

論文の内容の要旨

論文題目 Study of CO_x Methanation Mechanism over Supported Metal Catalysts
(担持金属触媒を用いた CO_xメタン化反応機構の検討)

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This thesis summarizes catalysts for selective CO methanation and CO₂ methanation which can be applied to CO removal techniques from hydrocarbon reformates and hydrogen carriers from renewable energies, respectively.

1. Selective CO methanation

In Japan, from 1980's, fuel cells have been regarded as a promising power generator with high efficiency and low environmental impact. They directly convert chemical energy into electrochemical energy and omit the intermediate steps of producing heat and mechanical power works of the most conventional power generation method. Polymer electrolyte fuel cells (PEFCs) are expected to be in the practical applications such as power sources for domestic uses and electric vehicles, and so on. In Japan, PEFC systems have been commercially available by the name of ENE-FARM since 2009, and 50000 units will have been installed by fiscal year 2013. The retail price of ENE-FARM is decreased from 3.5 million JPY (35000 USD) in 2009 to 2.0 million JPY (20000 USD) in 2013, but remains expensive for domestic facility. In order to spread ENE-FARM, it is necessary to manufacture ENE-FARM at a low cost and in large numbers. New Energy and Industrial Technology Development Organization (NEDO) in Japan has led a project "Development of PEFC Technologies for Commercial Promotion" since 2010 for the significant cost reduction of the full-fledged commercialization of residential PEFC co-generation systems. This project consists of the following 4 groups: a development of durable electrolyte materials, a development of CO tolerant anode catalysts, a development of CO removal processes from reformates, and a method to estimate the influence of impurities on fuel cell performance.

In the future hydrogen, as PEFC fuels, could be made from water electrolysis using carbon-neutral electricity sources, while hydrogen is presently made mainly from fossil fuels. PEFC are operated at low temperatures, and thus the anode is poisoned by CO contained in reforming gases. It is therefore necessary to reduce CO concentration below 10 ppm in the reforming gas. CO methanation has been regarded as a possible method to abate CO in the

reforming gases. Simultaneous CO₂ methanation is, however, an undesirable reaction in the CO removal because of highly exothermic nature and huge consumption of H₂. Consequently, a suitable catalyst must be developed to promote CO methanation and inhibit coincident CO₂ methanation. In addition, enhancement of low-temperature activity of CO methanation decreases the loading amount of methanation catalysts, resulting in downsizing CO removal units and, in consequence, cutting down the manufacture's cost. Taking into account application to CO removal units in commercial PEFC systems, the catalysts are also required to be stable for a long time.

In Chapter 2, selective CO methanation over Ru/Al₂O₃ and Ru/TiO₂ was investigated, and the effect of reduction treatment and the support materials on the selectivity and activity was examined. CO methanation activity was degraded over both Ru catalysts by raising reduction treatment temperature, which brought about Ru particle growth except for Ru/TiO₂ reduced at 600 °C. Ru/TiO₂ showed higher CO methanation activity than Ru/Al₂O₃ due to smaller Ru particle size. A close correlation was found between CO₂ methanation rate and perimeter length between Ru particle and support, which indicates that the interface was identified as the reaction sites of CO₂ methanation in CO and CO₂ coexisting atmosphere. CO₂ methanation over Ru/TiO₂ was suppressed in spite of long perimeter compared to Ru/Al₂O₃, stemming from the small amount of CO₂ adsorbed onto Ru/TiO₂. Ru/TiO₂ catalyst exhibited wider temperature window for selective CO methanation than Ru/Al₂O₃ catalyst.

In Chapter 3, selective CO methanation was investigated over Ru/TiO₂ prepared by a selective deposition method using NaOH and NH₃ aqueous solution as a pH adjuster. Control of pH by NH₃ solution resulted in small particle size of Ru (average 1.2 nm) and the formation of Na-free Ru/TiO₂, resulting in high CO methanation activity and wide temperature window for selective CO methanation at low temperatures.

