INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title : Electrocatalysing CO_2 Conversion to Value-added Products using Metal Oxides and Metal-Salen Complexes

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SHORT ABSTRACT

The electrochemical reduction of carbon dioxide (ERC) is a promising technique for storing energy and producing carbon-based chemicals from CO_2. The concentration of CO_2 is increased from 280 to 416.3 ppm (43.3%) over the past 60 years, which is about 66 ppm higher than the safety limit. This rise in CO_2 concentration causes an increase in global temperature by 1-2°C. This doctoral work researches in synthesizing catalysts for ERC into valuable products. The study begins with the synthesis of selected transition and main group metal oxides (Cu, Ni, and Pb). The Cu_2O, PbO and NiO nanoparticles were synthesized using a chemical route.

The electrochemical studies were conducted using the synthesized catalysts. A custom-made H-type reactor was tested for the electrochemical analyses throughout the study using 0.5 M aqueous $KHCO_3$ solution saturated with CO_2 (each catholyte and anolyte of 120 mL). The effects of fundamental electro-parameters were investigated through linear sweep voltammetry, cyclic voltammetry, and constant-potential analyses. The working electrodes (WEs) were prepared by brush coating the synthesized catalysts on the graphite plate. Platinum wire and Ag/AgCl (saturated 3 M KCl) were employed as the counter electrode (CE) and reference electrode (RE).

The Cu_2O electrocatalyst was active for the formation of mainly HCOOH (22%) with a trace amount of CH_3OH at a higher potential (−2.00 V vs. Ag/AgCl). In the constant-potential analysis, it was also found that the NiO as an electrocatalyst could produce only H_2 and was inactive in reducing CO_2. PbO could form HCOOH at different potentials (−1.40 to −2.20 V) and a maximum Faradaic efficiency (FE) of 23% was achieved at −2.00 V vs. Ag/AgCl. Using these metal oxide catalysts, the hydrogen evolution reaction (HER) was quite high which could adversely affect ERC. Thus, to increase the yield of value-added products and to supress the HER, the salen metal complexes (Cu, Ni, and Pb) were designed, synthesized and introduced in ERC.

At first, salen ligand **1** ($H_2L^{NO_2}$) was synthesized from the reaction of 4-Nitro-*o*-phenylenediamine and salicylaldehyde at 1:6 molar ratios. Ligand **1** was reacted with $Na_2S{\bullet}H_2O$ to produce salen ligand **2** ($H_2L^{NH_2}$). The metal complexes (**1**, **2,** and **4**) and **3** were synthesized by the metalation reaction from the ligand **2** and **1**, respectively, in the presence of triethylamine. The complexes were also brush-coated on the graphite plates and used as the Wes for ERC. Using Cu-salen complex (**1**) as an electrocatalyst, the ERC products were obtained in the order as $HCOOH>CH_3COOH>CH_3OH>C_2H_5OH$ with a total FE of 36%. The highest selectivity (SE) was achieved for the formation of non-alcoholic ERC products such as HCOOH (SE 35%) and CH_3COOH (SE 21%). Using Ni-salen complex (**2**), the abundance of the product formation was found in the order as $C_2H_5OH>HCOOH>CH_3OH$ with a higher FE (total 49%). The maximum FE and SE of ethanol production achieved was 29% and 50%, respectively, at −1.80 V vs. Ag/AgCl. Finally, two Pb(II)-salen complexes (**3** = $[Pb^{II}(L^{NO_2})]$, **4** = $[Pb^{II}(L^{NH_2})]$) could produce majorly C_2 products. While C_2H_5OH was formed as the single C_2 product with FE of 57% and SE of 66% in the presence of complex **3**. A mixture of C_1 and C_2 products, CH_3COOH (FE 36%, SE 54%), CH_3CHO (FE 12%, SE 14%) and CH_3OH (FE 12%, SE 14%) with a total FE of 68% was realized using complex **4**. Whereas, the NH_2 and NO_2 free $[Pb^{II}(L)]$ complex, primarily favored ERC to HCOOH and CH_3OH (FE 27%, SE 59%).

The incorporation of electron-withdrawing $-NO_2$ or electron-donating basic $-NH_2$ functional groups in the backbone of the parent ligand preferentially generated multiple electrons-multiple protons reduced C_2 products by stabilizing *CO, *CHO/*CH_3 intermediates and increased the availability of CO_2/CO near the electrode surface which could enhance the chance of CO_2 to be reduced. Thus, the metal complexes could not only supress the HER but also could produce a variety of C_1 as well as C_2 products with high FE than the metal oxides.