

Preparation of Pt-CeO₂ nanoparticles using supercritical hydrothermal method for low-temperature chemical looping steam methane reforming

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1. Introduction

Methane, a significant component of natural gas or biomass, is an eco-friendly and non-toxic fossil fuel with abundant reserves, and is attracting much attention as a bridge energy resource between conventional fossil fuels and new type of sustainable energies. The traditional steam methane reforming (SMR) process to produce hydrogen or syngas requires high-temperature conditions due to a tremendous endothermic reaction for the reforming step ($\Delta H^\circ = 206.3$ kJ/mol). Although the SMR process is industrially used, a solution to energy efficiency and cost-related problems has always been needed considering long-term operation under a high-temperature and high-pressure conditions [1].

Chemical looping steam methane reforming (CL-SMR) [2] is a promising process that can answer several issues mentioned above. Oxygen carriers partially oxidize methane in a methane conversion step, and the used oxygen carriers are regenerated while releasing hydrogen in a water-splitting step. Thus, this concept has the potential of a very innovative process as it can induce the separation of hydrogen while achieving high conversion in low-temperature operating environments.

In this study, highly active Pt loaded CeO₂ oxygen carriers were developed to activate the CL-SMR process at low-temperatures. The Pt was successfully loaded into cubic CeO₂ as sub-nano size scale, and the low-temperature operation of CL-SMR was investigated using the Pt-CeO₂.

2. Materials and Methods

First, cubic CeO₂ nanoparticles were synthesized using the flow-type reactor via supercritical hydrothermal method [3]. The obtained particles were once calcined under air flow. After that, H₂PtCl₆ hydrate was mixed with the nanoparticles under aqueous solution at 60 °C using magnetic stirrer and sonication. The products were washed and centrifuged several times. Finally, Pt-loaded cubic CeO₂ was obtained. For the further characterization and CL-SMR process, the products were calcined at 300 °C for 12 h under air flow.

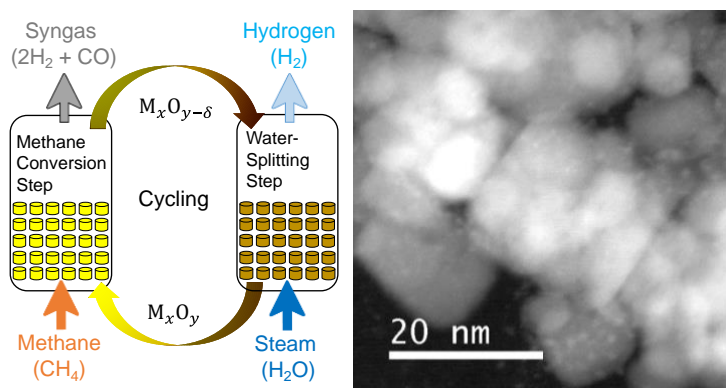


Figure 1 (left) The concept of CL-SMR using oxygen carriers; (right) Pt loaded cubic CeO₂ nanoparticles.

H₂-TPR and CL-SMR was performed using a fixed bed reactor (BELSORP CAT-II with BELMASS; Microtrac BEL Corp. 100 ml of Bubbler installed). For CL-SMR, all the samples were pretreated with oxygen or hydrogen for 30 min to control the oxidation state of oxygen carriers. Methane conversion was performed for 30 min while flowing 90% methane in Ar. After the reaction was completed, the mixture was sufficiently substituted with pure Ar for 40 min. Then, the saturated steam was made using a bubbler mounted on the equipment. The concentration of steam used was 11.8%. After reacting by adding steam for 30 min in a water-splitting step, the reaction was terminated by flowing Ar for another 40 min. The

discharged gas was sent to the micro gas chromatography (μ -GC, Agilent technology 490 micro GC, Ch.1: molsieve 5A PLOT, Ch.2: PolarPLOTQ module, TCD) through the moisture trap (Simple moisture remover HQ705, GL Science, Japan). The gas hourly space velocity (GHSV) was $1.63 \times 10^5 \text{ h}^{-1}$, and the weight hourly space velocity (WHSV) for CH_4 flow was $17.7 \text{ g} \cdot \text{g}^{-1} \cdot \text{CeO}_2 \cdot \text{h}^{-1}$ and for steam was $0.293 \text{ g} \cdot \text{g}^{-1} \cdot \text{CeO}_2 \cdot \text{h}^{-1}$, respectively.

