

# Study of CO<sub>x</sub> Methanation Mechanism over Supported Metal Catalysts

その他のタイトル	担持金属触媒を用いたCO <sub>x</sub> メタン化反応機構の検討
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博士論文（要約）

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（担持金属触媒を用いた CO<sub>x</sub>メタン化反応機構の検討）

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This thesis summarizes catalysts for selective CO methanation and CO<sub>2</sub> 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 CO<sub>2</sub> methanation is, however, an undesirable reaction in the CO removal because of highly exothermic nature and huge consumption of H<sub>2</sub>. Consequently, a suitable catalyst must be developed to promote CO methanation and inhibit coincident CO<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> and Ru/TiO<sub>2</sub> 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/TiO<sub>2</sub> reduced at 600 °C. Ru/TiO<sub>2</sub> showed higher CO methanation activity than Ru/Al<sub>2</sub>O<sub>3</sub> due to smaller Ru particle size. A close correlation was found between CO<sub>2</sub> methanation rate and perimeter length between Ru particle and support, which indicates that the interface was identified as the reaction sites of CO<sub>2</sub> methanation in CO and CO<sub>2</sub> coexisting atmosphere. CO<sub>2</sub> methanation over Ru/TiO<sub>2</sub> was suppressed in spite of long perimeter compared to Ru/Al<sub>2</sub>O<sub>3</sub>, stemming from the small amount of CO<sub>2</sub> adsorbed onto Ru/TiO<sub>2</sub>. Ru/TiO<sub>2</sub> catalyst exhibited wider temperature window for selective CO methanation than Ru/Al<sub>2</sub>O<sub>3</sub> catalyst.

In Chapter 3, selective CO methanation was investigated over Ru/TiO<sub>2</sub> prepared by a selective deposition method using NaOH and NH<sub>3</sub> aqueous solution as a pH adjuster. Control of pH by NH<sub>3</sub> solution resulted in small particle size of Ru (average 1.2 nm) and the formation of Na-free Ru/TiO<sub>2</sub>, 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/TiO<sub>2</sub>, Ru-Ni/TiO<sub>2</sub>, Ru-Co/TiO<sub>2</sub>, Ru-Fe/TiO<sub>2</sub>, Ru-La/TiO<sub>2</sub>, and Ru-K/TiO<sub>2</sub>, and examined the selectivity and activity. The addition of Co and La to Ru/TiO<sub>2</sub> 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/TiO<sub>2</sub> showed the widest temperature range for selective CO methanation in prepared bimetallic Ru-based catalysts. In order to shift the range of Ru-Ni/TiO<sub>2</sub> to lower temperature, I prepared the trimetallic catalyst Ru-Ni-La/TiO<sub>2</sub>. 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/TiO<sub>2</sub>. 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/TiO<sub>2</sub> and Ru-Ni-La/TiO<sub>2</sub>.

In Chapter 5, the removal of CO from reformat streams by selective CO methanation was investigated over TiO<sub>2</sub> 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/TiO<sub>2</sub> decreased the CO<sub>2</sub> conversion rate at 260 °C from 10 to 7.3 μmol min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. The use of Ru and Ni, thus, expands the temperature range of selective CO methanation. Transmission electron microscopy and temperature programmed reduction by H<sub>2</sub> confirmed that Ru species were in close proximity to Ni species on Ru-Ni/TiO<sub>2</sub>, indicating a decrease in direct contact between Ru and TiO<sub>2</sub>. Fourier transform infrared spectroscopy techniques revealed that the decomposition of the formate species, formed during CO<sub>2</sub> methanation, is slow over Ru-Ni/TiO<sub>2</sub>, in contrast to Ru/TiO<sub>2</sub>.

In Chapter 6, The effect of metal loading amounts on activity and selectivity of CO methanation over Ru/TiO<sub>2</sub>, Ni/TiO<sub>2</sub>, and Ru-Ni/TiO<sub>2</sub> was investigated. 0.1wt%Ru-10wt%Ni/TiO<sub>2</sub> was the suitable catalyst for selective CO methanation in prepared *x*wt%Ru-10wt%Ni/TiO<sub>2</sub> catalysts (*x* = 0.5, 0.2, and 0.1) due to sharp abatement in CO concentration and suppression of CH<sub>4</sub> production. With a decrease in Ru loading CO production via RWGS reaction was slow, meaning that 0.1wt%Ru-10wt%Ni/TiO<sub>2</sub> removes CO rapidly compared to 0.5wt%Ru-10wt%Ni/TiO<sub>2</sub>.

