PHOTOCATALYTIC CONVERSION OF METHANE TO METHANOL

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INTRODUCTION

Methane is produced as a by-product of coal gasification. Depending upon reactor design and operating conditions, up to 18% of total gasifier product may be methane. In addition, there are vast proven reserves of geologic methane in the world. Unfortunately, a large fraction of these reserves are in regions where there is little local demand for methane and it is not economically feasible to transport it to a market. There is a global research effort under way 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 utilizing 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). Currently, the direct oxidation of methane to methanol suffers from low methane conversion and poor methanol selectivity. A process for the direct oxidation of methane to methanol, in high yield and with high selectivity, is desirable.

Investigation of direct conversion of methane to transportation fuels has been an ongoing effort at PETC for over 10 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. The use of three relatively abundant and inexpensive reactants, light, water, and methane, to produce methanol, is attractive. Research in our laboratory is directed toward applying the techniques developed for the photocatalytic splitting of water[1,2] and the photochemical conversion of methane.[3,4]

OBJECTIVE

A long-term goal of our research group is the exploration of novel pathways for the direct oxidation of methane to liquid fuels, chemicals, and intermediates. The use of three relatively abundant and inexpensive reactants, light, water, and methane, to produce methanol is attractive. The products of reaction, methanol and hydrogen, are both commercially desirable, methanol being used as is or converted to a variety of other chemicals, and the hydrogen could be utilized in petroleum and/or chemical manufacturing.

BACKGROUND

It has been reported that methane may be converted to methanol, in a strictly photochemical reaction, 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 proposed reaction pathway, shown in Scheme 1, suggests initial production of hydroxyl radical. 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 an insoluble solid (Scheme 2).[3] The photolysis 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. The proposed mechanism invokes the coupling of two hydroxyl radicals to form hydrogen peroxide, which then decomposes to hydrogen and oxygen.

By combining these reactions, it should be possible to react hydroxyl radicals, generated with the photocatalyst and electron transfer reagent, 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.

Previous research by our group has confirmed literature reports[1,2] that it is possible to photolyze methane, saturated with water vapor, to produce methanol and hydrogen. In a modification of the above experiment, we were also able to photolyze methane sparged through a photochemical reactor filled with water. Recently, we began investigating the photocatalytic conversion of methane in water.

EXPERIMENTAL

The reactor, a commercially supplied quartz photochemical reaction vessel, was fitted to meet the needs of this research (Figure 1). 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, and an injection port. Deionized water was distilled prior to use.

The semiconductor photocatalysts were synthesized following a modification of the procedure in the literature[4]. Four dopants, copper, lanthanum, platinum, and a mixture of copper and lanthanum, were selected for study. After sintering, the catalyst is suspended, by mechanical stirring, in water (~750 mL) containing an electron-transfer reagent, methyl viologen dichloride hydrate. A mixture of methane (5 mL/min) and helium (16 mL/min) is sparged through the photocatalytic reactor. Helium is used as an internal standard for on-line analysis of the reactor effluent. Temperature of the reaction is maintained at ~94°C by circulation of heated (~120°C) silicon oil in the outer jacket of the reactor. Irradiation is accomplished by a high-pressure mercury-vapor quartz lamp. The spectral characteristics and energy output of the lamp are displayed in Figure 2. 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 by gas chromatography.

RESULTS

The first series of experiments were conducted with no catalyst in the reactor. During these experiments, an unexpected temperature dependance of the reaction was observed; photoconversion of methane decreased sharply with temperature and was not observed below ~70°C (Figure 3). Several experiments were performed where the temperature of the reactor was allowed to cycle between 60°C and 95°C. In all experiments, as the temperature of the reactor decreased, conversions of methane and the production of methanol decreased. The effect was reversible; when the reactor temperature increased above ~70°C, conversion of methane and the production of methanol increased.

