

多孔有机骨架:基于傅氏烷基化反应的合成与气体吸附性质

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摘要:通过傅氏烷基化反应成功地合成了基于四苯锗烷构筑单元的多孔有机骨架材料 PAF-9。用红外光谱,粉末 X 射线衍射,固体核磁共振,热重分析和低温氮气吸附-脱附表征了 PAF-9 材料的微结构与孔道性质。表征数据表明 PAF-9 具有非常高的热稳定性和化学稳定性,同时具有较高的比表面积。该 PAF 材料的 BET 比表面积为 $334 \text{ m}^2 \cdot \text{g}^{-1}$ 。此外,得到的 PAF 材料对二氧化碳具有较好的吸附能力。

关键词:傅氏烷基化;多孔有机骨架材料;气体吸附

中图分类号:O621.25 文献标识码:A 文章编号:1001-4861(2015)09-1855-05

DOI:10.11862/CJIC.2015.256

Porous Aromatic Frameworks: Synthesis via Friedel-Crafts Alkylation Reaction and Gas Sorption Property

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Abstract: A porous aromatic framework, PAF-9 derived from tetraphenylgermane as basic building unit, was synthesized via Friedel-Crafts alkylation reaction. The microstructure and pore property were investigated by FTIR spectroscopy, powder X-ray diffraction, solid state NMR, thermogravimetric analysis and low temperature N_2 adsorption-desorption measurements. The characterizations reveal that PAF-9 possess high thermal and chemical stability as well as high BET surface area of $334 \text{ m}^2 \cdot \text{g}^{-1}$. Additionally, the resulting PAF materials exhibit high CO_2 adsorption ability.

Key words: Friedel-Crafts alkylation reaction; porous aromatic framework; gas sorption

0 Introduction

Nowadays, one of the major causes of the global warming is the excessive CO_2 emission. CO_2 capture

and storage (CCS) technologies are urgently needed in twenty-first century^[1-3]. So it is important to synthesize novel porous materials as alternative candidates for CO_2 capture. Porous organic frameworks (POFs)

收稿日期:2015-05-31。收修改稿日期:2015-08-03。

国家重点基础研究发展计划(973 计划, No.2012CB821700, No.2014CB931804)、国家自然科学基金委重大国际(地区)合作研究项目(No.21120102034)资助项目。

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possess many advantage, including high surface area, low skeleton density, high chemical and thermal stability and have attracted considerable attention as a kind of sorption materials in CCS technologies. Various POFs materials, such as covalent organic frameworks (COFs)^[4-7], polymers of intrinsic microporosity (PIMs)^[8-9], conjugated microporous polymers (CMPs)^[10-11], crystalline triazine-based organic frameworks (CTFs)^[12-13], and porous aromatic frameworks (PAFs)^[14-16], have been created and synthesized. In particular, POF networks derived from diamond-like building units such as tetraphenylmethane were obtained, and most of them presented ultra-high surface area and excellent gas sorption ability^[17]. Several pioneering and effective strategies have been employed to construct POFs, including condensation reaction of boronic acids, the dibenzodioxane-forming reaction, palladium catalyzed Sonogashira-Hagihara cross-coupling reaction, palladium-catalyzed Suzuki cross-coupling reaction and trimerization reaction of aromatic nitrile compounds etc^[18]. However, these cross-couple reactions are usually catalyzed by expensive noble metals or transition metal catalysts which limit the development for extensive application of POFs in CCS technologies. It is worth to find a synthesis route with cheap catalysts to synthesize high surface area POFs. Under the circumstances, we explored to construct polymers with diamond-like structure which have high surface area via cost-effective cross-coupling reaction. Tan and Cooper group^[19-22] have reported a series of polymers with heterocyclic (pyrrole, thiofuran, furan, benzene, and biphenyl etc.) as monomers and formaldehyde dimethylacetal as an external cross-linker via Friedel-Crafts alkylation reaction. This kind of reaction is catalyzed by inexpensive FeCl_3 or AlCl_3 ^[23-24]. In the presence of Lewis acid, aromatic nuclei of monomers become active to achieve polymerization to produce polymers. Being inspired by this idea, we chose tetraphenylgermane as tetrahedral building unit and FeCl_3 as catalyst via Friedel-Crafts alkylation reaction under mild condition to produce the cost-effective porous aromatic frameworks (PAF-9). After the synthesis of PAF-9, we carried out characterizations

and discovered that PAF-9 has high surface area ($334 \text{ m}^2 \cdot \text{g}^{-1}$). So we further studied CO_2 sorption ability of PAF-9 and found out that PAF-9 had good sorption ability of CO_2 .

