CHAPTER I
INTRODUCTION

According to the crude oil depletion, the fluctuation of oil price, and the environmental concern about global warming by greenhouse gas emission, it is significantly important to find alternative energy sources. Natural gas, which is composed mostly of methane, has been considered as an alternative fuel for transportation such as cars, bus, and trucks. Natural gas vehicles (NGVs) show environmental advantages. From the combustion product point of view, it can be remarked: (i) it does not contain lead or heavy metals traces, ii) lack of suspended solid particles that are present when using gasoline, iii) absence of sulfur and subsequently no sulfur dioxide (SO_2) emissions, typical contaminant from transport. Compared to liquid fuels, the emissions of the NGV combustion produce up to 76% less CO, 75% less NOx, 88% less hydrocarbons and 30% less CO_2 (Sun *et al.*, 1997).

In spite of the advantages of natural gas, there is an important disadvantage, which is its low-energy density (heat of combustion/volume), which constitutes a limitation for some applications. Therefore, under standard conditions of pressure and temperature, the distance traveled by a vehicle per unit of fuel volume, using natural gas, corresponds to 0.12% of the gasoline (Solar *et al.*, 2010). Hence, the storage of this fuel, whether in quantity or density, plays an important role for its use in diverse kinds of transport. To increase the energy density of natural gas, there are three different methods to store natural gas, which are liquefied natural gas (LNG), compressed natural gas (CNG), and adsorbed natural gas (ANG). LNG is stored at the boiling point, 112 K (-161 °C), in a cryogenic tank at a pressure of 0.1 MPa, where the energy density is approximately 72% of the total gasoline (Solar *et al.*, 2010). However, this storage method shows multiple inconveniences. Mainly, LNG increases the temperature within the tank, so the pressure rises up and could result in a dangerous situation. Moreover, it requires a special insulated vessel, not to mention the associated high cost of liquefaction.

A widely used commercial method to increase the energy density of natural gas is CNG. Natural gas is compressed at a maximum pressure around 20-25 MPa, reaching 230 times higher density (230 v/v) than the one obtained for natural gas under STP conditions (Lozano-Castelló *et al.*, 2002a). A disadvantage is the risk of carrying highly compressed gas (20 MPa) within the vehicle. Modifications such as thick-walled and heavy tanks and complex safety valves would be required. In the case of ANG, pressures are relatively low, around 2 to 4 MPa at room temperature, which represents an interesting alternative for the transport and applications in a large scale. In contrast, this technology is not well developed and is still at scientific level (Alcañiz-Monge *et al.*, 1997). At this stage, study on storage by the ANG method is carried out using methane, major constituent of the natural gas to adsorb on porous materials such as graphite, carbon nanotubes, zeolites, and activated carbons. The advantage of this technique is using relatively low pressure and ambient temperature. On the other hand, a major problem to store natural gas in the ANG form is to use the right material that is suitable for storing and releasing methane at desired conditions (Inomata *et al.*, 2002, Lozano-Castelló *et al.*, 2002a and 2002b). Many researchers have focused on the improvement of materials to be used for ANG, particularly, carbon-based materials, which provide high adsorption capacity. Microporous activated carbons are the most attractive adsorbents for gas storage due to its high specific surface area and pore volume, which is believed to be suitable as an ANG adsorbent (Farzad *et al.*, 2007 and Prauchner and Rodríguez-Reinoso, 2008).

As carbon dioxide has higher adsorption capacity than methane on microporous activated carbon, it decreases the quantity of adsorbed methane on the activated carbon resulting in the low energy density (Yang *et al.*, 2011). However, activated carbon can be modified by chemical treatment to increase pore volume and surface hydrophobicity to enhance hydrophobic volatile organic compounds uptake (Li *et al.*, 2011). In this work, granular activated carbon was used as a natural gas storage adsorbent. The dynamic adsorption, 10 vol% methane and 10 to 30 vol% carbon dioxide, were used to study the adsorption capacity. The 3-cycle adsorption-desorption was used to investigate the adsorption stability. Moreover, effects of surface treatments on the methane adsorption were investigated. Competitive carbon dioxide and methane adsorption on activated carbon was also studied.