**Highly Active and Stable Ni-Ce-ZrO₂ Catalysts in Combined H₂O and CO₂ Reforming of Methane for Gas to Liquids (GTL)**

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**Introduction**

Due to high oil price, gas to liquids (GTL) technology to produce synthetic oil from natural gas attracts significant research interest. GTL technology is composed of synthesis gas production, Fischer-Tropsch synthesis and product work-up. The synthesis gas preparation section is an important part of the entire GTL complex. Therefore, the design of the synthesis gas preparation unit is critical for the economics of a GTL project [1]. Combined steam and carbon dioxide reforming of methane (CSCRM) offers great advantage to adjust H₂/CO ratio in the product synthesis gas by changing the feed H₂O/CO₂/CH₄ ratio to meet the requirements of Fischer-Tropsch synthesis [2]. Commercially, supported Ni catalysts have been used in SRM because Ni is economical compared with noble metal based catalysts [3]. However, supported Ni catalysts easily deactivate due to carbon formation in carbon dioxide reforming of methane (CRM) as well as in CSCRM. Recently, Xu and co-workers reported that the Ni catalyst supported by small nanoparticles of ZrO₂ or MgO could be highly active and stable for CRM [2,4]. In addition, Roh et al. reported that nano-sized Ni-Ce-ZrO₂ catalyst could be active and stable in CRM [5]. Thus, it is an important topic to develop active and stable catalysts in CSCRM. In this study, co-precipitated Ni-Ce-ZrO₂ catalysts have been optimized in CSCRM to achieve a H₂/CO ratio of 2, which is suitable for Fischer-Tropsch synthesis.

**Materials and Methods**

15%Ni-Ce-ZrO₂ with various Ce/Zr ratios were prepared by a co-precipitation method. The detailed preparation procedure was described elsewhere [5]. The prepared catalysts were characterized by BET, XRD, H₂-chemisorption, SEM and TEM. Activity tests were carried out at 800 °C under atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The detailed reaction procedure was described elsewhere [6]. The feed (H₂O + CO₂)/CH₄ ratio was fixed at 1.2. A space velocity of 265,000 cm³ gas fed/g cat-h was used to screen the catalysts in this study. Prior to each catalytic measurement, the catalyst was reduced in 10% H₂/N₂ at 700 °C for 1 h. The reactant gas stream consisted of H₂O, CO₂, and CH₄. Water was fed using a syringe pump and was vaporized at 150 °C upstream of the reactor. The reformate was chilled, passed through a trap to condensate residual water, and then flowed to the on-line GC.

**Results and Discussion**

Co-precipitated Ni-Ce-ZrO₂ catalysts with various Ce/Zr ratios have been tested with H₂O/CO₂/CH₄ ratio of 0.8/0.4/1.0 because H₂/CO ratio of 2 has been achieved in this reaction condition. Figure 1 shows CH₄ conversion with time on stream over co-precipitated Ni-Ce-ZrO₂ catalysts. Both Ni-Ce₀.₆Zr₀.₄O₂ and Ni-CeO₂ catalysts exhibited the highest CH₄ conversion with stability. It is interesting to note that with increasing Ce/Zr ratio the stability of the catalyst becomes better. According to XRD patterns, three catalysts, Ni-CeO₂, Ni-Ce₀.₆Zr₀.₄O₂ and 15%Ni-Ce₀.₆Zr₀.₄O₂ show cubic phase, while 15%Ni-Ce₀.₄Zr₀.₆O₂ illustrates tetragonal phase. In the case of 15%Ni-Ce₀.₄Zr₀.₆O₂, the XRD pattern shows the transition state from cubic to tetragonal but close to cubic phase. It is concluded that CeO₂ plays an important role in giving high activity as well as stability in CSCRM. This is due to high oxygen storage capacity of CeO₂, which stores and releases reversibly active oxygen species depending on the reaction condition.

**Significance**

Ni/Ce-ZrO₂ catalysts with high Ce content can be a good candidate catalyst for CSCRM due to high oxygen storage capacity.

**Figure 1.** CH₄ conversion with time on stream over Ni-Ce-ZrO₂ catalysts (T=800°C, H₂O/CO₂/CH₄ ratio of 0.8/0.4/1.0).

**References**