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Photocatalytic conversion of methane

Richard P. Noceti, Charles E. Taylor *, Joseph R. D'Este

U.S. Department of Energy, Pittsburgh Energy Technology Center, P.O. Box 10940, Pittsburgh, PA 15236-0940, USA

1. Introduction

Methane is 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 upon 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. Unfortunately, a large fraction of these methane reserves are in regions having little local demand and where it is uneconomical to transport it to a market. A global research effort is 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 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 methanol selectivity. A process for the direct oxidation of methane to methanol, in high yield and with high selectivity, is desirable.

Investigation of the 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 an attractive process option. Research in our laboratory is directed toward applying the techniques developed for the catalytic photolysis of water [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 reaction to occur with visible light instead of with ultraviolet. This greatly simplifies reactor design and will permit flexibility in the selection of the light source.

2. Objective

A long-term goal of our research group is to explore novel pathways for the direct conver-

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* Corresponding author. Tel.: +1 412 8926058; fax: +1 412 8924152; E-mail: ctaylor@orion.petc.doe.gov

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$$
\begin{aligned}
&(1)\ H_2O \xrightarrow[\lambda\ \geq 185\ \text{nm}]{h\nu} H_2 + \tfrac{1}{2}O_2\\
&(2)\ H_2O \xrightarrow[\lambda\ \geq 185\ \text{nm}]{h\nu} \tfrac{1}{2}H_2 + {\bullet}OH\\
&(3)\ CH_4 + {\bullet}OH \longrightarrow CH_3^{\bullet} + H_2O\\
&(4)\ CH_3^{\bullet} + H_2O \longrightarrow CH_3OH + \tfrac{1}{2}H_2
\end{aligned}
$$

Scheme 1. Photochemical conversion of methane.

sion of methane to liquid fuels, chemicals, and intermediates. The use of three abundant and inexpensive reactants – light, water, and methane – to produce methanol is attractive. The products of the reaction of interest, methanol and hydrogen, are both commercially desirable as fuels or chemical intermediates. The object of this research is to develop a method for the production of methanol and hydrogen using water, methane, and visible light.

3. 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 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 (1,1′-dimethyl-4,4′-bipyridinium dichloride). The proposed mechanism invokes the coupling of two hydroxyl radicals to form hydrogen peroxide, which decomposes to water and oxygen.

$$
\begin{aligned}
&(1)\ La/WO_3 \xrightarrow[\lambda\ \geq 410\ \text{nm}]{h\nu} e^-_{CB} + h^+_{VB}\\
&(2)\ e^-_{CB} + MV^{2+} \longrightarrow MV{\bullet}^+\\
&(3)\ h^+_{VB} + H_2O \longrightarrow H^+ + {\bullet}OH\\
&(4)\ MV{\bullet}^+ + H^+ \longrightarrow \tfrac{1}{2}H_2 + MV^{2+}\\
&(5)\ 2{\bullet}OH \longrightarrow H_2O_2 \longrightarrow \tfrac{1}{2}O_2 + H_2O
\end{aligned}
$$

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

Reference 5.

Scheme 2. Catalytic photolysis of water.

By combining these reactions, it should be possible to react hydroxyl radicals, generated with the photocatalyst and the 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, identical to Scheme 1.

Previous research by our group [6] has confirmed literature reports [1,2] that it is possible to photolyze methane, saturated with water va-

$$
\begin{aligned}
&(1)\ La/WO_3 \xrightarrow[\lambda\ \geq 410\ \text{nm}]{h\nu} e^-_{CB} + h^+_{VB}\\
&(2)\ e^-_{CB} + MV^{2+} \longrightarrow MV{\bullet}^+\\
&(3)\ h^+_{VB} + H_2O \longrightarrow H^+ + {\bullet}OH\\
&(4)\ MV{\bullet}^+ + H^+ \longrightarrow \tfrac{1}{2}H_2 + MV^{2+}\\
&(5)\ CH_4 + {\bullet}OH \longrightarrow CH_3^{\bullet} + H_2O\\
&(6)\ CH_3^{\bullet} + H_2O \longrightarrow CH_3OH + \tfrac{1}{2}H_2
\end{aligned}
$$

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

Scheme 3. Photocatalytic conversion of methane.

por, 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.

4. Experimental

The reactor, a commercially supplied quartz photochemical reaction vessel, was fitted to meet the needs of this research (Fig. 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 on the tungsten oxide catalyst base. In a typical experiment, the sintered catalyst is suspended, by mechanical stirring, in water (~ 750 ml) containing an electron-transfer reagent, methyl viologen dichloride. A mixture of methane (5 ml/min) and helium (16 ml/min) is sparged through the photocatalytic reactor. The helium is an internal standard for online 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 are displayed in Fig. 2. Note 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 by gas chromatography.

