PHYSICAL CHEMISTRY 2022

16th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

September 26-30, 2022
Belgrade, Serbia

Title: PHYSICAL CHEMISTRY 2022, 16th International Conference on Fundamental and Applied Aspects of Physical Chemistry (Proceedings) **ISBN** 978-86-82475-41-5
Volume II: ISBN 978-53-82475-43-9
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: ″Jovan″, <Printing and Publishing Company, Ilije Đuričića 19, Belgrade, 200 Copies
Number of pages: 6+320, Format A4, printing finished in December 2022

Text and Layout: ″Jovan″

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

200 - *Copy printing*

CONTENT

Volume II
Organizer IV
Comittes V
Sponsors VI
Material Science 321
Photochemistry, Radiation Chemistry, Photonics 391
Macromolecular Physical Chemistry 395
Environmental Protection, Forensic Sciences, Geophysical Chemistry, Radiochemistry, Nuclear Chemistry 437
Phase Boundaries, Colloids, Liquid Crystals, Surface-Active Substances 513
Complex Compounds 517
Food Physical Chemistry 535
Pharmaceutical Physical Chemistry 565
Index 633

PHYSICAL CHEMISTRY 2022

16th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by

The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of Russian Academy of Sciences

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry
Institute of Chemistry, Technology and Metallurgy
Vinča Institute of Nuclear Sciences
Faculty of Pharmacy

and

Institute of General and Physical Chemistry, Belgrade, Serbia

International Organizing Committee

Chairman: S. Anić (Serbia)
Vice-chairman: M. Gabrovska (Bulgaria)
A. A. Vedyagin (Russia)
S. N. Blagojević (Serbia)
Members: N. Cvjetićanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), A. Ivanović-Šašić (Serbia), D. Jovanović (Serbia), N. Jović-Jovičić (Serbia), M. Kuzmanović (Serbia), S. Maćešić (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović Bijelić (Serbia), B. Simonović (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), S. Veličković (Serbia), N. Vukelić (Serbia),

International Scientific Committee

Chairman: Ž. Čupić (Serbia)
Vice-chairman: V. Bukhtiyarov (Russia)
S. Todorova (Bulgaria)
B. Adnađević (Serbia)
Members: S. Anić (Serbia), A. Antić-Jovanović (Serbia), A. Azizoğlu (Turky), R. Cervellati (Italy), A. Clayton (Australia), A. Cristina Silva (Portugal) G. Ćirić-Marjanović (Serbia), V. Dondur (Serbia), R. Faria (Brasil), M. Fronczak (Poland), I. Grinvald (Russia), P. Humpolíček (Czech), M. Jeremić (Serbia), I. Kiss (USA), E. Kiš (Serbia), A.V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), T. Kowalska (Poland), G. Kyzas (Greece), G. Lente (Hungary), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), N. Ostrovski (Serbia), V. Parmon (Russia), J. Pérez-Mercader (USA) Z. Petkova Cherkezova-Zheleva (Bulgary), M. Plavšić (Serbia), J. Savović (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech), L. Schreiberova (Czech), D. Stanisavljev (Serbia), N. Stepanov (Russia), Zs. Szakacs (Romania), Z. Šaponjić (Serbia), Á. Tóth (Hungary), M. Trtica (Serbia), H. Varela (Brasil), V. Vasić (Serbia), Nadezda Vasilyeva (Russia), D. Veselinović (Serbia), V. Vukojević (Sweden), A. De Wit (Belgium)

Local Executive Committee

Chairman: S. N. Blagojević
Vice-chairman: A. Ivanović-Šašić
Members: M. Ajduković, I. N. Bubanja, D. Dimić, J. Dostanić, D. Drakulić, S. Jovanović, Z. Jovanović, D. Lončarević, J. Krstić, B. Marković, J. Maksimović, S. Marinović, D. Milenković, T. Mudrinić, M. Pagnacco, N. Potkonjak, B. Stanković, I. Stefanović, A. Todorović, M. Vasić, F. Veljković, M. Pejčić, G. Stevanović, H.Šalipur.K. Milošević, S. Pavlović, V. Kostić, B. Milovanović.

