

Hydrophobic Modification Experiment and Characterization of FDU-15 with Different Pore Diameter

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Abstract: Three ordered mesoporous carbon materials FDU-15 with different pore diameter were used. The pore size of FDU-15 can be achieved by changing the temperature and calcination atmosphere during template removal calcination. There are more polar functional groups on the inner and outer surfaces of FDU-15 pores. As a highly hydrophilic group, hydroxyl will make FDU-15 adsorb more water molecules. In practical application, water molecules and PAHs (polycyclic aromatic hydrocarbons) will produce competitive adsorption. At the same time, PAHs are mainly non-polar compounds, so non-polar adsorbents are more conducive to the adsorption of PAHs. In conclusion, the nonpolar functional groups on the surface of FDU-15 will reduce the adsorption of PAHs, which is also caused by the poor thermal and hydrothermal stability of FDU-15 material, which limits the application of FDU-15. Therefore, hydrophobic modification of FDU-15 can reduce the number of hydroxyl functional groups on its surface, adjust the surface hydrophobicity, enhance the hydrothermal stability and improve the adsorption performance of FDU-15 for PAHs. The silylation hydrophobic modification of adsorbent is studied, and the FDU-15 with different pore diameter is hydrophobically modified. It is expected to obtain a modified FDU-15 with the best pore size by comparing its adsorption isotherm, which can be put into practical use. The hydrophobic modification in this study adopts post transplantation method, and the modified samples are characterized by FT-IR to test the modification effect.

Keywords: FDU-15, adsorption, hydrophobic modification, characterization

1. Introduction

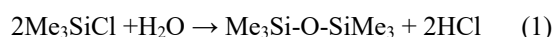
As a new synthetic porous material, ordered mesoporous materials are favored by researchers, developers and users because of their orderly and good pore distribution, adjustable mesoporous pore size, large pore volume and large specific surface area. Compared with traditional adsorbents, ordered mesoporous materials have many advantages such as large adsorption capacity, fast adsorption rate and low regeneration temperature.

Based on a large number of literature research and the former experiment, three kinds of fdu-15 with different pore sizes were selected for hydrophobic modification with trimethylchlorosilane (TMCs), characterized by FT-IR and bet, and the effects of the modification process were analyzed from two aspects of chemical composition and physical structure. The results can provide scientific basis and application reference for the practical application of mesoporous materials in the adsorption and purification of gaseous PAHs and the purification and treatment of organic polluted gases.

2. Hydrophobic modification process and phenomenon

2.1 Hydrophobic modification mechanism

TMCS (trimethylchlorosilane) is selected as the modifier in this study. The modifier is active and easy to hydrolyze. When exposed to humid air, the following reactions occur[1]:



The siloxane produced by hydrolysis is dehydrated and condensed with the hydroxyl group on the

surface of FDU-15, so as to reduce the hydroxyl functional group with strong hydrophilicity on the surface, so as to make FDU-15 hydrophobic[2].

2.2 Experimental phenomena of hydrophobic modification

The particle size of FDU-15 decreases by 40%-60% with the increase of calcination temperature, and its skeleton size will also decrease[3]. Therefore, during the modification experiment, it can be observed that the sample calcined at 1200°C is most evenly dispersed in toluene solution, while the other two samples have large particles. During the stirring process, more samples are attached to the stirring rotor, resulting in large loss. In the process of suction filtration, because the sample particles calcined at 1200°C are small, the main loss is that part of the sample powder is attached to the filter paper, which is difficult to collect.

Because the particle diameters of FDU-15-350 and FDU-15-600 are large and can not be well dispersed in toluene solution[4], 18H modification experiment is added to test whether the modification is successful when the sample is poorly dispersed in toluene solution. In addition, because the particles of FDU-15-1200 sample are small and powder, they are very evenly dispersed in toluene solution[5], and the modification experiment of 18H is not carried out.