In Chapter 4, I focused on selective CO methanation over Ru/TiO₂, Ru-Ni/TiO₂, Ru-Co/TiO₂, Ru-Fe/TiO₂, Ru-La/TiO₂, and Ru-K/TiO₂, and examined the selectivity and activity. The addition of Co and La to Ru/TiO₂ improved both CO methanation and reverse water gas shift reaction, while the addition of Ni raised only the activity for CO methanation. Thus Ru-Ni/TiO₂ showed the widest temperature range for selective CO methanation in prepared bimetallic Ru-based catalysts. In order to shift the range of Ru-Ni/TiO₂ to lower temperature, I prepared the trimetallic catalyst Ru-Ni-La/TiO₂. The catalyst exhibited the highest CO methanation activity among the prepared catalysts, resulting in a wider temperature range for selective CO methanation at low temperatures compared to Ru/TiO₂. The addition of La increased the electron density in the Ru species, which likely enhanced the dissociation of the C-O bond of CO on Ru probably due to back donation of electrons from Ru to CO. This led to high CO methanation activity over Ru-La/TiO₂ and Ru-Ni-La/TiO₂.

In Chapter 5, the removal of CO from reformat streams by selective CO methanation was investigated over TiO₂ supported Ru-Ni bimetallic and monometallic catalysts. As mentioned in Chapter 4, the combination of Ru and Ni enhanced CO methanation at low temperatures. The introduction of Ni into Ru/TiO₂ decreased the CO₂ conversion rate at 260 °C from 10 to 7.3 $\mu\text{mol min}^{-1} \text{g}_{\text{cat}}^{-1}$. The use of Ru and Ni, thus, expands the temperature range of selective CO methanation. Transmission electron microscopy and temperature programmed reduction by H₂ confirmed that Ru species were in close proximity to Ni species on Ru-Ni/TiO₂, indicating a decrease in direct contact between Ru and TiO₂. Fourier transform infrared spectroscopy techniques revealed that the decomposition of the formate species, formed during CO₂ methanation, is slow over Ru-Ni/TiO₂, in contrast to Ru/TiO₂.

In Chapter 6, The effect of metal loading amounts on activity and selectivity of CO methanation over Ru/TiO₂, Ni/TiO₂, and Ru-Ni/TiO₂ was investigated. 0.1wt%Ru-10wt%Ni/TiO₂ was the suitable catalyst for selective CO methanation in prepared $x\text{wt}\%\text{Ru}-10\text{wt}\%\text{Ni}/\text{TiO}_2$ catalysts ($x = 0.5, 0.2, \text{ and } 0.1$) due to sharp abatement in CO concentration and suppression of CH₄ production. With a decrease in Ru loading CO

production via RWGS reaction was slow, meaning that 0.1wt%Ru-10wt%Ni/TiO₂ removes CO rapidly compared to 0.5wt%Ru-10wt%Ni/TiO₂.

In Chapter 7, Selective CO methanation was carried out over 10wt%Ni/TiO₂ and 0.5wt%Ru-10wt%Ni/TiO₂, and the durability was examined. During the long-term test, both catalysts abated CO concentration from 0.25% (dry base) to less than 0.05 % above ca. 175 °C with CO₂ methanation suppressed. Ru-Ni/TiO₂ exhibited the high activity of CO methanation compared to Ni/TiO₂ during the test. Furthermore, for more than 5500 h, Ru-Ni/TiO₂ maintained a wide temperature window for selective CO methanation (> 50 °C), where CO and CH₄ concentrations were < 0.05% and < 1%, respectively, at a high gas hourly space velocity of 10000 h⁻¹. Over Ni/TiO₂ and Ru-Ni/TiO₂, CO₂ methanation activity was initially enhanced, and then stabilized. The initial promotion of CO₂ methanation activity is possibly due to the reduction of NiO which remained unreduced after the prereduction by H₂ at 450°C.

I expect that the key of selective CO methanation is the control of interfaces between active metals and support materials. If the interface can be blocked or the perimeter can be shortened, CO₂ methanation will be suppressed dramatically.

2. CO₂ methanation

While hydrogen can be produced via water electrolysis by renewable energy (such as biomass, solar, and wind energy), with zero greenhouse gas emissions, hydrogen is a gas at standard temperature and pressure and has many difficulties in storage and transportation. In order to overcome the difficulties, many studies have been conducted on the following hydrogen carriers: CH₄, NH₃, MeOH, dimethyl ether, formic acid, and organic chemical hydrides. An optimum hydrogen storage material is required to have the following properties: high hydrogen capacity per unit mass and unit volume, moderate temperature and pressure operation, reversibility, limited energy loss during charge and discharge of hydrogen, fast kinetics, a low cost of recycling and charging infrastructures, and a high level of safety. Especially CH₄, made from CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), has become a promising candidate as hydrogen source to be used in fuel processors. The advantage of CH₄ as a hydrogen carrier is non-toxicity in contrast to ammonia and methanol, and has a high energy density (3 times higher volumetric energy density than hydrogen). Moreover the well-developed infrastructures of natural gas can be adopted for methane, resulting in the easy storage and transportation of methane. Added to this, enormous carbon dioxide emitted into atmosphere can be recycled as the feedstock of CO₂ methanation, leading to the solutions to global warming. If the cost of green hydrogen production can be lowered, this attempt will succeed admirably.

