

CARBON DIOXIDE REDUCTION FROM HYDRATE PHASE ADSORBED ON METAL OXIDE PHOTOCATALYSTS

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ABSTRACT

It has been described that irradiation of CO₂ hydrate with visible light in the presence of activated zinc oxide as a photocatalyst, induces a photochemical reaction between CO₂ and water that leads to the formation of CH₃OH and CH₄ through a formic acid intermediate. This process is thought to be favored by the clathrate hydrate structure of the reagents (CO₂ and water). However, yields were quite low for any prospective industrial applications.

The present work relates to an improvement of this photochemical method by exploiting the known hydrate-promoting properties of some classes of surface-active molecules, such as the anionic surfactants sodium dodecylsulfate (SDS) and linear alkyl benzene sulfonates (LABSA). Conversion reactions were conducted into a stainless steel reactor provided with a thermostating jacket, gas inlets and outlets, and a quartz window, which was charged with either water or an aqueous solution of promoter (e.g., anionic surfactant), and activated metal oxide catalyst (e.g., ZnO). Contents of the reactor were then irradiated from a 50 W halogen lamp through the quartz window, and reactions were conducted for variable times of one to several hours. After each reaction, the gaseous headspace was sampled into a balloon. Results of analysis show that CO₂ conversion rates to CH₄ are measurably higher in the presence of a hydrate promoter.

Keywords: gas hydrates, carbon dioxide reduction, methane, photocatalysis, hydrate promoters

NOMENCLATURE

LABSA Linear Alkyl Benzene Sulfonic Acid (and salts thereof)
SDS Sodium Dodecylsulfate

INTRODUCTION

Utilization of carbon dioxide is a global issue due to the continuous increase in atmospheric CO₂ concentrations. Among the factors hindering the development of technologies for CO₂ utilization are the high costs of CO₂ capture, separation, purification, etc., and the energy requirements of chemical or physical conversion to useful molecules.[1] One recent approach to carbon dioxide sequestration involves its capture into clathrate hydrates, with subsequent storage in sub-sea fields with or without concurrent recovery of

natural gas.[2] It has been described [3] that irradiation of CO₂ hydrate with visible light in the presence of activated zinc oxide as a photocatalyst induces a photochemical reaction between CO₂ and water that leads to the formation of CH₃OH and CH₄ through a formic acid intermediate. This process is thought to be favored by the *clathrate hydrate* structure of the reagents (CO₂ and water). However, reported yields are quite low for any prospective industrial applications. Furthermore, the mechanisms are unknown and, generally, the background literature is virtually *nil*.

The present work relates to an attempt to understand and improve this photochemical method by exploiting the known hydrate-promoting properties [4] of some classes of surface-active molecules, such as the anionic surfactants sodium dodecylsulfate (SDS) and linear alkyl benzene sulfonates (LABSA). Interest

in hydrate promotion by surfactants has been increasing due to their large effects on formation kinetics. However, the supramolecular basis of such effects are still debated.[5,6] Meanwhile, attempts are under way to modulate the structure of surfactant molecules to gain both stronger effects (as promoters or inhibitors, respectively) and deeper knowledge.[7,8] Also, promotion of CO₂ hydrate by surfactants has recently been reported.[9]

In the present work, conversion reactions were conducted into a stainless steel reactor which was charged with aqueous solutions of promoters (e.g., anionic surfactant), and activated metal oxide catalyst (e.g., ZnO). The reactor was then pressurized with CO₂ gas up to 2-3 MPa, and cooled down to 0-10°C. Once the formation of CO₂ hydrate has been visually ascertained, light was irradiated from a 50 W halogen lamp through a quartz window, and reactions were conducted for variable times. After each reaction, the gaseous headspace was analyzed to show that CO₂ conversion rates to CH₄ are measurably higher in the presence of a hydrate promoter.

EXPERIMENTAL

1. Apparatus

Experiments were conducted into a pressurized vessel (Figure 1) made of AISI 321 stainless steel with an internal volume of 500 ml, fitted with AISI 316L tubing and fittings (Swagelok Co.). The reactor is provided with a jacket for circulating cooling fluid from a Julabo F12 thermostat, with a service temperature range of 0 to 90°C. The reactor is connected to a gas cylinder through a two-gauge pressure regulator (SOL SpA) with a downstream gauge range of 0 to 60 bar.

A large-diameter, high-pressure quartz window (SICO Technology GmbH, Bleiberg-Kreuth, Germany; satisfies EN 10204) is mounted into the reactor bottom and allows to visually monitor the progress of the reaction inside the reactor, and to irradiate the catalyst/hydrate slurry inside.

Water solutions inside the reactor were allowed to cool down to the preset temperature (0 to 5°C), then the reactor was pressurized with carbon dioxide (>99.5%, Rivoira, Italy). Experiments were conducted in triplicate to minimize errors due to the stochastic nature of hydrate nucleation.

