Doctoral Dissertation
Doctoral Program in Energy Engineering (36th Cycle)

Innovative Materials and Processes for Enhanced CO_2 Capture and Conversion

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Politecnico di Torino
July 31, 2024

Summary

The thesis aims to address the global challenge of increasing greenhouse gas emissions by developing and optimizing innovative Carbon Capture, Utilization, and Storage (CCUS) technologies. It focuses on the systematic development of experimental designs, simulations, and optimization models for three primary areas: membrane-based gas separation processes, ionic liquid CO_2 capture, and chemical looping CO_2 conversion.

Chapter 1 sets the stage by presenting the background of the study, emphasizing the environmental urgency, technological innovation, and economic viability of CCUS technologies. It outlines the research objectives, which include enhancing the efficiency, scalability, and economic attractiveness of these technologies to mitigate climate change.

The literature review delves into various CCUS technologies, including the use of bio-based ionic liquids for CO_2 capture, highlighting their synthesis, properties, and performance. It discusses different polymeric and mixed matrix membranes for CO_2 separation, their mechanisms, and material properties. The investigation of advanced perovskite materials for chemical looping processes is also covered.

Chapter 3 provides a detailed description of the experimental setup and modelling methodology. It explains the synthesis and characterization of Choline-Proline [Cho][Pro] ionic liquids for CO_2 capture, the fabrication, testing, and evaluation of polymeric and mixed matrix membranes, and the methodology for synthesizing and testing metal-doped $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ double perovskites. The experimental setups used in the research are described comprehensively.

The findings from the research are presented in chapter 4. Experimental tests on [Cho][Pro] solutions revealed that a 25%wt composition achieves the optimal balance of CO_2 absorption capacity and regeneration efficiency, with performance metrics including $20\,g_{CO_2}/kg_{sol}$, $0.8\,mol_{CO_2}/mol_{IL}$, 60% of regeneration

efficiency, and more than 90% CO_2 removal rate after 3 cycles. Over 30 absorption-regeneration cycles, the 25%wt solution demonstrated stable performance, maintaining a regeneration efficiency of approximately 55% and exhibiting minimal degradation.

A comparative analysis of membrane materials identified polyether ether ketone with beta nano sponge (PEEK+BNS) as the most stable option for gas separation across varying pressures, maintaining consistent CO_2 permeability (11–14 Barrer) and selectivity, ranging from 7 to 10 for CO_2/N_2 and around 5 for CO_2/CH_4. Although the polyether sulfone (PES) membranes showed the highest CO_2 permeability, 15 Barrer, their selectivity was favourable for flue gas application (CO_2/N_2 selectivity ranging between 6 and 12) but less effective for biogas application (CO_2/CH_4 selectivity between 1 and 5). For methane upgrade applications, the PEEK membrane outperformed other tested materials, achieving the highest CO_2/CH_4 selectivity (30 at 0.2 bar) and a CO_2 permeability of 15 Barrer, making them an efficient solution for methane upgrade.

Double perovskites exhibited optimal CO production during isothermal redox cycles at 850°C, achieving yields of 3330 μmol CO/g. Long-term stability tests showed a gradual decline in CO yield during the first 40 cycles, followed by stabilization at 1537 μmol CO/g after 250 cycles. This stability, combined with competitive CO yields, positions the material as a robust candidate for scalable chemical looping applications.

Chapter 5 applies the research findings to methane upgrade processes, focusing on the development of an optimized membrane-based system for methane recovery from natural gas hydrate reservoirs. The study evaluates various membrane materials and identifies the most cost-effective and technically efficient solution. The analysis of specific energy consumption and separation efficiency highlights the system's practicality and significant advantages. One of the membranes modelled in the study demonstrated exceptional performance, achieving a methane recovery rate of 97.5% and CO_2 purity of 99%. The specific electrical energy consumption was 4.6 MJ/kgCH4 with an economic analysis revealing production costs of $102 per tonne of methane and only $14 per tonne for CO_2 separation. Additionally, the integration of simultaneous CO_2 injection into the reservoir and the use of renewable electricity underscores the potential to produce carbon-neutral methane, contributing to sustainable energy solutions.

The conclusion summarizes the key contributions of the research, emphasizing the advancements in CCUS technologies and their potential impact on mitigating climate change. It suggests areas for further research to enhance the efficiency, scalability, and economic viability of CCUS technologies. The broader implications of the research findings for industry and policy are discussed, highlighting the importance of supportive frameworks for the adoption of CCUS technologies.