Pyrolysis-catalytic steam reforming of PE and PLA waste plastics for hydrogen-rich syngas production over high entropy catalysts and natural oyster shell

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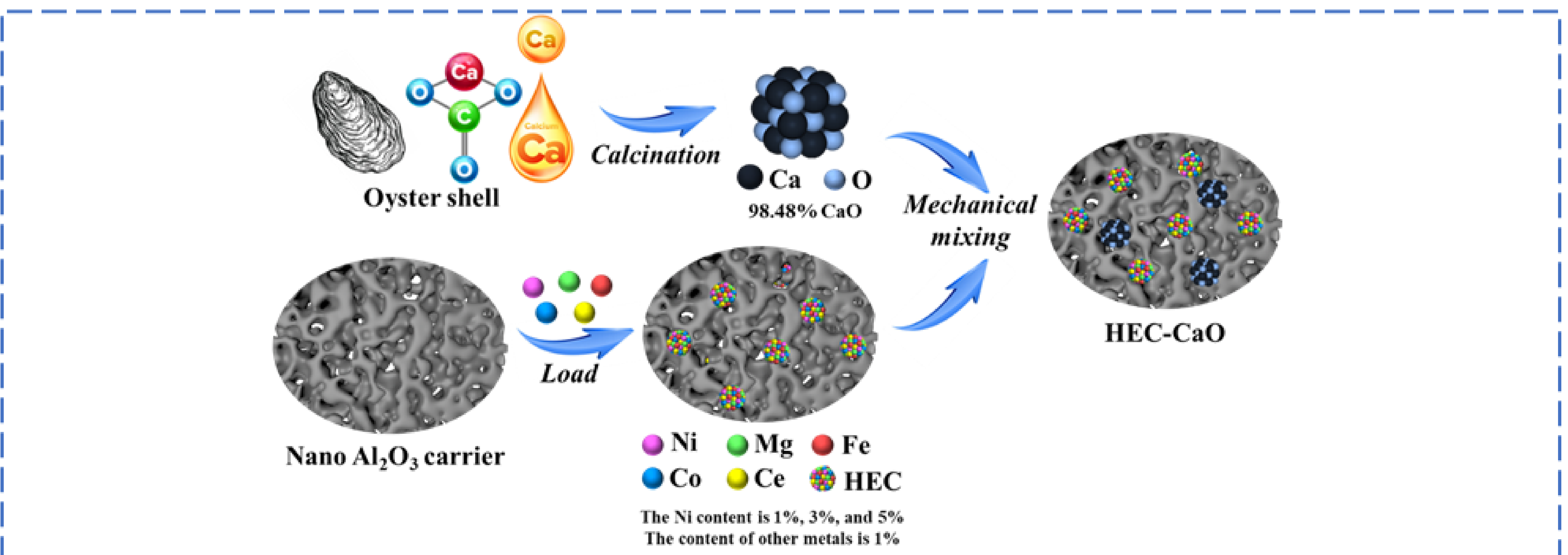
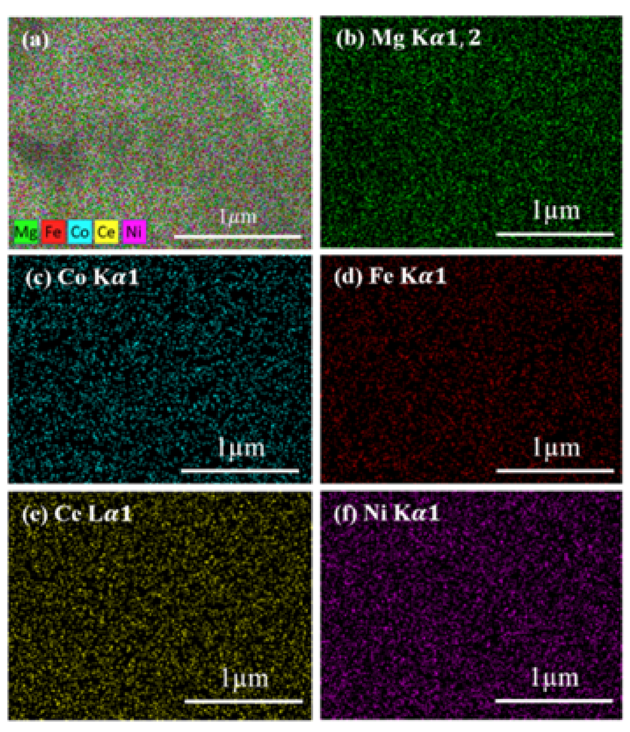
Abstract

