Abstract

Anthropogenic CO₂ emissions from fossil fuel consumption have opened a pandora's box of climatic and sustainability problems. Reducing CO₂ into fuels and carbon-based compounds on expenditure of intermittent renewable electricity resources (solar, wind) is a promising way to store this energy and close the carbon cycle. Electrochemical CO₂ reduction (ECR) requires highly efficient, robust and selective catalysts to selectively and efficiently convert CO₂ at lower overpotentials into fuels for commercialisation. This thesis begins with studying the role of various physico-chemical properties like morphology, phase, carbonaceous support, synergism between metal and GO support, and electrode fabrication of a copper nanocatalyst in ECR activity, selectivity and stability in acetonitrile electrolyte system into CO. Similar studies were done on Cu/Cu₃O-GO catalysts in aqueous KHCO₃ electrolyte solutions to transform CO₂ selectively into ethylene. An interplay between the electrode/electrolyte influences the mechanism of the ECR, resulting in different products. This was found true in the case of Cu/Cu₃O-GO catalysts also, where ECR in aprotic solvent like acetonitrile yielded CO and availability of reducible protons shifted reaction selectivity towards ethylene.

High electroactive surface area accelerates the ECR activity and kinks, and porous nature causes an increase in local pH around these shapes, which impedes hydrogen evolution reaction (HER). An extensively branched dendritic morphology has these optimum properties. We studied the role of applied potential, ascorbic acid concentration, temperature and time on the morphology of resultant catalyst and optimised the dendritic structure for maximum surface area and secondary branching. A plausible mechanism for the dendritic growth in electrodeposition was also explained. In wet-dimethylsulphoxide (DMSO), the optimised structure produced 33% ethane from CO₂ at -1.5 V (NHE). HER was inhibited on these structures. A shift from production of ethane in wet-DMSO to ethylene (faradaic efficiency of 43%), in KHCO₃ was observed which may be due to solvent effects at the interface. Presence
of solvent at inner Helmholtz layer can alter the product profile by controlling the reducible protons available to the electrode surface. Therefore, even if the catalyst structure is same change of solvents can alter the course. The effect of solvent was found more prominent in dendritic or uneven shapes than in simple and spherical shapes.

For methane production (100) facets on smaller rhombohedral copper catalysts are very efficient for ECR. Controlling the surface texture, finesse, and homogeneity by reverse pulse currents, and presence of surface modifying ionic liquids, catalysts converting CO$_2$ to CH$_4$ with an efficiency of 67.4% and at partial current density of 38 mA/cm$^2$ were prepared. A study of pulse nature and additive presence was done to gain more insights about the catalyst preparation and its activity.

Catalysts having porous and high surface area increase ECR activity, an ability to adsorb CO$_2$ and simultaneously having an active redox system for electron transfer to CO$_2$ should lead to higher currents for CO$_2$ reduction reaction. Copper metal-organic frameworks (CuMOFs) can act both as CO$_2$ adsorbents as well as redox metal centres for CO$_2$ reduction, but their electrochemical instability limits their potential use. To surmount this problem, simple groups like NH$_2$ were used as replacements on free surface -COOH groups on CuMOFs. This simple transformation increased both ECR activity and electrochemical stability of these CuMOFs. HER is suppressed while hydrocarbons were favoured over simple CO.

Overall, this thesis is outlining the implementation of theoretically predicted and empirically realised catalyst properties in a single catalyst system to enhance the ECR activity and selectivity into energy-dense hydrocarbons like ethylene and methane.
**Journal Publications**


**Book Chapter**


**Papers Presented in Conferences**


3. Rashid, N.; Ingole, P. P.; Reduction of CO2 into value added chemicals (OP). International conference for nanotechnology and material sciences, Department of Chemistry, Delhi University, New Delhi, 3-5 March, 2016.


8. Rashid, N.; Ingole, P. P.; Electrochemical Reduction of Carbon Dioxide on Copper MOFs: Effect of Ligand Functional Groups on Efficiency and Selectivity. (OP), MRS Boston, USA 01-Dec to 06 Dec 2019.


**Workshops Attended**

1. Attended workshop on spectro-electrochemistry at Department of Chemistry, University of Delhi, from 17-18 June, 2015.