3. Results and discussion

H_2 -TPR was performed as shown in Figure 2. The TPR profiles were obtained by increasing the temperature while flowing 10% of hydrogen. In the case of Pt- SiO_2 , almost no the hydrogen reduction peak was observed. This indicates that there is nearly no interaction between Pt and SiO_2 . In the case of cubic CeO_2 , a small peak was observed in the relatively low temperature region. This is a feature of the crystal facet-controlled CeO_2 [4]. Oxygen release ability is confirmed between 300–500 °C, but most oxygen is released around 800 °C. In contrast, Pt-cubic CeO_2 shows a completely different behavior. A peak that did not appear in the previous two samples appeared strongly around 250 °C. This indicates a strong interaction between Pt and cubic CeO_2 , that is, interface oxygen species [5], which have a very strong oxidizing activity.

Next, the possibility of CL-SMR process was evaluated using Pt-cubic CeO_2 . Figure 3 shows the results of methane-steam 10 cyclic operation under gas-rich condition. First, it was confirmed that hydrogen and CO were mainly generated in the methane step and high concentration of hydrogen was generated in the steam step. Second, as the cycle was repeated, the gas production was decreased, but reached a certain level, demonstrating the good feasibility of the low temperature CL-SMR. Although the gas production was lower than in the initial stage of the reaction, it was maintained at a sufficiently high level considering the amount of oxygen carriers introduced. In addition, since the ratio of hydrogen and CO is maintained close to 3:1, which shows good mass balance results, it can be inferred that the process was operated with little formation of carbon additives such as coke.

4. Conclusions

This study used the facet-controlled CeO_2 nanoparticles as oxygen carriers produced under the hydrothermal synthesis method. Pt was loaded to increase interaction potential between Pt and CeO_2 , and oxidation potential was greatly improved even at a relatively low temperature. In addition, high activity and stability at a relatively low temperature were confirmed by examining the material's performance through the oxidation potential test and the CL-SMR cyclic operation.

References

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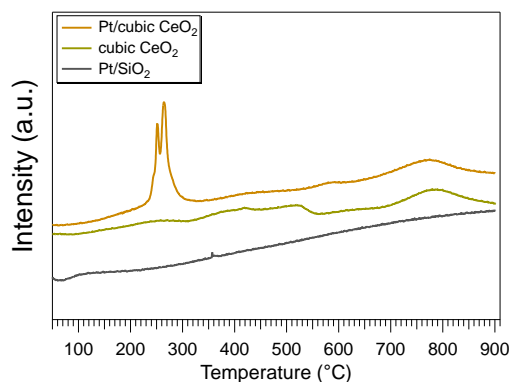


Figure 2 Comparison of oxidative potential between oxygen carriers using H_2 -TPR profiles.

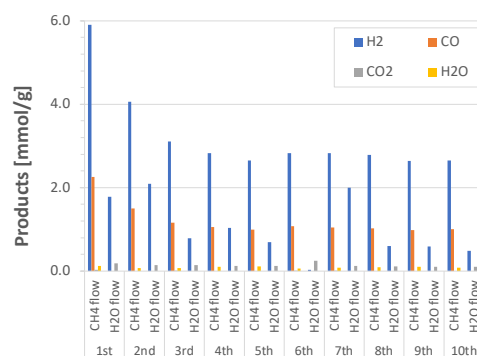


Figure 3 CH_4 - H_2O cyclic operation at 500 °C using Pt-cubic CeO_2 oxygen carrier.