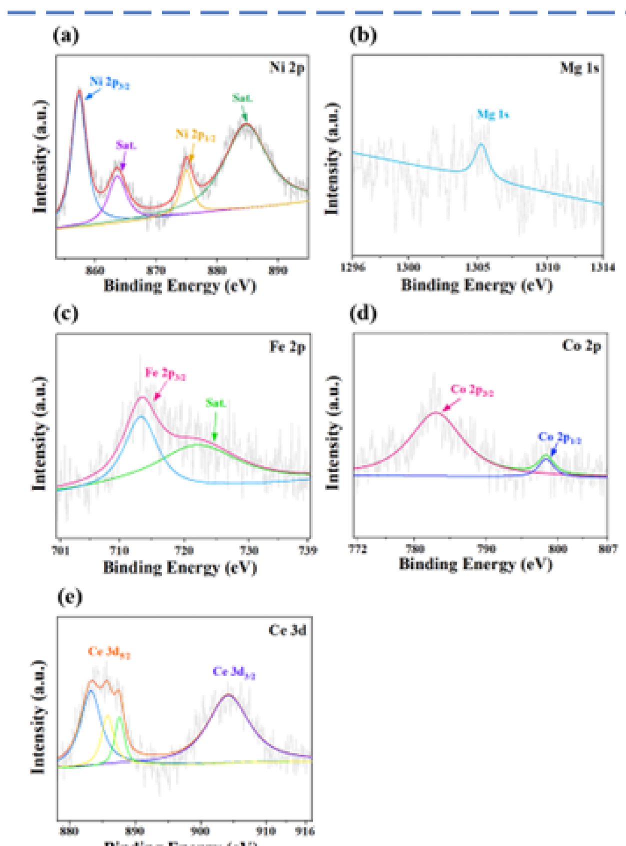
The incessant rise in the requisition for plastic commodities has resulted in the swift accrual of plastic waste. Consequently, the pyrolytic reforming of solid plastic waste to produce hydrogen is emerging as a promising method. The purpose of this study is to explore a high-yield hydrogen production method from PE and PLA high-molecular-weight plastics via pyrolysis and catalytic steam reforming in a two-stage reactor system. The selection of PE and PLA plastics as experimental materials is of significant importance. High-entropy catalysts (HECs) with well-defined structures and clear morphologies were prepared using the impregnation method. The study investigated the effects of nickel loading (wt.%), reaction temperature, reaction time, steam input, and the addition of CaO on the hydrogen gas production performance. The results show that after adding the HECs, the maximum hydrogen production rate of PE increased by about 33 times, and the maximum hydrogen production rate of PLA increased by about 14 times, reaching 278.42 μmol·s^{-1}·g_{Cat}^{-1}·g_{PE}^{-1} respectively. and 224.74 μmol·s^{-1}·$g_{Cat.}^{-1}$·g_{PLA}^{-1}. The addition of CaO adsorbent moderately improved hydrogen yield, but the effect was not pronounced. In the steam reforming reaction, the presence of metals such as Ni, Mg, Fe, Co, and Ce played catalytic roles. The experimental approach employed in this study demonstrated excellent hydrogen-producing capabilities. It provides a novel method for efficiently producing hydrogen from high-molecular-weight polymeric plastics through pyrolysis and catalytic steam reforming.

