New developments in the photocatalytic conversion of methane to methanol

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Abstract

Investigation of direct conversion of methane to transportation fuels has been an on-going effort at FETC for over 14 years. One of our current areas of research is the conversion of methane to methanol, under mild conditions, using light, water, and a semiconductor photocatalyst. Research in our laboratory is directed toward adapting the chemistry developed for photolysis of water to that of methane conversion. The reaction sequence of interest uses visible light, a doped tungsten oxide photocatalyst and an electron transfer molecule to produce a hydroxyl radical. Hydroxyl radical can then react with a methane molecule to produce a methyl radical. In the preferred reaction pathway, the methyl radical then reacts with an additional water molecule to produce methanol and hydrogen. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Methane may be produced as a by-product of coal gasification, either in a stand-alone process or as part of the direct or indirect liquefaction of coal. Depending on the gasifier design and operating conditions, up to 18% of the total gaseous product may be methane. In addition, there are vast proven reserves of geologic methane in the world. A global research effort is underway in academia, industry, and government to find methods to convert methane to useful, more readily transportable and storable materials. Methanol, the initial product of methane oxidation, is a desirable product of conversion because it retains much of the original energy of the methane while satisfying transportation and storage requirements. A liquid at room temperature, methanol could be transported to market using the existing petroleum pipeline and tanker network and distribution infrastructure. Methanol may be used directly as a fuel or may be converted to other valuable products (i.e. other transportation fuels, fuel additives, or chemicals). At present, the direct oxidation of methane to methanol suffers from low methane conversion and poor selectivity to methanol. A process for the direct oxidation of methane to methanol, with high yield and high selectivity, is desirable.

A long-term goal of our research group is to explore and evaluate novel pathways for the direct conversion of methane to liquid fuels, chemicals, and intermediates. One of our current areas of research, the conversion of methane to methanol, under mild conditions, using light, water, and a semiconductor photocatalyst is the topic of this report. The use of three relatively abundant and inexpensive reactants — light, water, and methane — to produce methanol is an attractive process option. The products of the reaction of interest, methanol and hydrogen, are both commercially desirable as fuels or chemical intermediates. Research in our laboratory is directed toward applying the techniques developed for the catalytic photolysis of water

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$$(1)\ H_2O \xrightarrow[\lambda < 185\ nm]{h\nu} H_2 + \tfrac{1}{2}O_2$$

$$(2)\ H_2O \qquad \tfrac{1}{2}H_2 + \bullet OH$$

$$(3)\ CH_4 + \bullet OH \qquad CH_3\bullet + H_2O$$

$$(4)\ CH_3\bullet + H_2O \qquad CH_3OH + \tfrac{1}{2}H_2$$

Scheme

[1,2] and the photochemical conversion of methane to methanol [3,4]. The main advantage of using a photocatalyst to promote the photoconversion of methane to methanol is that the presence of the catalyst, in conjunction with an electron transfer agent, allows the reaction to occur in the presence of visible light instead of ultraviolet (UV) light. This greatly simplifies reactor design and permits flexibility in the selection of the light source.

2. Background

It has been reported [1,2] that methane may be photochemically converted to methanol by first sparging it through a heated (~90°C) water bath, in order to saturate it with water vapor, and then exposing it to ultraviolet light at a wavelength of 185 nm in a quartz photochemical reactor. The suggested reaction pathway, shown in Scheme 1, proposes the initial production of hydroxyl radical through photolysis of water. This radical may then react with a methane molecule to produce methyl radical. In the preferred reaction, the methyl radical then reacts with another water molecule to produce methanol and hydrogen. Catalytic photolysis of water to hydrogen and oxygen occurs during irradiation of liquid water with visible light (at wavelengths longer than 410 nm) in the presence of a solid photocatalyst suspended in the solution (Scheme 2) [5]. The photolytic sequence of interest initially produces a hydroxyl radical through the reaction of water in the presence of a doped tungsten oxide photocatalyst and an electron transfer molecule, methyl viologen dichloride hydrate (1,1′-dimethyl-4,4′-bipyridinium dichloride). The proposed mechanism invokes the coupling of two hydroxyl radicals to form hydrogen peroxide, which de-

