Insights into the Oxygen Evolution Step of the Thermochemical Iodine-Sulfur (I-S) Process for Hydrogen Production

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by

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Dedicated to my beloved family, my grandmother late Prakashvati Pathak and my grandfather late Om Prakash Pathak

“Education is the most powerful weapon which can use to change the world”

-Nelson Mandela

CERTIFICATE

This is to certify that the thesis titled "**Insights into the Oxygen Evolution Step of the Thermochemical Iodine-Sulfur (I-S) Process for Hydrogen Production**" being submitted by Mr. Shailesh Pathak to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemical Engineering is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the requisite standard.

The work presented in this thesis is original and has 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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ABSTRACT

In the last few decades, greenhouse gas emission has increased very rapidly due to a surge in energy demand which results in a rise in global temperature. Hydrogen is an alternative source of energy because it is a non-polluting, eco-friendly, and regenerating nature which makes it a most attractive fuel source. Thermochemical decomposition of water in the Iodine-Sulfur (I-S) cycle for hydrogen production is the most reliable and propitious because of its higher efficacy of 56 %. I-S process involves mainly three reactions namely, Bunsen reaction, sulfuric acid decomposition, and hydro iodic cycle decomposition**.** Among them, thermal decomposition of sulfuric acid is highly corrosive and very energy-intensive usually requires a high temperature of approximately 973-1173 K and exhibits a large kinetic barrier (73-150 kJ/mol). Finding ways to circumvent the high energy consumption may render a path towards enabling a more efficient, and more economically viable low-temperature process.

This research is focused on the estimation of thermodynamic properties including phase behavior and chemical speciation, finding a suitable catalyst, and reactor design for high energy demanding sulfuric acid decomposition for hydrogen production. In this work, metal oxides and spinels are supported over mesoporous silica and pretreated silicon carbide. These catalysts were characterized through XRD, FESEM, HRTEM, and BET following activity and 100 h long-run stability testing. Iron oxide and spinels dispersed on a silica surface grown on a SiC support material are found to be the best catalyst for an endothermic high temperature and highly corrosive reaction condition such as sulfuric acid decomposition. The combined theoretical and experimental findings not only allow us to design cheaper and stable catalysts but also provide an atomistic insight into the mechanism of the metal-support interaction. Consequently, the successful tuning of the latter helps in the enhancement of overall activity and stability. The high activity and stability are ascribed to the presence of oxygen deficit sites in the catalyst developed for the model reaction under consideration.

After that, the reaction kinetics of sulfuric acid decomposition over highly active and thermally stable Fe_2O_3/SiC-Pretrt catalyst is investigated in a fixed-bed quartz reactor. To scale-up the process and improve the heat transfer and integration, the influences of

the different sizes and shapes of the catalyst pellet on the reaction performance and effectiveness factor are estimated. Further, both decomposition and recuperation can be achieved simultaneously through effective reactor structure optimization.

सारांश

पिछले कुछ दशकों में, ऊर्जा की मांग में वृद्धि के कारण ग्रीनहाउस गैस उत्सर्जन में बहुत तेजी से वृद्धि हुई है जिसके परिणामस्वरूप वैश्विक तापमान में वृद्धि हुई है। हाइड्रोजन ऊर्जा का एक वैकल्पिक स्रोत है क्योंकि यह एक गैर-प्रदूषणकारी, पर्यावरण के अनुकूल और पुन: उत्पन्न करने वाली प्रकृति है जो इसे सबसे आकर्षक ईंधन स्रोत बनाती है। हाइड्रोजन उत्पादन के लिए आयोडीन-सल्फर (आई-एस) चक्र में पानी का थर्मोकेमिकल अपघटन 56% की उच्च प्रभावकारिता के कारण सबसे विश्वसनीय और अनुकूल है। आई-एस प्रक्रिया में मुख्य रूप से तीन प्रतिक्रियाएं शामिल हैं, अर्थात् बन्सन प्रतिक्रिया, सल्फ्यूरिक एसिड अपघटन, और हाइड्रो आयोडिक चक्र अपघटन। उनमें से, सल्फ्यूरिक एसिड का थर्मल अपघटन अत्यधिक संक्षारक होता है और बहुत ऊर्जा-गहन आमतौर पर लगभग 973-1173 K के उच्च तापमान की आवश्यकता होती है और एक बड़ा गतिज अवरोध (73-150 kJ/mol) प्रदर्शित करता है। उच्च ऊर्जा खपत को रोकने के तरीके खोजना एक अधिक कुशल, और अधिक आर्थिक रूप से व्यवहार्य कम तापमान प्रक्रिया को सक्षम करने की दिशा में एक मार्ग प्रस्तुत कर सकता है।