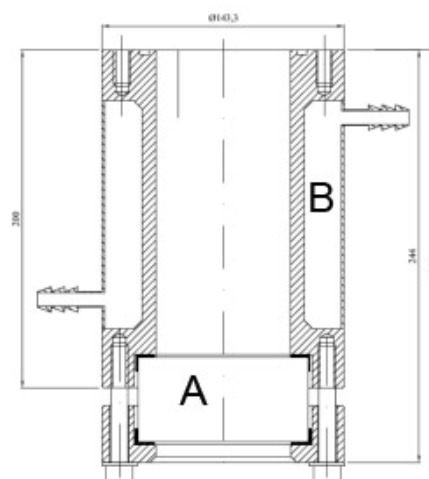
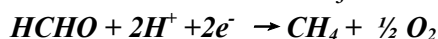
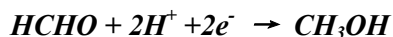
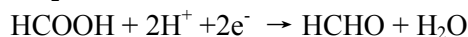
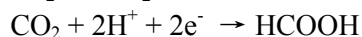
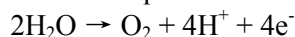


Figure 1 High-pressure reactor. A: quartz window; B: cooling jacket.

2. Photocatalyst

Zinc oxide (ACS, >99.0%, Sigma-Aldrich, Italy) was used as a photocatalyst. Before use, it was activated by heating into a muffle furnace set at 400°C for 4 hrs. This activation process is believed to create local gradients of surface regions poor in oxygen atoms and rich in Zn²⁺ ions, and surface regions where such a defective lattice barely exists.[3] Those surface gradients are believed to give rise to the reaction of water to give oxygen, protons and electrons, which in turn react with CO₂ to give formic acid and formaldehyde intermediates. Formaldehyde is then reduced to methanol and methane, according to the following balanced equations:



3. Promoters

Surfactant promoters used were the well-known sodium dodecyl sulfate (SDS; >98%, Fluka) and

linear alkyl benzene sulfonic acid (LABSA; >96%, Ronas Chemical, China).

4. Gas Analysis System

The gas analysis system is composed by two IR sensors specific for CO₂ and CH₄, respectively (Dynament, UK). These produce an electrical signal (tension, Volts) which is proportional to the concentration of CO₂ or CH₄, respectively, into the gas stream. The sensor for CH₄ has a measuring range of 0-100% with 0.1% resolution and 2% precision. The sensor for CO₂ has a measuring range of 0-100% with 1% resolution and 1% precision. These sensors were wired into a processor-controlled board for data acquisition. Processor (Arduino, arduino.cc) and wirings were programmed and built by RDPower (RDPower s.r.l., Terni, Italy). Data from the sensors were obtained as % of CO₂ and CH₄, the relation being: %CH₄ = 100 - %CO₂.

5. Experimental procedure

The general experimental procedure was as follows: the reactor was charged with 50 ml MilliQ water and 50 g ZnO (previously activated as described above, and kept under vacuum). The reactor flange was screwed close. The slurry was stirred at 250 rpm by means of a magnetic stir bar, and the temperature was controlled to a set value (0.5-5°C) through a water-glycol cooling system (Julabo F12). The reactor was then pressurized with CO₂ from the cylinder and through a high-pressure line (Swagelok, Nordival, Italy), and pressure values were controlled in the range of 2-3 MPa by acting on a pressure regulator provided with pressure gauge (Swagelok, Nordival, Italy). At this point, the system is under hydrate forming conditions, and after a variable induction time has elapsed, formation of CO₂ hydrate crystals is observed visually through the quartz window. A variable formation time is then allowed (see below), and then, irradiation with a 50 W halogen lamp is conducted through the window for variable times in the range of 1-3 hrs. Following irradiation, CO₂ gas in the headspace is vented, cooling is stopped and hydrate is left melting to release guest molecules. Gases resulting from hydrate dissociation are then supplied to the gas analysis system via a micrometric valve which allows to supply a very low flow rate to the sensors. The entire process was carried out under N₂ into a flexible dry box.

RESULTS AND DISCUSSION

First, control experiments were conducted outside the hydrate stability zone (HSZ) with promoter (*i*, *ii*), and without a promoter but within the HSZ (*iii*). Control experiments were conducted as follows:

(*i*) *low temperature, ambient pressure*

300 ppm SDS, formation time: 2h, irradiation time: 3h.

Table 1:

Temperature, °C	% CH ₄ max*
2.0	ND
1.0	ND

*As compared to moles of CO₂; ND = not detected (below the detection limit of IR sensor).

(*ii*) *room temperature (20 °C), high pressure*

300 ppm SDS, formation time: 2h, irradiation time: 3h.

Table 2:

Pressure, bar	% CH ₄ *
20	ND
30	ND

* As compared to moles of CO₂; ND = not detected (below the detection limit of IR sensor).

(*iii*) *Without promoter*

formation time: 2h, irradiation time: 3h; CO₂ pressure: 30 bar.

