Contents lists available at SciVerse ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Effect of synthesized silver nanoparticles in promoting methane hydrate formation at 4.7 MPa and 5.7 MPa

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ABSTRACT

Using gas hydrates as materials for storage and transportation of natural gas have attracted much attention in recent years. However, there are two barriers in industrializing this new method. Firstly, methane hydrate induction time is relatively high. On the other hand the amount of gas trapped in methane hydrate crystals is too low. In this survey, silver nanoparticles were synthesized using a chemical reduction method and introduced to the hydrate reactor. Experiments were conducted at initial reactor pressures of 4.7 MPa and 5.7 MPa. At each pressure three independent experiments were performed. According to the results, in the presence of silver nanoparticles, methane hydrate induction time decreased by 85% and 73.9%, and the amount of methane trapped in hydrate crystals increased by 33.7% and 7.4% at the pressures of 4.7 MPa and 5.7 MPa respectively.

Keywords: Silver nanoparticles; Methane; Hydrate; Induction time

1. Introduction

Many researchers have studied methane hydrate formation conditions aimed normally at promotion (Ganji et al., 2007b) or inhibition (Xiao et al., 2010). Since each volume of methane hydrate can contain as much as 184 volumes of methane at standard temperature and pressure (Sloan and Koh, 2008), hydrates are currently considered as a new technology for natural gas storage and transport.

To industrialize this new technology, it is necessary to increase methane hydrate formation rate and storage capacity. In fact, the reaction between methane and water is very slow during formation process.

Various methods were used to promote gas hydrates formation. Addition of surfactants (Ganji et al., 2007a,b; Kwon et al., 2011; Mohammadi et al., 2011, accepted for publication-a, accepted for publication-b) has been the most popular one. Ganji et al. (2007a,b) have reported remarkable promotional effects of SDS (an anionic surfactant) on methane hydrate formation process.

Some other methods like applying ultrasonic (Liu et al., 2003a) and magnetic fields (Liu et al., 2003b) have been studied too. Although favorable effects were reported of these methods, but it is hard to use them in practice.

Li et al. (2006) employed copper nanoparticles as an additive to promote HFC134a gas hydrate formation for the first time. Lee et al. (2007) showed poor promotional effects of triple nanoparticles on methane hydrate formation process. In addition, increasing methane hydrate storage capacity and decreasing of the induction time were reported by Park and Kim (2010) using carbon nanotubes. Increasing heat transfer coefficient in the presence of these conductive nanoparticles was mentioned as the main reason for this promotional effect in these researches. In this survey silver nanoparticles were chosen. Silver has the highest heat transfer coefficient among all metals.

2. Experimental

2.1. Synthesis of silver nanoparticles

Various methods have been proposed to synthesize silver nanoparticles (Aswathy et al., 2011; Bonsak, 2010; Ghader et al., 2007; Lupu, 2010; Scaiano et al., 2006; Zhang et al., 2006). In this study, a suitable chemical method has been chosen to synthesize these nanoparticles. This method has been described below.

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Received 23 May 2012; Received in revised form 17 November 2012; Accepted 7 December 2012
0263-8762/$ – see front matter
http://dx.doi.org/10.1016/j.cherd.2012.12.001

Nomenclature

P	pressure, MPa
T	absolute temperature, K
t	time, min
n	number of moles
V	volume, m^3
Z	compressibility factor (dimensionless)
R	universal gas constant, 8.314 J mol^{-1} K^{-1}

2.1.1. *Materials*

Sodium borohydride ($NaBH_4$) and tri-sodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) were purchased from Merck, Germany. Silver nitrate ($AgNO_3$) was obtained from PanReac, Spain. All of these chemicals were used as received.

2.1.2. *Synthesis method*

A chemical reduction method (Bonsak, 2010; Jana et al., 2001) was employed to synthesize silver nanoparticles. First 20 ml aqueous solution with concentration of 0.25 mM $AgNO_3$ and 0.25 mM trisodium citrate was prepared. During stirring this solution, 0.6 ml of 10 mM $NaBH_4$ was added. Stirring was stopped after 3 min. In this route sodium borohydride acted as the reducing agent and trisodium citrate as the stabilizer. The chemical reaction of this synthesis process can be written as (Solomon et al., 2007):

$$AgNO_3 + NaBH_4 \rightarrow Ag + 0.5H_2 + 0.5B_2H_6 + NaNO_3$$

Some samples were prepared on glass slides and was imaged using SEM. The image is shown in Fig. 1.

Using Image J 1.43 software, the size distribution of silver nanoparticles was obtained. This is shown near SEM image. According to this image, silver nanoparticles diameter is between 50 and 75 nm. EDX analysis showed the purity of synthesized silver nanoparticles. The spectrum is shown in Fig. 2. Presence of calcium and silicon is believed to be from the glass slide.

