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Study of metal-organic framework MIL-101(Cr) for natural gas (methane) storage and compare with other MOFs (metal-organic frameworks)

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ABSTRACT

Natural gas, containing mainly methane (CH_4), has the potential to substitute petroleum as fuel for vehicles. However, the storage of natural gas at adequately high densities to fulfil the requirement of driving range is a challenging task. One prospective solution is the use of porous materials to adsorb natural gas at lower pressures and temperatures resulting in higher density storage. In this article, we present an extensive study on synthesis, characterization and property evaluation of MIL-101(Cr) MOF (metal-organic framework) for CH_4 adsorption. At 298 K, it is observed that the total volumetric uptake of CH_4 on MIL-101(Cr) MOF is about (i) 150 cm^3/cm^3 at 35 bar, (ii) 215 cm^3/cm^3 at 65 bar, and (iii) 30 cm^3/cm^3 at 5 bar. Further, we have demonstrated a novel idea to store CH_4 on MOFs in an ANG (adsorbed natural gas) vessel below critical point temperature employing LNG (liquefied natural gas) regasification. This LNG–ANG coupling improves the competitiveness of ANG storage and increases the CH_4 working capacity. Employing LNG-ANG coupling, it is found that MIL-101(Cr) exhibits high CH_4 delivery or working capacity which is (i) 240 cm^3/cm^3 for the operating parameters ranging from 6 bar at 160 K to 5 bar at 298 K, and (ii) 125 cm^3/cm^3 for the operating parameters varying from 1.2 bar at 160 K to 5 bar at 298 K.

1. Introduction

The depletion of fossil fuel reservoirs and the escalating threat of global warming due to harmful emissions of greenhouse gases have put clean energy research. NG (Natural gas) has the potential to replace the existing hydrocarbon-based fuel such as petroleum. NG, consisting mainly of methane (CH_4), has the maximum H to C ratio than any other hydrocarbon-based fuel, thus resulting lower release of CO and CO_2 per unit of energy generation due to its combustion [1]. In addition, NG results lower SOx and NOx emissions, making it significantly cleaner fuel than gasoline [2]. The abundant worldwide reserves of NG is expected to be an increasing demand as a clean energy source due to its cheaper availability, cleaner ignition and higher competition for oil reserves [3]. However, the wide-spread use of the NG is limited to its low energy density and the consequent necessity of its storage either at very high pressure or as a liquefied natural gas [4].

The transportation of NG is generally conducted in its liquid form. Conventionally, there are three different ways of natural gas storage namely (i) the CNG (compressed natural gas), (ii) the LNG (liquefied natural gas), and (iii) the ANG (adsorbed natural gas). For example, the use of CNG is limited to costly multi-stage gas compressors which consume high energy and require weighty, large fuel tanks [5]. The use of LNG is limited to the difficulties of handling a cryogenic fuel [6]. As an alternative to LNG and CNG, the ANG system can be designed with porous adsorbents to store NG at relatively low pressure that would permit light-weight fuel tanks which would be optimally incorporated into the limited space [7].

The US DOE (Department of Energy) has fixed CH_4 storage targets for adsorbents at 350 cm^3 CH_4 (STP) per cm^3 adsorbent and 0.5 g CH_4 per g adsorbent at ambient conditions [5]. The storage of CH_4 on adsorbents at ambient temperature requires (i) extra cooling energy due to higher enthalpy of adsorption, and (ii) higher time to reach thermal equilibrium during charging of CH_4 on porous adsorbents. Due to the availability of LNG and its re-gasification issues at comparatively lower pressures, the storage of CH_4 at lower temperature is an important research area [8–10].

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One possible solution as shown in Fig. 1 is the coupling of LNG vaporization and ANG tank filling process, which utilizes the exergy of LNG vaporization fluid. The latent heat of LNG vaporization is utilized to precool the ANG adsorption bed. The filling of cold ANG tank can be performed at lower pressure as adsorption process highly depends on temperature. In that case, the multi-stage gas compressor is not needed to pump the required amount of gas in the vessel, which saves energy. Thus, the coupling of LNG and ANG not only helps to avoid the complexity of re-gasification of NG at ambient condition but also improves the overall exergy efficiency of the storage chamber up to 25% depending on filling temperatures and pressures [11].

Currently most transcontinental transport of NG is performed by LNG. The ANG system could be an ideal proposition for CH_4 storage at low temperature. To implement the ANG technique in practical applications, the adsorption characteristics of CH_4 + porous adsorbent material must be well known at the cryogenic temperatures and low pressure ranges (120 K–190 K and P < 15 bar). So far major attention to ANG is put on its storage and application at ambient conditions [1,3,12–16], not many works regarding cryo-adsorption have been reported in the literature. It should be noted that one can store CH_4 on adsorbents at lower pressures (<15 bar) and temperatures (<200 K) in a confined vessel but the discharge of CH_4 is viable at ambient conditions.