Table 3:

Temperature, °C	% CH ₄ *
2.0	2.1
1.0	2.4

* As compared to moles of CO₂

As is clear from the control experiments, irradiation outside the HSZ is poorly effective in reducing carbon dioxide to methane. Due to the detection limit of the sensors, however, we cannot rule out that formation of methane in low amounts is also possible under those conditions. Table 3 shows that a detectable amount of methane is formed also with no promoter added, which is a first support to the importance of hydrate formation in the photoreduction of CO₂.

To test hydrate effects further, we varied temperature, hydrate formation time and irradiation time, pressure, and promoter (SDS and LABSA).

(*iv*) *effect of temperature, formation time, and*

promoter

300 ppm SDS; formation time, 1h, irradiation time: 3h; CO₂ pressure: 30 bar.

Table 4:

Temperature, °C	% CH ₄ *
5.0	4.2
4.0	4.6
3.0	5.8
2.0	6.6
1.0	6.4

* As compared to moles of CO₂

Table 5: As in Table 4, but formation time is 2h

Temperature, °C	% CH ₄ *
5.0	4.6
4.0	5.0
3.0	6.5
2.0	7.2
1.0	6.9

* As compared to moles of CO₂

Table 6: As in Table 4, but formation time is 3h

Temperature, °C	% CH ₄ *
5.0	4.5
4.0	5.1
3.0	6.4
2.0	7.3
1.0	7.0

* As compared to moles of CO₂

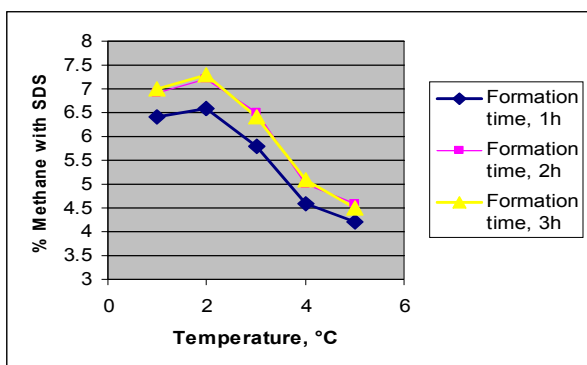


Figure 2: Methane % yields with SDS at different formation times

Table 7: 300 ppm LABSA, formation time, 1h; irradiation time, 3h; CO₂ pressure, 30 bar.

Temperature, °C	% CH ₄ *
5.0	5.0
4.0	5.6
3.0	6.9
2.0	7.8
1.0	7.8

* As compared to moles of CO₂

Table 8: as in Table 7, except formation time is 3h.

Temperature, °C	% CH ₄ *
5.0	5.2
4.0	5.8
3.0	7.0
2.0	8.3
1.0	8.1

* As compared to moles of CO₂

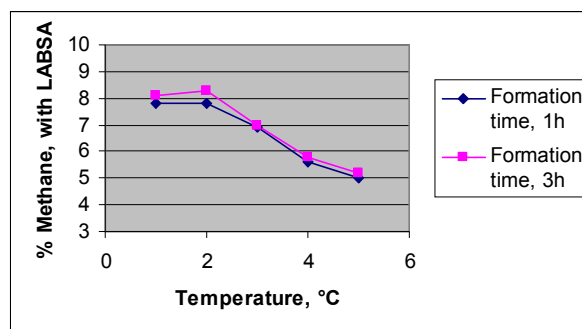


Figure 3: Methane % yields with LABSA at different formation times

Based on the above results, some discussion is in order. First, we found that hydrate formation is essential for any photoreduction of CO₂ to take place. In fact, experiments conducted outside the hydrate region for CO₂ reveal no methane formation within the detection limit of our sensors. Secondly, CO₂ hydrate formation with no promoter added was conducive to a certain (very limited) methane production, which hints to a fundamental role of hydrate in the optimization of electron and proton transfer to CO₂ for the formation of a formic acid intermediate.

On the other hand, promotion of hydrate formation, as caused by SDS and LABSA, strongly increases the CH₄ yields. While the mechanisms underlying this effect are still not clear, we may hypothesize that promoted hydrates have higher occupancy than non-promoted ones, and this might lead to a greater concentration of “immobilized” CO₂ onto the catalyst surface.

As relates to the other parameters scrutinized, it suffices to say that the higher the formation or irradiation time, the higher the yield of methane produced, except for a levelling of the conversion yields when formation times exceed 2 hrs.

This preliminary work shows in a straightforward manner that CO₂ reduction to CH₄ is feasible by using appropriate combinations of activated photocatalysts, hydrate-forming conditions, and well-known commercial surfactants as hydrate promoters. Work is in progress for the synthesis and characterization of novel hydrate promoters that might give rise to higher conversion yields to CH₄. In fact, energy balance calculations (to be published elsewhere) show that conversion yields of 20-25% (depending on the compression and refrigeration techniques adopted) would represent a feasible target to a net positive energy balance.

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