ELECTROCHEMICAL REDUCTION OF CO_2 ON COPPER DERIVED SURFACES

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ELECTROCHEMICAL REDUCTION OF CO_2 ON COPPER DERIVED SURFACES

by

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To my father, a sun which nourishes me,

my mother, a moon that soothes me,

and

everyone who strives for a better change.

Certificate

This is to certify that the dissertation entitled "**ELECTROCHEMICAL REDUCTION OF CO_2 ON COPPER DERIVED SURFACES**" being submitted by **Nusrat Rashid** to the Indian Institute of Technology Delhi, for fulfilment of the requirements for the award of **Doctor of Philosophy** in Chemistry is a record of bona-fide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis. The results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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In the name of Allah, the most gracious and the most merciful

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Nusrat Rashid

Abstract

Anthropogenic CO_2 emissions from fossil fuel consumption have opened a pandora's box of climatic and sustainability problems. Reducing CO_2 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 CO_2 reduction (ECR) requires highly efficient, robust and selective catalysts to selectively and efficiently convert CO_2 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/Cu_xO-GO catalysts in aqueous $KHCO_3$ electrolyte solutions to transform CO_2 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/Cu_xO-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 CO_2 at -1.5 V (NHE). HER was inhibited on these structures. A shift from production of ethane in wet-DMSO to ethylene (Faradaic efficiency (FE) of 43%), in $KHCO_3$ 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.

सार

जीवाश्म ईंधन की खपत से मानवजनित CO_2 उत्सर्जन ने जलवायु और स्थिरता की समस्याओं के एक पैंडोरा बॉक्स को खोल दिया है। आंतरायिक नवीकरणीय बिजली संसाधनों (सौर, पवन) के व्यय पर CO_2 को ईंधन और कार्बन-आधारित यौगिकों में कम करना इस ऊर्जा को संग्रहीत करने और कार्बन चक्र को बंद करने का एक आशाजनक तरीका है। इलेक्ट्रोकेमिकल CO_2 परिवर्तन (ECR) को अत्यधिक कुशल, मजबूत और चयनात्मक उत्प्रेरक की आवश्यकता होती है जो व्यवसायीकरण के लिए CO_2 को कम ओवरपोटेंशियल्स में ईंधन में कुशलतापूर्वक परिवर्तित कर सकें। यह थीसिस विभिन्न भौतिक-रासायनिक गुणों की भूमिका का अध्ययन करने के साथ शुरू होती है जैसे आकृति विज्ञान, चरण, कार्बोनेस समर्थन, धातु और गो समर्थन के बीच तालमेल, और ECR गतिविधि में एक तांबे नैनोकैटलिस्ट के इलेक्ट्रोड निर्माण, सीओ में एसीटोनिट्राइल इलेक्ट्रोलाइट सिस्टम में चयनात्मकता और स्थिरता। CO_2 को एथिलीन में बदलने के लिए जलीय $KHCO_3$ इलेक्ट्रोलाइट समाधान में Cu/Cu_xO-GO उत्प्रेरक पर अध्ययन किया गया था। इलेक्ट्रोड / इलेक्ट्रोलाइट के बीच एक परस्पर क्रिया ECR के तंत्र को प्रभावित करती है, जिसके परिणामस्वरूप विभिन्न उत्पाद होते हैं। यह Cu/CuxO-GO उत्प्रेरकों के मामले में भी सच पाया गया, जहां एसीटीऑनिट्राइल जैसे एप्रोटिक विलायक में ECR CO उपजते हैं और रिड्यूसियल प्रोटॉन की उपलब्धता ने एथिलीन के प्रति प्रतिक्रिया चयनात्मकता को स्थानांतरित कर दिया है।

