CHAPTER I
INTRODUCTION

Natural gas is a mixture of gases consisting of mostly methane and other gases like ethane, propane, nitrogen, helium, sulfur compounds, and water vapor (naturalgas.org). Although it is non-renewable energy, it is one of the cleanest energy. It bums cleaner and emits lower levels of pollutions than other fossil fuels because of its low-carbon-to-hydrogen ratio. It can be used as a fuel for vehicles called Natural Gas Vehicles (NGVs). Now, there are three commercial technologies for natural gas storage: compressed natural gas (CNG), liquefied natural gas (LNG), and adsorbed natural gas (ANG). For CNG, natural gas is stored in a high-pressure tank. Natural gas is maintained as cryogenic liquid at a very low temperature for the LNG. For ANG, natural gas is stored in porous media at a standard temperature and pressure (www.afsglobal.com). Recently, natural gas hydrate technology has drawn much attention as a new technology for natural gas storage and transportation. The advantage of natural gas hydrates is it has higher gas storage capacity than ANG, and it requires less energy and safer than LNG and CNG (Fakharian *et al.*, 2012; Najibi *et al.*, 2008; Zanota *et al.*, 2005).

Gas hydrates or clathrate are crystalline solid compounds consisting of a gas molecule such as methane, carbon dioxide, ethane, propane, and butane surrounded by a cage of water molecules. They are stable under high pressure and low temperature. Gas hydrates were found all over the world in the sediments of continental margins and in permafrost regions at Arctic polar. First, gas hydrates were known as a major problem for exploration and production of petroleum technologies because it occurs inside the pipe line and blocks transportation of petroleum products. After that, gas hydrates were discovered to accommodate a large amount of natural gas. For example, one volume of hydrates can encage about 150 to 180 volumes of gas at STP (Saw *et al.*, 2014). Hence, gas hydrates become attractive as an energy potential resource that can meet energy demands in the future. However, there are many challenges for artificial hydrate storage, such as slow formation rate gas content, stability, and unreacted water in the system that hinders the production of gas hydrate storage and transportation of natural gas in industrial.

The hydrate formation can be promoted by, for example, high driving force, mechanical mixing, and surfactants. The drawbacks of vigorous stirring and driving force methods are enormous energy required for operation in industrial scale. For surfactants, the stability of gas storage is decreased (Ganji *et al.*, 2007a; Ganji *et al.*, 2007b). Then, the researchers discovered that the presence of porous media can promote gas storage capacity and hydrate formation rate. The use of porous media can save cost and energy to form gas hydrates. The porous media like activated carbon provide higher gas-water contact area than pure water system so it can enhance gas capacity and formation rate of hydrates (Cha *et al.*, 1998; Zhong *et al.*, 2013).

Among porous media, recently, there is a report on the use of hollow silica for methane hydrate formation. Hollow silica is synthesized silica with inner void. It becomes attractive for many applications because of its unique properties such as large cavity, low density, high pore volume, high porosity, high specific area, and good thermal insulation (Chen *et al.*, 2013). Hollow silica as a gas storage can reach the U.S. Department of energy (DOE) set target, 180 cm^3(STP) cm^{-3}, for methane storage at 298 K and 3.5 MPa. The hydrate formation in hollow silica matrix can form at a moderate pressure, which is significantly lower than pure water system at the same hydrate yield (Prasad *et al.*, 2014).

Although there are a number of studies on how role porous material affects methane hydrate formation, very few have addressed effects of different porous materials on the hydrate formation. Thus, the aim of this research was to comparatively study the methane hydrate formation and dissociation in the presence of hollow silica and activated carbon in terms of kinetics as gas consumed and percentage of water conversion to hydrates and also studied in terms of thermodynamics views to improve methane gas storage and transportation.