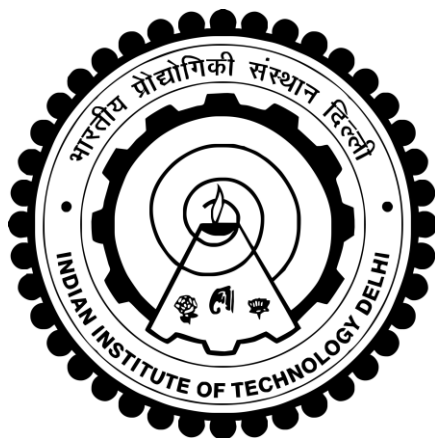


SYNTHESIS OF BLUE HYDROGEN, CNTS, AND GRAPHENE GRAFTED CNTS FROM METHANE IN FLUIDIZED BED REACTOR

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBURARY 2022**

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by

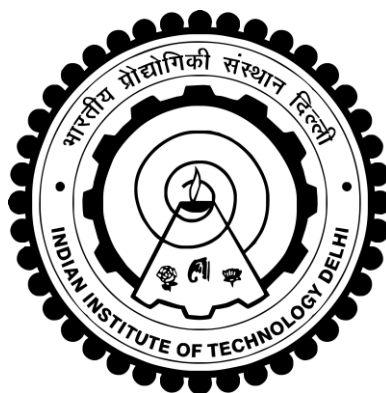
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Submitted

In fulfillment of the requirements of the Degree of Doctor of Philosophy

TO THE



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBURARY 2022

**DEDICATED TO MY LOVING
PARENTS AND SISTER**

CERTIFICATE

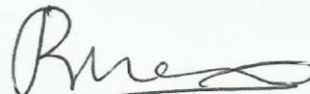
This is to certify that the thesis entitled **“SYNTHESIS OF BLUE HYDROGEN, CNTS, AND GRAPHENE GRAFTED CNTS FROM METHANE IN FLUIDIZED BED REACTOR”**, submitted by **Mr. Kaushal R. Parmar** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of the original bonafide research work carried out by him. **Mr. Kaushal R. Parmar** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge, has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.



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indirectly in the completion of my research work. Last but not least, a note of heartfelt devotion to almighty GOD, who made me capable of accomplishing this acclivitous task.

A handwritten signature in blue ink, appearing to read 'Kaushal', with a horizontal line and a small flourish underneath.

KAUSHAL R. PARMAR

ABSTRACT

Energy is the most prominent need of today's world, and developing sustainable and reliable energy sources is one of the major challenges. Due to an increase in the global population, the demand for clean energy sources, i.e., sources with a minimum negative impact on the environment is continuously increasing. Contemporary research has focused on developing energy sources that reduce fossil fuel consumption without creating adverse environmental effects. Hydrogen energy seems to be the most appropriate solution due to its high energy density and clean-burning ability. The production of green hydrogen (i.e., from renewable electricity) and blue hydrogen (i.e., from fossil fuel with carbon capture) are most explored nowadays due to environmental concerns.

Due to a lack of infrastructure and technological advancement, green hydrogen production is not currently economically feasible. This work aims to develop a technology that can produce blue hydrogen and has the potential to compete with commercial hydrogen production technologies. The methane decomposition (MD) process has the potential to produce blue hydrogen by capturing carbon as valuable carbon nanotubes. As one of the products is valuable carbon nanotubes (CNTs), the overall feasibility of the process can be governed by the quality and the cost of produced CNT. A series of catalysts were prepared from transition metals such as Ni and Fe using Cu, Zn as promoters, and alumina as support. A fluidized bed reactor was utilized for the methane decomposition reaction considering commercialization aspects. The catalysts were prepared by the wet-impregnation method, and their hydrodynamic behavior was studied by cold flow studies. The catalysts were characterized by various analytical techniques such as X-ray diffraction (XRD), temperature-programmed reduction (TPR), surface area analysis (BET-BJH), field-emission scanning electron microscopy (FESEM),

high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), Raman spectroscopy, and thermogravimetric analysis (TGA) to comprehend the properties of catalysts (calcined, spent) and produced carbon materials (i.e., carbon nanotubes, graphene grafted CNTs).

