REPORTS

A Mercury-Catalyzed, High-Yield System for the Oxidation of Methane to Methanol

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A homogeneous system for the selective, catalytic oxidation of methane to methanol via methyl bisulfate is reported. The net reaction catalyzed by mercuric ions, Hg(II), is the oxidation of methane by concentrated sulfuric acid to produce methyl bisulfate, water, and sulfur dioxide. The reaction is efficient. At a methane conversion of 50 percent, 85 percent selectivity to methyl bisulfate (~43 percent yield; the major side product is carbon dioxide) was achieved at a molar productivity of 10^{-7} mole per cubic centimeter per second and Hg(II) turnover frequency of 10^{-3} per second. Separate hydrolysis of methyl bisulfate and reoxidation of the sulfur dioxide with air provides a potentially practical scheme for the oxidation of methane to methanol with molecular oxygen. The primary steps of the Hg(II)-catalyzed reaction were individually examined and the essential elements of the mechanism were identified. The Hg(II) ion reacts with methane by an electrophilic displacement mechanism to produce an observable species, CH_3HgOSO_3H, **1**. Under the reaction conditions, **1** readily decomposes to CH_3OSO_3H and the reduced mercurous species, Hg_2^{2+}. The catalytic cycle is completed by the reoxidation of Hg_2^{2+} with H_2SO_4 to regenerate Hg(II) and byproducts SO_2 and H_2O. Thallium(III), palladium(II), and the cations of platinum and gold also oxidize methane to methyl bisulfate in sulfuric acid.

One of nature's great challenges to the scientist is the selective oxidation of methane (the primary component in natural gas) to methanol or another efficiently transportable material. Methane is an abundant resource that could serve as an efficient fuel source and chemical feedstock. The known and projected world reserves of natural gas, more than 9000 trillion cubic feet (250,000 trillion liters), are comparable to those of petroleum (*1*). However, petroleum is today's primary energy source and chemical feedstock, and the current use of methane is relatively small. If methane could be used efficiently, it could replace projected dwindling petroleum reserves in the 21st century. Efficient utilization of methane is challenging because the largest reserves are in remote locations, far from centers of consumption. This situation, coupled with the gaseous state and low boiling point of methane (−164°C), makes this resource too expensive to transport (*2*). An obvious solution is the conversion of methane to methanol or other efficiently transportable liquid material at the remote site before transportation. Such processes have been developed, but current technology based on the high-temperature (>900°C), energy-intensive conversion of methane and water to carbon monoxide and hydrogen is uneconomical. The scientific and engineering community accepts as a general, conservative guideline that a high-selectivity (≥85%), high-conversion (≥30%) (*3*) process for the oxidation of methane to methanol with molecular oxygen as the final oxidant could provide the basis for an economical process for the conversion of methane to a transportable material (*4*).

Methane is a very unreactive molecule, as demonstrated by the high C–H bond strength [D(C–H) = 438.8 kJ/mol], high ionization potential (12.5 eV), low proton affinity (4.4 eV), and low acidity (pK_a = 48) of the molecule. Methane can be made to react by using very reactive species. Radicals are among the most reactive species, and radical chemistry has been traditionally used for reaction with methane. These species can be generated under very forcing conditions or with very reactive reagents. However, under these conditions, the initial (and more useful) products (*5*) of reaction are more reactive than methane, and selective reaction of methane in high yield is very difficult. Thus, reactions with oxygen can be accomplished but require temperatures above 700°C. Under these conditions, only low selectivities (<30%) to methanol have been reported at methane conversions above 10%, giving ~3% overall yields (*6*). Reactions with more reactive species such as chlorine can be carried out at 350°C, but the reaction selectivity to methyl chloride is still low and significant amounts of polychlorinated methanes are generated (*7*). Given the low proton affinity and acidity of methane, it would not be expected that reaction of typical acids or bases with methane would occur at temperatures lower than those of radical processes. This unreactivity has been found to be the case. Only with extremely reactive species, such as protons in "superacid" media (SbF_5/HF), are reactions with methane observed at lower temperatures (*8*). However, these reactions are stoichiometric or use expensive reagents and thus are not practical for the large-scale oxidation of methane.