उच्च इलेक्ट्रोएक्टिव सतह क्षेत्र ECR गतिविधि को तेज करता है और डूब जाता है, और झरझरा प्रकृति इन आकृतियों के आसपास स्थानीय पीएच में वृद्धि का कारण बनती है, जो हाइड्रोजन विकास प्रतिक्रिया (HER) को बाधित करती है। एक व्यापक रूप से शाखाओं में बँधी हुई आकृति विज्ञान में ये इष्टतम गुण हैं। हमने परिणामी उत्प्रेरक की आकृति विज्ञान पर लागू क्षमता, एस्कॉर्बिक एसिड सांद्रता, तापमान और समय की भूमिका का अध्ययन किया और अधिकतम सतह क्षेत्र और माध्यमिक शाखा के लिए वृक्ष के समान संरचना को अनुकूलित किया। इलेक्ट्रोडोडेपोशन में वृक्ष के समान विकास के लिए एक प्रशंसनीय तंत्र भी समझाया गया था। गीले-डाइमिथाइलसल्फॉक्साइड (DMSO) में, अनुकूलित संरचना - 1.5 V (NHE) पर CO_2 से 33% इथेन का उत्पादन करती है। इन संरचनाओं पर HER को रोक दिया गया था। $KHCO_3$ में एथिलीन (फैराडिक दक्षता (FE)) के ओले-डीएमएसओ में ईथेन के उत्पादन से शिफ्ट किया गया था, जो इंटरफ़ेस में विलायक प्रभाव के कारण हो सकता है। भीतरी हेल्महोल्ज़ परत में विलायक की उपस्थिति इलेक्ट्रो सतह तक उपलब्ध रेड्यूसबल प्रोटॉन को नियंत्रित करके उत्पाद प्रोफ़ाइल को बदल सकती है। इसलिए, भले ही उत्प्रेरक संरचना सॉल्वैंट्स का एक ही परिवर्तन है पाठ्यक्रम को बदल सकता है। सरल और गोलाकार आकृतियों की तुलना में विलायक का प्रभाव वृक्ष के समान या असमान आकार में अधिक प्रमुख पाया गया।

ECR के लिए मीथेन प्रोडक्शन (100) के लिए छोटे रॉमबॉडरल कॉपर उत्प्रेरकों पर पहलू बहुत कुशल हैं। रिवर्स पल्स धाराओं द्वारा सतह की बनावट, चालाकी और समरूपता को नियंत्रित करना, और सतह को संशोधित आयनिक तरल पदार्थों की उपस्थिति, 67.4% की दक्षता के साथ CO_2 को CH_4 में परिवर्तित करने वाले उत्प्रेरक और 38 m/cm^2 के आंशिक वर्तमान घनत्व पर तैयार किए गए थे। उत्प्रेरक तैयारी और इसकी गतिविधि के बारे में अधिक जानकारी प्राप्त करने के लिए पल्स प्रकृति और योज्य उपस्थिति का अध्ययन किया गया था।

झरझरा और उच्च सतह क्षेत्र वाले उत्प्रेरक ईसीआर गतिविधि को बढ़ाते हैं, CO_2 को विज्ञापित करने की क्षमता और साथ ही साथ CO_2 में इलेक्ट्रॉन हस्तांतरण के लिए सक्रिय रेडॉक्स प्रणाली होने से CO_2 में कमी की प्रतिक्रिया के लिए उच्च धाराओं का नेतृत्व करना चाहिए। कॉपर मेटल-ऑर्गेनिक फ्रेमवर्क (CuMOF) दोनों CO_2 adsorbents के साथ-साथ CO_2 परिवर्तन के लिए redox धातु केंद्रों के रूप में कार्य कर सकते हैं, लेकिन उनकी विद्युत अस्थिरता उनके संभावित उपयोग को सीमित करती है। इस समस्या को दूर करने के लिए, NH_2 जैसे सरल समूहों का उपयोग CuMOFs पर मुक्त सतह -COOH समूहों पर प्रतिस्थापन के रूप में किया गया था। इस सरल परिवर्तन ने ईसीआर गतिविधि और इन CuMOFs की विद्युत रासायनिक स्थिरता दोनों को बढ़ाया। एचईआर को दबा दिया गया है जबकि हाइड्रोकार्बन को साधारण सीओ से अधिक पसंद किया गया।

कुल मिलाकर, यह थीसिस ईसीआर गतिविधि और एथिलीन और मीथेन जैसे ऊर्जा-घने हाइड्रोकार्बन में चयनात्मकता को बढ़ाने के लिए एक एकल उत्प्रेरक प्रणाली में सैद्धांतिक रूप से अनुमानित और अनुभवजन्य रूप से उत्प्रेरक गुणों के कार्यान्वयन को रेखांकित कर रही है।

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