The performance of the catalysts was evaluated in the bubbling fluidized bed reactor over a wide range of operating conditions. A hydrodynamic study was carried out to identify the catalyst particle size and other parameters such as minimum fluidization velocity (U_{mf}) and superficial velocity. A 60%Ni-5%Cu-5%Zn/ Al_2O_3 catalyst with 125 μm (avg.) particle size provided more than 90% initial methane conversion at 750 °C. The produced carbon was in the form of valuable carbon nanotubes with a length up to 5 μm , outside diameter of 60-80 nm, and Raman ratio (i.e., ID/IG) of 0.5. The produced CNTs were extracted from the spent catalyst by a newly developed non-destructive ultrasonication process. The reusability of the catalyst was checked by performing five reaction-regeneration cycles, including carbon nanotube extraction by ultrasonication. It was observed that 60%Ni-5%Cu-5%Zn/ Al_2O_3 catalyst regained its initial activity after each regeneration cycle without any significant loss in activity. A total of five reaction-regeneration cycles were performed, and the catalyst was able to provide >90% initial methane conversion after the fifth regeneration cycle. After each reaction cycle, the produced carbon nanotubes were characterized by various characterization tools, and no degradation in the CNT quality was observed.

In order to observe the continuous change in hydrodynamic behavior of the catalyst due to CNT deposition, a hydrodynamic study was performed in the fluidized bed reactor at reaction conditions on different amounts of CNT deposited catalysts. Based on the latest literature, an economic analysis was carried out to find the break-even point between SMR and MD process.

The selling cost of the carbon nanotube was predicted by comparing the physical properties between produced and commercial carbon nanotubes. Efforts were made to reduce the cost of the catalyst by lowering the active metal content. A 20%Ni-1.7%Cu-1.7%Zn/Al₂O₃ catalyst provided >80% initial methane conversion, which remained stable up to 2h (>70%) with a high amount of CNTs (i.e., 18 g_{CNT} g_{metal}⁻¹). The effect of metal-support interaction on hydrogen yield and carbon nanotube growth mechanism was also studied.

The produced carbon nanotubes were also utilized as an autocatalyst for methane decomposition reaction to avoid the catalyst's regeneration. For that, 60%Ni-5%Cu-5%Zn/Al₂O₃ and 30%Fe-2.5%Cu-2.5%Zn/Al₂O₃ catalysts were tested in a 750-950 °C temperature range. At 900 °C, after deposition of 50 g CNTs, 60%Ni-5%Cu-5%Zn/Al₂O₃ catalyst provided 30% constant conversion for 40 h without any deactivation. The product gas with 30% H₂-70% CH₄ (called hythane gas) can be used as a potential fuel for an automotive application. While using produced carbon nanotube as an autocatalyst, a new form of carbon (i.e., graphene grafted carbon nanotube) was identified. Its growth mechanism and physical properties were explored by various analytical techniques such as FESEM, EDX mapping, HRTEM, Raman spectroscopy, and TGA. It was observed that graphene grafted CNTs are highly crystalline and more thermal stable than produced carbon nanotubes. Further, the methane decomposition mechanism on existing CNTs was studied and explained by various analytical tools. The produced carbon nanotube was utilized to produce ultra-light, flexible, highly porous aerogel materials. Prepared silica-CNT-CMC aerogel was utilized in an oil adsorption application, and 1 g carbon nanotube aerogel can adsorb 28 g of oil.

सार

ऊर्जा आज की दुनिया की सबसे प्रमुख जरूरत है, और स्थायी और विश्वसनीय ऊर्जा स्रोतों का विकास प्रमुख चुनौतियों में से एक है। वैश्विक जनसंख्या में वृद्धि के कारण, स्वच्छ ऊर्जा स्रोतों, यानी पर्यावरण पर न्यूनतम नकारात्मक प्रभाव वाले स्रोतों की मांग लगातार बढ़ रही है। समकालीन अनुसंधान ने ऊर्जा स्रोतों को विकसित करने पर ध्यान केंद्रित किया है जो प्रतिकूल पर्यावरणीय प्रभाव पैदा किए बिना जीवाश्म ईंधन की खपत को कम करते हैं। हाइड्रोजन ऊर्जा अपने उच्च ऊर्जा घनत्व और स्वच्छ जलने की क्षमता के कारण सबसे उपयुक्त समाधान प्रतीत होती है। पर्यावरण संबंधी चिंताओं के कारण आजकल हरित हाइड्रोजन (अर्थात, नवीकरणीय बिजली से) और नीले हाइड्रोजन (यानी, जीवाश्म ईंधन से कार्बन कैप्चर के साथ) का उत्पादन सबसे अधिक किया जाता है।