1 Experimental

1.1 Materials and measurements

Tetraphenylgermane (5 g, 98%) and formaldehyde dimethyl acetal (FDA, 500 mL, 98%) were purchased from Alfa Aesar. CaH_2 (100 g, 95%) was purchased from Aladdin. Other chemicals and reagents were purchased from commercial suppliers without further purification unless otherwise stated. Methylene dichloride (CH_2Cl_2 , 500 mL, 99%, Beijing Chemical Works) was dehydrated with CaH_2 .

The Fourier transform infrared spectroscopy (FTIR) spectra (film) were recorded using IFS 66V/S Fourier transform infrared spectroscopy. Solid-state ^{13}C CP/MAS NMR measurements were performed on a Bruker Avance III model 400 MHz spectrometer at a MAS rate of 5 kHz. The powder X-ray diffraction (PXRD) was performed by a Rigaku D/MAX2550 diffractometer using $\text{Cu } K\alpha$ radiation ($\lambda=0.15418 \text{ nm}$), 50 kV, 200 mA with scanning rate of $4^\circ \cdot \text{min}^{-1}$ (2θ). Scanning electron microscopy (SEM) analysis was performed on a JEOS JSM 6700. Transmission electron microscopy (TEM) was recorded using a JEOL JEM 3010 with an acceleration voltage of 300 kV. Thermogravimetric analysis (TGA) was performed using a Netzsch Sta449c thermal analyzer system at a heating rate of $10^\circ \text{C} \cdot \text{min}^{-1}$ in air. The gas adsorption-desorption isotherms data were obtained from a Quantachrome Autosorb-iQ2 analyzer.

1.2 Synthesis

Tetraphenylgermane (1 mmol, 0.38 g) and FeCl_3 (4 mmol, 0.65 g) were added into a 100 mL round-bottom-flask, and the system of mixture was degassed to vacuum and aerated with Ar and sealed by three freeze-pump-thaw cycles. Then FDA (4 mmol 0.36 mL) and CH_2Cl_2 (10 mL) were injected into the system through a syringe. The polymerization fused aromatic monomers with 4 equivalents of FDA (depending on the number of aromatic reaction sites available). The

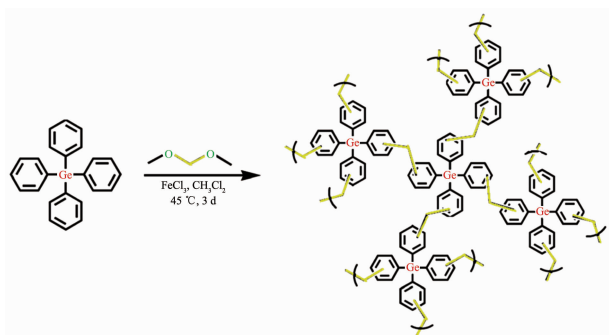


Fig.1 Synthetic pathway of PAF-9

mixture was heated at 45 °C for 3 d to produce the polymer. After cooling down to room temperature, the product was washed by 1 mol · L⁻¹ hydrochloric acid solution, methanol and acetone until the filtrate liquor was nearly colorless. Then the product was Soxhlet extracted for 24 h with methanol, tetrahydrofuran and dichloromethane separately to remove monomers and catalyst residues thoroughly, and dried under vacuum to give PAF-9 as brown powder (95% yield).

2 Results and discussion

2.1 FTIR spectra

Comparisons of the FTIR spectra of monomers and products were performed to confirm the reaction degree of the polymerization. As shown in Fig.2, the appearance of intense saturated C-H bands (at 2 904 cm⁻¹) of PAF-9 reveal that the networks are linked by methylene groups as desired. The peaks at 1 600~1 450 cm⁻¹ belong to aromatic C=C stretching vibrations and the peaks at 900~650 cm⁻¹ belong to aromatic C-H deformation vibrations. These indicate the phenyl rings in the PAF-9 network.

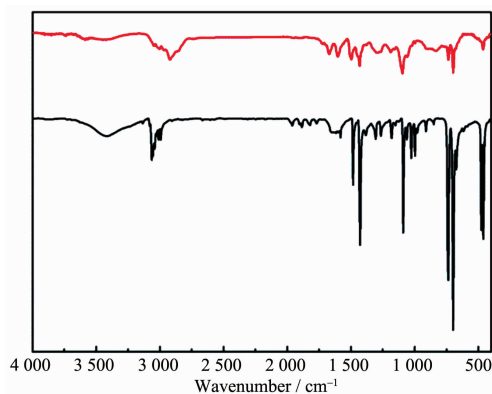
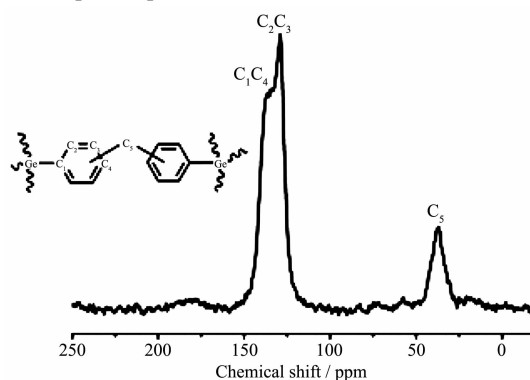


