Design of highly selective PDMS membranes for CO_2 separation

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In this study we employ density functional theory to investigate the binding interaction between polydimethylsiloxane and CO_2 for application in gas separation membranes and sequential reduction and utilization.[1,2] The binding strength has been studied systematically as a function of the monomer conformational rotations in the polymer chain. Our work identified major differences between the CO_2 interaction with the helical conformation and the linear conformation of polydimethylsiloxane polymer chains. We have further estimated dependence between the CO_2 binding strength and the polydimethylsiloxane polymer chain curvature by systematically evaluating the CO_2 binding to cyclic polydimethylsiloxane oligomers. The enhanced CO_2 interaction with helical chains and cyclic oligomers was attributed to cooperative, confinement effects, and local electron density distribution at the Si–O–Si fragments. The binding modes were identified using vibration frequency analysis.

Our study showed maximum binding interaction for 8-member cyclic oligomer. We used frequency analysis to estimate binding modes, and we found major interactions between CO2 and PDMS methyl groups. We compared the CO_2 vibration mode at 2470 cm^{-1} for linear and helical PDMS chain. We verified that in the case of helical geometry the CO_2 interacts (concerted vibrations) with multiple methyl groups while in the case of linear geometry CO_2 interacts with two methyl groups only. Thus, we conclude that the helical PDMS geometry offers multiple interaction sites for CO_2 which results in stronger binding. Such confinement effect has been previously reported for CH_4 activation in small pore zeolite materials. We have shown using ReaxFF dynamics that at 300 K the helical PDMS conformation does not undergo changes to linear conformation while at 800 K the helical conformation readily unwraps to linear conformation. Thus, we can propose the mechanism of CO_2 absorption at low temperature by helical PDMS conformation and CO_2 release by transformation of helical to linear PDMS at high temperature. We elucidated the effect the Si atoms play on the CO_2 selectivity as polarization on the O and H atoms which enhances the quadrupole interaction.

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2) M. Sun, A. Staykov, M. Yamauchi, *ACS Catal.* **2022** *12*, 14856-14863.