AMINE-FUNCTIONALIZED POROUS POLYMERS FOR SELECTIVE CO_2 ADSORPTION

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Abstract

Porous materials have always attracted high scientific interest because of their outstanding performance and potential applications in various fields, including adsorption and gas separation. Hyper-crosslinked polymers (HCLPs) have several advantages over other porous materials, they show extremely high surface areas and porosity, low density, outstanding adsorption properties, high chemical, and thermal stability.
Herein, we reported a synthesis, characterization, and the CO_2 (and other gases) adsorption performance of series of novel styrene-divinylbenzene based HCPs. The material was prepared in two steps. The first step involved the radical copolymerization of divinylbenzene (DVB) and 4-vinylbenzyl chloride (VBC), under solvothermal condition to generate porous polymers with high surface area above 700 $m^2 g^{-1}$. In the second step, various polyamine species were applied to react with the alkyl chloride groups and functionalize the pore surface to improve the CO_2/N_2, CO_2/CH_4 and CO_2/H_2 selectivity.

Introduction

The increasing release of CO_2 to the atmosphere due to human activities has initiated considerable interest in the development of new materials and technologies for CO_2 capture. A cheap alternative solution represents a design and synthesis of microporous organic polymers, porous materials generally possess low skeletal density, in which the precise control over the material's chemical composition and textural properties can lead to a significant enhancement in gas storage[1]. This work is focused on the synthesis of hypercrosslinked vinylbenzyl chloride (VBC) - divinylbenzene (DVB) microporous material and its application for CO_2 capture and gas separation[2].

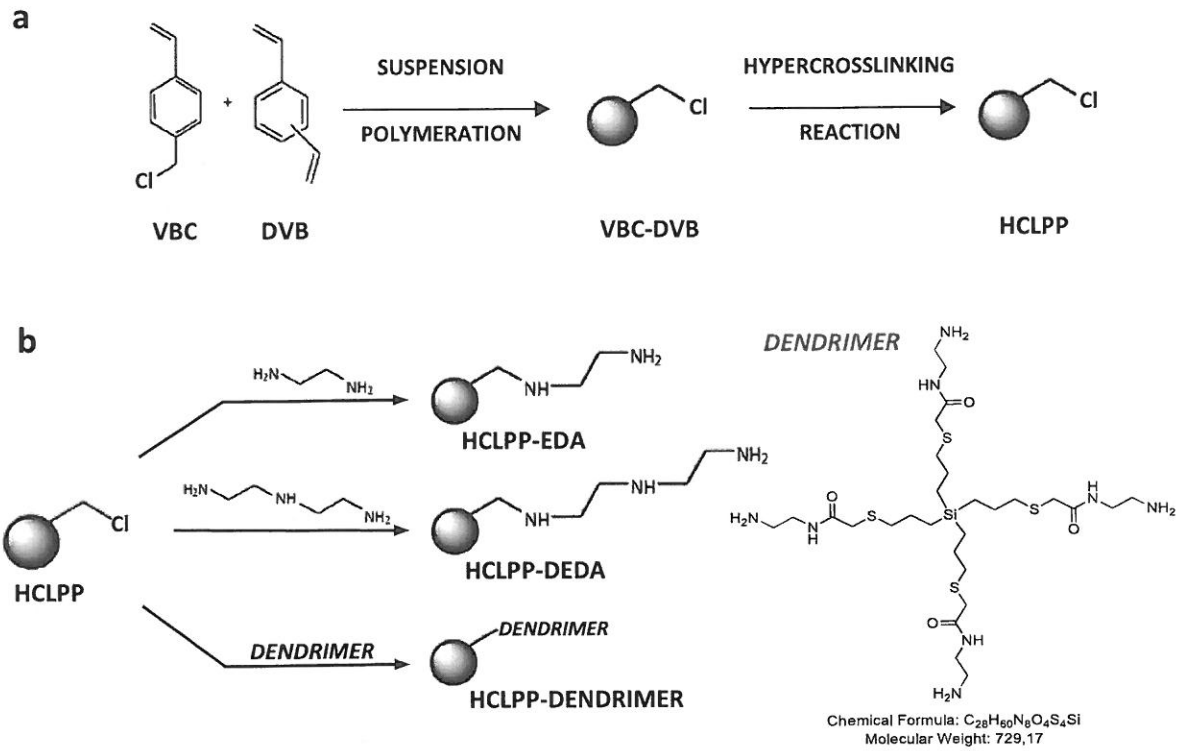
Experiment

Material

All chemicals needed to synthesis of the hypercrosslinked vinylbenzyl chloride (VBC) - divinylbenzene (DVB) microporous material were purchased from Sigma Aldrich. Pure gases used for the solubility and permeation experiments were purchased from Linde Gas with a stated purity of at least 99.995%.