Fig.2 FTIR spectra of PAF-9 (red) and tetraphenylgermane (black)

2.2 Solid State ¹³C CP/MAS NMR spectra

Further investigation of the local structures of the PAF-9 was performed by solid-state ¹³C CP/MAS NMR studies. Three different types of resonance peaks are clearly observed in the ¹³C CP/MAS NMR spectra of PAF-9 (Fig.3). The strong signals in the range of 140~125 ppm are attributed to the aromatic carbon atoms. The peak at 127 belongs to the aromatic C (C₂, C₃) connected to H and the peak at 138 belongs to the aromatic C (C₁, C₄) connected with other atom or persad. Moreover, the signal near 37 is related to the methylene carbon atoms (C₅), thus further indicating the FDA participation in the reaction.

Fig.3 ¹³C CP/MAS NMR spectrum of PAF-9

2.3 Powder X-ray diffraction

PXRD was carried out to identify the crystallinity of PAF-9 materials. No intense peaks but only a broad peak in Fig.4 indicate that the texture of the polymer is amorphous which is caused by the irreversibility of Friedel-Crafts alkylation reaction and the introduction of flexible persad (methylene).

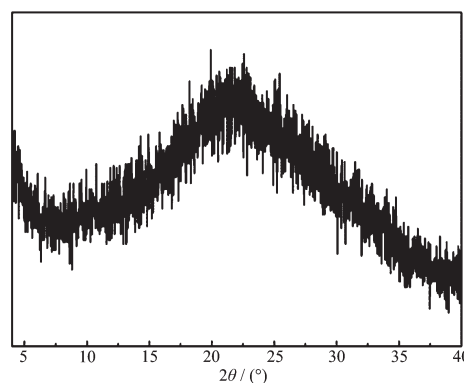


Fig.4 PXRD pattern of PAF-9

2.4 SEM and TEM

The morphology and particle size of PAF-9 were

investigated by SEM measurement. SEM image (Fig. 5a) shows that PAF-9 is amorphous and most particles are micro-sized irregular blocks. TEM analyses (Fig. 5b) shows that PAF-9 is clearly porous textures, although the arrangement of the pores was random.

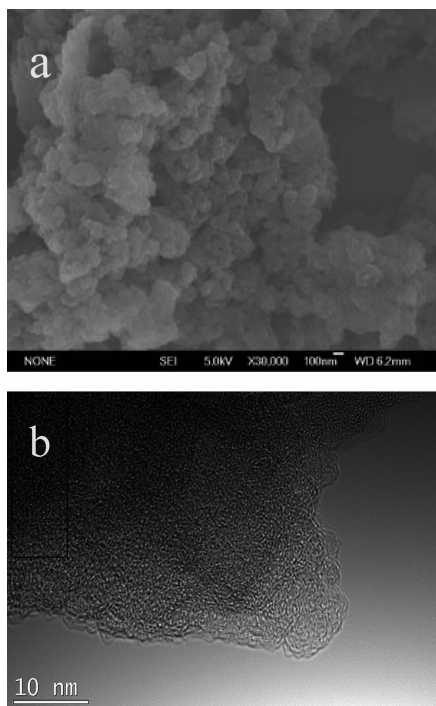


Fig.5 SEM (a) and TEM (b) images of PAF-9

2.5 Thermogravimetric analysis

TGA analysis under air conditions was used to investigate the structure stability of the polymers. Fig. 6 exhibits that PAF-9 displays high thermal stability. The decomposition temperature of PAF-9 is above 400 °C. In addition, PAF-9 materials cannot be dissolved and decomposed in common organic solvents, such as DMF, THF, CHCl₃ and so on, indicating high thermal and chemical stability.

