

Effect of Different Parameters on Activated Carbon Methane storage

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Introduction

Adsorbent Natural Gas (ANG) has been studied for a long time as a useful technology for improvement of NG's energy density and its storage. Its higher operation security and lower cost has differed it among other storage processes. In ANG technology, we are pursuing to achieve high storage capacity, swift kinetic of gas adsorption and desorption and efficient cyclability under modest thermodynamic conditions [1]. By now, among various organic adsorbents studied in industrial processes, activated carbon (AC) has demonstrated higher capacity in natural gas storage. To have a high storage capacity, our samples structures should have three dominant characteristics: high micropore volume, high surface area (more than 1000 m²/g) and an average pore size between 8 and 15 Å [2]. Different subjects can affect on AC surface structure and its adsorption capability. Impregnation ratio, carbonization time and temperature play the main roles in it. Till now, several researches have been carried out to optimize these factors [3,4,5].

Experimental

In this research, we synthesized two samples of carbon structure and studied the effect of activating agent, impregnation ratio (R-ratio of phosphorous or zinc mass per gram of precursor) and physical activation on the methane adsorption capability.

Walnut shell, as the carbon source used in our study, was activated by two prevalent agents: ZnCl₂ and H₃PO₄.

For chemical activation, the precursors (particle size 0.5-1 mm) were first impregnated with solution of the chemical by stirring the mixture at 60 °C. The solution concentration was adjusted to provide the desired impregnation ratio (0.75, 0.82, 1 and 1.1, 1.15, 1.5 for ZnCl₂ and H₃PO₄ activation respectively). The reached samples were dried in an oven for 12 h. Then, the impregnated and dried samples were carbonized (up to 550 °C for 160 min (6 °C/min) for activation with ZnCl₂ and up to 450 °C for 55 min (4 °C/min) for activation with H₃PO₄) under N₂ flow and subsequently washed with a solution (HCl/distilled water : 1/1) to remove the chemicals and impurities. They were rinsed by distilled water for several times to be neutralized and then dried in the oven.

For physical activation, above samples were heat treated under a gas flow (consists of 90 percent N₂ and 10 percent CO₂) at 900 °C for 5 h.

As shown in Fig. 1, such an apparatus was devised and used to measure gas uptake. At the beginning of the adsorption test, the sample column was filled approximately with two grams of AC sample. To release all the existing gases, it was degassed at 150 °C in vacuum pressure. After about two hours, the column was cooled and put in a water bath with constant temperature. Note that during the test both tanks were kept in the constant ambient temperature due to get an isothermal adsorption.

At first, we let the storage tank to get to pressure we need. Next the stored gas is led to the sample column to be adsorbed. Finally, the time of adsorption and the equilibrium pressure will be recorded. This test will be also repeated with Helium gas as a voucher. Since the pressure gradient in methane test doesn't stand for the amount of gas adsorbed, the pressure difference recorded during Helium test should have been subtracted from previous data. Subsequently, the reported pressure gradient will be used to account the mass of adsorbed gas.

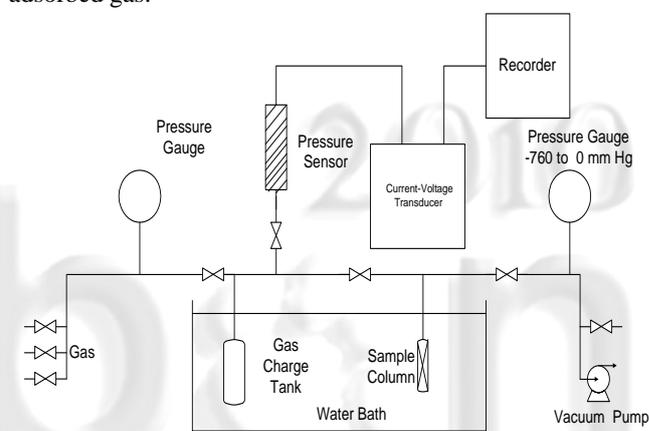


Fig. 1 schematic of experimental apparatus for gas adsorption

Results and Discussion

Comparison of methane adsorption isotherms shows that among the ACs activated with ZnCl₂, AC2R0.82 (the sample with impregnation ratio: 0.82) has the most capability in methane adsorption (Fig. 2-130 cc CH₄/g adsorbent, at 35 bar). In this case the maximum adsorption capacity by the other two samples, AC2R1 and AC2R0.75, was reported 122 and 111 cc CH₄/g adsorbent, respectively. The carbons activated with H₃PO₄ showed a reverse behavior in methane adsorption with physical activation. The adsorption ability of above samples declined to 109, 126 and 111 cc CH₄/g adsorbent for AC₂R0.75CO, AC₂R0.82CO and AC₂R1CO consecutively. This can be seen as a result of inordinate increase in pores' size due to the oxidation of superficial atoms by CO₂.