Synthesis of porous polymer

The hypercrosslinked vinylbenzyl chloride (VBC) - divinylbenzene (DVB) microporous polymer was prepared and functionalized in two steps as shown in Scheme 1. The first step involved the suspension polymerization of divinylbenzene (DVB) and 4-vivylbenzyl chloride (VBC). Then, the resulting polymer was hypercrosslinked under conditions given in Scheme 1a. In the second step, various polyamine species were applied to react with the alkyl chloride groups and functionalize the pore surface to improve selectivity of material to CO_2 (see Scheme 1b).



Scheme 1 (a) Synthesis of hyper-crosslinked porous polymer (HCLPP) and (b) the post-polyamine functionalization by ethylenediamine, diethylenetriamine and dendrimer[4].

Gas adsorption measurement

The measurement of the absorption isotherms was based on the volumetric method[3]. The adsorption of pure gas in prepared materials was measured using an apparatus shown in Figure 1.
The thermostated apparatus consists of two chambers with calibrated volumes V_1 and V_2 separated by a valve. Pressure in the apparatus is measured by pressure transducer. In the case of liquid measurement, the apparatus is placed on a magnetic plate that mixes the sample to accelerate the achievement of the absorption equilibrium. The constant temperature of the whole system during the absorption experiment was provided by a heated box.

Before the experiment the weighted amount of sample was placed in the adsorption chamber, V_2. The system was thermostated at experimental temperature 25 °C. The apparatus was evacuated in order to remove dissolved gases and impurities at least 5 h at temperature 80 °C. Then the chamber V_2 is closed, while the volume V_1 is filled with a studied gas at a certain pressure p_1. At the start of measurement, the volumes V_1 and V_2 are connected and the pressure value inside apparatus was monitored by computer. The pressure first dropped immediately to a certain value due to the interconnection of the chambers. Subsequently, the pressure value decreased already more slowly, it corresponds to the adsorption of gas in the sample material. After reaching the equilibrium the pressure p_{eq} is subtracted and use to determination of adsorbed amount of gas in sample. The time needed to achieve equilibrium is about 3 hours.

