ABSTRACT

Attaining net-zero carbon emissions necessitates substantial decreases in the consumption of carbon-based fuels for energy production and industrial activities. The steel industry, reliant on carbon as a reducing agent, and the energy sector, heavily dependent on fossil fuels, are significant contributors to greenhouse gas emissions. Replacing traditional fuels with cleaner alternatives like syngas (H_2 + CO) or hydrogen presents a viable route to decarbonization. Most hydrogen and syngas are produced through steam or dry methane reforming, energy-intensive processes that create significant CO_2 emissions, constraining their environmental and economic advantages.

Chemical looping (CL) offers a viable alternative for generating clean energy. This process comprises a reduction and oxidation (redox) reaction sequence wherein carbonaceous fuels are indirectly oxidized utilizing oxygen carrier (OC) particles made of reducible transition metal oxides. These OCs provide lattice oxygen for fuel conversion, facilitating syngas or H_2 production without supplementary gas separation. Despite the superior performance of synthetic Ni-, Fe-, and Cu-based OCs, which are frequently improved with oxides like ZrO_2 and CeO_2, their high cost and difficulty of synthesis prevent large-scale deployment. Mining byproducts and low-grade ores, abundant in transition metal oxides, present a sustainable and economical substitute as oxygen carriers.

This study assesses COB, a mining byproduct, as an economical oxygen carrier for chemical looping. The reactivity of COB with methane (CH_4) was evaluated using experimental and theoretical approaches. Experiments conducted at 750 °C validated its reducibility, and 20 redox cycles yielded 12.2 mmol/g OC of H_2 with a H_2/CO ratio of 0.87, confirming syngas production. Phase analysis indicated that COB predominantly transformed into magnetite/spinel phases due to thermodynamic constraints, whereas incomplete re-oxidation resulted in a progressive decline in reactivity. The oxygen carrier was systematically modified to improve performance, utilizing thermodynamic calculations and molecular dynamics simulations. Based on the findings, a composite material was created by combining COB with naturally occurring magnesite ore in a 3:1 ratio, subsequently subjected to high-temperature calcination at 1100 °C for 8 hours. The modified OC demonstrated enhanced hydrogen yields and redox stability over 20 cycles in a fluidized bed reactor at 750 °C. Furthermore, chemical looping steam reforming at 950 °C utilizing COB and the modified OC generated a pure hydrogen stream free of CO contamination. The findings indicate the viability of utilizing mining waste-derived organic compounds as sustainable, economical resources for syngas and hydrogen generation, aiding the transition to net-zero carbon energy systems.

Keywords: Mining waste; Chemical looping technique; Methane reforming; Steam reforming; Oxygen carrier; H_2 yield; Fluidized bed reactor; Molecular dynamics.