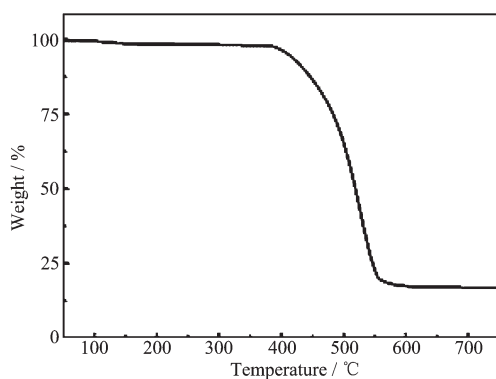


Fig.6 TGA plots of PAF-9

2.6 N₂ sorption measurements

The pore character of PAF-9 was studied by N₂ sorption isotherm measured at 77 K under 1 013 kPa. As indicated in Fig.7, a sharp uptake at low relative pressures and a distinct hysteresis loop in the desorption branch are observed indicating that PAF-9 possesses both microporous and mesoporous texture. The adsorption isotherm of PAF-9 increases rapidly at $P/P_0 \approx 1.0$ which might be attributed to the surface adsorption of assembled small particles. The apparent surface area of PAF-9 calculated from the Brunauer-Emmett-Teller (BET) model is 334 m²·g⁻¹. Meanwhile, the pore size distribution calculated via nonlocal density functional theory (NLDFT) gives two narrow peaks at 1.68 and 3.80 nm, further proving the micro-mesoporous network of PAF-9.

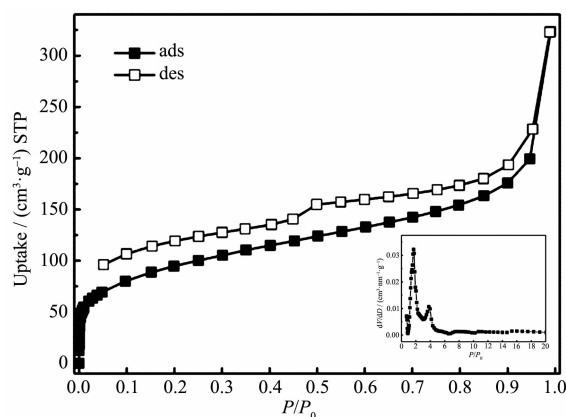


Fig.7 N₂ sorption isotherms and pore size distribution (inset) of PAF-9

2.7 CO₂ adsorption measurements

The high surface area and permanent porosity make PAF-9 an outstanding candidate for gas sorption such as CO₂. Herein, CO₂ sorption isotherms are collected at 273 and 298 K. As shown in Fig.8a, under STP condition, the CO₂ uptakes of PAF-9 at 273 and 298 K are 28 cm³·g⁻¹ and 17 cm³·g⁻¹ respectively. The heat of adsorption (Q_{st}) for CO₂ calculated from adsorption data from 273 and 298 K, using the Clausius-Clapeyron equation, is 32 kJ·mol⁻¹ (Fig.8b). The results indicate that PAF-9 has comparative CO₂ sorption capacity with other reported POF materials^[25-26] and is possible to be a cost-effective material in CCS technologies.

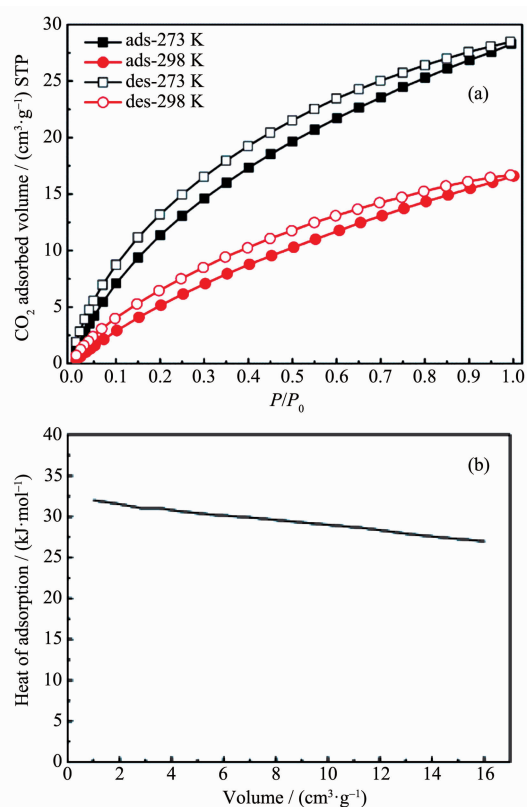


Fig.8 CO₂ sorption isotherms measured at 273 and 298 K (a) and Q_{st} for CO₂ (b) of PAF-9

3 Conclusions

In summary, the PAF materials (PAF-9) based on tetrahedral building blocks was synthesized by simple one-step Friedel-Crafts alkylation reaction in the presence of inexpensive catalyst FeCl₃. The properties of PAF-9 materials were investigated and discussed. Characterizations indicate that the PAF-9 materials display high thermal and chemical stability as well as high surface area. In addition the PAF-9 materials exhibit potential application in CO₂ capture.

Acknowledgments: We are grateful for the financial support of National Basic Research Program of China (973 Program, Grant No.2012CB821700 and Grant No.2014CB931804), Major International (Regional) Joint Research Project of NSFC (Grant No.21120102034).

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