Generally, in our studies, ACs activated with H₃PO₄ exhibited more ability to methane uptake than those activated with ZnCl₂. From the isotherms of the shells activated with H₃PO₄, it was clear that AC₃R1.5CO, with the impregnation ratio of 1.5, had the best adsorption with capacity of 158 cc

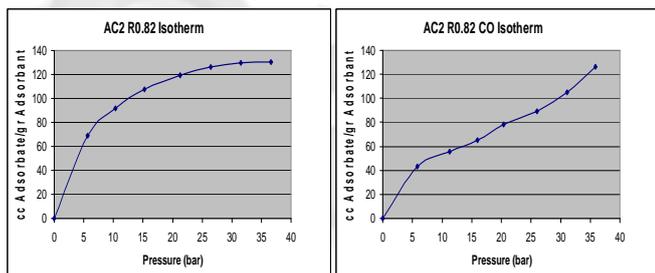
CH₄/g adsorbent at 35 bar (Fig. 3-b), whereas the two other samples, AC₃R1.15CO and AC₃R1CO, achieved their maximum adsorption capacity in 145 and 121 cc CH₄/g adsorbent.

Moreover, it is concluded that physical activation has a positive effect on the adsorption capacity of ACs activated with H₃PO₄. In this case, the adsorption capacity increased under physical treatment. It can be caused by the enhancement in micropore volume fraction due to the oxidation of superficial atoms. Although for ACs activated with H₃PO₄, methane adsorption capacity improved with R increasing, this manner wasn't true for other materials. For the AC samples activated with ZnCl₂, adsorption capability increased and then decreased by the enhancement of R from 0.75 to 1.

The specifications of the two samples which showed the highest methane adsorption capacity are summarized in Table 1.

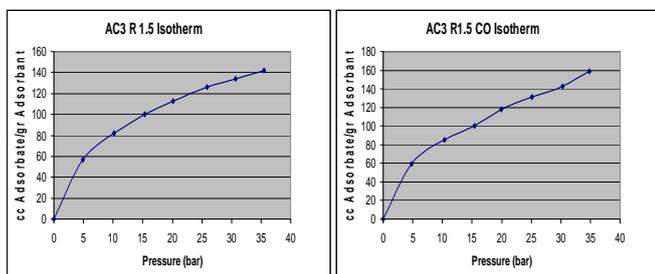
Table 1. Best samples and their characteristics.

Best Samples	AC2R0.82	AC ₃ R1.5CO
Activation Agent	ZnCl ₂	H ₃ PO ₄
Impregnation Ratio	0.82	1.5
Activation Time (min)	160/300	55/300
Chemical/Physical		
Activation Temperature (°C)	550/900	450/900
Chemical/Physical		
Maximum Methane Adsorption (cc CH ₄ /g adsorbent)	130	158
BET Surface Area (m ² /g)	1496.5	1479
Average Pore Diameter (Å)	21	28



a **b**

Fig. 2 methane adsorption isotherms for AC2R0.82, best sample activated with ZnCl₂, (a) before physical activation, (b) after physical activation.



a **b**

Fig. 3 methane adsorption isotherms for AC3R1.5, best sample activated with H₃PO₄, (a) before physical activation, (b) after physical activation.

Conclusions

In the present work, we synthesized some activated carbons from walnut shell and studied the effect of activating agent, impregnation ratio (R) and physical activation on their methane adsorption capacities. The results exhibited that ACs activated with H₃PO₄ had more capability to methane adsorption than those activated with ZnCl₂. As another observation, methane adsorption capacity improved with R increasing for ACs activated with H₃PO₄, but had ups and downs for ACs activated with ZnCl₂.

Moreover, in contrast with the other samples, it is concluded that physical activation has a negative effect on the adsorption capacity of ACs activated with ZnCl₂. This reduction in the amount of methane storage may be as a result of inordinate increase in the pores' size due to the oxidation of superficial atoms by CO₂. The best sample of our study is AC₃R1.5CO which shows storage capacity of 158 cc CH₄/g adsorbent at 35 bar pressure.

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