Enhancement of CH$_4$-water mass transfer using methyl-modified mesoporous silica nanoparticles

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Abstract−Surface-modified mesoporous silica nanoparticle (MSN) with methyl groups was used to enhance the CH$_4$-water volumetric mass transfer coefficient (k$_L$a) and the solubility of CH$_4$ in water. Two types of samples were tested: unmodified MSN and methyl-modified MSN. The mass transfer for each type of sample was measured every 20 s by gas chromatography. The results showed that the methyl-modified MSN, which have both hydrophobic and hydrophilic properties on the surface, exhibited higher CH$_4$-water volumetric mass transfer coefficient and solubility in water. The dissolved concentrations of CH$_4$ were enhanced by 10.7% and 27.8%, and the volumetric mass transfer coefficient were enhanced by 28.6% and 84.7%, respectively, by using unmodified MSN and methyl-modified MSN.

Keywords: Methane (CH$_4$) Gas, Mass Transfer, Gas Fermentation, Mesoporous Silica Nanoparticle (MSN), Surface Modification

INTRODUCTION

The use of fossil fuels has increased rapidly since the 19th century. As a result, methane (CH$_4$), carbon monoxide (CO), and carbon dioxide (CO$_2$) have greatly increased in the atmosphere and play a major role in the greenhouse effect. Attempts are being made to reduce emissions of greenhouse gases. Gas fermentation is a particularly promising solution, because it provides a pathway for converting biomass to a usable energy source. It has the advantages of relatively low cost and high efficiency [1,2]. Microorganisms such as *Rhodospirillum rubrum*, *Acetobacterium woodii*, and *Clostridium acetobutylicum* produce diverse fuels and energy sources such as methanol, ethanol, and acetic acid as a byproduct of their metabolism of a variety of gases [3-5]. CH$_4$ is one of the major contributors to global warming and is about 23 times more potent than CO$_2$. Therefore, a study of CH$_4$-oxidizing microorganisms is urgently needed [6].

In gas fermentation with microorganism oxidation of CH$_4$, methane is the sole carbon energy source to methanotrophs for producing valuable chemicals [7]. Accordingly, CH$_4$ can be reduced and converted to useful chemicals at CH$_4$ sources such as landfills using fermentation. However, the solubility of CH$_4$ in the culture medium and the CH$_4$-liquid mass transfer rate are limited. The relatively low solubility and mass transfer rate reduce the product yield [8].

Therefore, to improve the efficiency of CH$_4$ fermentation, enhancement of the CH$_4$-liquid mass transfer rate is necessary. However, studies of CH$_4$ are few, compared to CO and CO$_2$. In particular, little attention has been paid to approaches for enhancing the CH$_4$-liquid volumetric mass transfer coefficient and solubility. Therefore, this study is an important first step toward enhancing the CH$_4$-water volumetric mass transfer coefficients and solubility using nanoparticles at atmospheric pressure.

Gas-liquid mass transfer is affected by the reactor type, additive system, and power inputs. Several previous studies have been conducted to enhance gas-liquid mass transfer. For example, different impeller types in a stirred tank reactor were studied, and the dual impeller type had a higher volumetric mass transfer coefficient than the single impeller type reactor, by up to 27% [9]. However, considerable power input was required by the dual impeller type reactor, which resulted in the lowest mass transfer rate per unit power input [10]. Other methods to enhance gas-liquid mass transfer rates have been studied, such as adding salts, alcohols, and particles [11-14].

Among these, a 600% enhancement in the oxygen (O$_2$)-liquid mass transfer rate has been observed using coated nanoparticles with a surfactant and oleic acid in a dispersed agitated reactor at <1% nanoparticle volume [15]. Many researchers have reported that addition of particles enhances the gas-liquid mass transfer coefficient [16-18]. However, most of these studies evaluated CO, CO$_2$, and O$_2$, with relatively few assessing CH$_4$. In general, there are four primary mechanisms accounting for enhancement of gas-liquid mass transfer by particles: 1) the hydrodynamic effect, 2) shuttling, 3) stabilization of bubbles and 4) reaction enhancement [19,20]. In these mechanisms, gas-liquid mass transfer is affected by the amount, surface area, characteristics, and size of the particles. Mesoporous

silica nanoparticles (MSNs) are of great interest because their surfaces can be easily modified with various functional groups and they have porous surfaces with substantial adhesion capacity. Hence, MSNs may be appropriate for enhancement of the CH$_4$-liquid mass transfer rate with surface properties combining hydrophilicity and hydrophobicity [16,21]. In this study, MSNs were synthesized and their surface characteristics were modified with methyl groups to produce both hydrophilicity and hydrophobicity to enhance the CH$_4$-water volumetric mass transfer coefficient (k$_L$a) and the solubility in water.