In Chapter 7, Selective CO methanation was carried out over 10wt%Ni/TiO<sub>2</sub> and 0.5wt%Ru-10wt%Ni/TiO<sub>2</sub>, 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 CO<sub>2</sub> methanation suppressed. Ru-Ni/TiO<sub>2</sub> exhibited the high activity of CO methanation compared to Ni/TiO<sub>2</sub> during the test. Furthermore, for more than 5500 h, Ru-Ni/TiO<sub>2</sub> maintained a wide temperature window for selective CO methanation (> 50 °C), where CO and CH<sub>4</sub> concentrations were < 0.05% and < 1%, respectively, at a high gas hourly space velocity of 10000 h<sup>-1</sup>. Over Ni/TiO<sub>2</sub> and Ru-Ni/TiO<sub>2</sub>, CO<sub>2</sub> methanation activity was initially enhanced, and then stabilized. The initial promotion of CO<sub>2</sub> methanation activity is possibly due to the reduction of NiO which remained unreduced after the prereduction by H<sub>2</sub> 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, CO<sub>2</sub> methanation will be suppressed dramatically.

## **2. CO<sub>2</sub> 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: CH<sub>4</sub>, NH<sub>3</sub>, 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 CH<sub>4</sub>, made from CO<sub>2</sub> 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 CH<sub>4</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> decomposition ( $\text{CO}_{2\text{ads}} \rightarrow \text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$ ) at less than 100 °C. The CO<sub>2</sub> reduction to CO is considered to be a rate-determining step of CO<sub>2</sub> 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 CH<sub>4</sub> selectivity. It is, therefore, important to enhance the reaction rate of RWGS reaction and CO methanation at low temperatures.

In Chapter 8, CO<sub>2</sub> methanation was performed over 10wt%Ni/CeO<sub>2</sub>, 10wt%Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 10wt%Ni/TiO<sub>2</sub>, and 10wt%Ni/MgO, and the effect of support materials on CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity was examined. Catalysts were prepared by a wet impregnation method, and characterized by BET, XRD, H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD. Ni/CeO<sub>2</sub> showed high CO<sub>2</sub> conversion especially at low temperatures compared to Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and the selectivity to CH<sub>4</sub> was very close to 1. The surface coverage by CO<sub>2</sub>-derived species on CeO<sub>2</sub> surface and the partial reduction of CeO<sub>2</sub> surface could result in the high CO<sub>2</sub> conversion over Ni/CeO<sub>2</sub>. In addition, superior CO methanation activity over Ni/CeO<sub>2</sub> led to the high CH<sub>4</sub> selectivity.

In Chapter 9, the effect of CeO<sub>2</sub> loading amount of Ru/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> on CO<sub>2</sub> methanation activity and CH<sub>4</sub> selectivity was studied. The CO<sub>2</sub> conversion rate was increased by adding CeO<sub>2</sub> to Ru/Al<sub>2</sub>O<sub>3</sub>, and the order of CO<sub>2</sub> conversion rate at 250 °C is Ru/30%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> > Ru/60%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> > Ru/CeO<sub>2</sub> > Ru/Al<sub>2</sub>O<sub>3</sub>. With a decrease in CeO<sub>2</sub> loading of Ru/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> from 98% to 30%, partial reduction of CeO<sub>2</sub> surface was promoted and the specific surface area was enlarged. Furthermore, it was observed using FTIR that the intermediates of CO<sub>2</sub> methanation, such as formate and carbonate species, reacted with H<sub>2</sub> faster over Ru/30%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Ru/CeO<sub>2</sub> than over Ru/Al<sub>2</sub>O<sub>3</sub>. These could result in the high CO<sub>2</sub> conversion rate over CeO<sub>2</sub>-containing catalysts. As for the selectivity to CH<sub>4</sub>, Ru/30%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> exhibited high CH<sub>4</sub> selectivity (> 0.995) compared with Ru/CeO<sub>2</sub> (0.986), due to prompt CO conversion into CH<sub>4</sub> over Ru/30%CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

In this thesis, new catalysts with high CO<sub>2</sub> methanation activity and selectivity were developed using CeO<sub>2</sub>. The catalysts showed the high initial performance. On the other hand, long-term stability of CeO<sub>2</sub>-containing catalysts should be enhanced. For example, CO<sub>2</sub> conversion over my Ni/CeO<sub>2</sub> at 350 °C was rapidly decreased from 80 to 40% in only 200 h. Thus the deactivation mechanism of CeO<sub>2</sub>-containing catalysts should be investigated. As one of the solutions, dispersing CeO<sub>2</sub> on the other metal oxides, such as zeolite and Al<sub>2</sub>O<sub>3</sub>, is expected to enhance stability compared to CeO<sub>2</sub> alone. The interaction between CeO<sub>2</sub> and metal oxides will prevent CeO<sub>2</sub> from sintering, leading to high stability of the catalysts. Furthermore, CeO<sub>2</sub>-based mixed oxides (Sm<sub>x</sub>Ce<sub>y</sub>O<sub>z</sub>, Gd<sub>x</sub>Ce<sub>y</sub>O<sub>z</sub>, etc.) are anticipated to become a promising candidate as support materials of CO<sub>2</sub> 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 CeO<sub>2</sub>-based mixed oxides show a high durability in CO<sub>2</sub> methanation.