We describe the use of Hg(II) to catalyze the selective oxidation of methane to methanol, through methyl bisulfate, in high yield, ~43% (*9*). The reaction occurs under mild conditions (180°C) with reagents that can potentially be used on a large scale. The keys to this discovery are the novel use of Hg(II) as a catalyst for the oxidation of methane through an electrophilic displacement reaction (*10*) and the production of the monomethyl ester of sulfuric acid, methyl bisulfate, as a methanol precursor that is less reactive than methane.

A significant amount of work exploring the electrophilic reactions of alkanes with transition metals has been reported (*11*, *12*). However, to our knowledge, the electrophilic reaction of methane with Hg(II), a posttransition metal, has not been reported (*13*). Hg(II) is a "soft" (*14*), powerful electrophile with good oxidizing properties (*15*). Consistent with these properties, this cation is known to readily activate (*16*) arenes by electrophilic displacement, generating stable aryl mercury species (Eq. 1) (*11*, *12*):

$$\mathrm{ArH} + \mathrm{Hg(II)} \rightarrow \mathrm{Ar{-}Hg(II)} + \mathrm{H}^+ \quad (1)$$

Related electrophiles, palladium(II) and platinum(II), have also been reported to activate and oxidize arenes (*17*). These species as well as Co(III) have been reported to react with methane, presumably through a methyl metal species (Eq. 2), to produce methyl esters in the cases of Pd(II) (*18*) and Co(III) (*19*) and methanol and methyl chloride in the case of Pt(II) (*12*):

$$\begin{gathered}\mathrm{CH_4} + \mathrm{M}^{n+} \rightarrow [\mathrm{CH_3{-}M}^{n+}] + \mathrm{H}^+ \rightarrow \\ \mathrm{CH_3X} + \mathrm{M}^{(n-2)+} \\ \mathrm{X} = \mathrm{CF_3CO_2},\ \mathrm{OH},\ \mathrm{Cl} \\ \mathrm{M}^{n+} = \mathrm{Pd}^{2+},\ \mathrm{Pt}^{2+},\ \mathrm{Co}^{3+} \qquad (2)\end{gathered}$$

The reactions with Pt(II), first reported by Shilov in 1972, have played a central role in focusing attention on the important field of alkane chemistry with transition metals. However, the Pt(II), Pd(II) and Co(III) systems are all characterized by low yields, and only limited success has been reported in making these reactions catalytic in the metals.

We have found that the stoichiometric reaction of methane with mercuric triflate in triflic acid at 180°C results in an almost quantitative yield of methyl triflate based on added mercuric triflate (*20*). In this

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reaction, the mercuric triflate is reduced to mercurous triflate (no metallic mercury is observed) as shown in Eq. 3:

$$CH_4 + 2\ Hg(CF_3SO_3)_2 \rightarrow CF_3SO_3CH_3 + CF_3SO_3H + Hg_2(CF_3SO_3)_2 \quad (3)$$

The reaction was also found to proceed efficiently in 100% sulfuric acid to produce the corresponding methyl ester, methyl bisulfate. Moreover, in this solvent the reaction is catalytic in mercuric ions, with sulfuric acid playing the role of oxidant. The reaction stoichiometry is shown in Eq. 4:

$$CH_4 + 2\ H_2SO_4 \xrightarrow{Hg(II)} CH_3OSO_3H + 2\ H_2O + SO_2 \quad (4)$$

Consistent with this stoichiometry, the coproduction of sulfur dioxide was observed. The reaction is quite efficient and, to our knowledge, unprecedented. In batch reactions, methane conversions as high as 50% at 85% selectivity to methyl bisulfate (~43% yield; the major side product is carbon dioxide) and molar productivity rates of 10^{-7} mol cm^{-3} s^{-1} with Hg(II) turnover frequencies of 10^{-3} s^{-1} have been observed (*21*). Consistent with the high yield of methyl bisulfate, control experiments have shown that the rate of oxidation of methyl bisulfate by the Hg(II)–sulfuric acid system is less than the rate of oxidation of methane. The methyl bisulfate solution produced in the reaction can be readily hydrolyzed (Eq. 5) and the methanol can be isolated by distillation:

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4 \quad (5)$$

Gas chromatographic–mass spectrometric (GC-MS) analyses of isolated samples of methanol produced from ^{13}C-enriched methane confirmed that the methanol is produced from the oxidation of methane (and not some carbon-containing contaminant). Thallium(III), palladium(II), and the cations of platinum and gold have also been shown to oxidize methane in triflic and sulfuric acids to the corresponding methyl esters.

The conversion of methane to methanol with the concomitant reduction of sulfuric acid to sulfur dioxide (Eqs. 4 and 5) cannot, as such, be the basis for an economical synthesis of methanol. However, sulfuric acid is the single largest commodity chemical produced in the world today and is prepared from the oxidation of sulfur dioxide. Thus, the technology for the reoxidation of sulfur dioxide to sulfuric acid (through sulfur trioxide) with air (20% oxygen) is practiced on a large scale and is relatively inexpensive. By combining this step with reactions shown in Eqs. 4 and 5, a potentially practical process can be described. Such an integrated scheme is shown in Scheme 1.

Step 1

$$CH_4 + 2\ H_2SO_4 \xrightarrow{M} CH_3OSO_3H + 2\ H_2O + SO_2$$

Step 2

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4$$

Step 3

$$SO_2 + 1/2\ O_2 + H_2O \rightarrow H_2SO_4$$

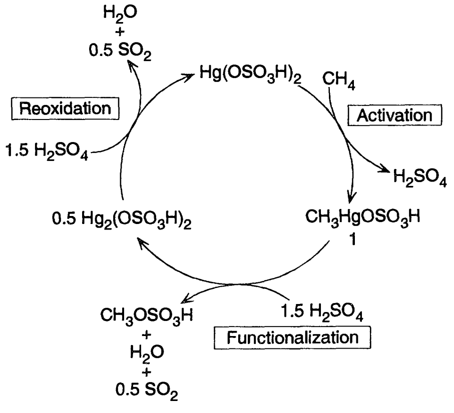
Net

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

Scheme 1.

In this scheme, sulfuric acid functions as an oxygen-atom transfer reagent. The net transformation of the established steps is the selective oxidation of methane to methanol with molecular oxygen. Compared to the typical 3% yields obtained for the gas-phase oxidation of methane to methanol (*6*), the ~43% methanol yield disclosed in this report represents a significant advance.

The catalyzed oxidation of methane by mercuric ions is a remarkably efficient reaction. Understanding the molecular basis for such a system would be valuable to the continuing search for even more efficient methane oxidation catalysts. Three key steps in the catalytic sequence have been established. The working model based on the available data is shown in Scheme 2.



Scheme 2.

The activation of methane is proposed to occur through a net electrophilic displacement reaction with mercuric bisulfate to produce methyl mercuric bisulfate, **1**. This species then decomposes to the product and the reduced species, mercurous bisulfate, in the functionalization step. In the reoxidation step, the mercurous bisulfate is oxidized by sulfuric acid, regenerating mercuric bisulfate.