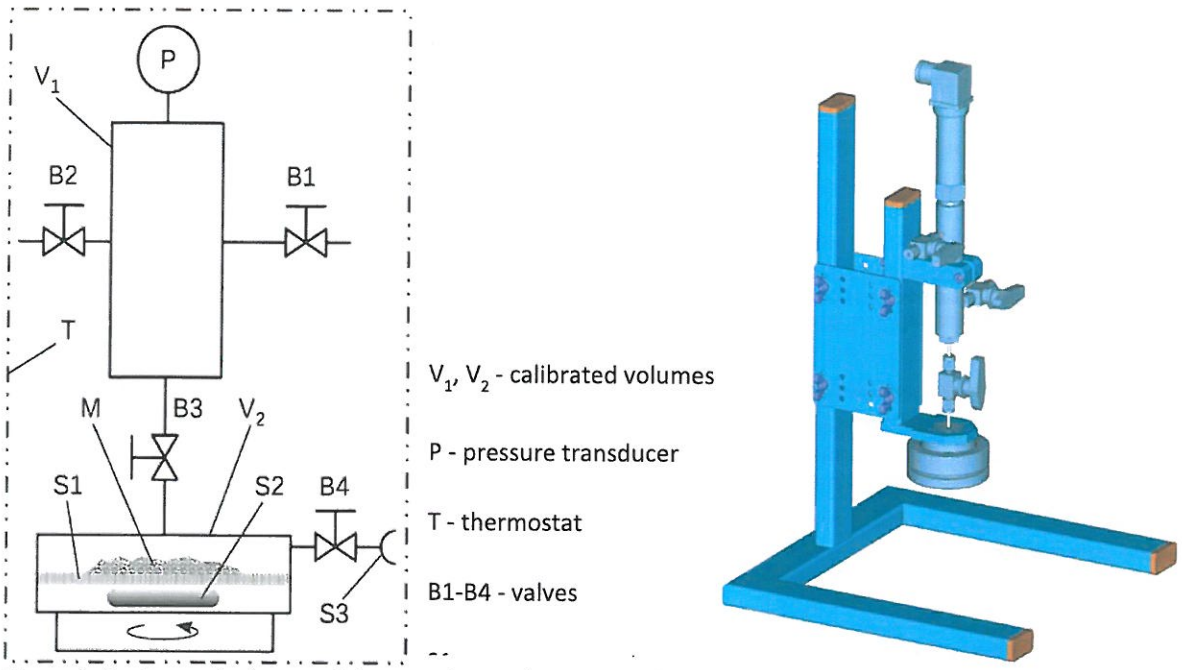


Figure 1. Design and schema of the experimental apparatus for gas adsorption capacity measurement.

The gas amount adsorbed in the material is calculated from the balance as the difference of the initial and the equilibrium amounts:

$$N_{(adsorbed)} = N_{(gas\ initially)} - N_{(rest\ gas\ in\ equilibrium)} \quad (1)$$

$$N_{(adsorbed)} = \frac{p_1 V_1 - p_{eq}(V_1 + V_2 - V_x)}{RT} \quad (2)$$

The ideal gas state eq. (3) is used to the moles in gas phase calculation (*N* gas moles number):

$$N = \frac{pV}{RT} \quad (3)$$

The adsorbed amount is related to the material weight *m* to determine the adsorbed phase concentration, *q*:

$$q = \frac{N_{(adsorbed)}}{m} \quad (4)$$

Discussion and result analysis

Characterization

The surface properties of the produced materials were characterized by gas adsorption analysis, see Table I. The results revealed that pristine hyper-crosslinked porous polymer showed the highest Brunauer-Emmett-Teller surface area (S_{BET} = 757 $m^2\ g^{-1}$). It was found that reaction of prepared porous material with polyamine species (amines and amine groups containing dendrimer) decreased the specific surface area and the total volume of pores as well, wherein in the case of modification by dendrimer the decrease was smaller than for amines.

Table I
Texture properties of pure and functionalized porous polymers HCLPP based on VBC

Sample	S_{BET}[a] [m^2g^{-1}]	S_{meso}[b] [$m^2 g^{-1}$]	V_{tot}[c] [$mm^3_{liq} g^{-1}$]	V_{micro}[d] [$mm^3_{liq} g^{-1}$]	ρ_{He}[e] [$g^1 cm^{-3}$]
HCLPP	757	310	408	226	1.15
HCLPP-EDA	283	93	157	97	1.18
HCLPP-DETA	277	132	159	76	1.16
HCLPP-DENDRIMER	616	194	341	218	1.69

[a]S_{BET} specific surface area calculated by the BET method; [b]S_{meso} specific surface area of mesopores (*t*-plot method); [c]V_{tot} specific total volume of pores; [d]V_{micro} specific volume of micropores (*t*-plot method); [e]ρ_{He} skeletal density (Helium pycnometry)

Elemental analysis of prepared polymers was investigated by EDX method and obtained data are given in Table II. It can be seen that after functionalization of porous polymer the nitrogen content in material considerably increased, after modification by amines on value higher than 8 % and in case of dendrimer on lower value about 5 %. At the same time, the chlorine content is lower, indicating a reaction with the chloride units.
These data can indicate that the reaction of the pristine polymer with dendrimer was not so effective as the reaction with amines.

Table II
EDX analysis of pure and functionalized porous polymers HCLPP based on VBC

Sample	*C* [%]	*Cl* [%]	*N* [%]	*S* [%]	*Si* [%]
HCLPP	93.49	0.40	1.66	-	0.05
HCLPP-EDA	82.96	0.07	8.43	-	0.09
HCLPP-DETA	85.09	0.05	8.76	-	0.07
HCLPP-DENDRIMER	90.62	0.29	5.18	0.19	0.20

Gas adsorption

The experimental results for the gas adsorption in the synthesized porous polymer and functionalized variants at temperatures of 25 °C evaluated from adsorption isotherm for pressure 1 bar are presented in Table III.

