



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
SHORT ABSTRACT OF THESIS

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**SHORT ABSTRACT**

Rise in the atmospheric concentration of carbon dioxide is believed to play a significant role in global warming through the greenhouse effect. Separation of CO<sub>2</sub> from the flue gas emissions from power plants is important to reduce the amount of CO<sub>2</sub> released into the atmosphere. 'Sweetening' of natural gas is another important industrial operation involving the separation of CO<sub>2</sub> from a gas mixture. Adsorptive separation of CO<sub>2</sub> using porous materials such as zeolites, mesoporous silicas, metal organic frameworks (MOFs), porous carbons etc. is an attractive alternative to conventional amine scrubbing due to lower regeneration energy requirements. Mesoporous silica such as MCM-41 and SBA-15 are an important class of adsorbents that can be readily modified through functionalization or other means due to their large, regularly arranged pores. Microporous metal-organic frameworks (MOFs) represent another class of adsorbents that can be modified through functionalization of the organic linker groups.

In this work, realistic molecular models of pure and modified MCM-41 and representative models of SBA-15 have been developed to study CO<sub>2</sub> separation on mesoporous silica using grand canonical Monte Carlo (GCMC) simulations. Structural characterization of the developed MCM-41 models compared favorably with experimental data available in literature. Further, the simulated adsorption isotherm and calculated isosteric heat of adsorption of pure CO<sub>2</sub> showed good agreement with reported experimental values. Simulations of CO<sub>2</sub>/N<sub>2</sub> mixture adsorption showed selectivities of CO<sub>2</sub> over N<sub>2</sub> to be in the range 4–10. Further studies on adsorption of ternary and quaternary bulk gas mixtures containing water vapor and O<sub>2</sub> did not reveal any significant effect on CO<sub>2</sub> adsorption and CO<sub>2</sub>-N<sub>2</sub> selectivity. Next, to study the effect of pore size and microporosity of pore walls, models having larger mesopore diameter of ~75 Å were developed, and representative models of SBA-15 were generated by carving different numbers of micropores across the pore walls. GCMC simulations were used to study the adsorption of pure gases as well as gas mixtures of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>. Increase in mesopore size resulted in reduced specific surface area and CO<sub>2</sub> uptake, whereas with increase in wall microporosity, the uptake of CO<sub>2</sub> was observed to first decrease and then increase. The SBA-15 models are more selective toward CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub>. At low pressures, the selectivities were higher for models

with wall microporosity. The MCM-41 models were modified by incorporation of the ionic liquid (IL) 1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide [C4Pyr<sup>+</sup>][TF2N<sup>-</sup>] at two different loadings. The MCM-41 model with lower loading of IL showed significantly higher adsorption of pure CO<sub>2</sub> than pristine MCM-41. Molecular dynamics simulation of pure CO<sub>2</sub> in IL-loaded MCM-41 models revealed that CO<sub>2</sub> molecules prefer locations near the pore walls as well as in the pore interior around IL molecules. The CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities were highest for the MCM-41 with larger IL loading, with values almost twice that for pure MCM-41. Thus, modifying the mesopores of MCM-41 with IL can result in significant enhancement in CO<sub>2</sub> adsorption and selectivity.

For studies on adsorptive separation of CO<sub>2</sub> on MOFs using GCMC simulations, zirconium-based UiO-66 and UiO-67, and functionalized copper-based Cu-BTC have been considered. The two Zr-based MOFs studied are topologically similar but have channels and cages of different sizes. The amount of gas adsorbed as well as the isosteric heats of adsorption show the order CO<sub>2</sub> > CH<sub>4</sub> > CO > N<sub>2</sub> on both UiO-66 and UiO-67. Isosteric heats of adsorption and gas uptake at low pressures were higher in the case of UiO-66 due to the presence of smaller cages leading to stronger interactions. At higher pressures, gas uptake in UiO-67 was larger because of larger cages and greater surface area. CO<sub>2</sub> was observed to preferentially adsorb near the organic linkers in the smaller cages of the MOFs. The binary mixture selectivity of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> was significantly higher for adsorption in UiO-66 than in UiO-67 because of the narrow window size and smaller cages in UiO-66. Finally, the effect of pore modification on CO<sub>2</sub> adsorption was studied using different functionalized Cu-BTC MOFs having iodo-, single methyl and two methyl functional groups grafted to the organic linkers. At low pressures (< 1 bar), adsorption of CO<sub>2</sub> was seen to be higher for the iodo-functionalized Cu-BTC. However, at higher pressures, CO<sub>2</sub> uptake was highest for the unmodified Cu-BTC because of its larger pore volume. Moreover, selectivity of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> was found to be higher for the iodo-functionalized Cu-BTC at high pressures (> 2 bar). In the low-pressure regime, Cu-BTC functionalized with two methyl groups showed higher selectivity of CO<sub>2</sub> over N<sub>2</sub>. The geometric characteristics of the pore such as pore size, surface area and volume, and the interaction environment within the pores strongly affect CO<sub>2</sub> adsorption and hence, can be tuned to enhance CO<sub>2</sub> uptake and selectivity.