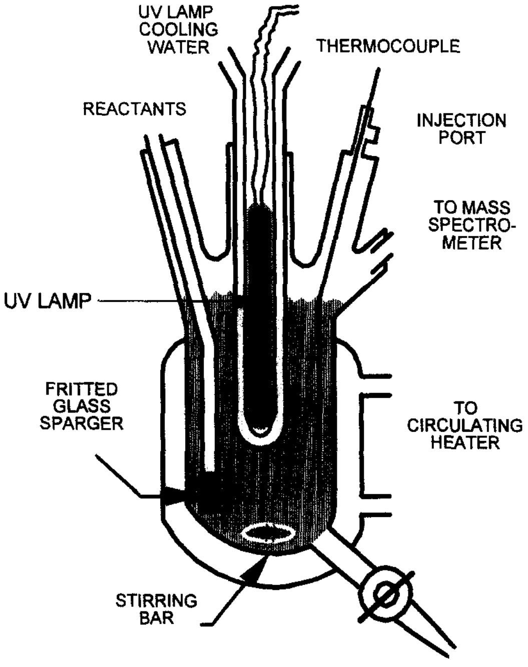

Fig. 1. Schematic of photocatalitic reactor.

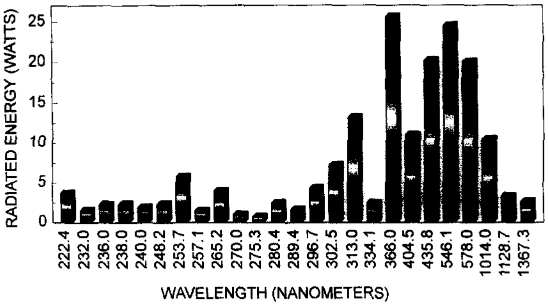

Fig. 2. High-pressure quartz mercury-vapor lamp spectral energy distribution.

5. Results

The first series of experiments was conducted with no photocatalyst in the reactor. During these experiments, a temperature dependence of the reaction was observed; photoconversion of methane decreased sharply with decreased temperature and was not observed below ~ 70°C. This observation implies that a non-photochemical process is part of the reaction sequence.

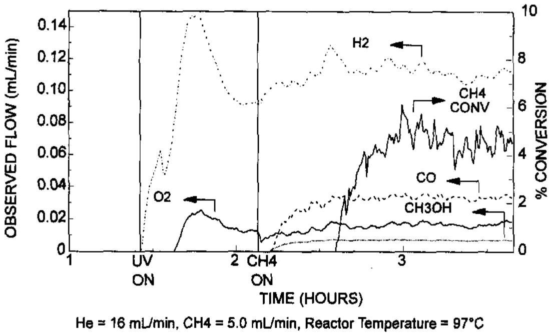

Fig. 3. Typical results of noncatalytic methane photoconversion.

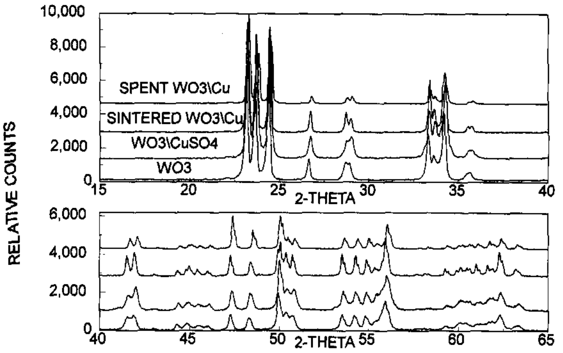

Fig. 4. X-ray spectra of copper-doped photocatalysts.

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 and were not observed below ~ 70°C. The effect was reversible; when the reactor temperature increased above ~ 70°C, conversion of methane and the production of methanol resumed and increased with temperature.

Fig. 3 shows the result of an experiment without photocatalyst where the reactor temperature was maintained at 97°C during the run. Note that conversions of methane remain relatively constant at ~ 4% and production of hydrogen, methanol, oxygen, and carbon monoxide remain constant during the experiment.

The four doped tungsten oxide catalysts (noted above) 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 at%, 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 2-theta values of 28.8° and 42.0° (Fig. 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. Fig. 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 (Fig. 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

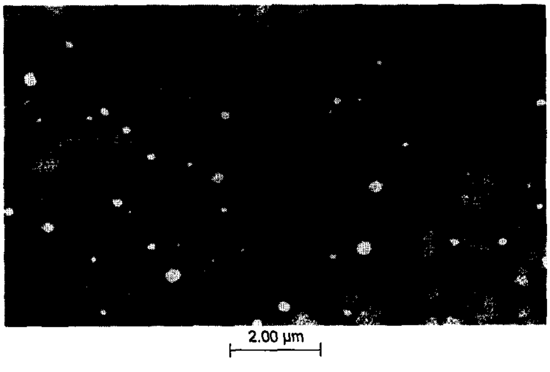

Fig. 5. Backscatter SEM of WO_3 /Pt photocatalyst.