The drop in reactor temperature in the above experiments was a result of the cooling water for UV lamp overpowering the capacity of the external circulating heater. The cooling water, supplied from the tap, is circulated through the UV lamp immersion jacket. When the UV lamp is turned on, the cooling water flow also begins, removing heat from the lamp and, unavoidably, the reactor, resulting in relatively large temperature excursions. Replacement of the heater with one of larger capacity, addition of a nitrogen cooling line, and a decrease in water flow permitted control of temperature to within 1°C throughout the reaction.

Four doped tungsten oxide catalysts were synthesized and used in this study. The catalysts were analyzed by scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), x-ray diffraction (XRD), and electron spectroscopy for chemical analysis (ESCA). 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 because the level of doping, ~4 atom percent, is below the detection limits of these instruments. The sintering process produced differences that were detectable by SEM and XRD. After sintering, XRD data show 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 2-theta values of 28.8° and 42.0° (Figure 4). Analysis of the sintered, doped tungsten oxides by SEM revealed that the sintered materials contained larger crystallites with smoother edges.

SEM and EDS analysis of the platinum-doped tungsten oxide photocatalyst after sintering showed the presence of platinum particles on the surface of the tungsten oxide. Figure 5 is a "back-scatter" photomicrograph of the sintered, platinum-doped tungsten oxide photocatalyst (the bright spheres are platinum). Analysis of the sintered platinum-doped tungsten oxide by ESCA (Figure 6) revealed that the platinum on the surface is Pt^0.

The catalysts were 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.

Figure 7 shows the results of an typical photocatalytic methane conversion experiment. Methane conversions are ~4% with hydrogen and methanol as the main products of reaction. Gas chromatographic analysis (Figure 8) of the liquid product, condensed at 0°C, revealed the presence of methanol and acetic acid. The peak at 41.854 minutes in the GC trace was not able to be identified. Further analysis, in an attempt to identify the component 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 by the helium that is used as an internal standard.

As noted previously, the proposed reaction sequence of interest initially produces hydroxyl radical which then reacts to produce methanol. To test the validity of this sequence, a 30% solution of hydrogen peroxide, a good source of hydroxyl radicals, was injected into the reactor during photocatalytic methane conversion. Figure 9 shows the results typical of the peroxide injection experiments. After peroxide injection, conversion of methane increases from ~4% to ~10%. Methanol production increases 17 fold, and carbon dioxide increases 5 fold, along with modest increases in hydrogen and carbon monoxide.

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. Conversion of methane and the production of methanol are augmented by the addition of hydrogen peroxide, indicating that hydroxyl radical is an intermediate.

FUTURE PLANS

Research during the next fiscal year will be focused on developing the photocatalyst. Studies on the effect of radical propagation/initiators on the reaction will also investigated.

ACKNOWLEDGMENT

We would like to acknowledge the technical assistance of Richard R. Anderson, John Baltrus, J. Rodney Diehl, Elizabeth A. Frommell, Neil Johnson, Donald V. Martello, and Joseph P. Tamilia.

DISCLAIMER

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.

REFERENCES

1. Ogura, K.; Kataoka, M. *J. Mol. Cat.* **1988**, *43*, 371-79.
2. Ogura, K.; Migita, C.T.; Fujita, M. *Ind. Eng. Chem. Res.* **1988**, *27*, 1387-1390.
3. Ashokkumar, M.; Maruthamuthu, P. *J. Mat. Sci. Lett.* **1898**, *24*, 2135-2139.
4. Maruthamuthu, P.; Ashokkumar, M. *Int. J. Hydrogen Energy* **1989**, *14(4)*, 275-277.

SCHEME 1. Catalytic Photolysis of Water

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

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

MARUTHAMUTHU, P.; ASHOKKUMAR, M.; GURUNATHAN, K.; SUBRAMANIAN, E.; SASTRI, M.V.C. *INT. J. HYDROGEN ENERGY* 1989, *14(8)*, 525-8.

