Studies on Catalytic Decomposition of Hydrogen Iodide in Sulphur Iodine Cycle for Hydrogen Production

Submitted by

Sony

Chemical Engineering Department
Indian Institute of Technology Delhi
July 2023

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in fulfillment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

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DEDICATED
TO
MY FAMILY
AND
MY GURUS

CERTIFICATE

This is to certify that the thesis entitled "**Studies on Catalytic Decomposition of Hydrogen Iodide for Hydrogen Production in Thermochemical Sulphur-Iodine (SI) Cycle"** being submitted by **Sony** to the Department of Chemical Engineering, Indian Institute of Technology, Delhi, in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Chemical Engineering, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis.

The research reports and results presented in this thesis have not been submitted, in part or whole, to any other university or institute for the award of any degree or diploma.

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Abstract

Nowadays, increasing global energy demand, fossil fuel dependence for energy generation, and resulting CO_2 emissions multiply economic and environmental concerns. On the other hand, hydrogen is a clean energy carrier that can eliminate greenhouse gas emissions and meet future energy needs. Sulfur-Iodine (SI) thermochemical cycle is a highly efficient, eco-friendly, and lower temperature (∼900^{o}C) water-splitting process for hydrogen production. There are three main reactions in the cycle: Bunsen reaction, sulphuric-acid decomposition, and hydrogen iodide (HI) decomposition. HI decomposition is an essential step of this cycle because hydrogen is formed here. It is an endothermic, reversible, and equilibrium-limiting reaction. There is no remarkable conversion of HI without the catalyst, even at 550^{o}C. The literature primarily focussed on Pt-based catalysts and costly hydrogen-permeable membranes, which affect the overall cost of the cycle. Hence, there is a need for cost-effective, active, and stable catalysts and a feasible approach for attaining conversion above equilibrium in a fixed bed continuous flow reactor. In the present study, NiO-ZrO_2 in xerogel form was synthesized by a single-step epoxide-driven sol-gel method with different nickel content that showed HI conversion of 23.6% at 550^{o}C. The catalyst (5 wt% NiO-ZrO_2) was tested with an adsorbent for iodine removal to increase the conversion above equilibrium. Activated Carbon (AC) was selected as an iodine adsorbent and potentially exhibited catalytic properties for HI decomposition reaction. The catalyst and adsorbent were arranged in different assemblies inside the reactor bed to find a suitable configuration. The intermixed assembly showed maximum conversion at 500^{o}C, i.e., 25.6%, which was 2.6% above the equilibrium value. The catalyst and synthesized adsorbent (5 wt% iodine impregnated on AC) were investigated to confirm the role of adsorbed iodine in intermixed assembly at 500^{o}C. It has been observed that a significant conversion of ~35% was achieved, indicating I_2/AC adsorbent triggered the conversion owing to its intervention that allowed the system to cross the equilibrium barrier. The long endurance test measured with catalyst and I_2/AC in the intermixed assembly at 500^{o}C showed excellent stability of ∼50 h. Thus, this increase in conversion beyond equilibrium through iodine removal in a packed bed continuous flow reactor is a practically feasible, stable, and economical approach.