$$(1)\ La/WO_3 \xrightarrow[\lambda \geq 410\ nm]{h\nu} e^-_{CB} + h^+_{VB}$$

$$(2)\ e^-_{CB} + MV^{2+} \longrightarrow MV\bullet^+$$

$$(3)\ h^+_{VB} + H_2O \longrightarrow H^+ + \bullet OH$$

$$(4)\ MV\bullet^+ + H^+ \qquad \tfrac{1}{2}H_2 + MV^{2+}$$

$$(5)\ 2\bullet OH \longrightarrow H_2O_2 \longrightarrow \tfrac{1}{2}O_2 + H_2O$$

band, h^+_{VB} = positive hole in valance band

Scheme 2.

$$(1)\ La/WO_3 \xrightarrow[\lambda \geq 410\ nm]{h\nu} e^-_{CB} + h^+_{VB}$$

$$(2)\ e^-_{CB} + MV^{2+} \longrightarrow MV\bullet^+$$

$$(3)\ h^+_{VB} + H_2O \longrightarrow H^+ + \bullet OH$$

$$(4)\ MV\bullet^+ + H^+ \longrightarrow \tfrac{1}{2}H_2 + MV^{2+}$$

$$(5)\ CH_4 + \bullet OH \longrightarrow CH_3\bullet + H_2O$$

$$(6)\ CH_3\bullet + H_2O \longrightarrow CH_3OH + \tfrac{1}{2}H_2$$

e^-_{CB} = electron in conduction band, h^+_{VB} = positive hole in valance band

Scheme

composes to water and oxygen. The use of a semiconductor allows an electron in the filled electron level to be promoted, across the forbidden band, to the conduction band when a photon of the proper energy strikes the surface. This electron is then available for reaction.

By combining these reactions [6], hydroxyl radicals, generated with the photocatalyst and the electron transfer reagent, should react with methane to produce methyl radicals. In our proposed reaction pathway (Scheme 3), methyl radicals react with an additional water molecule to form methanol and hydrogen, identical to Scheme 1.

3. Experimental

The reactor, a commercially supplied quartz photochemical reaction vessel, was fitted to meet the needs of this research [7]. This included use of a Teflon-coated magnetic stirring bar in the reactor, a fritted glass sparger, a nitrogen line used to cool the

UV lamp, an injection port, and a Pyrex® UV filter. Deionized water was distilled prior to use.

3.1. Photochemical conversion of methane

In the first series of experiments, the reactor was filled with 1 l of deionized-distilled water heated to 90°C by an external recirculating, thermostated bath. The feed gas consisted of helium and methane with flows of 16.00 and 5.00 ml/min, respectively. The gases were introduced to the reactor through a fritted-glass sparger. A Teflon®-coated magnetic stir bar was used to assist in dispersion of the gases in the solution. This configuration is a modification to the one reported in the literature [1]. All gases were heated to 80°C prior to entering the reactor. The gas stream was irradiated with a high-pressure, quartz, mercury-vapor lamp. The exit gas stream was analyzed by an on-line quadrupole mass spectrometer capable of distinguishing between methanol and dioxygen, both of which exhibit a parent peak at 32 AMU. All streams exiting the reactor were passed through a cold trap operating at 0°C prior to being vented.

3.2. Catalytic photolysis of water

The semiconductor photocatalysts were synthesized following the procedure in the literature [4] with minor modifications to the procedure. Four dopants, copper, lanthanum, platinum, and a mixture of copper and lanthanum, were selected for study on the tungsten oxide catalyst base. The catalysts were sintered in quartz boats under a flow of helium using a ramp and soak profile.

