CO_2 capture on the amino-modified mesoporous silica

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Significance and Relevance

The primary amine (propyl amine) and cyclic amine (piperazines) modified mesoporous silicas were successfully synthesized by a post-synthesis procedure. The used mesoporous silicas were prepared by two procedures: from rice husks as silica source without template and by sol-gel process with the application of carboxylic acids as template. High capacity for CO_2 adsorption was determined for all modified materials in dry and wet conditions and total desorption was achieved at 60 °C. The leaching of the adsorption sites was not detected. The high CO_2 uptake and straightforward preparation make the herein-reported modified silicas the CO_2 capture materials of the future.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling/ Air cleaning and combustion
Preferred presentation: Oral only

Introduction and Motivations

The increasing emission of greenhouse gases and their severe effect on the climate has come into the spotlight as a major challenge to sustainable development [1–3]. 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.

In the present study, we have developed new primary amine and cyclic amine modified mesoporous silicas that possess remarkably high CO_2 capture.

Materials and Methods

Mesoporous silicas were prepared by two synthesis procedures **(Scheme 1)**. 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°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°C for 3 hours. Then the rice flakes were calcined at 500 °C for 6 h, with 5 °C/min heating rate [2].

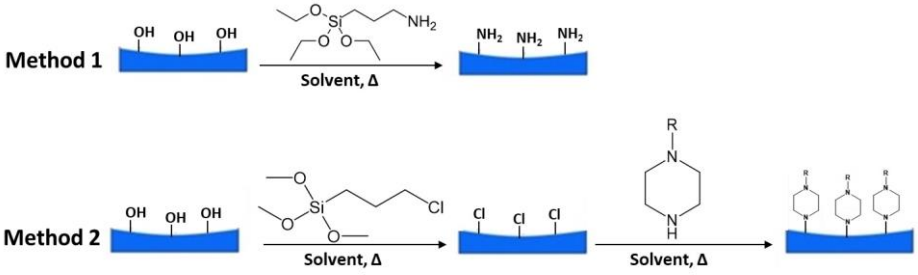

Figure 1. Scheme for synthesis of the modified mesoporous silicas

Modification of the mesoporous silicas with propylamino groups was accomplished by reaction with 3-amino-propyltriethoxysilane (APTES) in ethanol. 1 g mesoporous silica was added to 1 ml APTES in 10 ml of ethanol and was stirred at 50 °C for 5 h (Scheme 1, method 1). After that the samples were washed with several portions of solvent, and finally with water and dried at room temperature.

A total of 0.7 g of the corresponding modified mesoporous materials were suspended in 7.0 mL of dry toluene and 0.71 g of piperazine was added (Scheme 1, method 2). 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 per-formed 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 propyl amine and 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 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 propylamino groups and piperazine results in a high isosteric heat of adsorption due to the strong interaction between functional groups and CO_2 molecules. The highest adsorption capacity for CO_2 adsorption was determined for the piperazines modified mesoporous silica. 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

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