanol selectively from methane. The third would be most desirable of all.

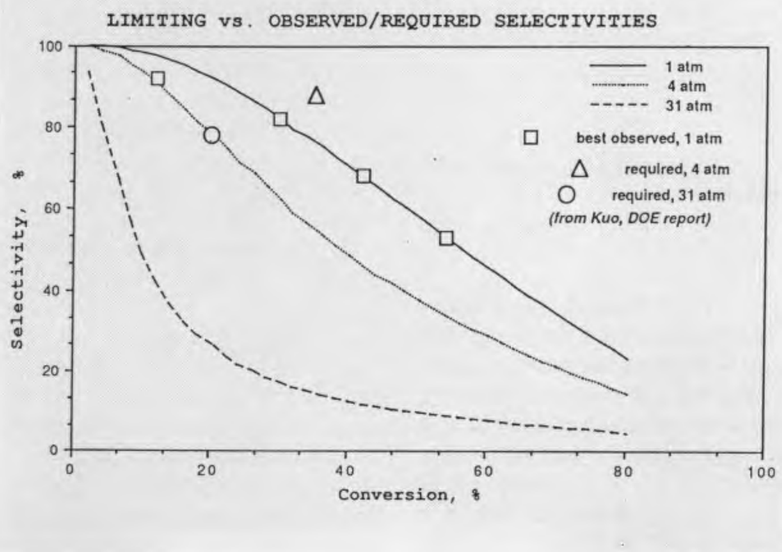
Circumventing the limitation will require approaches that are mechanistically entirely distinct from oxidative coupling, which might be found in the realms of homogeneous, biological, or even possibly novel heterogeneous catalysts. One attactive possibility is shown in Scheme II. Here hydroxylation of an alkane is achieved using reagents – Pt II/IV complexes – that are stable to oxygen and hence could conceptually be used in a catalytic alkane oxidation scheme, although only stoichio-metric oxidation has been achieved to date. We have shown[3] by reaction such as:

$$CH_3CH_2OH + PtCl_6^{2-} + H_2O \rightarrow HOCH_2CH_2OH + PtCl_4^{2-} + 2HCl \quad \textit{(inter alia)}$$

that the selectivity of these reactions is completely different from that of the radical-based processes discussed above: unactivated positions such as $-CH_3$ are as reactive as or even slightly more reactive than $-CH_2OH$, offering the possibility, for example, of converting methane to methanol with much better yield than has yet been achieved (about 5%) using traditional heterogeneous catalysts.

Clearly this is a long-term approach to the problem, which appears much more suited to academic than industrial research; but as I have tried to show, such focus on the long term is necessary if substancial progress towards the solution of this major challenge is to be made. Strong interactions between industry and academia – wether in the form of direct industrial support for academic research, establishment of consortia, or new types of arrangements – will also be essential, so that advances in fundamental understanding can be most directly applied to the technical and practical hurdles that must be overcome.

FIGURE 2



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*[1] *Lição Plenária proferida no 13.º Encontro da SPQ.*

*[2] *Division of Chemistry and Chemical Engineering*
California Institute of Technology
Pasadena, CA, USA