博士（理　学）　ラジェシ　ビー　ビニワーレ

学位論文題名

Catalysis in Octane Reforming and Cyclohexane Dehydrogenation Reactions using Plasma-Spray Pulsed Reactors and their Thermographic Reaction Analysis for Hydrogen Production, Storage and Supply

（水素の製造，貯蔵及び供給のためのプラズマーパルス噴霧型反応器を用いるオクタン改質反応及びシクロヘキサン脱水素反応の触媒作用及び熱画像反応解析に関する研究）

学位論文内容の要旨

Catalytic processes for hydrogen production, storage & supply, and utilization are being considered as most important issues for application of clean energy resources, therefore the environmental and energy resource related catalysis is of current interest. In present study two important aspects namely, hydrogen production and; storage and supply are addressed. Hydrogen production was carried out via autothermal reforming of iso-octane. Catalytic dehydrogenation of cyclohexane was studied for hydrogen storage and supply application through catalytic reaction of dehydrogenation of cycloalkanes. Novel reactors using spray pulsed mode injection of liquid reactant and application of plasma for enhancement of catalytic activity was used in this study.

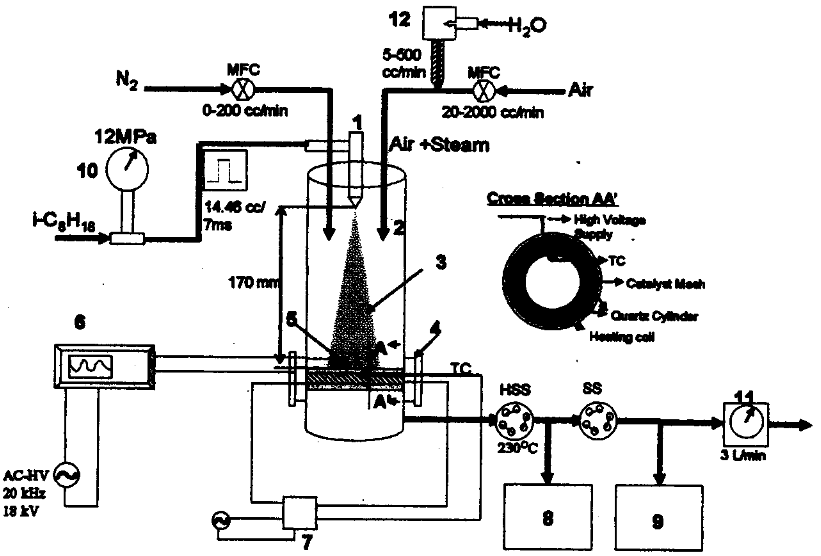

Figure 1: Experimental setup for Plasma-Spray Pulsed Reactor, the legends are as following 1) Atomizer, 2) Reactor, 3) Fuel Spray 4) Connecting Flanges (Insulators), 5) Mesh Type Catalyst, 6) Oscilloscope, 7) Temperature Controller, 8) FID GC, 9) TCD GC, 10) High Pressure Supplier, 11) Gas

Flow Meter, 12) Micro feeder pump, AC-HV: High Voltage, MFC: Mass Flow Controller, HSS: Heated Sample Selector, SS: Sample Selector, TC: Thermocouple

In the first chapter a brief introduction to hydrogen as clean fuel is given. Utilization of hydrogen in various types of fuel cells, hydrogen production routes and various methods of hydrogen storage are discussed.

Iso-octane is used in this study to simulate the reforming of gasoline under autothermal conditions and the results are reported in chapter 2. A steam/carbon ratio equal to 1 and an equivalence ratio equal to 0.32 was used for reforming at temperatures of 600 and 700 °C on Ni-Mn, Ni-W and Rh-Ce catalysts supported on alumina mesh. A novel spray-pulsed reactor for providing atomized iso-octane in pulses was used to create alternate wet and dry conditions for improving the catalyst reactant contact which resulted in enhanced hydrogen production rates. The maximum hydrogen yield obtained is 4 moles of hydrogen per mole of iso-octane. Based on the product analysis optimized condition for higher hydrogen production and high H_2/CO ratio has been deduced. Further, the effect of non-thermal plasma in combination with catalyst on reaction was tested under spray-pulse injection of iso-octane. Plasma catalytic hybrid system results into higher activity at particular conditions.

Chapter 3 deals with efficient storage and supply of hydrogen both on weight and volume basis without any contamination of other gases such as CO. Dehydrogenation of cyclohexane over Pt/alumite and Pt/activated carbon cloth catalysts was carried out for hydrogen storage and supply to fuel cell applications. Unsteady state was created using spray pulsed injection of cyclohexane to facilitate the endothermic reaction to occur efficiently. Higher temperature of the catalysts surface is more favorable for this reaction, thus the heat transfer phenomena and temperature profile under alternate wet and dry conditions created using spray pulsed injection becomes important. IR thermography was used for monitoring of temperature profile of the catalyst surface simultaneously with product analysis. The heat flux from the plate type heater to the catalyst was estimated (10-15 kW/m^2) using a rapid temperature recording and thermocouple arrangement. The analysis of temperature profiles, reaction products over two different supports namely activated carbon cloth and alumite reveals that the more conductive support such as alumite is more suitable for dehydrogenation of cyclohexane.