In a typical photocatalytic experiment, 1.0000 g of the sintered catalyst is suspended, by mechanical stirring, in water (~750 ml containing 0.0450 g of an electron-transfer reagent, methyl viologen dichloride. Helium (16 ml/min) is sparged through the photocatalytic reactor. The helium is an internal standard for on-line analysis of the reactor effluent. The reaction temperature is maintained at ~94°C by circulation of heated (~120°C) silicone oil in the outer jacket of the reactor. A high-pressure mercury-vapor quartz lamp is used as the light source. The spectral characteristics and energy output of the lamp, supplied by the lamp's manufacturer, show that ~46% of the radiated energy of the (UV) lamp used in this study is in the visible region. The outer surface of the lamp is cooled by a stream of nitrogen gas, while the lamp's immersion well is cooled by a flow of tap water. The gaseous products of reaction are analyzed on-line and in real-time by a quadrupole mass spectrometer. Liquid products are condensed from the gas stream at 0°C and analyzed using a HP 5890A capillary gas chromatograph

3.3. Photocatalytic conversion of methane

The rector configuration described for catalytic photolysis of water above was also used for the following experiments with the exception that the gas feed was a mixture of methane (5 ml/min) and helium (16 ml/min). For use in the last series of experiments, a UV filter, consisting of Pyrex® glass, was constructed to fit around the mercury-vapor lamp. The absorption spectrum reveals that radiation below ~310 nm is absorbed by the filter, removing the UV component from the reaction.

4. Results

4.1. Photochemical conversion of methane

Conversion of methane rapidly increases to >97% after the UV lamp is turned on. After ~3 min, methane conversion decreases rapidly (during the next 3 min) to ~10%, followed by a slow (~12 h) drop to 0%. The production of methanol follows a similar pattern, offset in time from the methane conversion peak by the sweep volume of the reactor.

The rapid drop off in conversion of methane was puzzling until the reactor temperature was plotted with conversion data (Fig. 1). We observed a correlation between methane conversion and reactor temperature. When the temperature of the reactor dropped below ~80°C, conversion of methane and production of methanol sharply decreased. The drop in reactor temperature was the result of the cooling of the UV lamp by passing cold tap water (~17°C) through the immersion well jacket. In the reactor configuration used in these experiments, the reactor was heated to 90°C

[1] Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

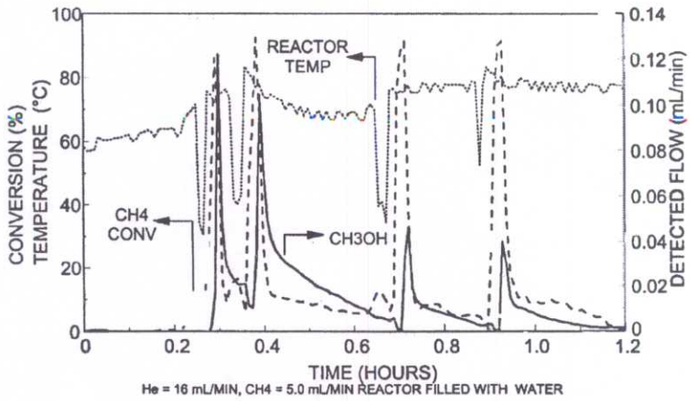

Fig. Typical results of photochemical conversion of methane.

by the external circulating bath and the reactants were passed through the reactor. When steady state flow and temperature conditions had been achieved, lamp cooling water was allowed to flow through the immersion well jacket and the UV lamp was turned on. The cooling effect of the water in the immersion well jacket not only compensated for heat produced by the UV lamp, but also overwhelmed the reactor's external circulating heater. Attempts to minimize the temperature difference between the lamp cooling water and the reactor had limited success. The use of heated water (~40°C) in the immersion well jacket without additional lamp cooling resulted in a lamp life on the order of several minutes. The use of a larger capacity external circulating bath solved the problem and allowed us to control the temperature of the reactor and compensate for the lamp's cooling water effects.