SCHEME 2. Photochemical Conversion of Methane

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

(2) $H_2O \xrightarrow[\lambda \geq 185\ nm]{h\nu} \frac{1}{2} H_2 + {\bullet}OH$

(3) $CH_4 + {\bullet}OH \longrightarrow CH_3{\bullet} + H_2O$

(4) $CH_3{\bullet} + H_2O \longrightarrow CH_3OH + \frac{1}{2} H_2$

OGURA, K.; KATAOKA, M. *J. MOL. CATAL.* 1988, *43*, 371-9.

SCHEME 3. Photocatalytic Conversion of Methane

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

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

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

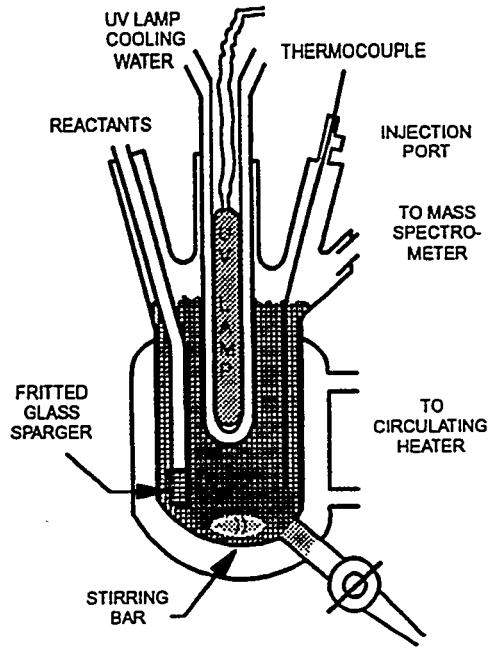

FIGURE 1. Schematic of Photocatalytic Reactor

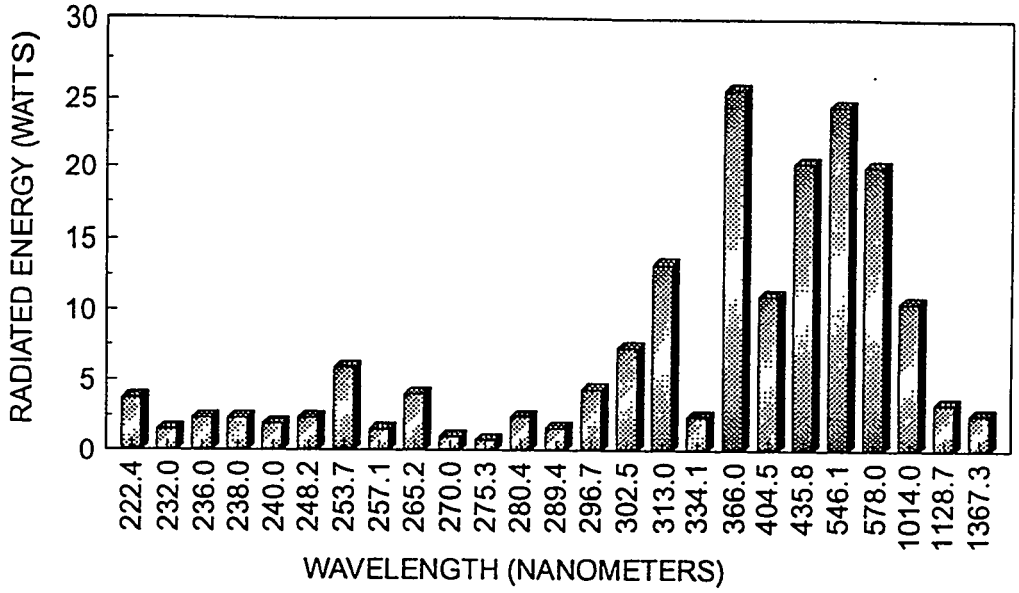

FIGURE 2. High-Pressure Quartz Mercury-Vapor Lamp Spectral Energy Distribution

Ace Glass Inc. Data Sheet

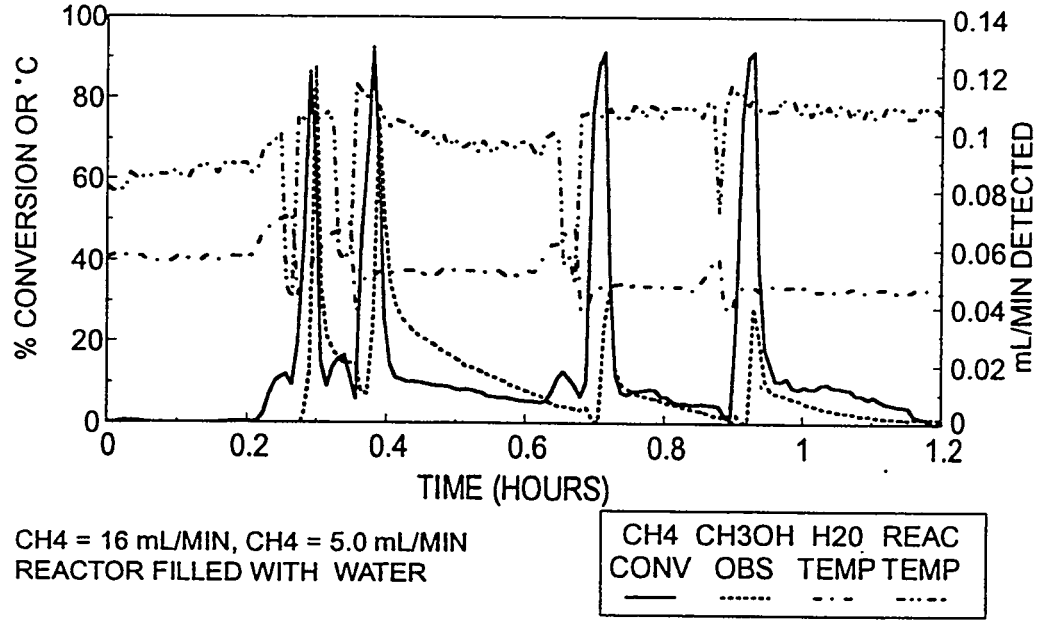

