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DDR zeolite membrane reactor for enhanced HI decomposition in IS thermochemical process

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ABSTRACT

The third section of closed loop Iodine Sulphur (IS) thermochemical cycle, dealing with HI_x processing, suffers from low equilibrium decomposition of HI to hydrogen with a conversion value of only ~22% at 700 K. Here, we report a significant enhancement in conversion of HI into hydrogen (up to ~95%) using a zeolite membrane reactor for the first time. The all silica DDR (deca dodecasil rhombohedral) zeolite membrane with dense, interlocked structure was synthesized on the seeded clay alumina substrate by sonication mediated hydrothermal process. The synthesized membranes along with seed crystals were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDX). Corrosion studies were carried out by exposing the membrane samples to simulated HI decomposition reaction environment (at 450 °C) for different durations of time upto 200 h. The FESEM, EDX and XRD analyses indicated that no significant changes occurred in the morphology, composition and structure of the membranes. Iodine adsorption on to the membrane surface was observed which got increased with the exposure duration as confirmed by secondary ion mass spectrometry studies. A packed bed membrane reactor (PBMR) assembly was fabricated with integration of in-house synthesized zeolite membrane and Pt-alumina catalyst for carrying out HI decomposition studies. The tube side was chosen as reaction zone and the shell side as the permeation zone. The HI decomposition experiments were carried out for different values of temperature and feed flow rates. DDR zeolite based PBMR was found to enhance the single-pass conversion of HI up to ~95%. The results indicate that for achieving optimal performance of PBMR, it should be operated with space velocities of 0.2–0.3 s⁻¹ and temperature in the range of 650 K–700 K with permeate side vacuum of

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0.12 kg/cm². It is believed that the in-house developed zeolite PBMR shall be a potential technology augmentation in making the IS thermochemical cycle energy efficient.

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Introduction

It is the need of hour to look for alternate sources of energy to reduce the load on fossil fuels. Since energy needs will continue to increase due to the urge for better quality of life, population growth and industrialization in the country, the new technology must be expandable and the augmentation to the existing technologies is inevitable. Future energy sources must be environmental friendly while the associated technologies for its extraction must be efficient as well as economical. Keeping these factors into account, it is believed that hydrogen is poised to be the next big revolution in the energy market. Today most of the hydrogen production comes from hydrocarbons: oil (30%), coal (18%) and natural gas (48%). Only 4% of hydrogen is produced from electrolysis of water [1]. It is necessary to have sustainable means of massive hydrogen energy production with non fossil energy sources. One of the promising ways to produce hydrogen sustainably is the thermochemical splitting of water using high temperature energy from the sun or nuclear sources. Iodine Sulphur (IS) thermochemical cycle has been identified as one of the promising routes of hydrogen production owing to its ability to produce hydrogen from water in a sustainable manner using nuclear heat in which high temperature nuclear reactors can act as the heat source [2–7].

HI decomposition reaction of HI_x processing section is one of the important steps of the IS cycle which can dictate the overall efficiency of the entire IS process. The excess addition of iodine beyond the stoichiometric requirement (which is unavoidable) to bring about the phase separation between HI and H₂SO₄ phase makes the HI_x phase difficult to process further. The HI_x mixture, in addition, is having an azeotropic composition of HI with water. The most important candidate technology to process HI_x phase which can lead to hydrogen generation is reactive distillation, which is a single-step process. Looking at the intricate issues associated with reactive distillation path (a pressure requirement upto 30 bar, severe corrosion because of high pressure operation, material issues etc.), an alternative path encompassing electro-electrodialysis (EED) coupled with membrane reactor (MR) can be a suitable option to be targeted in parallel. HI decomposes to hydrogen and iodine over a catalyst at approximately 450 °C in vapour phase. However, the reaction is equilibrium limited and current conversion is only about 22%. The low decomposition ratio leads to the increase of the amount of recycle materials (HI, I₂, H₂O) and therefore decreases the thermal efficiency [8]. In order to overcome the low efficiency due to the poor equilibrium decomposition of HI, ongoing research is dedicated toward development of a hydrogen permselective membrane reactor. The employment of catalytic membrane reactor would ensure overcoming the single pass equilibrium

conversion [4,9]. Membrane is the heart of membrane reactor and if the hydrogen produced is removed from the reaction mixture by a separation membrane in-situ, the equilibrium limitations can be overcome and conversion of the reaction shall improve, which in turn should enhance the overall thermochemical efficiency of the IS cycle. The status review of various hydrogen permselective membranes was made by Kluiters in 2004 [10]. The hydrogen produced in the reaction zone can be removed from the reaction mixture by a permselective membrane in-situ, thereby overcoming the equilibrium limitation of the reaction. Transport of hydrogen through a porous membrane can follow different mechanisms such as Knudsen diffusion, solution diffusion, capillary condensation and molecular sieving [11]. Although studies on MRs based on palladium [12], dense perovskite [13], zeolite [14] and inorganic MR [15–18] have already been reported, nevertheless their application in HI decomposition studies is not available. Membrane reactor fabrication involves two stages: first, the preparation of membrane with reasonable hydrogen permselectivity; second, the fabrication of a membrane reactor assembly with integration of membrane and catalysts in place. A significant amount of effort is required to fabricate a membrane reactor, integrating the membrane tubes into the reactor housing and ensuring the leak tightness of the entire system to establish a synergy between reaction and separation.

The high temperature and corrosive environment of the HI_x processing section requires development of state-of-art membranes [19]. Inorganic membranes are chemically and thermally stable with high permeability and selectivity for small gas molecules like H₂ and He with respect to other larger ones [20–22]. Various types of inorganic membranes for separation of H₂ from HI reaction mixture have been developed [23–29]. The application of silica membranes in HI decomposition reaction has been studied [4,30] in order to improve single-pass conversion of HI. A major disadvantage of silica membrane is its amorphous nature which is highly reactive in presence of moisture. Zeolite membranes belong to a special class of porous inorganic membranes with well defined intracrystalline nano-pores. Hence, as a better alternative to silica membranes and to overcome its disadvantages, we have proposed all silica zeolite, i.e., DDR (deca dodecasil rhombohedral) zeolite membrane for separation of H₂ from HI decomposition reaction. They have superior thermal, mechanical, chemical and high pressure stability and also hydrophobic in nature which makes it the suitable material for using in HI corrosive atmosphere. Kinetic diameter of hydrogen (0.29 nm) is very small compared to other gases and hence a small pore sized DDR (0.36 nm–0.44 nm) zeolite can easily separate hydrogen from other gases or vapours with large value of kinetic diameter. The pore size of DDR zeolite

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