During experiments where the reactor temperature was maintained at 97°C during the run, conversions of methane remain relatively constant at ~4% and production of hydrogen, methanol, oxygen, and carbon monoxide remain constant during the experiment. The large oscillations previously observed in the conversion of methane and the production of methanol were not observed during these experiments.

4.2. *Catalytic photolysis of water*

Four doped tungsten oxide catalysts (noted above) were synthesized and used in this study. The catalysts were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). For all catalysts, except the platinum-doped tungsten oxide, these techniques were not able to detect any differences between the tungsten oxide, as received, and the unsintered-doped oxide. This is due to the level of doping, ≤ 4 atom percent, which is below the detection limits of these instruments. The sintering process produced differences that were detectable by SEM and XRD. After sintering, XRD data showed the doped tungsten oxides to be more crystalline than the unsintered materials as evidenced by the separation of a broad diffraction peak into two separate peaks having 2θ values of 28.8° and 42.0° [7]. Analysis of the sintered, doped tungsten oxides by SEM revealed that the sintered materials contained larger crystallites with smoother edges.

The catalysts were each tested for their ability to catalytically photolyze water prior to their use in the methane conversion experiments. We were able to reproduce photolysis results reported in the literature [4] using these catalysts under similar conditions.

4.3. *Photocatalytic conversion of methane*

All of the following experiments were conducted with the photocatalyst suspended in water and the electron transfer agent in the reactor. Fig. 2 shows the results of a typical photocatalytic methane conversion

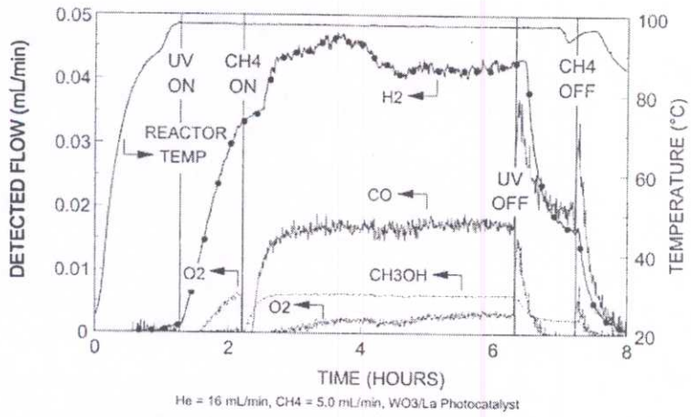

Fig. 2. Typical results of photocatalytic conversion of methane.

experiment. Methane conversions are ~4% with hydrogen, methanol, and carbon monoxide as the main products of reaction. Note that after the UV lamp is turned off, the detected flow of methanol decreases slowly to zero (over ~2 h). This is due to stripping of dissolved methanol from the water in the reactor by the reactant gases.

Gas chromatographic analysis of the liquid product that had condensed in the trap at 0°C revealed the presence of methanol and acetic acid. Further analysis to identify other components by GC-MS was not possible due to the low concentration of products in the trap. The products were diluted by water carried over from the reactor in the flow of helium that is used as an internal standard.

As noted previously, the proposed reaction sequence of interest initially produces a hydroxyl radical, which then reacts with methane to produce methanol. To test the validity of this hypothesis, a 30% solution of hydrogen peroxide, a good source of hydroxyl radicals, was injected into the reactor during photocatalytic methane conversion. Fig. 3 (a different photocatalyst preparation than shown in Fig. 2) shows results typical of the hydrogen peroxide solution injection experiments.

After injection of hydrogen peroxide solution, methane conversion increases from ~4% to ~10%, methanol production increases 17-fold, and carbon dioxide increases fivefold, along with modest increases in hydrogen and carbon monoxide production. Introduction of hydroxyl radicals to the reactor leads to a greater fraction of product going to methanol as evidenced by methane conversion increasing 2.5 times, whereas methanol production increases 17 times. The increase in carbon dioxide is from 'deep' oxidation of methane and/or further oxidation of the carbon-containing products. Note the drop in methane conversion to zero for approximately 12 min after injection of the hydrogen peroxide solution. Prior to injecting hydrogen peroxide solution, a steady-state condition existed between the methane dissolving in the water and methane being consumed. It is likely that the introduction of excess hydroxyl radicals depleted the dissolved methane. At the temperature where the reactions were conducted, the solubility of methane in water is 0.017 ml of methane per ml of water [8]. This resulted in little methane available for conversion until steady-state conditions could be re-established.