FIGURE 3. Temperature Dependence of Methane Photoconversion Reaction

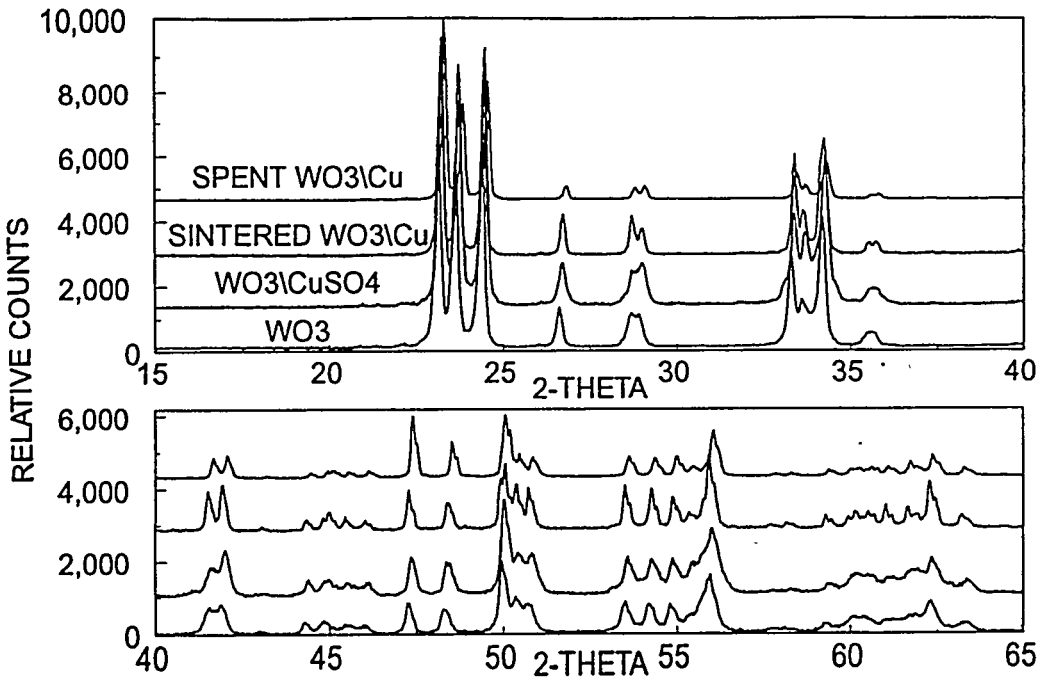

FIGURE 4. X-ray Spectra of Copper-Doped Photocatalysts

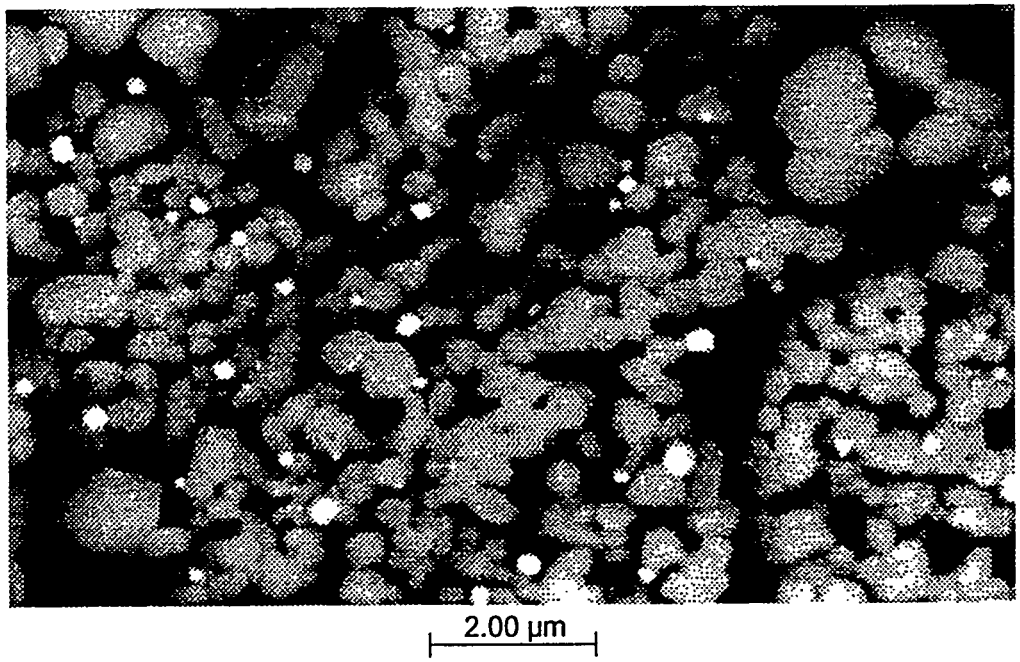

FIGURE 5. Backscatter SEM of WO_3\Pt Photocatalyst

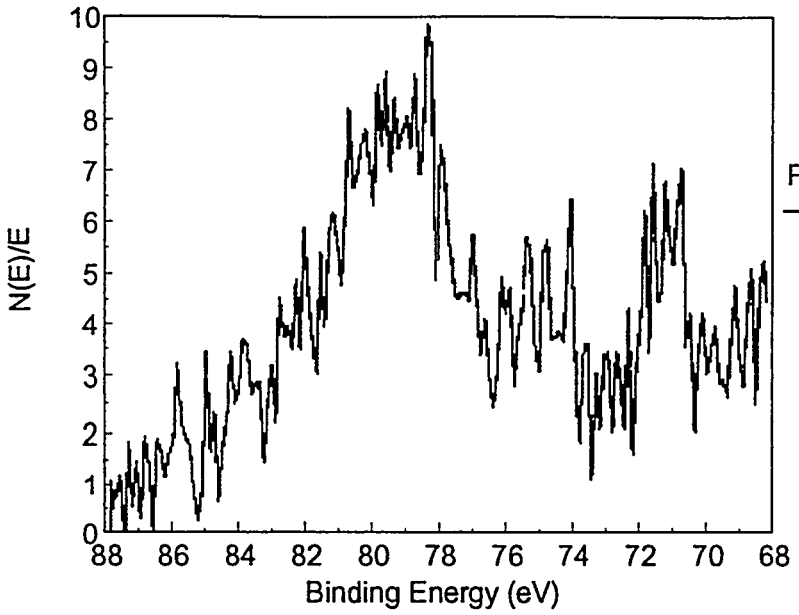

FIGURE 6. ESCA Survey of WO_3\Pt Photocatalyst