SPONSORS

Ministry of Education, Science and Technological Development of the Republic Serbia

Institute of General and Physical Chemistry, Belgrade

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of Republic of Serbia, Belgrade

University of Belgrade, Faculty of Physical Chemistry, Belgrade

CO_2 CAPTURE BY AMINE POROUS POLYMERIC SORBENT

B. M. Marković, T. T. Tadić, A. B. Nastasović, N. Radić and Z. M. Vuković

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (bojana.markovic@ihtm.bg.ac.rs)

ABSTRACT

In this report, magnetic porous polymer functionalized with pentaethylenehexamine (mP-PEHA) was tested as CO_2 sorbent. The sorbent mP-PEHA was characterized by Fourier transform infrared spectroscopy in ATR mode (FTIR-ATR), scanning electron microscopy (SEM) and mercury porosimetry. CO_2 adsorption was determined using a pulse gas chromatographic method. At optimal adsorption conditions (20 °C), the CO_2 sorption capacity reached 10.8 ml CO_2/g (0.48 mmol CO_2/g). Temperature-programmed desorption (TPD) experiments were conducted to calculate the activation energy of CO_2 desorption. Low activation energy (18.34 kJ/mol) and high desorption rate, with a stable uptake in five adsorption/desorption cycles, suggest mP-PEHA as potentially excellent sorbent for CO_2 absorption.

INTRODUCTION

The increasing anthropogenic carbon dioxide (CO_2) emission is considered as the main cause of global warming. Various types of adsorbents can be potentially used for CO_2 captures, such as zeolites, porous organic polymers (POPs), porous carbons, and mesoporous materials [1]. The introduction of various amine groups into porous materials results in sorbents with high CO_2 capture capacity, selectivity, regenerability, and stability [2]. In this study, CO_2 adsorption/desorption performances of chemically stable pentaethylenehexamine (PEHA)-grafted magnetic porous polymer (mP-PEHA) with adjustable surface chemistry and pore structure were tested. The CO_2 uptake, thermodynamics and kinetics and adsorption/desorption cycle stability were determined. The performance of mP-PEHA was investigated over a range of CO_2 partial pressures.

EXPERIMENTAL

Magnetic porous polymer (mP) was prepared following the procedure described elsewhere [3]. Post-functionalization of mP with pentaethylenehexamine (PEHA) was done in a typical procedure, i.e., 7.2 g of mP and 17.7 g of PEHA were added to 300 ml of toluene and heated under stirring at 80 °C for 6 h. The sample mP-PEHA was filtered, washed with ethanol, and dried under vacuum at 40 °C.The amino groups content (C_{AG}) was determined as described in the literature [3]. FTIR-ATR spectra were taken in the range 4000–400 cm^{-1} using a Nicolet 380 spectrometer. The scanning electron microscopy (SEM) micrographs were obtained on JEOL JSM-6460LV. Pore size distributions were collected by a high-pressure mercury intrusion porosimeter Carlo Erba Porosimeter 2000 (Washington, USA, software Milestone 200). The porosity parameters (specific pore volume, V_p, pore diameter which corresponds to half of the pore volume, $D_{V/2}$, and specific surface area, $S_{s,Hg}$) were determined as described in the literature [4].

The CO_2 uptake measurements were performed using a pulse gas chromatographic method. CO_2 desorption was obtained by temperature programmed desorption tests with constant carrier gas stream flow. The experiments were performed on sample mP-PEHA (0.0150 g) in dynamic conditions in a flow system. The content of CO_2 was analyzed online by GC Shimadzu 8a, equipped with a TCD detector using a stainless steel column; 6.5 ft. long and 1/8 in. in diameter, containing 80/100 mesh HayeSep D. For adsorption experiments, the sample was exposed to pulses

of 0.1 ml CO_2 inserted into carrier gas stream (He - 2400 ml/h) at 20 °C. For temperature-programmed desorption tests, the sample was saturated with CO_2 at 20 °C. After that, desorption was performed at heating rates of 10, 20, 30, 40, and 50 °C/min, in the temperature range 20-200 °C with holding of temperature at 200 °C for 2 min. For determination of regeneration stability of mP-PEHA five CO_2 adsorption-desorption cycles were performed, consisting of CO_2 adsorption at 20 °C until saturation, and desorption at 20 to 200 °C (heating rate 30 °C/min), with 2 minutes of retention at 200 °C. After each desorption, for the next cycle, the sample was cooled to an initial adsorption temperature of 20 °C. The reproducibility of the results was verified by performing each test several times.

RESULTS AND DISCUSSION

Characterization of the sorbent

Since the practical application and CO_2 adsorption performances of amino-functionalized porous sorbents strongly depend on their characteristics such as morphology, particle chemistry (amine groups content and location), and pore structure (specific surface area, specific pore volume, pore size, and distribution), a detailed characterization of mP-PEHA was done. In FTIR-ATR spectra (Figure 1a), peaks confirming amino-functionalization are clearly visible, i.e. peaks for δ(NH) and shoulder δ(NH_2), at ~1570 cm^{-1} and ~1650 cm^{-1}, respectively. Also, the magnetic nature of the sorbent is corroborated with the peak for Fe-O vibrations at ~590 cm^{-1}[3].