Four doped tungsten oxide photocatalysts were prepared: platinum, lanthanum, copper, and a 50/50 molar mixture of copper and lanthanum. These catalysts were tested for catalytic activity against a blank experiment, where all reaction conditions were identical except, that in the blank, no catalyst was present. Fig. 4 displays the results for these experiments. After steady-state conditions for the reactions were established (the reactor was at operating temperature and was being irradiated by the UV lamp), methane flow was started. In Fig. 4 the production of methanol as

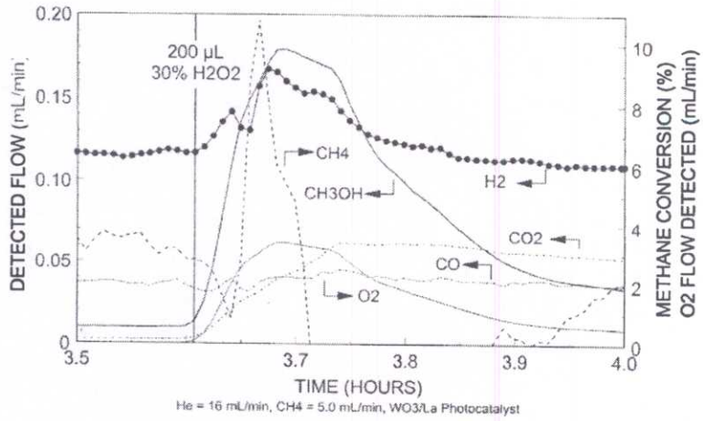

Fig. 3. Results of hydrogen peroxide addition.

a function of time is displayed. As shown in this figure, the lanthanum doped catalyst exhibits an increase in methanol production over the non-catalytic reaction. The platinum and lanthanum/copper doped catalysts exhibit approximately the same production of methanol as the non-catalytic reaction. The presence of copper on tungsten oxide inhibits the production of methanol.

Prior to the introduction of methane to the reactor, the non-catalytic reaction produces the most hydrogen. The catalyzed systems that produce hydrogen in significant quantities are the lanthanum and the lanthanum/copper doped catalysts. After methane flow begins, the lanthanum catalyst exhibits a larger increase in hydrogen production than the non-catalyzed system.

The results of the addition of 200 µl of 30% hydrogen peroxide solution to the reactor converting methane under steady-state conditions is shown in Fig. 5. All of the catalysts exhibited greater peak production of methanol than the non-catalytic reaction after injection of hydrogen peroxide solution. The lanthanum-doped catalyst exhibited the largest increase of all catalysts with the copper-doped catalyst exhibiting the least. The effects on the production of hydrogen were not as dramatic as those observed for

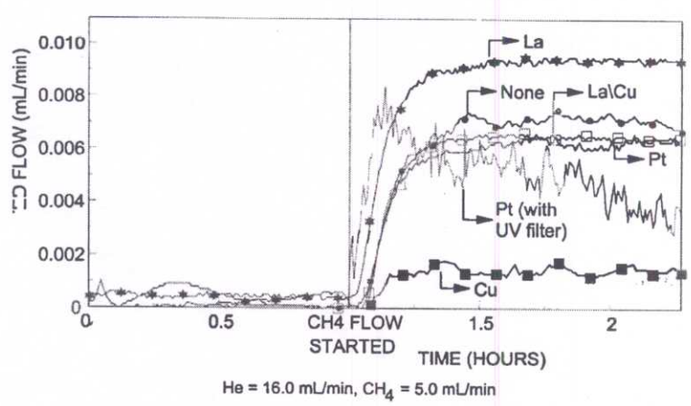

Fig. 4. Methanol production from doped WO_3.