Table III
Gas adsorption performance of pure and functionalized porous polymers HCLPP based on VBC*

Sample	CO_2 [mmol g^{-1}]	CH_4 [mmol g^{-1}]	N_2 [mmol g^{-1}]	H_2 [mmol g^{-1}]	O_2 [mmol g^{-1}]
HCLPP	1.01	0.31	0.090	0.021	0.012
HCLPP-EDA	0.91	0.13	0.033	0.015	0.047
HCLPP-DETA	0.82	0.13	0.029	0.012	0.042
HCLPP-DENDRIMER	1.10	0.24	0.063	0.017	0.089

* Amount of captured gases in porous material at 1 bar.

The polymer modification led in most of cases to the decrease of gas adsorption, except for oxygen. This could be due to a reduced surface area of amine-functionalized forms of polymer. However, the selectivity of the material to the gas separation after animation increased in all cases, only CH_4/H_2 selectivity was lower, see Table IV.

Table IV
Selectivity performance of pure and functionalized porous polymers HCLPP based on VBC*

Sample	CO_2/CH_4 [-]	CO_2/N_2 [-]	CO_2/H_2 [-]	O_2/N_2 [-]	CH_4/H_2 [-]
HCLPP	3.3	11.2	48.1	0.1	14.8
HCLPP-EDA	7.0	27.5	60.6	1.6	8.7
HCLPP-DETA	6.3	28.3	68.3	1.3	10.8
HCLPP-DENDRIMER	4.6	17.5	64.7	1.4	14.1

The adsorption (and desorption) isotherms of CO_2 in all studied materials up to 10 bars are shown in graphs in Figure 2. The original polymer and its dendrimer modified form showed a higher CO_2 capacity compared to the amine variants. However, when the CO_2 capacity is related to the material surface area, the amine modified polymer appears to be the most effective CO_2 adsorbent, see Figure 3.

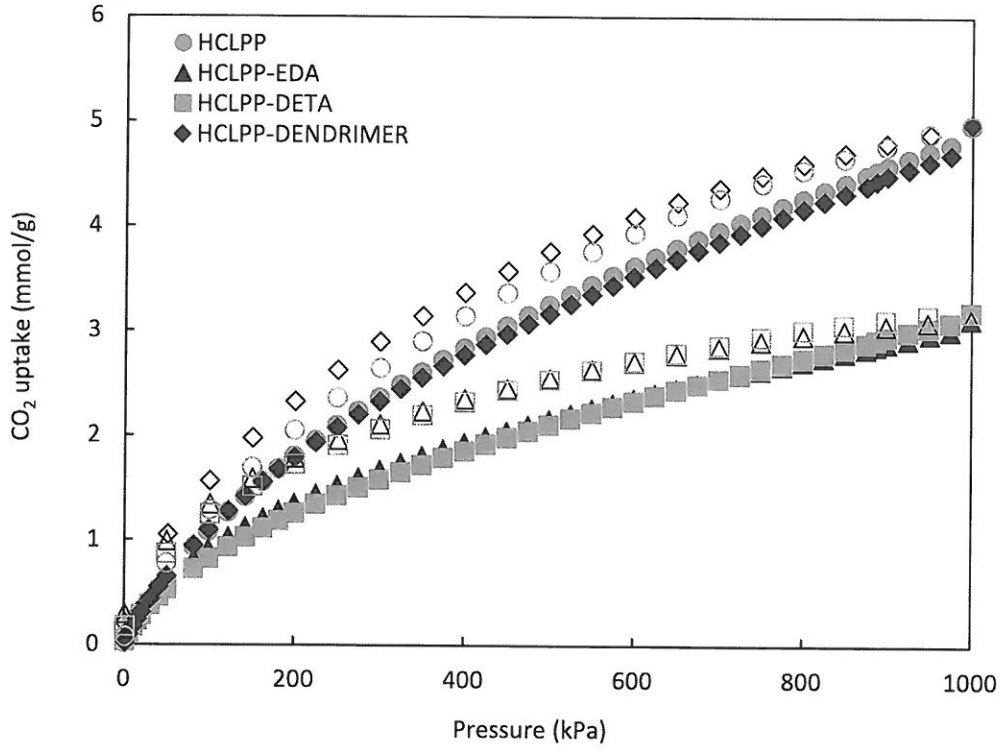


Figure 2. The CO_2 adsorption isotherms in the porous polymer materials at temperature 25 °C, adsorption (full points) and desorption (empty points).