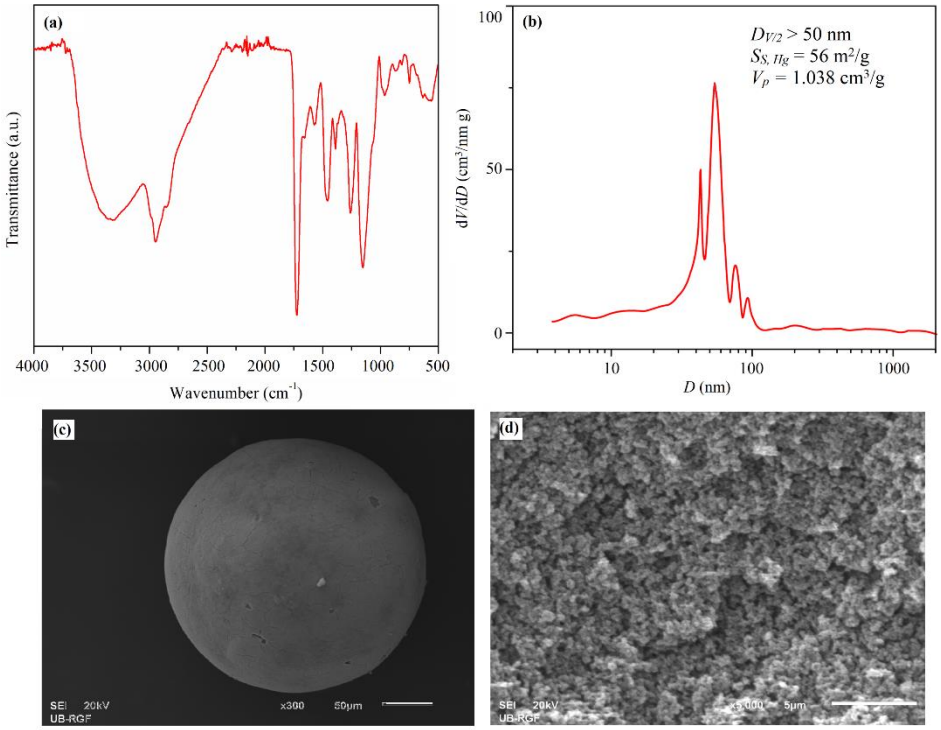

Figure 1. FTIR spectra (a), differential curve of the pore size distribution (b) and SEM microphotographs of particle surface (c) and cross-section (d) for mP-PEHA.

The differential curve of pore volume distribution curves and calculated porosity parameters are given in Figure 1b. As seen, mP-PEHA is macroporous in nature ($D_{V/2}$> 50 nm) with $S_{S,\,Hg}$ = 56 m^2/g and V_p = 1.038 cm^3/g. SEM images of mP-PEHA show a regular globular shape and smooth surface of the particles (Figure 1c), as well as a highly developed three dimensional internal porous

structure composed of a large number of globules and opened pores at the particle cross-section (Figure 1d).

CO_2 Adsorption tests

After successive insertion of a small constant volume of CO_2, polymer mP-PEHA had an adsorption capacity of 10.76 ml CO_2/g (0.48 mmol CO_2/g) which corresponds to the normalized value per unit area of 0.19 ml CO_2/m^2 (8.57 10-3 mmol CO_2/m^2).

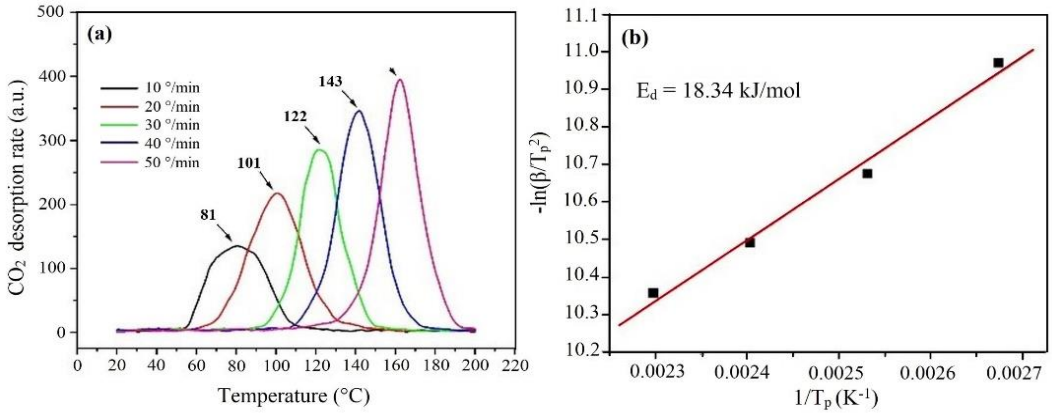

Figure 2.CO_2 desorption vs. temperature (a), relationship between the maximum desorption temperature (T_p) and the heating rate (β) for CO_2 desorption (b) from mP-PEHA [adsorption conditions: He flow rate, 2400 mL/h; adsorption temperature, 20 °C; desorption conditions: carrier gas (He) flow rate, 2400 mL/h; temperature regime: linear increase from 20 to 200 °C, holding at 200 °C for 2 min, heating rates 10, 20, 30, 40, and 50 °C/min; sorbent mass: 0.0150 g].