EXPERIMENTAL METHODS

1. Materials

Ammonium hydroxide (28.0-30.0% NH$_3$ basis), tetraethyl orthosilicate (TEOS) (98%) (No. 131903), and triethoxymethylsilane (99%) (No. 175579) were acquired from Sigma-Aldrich (USA). *n*-Octadecyltrimethoxysilane (85%) (No. O0256) was purchased from TCI (Japan). Ethanol (94%) was obtained from Daejung (Korea). Methane gas (30 vol%) was acquired from Dong-A Industrial Gases Co. (Korea). Deionized water (Milli-Q) was purchased from Merck Millipore (Germany). The gas flow meter (gas mixer) was obtained from Hanil (Korea). The temperature controller and stirrer (HSD180) was purchased from Misung Scientific Co. (Korea). The high-resolution transmission electron microscope (TEM; JEM-2100F) was manufactured by JEOL (Japan). The gas chromatograph (YL-6500) was purchased from Young Lin Instrument Co. (Korea). The Fourier transform infrared spectrometer (FT-IR; FTS-3000) was manufactured by Bio-Rad (USA).

2. Synthesis of the Mesoporous Silica Nanoparticles

For synthesis of the MSNs, 10 mL deionized water, 75 mL ethanol, and 3 mL ammonium hydroxide were mixed in a 250-mL round bottom flask and stirred with a magnetic stir bar for 10 min, followed by addition of 6 mL TEOS and the stirring for 2 h. Subsequently, 5 mL TEOS and 2 mL *n*-octadecyltrimethoxysilane were mixed and then added to the flask, stirring for 1.5 h. The solution was washed three times with ethanol and dried in an oven at 80 °C. The product was calcined for 6 h at 550 °C to remove all organic residues on the silica surface. The surfaces of the synthesized nanoparticles were analyzed by TEM [22].

3. Surface Modification of the Mesoporous Silica Nanoparticles

Ethanol (16 mL), and deionized water (4 mL) were added to 0.1 g of MSNs and the mixture was sonicated. The solution was stirred for 10 min and triethoxymethylsilane (8 mL) was added. The mixture was heated to 70 °C with stirring for 3 h. The resultant was washed with ethanol several times and dried in an oven at 80 °C [16]. The modified surface was analyzed by FT-IR [23].

4. Measurement of CH$_4$ Solubility in Water

A 250-mL media bottle was filled with 200 mL deionized water. The surface-modified MSNs (0, 0.05, 0.15, 0.25, and 0.35 wt%) were then dispersed in the water by sonication. The mixture was stirred (200 rpm), placed on the temperature controller, and maintained at 28 °C at atmospheric pressure. CH$_4$ gas was injected into the solution at a flow rate of 3 L/min and the solution was sampled at 300 s. After centrifugation to consolidate the nanoparticles, the supernatant was analyzed with gas chromatography (GC).

To measure solubility over time, a mixture of 200 mL deionized water and 0.25 wt% surface-modified MSNs was prepared. The mixture was placed on the temperature controller and held at a constant temperature of 28 °C with stirring (200 rpm) and a CH$_4$ gas flow rate of 3 L/min. Samples were collected from 20 to 300 s. The supernatant of the centrifuged sample was analyzed with a GC equipped with a capillary column (GS-CarbonPLOT) and pulsed discharge detector. The pulsed discharge detector temperature was 160 °C. The carrier gas was He at 0.069 MPa. The flow rate was 4 ml/min. The valve temperature was 120 °C and the capillary temperature was 150 °C. The oven temperature was programmed to begin at 35 °C and increase at a rate of 50 °C·min^{-1} to 150 °C.

RESULTS AND DISCUSSION

1. Characterization of Methyl-modified Mesoporous Silica Nanoparticles

To enhance the mass transfer of gas in water, the MSNs with a uniform diameter were prepared by a slight modification of the Unger procedure [24]. The MSNs were composed of a silica core and mesoporous shell, which significantly increased the surface area compared to nonporous spherical silica nanoparticles. The increased surface area of the MSNs is important in increasing the mass transfer between the liquid and the gas. As shown in Fig. 1, the MSN diameter was about 350 nm, with the diameter of the solid core about 280 nm and the thickness of the mesoporous shell about 70 nm.