बुनियादी ढांचे और तकनीकी प्रगति की कमी के कारण, वर्तमान में हरित हाइड्रोजन का उत्पादन आर्थिक रूप से संभव नहीं है। इस कार्य का उद्देश्य एक ऐसी तकनीक विकसित करना है जो नीले हाइड्रोजन का उत्पादन कर सके और इसमें वाणिज्यिक हाइड्रोजन उत्पादन प्रौद्योगिकियों के साथ प्रतिस्पर्धा करने की क्षमता हो। मीथेन अपघटन (एमडी) प्रक्रिया में कार्बन को मूल्यवान कार्बन नैनोट्यूब के रूप में कैप्चर करके नीले हाइड्रोजन का उत्पादन करने की क्षमता है। चूंकि उत्पादों में से एक मूल्यवान कार्बन नैनोट्यूब (सीएनटी) है, प्रक्रिया की समग्र व्यवहार्यता गुणवत्ता और उत्पादित सीएनटी की लागत से नियंत्रित हो सकती है। उत्प्रेरकों की एक श्रृंखला Ni और Fe जैसे संक्रमण धातुओं से Cu, Zn को प्रवर्तक के रूप में, और एल्यूमिना को समर्थन के रूप में उपयोग करके तैयार की गई थी। व्यावसायीकरण पहलुओं पर विचार करते हुए मीथेन अपघटन प्रतिक्रिया के लिए एक द्रवीकृत बिस्तर रिएक्टर का उपयोग किया गया था। उत्प्रेरक गीले-संसेचन विधि द्वारा तैयार किए गए थे, और उनके हाइड्रोडायनामिक व्यवहार का अध्ययन शीत प्रवाह अध्ययन द्वारा किया गया था। उत्प्रेरकों को एक्स-रे विवर्तन (एक्सआरडी), तापमान-क्रमादेशित कमी (टीपीआर), सतह क्षेत्र विश्लेषण (बीईटी-बीजेएच), क्षेत्र-उत्सर्जन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एफईएसईएम), उच्च-रिज़ॉल्यूशन ट्रांसमिशन इलेक्ट्रॉन जैसी विभिन्न विश्लेषणात्मक तकनीकों की विशेषता थी। माइक्रोस्कोपी (एचआरटीईएम), परमाणु बल माइक्रोस्कोपी (एएफएम), रमन स्पेक्ट्रोस्कोपी, और थर्मोग्रैविमेट्रिक विश्लेषण (टीजीए)

उत्प्रेरक (कैलकलाइंड, खर्च किए गए) और उत्पादित कार्बन सामग्री (यानी, कार्बन नैनोट्यूब, ग्राफीन ग्राफटेड सीएनटी) के गुणों को समझने के लिए।

उत्प्रेरकों के प्रदर्शन का मूल्यांकन बुदबुदाती द्रवीकृत बिस्तर रिएक्टर में परिचालन स्थितियों की एक विस्तृत श्रृंखला में किया गया था। उत्प्रेरक कण आकार और अन्य पैरामीटर जैसे न्यूनतम द्रवीकरण वेग (यूएमएफ) और सतही वेग की पहचान करने के लिए एक हाइड्रोडायनामिक अध्ययन किया गया था। 125 माइक्रोन (औसत) कण आकार के साथ 60%Ni-5%Cu-5%Zn/Al₂O₃ उत्प्रेरक ने 750 डिग्री सेल्सियस पर 90% से अधिक प्रारंभिक मीथेन रूपांतरण प्रदान किया। उत्पादित कार्बन मूल्यवान कार्बन नैनोट्यूब के रूप में था जिसकी लंबाई 5 माइक्रोन तक, बाहरी व्यास 60-80 एनएम और रमन अनुपात (यानी, आईडी / आईजी) 0.5 था। उत्पादित सीएनटी को एक नव विकसित गैर-विनाशकारी अल्ट्रासोनिकेशन प्रक्रिया द्वारा खर्च किए गए उत्प्रेरक से निकाला गया था। अल्ट्रासोनिकेशन द्वारा कार्बन नैनोट्यूब निष्कर्षण सहित पांच प्रतिक्रिया-पुनर्जनन चक्रों का प्रदर्शन करके उत्प्रेरक की पुनः प्रयोज्यता की जाँच की गई थी। यह देखा गया कि 60%Ni-5%Cu-5%Zn/Al₂O₃ उत्प्रेरक ने गतिविधि में किसी भी महत्वपूर्ण नुकसान के बिना प्रत्येक पुनर्जनन चक्र के बाद अपनी प्रारंभिक गतिविधि को पुनः प्राप्त कर लिया। कुल पांच प्रतिक्रिया-पुनर्जनन चक्र किए गए, और उत्प्रेरक पांचवें पुनर्जनन चक्र के बाद >90% प्रारंभिक मीथेन रूपांतरण प्रदान करने में सक्षम था। प्रत्येक प्रतिक्रिया चक्र के बाद, उत्पादित कार्बन नैनोट्यूब को विभिन्न लक्षण वर्णन उपकरणों द्वारा चित्रित किया गया था, और सीएनटी गुणवत्ता में कोई गिरावट नहीं देखी गई थी।