3. FT-IR analysis

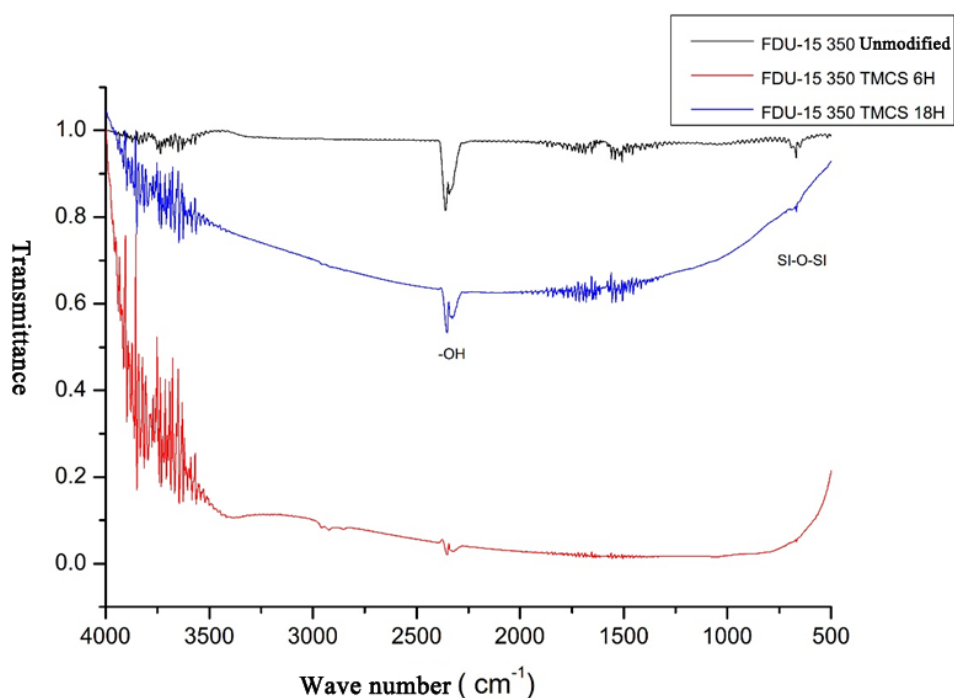


Figure 1: Comparison of FT-IR before and after FDU-15-350 modification under different reaction time

Figure 1 shows FDU-15 calcined at 350°C and modified for 6H and 18H respectively, which are compared with unmodified samples. In the figure above, the bending vibration peak of -OH hydroxyl functional group is at 2300cm⁻¹, and the stretching vibration peak of Si-OH silicon hydroxyl functional group is at 3700cm⁻¹. These two peaks reflect the number of hydroxyl functional groups on the sample surface[6]. It can be seen from the figure that the hydroxyl functional groups on the surface of the modified sample are significantly reduced, indicating that the hydrophobic modification is successful. However, although the hydroxyl functional groups of the samples with modification time of 18H are less than those of the unmodified samples, they are more than those of the samples with modification time of 6H, which may be due to the long reaction time and the attachment of some modifiers to the sample pores.

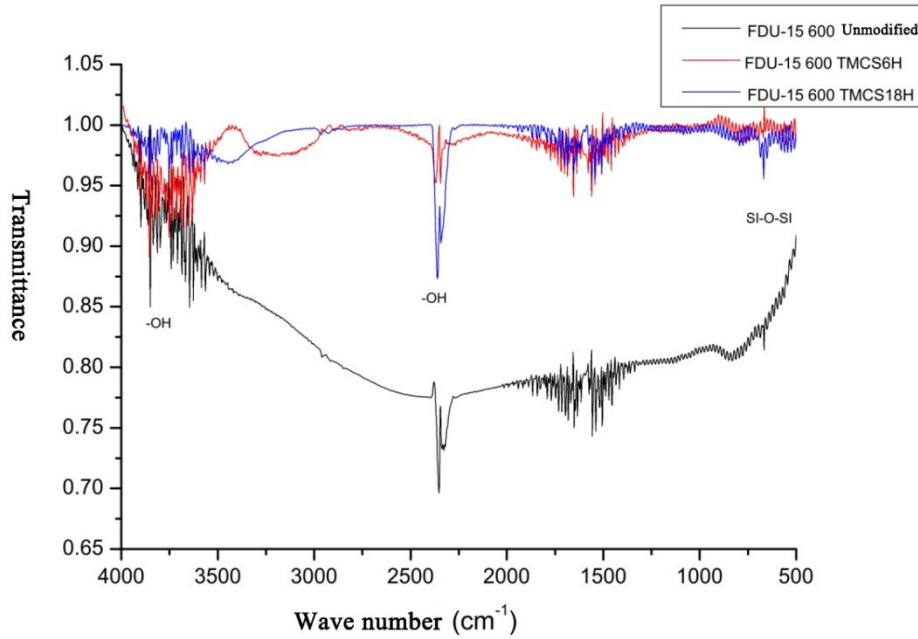


Figure 2: Comparison of FT-IR before and after FDU-15-600 modification at different reaction times