Silica particles composed of Si-OH bonds have a hydrophilic character because the hydroxyl group is polar [25]. According to Kim et al. [16], hydrophilic silica nanoparticles showed to be more effective at enhancing CO, CO$_2$ and H$_2$ mass transfer than hydrophobic nanoparticles. Because the hydrophobic nanoparticles were
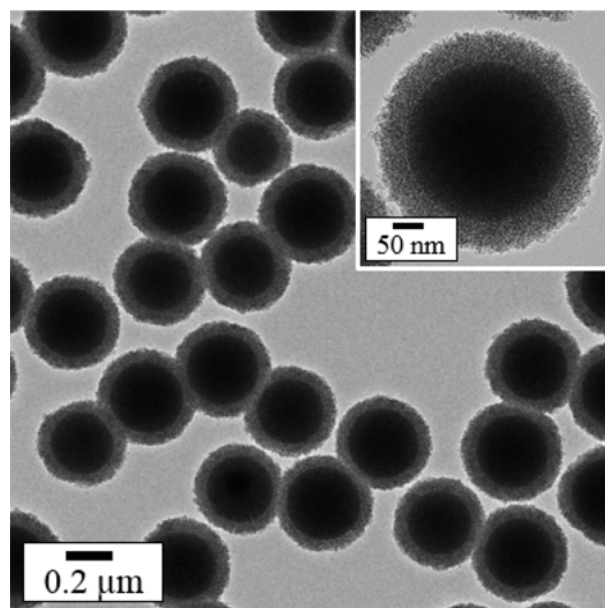

Fig. 1. TEM images of the MSNs. Scale bar, 0.2 μm. The inset shows a high-resolution TEM image of a randomly selected MSN. Scale bar, 50 nm.
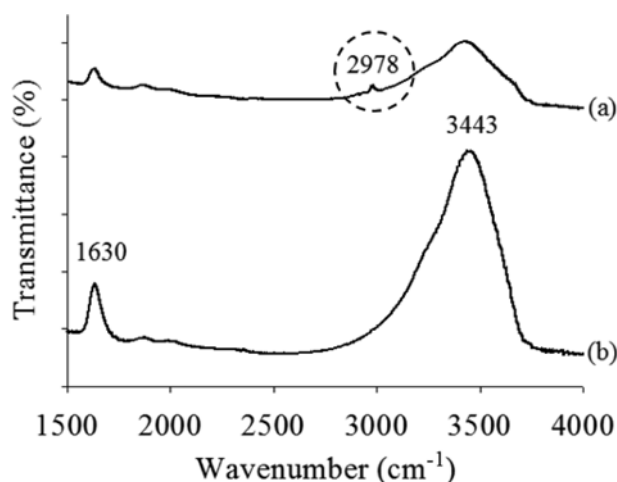
Fig. 2. FT-IR spectra of (a) surface-modified MSNs with methyl groups and (b) unmodified MSNs. The circled point is the peak corresponding to the methyl groups.

Fig. 3. Measurement of CH_4 solubility (a) methyl-modified MSNs, (b) unmodified MSNs, and (c) no MSNs in water at the CH_4 flow rate of 3 L/min.

not well dispersed in the aqueous solution, they could not come into contact with the gas bubbles in the aqueous solution.

Ruthiya et al. [19] proposed that the increase of gas-liquid mass transfer is based on the adhesion of nanoparticles to the gas-liquid interface. The gases, including CH_4, are essentially hydrophobic, so hydrophobicity in MSNs is important for the induction of shuttling or grazing effects, hydrodynamic effects at the gas-liquid boundary, and changes at the specific gas-liquid interfacial area. Therefore, a suitable balance of hydrophilic properties inhibiting aggregation and hydrophobic properties to retain more CH_4 gas is required for the nanoparticles to improve the mass transfer of CH_4.

To confer hydrophobicity to hydrophilic MSNs, triethoxymethylsilane was added to the MSNs for modification of the mesoporous surfaces with methyl groups. FT-IR spectra for the unmodified MSNs and methyl-MSNs are shown in Fig. 2. In Fig. 2(b), two separate peaks (1,630 and 3,443 cm^{-1}) can be seen for the silica surface, while a peak at 2,978 cm^{-1} appears in Fig. 2(a), indicates methyl groups on the surface of the MSNs.

