ORDERED NANOPOROUS CARBON AS PROMISING NOVEL METHANE ADSORBENT FOR ADSORBED NATURAL GAS TECHNOLOGY


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Introduction
Nanoporous carbon materials are extensively used as adsorbents for different purposes [1,2] such as separation and refining of gases and chemicals. Many researchers proved that methane can be stored by adsorption on porous carbon materials (adsorbed natural gas, ANG) with relatively high energy density at room temperature and pressures about 35 bar [3–4]. Ordered mesoporous carbon is a newly industrial material with wide important possible applications [5-10]. Pore size control is an important issue in the synthesis of ordered nanoporous carbon material.

In the present study, nanoporous carbon structures were synthesized with relatively controlled pore diameters and used as methane adsorbent. The results showed their potential application for natural gas storage.

Experimental
Ordered Nanoporous Carbon with Furforil Alcohol
For synthesizing sample named MCMF800, firstly, MCM41 was mixed well with a solution of para toluene sulfonic acid in ethanol for 2 hours. Then the sample was dried at 80 °C over night. Next, 0.774 gr of furforil alcohol was added and mixed for another 2 hours. The sample was placed in a tubular quartz reactor and heated up to 800°C with a ramp of 2°C/min and maintained for 2 hours. Finally, the resulted composite was rinsed in hydrofluoric acid to eliminate the template, and dried in an oven at 80 °C over night.

In order to study the effect of template structure on the adsorption capacity the above procedure was repeated with mordenite to synthesize a sample named mordenite F800.

Ordered Mesoporous Carbon with Sucrose
Three other adsorbents were synthesized by different amount of sucrose. Firstly, desired amount of MCM-41 was added to a solution of sulfuric acid, distilled water and sucrose in a Teflon beaker and mixed well. Then it was dried in an oven at 100°C. The resulted sample was divided into 3 equal parts which first one was heated to 160 °C under open atmosphere for 4-5 hours followed by heating up to 800°C under nitrogen atmosphere with a ramp of 10°C/min (Sample MCM S800A) and immediately cooled down naturally.

Second part of mentioned above mixture was added to a mixture of distilled water, 0.6 gr of sulfuric acid and 6.6 gr of sucrose and dried at 100°C. Then, it was heated at 160°C for 4-5 hours. Finally, the pyrolysis step was done by heating upto 800°C (Sample MCM S800B).

Results and discussions
Carbon nanoporous material with Furforil alcohol
From pore size distribution diagrams, the mean pore diameter of the sample MCM F800 is about 39 Å which is much more than the diameter of methane molecules; therefore this sample can not have a high storage capacity. Figure 1 shows the methane adsorption isotherm which increases from about 20cc/gr at pressure of 5 bar to approximately 49cc/gr at 35 bar. This is a low capacity for methane storage expected from mesoporous carbon nanostructures.

![Figure 1. Methane adsorption isotherm of sample MCM F800.](image1)

The average pore diameter of mordenite F800 is about 42 Å which is even higher than the previous sample. Also, its BET surface area is about 25% lower than the BET surface area of MCM F800 (405m²/gr). This causes that the carbon nanostructure by mordenite adsorbed just 43cc/gr that is about...
12% lower than the maximum capacity of MCM F800 Figure 2. Therefore one may conclude that MCM-41 is better template for synthesizing of ordered mesoporous carbon adsorbent.

**Carbon mesoporous materials with sucrose**

The BET surface areas of samples MCM S800A, B and C are 824, 741, 718 m²/g, respectively. From pore size distribution diagrams, it can be concluded that the pore volume of sample MCM S800A is the lowest among all three samples. On the other hand, the mean pore diameter of sample MCM S800A is about 48 Å which is less than that in sample MCM S800B (56 Å) and sample MCM S800C (59 Å). These confirm that the micro pore volume ratio of sample A is the highest among two other ones.

![Figure 3. Methane adsorption isotherm of MCM S800A.](image)

The methane adsorption isotherms of sample MCM S800A, B and C are illustrated in figure 3, 4, and 5, respectively. It is showed that the methane capacity of sample MCM S800A is remarkably higher than the capacity of sample MCM S800B and C. This can be explained according to the synthesis steps during the preparation procedures, which may allow forming a kind of open ended carbon nanotubes adsorbing methane molecules at the inner and outer surfaces after partially filled template elimination. That may be why the BET surface area of the sample MCM S800A is the highest among all samples. In addition, it can be very interesting to note that all samples show a sudden rise in their isotherm curves at pressures around 25 bar which may caused by variation in the adsorption mechanism. In case of sample MCM S800A the sudden growth in adsorption capacity is occurred at a little higher pressure which shows that the formation of tubular structures causes to change the adsorption mechanism at relatively higher pressures because of specific curved structures and methane adsorption on the nanotubes inner surfaces.

**Conclusion**

Different ordered nanoporous carbon adsorbents were prepared and used for methane storage at low pressures (e.g. 5-35 bar). According to isotherm curves, sucrose had more improved performance compared to furforil alcohol in methane adsorption. moreover, the results showed that the carbon nanoporous synthesized by partially filling of MCM-41 had the highest BET surface area and adsorption capacity of 824 m²/g and 112 cc CH₄/g, correspondingly. This can be as a result of open ended carbon nanotubes formation inside the ordered pores of MCM-41 which also can cause a shift in variation of adsorption mechanism to higher pressures.

![Figure 4. Methane adsorption isotherm of MCM S800B.](image)

![Figure 5. Methane adsorption isotherm of MCM S800C.](image)

**References**