UV–vis absorption spectra peak is on 400 nm, the conventional peak of silver metal nanoparticles (Aswathy et al., 2011; Bonsak, 2010; Ghader et al., 2007; Jana et al., 2001; Lupu, 2010; Scaiano et al., 2006; Solomon et al., 2007). The spectrum is shown in Fig. 3.

2.2. *Effects of silver nanoparticles on methane hydrate formation process*

2.2.1. *Apparatus*

The schematic diagram of methane hydrate formation apparatus is shown in Fig. 4. The reactor is a batch one and its volume is 460 cm^3. A mixture of water and alcohol is used to cool the system. In this setup a mechanical system accompanied with an electromotor was employed to agitate the mixture of water and methane in the reactor. The whole reactor was insulated to prevent any heat loss. One platinum resistance thermometer (Pt 100) is inserted into the reactor to measure temperature of the system within a precision of ±0.01 K. Pressure is measured by a BD pressure transducer within a precision of ±0.01 MPa for the operating range. The temperature and pressure are monitored and recorded in a computer by means of a data acquisition interface.

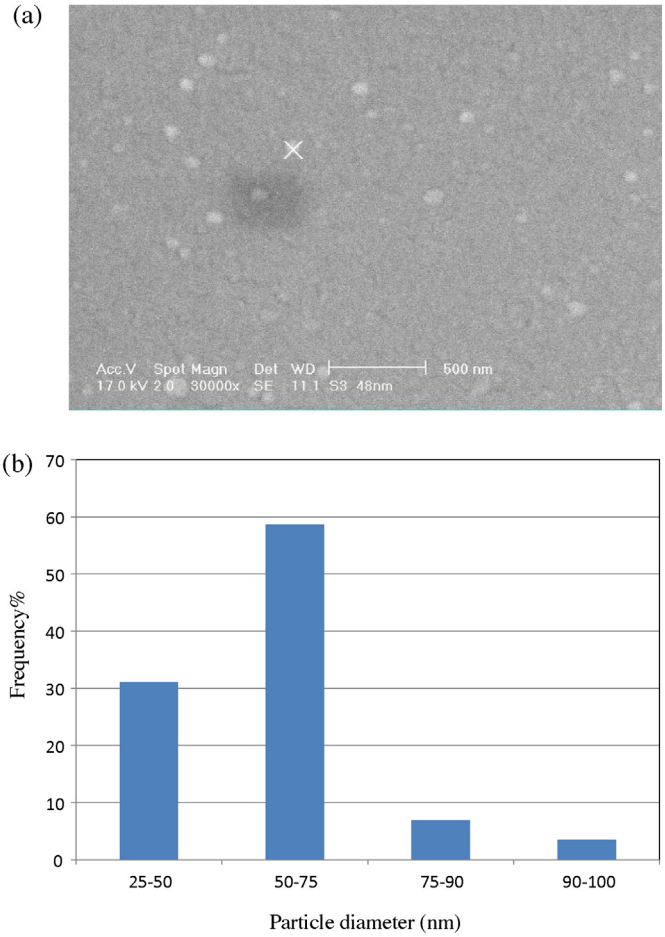

Fig. 1 – (a) SEM image and (b) size distribution of synthesized silver nanoparticles.

2.2.2. *Experimental procedure*

To do each experiment first of all, water or aqueous solution containing silver nanoparticles or trisodium citrate was poured into the reactor. Then methane gas with purity of 99.9% was injected until the final pressure was reached at 283.15 K. After that cooling system was turned on while its temperature was adjusted on 275.15 K. When the electromotor was turned on, data recording was started. The reactor temperature and pressure were recorded each 10 s. These data are plotted using Excel 2007 software.

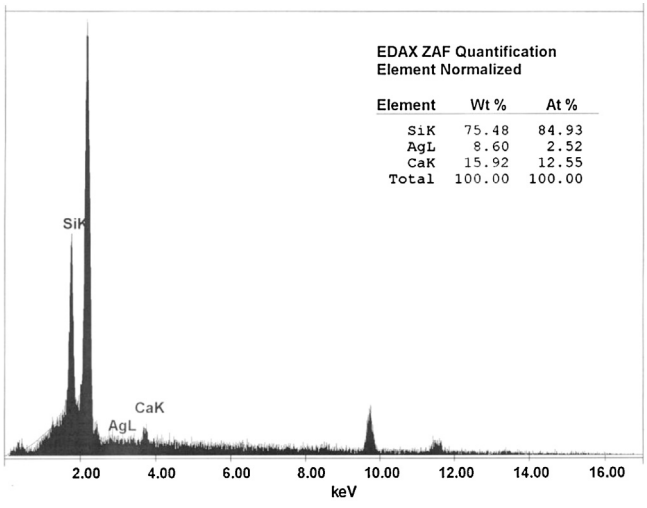

Fig. 2 – EDX analysis of synthesized nanoparticles.