CO_2 capture on cyclic amino-modified mesoporous silica obtained from biomass wastes

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Introduction

Industrialized societies overuse the energy and raw material resources of the Earth to maintain and continually enhance their standard of living. As a result, environmental problems, such as climate change and air pollution, driven by greenhouse gas emission, have become the most important issue to be solved [1]. Potential solutions focus on the development of carbon-free or low carbon technologies that minimize waste production, or align with the principles of the circular economy by reusing waste materials. A variety of documents from the scientific community and policy-makers raise awareness and advocate for a transition towards a resource-efficient and competitive economy. The European Green Deal is a new EU strategy aiming to combat climate change by no net emissions of (GHGs) by 2050. In recent years, the adsorption of CO_2 on nanoporous materials with a high specific surface area has been the subject of extensive research. The physical characteristics and surface chemical properties of porous materials determine their CO_2 adsorption capacity, as well as their selectivity and stability in the presence of other contaminants and water vapor. Using biomass wastes for synthesis of mesoporous silicas can reduce the expenses of adsorbent production. For example, rice husks contain 12-18 % silicon, making them a suitable source for synthesizing mesoporous silica. Moreover, carboxylic acids produced from biomass waste can be used as cheap and effective templates for synthesis of mesoporous silicas with high surface area.

In the present study, we have developed new cyclic amine modified mesoporous silicas, obtained from biomass wastes, that possess remarkably high CO_2 capture.

Materials and Methods

Mesoporous silicas were prepared by two synthesis procedures. Mesoporous silica materials were synthesized using citric acid as the template and tetraethylorthosilicate as the silica source in aqueous solution. The applied sol–gel process was performed at 30-60^{o}C, the molar ratio of citric acid/TEOS= 1–6. The obtained mesoporous silica materials were calcined at 500 °C for 6 h, with 5 °C/min heating rate. In the second approach rice husk was subjected to acid treatment with 5% citric acid at 50^{o}C for 3 hours. Then the rice husks were calcined at 500 °C for 6 h, with 5 °C/min heating rate [2].

Modification of the mesoporous silicas with cyclic amine was accomplished by post synthesis reaction with piperazines in two steps **(Figure 1)**.

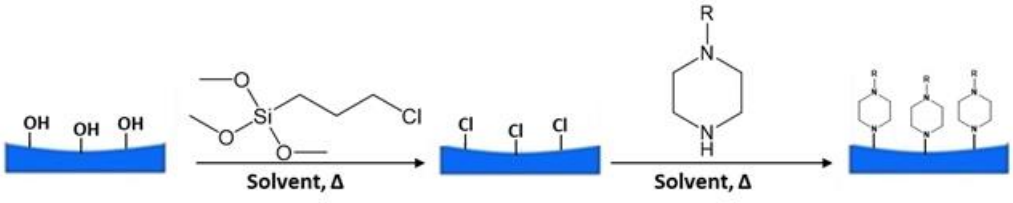

Figure 1. Scheme for synthesis of the modified mesoporous silicas

In the first step, the initial mesoporous silicas were suspended in dry toluene, and (3-chloropropyl)trimethoxysilane was added. The mixture was refluxed for 48 h. The modified

silica was filtered and washed with toluene. In the second step, the chloropropyl -modified mesoporous materials were suspended in dry toluene and piperazines were added. Then a few drops of NEt_3 were added and the reaction mixture was refluxed for 72 h. The solid phase was filtered and washed consecutively with toluene and ethanol.

The initial and modified materials were characterized by XRD (Bruker AXS Advanced X-ray Solutions GmbH, Karlsruhe, Germany), N_2 physisorption (Quantachrome instruments AUTOSORB iQ-MP-AG, Boynton Beach, FL 33426, USA), thermal analysis (STA449F5 Jupiter of NETZSCH Gerätebau GmbH (Netzsch, Germany), and solid-state NMR (Bruker Avance II+ 600 NMR spectrometer (Karlsruhe, Germany).

CO_2 adsorption experiments were performed in dynamic conditions in a flow system. The sample (0.40 g adsorbent) was dried at 150 °C for 2 h, and 3 vol.% CO_2/N_2 at a flow rate of 30 mL/min was applied for the experiments. The gas was analyzed online by GC NEXIS GC-2030 ATF with 25 m PLOT Q capillary column. The experiments for CO_2 and water vapor adsorption (3 vol.% CO_2 plus 1 vol.% water vapor) were performed at a flow rate of 30 mL/min. The amounts of adsorbed CO_2 and water vapor in the adsorbents were determined and used to calculate the adsorption capacity.

Results and Discussion

The piperazines modified mesoporous silicas were successfully synthesized by a post-synthesis procedure. The procedure for preparation of the modified mesoporous materials does not affect the structural characteristics of the initial mesoporous silicas strongly. The obtained piperazines modified mesoporous materials showed high specific surface area due to the preservation of mesoporous structure during the modification procedure. High capacity for CO_2 adsorption was determined for all modified materials in dynamic and static conditions, with some differences depending on the functional groups. The formation of chemisorbed CO_2 functionalities in the form of a bicarbonate ion (HCO_3^-) as well as the presence of physiosorbed CO_2 was evidenced by solid-state NMR.

The modification with piperazines results in a high isosteric heat of adsorption due to the strong interaction between functional groups and CO_2 molecules. The total CO_2 desorption from the modified materials was achieved at 60 °C. The leaching of the adsorption sites was not detected after three consecutive adsorption cycles. The high CO_2 uptake and straightforward preparation make the herein-reported modified silicas the CO_2 capture materials of the future.

References

1. J.C. Navarro, F.M. Baena-Moreno, M.A. Centeno, O.H. Laguna, J.F. Almagro, J.A. Odriozola, *Renewable and Sustainable Energy Reviews*, **2023**, *184*, 113537.
2. M. Popova, V. Mitova, M. Dimitrov, C. Rosmini, I. Tsacheva, P. Shestakova, D. Karashanova, I. Karadjova, N. Koseva, *Molecules*, **2024**, *29*, 3540.

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