Highly effective ANG process requires the adsorbent materials with large adsorptive capacity and good kinetics performances. It has been found that the MOFs (metal-organic frameworks) are the most potential adsorbents [17,18] due to large surface area, permanent porosity and thermodynamic stability [19–21]. The MOFs are built by assembling clusters of metal ions with the multidentate organic linkers to form a three-dimensional structure [22]. MOFs can be used as NG-storage materials with tunable surface chemistry and structures. The exposed metal sites in MOFs enhance the storage capabilities at low pressures [23], whereas the bigger pore sizes increase the uptakes at high pressures [24].

To explore the adsorption characteristic of CH_4, a MOF (metal-organic framework) named chromium (III) terephthalate [MIL-101(Cr)] (MIL stands for materials of institut Lavoisier) was chosen as the focal point of this study. Previously CH_4 adsorption studies were reported on MIL-101(Cr) [25–27], copper based MOFs such as HKUST-1 [5,26–32], PCN-14 [33], UTSA-20 [34,35], NU-111 [36], NU-125 [37], nickel based MOF such as Ni-MOF-74 [38,39] and activated carbon, MaxsorbIII [40]. We have focused on chromium based MOF, MIL-101(Cr) for the adsorption study of CH_4 and compared our adsorption isotherm results with the previously reported MOFs [32]. Interestingly, MIL-101(Cr) possesses numerous unprecedented features such as zeotype architecture including mesoporous cages and microporous windows, huge cell volume, large surface area, and many unsaturated chromium sites [41–43]. The MIL-101(Cr) framework is constructed from a hybrid solid superterahedral building unit, which is formed by the linkage of 1,4-benzenedicarboxylate (BDC) ligands and trimeric chromium(III) octahedral clusters [44].

In this work, we present an extensive study on synthesis, characterization and property evaluation of MIL-101(Cr) MOF for the adsorption of CH_4. The MIL-101(Cr) was synthesized by the hydrothermal reaction method using a modified fluorine free synthesis route. The synthesized materials were characterized by various experimental techniques including XRD (X-ray diffraction), SEM (scanning electron microscope), N_2 adsorption/desorption isotherms, TGA (thermogravimetric analysis) and FTIR (Fourier transform infrared) spectroscopy. The amount of CH_4 uptakes on MIL-101(Cr) were measured for the temperatures ranging from 125 K to 298 K and the pressures varying from the Henry's region to 10 bar. The experimental data were further analysed employing the GCMC (grand canonical Monte Carlo) simulation. The main objective of this work is the study of CH_4 adsorption on MIL-101(Cr) under LNG-ANG coupling conditions, which could be valid for the re-gasification of CH_4 from LNG terminals. The methane uptakes data are compared with those of other existing copper (II) and

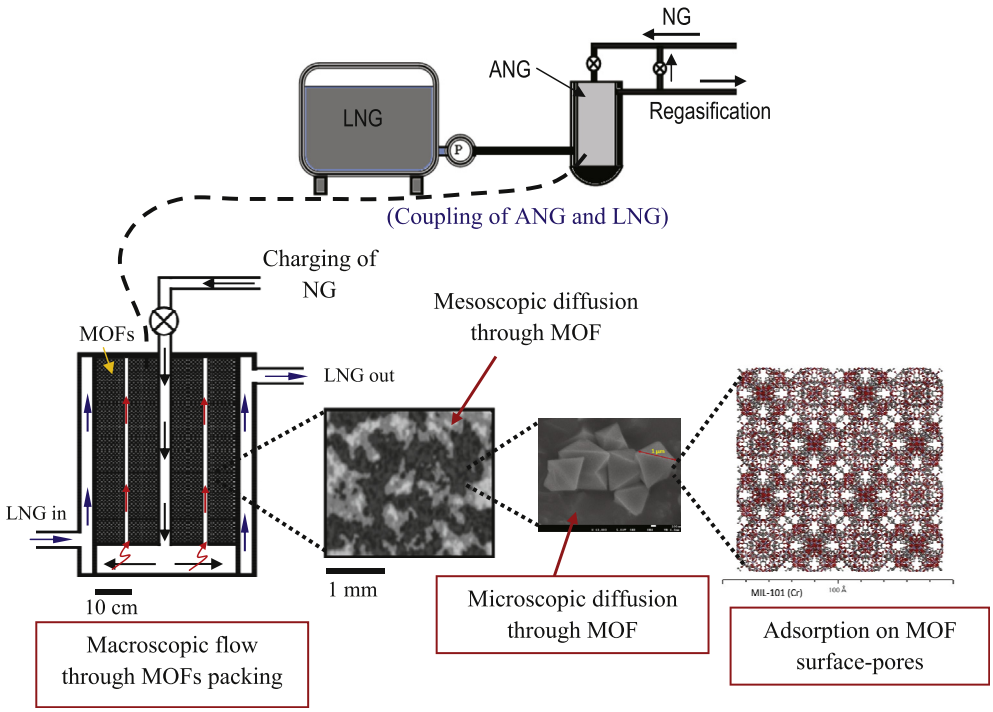

Fig. 1. Scheme of LNG regasification and ANG tank filling system. The complexity of the mass transport in MOF-packing beds of ANG is reflected by four different sizes scales: macroscopic flow, mesoscopic diffusion, microscopic pore diffusion, and adsorption processes on the MOF crystallite surface.