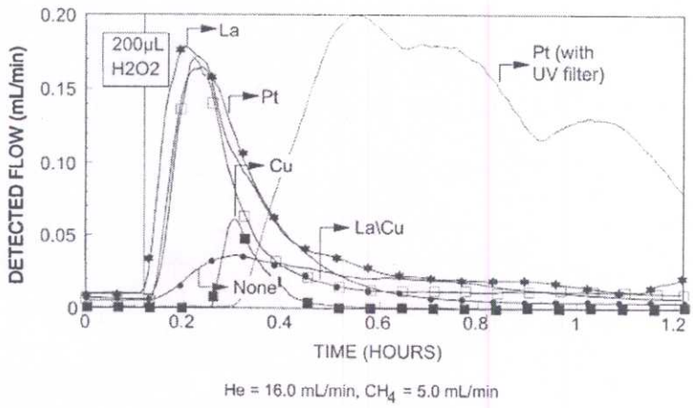

Fig. 5. Methanol production from doped WO_3.

methanol production with hydrogen peroxide solution injection. All reactions in the presence of catalysts exhibited a slight increase in hydrogen production while the non-catalytic reaction exhibited a decrease in hydrogen production until the hydrogen peroxide was consumed.

4.4. Photocatalytic conversion of methane with visible light

As noted previously, the photocatalyst is reported to function at wavelengths >410 nm. All results reported above were obtained using the UV lamp's total spectrum output In order to separate reactions initiated by radiation with UV light from reactions initiated by visible light, a filter was constructed to block the UV portion of the lamp's energy output. The filter, a Pyrex® sleeve fitted around the lamp, absorbs nearly all radiation below ~310 nm (Fig. 6). Note that the total energy output of the lamp with the filter installed is ~50% of that without the filter.

Experiments using the filter around the lamp were conducted under conditions described above. The results of a typical experiment are shown in Fig. 7. Note that hydrogen production is observed ~3 min after the lamp is turned on. Methanol, carbon monoxide

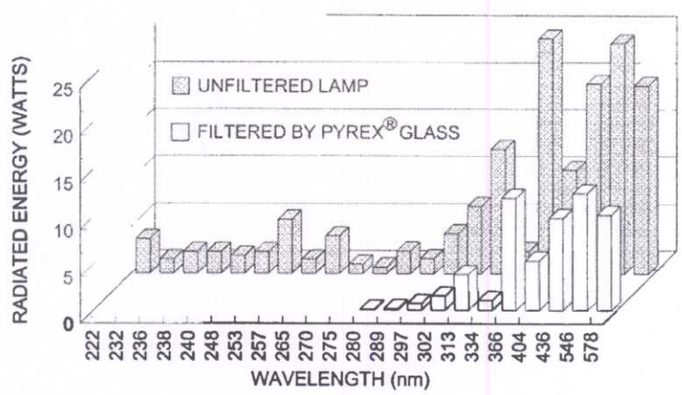

Fig. 6. High-pressure quartz mercury-vapor lamp spectral energy distribution.

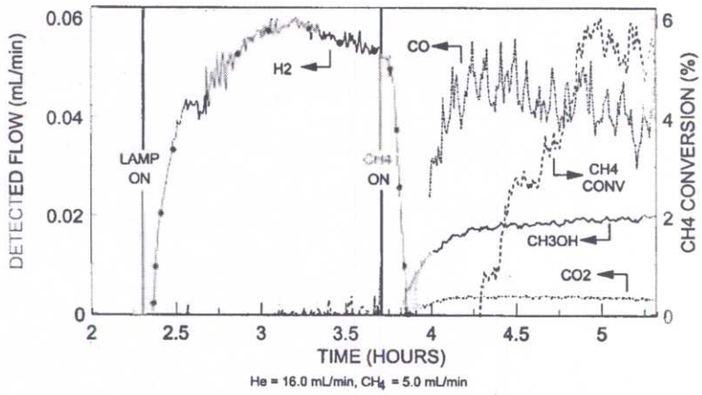

Fig. 7. Typical results of photocatalytic methane conversion, Pyrex® filter installed.