2. Enhancement of CH_4 Solubility by Using Methyl-modified Mesoporous Silica Nanoparticles

The gas-liquid mass transfer system was composed of a temperature sensor and gas flow rate regulator. It was designed to maintain a constant room temperature (28 °C) to hold the solubility constant and to inject CH_4 gas at a steady flow rate (3 L/min) using regulators with gentle magnetic stirring. The temperature and injection rate have a significant effect on determination of the mass transfer rate; thus, it was important to hold these factors constant.

To evaluate the enhancement of CH_4 solubility in water by using methyl-modified MSNs, two types of samples were tested at 0.25 wt% concentration of nanoparticles: unmodified MSN and methyl-modified MSN. No nanoparticles were used in control experiment. Under the conditions studied, the dissolved CH_4 concentration in water starts to saturate above 250 s (Fig. 3). When saturated, the average CH_4 concentration in water was 6.190 mg/L for control experiment and 6.852 mg/L with injection of unmodified MSNs. The highest saturation concentration, 7.902 mg/L, was obtained
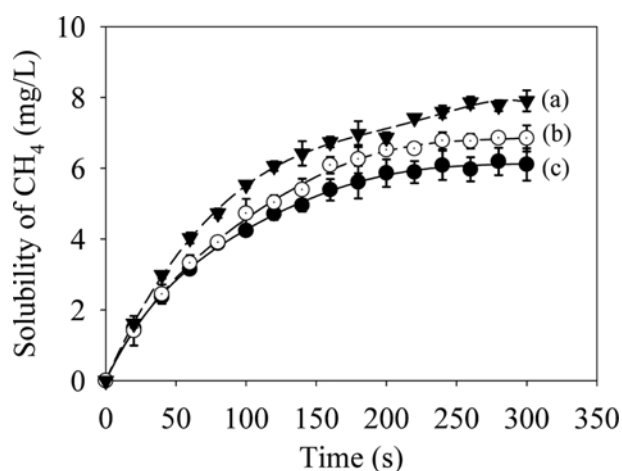
for the surface-modified MSNs with methyl groups. This represents 27.8% improved CH_4 solubility for the methyl-MSNs over the control experiment and 15.3% over the unmodified MSNs. These results demonstrate that methyl modification of hydrophilic nanoparticles is effective in increasing the solubility of CH_4.

To evaluate the effect of methyl-modified MSNs concentration on CH_4 solubility in water, various concentrations of methyl-modified MSNs were tested (0.05, 0.15, 0.25, 0.35 wt%), and then dissolved CH_4 concentrations measured. Fig. 4 shows the relationship between the solubility of CH_4 and the amount (wt%) of injected methyl-modified MSNs in water. The solubility of CH_4 increased steadily with the nanoparticle concentration, because a greater concentration of nanoparticles in water increased the nanoparticle surface area for gas collection. For the 0.25 wt% injection, clear enhancement of solubility was observed compared to the non-injection case. The difference in CH_4 solubility was about 2 mg/L, or an increased solubility of about 27.8%. However, above 0.25 wt%, the solubility of CH_4 became saturated, although the nanoparticle surface area
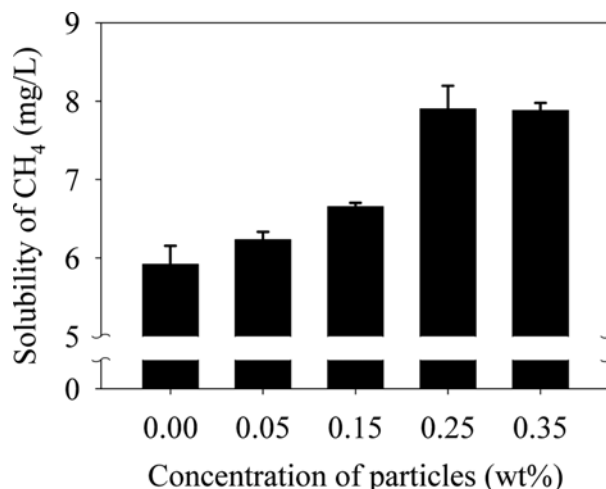

Fig. 4. Effect of the concentration of surface-modified MSNs with methyl groups on CH_4 solubility.

increased. At this point, there was a greater surface area than required by the injected CH$_4$ gas. Therefore, under these conditions, 0.25 wt% of methyl-modified MSNs was found to be a suitable concentration for enhancing CH$_4$ solubility.

