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Novel Amide Based Polymeric Ionic Liquids: Potential Candidates for CO_2 capture

Project Acronym: NABPIL

Project No: 629050

Carbon dioxide (CO_2) is a major greenhouse gas and a significant contributor towards global warming and climate change. The main objective of NABPIL Project was to design, produce, characterize and test new class of novel amide based polymeric ionic liquids for CO_2 capture and separation from the fuel as well as landfill gas. The idea was to develop novel ionic materials that have high CO_2 sorption capacity and are cost effective at the same time. Furthermore, selectively capturing CO_2 is of particular interest in this project and gave information about relationship between macromolecular structure and its affinity with the CO_2. The nature of project was highly multidisciplinary and bridges Chemistry, Environmental and Materials Science. Among all CO_2 capture technologies, adsorption is the one with possible energy savings as compared to conventional solvent processes and was used in the present work to study the sorption capacities of new ionic materials in powder form. There are many advantages of using the polymeric ionic liquids (PILs) in powder form because they don´t generate as much waste and can be disposed off without too much environmental preventative measures. The polymeric ionic liquid solid sorbents were evaluated for CO_2 capture as well as separation performance, and the results are highly encouraging because some of the PILs even surpassed the highest values reported in literature to date for such type of materials. Moreover, quantum chemical calculations were also carried out to ensure the possible affinity of amide ionic polymers for CO_2 capture.

Interestingly, theoretical calculations inferred that the amide link in these polymers is the focal point for interaction of CO_2 molecules. It is well known that amide is a fascinating functional group possessing binary interaction sites (N-H & C=O) and also mildly basic in nature that facilitates better capture of CO_2 leading to superior adsorption capacities. Keeping in view these intriguing aspects, we planned and carried out the whole study based on incorporation of amide functionality in ionic polymers.

The two work packages (WP1 and WP2) comprising Task 1, 2, 3, 4 & 5 have successfully been achieved according to the proposed timeline of the project i.e., amide based polymer ionic liquids produced via solution polymerization technique at low temperature under anhydrous conditions yielding different type of novel polyamides (Task 1). The primary aim was to optimize the reaction conditions and parameters, and the best experimental conditions for polymerization process were employed. A series of monomers including bi-, tri- and tetra functional groups were exploited to yield various permutations of novel polyamides with different architectures ranging from linear to extended ones. Moreover, use of tetra-functional monomers helped us to generate 3D-network structures to render high porosity. These reactions between amines and acid chlorides are exothermic in nature. Therefore, polymerization reaction was performed at low temperature in ice to avoid any side reaction. A stoichiometric amount of triethylamine was also added to quench the HCl formed during the polymerization reaction. Various combinations of monomers have successfully been explored resulting in different novel polyamides. Task 2 has efficiently been accomplished and in this task, abovementioned synthesized polyamides subsequently were subjected to quaternization reaction. Quaternization is the most critical step in the formation of polymeric ionic liquids. Different polymeric salts were prepared from the corresponding alkylating agents and nitrogen bases of the polyamides synthesized in the Task 1. Various type of alkylating agents such as alkyl bromide, alkyl iodide and trifluoromethanesulfonate were exploited for quaternization. Afterward, the reaction mixture was processed to isolate the purified product to yield amide based PILs. The nature of counter ion significantly influences the CO_2 sorption. Therefore, the next step involved the anion exchange or metathesis reaction to replace halide/sulfonate counter-anions with more hydrophobic and stable anions like inorganic anions, sulfonimides and cyano anions such as tetrafluoroborate, hexafluorophosphate, NTf_2, $B(CN)_4$, $N(CN)_2$, $C(CN)_3$, etc. The synthetic part of the project (Task 1 & Task 2) was smoothly completed.

Alternatively, the PILs were also synthesized by making ionic monomers first and then their polymerization correspondingly. This route was also effective in generating PILs successfully. The characterization for the chemical structure, morphology, crystallinity and thermal stability (Task 3) of these new materials was carried out at POLYMAT, Spain. The structure elucidation of the novel polyamides and their amide based PILs was performed using FTIR and NMR spectroscopy and elemental analysis (Task 3). Thermal stability of both polyamides and their PILs was monitored by thermogravimetric analysis. Single-crystal X-ray diffraction was carried out to determine the crystal structures of some of the synthesized monomers. Wide angle X-ray diffraction was performed to illustrate the crystalline or amorphous behaviour of these materials. Surface morphology of these materials was investigated by Scanning Electron Microscopy (SEM) and internal morphological studies were recorded by Transmission Electron Microscopy (TEM). Task 4 involved the determination of surface area and porosity of these new ionic materials followed by the CO_2 adsorption tests carried out in collaboration with King Abdullah University of Science and Technology (KAUST), Saudi Arabia. The CO_2 sorption capacities of these materials were also compared with already well known sorbents. Last Task 5 covers the theoretical quantum chemical calculations and which showed good agreement with the experimental results. Moreover, theoretical calculations provide evidence of interaction of CO_2 molecules exclusively with the amide functionality present in the PILs.