（様式課程博士３）

学 位 論 文 の 要 旨

専　攻　名	工学　専攻	ふりがな 氏　　名	イュイ　リン 兪　　琳　印
学位論文題目	プロパンの低温水蒸気改質用担持 Rh 触媒の研究開発		

In recent years, energy saving with technological innovation has been strongly demanded in the world because energy and environmental issues have been taken up. Fuel cells can directly convert chemical energy into electrical energy with higher efficiency than conventional internal-combustion engines and it has attracted increasing attentions as environment-friendly power generation device. Solid oxide fuel cell (SOFC) show highest energy conversion efficiency among different types of fuel cells, contribute to reduce amount of emitted CO_2, and is expected as new power generator in the new generation. At present, operation temperature of the SOFC system is so high (700-1000 °C) that it takes a while start and shutdown the system and deterioration of the component parts are easily induced. Hence, there are many researches for lowering the operation temperature of the SOFCs.

Liquefied petroleum gas (LPG) composing mainly of propane (C_3H_8) is one of the potential sources for fuel cell applications due to their higher energy density than natural gas, easy storage and well-established distribution infrastructures for the fuels. Although SOFC can convert LPG directly, it is widely known that the heavier hydrocarbons can induce coking on the electrode of FC stacks and in the pipe of the systems. Hence, pre-reforming is an important preliminary step for the SOFC and eliminates heavier hydrocarbons by converting to CH_4, H_2 and CO_xs at low temperatures such as 300-400 °C where the waste-gas is exhausted from the FC stack. Therefore, noble pre-reforming catalyst which shows high activity at the temperature is demanded.

In Chapter 3, Rh is supported on different kinds of oxide carriers and we investigated their catalytic behaviors for steam reforming of propane at low temperature. As the results, Rh/TiO_2 catalyst exhibited highest catalytic activity compared with other oxide supported catalysts. Therefore, we investigated the physicochemical properties of all catalysts. But, it was found that better propane-converting ability of catalysts was not explained by the increase in number of Rh active sites. These results indicate properties of the support rather than characters of the Rh are crucial for determining activity of the catalysts.

In Chapter 4, Rh is supported on $Ce_{1-x}Zr_xO_2$ oxide carriers with different cerium to zirconium molar ratio and we investigate their catalytic behaviors for steam reforming of propane at low temperature. As a comparison, conventional Rh/γ-Al_2O_3 catalysts are used. Rh/$Ce_{0.25}Zr_{0.75}O_2$ catalyst was found to show highest activity among the catalysts studied. We have found that Rh/$Ce_{0.25}Zr_{0.75}O_2$ exhibited highest propane steam reforming activity among Rh/$Ce_xZr_{1-x}O_2$ and Rh/γ-Al_2O_3 at low temperature. In addition to the conventional water adsorption and subsequent activation mechanism on the oxide supports, H_2O is activated over oxygen defect sites formed over the Rh/$Ce_{0.25}Zr_{0.75}O_2$ catalyst, owing to excellent redox ability of the support material. This results in promotion of propane steam reforming and subsequent water gas shift reaction at the temperature.

In Chapter 5, we found that the crystal structure of the TiO_2 anchoring Rh particles is crucial for the catalytic activity of Rh/TiO_2 catalysts for propane pre-reforming at the low temperatures. The SMSI induced during H_2 pre-reduction is optimized over Rh/TiO_2 with a rutile structure and catalyzes the reaction effectively. The resultant activity is much higher than conventional Rh/γ-Al_2O_3. In contrast, SMSI was too strong for Rh/TiO_2 with an anatase structure, and thus the surface of Rh particles was covered mostly with partially reduced TiO_2. The resultant activity was very low. This study emphasizes that the structure of supports affect metal support interactions and determines catalytic behavior, even if the elemental composition of the supports is the same.

The above results clearly demonstrated the effectiveness of the properties of the support for improvement in low temperature catalytic activity for steam reforming of propane, which indicates that developed catalysts are a promising candidates for the pre-reforming of hydrocarbons for the SOFC applications highly desirable for realizing sustainable society using only limited amount of energy.

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（様式課程博士８）

学位論文審査結果の要旨

専　　　　攻	工学　専攻	氏　　　名	兪　琳
論　文　題　目	プロパンの低温水蒸気改質用担持 Rh 触媒の研究開発		
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審査結果の要旨（1000 字以内）

本研究では、燃料電池のなかで最も高い発電効率を有する固体酸化物形燃料電池(SOFC)で使用する炭化水素の水蒸気改質反応について、実用化する上での以下の課題を克服すべく、触媒の開発を行った。

SOFC では、液化石油ガスなどの燃料と水蒸気をプレ改質器で水素やメタンなどに変換した後に燃料電池本体に供給する。しかし、C_2（エタン、エチレン）以上の炭化水素が生成ガス中に残留すると、SOFC の電極上や配管内で熱分解し炭素が析出する問題がある。また、SOFC の排熱をプレ改質器に利用するには、低温で高い活性を示す触媒が求められる。さらに、触媒には高い炭素析出抑制能と耐久性も必要である。そこで、液化石油ガスの主成分であるプロパンを用い、高価であるが他の金属と比較して高活性を示す Rh を少量含む、酸化物担持 Rh 触媒の開発について検討した。

- $Rh/Ce_{0.25}Zr_{0.75}O_2$ が 350℃の低温において従来型の Rh/Al_2O_3 よりも 2.4 倍の活性を示した。また、この原因が担体の優れた酸化還元能により水蒸気を効率的に活性化できるためであることを明らかにした。さらに、この高い酸化還元能によって析出炭素の前駆体が効率的に除去され、この触媒が優れた炭素析出抑制能と高い耐久性を示すことを明らかにした。

- Rh/TiO_2 の活性が TiO_2 の相構造（アナターゼ、あるいはルチル）に依存すること、ルチル型の TiO_2 を担体に用いると高活性を示すことを見出した。Rh/TiO_2（アナターゼ）では、Rh ナノ粒子が担体に覆われ Rh に反応ガスが接触できず活性を示さないが、Rh/TiO_2（ルチル）では、Rh ナノ粒子の一部が担体に覆われるため Rh に反応ガスが接触し高活性を示した。つまり、金属ナノ粒子と担体の強い相互作用を最適化することで高機能触媒の開発に成功した。また、この触媒が高い炭素析出抑制能と耐久性を持つことも見出した。

以上のように、材料の特性を利用した新しい触媒の構築に成功した。この成果は触媒などの材料開発のみならず工学の発展に寄与するところが大きい。また、論文審査会や論文公聴会における著者の説明は明確であり、質問に対しても的確に回答がなされた。よって本論文は博士（工学）の学位論文に値すると認められる。