Figure 2 shows the samples with FDU-15 calcination temperature of 600°C and modification time of 6H and 18H respectively, which are compared with the unmodified samples. It can be seen from the figure that the bending vibration peak of -OH hydroxyl functional group is at 2300 cm^{-1} and the stretching vibration peak of Si-OH silicon hydroxyl functional group is at 3700 cm^{-1} . These two peaks reflect the number of hydroxyl functional groups on the sample surface. The spectral peak at 795 cm^{-1} in the figure is the asymmetric stretching vibration peak of Si-O-Si bond, representing the number of siloxanes on the sample surface[7]. It can be seen from the figure that the hydroxyl functional groups on the surface of the modified sample are significantly reduced, indicating that the hydrophobic modification is successful, and the peak of siloxane is significantly steeper, indicating that a large amount of siloxane is generated on the surface of FDU-15 sample. In the figure, the number of hydroxyl groups on the surface of the sample with modification time of 18H is more than that of the sample without modification. This is because the pore diameter of FDU-15-600 is smaller than that of FDU-15-600, which is easier to be blocked by modifier in the long-term modification process[8].

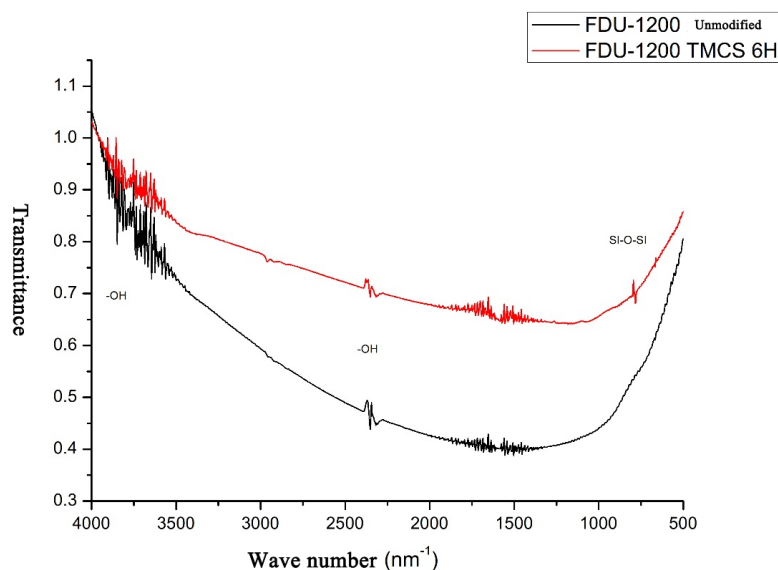


Figure 3: Comparison of FDU-15-1200 FT-IR before and after hydrophobic modification

Figure 3 shows a sample of FDU-15 calcined at 1200°C for 6H and compared with the unmodified

sample. Because the sample itself is powder, it is better dispersed in toluene in the modification process, and the modification effect of the sample with modification time of 18H decreases from FT-IR analysis, so the sample is not subject to 18H modification experiment[9]. It can be seen from the figure that the number of hydroxyl functional groups on the surface of the modified sample is significantly reduced, indicating that the hydrophobic modification is successful.

After FT-IR analysis of the above samples, it can be known that the hydrophobic modification of FDU-15 with different pore diameter is successful, and the next experiment can be carried out. The adsorption performance can be obtained from the subsequent dynamic adsorption test.

4. Bet analysis

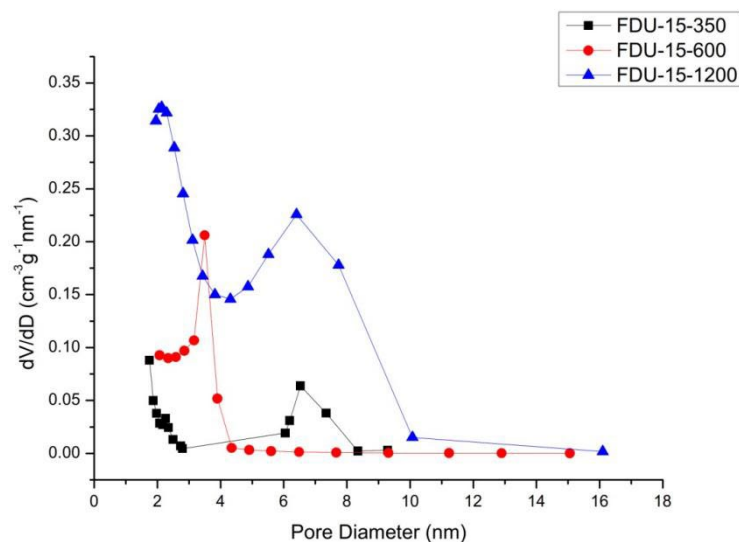


Figure 4: Pore size distribution of unmodified FDU-15 samples with different pore diameter