Fabrication and characterization of the HEC



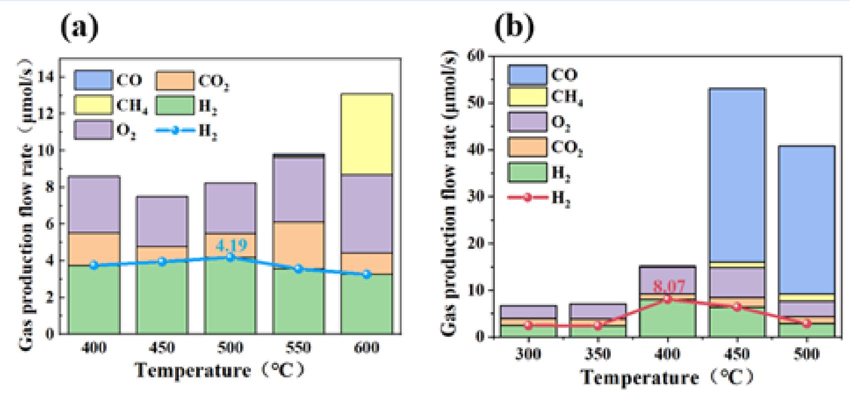
- This study utilized Al_2O_3 as a carrier and employed the impregnation method to prepare a loaded HEC.



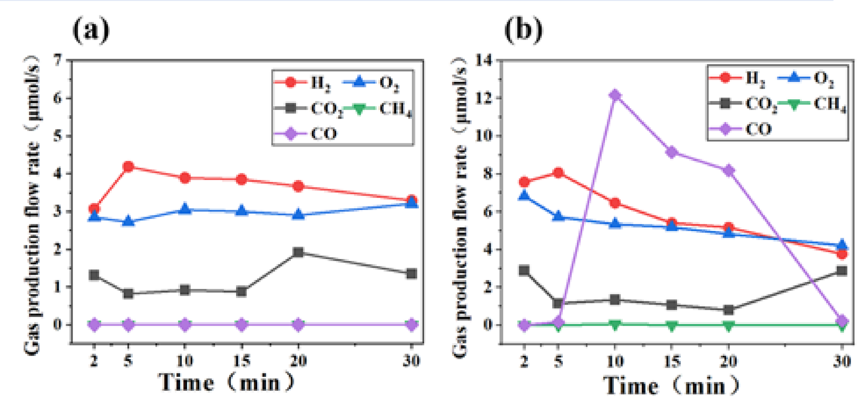


- The HEC has a good morphology, excellent pore size and specific surface area.

Simple pyrolysis and catalytic reforming

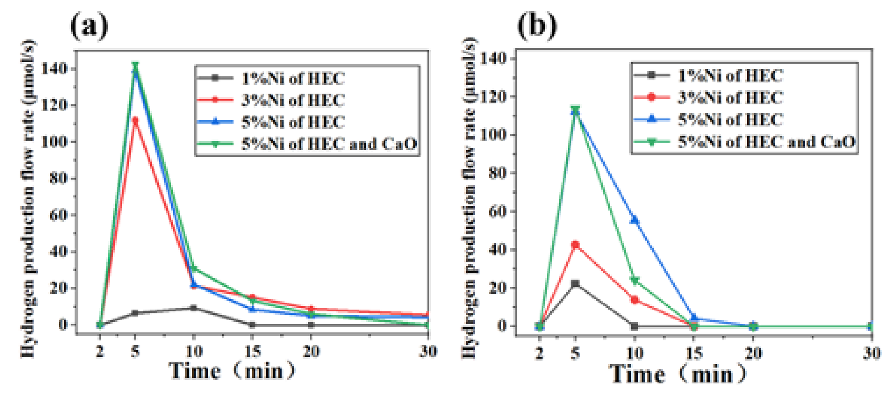


Gas product at different temperatures (a) PE, (b) PLA

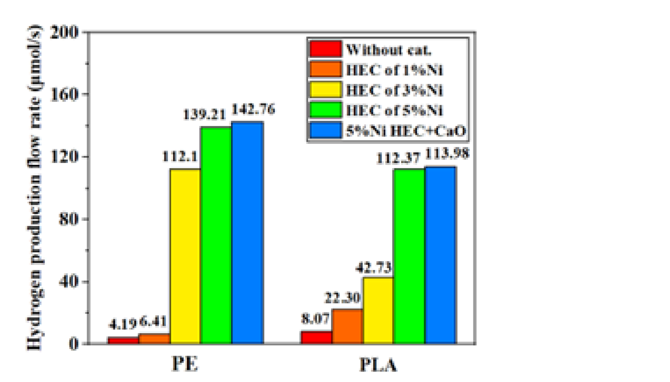


Hydrogen production rate as a function of time (a) PE, (b) PLA

- The optimal temperatures for PE and PLA plastics are 500°C and 400°C.
- The large amount of CO produced by PLA is caused by high temperature and oxygen-deficient conditions.