With the specific interest to use Pt-less catalysts or to minimize the use of Pt in catalysts, dehydrogenation of cyclohexane to benzene was carried out over Ni supported on activated carbon cloth (Ni/ACC). The results are reported in chapter 4. A synergistic effect was observed in the case of the promoted catalysts (20 wt% Ni+0.5 wt% Pt) wherein, the hydrogen production was enhanced by ca 1.5 times as compared to the Ni only catalyst and ca 60 times as compared to 0.5 wt% monometallic Pt catalyst. Selectivity towards dehydrogenation observed to be enhanced by addition of Pt into Ni/ACC catalysts. Catalysts were characterized using XRD, TEM and H_2 chemisorptions. Stable Ni metallic catalyst was observed with average particle size of ca 10 nm.

In conclusion I have demonstrated the use of spray-pulsed reactor for enhanced hydrogen production in both the cases, namely, autothermal reforming of iso-octane and dehydrogenation of cyclohexane. Use of plasma-catalytic hybrid system is demonstrated for enhancement in hydrogen production. Further use of IR thermography for monitoring multiphase phenomena during strongly endothermic reaction of dehydrogenation of cyclohexane is reported for the first time and was used for optimization of operating conditions. Also the Pt-less catalysts are reported in this study for dehydrogenation of cyclohexane with synergistic effect in the case of promoted catalysts using a small amount of Pt. The results reported in this study would be beneficial for advancement in hydrogen production and; storage and supply for fuel cell applications.

学位論文審査の要旨

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Catalysis in Octane Reforming and Cyclohexane Dehydrogenation Reactions using Plasma-Spray Pulsed Reactors and their Thermographic Reaction Analysis for Hydrogen Production, Storage and Supply

(水素の製造，貯蔵及び供給のためのプラズマーパルス噴霧型反応器を用いるオクタン改質反応及びシクロヘキサン脱水素反応の触媒作用及び熱画像反応解析に関する研究)

申請学位論文は、プラズマ放電及びパルス噴霧型反応器を用いる新しい触媒反応場を環境及び水素エネルギー関連の触媒反応に応用して、その構造特性と触媒作用について特に、シクロヘキサンの脱水素反応における触媒表面の熱動力学的反応解析の研究を行なったものである。近い将来の水素・燃料電池社会に向けて、環境負荷が少ない水素製造及び水素貯蔵・供給技術の開発は触媒研究の重要な課題である。申請者は、まず燃料電池自動車用水素の供給のためのガソリン改質反応について、イソオクタンをモデル物質としてとりあげ、Ni-MnやRh-Ce触媒とプラズマ放電を組み合わせた水蒸気改質反応での水素生成活性とH_2/COモル比について研究を行なった。その結果、熱触媒反応やプラズマ放電反応それぞれ単独と比較して、組み合わせ反応場においてより低温域において高い水素生成速度が得られた。またイソオクタンのパルス噴霧間隔を最適にする触媒表面の液膜形成条件での反応解析を行い、これによりイソオクタン改質反応における最大水素発生速度が観察された。さらに、高密度、軽量で安全に水素を貯蔵・運搬できる有機ハイドライドの一つであるシクロヘキサンの脱水素反応に対する触媒構造とパルス噴霧型反応場の研究をおこなった。活性炭やアルミナ担持Pt触媒上でのシクロヘキサン脱水素反応は吸熱に伴う熱供給律速であることが赤外線サーモグラフによる触媒表面温度の時間分解測定によりわかった。熱板から触媒膜に対する熱流の移動速度と最適なパルス噴霧間隔で供給されたシクロヘキサンの触媒表面における液膜形成過程について熱画像反応解析を行い触媒と熱板との接触界面が重要であることがあきらかにされた。この結果に基づいてアルマイト触媒膜が研究開発されて、活性炭やアルミナ担持触

媒などの従来触媒にくらべて、単位Pt量当たり100倍以上の高速でシクロヘキサンから水素を取り出すことが可能になった。さらに、申請者はシクロヘキサンの脱水素化反応に低活性のニッケル触媒に極微量（0.5%）の白金を添加することにより高活性で高選択率な水素生成が起こることを見出してその反応解析を進めた。燃料電池の実用化にむけて白金使用量の低減化や非白金触媒化のための興味ある研究成果である。このように、申請者は、プラズマ放電及びパルス噴霧型反応器を用いてイソオクタンの水蒸気改質反応やシクロヘキサンの脱水素化反応での水素生成速度に及ぼすプラズマ放電ー触媒組み合わせ反応場での反応解析を進めて触媒表面での活性液膜形成と触媒への熱流体の伝導効率の重要性を明らかにするとともに、従来法では得られない高速な水素生成反応を見出した。これらの環境及び水素エネルギーに関連した触媒作用の研究成果はCatal. Lett., Appl. Catal. などの権威ある国際的学術誌に５件が掲載発表されている。これは要するに、著者は、プラズマ放電及びパルス噴霧型反応器を用いたイソオクタンの水蒸気改質反応やシクロヘキサンの脱水素反応において、特殊反応場の反応解析と新規な赤外線レーザー熱画像測定法を応用して触媒表面の精密な温度分布のその場観察に成功して触媒評価と反応解析の進展に貢献するところ大なるものがある。

よって著者は、北海道大学（理学）の学位を授与される資格あるものと認める。