CO is one of the intermediates in CO₂ methanation and produced in the following reactions: reverse water gas shift reaction (RWGS reaction, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) at more than 200 °C and CO₂ decomposition ($\text{CO}_{2\text{ads}} \rightarrow \text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$) at less than 100 °C. The CO₂ reduction to CO is considered to be a rate-determining step of CO₂ methanation. Endothermic RWGS reaction is favored thermodynamically and kinetically at high temperatures. The successive CO methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) is, however, of exothermic nature, and thus lower reaction temperature is desirable for higher CH₄ selectivity. It is, therefore, important to enhance the reaction rate of RWGS reaction and CO methanation at low temperatures.

In Chapter 8, CO₂ methanation was performed over 10wt%Ni/CeO₂, 10wt%Ni/ α -Al₂O₃, 10wt%Ni/TiO₂, and 10wt%Ni/MgO, and the effect of support materials on CO₂ conversion and CH₄ selectivity was examined. Catalysts were prepared by a wet impregnation method, and characterized by BET, XRD, H₂-TPR and CO₂-TPD. Ni/CeO₂ showed high CO₂ conversion especially at low temperatures compared to Ni/ α -Al₂O₃, and the selectivity to CH₄ was very close to 1. The surface coverage by CO₂-derived species on CeO₂ surface and the partial reduction of CeO₂ surface could result in the high CO₂ conversion over Ni/CeO₂. In addition, superior CO methanation activity over Ni/CeO₂ led to the high CH₄ selectivity.

In Chapter 9, the effect of CeO₂ loading amount of Ru/CeO₂/Al₂O₃ on CO₂ methanation activity and CH₄ selectivity was studied. The CO₂ conversion rate was increased by adding CeO₂ to Ru/Al₂O₃, and the order of CO₂ conversion rate at 250 °C is Ru/30%CeO₂/Al₂O₃ > Ru/60%CeO₂/Al₂O₃ > Ru/CeO₂ > Ru/Al₂O₃. With a decrease in CeO₂ loading of Ru/CeO₂/Al₂O₃ from 98% to 30%, partial reduction of CeO₂ surface was promoted and the specific surface area was enlarged. Furthermore, it was observed using FTIR that the intermediates of CO₂ methanation, such as formate and carbonate species, reacted with H₂ faster over Ru/30%CeO₂/Al₂O₃ and Ru/CeO₂ than over Ru/Al₂O₃. These could result in the high CO₂ conversion rate over CeO₂-containing catalysts. As for the selectivity to CH₄, Ru/30%CeO₂/Al₂O₃ exhibited high CH₄ selectivity (> 0.995) compared with Ru/CeO₂ (0.986), due to prompt CO conversion into CH₄ over Ru/30%CeO₂/Al₂O₃.

In this thesis, new catalysts with high CO₂ methanation activity and selectivity were developed using CeO₂. The catalysts showed the high initial performance. On the other hand, long-term stability of CeO₂-containing catalysts should be enhanced. For example, CO₂ conversion over my Ni/CeO₂ at 350 °C was rapidly decreased from 80 to 40% in only 200 h. Thus the deactivation mechanism of CeO₂-containing catalysts should be investigated. As one of the solutions, dispersing CeO₂ on the other metal oxides, such as zeolite and Al₂O₃, is expected to enhance stability compared to CeO₂ alone. The interaction between CeO₂ and metal oxides will prevent CeO₂ from sintering, leading to high stability of the catalysts. Furthermore, CeO₂-based mixed oxides (Sm_xCe_yO_z, Gd_xCe_yO_z, etc.) are anticipated to become a promising candidate as support materials of CO₂ methanation catalysts. These oxides have been utilized as the anode of solid oxide fuel cells under the reduction atmosphere at high temperatures (ca. 1000 °C), which can mean that the catalysts using CeO₂-based mixed oxides show a high durability in CO₂ methanation.