In the activation step, an electrophilic displacement mechanism is assumed because of the similarity of this reaction to other electrophilic reactions involving hydrocarbons and metal electrophiles, such as the reactions of Pt(II) with alkanes (Eq. 2) and the well-established electrophilic substitution reaction of arenes with Hg(II) (Eq. 1). Thus, weakly basic counteranions to Hg(II) have been found to facilitate the reaction, whereas electron withdrawing groups substituted for a C–H bond on methane disfavored reaction. We have observed that methane activation occurs readily (in the corresponding acids) with the weakly basic and poorly coordinating anions, triflate and bisulfate, as counteranions to Hg(II). However, less activation is observed with the more basic and better coordinating acetate anion ($CH_3CO_2^-$). The observed lower rate of oxidation of methyl bisulfate and triflate compared to methane is also consistent with an electrophilic process (if we assume that the activation step is the slowest step in the overall oxidation). Bisulfate and triflate groups are electron withdrawing, and substitution of these groups for a C–H bond of methane would be expected to retard participation of the C–H bonds of these substituted species in electrophilic reactions. Processes involving free radicals are not considered likely based on the high selectivity of the reaction. Another possible mechanism, oxidative addition (*22*) to produce an intermediate Hg(IV) species, has been considered but is deemed unlikely because it would require participation and disruption of the stable $5d^{10}$ filled shell configuration of Hg(II).

Two pieces of evidence have been obtained for the involvement of the activation step as shown in Scheme 2 to produce methyl mercuric bisulfate, **1**. Direct observations of crude reaction mixtures by ^{13}C (and ^{199}Hg) nuclear magnetic resonance (NMR) spectroscopy show that **1** is present at a low steady-state concentration during the reaction with methane (Fig. 1). The use of ^{13}C-enriched methane confirms that this species is produced by reaction with methane and not by some contaminant. The identity of intermediate **1** was confirmed by comparison to a sample prepared independently by treatment of dimethyl mercury with one equivalent of sulfuric acid (Eq. 6):

$$Hg(CH_3)_2 + H_2SO_4 \rightarrow CH_3HgOSO_3H + CH_4 \quad (6)$$

Further evidence that **1** is produced by methane activation was provided by the reaction of CH_4 with $^2H_2SO_4$ in the presence of Hg(II). Under these conditions, deuterium incorporation into the CH_4 was observed by GC-MS analyses. This result

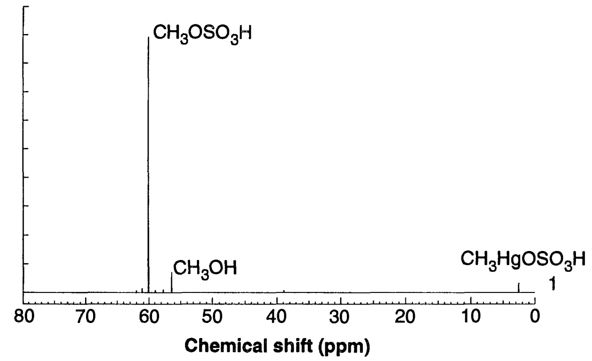


Fig. 1. The ^{13}C NMR spectrum of the crude reaction mixture resulting from the oxidation of $^{13}CH_4$ (100% enriched) with $Hg(OSO_3H)_2$ in H_2SO_4.

can be explained by the formation of **1** by methane activation with Hg(II), followed by deuterolysis of **1** to produce $CH_3{}^2H$ (Eq. 7):

$$CH_4 + Hg(II) \xrightarrow{-H^+} CH_3\text{–}Hg(II) \xrightarrow{^2H^+} CH_3{}^2H + Hg(II) \qquad (7)$$

Independent reactions of **1** with H_2SO_4 confirmed that protolysis, the microscopic reverse of the activation step, occurs at 180°C to produce $Hg(OSO_3H)_2$ and methane. These two sets of data provide strong evidence for the formation of **1** by the activation step proposed in Scheme 2. Our observations do not imply that $Hg(OSO_3H)_2$ is the species that activates methane. At this time, the identity of this species is unknown. However, a likely candidate is the solvated cation $[Hg(OSO_3H)]^+$, which is produced by autoionization of $Hg(OSO_3H)_2$ (*23*).