and carbon dioxide are detected ~6 min after methane flow is started. Also note that hydrogen production decreases rapidly after the flow of methane is started. Methane conversion leveled off at ~5.5%. The addition of 200 μl of 30% hydrogen peroxide solution after the reaction had reached steady-state conditions is shown in Fig. 8. After addition of the hydrogen peroxide solution, production of methanol increased 25-fold, carbon dioxide production increased 50-fold, and methane conversion peaked at 9%.

As mentioned above, the filter decreases the energy output of the lamp by ~50%. We would expect a corresponding decrease in conversion of methane and production of products if the lamp's energy output was the limiting factor in the experiment. Comparison of reactions using the full spectrum and only the visible region of the lamp are shown in Figs. 4 and 5. These experiments were conducted using the same WO_3/Pt semiconductor catalyst. Under steady-state conditions, conversion of methane and production of products, with the exception of hydrogen production, are identical. When the UV filter is employed (Fig. 4), hydrogen production decreases to zero after the flow of methane is started, where as for the unfiltered lamp, production of hydrogen decreases after methane flow is started but levels off at ~0.01 ml/min. Experimental

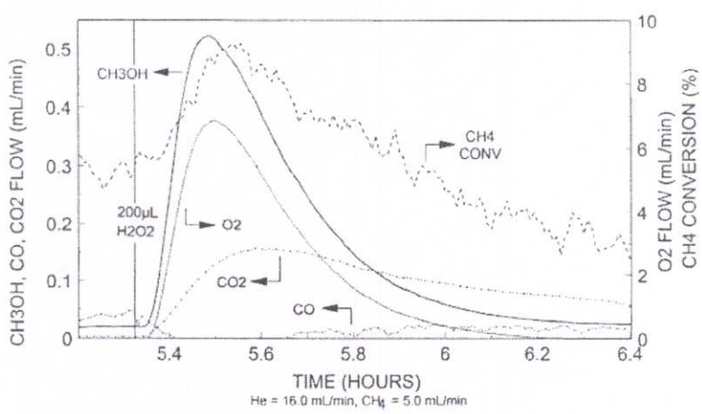

Fig. 8. Typical results of hydrogen peroxide addition, Pyrex® filter installed.

data suggests that the difference in hydrogen production is due to the UV component of the lamp. Addition of 200 μl of 30% hydrogen peroxide solution (Fig. 5) gave similar results between the two lamps. The main exception was the significantly greater production of oxygen in the filtered experiment.

5. Conclusions

We have reproduced the results reported in the literature for both methane photolysis and catalytic photolysis of water. In experiments that combine elements of both systems, methane and water have been converted to methanol, hydrogen, and acetic acid by a doped semiconductor photocatalyst at temperatures of ~94°C and atmospheric pressure.

Under the conditions used in these experiments, the photocatalytic reaction produced 1.7 g of methanol-per gram of catalyst-per hour in the steady-state mode and produced 43 g of methanol-per gram of catalyst-per hour when hydrogen peroxide solution was added.

The use of a filter removed the UV component from the lamp. Experimental results show that little difference between the filtered and unfiltered lamp was observed in the case of the platinum-doped tungsten oxide sample. This indicates that the photocatalyst is operating using visible light, the UV portion of the lamp's output is negligible in the photocatalytic conversion of methane to methanol, and that a limiting factor in conversion may be the solubility of methane in water.

In all experiments, conversion of methane and the production of methanol are augmented by the addition of hydrogen peroxide solution, consistent with the postulated mechanism that invokes a hydroxyl radical as an intermediate in the reaction sequence. The use of other radical initiators would be of interest to determine if the enhanced conversion could be sustained.

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