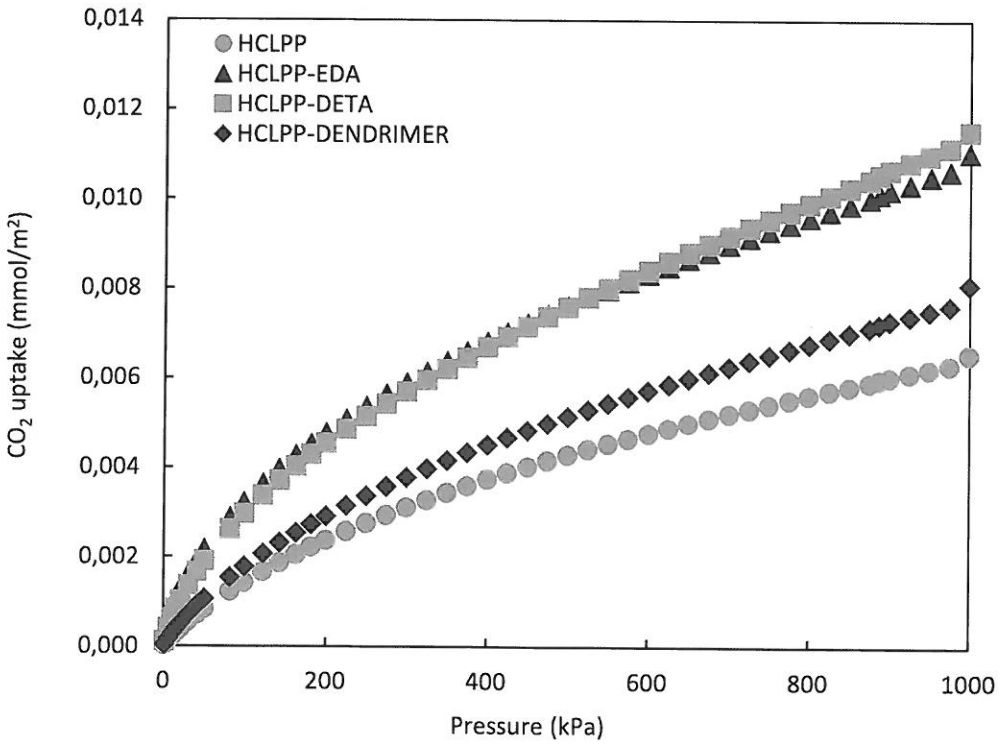


Figure 3. The CO_2 adsorption in the porous polymers at temperature 25 °C related to the specific surface area of material.

Conclusion

New porous polymeric adsorbent with a high apparent surface area showing selective CO_2 adsorption over CH_4 and N_2 and H_2 was prepared by suspension polymerization of vinylbenzyl chloride and divinylbenzene, followed by modification with polyamines and dendrimer containing amino groups resulting in an enhanced CO_2/CH_4, CO_2/N_2 and CO_2/H_2 selectivity. Produced polymer represents a promising organic porous material for CO_2 capture from gas mixtures. We plan to use the developed porous polymer and its amine-functionalized forms as fillers for preparation of mixed matrix membranes with improved CO_2/CH_4 and CO_2/N_2 separation performance[5].

Acknowledgement

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References

1. Luo YL., Tan BE.: *Porous Materials for Carbon Dioxide Capture Book Series: Green Chemistry and Sustainable Technology*. Springer, New York 2014.
2. Veverka P., Jeřábek K.: React. Funct. Polym. *41*, 21 (1999).
3. Uchytil P., Petrickovic R., Thomas S., Seidel-Morgenstern A: Separ. Pur. Technol. *33*, 273 (2003).
4. Stastna L.C., Krupkova A, Petrickovic R., Mullerova M., Matousek J., Kostejn M., Curinova P, Jandova V., Sabata S., Strasak T.: ACS Sustain. Chem. Eng. *8*, 11692 (2020).
5. Setnickova K., Sima V., Petrychkovych R., Reznickova J., Uchytil P.: Separ. Pur. Technol. *160*, 132 (2016).