The evidence for the involvement of the functionalization step shown in Scheme 2 is straightforward and quite compelling. Independently synthesized methyl mercuric bisulfate, **1**, is quite stable in concentrated sulfuric acid at room temperature. However, at 180°C, **1** decomposes cleanly to methyl bisulfate, sulfur dioxide, mercurous bisulfate, and methane at a rate that is consistent with the intermediacy of **1** in Scheme 2. The evidence for the reoxidation step shown in Scheme 2 is also straightforward. Hot concentrated sulfuric acid is a powerful oxidant and was observed to rapidly oxidize mercurous bisulfate to mercuric bisulfate with the formation of sulfur dioxide.

The Hg(II)–sulfuric acid system described in this report provides important precedent that true catalytic systems can be developed for the selective, low-temperature, overall oxidation of methane to methanol. A novel use of sulfuric acid as an effective oxygen-atom transfer reagent for methane oxidation is also demonstrated. This work further demonstrates that the posttransition metal, isoelectronic d^{10} ions Hg(II) and Th(III) can be used for selective oxidation of methane. The catalytic Hg(II)–sulfuric acid system is well suited for study because the key intermediates can be synthesized and examined under controlled conditions. Few truly catalytic systems can be examined in such detail. Thus far, the strong evidence for intermediacy of methyl mercury species in the activation of methane adds credibility to the general supposition that the electrophilic, metal-mediated oxidation of alkanes can occur through intermediate alkyl metal species (*12*). The information gained from the discovery and study of this system should be useful in guiding the development of more efficient systems.

REFERENCES AND NOTES

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2. This is due to the low energy density of methane, 1344 kJ/liter (at 50 bar, 25°C), and the high cost of transportation by methods involving liquefaction or pipeline. For comparison, the energy density of methanol is 15,834 kJ/liter (under standard conditions).
3. The percent conversion is defined as $(\{[CH_4]_{initial} - [CH_4]_{final}\}/[CH_4]_{initial}) \times 100$; the percent selectivity to CH_3OH is defined as $([CH_3OH]/\{[CH_4]_{initial} - [CH_4]_{final}\}) \times 100$; and the percent yield is defined as (% conversion) × (% selectivity). Achieving high selectivity at 30% conversion is much more challenging than at low (<5%) methane conversion because as product builds up with increasing conversion it can become the preferred substrate for overoxidation. High conversions and selectivities are required to obtain the efficiencies of scale necessary for economical operation of large capital plants.
4. The 30% methane conversion and 85% selectivity represent conservative minimum requirements for a hypothetical process based on the direct conversion of methane to methanol with molecular oxygen. As the complexity of the process increases, it is expected that higher conversions and selectivities will be required for commercial economics. See N. D. Parkyns, *Chem. Br.* **9**, 841 (1990); G. J. Hutching and R. W. Joyner, *Chem. Ind.* **16**, 575 (1991); M. G. Poirier, A. R. Sanger, R. Alan, K. J. Smith, *Can. J. Chem. Eng.* **69**, 1027 (1991); J. M. Fox III, T. Chen, B. D. Degen, *Chem. Eng. Prog.* **86**, 42 (1990); E. E. Wolf, Ed., *Methane Conversion by Oxidative Processes: Fundamental and Engineering Aspects* (Van Nostrand Reinhold, New York, 1992).
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9. International application published under the Patent Cooperation Treaty, WO 92/14738.
10. "Electrophilic displacement" is used to describe a process involving the heterolytic cleavage of the C–H bond by formal displacement of a proton from a C–H bond: $M^{n+} + CH \rightarrow [M\text{–}C]^{(n-1)+} + H^+$.
11. This area has been reviewed by Shilov in (*12*) and by A. Sen, *Acc. Chem. Res.* **21**, 421 (1988).
12. A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes* (Reidel, Dordrecht, 1984).
13. Low conversion (<1%) mercury-photosensitized reactions of methane have been reported; R. R. Ferguson and R. H. Crabtree, *New J. Chem.* **13**, 647 (1989). This photochemical reaction occurs via the photoexcited $^3P_1$ state of mercury atoms and is unrelated to the work discussed in this report.
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15. The standard potential $E^0[Hg(II)/Hg(I)] = 0.9$ V; C. A. McAuliffe, *The Chemistry of Mercury* (Macmillan, London, 1977). These properties are a direct consequence of the high nuclear charge, large size, proximity of the *s* orbital to the nucleus, and the excellent shielding characteristics of the filled *d* shell electronic configuration of Hg(II), [Xe] $5d^{10}\ 6s^0$. Frontier orbital considerations indicate that the lowest unoccupied molecular orbital of Hg(II), the $6s^0$ atomic orbital, is both spatially and energetically well suited to interact with the highest occupied molecular orbital of CH_4.
16. "Activation" is used to describe a process where substitution of a stronger C–H bond (375 to 440 kJ/mol) occurs to produce a weaker metal-carbon bond (210 to 335 kJ/mol). "Functionalization" is used to refer to a process where the metal-carbon bond is replaced by any bond except a C–H bond.
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20. Reactions were carried out under 34.5 bar meth-

