

Oxygen vacancy enhanced Ni-CeO₂ catalysts by using cellulose assisted combustion synthesis for dry reforming of methane

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Highlights

- The catalysts prepared by cellulose combustion or normal impregnation method.
- The catalysts showed higher oxygen storage capacity than normal impregnated samples.
- The increased oxygen storage capacity influenced increasing the conversion rate of CH₄ and CO₂.
- It also had an effect on additional CO₂ utilization through the reverse water-gas shift reaction.

1. Introduction

Dry reforming of methane (DRM, $\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$) is catching the spotlight to prevent climate change, which is strongly induced by the emission of greenhouse gases such as CO₂ and CH₄. It is an attractive way in carbon capture and utilization (CCU) technology because it utilizes two main greenhouse gases, but it requires the development of catalyst which has strong sintering- and coke-resistance to ensure stable catalytic performance. On the other hand, the oxygen vacancy of the catalysts is a notable catalytic property that can address problems associated with catalyst deactivation by providing an anchoring effect for the active metal and mobile oxygen on the surface. Our group has conducted various studies to improve oxygen storage capacity by intentionally inducing oxygen defects in CeO₂.¹

This study is about enhancing the oxygen vacancy of catalysts using the cellulose combustion method. The specific goal is to increase the amount defect site in the CeO₂ lattice during the process of carbon source depriving oxygen during the crystallization step and the rapid synthesis process through combustion. For a quantitative analysis for oxygen defects on the catalysts, various characterizations including XAFS, H₂-CO₂ pulse reaction, XPS, Raman, TGA, TPO, XRD were conducted. In addition, the relationship between physicochemical properties of catalysts and catalytic performance was also studied.

2. Methods

The Ni-CeO₂ catalysts were prepared using a cellulose combustion method with different Ni loading. The precursors of Ni(NO₃)₂·6H₂O (Junsei, 97%), and Ce(NO₃)₃·6H₂O (Aldrich, 99%) were simultaneously dissolved in distilled water at room temperature. The Ni was loaded from 5 to 20 wt.%. The catalyst was synthesized by drying cellulose paper that absorbed the precursor solution at room temperature. And then the dried cellulose paper was combusted and calcined 700 °C for 6 h. The prepared catalysts were marked as x wt.% Ni CeO₂_CACS (x = 5, 10, 15, 20).

3. Results and discussion

The H₂-CO₂ pulse reaction was conducted to estimate oxygen storage capacity of the catalysts. The catalysts prepared by cellulose combustion method showed higher oxygen storage capacity than normal impregnated samples.^{2,3} It strongly suggests that the cellulose combustion method affects that their oxygen storage capacity. As a results of dry reforming of methane, among the prepared catalysts, the 15 wt.% Ni CeO₂_CACS catalyst showed the highest CH₄ and CO₂ conversion. This is possibly due to its higher oxygen storage capacity and the number of active sites.

Table 1. Oxygen storage capacity of catalysts

Sample	Oxygen storage capacity ($\mu\text{mol/g}$)	References
5 wt.% Ni CeO ₂ _CACS	851	Present work
10 wt.% Ni CeO ₂ _CACS	834	Present work
15 wt.% Ni CeO ₂ _CACS	892	Present work
20 wt.% Ni CeO ₂ _CACS	839	Present work
15 wt.% Ni/Ce-ZrO ₂	215	[2]
CeO ₂	357	[3]

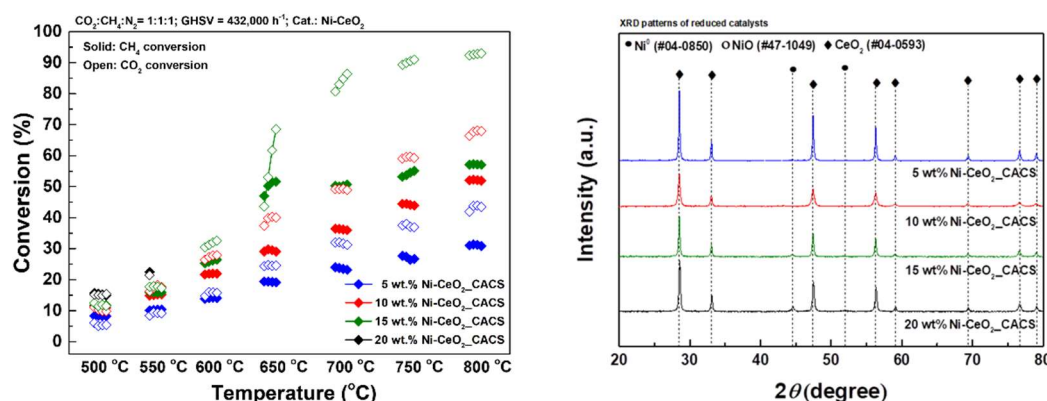


Figure 1. CH₄ and CO₂ conversion with time on stream over the catalysts (reaction conditions: T = 500 - 800 °C, GHSV = 432,000 h⁻¹) and XRD pattern of reduced samples.

4. Conclusions

The catalysts prepared by cellulose combustion method showed higher oxygen storage capacity than normal impregnated samples. The enhanced oxygen storage capacity affected Ni crystallite size. This induced increase of the number of Ni active site on the surface of the catalyst. In addition, the CO₂ conversion rate was much higher than CH₄ conversion rate. This phenomenon strongly suggests that reverse water-gas shift (RWGS) reaction was occurring. Consequently, the increased oxygen storage capacity not only influenced increasing the conversion rate, but also had an effect on additional CO₂ utilization through the RWGS reaction.

References

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Keywords

“Dry reforming of methane” “Oxygen vacancy” “Cellulose assisted combustion method” “Reverse water gas shift”.