सार

आजकल, बढ़ती वैश्विक ऊर्जा मांग, ऊर्जा उत्पादन के लिए जीवाश्म ईंधन पर निर्भरता और परिणामस्वरूप CO_2 उत्सर्जन से आर्थिक और पर्यावरणीय चिंताएँ बढ़ गई हैं। दूसरी ओर, हाइड्रोजन एक स्वच्छ ऊर्जा वाहक है जो ग्रीनहाउस गैस उत्सर्जन को खत्म कर सकता है और भविष्य की ऊर्जा जरूरतों को पूरा कर सकता है। सल्फर-आयोडीन (SI) थर्मोकेमिकल चक्र हाइड्रोजन उत्पादन के लिए एक अत्यधिक कुशल, पर्यावरण-अनुकूल और कम तापमान (~900°C) जल-विभाजन प्रक्रिया है। चक्र में तीन मुख्य रिएक्शन हैं: बन्सेन रिएक्शन, सल्फ्यूरिक-एसिड अपघटन, और हाइड्रोजन आयोडाइड (HI) अपघटन। HI अपघटन इस चक्र का एक आवश्यक चरण है क्योंकि हाइड्रोजन यहीं बनता है। यह एक एंडोथर्मिक, प्रतिवर्ती और ईक्वलिब्रीअम-सीमित रिएक्शन है। उत्प्रेरक के बिना 550°C पर भी HI का कोई उल्लेखनीय कन्वर्ज़न नहीं होता है। साहित्य मुख्य रूप से प्लैटिनम-आधारित उत्प्रेरक और महंगी हाइड्रोजन-पारगम्य झिल्लियों पर केंद्रित है, जो चक्र की समग्र लागत को प्रभावित करते हैं। इसलिए, एक पैक्ड-बेड निरंतर प्रवाह रिएक्टर में संतुलन से ऊपर कन्वर्ज़न प्राप्त करने के लिए लागत प्रभावी, सक्रिय और स्थिर उत्प्रेरक और एक व्यवहार्य दृष्टिकोण की आवश्यकता है। वर्तमान अध्ययन में, ज़ेरोजैल रूप में $NiO\text{-}ZrO_2$ को अलग-अलग Ni wt% के साथ एकल-चरण एपॉक्साइड-संचालित सोल- जैल विधि द्वारा संश्लेषित किया गया था, जिसमें 550°C पर 23.6% का HI कन्वर्ज़न दिखाया गया था। ईक्वलिब्रीअम से ऊपर कन्वर्ज़न बढ़ाने के लिए उत्प्रेरक (5 wt% $NiO\text{-}ZrO_2$) का आयोडीन हटाने के लिए एक अधिशोषक के साथ परीक्षण किया गया था। एक्टिवेटेड कार्बन (AC) को आयोडीन अवशोषक के रूप में चुना गया था और संभावित रूप से HI अपघटन प्रतिक्रिया के लिए उत्प्रेरक गुण प्रदर्शित किए गए थे। उपयुक्त विन्यास खोजने के लिए उत्प्रेरक और अवशोषक को रिएक्टर-बेड के अंदर अलग-अलग असेंबली में व्यवस्थित किया गया था। इंटरमिक्स्ड असेंबली ने 500°C पर अधिकतम कन्वर्ज़न दिखाया, यानी, 25.6%, जो ईक्वलिब्रीअम मूल्य से 2.6% अधिक था। 500°C पर इंटरमिक्स्ड असेंबली में सोखने वाले आयोडीन की भूमिका की पुष्टि करने के लिए उत्प्रेरक और संश्लेषित अधिशोषक (AC पर संसेचित 5 wt% आयोडीन) की जांच की गई। यह देखा गया है कि ~35% का एक महत्वपूर्ण कन्वर्ज़न प्राप्त किया गया था, जो दर्शाता है कि I_2/AC अधिशोषक ने अपने इंटरवेंशन के कारण कन्वर्ज़न को ट्रिगर किया जिसने सिस्टम को संतुलन बाधा को पार करने की अनुमति दी। 500°C पर इंटरमिक्स्ड असेंबली में उत्प्रेरक और I_2/AC के साथ मापे गए लंबे एंडुरेंस परीक्षण ने ~50 घंटे की उत्कृष्ट स्थिरता दिखाई। इस प्रकार, एक पैक्ड-बेड निरंतर प्रवाह रिएक्टर में आयोडीन हटाने के माध्यम से संतुलन से परे कन्वर्ज़न में यह वृद्धि व्यावहारिक रूप से व्यवहार्य, स्थिर और किफायती दृष्टिकोण है।

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Å	Angstrom
AC	Activated carbon
atm	Atmosphere
BE	Binding energy
BET	Braunauer-Emmett-Teller
BJH	Barret-Johner-Halenda
BTOE	Billion tons of oil equivalent
CB	Carbon black
CEA	French Alternative Energies and Atomic Energy Commission
CMS	Carbon molecular sieve
CNT	Carbon nanotube
CRT	Cathode ray tube
CTAB	Hexadecyltrimethylammonium bromide
DDR	Deca dodecasil rhombohedral
d_{hkl}	Interplanar distance of the crystal, å
DI	Deionized
D_p	Average crystallite size (mm)
EDX	Energy dispersive x-ray spectroscopy
EDX	Energy dispersive x-ray spectroscopy
ENEA	Agency for energy efficiency
FESEM	Field-emission scanning electron microscopy
FTIR	Fourier transform infrared
FWHM	Full-width half maxima
GA	General atomics
GC	Gas chromatography

GHG	Green house gas
GNS	Graphene nanosheet
GR	Graphite
Gt	Gigatonne
HC	Hydrocarbon
HRTEM	High-resolution transmission electron microscopy
HTGR	High-temperature gas-cooled reactor
IAEA	International atomic energy agency
ICP-MS	Inductively coupled plasma-mass spectroscopy
I_D	Intensity of D band
IEA	Interantional energy agency
I_G	Intensity of G band
IUPAC	International union of pure and applied chemistry
JAERI	Japan atomic energy agency
JCPDS	Joint committee on powder diffraction standards
JRC	Joint research center
keV	Kilo electron volt
KIER	Korea institute of energy research
L_a	Crystallite lateral diameter
MOFs	Metal-organic frameworks
MWCNT	Multiwalled carbon nanotube
NCLI	National chemical laboratory for industry
nm	Nanometer
ppm	Parts per million
SAED	Selective area electron diffraction
S_{BET}	Surface area of catalyst (m^2 g^{-1})
SEM	Scanning electron microscopy

SI	Sulphur iodine
SSA	Specific surface area
T	Temperature (°C)
TCD	Thermal conductivity detector
TOS	Time on stream
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ΔG	Gibb’s free energy (kJ/mol)
ΔH	Heat of reaction (kJ/mol)
θ	Diffraction angle (degree)
λ	Wavelength (nm)
η	Active site