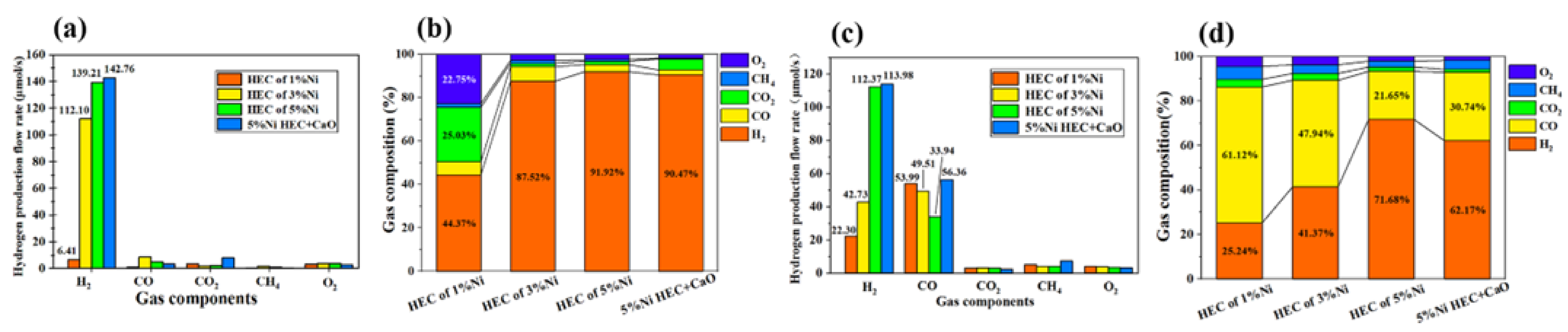


Hydrogen production rate catalytic reforming (a) PE, (b) PLA



Hydrogen production of PE and PLA plastics with HEC

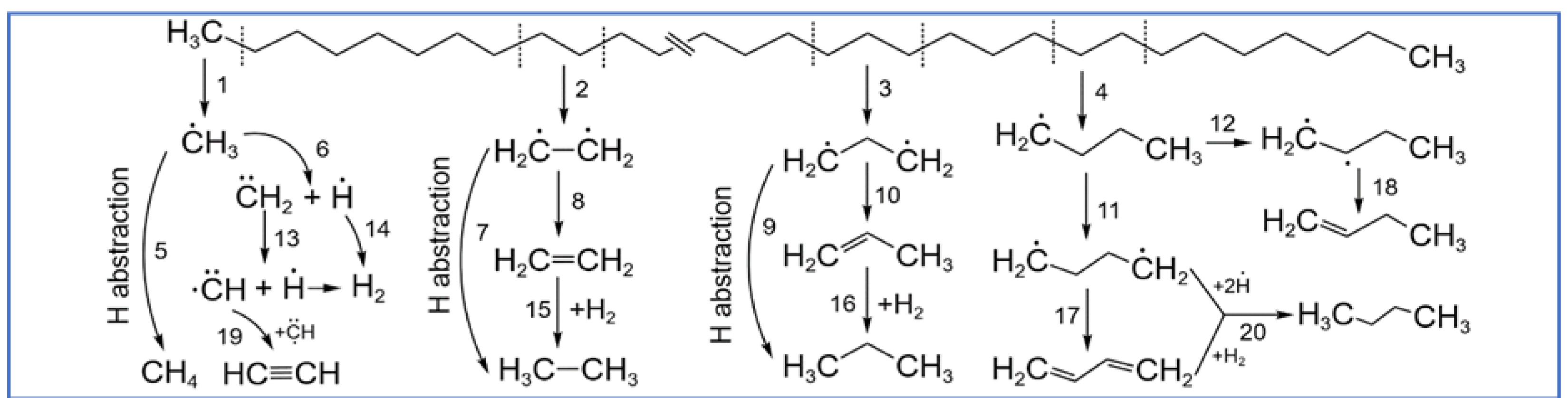
- The hydrogen production of HEC with different Ni loadings is: 5% > 3% > 1%.
- HEC can significantly improve the catalytic pyrolysis hydrogen production effect of PE and PLA .



