"Jadeite Hydrogen" from catalytic decomposition of non-methane hydrocarbons

Bofan Li[1], Ruijing Jiao[1], Chaojie Cui[1,2,*], Weizhong Qian[1,2,*], Fei Wei[1,2], Yong Jin[1]

1 Department of Chemical Engineering, Tsinghua University, Beijing, 100084, China; 2 Ordos Laboratory, Ordos, Inner Mongolia, 017000, China

**Correspondence: qianwz@tsinghua.edu.cn (W. Q.); cuicj06@tsinghua.edu.cn (C. C.)*

Highlights

- Volatile C2-C5 hydrocarbons and LCO were transformed into clean hydrogen and CNTs.
- The selectivity of H2 in the gaseous product was 71% - 95%.
- The relationship between gas and solid products was studied for the first time.
- Three deactivation mechanisms of the catalyst were proposed.

1. Introduction

Hydrogen is one of the most important matters for clean energy and green chemicals worldwide in the era of carbon neutrality [1]. To stress its cleanness for sustainable development, hydrogen is classified into green, blue, and grey ones, respectively, depending on the sources (from renewable solar, wind, biomass, or fossil fuels) and the treatment of CO_2 (released or stored) [2]. Although the capacity of green H_2 (from water electrolysis with green electricity) is ever-increasing, the absolute amount is still too small to meet the huge demand for various industries in the next decade [3]. The technology of carbon capture utilization and storage (CCUS) is also on a demo scale, owing to the limitation of storing zone and huge storing cost [4]. An alternative route of "Turquoise hydrogen", from the thermal decomposition of methane, was aimed to fill the gap in clean hydrogen supply [5]. However, the endothermic transformation of inert methane, operating at high temperatures (1100-1300K), is highly energy-consumptive and with low efficiency. Recycle of huge untransformed methane also implies huge carbon release [6]. In addition, considering the economical dispensing distance of H_2, it is highly desirable to obtain relatively clean H_2 with distributed sources at low cost.

Herein, we proposed a new concept of "jadeite hydrogen" from the non-oxidative catalytic decomposition of non-methane fossil fuels, such as ethane, pentane, liquefied petroleum gas (LPG) and even light recycled oil (LCO). These raw materials can be considered as the distributed sources, since various factories in the industry of oil refinery, coal and biomass transformation own these resources and the as-produced clean H_2 can be directly used in situ without costive storage and dispense.

2. Methods

Ethane, LPG pentane, and LCO were used as the carbon source and were fed from the bottom of the reactor with the addition of N_2 as the inert carrier gas. In general, 10-30 g $Fe/Mo/Al_2O_3$ catalysts were placed into the stainless-steel made fluidized bed reactor with an inner diameter of 50 mm. The reaction temperature was 973-1073 K and the space velocity of the carbon source was 0.34-0.71 h^{-1}. The operation pressure was ambient pressure at the exit of the reactor.

3. Results and discussion

In our technique, targeted gaseous products were mainly hydrogen with few methane, CO, CO_2 and carbon elements in raw materials and were mainly fixed as highly valuable carbon nanotubes (CNTs) rather than the cheap carbon black. In addition, we proposed the use of the molar ratio of H_2/all gaseous carbon products (CH_4, CO, CO_2, etc.) as the green index (GI) for evaluating the quality of H_2. The present technology ensured the GI value of jadeite hydrogen in the range of 3-42, far outweighing grey hydrogen (0.03-0.3) in the current industry, even surpassing blue hydrogen (10-15). These encouraging results would stimulate the development of production technologies of jadeite hydrogen, balancing the cleanness and the available amount and acceptable cost and contributing to a practical road map toward carbon-neutral future.

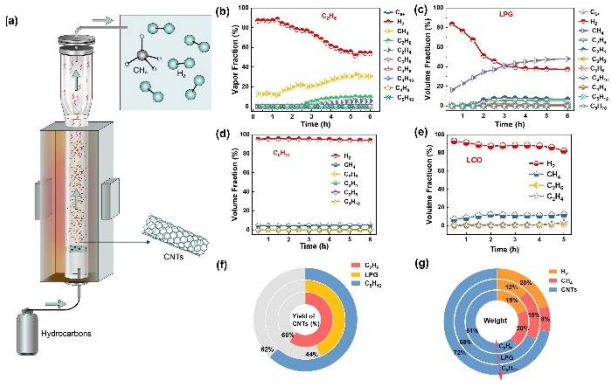

Figure 1. Hydrogen and CNTs production from the catalytic decomposition of hydrocarbons.

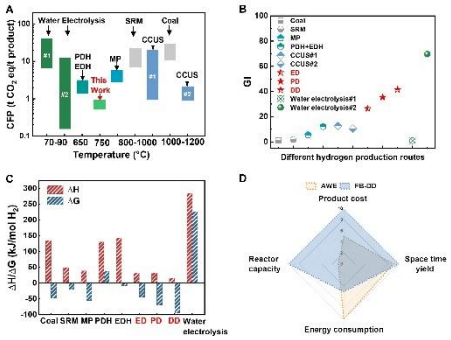

Figure 2. Comparison of GI and CFP between this work and current industry.

4. Conclusions

We offered a new route to produce jadeite hydrogen from hydrocarbons (ethane, pentane, diesel) and first proposed a universal concept of GI. Using nanosized Fe catalyst, GI values can be high up to 22-42 and the yield of CNTs could also be promoted from 48% to 69%. With the volume increase of CNTs inside the reactor, GI was decreased to 3-5, but it was still far higher than most grey hydrogen. The present GI value exceeded most technology for grey H_2 in the industry and approached that of blue H_2 gaining interest in filling the gap between the absolute capacity of green H_2 and the huge amount by not clean grey H_2. Our finding indicated that the catalyst was not truly deactivated from the perspective of activity, but just from the production and selectivity of H_2, which deserved further investigation.

References

[1] Yilmaz F, Ozturk M, Selbas R. Design and thermodynamic analysis of coal-gasification assisted multigeneration system with hydrogen production and liquefaction. Energy Conversion and Management 2019;186:229-40. https://doi.org/https://doi.org/10.1016/j.enconman.2019.02.053.

[2] Marquevich M, Sonnemann GW, Castells F, Montané D. Life cycle inventory analysis of hydrogen production by the steam-reforming process: comparison between vegetable oils and fossil fuels as feedstock. Green Chemistry 2002;4(5):414-23. https://doi.org/10.1039/B203742B.

[3] Serban M, Lewis MA, Marshall CL, Doctor RD. Hydrogen Production by Direct Contact Pyrolysis of Natural Gas. Energy & Fuels 2003;17(3):705-13. https://doi.org/10.1021/ef020271q.

[4] Chi J, Yu H. Water electrolysis based on renewable energy for hydrogen production. Chinese Journal of Catalysis 2018;39(3):390-4. https://doi.org/https://doi.org/10.1016/S1872-2067(17)62949-8.

[5] Proost J. Critical assessment of the production scale required for fossil parity of green electrolytic hydrogen. International Journal of Hydrogen Energy 2020;45(35):17067-75. https://doi.org/https://doi.org/10.1016/j.ijhydene.2020.04.259.

[6] Machhammer O, Bode A, Hormuth W. Financial and Ecological Evaluation of Hydrogen Production Processes on Large Scale. Chemical Engineering & Technology 2016;39(6):1185-93. https://doi.org/https://doi.org/10.1002/ceat.201600023.

Keywords

jadeite hydrogen; hydrogen production; green index; carbon nanotubes.