論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Process Intensification of Methane Pyrolysis using Molten Metal Bubble Column for Hydrogen Production
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12556号, 授与年月日:2023年9月22日, 学位の種別:課程博士, 審査員:関口 秀俊,多湖 輝興,下山 裕介,松本 秀行,森 伸介
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12556号, Conferred date:2023/9/22, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 系 応用化学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of (Engineering)
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The objective of this study is to investigate the process intensification of methane pyrolysis for hydrogen production using the molten metal bubble column (MMBC) with tin as the medium. Process intensification in this research is pursued to attain several advantages, including enhanced process efficiency, improved product quality, and reduced environmental impact. These benefits can be realized through improved heat transfer, catalytic surface reactions, and carbon separation properties provided by the MMBC.

The research aims to examine the impact of adding metals with higher catalytic activity, such as copper (Cu) and nickel (Ni), to the tin column on reaction kinetics and carbon production. Additionally, the research delves into the mathematical investigation of the influence of bubble diameter and the resulting surface-to-volume ratio on catalytic reactions. Moreover, a preliminary proposal is made for a combined molten metal bubble reactor with plasma discharge as a means for further process intensification.

Chapter 2: Experiments of Molten Metal-Based Methane Pyrolysis

Hydrogen was produced via methane pyrolysis conducted in a MMBC at different molten metal temperatures and media. The reactor was an alumina tube, and a quartz gas-injection tube was inserted into the molten metal column to bubble the nitrogen-diluted methane feed via the molten metal. Compared to the tubular reactor, the pure tin proved that the process was intensified by using a MMBC. The effects of adding catalytic active metals, such as nickel and copper, to the tin base metal were investigated. The presence of catalytic active metals significantly improved the pre-exponential factor and also increased the apparent activation energy. This phenomenon requires further investigation. Both tin–nickel and tin–copper alloys showed improved reaction rates in general.

The carbon produced during the reaction was analyzed using SEM with EDS, XRD, and Raman spectroscopy. The SEM images show that carbon collected from molten metal surfaces exhibited unique stacked-grain structures, and tin was also present as an impurity. The presence of catalytic active metals decreased Raman peak ratio of I_D/I_G, which implies that the carbon became less amorphous. There is a need to further improve this process to obtain higher quality products with higher purity and better morphology.

For comparison and further study of the catalytic reaction phenomena, a horizontal reactor was built to study the effect of the presence of a catalytic surface in the reactor.

Chapter3: Catalytic Surface Reaction Kinetic Analysis

The experimental results for methane pyrolysis in the molten metal bubble column were analyzed using different kinetic design equations. The fraction of surface reaction in the total reaction was calculated to

prove the dominance of the catalytic surface reaction with a fraction above 0.7 for all metals within the studied temperature range. The equation separating the catalytic surface reaction and the bubble gas phase reaction resulted in lower activation energies than the overall reaction equation but yielded the same trend for different metals. The resulting values for the catalytic surface reaction rate constant (k_c) showed that the 5% Ni–Sn alloy would perform best at all temperatures among the studied media. At the same time, the catalytic surface reaction rate constant for alloys with different Cu concentrations changes with temperature, suggesting the possible existence of an optimum Cu content.

Moreover, the equation was applied to the horizontal reactor and results were compared to experimental results which showed good alignment and also proved that the catalytic surface reaction fraction in the horizontal reactor is minor, which again elucidates the importance of the bubbling concept.

Finally, conversion was estimated at different conditions by solving the differential equation that separates surface and bulk reactions. The calculations showed the importance of the proper selection of orifice diameter and/or reaction medium and their effects on conversion. The differential model can be used for the initial selections of design parameters for future design stages.

Chapter 4: Plasma-assisted Molten Metal-Based Methane Pyrolysis

Plasma discharge was added to the horizontal and the MMBC reactors after the modifications of the experimental setup. The experiments were conducted to investigate the possibility as well as the effect of combining two different hydrogen generation technologies. Despite the slight increase in hydrogen composition, this experiment was a proof of the concept. Experimental evidence has confirmed that the inclusion of plasma discharge in a MMBC can enhance the production of hydrogen, especially at lower temperatures where the conversion is very limited. Nevertheless, continuous operation is not yet possible due to the carbon generation, which creates a short-circuit and stops the plasma discharge. Further modifications in the reactor design are necessary to solve the carbon generation issue at the discharge gap.

Conclusion

In conclusion, this study focuses on process intensification for methane pyrolysis using the MMBC with tin as the medium. The addition of catalytic active metals improves reaction kinetics and carbon production. The catalytic surface reaction dominates the overall reaction. Furthermore, the inclusion of plasma discharge enhances hydrogen production, but challenges related to carbon generation require attention for continuous operation.