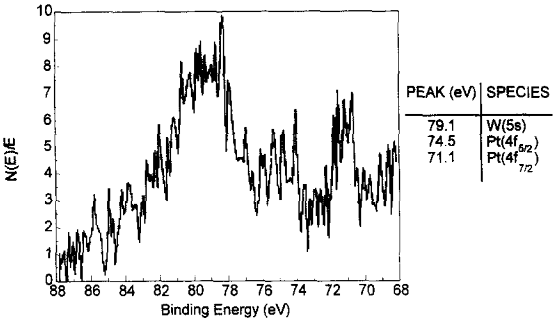

Fig. 6. ESCA survey of WO_3 /photocatalyst.

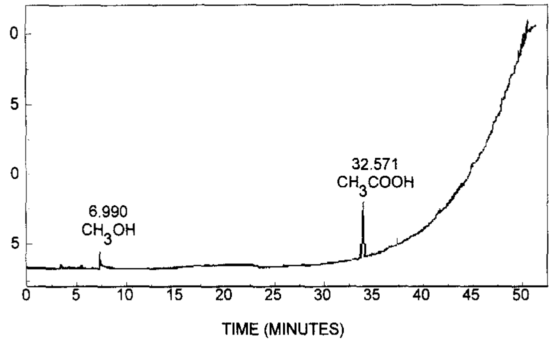

Fig. 8. GC of condensed liquid product.

the literature [4] using these catalysts under similar conditions.

All of the following experiments were conducted with the photocatalyst and electron transfer agent in the reactor. Fig. 7 shows the results of a typical photocatalytic methane conversion experiment. Methane conversions are ~ 4% with hydrogen and methanol 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). It was hypothesized that this behavior was due to stripping of methanol from the water in the reactor by the reactant gases. To confirm this, methanol was injected into the reactor, previously filled with 750 ml water at the operating temperature, and the concentration of methanol in the gas flow from the reactor was measured. Behavior similar to the reaction experiment was observed.

Gas chromatographic analysis (Fig. 8) of the liquid product that had condensed at 0°C revealed the presence of methanol and acetic acid. The peak at 41.854 min in the GC trace was not identified. Further analysis 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 flow of helium that is used as an internal standard. Analysis of subsequent samples from the cold trap showed the presence of methanol and acetic acid only.

As noted previously, the proposed reaction sequence of interest initially produces 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. 9 (a different catalyst preparation than Fig. 7) shows the results typical of the peroxide injection experiments. After peroxide injection, conversion of methane increases from

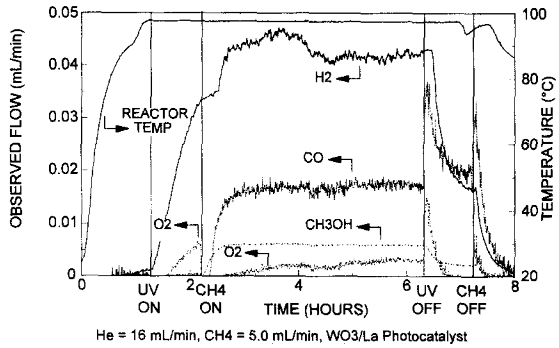

Fig. 7. Typical results of photocatalytic methane conversion.

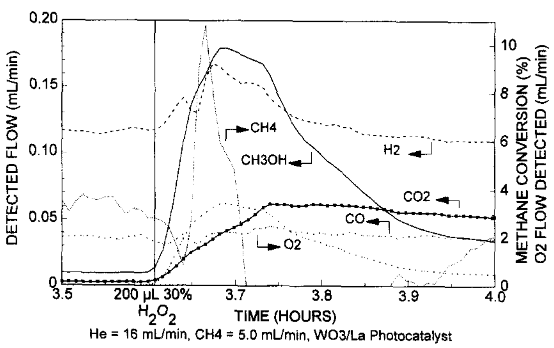

Fig. 9. Results of hydrogen peroxide addition.

~4% to ~10%, methanol production increases 17 fold, and carbon dioxide increases 5 fold, along with modest increases in hydrogen and carbon monoxide. 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. Prior to injection of hydrogen peroxide, 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. This resulted in little methane was available for conversion until steady-state conditions could be reestablished.

6. 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, consistent with the postulated mechanism that proposes hydroxyl radical as an intermediate in the reaction sequence.

7. Future plans

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

8. 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.

Acknowledgements

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