ane (containing 3% Ne as internal standard), at 180°C for 3 hours with 10 ml of triflic acid containing 2.0 mmol of mercury(II) triflate in a 50-ml high-pressure Autoclave Engineers Hastaloy-C reactor equipped with Desperi-Max gas liquid mixer. Quantitative analysis of the samples was challenging; GC analysis of the crude reaction mixtures was inadequate. Routine analyses were carried out with high-performance liquid chromatography to quantify the methanol produced by hydrolysis of a reaction aliquot. In selected cases, qualitative and quantitative ^{13}C NMR analyses of the crude reaction mixtures with acetic acid as an internal standard (added after reaction) were used to confirm the results. In reported cases, the mass balance on methane was >90%. This mass balance was obtained by accounting for unreacted methane, methyl bisulfate (as methanol after hydrolysis), and carbon dioxide. To obtain good mass balance, the methane-Ne mixture was dispensed from a known-volume, known-pressure reservoir. This procedure allowed the total moles of methane delivered to the reactor to be determined. The moles of methane remaining after reaction and carbon dioxide produced were determined by GC analysis of the gas phase by using Ne as an internal standard.

21. Reactions were carried out as described in (*20*) but with a 1-liter Hastaloy-C reactor and 300 ml of a 0.1 M solution of $Hg(OSO_3H)_2$ in 100% sulfuric acid. Higher selectivities were achieved at lower conversions. The selectivity was observed to decrease at higher conversions.
22. Oxidative addition of methane to Hg(II) would be formally described as involving the formation of methyl mercury(IV) hydride, $(CH_3)(H)Hg(IV)$.
23. An intriguing possibility is that a complex involving coordinated methane and solvated $[Hg(OSO_3H)]^+$ might be an intermediate on the reaction pathway to **1**. Such coordinated complexes have been proposed; see R. A. Periana and R. G. Bergman, *J. Am. Chem. Soc.* **108**, 7332 (1986).
24. We are deeply indebted to H. Taube, Marguerite Blake Wilbur Professor Emeritus at Stanford University and Scientific Advisor to Catalytica, Inc., for the insight and guidance provided during all phases of our investigation of selective methane oxidation. The results described here were obtained in the course of a joint research and development program among Petro-Canada, Techmocisco, Inc., a wholly owned subsidiary of Mitsubishi Oil Co., Ltd., and Catalytica, Inc.

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Production of Syngas by Direct Catalytic Oxidation of Methane

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The reaction between methane and oxygen over platinum and rhodium surfaces in metal-coated ceramic monoliths can be made to produce mostly hydrogen and carbon monoxide (greater than 90% selectivity for both) with almost complete conversion of methane and oxygen at reaction times as short as 10^{-3} seconds. This process has great promise for conversion of abundant natural gas into liquid products such as methanol and hydrocarbons, which can be easily transported from remote locations. Rhodium was considerably superior to platinum in producing more H_2 and less H_2O, which can be explained by the known chemistry and kinetics of reactants, intermediates, and products on these surfaces.