सीएनटी जमा होने के कारण उत्प्रेरक के हाइड्रोडायनामिक व्यवहार में निरंतर परिवर्तन का निरीक्षण करने के लिए, सीएनटी जमा उत्प्रेरक की विभिन्न मात्राओं पर प्रतिक्रिया की स्थिति में द्रवित बिस्तर रिएक्टर में एक हाइड्रोडायनामिक अध्ययन किया गया था। नवीनतम साहित्य के आधार पर, एसएमआर और एमडी प्रक्रिया के बीच ब्रेक-ईवन बिंदु खोजने के लिए एक आर्थिक विश्लेषण किया गया था। उत्पादित और वाणिज्यिक कार्बन नैनोट्यूब के बीच भौतिक गुणों की तुलना करके कार्बन नैनोट्यूब की बिक्री लागत का अनुमान लगाया गया था। सक्रिय धातु सामग्री को कम करके उत्प्रेरक की लागत को कम करने का प्रयास किया गया। 20%Ni-1.7%Cu-1.7%Zn/Al₂O₃ उत्प्रेरक प्रदान किया गया >80% प्रारंभिक मीथेन रूपांतरण, जो 2h (>70%) तक CNTs (यानी, 18 gCNT g_{metal}⁻¹) की उच्च मात्रा के साथ स्थिर रहा।

हाइड्रोजन उपज और कार्बन नैनोट्यूब विकास तंत्र पर धातु-समर्थन बातचीत के प्रभाव का भी अध्ययन किया गया था।

उत्प्रेरक के पुनर्जनन से बचने के लिए उत्पादित कार्बन नैनोट्यूब का उपयोग मीथेन अपघटन प्रतिक्रिया के लिए एक ऑटोकैटलिस्ट के रूप में भी किया गया था। उसके लिए, 60%Ni-5%Cu-5%Zn/Al₂O₃ और 30%Fe-2.5%Cu-2.5%Zn/Al₂O₃ उत्प्रेरक का परीक्षण 750-950 डिग्री सेल्सियस तापमान रेंज में किया गया था। 900 डिग्री सेल्सियस पर, 50 ग्राम सीएनटी के जमाव के बाद, 60%Ni-5%Cu-5%Zn/Al₂O₃ उत्प्रेरक ने बिना किसी निष्क्रियता के 40 घंटे के लिए 30% निरंतर रूपांतरण प्रदान किया। 30%H₂-70%CH₄ (हाइथेन गैस कहा जाता है) के साथ उत्पाद गैस का उपयोग ऑटोमोटिव अनुप्रयोग के लिए संभावित ईंधन के रूप में किया जा सकता है। एक ऑटोकैटलिस्ट के रूप में उत्पादित कार्बन नैनोट्यूब का उपयोग करते समय, कार्बन के एक नए रूप (यानी, ग्राफीन ग्राफटेड कार्बन नैनोट्यूब) की पहचान की गई थी। FESEM, EDX मैपिंग, HRTEM, रमन स्पेक्ट्रोस्कोपी और TGA जैसी विभिन्न विश्लेषणात्मक तकनीकों द्वारा इसके विकास तंत्र और भौतिक गुणों का पता लगाया गया। यह देखा गया कि ग्रेफीन ग्राफटेड सीएनटी उत्पादित कार्बन नैनोट्यूब की तुलना में अत्यधिक क्रिस्टलीय और अधिक तापीय स्थिर होते हैं। इसके अलावा, मौजूदा सीएनटी पर मीथेन अपघटन तंत्र का अध्ययन किया गया और विभिन्न विश्लेषणात्मक उपकरणों द्वारा समझाया गया। उत्पादित कार्बन नैनोट्यूब का उपयोग अल्ट्रा-लाइट, लचीली, अत्यधिक झरझरा एयरजेल सामग्री के उत्पादन के लिए किया गया था। तैयार सिलिका-सीएनटी-सीएमसी एयरजेल एक तेल सोखना अनुप्रयोग में उपयोग किया गया था, और 1 ग्राम कार्बन नैनोट्यूब एयरजेल 28 ग्राम तेल को सोख सकता है।

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