Hydrogen production rates and composition percentage of pyrolysis gas with catalyst (a)-(b)PE, (c)-(d)PLA

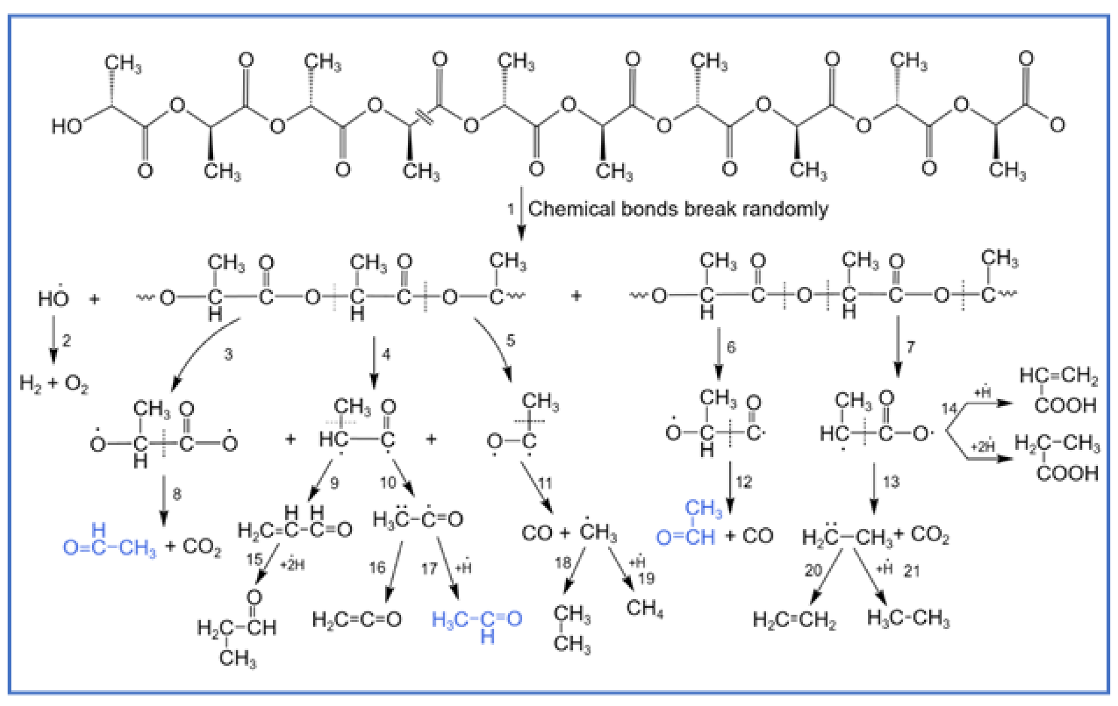
- The addition of CaO increases the hydrogen production, but the percentage of hydrogen is lower.
- The CaO adsorbent has little effect on hydrogen production of PE and PLA plastics.

Mechanistic analysis



Mechanistic Analysis of Gaseous Product during the Pyrolysis of PE

- The primary are the cleavage of C–C bonds, leading to the formation of smaller intermediate radical species (steps 1, 2, 3, and 4).
- Numerous secondary reactions includes further bond cleavage, dehydrogenation reactions, recombination reactions, isomerization reactions, cyclization reactions, and diolefin synthesis reactions, among others.
- The combination of hydrogen free radicals generated from cracking results in the target product, hydrogen (step 14).



Mechanistic Analysis of Gaseous Product during the Pyrolysis of PLA

- PLA undergoes random cleavage, generating complex oligomer radicals (step 1).
- As the pyrolysis reaction progresses, covalent bonds further cleave to produce small radical species or products.
- Hydroxyl radicals generated from cracking combine to produce the target products, hydrogen and oxygen (step 2).

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