यह शोध चरण व्यवहार और रासायनिक विशिष्टता सहित थर्मोडायनामिक गुणों के आकलन पर केंद्रित है, हाइड्रोजन उत्पादन के लिए सल्फ्यूरिक एसिड अपघटन की मांग करने वाली उच्च ऊर्जा के लिए एक उपयुक्त उत्प्रेरक और रिएक्टर डिजाइन की खोज करता है। इस काम में मेसोपोरस सिलिका और प्रेट्रेटेड सिलिकॉन कार्बाइड के ऊपर मेटल ऑक्साइड और स्पिनल्स को सहारा दिया जाता है। इन उत्प्रेरकों को एक्सआरडी, एफईएसईएम, एचआरटीईएम, और बीईटी निम्नलिखित गतिविधि और 100 घंटे लंबे समय तक चलने वाली स्थिरता परीक्षण के माध्यम से चित्रित किया गया था। एक SiC समर्थन सामग्री पर उगाए गए सिलिका सतह पर फैले आयरन ऑक्साइड और स्पिनल्स को एंडोथर्मिक उच्च तापमान और अत्यधिक संक्षारक प्रतिक्रिया स्थिति जैसे सल्फ्यूरिक एसिड अपघटन के लिए सबसे अच्छा उत्प्रेरक पाया जाता है। संयुक्त सैद्धांतिक और प्रायोगिक निष्कर्ष न केवल हमें सस्ते और स्थिर उत्प्रेरक डिजाइन करने की अनुमति देते हैं, बल्कि धातु-समर्थन बातचीत के तंत्र में एक परमाणु अंतर्दृष्टि भी प्रदान करते हैं। नतीजतन, बाद की सफल ट्यूनिंग समग्र गतिविधि और स्थिरता को बढ़ाने में मदद करती है। उच्च गतिविधि और स्थिरता को विचाराधीन मॉडल प्रतिक्रिया के लिए विकसित उत्प्रेरक में ऑक्सीजन की कमी वाली साइटों की उपस्थिति के लिए जिम्मेदार ठहराया गया है।

उसके बाद, अत्यधिक सक्रिय और ऊष्मीय रूप से स्थिर Fe_2O_3/SiC-Pretrt उत्प्रेरक पर सल्फ्यूरिक एसिड के अपघटन की प्रतिक्रिया कैनेटीक्स की जांच एक निश्चित-बेड क्वार्ट्ज रिएक्टर में की जाती है। प्रक्रिया को बढ़ाने और गर्मी हस्तांतरण और एकीकरण में सुधार करने के लिए, प्रतिक्रिया प्रदर्शन और प्रभावशीलता कारक पर उत्प्रेरक गोली के विभिन्न आकारों और आकारों के प्रभावों का अनुमान लगाया जाता है। इसके अलावा, प्रभावी रिएक्टर संरचना अनुकूलन के माध्यम से अपघटन और ऊर्जा पुनःप्राप्ति दोनों को एक साथ प्राप्त किया जा सकता है।

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Thesis contributions

1. **S. Pathak,** S. Saini, K. Kondamudi, S. Upadhyayula, S. Bhattacharya**,** Insights into enhanced stability and activity of silica modified SiC supported iron oxide catalyst in sulfuric acid decomposition, Applied Catalysis B: Environmental 284 (**2021**) 119613 **(IF=19.503).**
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8. **S. Pathak**, S. Upadhyayula Kinetics of the sulfuric acid decomposition over Fe_2O_3/SiC-Pretrt catalyst: elucidation of kinetics and mechanism, (to be communicated).

International Conference

1. **S. Pathak**, A. Goswami, K. Kondamudi, F. Parveen, D. Parvatalu, S. Upadhyayula*,* Kinetic Modelling and 2-D Simulations of Catalyst Pellets for Sulfuric Acid Decomposition, International Symposium on Homogenous and Heterogeneous Catalysis 2018 (ISHHC 18), Sydney, Australia, 25-28 July, 2018
2. **S. Pathak**, S. Upadhyayula, D. Parvatalu, "An Unified Algorithms Based eNRTL Model for Aqueous Sulfuric Acid System" EuropaCAT Germany, 2019 19-23 Aug, 2019.

Patents

1. **S. Pathak**, S. Upadhyayula, D. Parvatalu Process for treatment of catalysts to enhance the catalytic activity for sulfuric acid decomposition and hydrogen production (under preparation)