A series of TPD experiments were conducted at different heating rates (Figure 2a). A plot $\ln(RT_p^2/\beta)$-$1/T_p$ (Figure 2b) was obtained according to the equation (1) [5]:

$$\ln\left(\frac{RT_p^2}{\beta}\right) = \frac{E_d}{R}\left(\frac{1}{T_p}\right) + \ln\left(\frac{E_d}{k_0}\right) \quad (1)$$

where: R is the gas constant, T_p is the peak temperature, β is the heating rate (K/min), E_d is the activation energy for desorption (kJ/mol) and k_0 is the desorption rate coefficient (min^{-1}).

From a linear relationship with a high correlation coefficient (R^2=0.994) (Figure 2b), the activation energy of desorption was calculated to be ~ 18 kJ/mol. Polymer mP-PEHA showed comparable CO_2 adsorption capacity but lower CO_2 desorption energies than their analog amine-modified commercial zeolites [6]. The molecular structures of the amines and their reactions with CO_2 are the main factors affecting polymer properties in CO_2 capture. Thus, the good adsorption-desorption properties of mP-PEHA were attributed to the optimal molecular structure of pentaethylenehexamine which is the main constituent of this polymer. The low activation energies obtained for CO_2 desorption indicate a high CO_2 desorption rate and fast surface regeneration for the energy-saving applications of mP-PEHA in CO_2 capture.

Multiple CO_2 adsorption-desorption cyclic tests were performed to evaluate possible practical applications. As seen (Figure 3), mP-PEHA exhibited high performance in terms of efficient and

cyclic regeneration, since adsorption capacity maintained almost the same after five successive adsorption-desorption cycles.

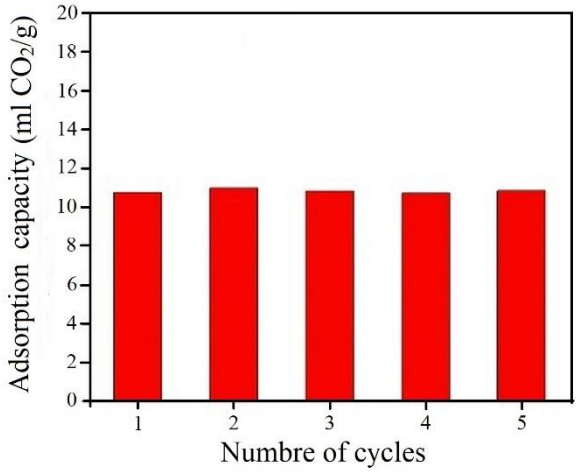

Figure 3. Adsorption-desorption properties of mP-PEHA in repeated cycles of CO_2 adsorption.

CONCLUSION

CO_2 adsorption-desorption properties of mP-PEHA suggests potentially excellent sorbent with a CO_2 adsorption capacity of 10.76 ml CO_2/g (0.48 mmol CO_2/g). It was shown that mP-PEHA could be regenerated successfully in the temperature range from 81 to 162 ^oC, with a stable uptake of ~10.8 ml CO_2/g (0.48 mmol CO_2/g) in five adsorption/desorption cycles. The obtained results showed that CO_2 adsorption on mP-PEHA is comparable to amine-modified commercial materials, Moreover, mP-PEHA showed easier and faster desorption, without reducing the adsorption capacity.

Acknowledgment

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200026).

REFERENCES

[1] G. Singh, J. Lee, A. Karakoti, R. Bahadur, J. Yi, D. Zhao, K. AlBahily, and A. Vinu, Chem. Soc. Rev., 49 (2020) 4360.
[2] A. M. Varghese, and G. N. Karanikolos, Int. J. Greenh. Gas Control, 96 (2020) 103005.
[3] B. M. Marković, Z. M. Vuković, V. V. Spasojević, V. B. Kusigerski, V. B. Pavlović, A. E. Onjia, A. B. Nastasović, J. Alloys Compd., 705 (2017) 38.
[4] F. Rodríguez-Reinoso, and A. Sepúlveda-Escribano in: Handbook of Surfaces and Interfacesof Materials, Vol. 5, H. Nalwa (Ed.), Elsevier: Amsterdam, The Netherlands. 2001.
[5] X. Li, H-F. Guo, and H-M. Chen, Adsorp. Sci. Techol., 24 (2006) 907.
[6] H. Cheng, H. Song, S. Toan, K. A. M. Gasem, M. Fan, and F. Cheng, Chem. Eng. J., 406 (2011) 126882.