3. Effect of Methyl-modified Mesoporous Silica Nanoparticles on CH$_4$-water Volumetric Mass Transfer Coefficient

To determine the effect of methyl-modified MSNs on CH$_4$-water volumetric mass transfer coefficient, the CH$_4$ content in water was measured every 20 s for 5 min using GC for each of the three types of samples described above: no MSNs, unmodified MSNs and methyl-modified MSNs. Because it was difficult to directly calculate the CH$_4$-water interfacial area, k$_L$a was determined using Eq. (2):

$$N_a = k_L a(C^* - C) \tag{1}$$

$$\ln[(C^* - C)/(C^* - C_0)] = k_L a(T - T_0) \tag{2}$$

where N$_a$ is the rate of gas transfer per unit of time (mg·L^{-1}·s^{-1}), k$_L$ is the liquid phase mass transfer coefficient (m·s^{-1}), a is the gas-liquid interfacial area per unit volume of fluid (m^2·m^{-3}), C* is the saturation concentration (mg·L^{-1}), C is the dissolved concentration (mg·L^{-1}), C$_0$ is the initial concentration (mg·L^{-1}) at T$_0$, T$_0$ is the initial time (s), and T is the elapsed time (s). N$_a$ is described by Eq. (1) and Eq. (2) was obtained by integration of Eq. (1). Eq. (2) was plotted as a linear graph based on the concentration data obtained from the solubility experiment (Fig. 5). k$_L$a was obtained from the slope of the line (Table 1) [26-28].

The volumetric mass transfer coefficient, which reflects the degree of gas transfer, depends on the bubble condition, injection rate, gas retention, surface tension and viscosity, etc. Injection of methyl-modi-

fied MSNs enhances the mass transfer coefficient through modification of several factors. As expected, the highest k$_L$a was obtained for the methyl-modified MSNs. The k$_L$a was increased by 84.7% over that of the control experiment, in which no MSNs were used. Thus, injection of methyl-MSNs effectively enhances the CH$_4$-water mass transfer rate.

CONCLUSION

We have developed an enhanced CH$_4$-water mass transfer system. To increase CH$_4$ solubility in water, MSNs were injected into solution, increasing the k$_L$a with the NSN surface area. The porosity and methyl-modified surface of nanoparticles are critical factors enhancing CH$_4$ mass transfer to water. The use of functional nanoparticles such as methyl-modified MSNs is a promising method for increasing mass transfer and producing eco-friendly energy using CH$_4$ or other residual gases.

ACKNOWLEDGEMENTS

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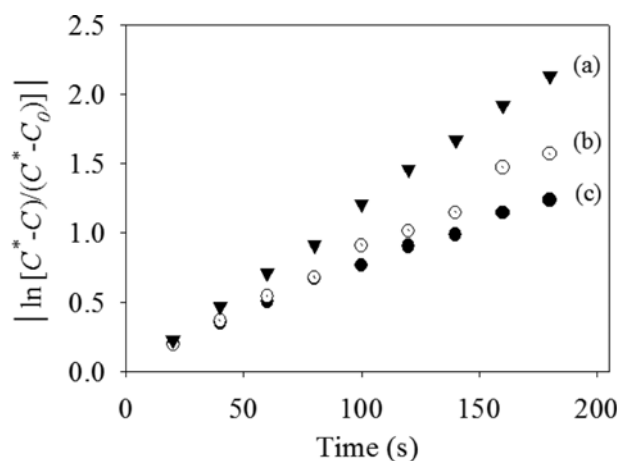15. B. Olle, S. Bucak, T. C. Holmes, L. Bromberg, T. A. Hatton and

Fig. 5. The absolute value of the change in concentration over time in the reactor at a CH$_4$ flow rate of 3 L/min. The graph of (a) methyl-modified MSNs, (b) unmodified MSNs, and (c) No MSNs. The slope of the lines corresponds to the volumetric mass transfer coefficient (k$_L$a).

Table 1. Volumetric mass transfer coefficient (k$_L$a) in the reactor at a CH$_4$ flow rate of 3 L/min

	Untreated	MSNs	Methyl-modified MSNs
k$_L$a (h^{-1})	22.68±0.21	29.16±0.55	41.88±1.15

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