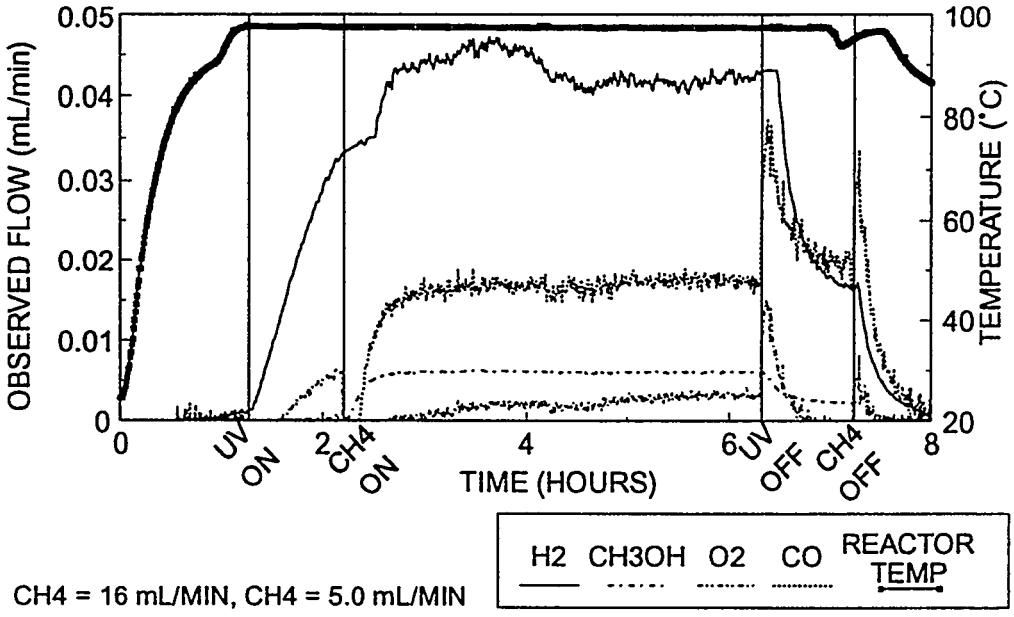

FIGURE 7. Typical Results of Photocatalytic Methane Conversion

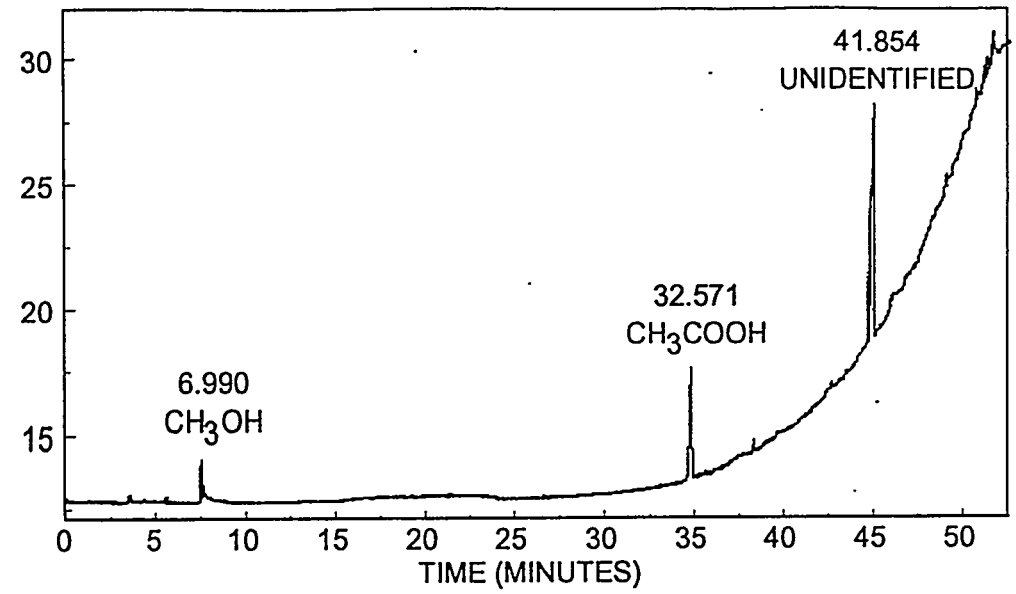

FIGURE 8. GC of Condensed Liquid Product

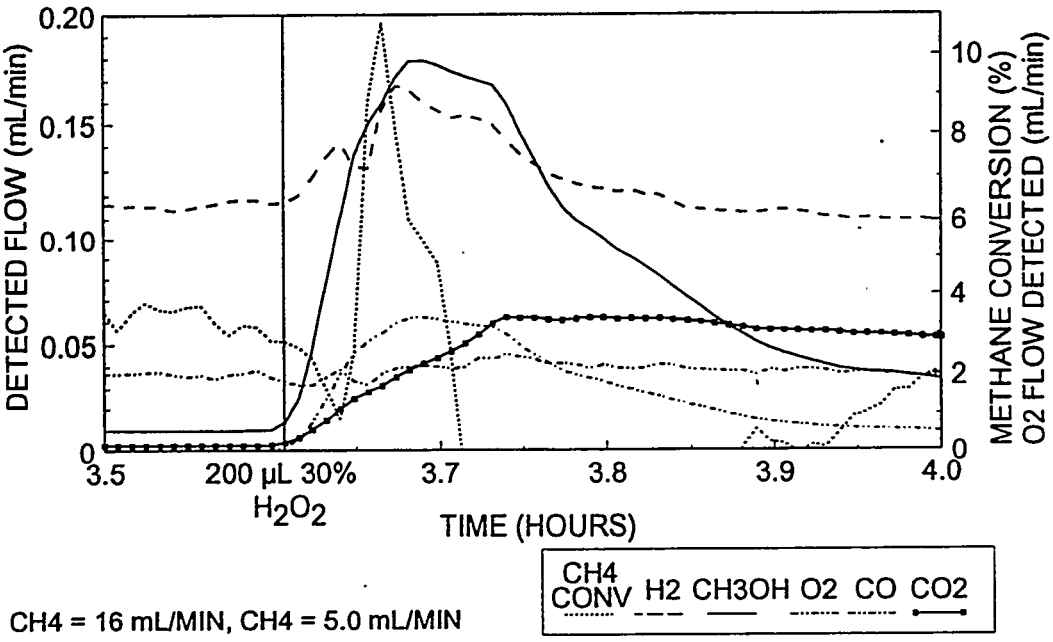

FIGURE 9. Results of Hydrogen Peroxide Addition