博士論文審査結果の要旨

博士論文審査委員会

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論文題目	Falsification of the mathematical models of methane reforming process using generalized least squares method

〔論文審査の要旨〕

申請者の博士論文は、固体酸化物形燃料電池のアノード材料をメタンの水蒸気改質の触媒として使用した場合の反応速度を対象とし、実験データから反応速度式に含まれる活性化エネルギー、頻度因子、反応次数を推定する新たな枠組みを提案するものである。

この博士論文について、予備審査を 2015 年 4 月 30 日（木）16:30 から豊洲キャンパスの 403 教室にて実施した。主査の他、本学から３名、学外から１名、合計４名の審査員が出席した。予備審査では、論文の内容についての説明とそれについての質疑を行った。論文全般に対する審査員の意見は概ね好意的であり、本文の構成および内容については特に問題ないと評価され、博士論文として十分な水準にあることを確認した。いくつか不備な点が指摘され、修正を要することが明らかとなったが、いずれも大幅な修正を必要とするようなものではなかった。審査委員からの指摘事項については、最終原稿を纏めるにあたって加筆・修正するよう申請者に指導を行った。その後、申請者により 13 箇所の修正が施された論文原稿が提出されたので、それをもって最終審査を実施することとした。

最終審査は、2015 年 7 月 23 日（木）16:30 から大宮キャンパスの 5441 教室にて実施した。主査の他、本学から３名、学外から１名、合計４名の審査員が出席し、ポスドク研究員や学生ら 10 名程度の聴講者があった。修正された部分を含めて論文内容について説明してもらった上で質疑を行った。論文で示された反応速度式についての研究成果が、将来的によりミクロな視点からどのように発展しうるかという質疑は、申請者の今後の研究活動の一つの指針を示すものであり有意義な意見交換であったと考えられる。一方で、審査委員からスペルミスなどの軽微な誤記の指摘があったので、修正するよう指示した。

発表と質疑が終了した後、審査委員による合否判定の審議を行った。審査委員が記入した学位審査評価シートの評価点は、４つの評価項目「専門性」「広範な教養」「業績」「コミュニケーション能力」のすべてにおいて、地域環境システム専攻が定める採点基準を満たしており、学位審査合格と認められた。最終的に投票を行い、合格と判定した。

以上の通り、主査および審査委員４名による審査の結果、申請者の博士論文の内容とこれまでの業績、研究者としての能力は、博士の学位に相応しいものと評価された。

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論 文 要 旨
Thesis Abstract

(2015/06/26) 2015 年 7 月 1 日

※報告番号	第 号	氏 名 (Name)	SCIAZKO Anna

主論文題名 (Title)

Falsification of the mathematical models of methane reforming process using generalized least squares method

内容の要旨 (Abstract)

The presented research for methane/steam reforming process attempted to provide the comprehensive description of the methane/steam reforming process dedicated for Solid Oxide Fuel Cell (SOFC). Despite the fact that methane/steam reforming is currently one of the most popular industrial methods for hydrogen production, the kinetic of the reaction is not fully described. The derived empirical models of the process are significantly divergent among themselves. The objective of dissertation is essential in the context of the lack of the consistency among the derived reaction kinetics of the methane/steam reforming presented in the literature. Therefore, the comprehensive analysis from both of experimental and computation stand points have to be proposed as the systematic and reliable strategies.

Generally, the quality of the mathematical model of the physical phenomena is decreased because of the uncertainties derived from the model simplifications, assumed values of thermo-psychical constants and uncertainties of the experimental measurements. The conducted research proposes the experimental and numerical analyses of the methane/steam reforming process using the Generalized Orthogonal Least Squares (GLS) method. The GLS algorithm is applicable for finding the most probable approximation of the unknown parameters, which define the reliability of the derived reforming reaction rate and provides a criteria for the quantifications of the mathematical models describing the physical process.

In the scope of thesis the following topics were concerned and discussed: in Chapter 1 the theoretical basis of the methane/steam reforming process were explained with the motivation for the proposed research. Chapter 2 summarizes the mathematical deliberation of the Generalized Least Squares Method and the potential benefits of its incorporation into the determination of the kinetic of the highly nonlinear chemical process. The classical methods of deriving methane/steam reforming kinetic were introduced in Chapter 3, with the focus on the determination of the parameters in the power law expression describing methane/steam reforming. The experimental

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studies, conducted as part of this dissertation were described in Chapter 4 and supplementary data concerning the experimental setup and prepared catalysts were given in Appendices A and B, respectively. Chapter 5 is divided into two parts. Firstly, the classical approaches to modelling and investigating the methane/steam reforming process were applied to the experimental studies on nickel cermet catalyst with volumetric composition of Ni equaled 60%. The updated experimental conditions were applied to the analyses in the second part of Chapter 5. The influence of the volumetric composition of nickel cermet catalyst was experimentally investigated. The reaction order rates for various catalytic materials were provided and compared with literature findings for SOFC dedicated catalysts. The results were found to be convergent and independent on the volumetric composition in terms of reaction orders. In Chapter 6 a novel approach to evaluate the reaction kinetics of the methane/steam reforming process by adopting an Orthogonal Least Squares method was introduced. The advantages of such an approach enable a more general analysis of the problem and provide more precise information about obtained results, which includes their uncertainty. The Generalized Least Square (GLS) method was applied to the calculation of the empirical parameters of the methane/steam reforming reaction on a Ni/YSZ SOFC anode cermet catalyst. A critical comparison of the obtained results with the literature data and discussion on the possible reasons for the essential discrepancies between various studies are presented in Chapter 7. The GLS method has the potential to provide objective criteria for the formal evaluation and falsification of different mathematical models of the methane reforming process. The studies in Chapter 8 particularly focused on the importance of the mathematical expressions, of the physical phenomena occurring in the chemical reforming system. The analysis was conducted in the light of improving the precise quantification of uncertainties found in the evaluation of the chemical reaction process and providing a reliable reaction rate equation.

The proposed algorithm of GLS can be easily adapted to the mathematical modelling of the fuel reforming process for different catalysts and experimental conditions. Also, the various constraint models can be easily implemented, as they do not change the structure of the numerical algorithm but only insert an additional procedure. The application of the GLS method can provide a great benchmark in the evaluation of the chemical process and qualify the level of mathematical modelling of reaction processes. Therefore it can be stated, that the proposed comprehensive description with respect to the simultaneous numerical-experimental methodology in the form of the Generalized Least Squares method introduces novel quality and reliability into studies on highly nonlinear catalytic reactions.

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