Natural gas is our most abundant, clean, and easily extractable energy source. However, most methane (CH_4) is in locations far from consumption sites, and its transportation is expensive as gas and hazardous as liquid or compressed gas. Therefore, it is desirable to convert methane into liquid products for more efficient utilization. The conventional route to liquid fuel production is through a syngas intermediate, a CO + H_2 mixture, which can then be easily reacted to form either methanol (CH_3OH) (*1*) over Cu/ZnO catalysts:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (1)$$

or to hydrocarbons through the Fischer-Tropsch process (*1*) over Fe and Ru catalysts:

$$nCO + 2nH_2 \rightarrow (CH_2)_n \qquad (2)$$

Syngas is typically produced by reacting CH_4 with H_2O at ~800°C to produce a mixture of CO, H_2, H_2O, and CO_2 in a process termed steam reforming (*1*):

$$CH_4 + H_2O \rightarrow CO, CO_2, H_2, H_2O \qquad (3)$$

The products are then converted into a 2:1 H_2/CO mixture (syngas) or into a H_2 + CO_2 mixture (hydrogen generation) by adding excess steam in the water gas shift reaction (*1*):

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4)$$

The conventional production of syngas or of H_2 therefore requires at least two reactors, a steam reformer and shifter, and excess CO_2 by-product is necessarily produced that must be vented. Residence times in each of these reactors are on the order of 1 s, so the size of a world-scale liquid fuel plant is very large.

An alternative method to produce hydrocarbons, particularly ethylene, is oxidative coupling (*2, 3*), in which CH_4 and O_2 flow over a mixed oxide catalyst which produces gaseous CH_3 radicals that ultimately form ethane and ethylene. Although this process is a topic of active research, it currently is limited by either low conversion of CH_4 or low selectivity to hydrocarbon products. Several publications have also appeared in which CO and H_2 are produced with only CH_4 and O_2 reactants (*4–9*). These processes were thought to involve first the oxidation of CH_4 primarily to H_2O, CO, and CO_2 followed by reaction of CH_4 with H_2O (reaction 2) and the water gas shift reaction (reaction 4), giving fairly long reactor residence times of 0.01 to 1 s. In fact, some H_2 may be formed initially in those experiments by the direct oxidation reaction (*5*). However, because the catalyst and reaction conditions are not optimized for this reaction, the formation of syngas by the direct oxidation reaction is not believed to be the primary route of H_2 generation (*4–9*).

We have produced syngas in nearly a 2:1 ratio by the direct catalytic oxidation of CH_4:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (5)$$

by using oxygen or air over Pt or Rh surfaces and feed gases near room temperature in a single monolith reactor with extremely short residence times. This reaction is entirely a surface process because homogeneous reaction in flames requires a combustible reactant mixture and would proceed by free-radical intermediates, thus generating very little H_2.

It is, of course, very surprising that combustion of CH_4 in O_2 should produce H_2 because: (i) the H_2 + O_2 reaction is very fast at high temperatures, either homoge-

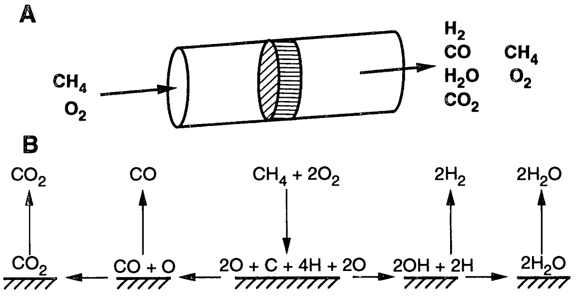

Fig. 1. (**A**) Sketch of the experimental reactor. (**B**) Schematic illustration of the adsorption, desorption, and surface reaction steps for which whose kinetic parameters are given in Table 1 and for which energies are shown in Fig. 3.

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