Figure 4 shows the pore size distribution of FDU-15 samples with different pore diameter. It can be seen that the pores of FDU-15 samples calcined at 1200°C are mainly concentrated near micropores and mesopores. Due to the poor accuracy of the detection instrument, the micropores less than 2nm cannot be reflected, and FDU-15 calcined at 1200°C has a double pore structure[10]. The channels of FDU-15 samples calcined at 600°C are concentrated between 3-4 nm. The calcination temperature is 350°C The FDU-15 sample channels are mainly distributed in the range of 2nm and 6-7nm[11]. It can be seen that the number of micropores of FDU-15 samples with different pore diameter increases after modification, and the difference between FDU-15 samples at 1200°C is small. The increase in the number of micropores is due to the formation of microporous structure because some smaller mesoporous channels in the sample are occupied by modifier TMCS molecules[12]. However, the samples calcined at 1200°C have a double pore structure. After some microporous structures are occupied by modifier TMCS molecules, the pore structure disappears. After some mesoporous channels with smaller pore diameter become micropores, the overall number of micropores changes little, which may lead to that the adsorption performance of FDU-15 samples calcined at 1200°C after modification is not as good as that before modification. After modification, the pore size of each diameter of each sample decreases, which is also caused by the fact that the modifier TMCS molecule occupies the pore[13].

5. Conclusions

We used modifier TMCS (trimethylchlorosilane) to hydrophobically modify FDU-15 with different pore diameter by post transplantation method. By changing the modification reaction time, we obtained 8 groups of FDU-15 samples that can be used for subsequent dynamic adsorption tests, characterized them by FT-IR and BET, analyzed the effect of the modification process from two aspects of chemical composition and physical structure, and obtained the following conclusions:

- (1) Three FDU-15 samples with different pore diameter were hydrophobically modified by TMCS.

FT-IR analysis showed that the hydrophobic modification experiment significantly reduced the number of hydrophilic groups and hydroxyl groups on the surface.

(2) After BET analysis of some of the above samples, it can be seen that after modification, the mesoporous channels of FDU-15 samples have not been damaged, there are still mesopores that can be used for PAHs adsorption at high concentration, and micropores beneficial to micropore filling behavior at low concentration are added.

References

- [1] Ziyi Li. *Experimental study and molecular simulation of adsorption of gaseous polycyclic aromatic hydrocarbons by mesoporous materials*[D]. University of Science and Technology Beijing, 2017.
- [2] Jianfei Song. *Studies on the adsorption of VOCs by activated carbons and the structure-activity relationship*[D]. Central South University, 2014.
- [3] Jinying Xi, Junliang Wu, Hongying Hu, et al. *Application status of industrial VOCs gas treatment techniques*[J]. *China Environmental Science*, 2012,32(11):1955-1960.
- [4] Keliang Wang. *Experimental and molecular simulation study on the preparation of ordered mesoporous carbons and naphthalene adsorption performance*[D]. South China University of Technology, 2012.
- [5] Davies J I, Evans W C. *Oxidative metabolism of naphthalene by soil pseudomonads. The ring-fission mechanism*[J]. *Biochemical Journal*, 1964, 91(2): 251.
- [6] Haifeng Huang, Xiang Chu, Hanfeng Lu, et ai. *Study on dynamic adsorption of VOCs on two mesoporous molecular sieves*[J]. *Chinese Environmental Science*, 2010, 30(4):442-447.
- [7] Mastral A M, García T, Callén M S, et al. *Removal of naphthalene, phenanthrene, and pyrene by sorbents from hot gas*[J]. *Environmental science & technology*, 2001, 35(11): 2395-2400.
- [8] Li Z, Liu Y, Yang X, et al. *Desorption kinetics of naphthalene and acenaphthene over two activated carbons via thermogravimetric analysis*[J]. *Energy & Fuels*, 2015, 29(8): 5303-5310.
- [9] Hongcang Zhou, Huaxia Cai, Hongbin Xue, et al. *Static adsorption mechanism of naphthalene on carbonaceous sorbents*[J]. *Research of Environmental Sciences*, 2010,23(05):685-662.
- [10] Dongmei Liu, Bichun Huang, Daiqi Ye. *Study on adsorption of naphthalene on ordered mesoporous carbons*[J]. 2009(09): 23-28+40.
- [11] Hua Huang, Yaxiong Wang, Jingchun Tang, et al. *Properties of maize stalk biochar produced under different pyrolysis temperatures and its sorption capability to naphthalene*[J]. *Environmental Science*, 2014(05): 1884-1890.
- [12] Kondo Jingyi, Ishikawa Daxiong, Abe yufu. *Adsorption science*[M]. Beijing: Chemical Industry Press, 2006.
- [13] Peiran Guo, Shilin Hu. *Hydrophobic modification of ni-mof-74 and its effect on co adsorption performance*[J]. *Atomic Energy Science and Technology*, 2020,54(07):1192-1198.