九州大学 エネルギーウィーク 2021

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KYUSHU UNIVERSITY

QPIT Kyushu University Platform of Inter-/Transdisciplinary Energy Research

Synthesis of Flowerlike $Ce_{1-x}Zr_xO_2$ as Catalyst Support for Hydrogen Production from Biogas

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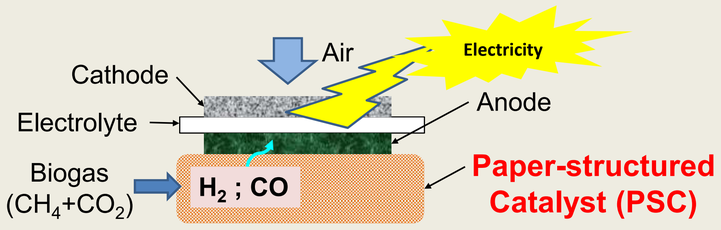
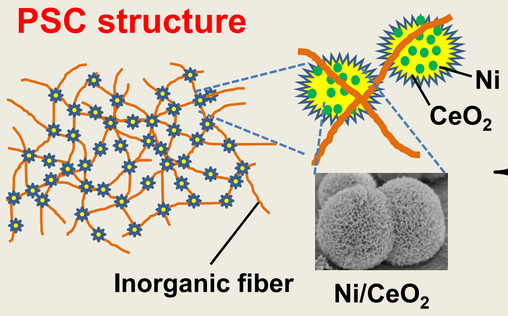
Subtitle: Ni-loaded ceria microspheres for biogas reforming

INTRODUCTION

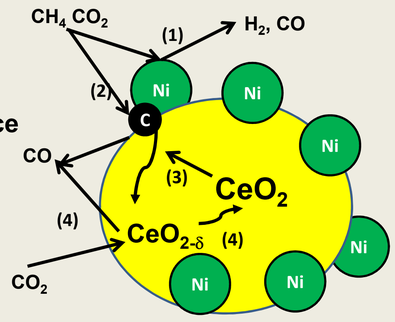
Our concept of direct-internal reforming (DIR)-SOFC



PSC structure



- Improve the catalytic performance
- Anti-carbon deposition
- Anti-sintering



Oxygen storage capacity (OSC) of Ceria

$$CeO_2 \underset{H_2O/CO_2}{\overset{H_2/CO}{\rightleftharpoons}} CeO_{2-\delta} + \delta/2\ O_2$$

(1) $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$

(2) $CH_4 \rightarrow 2H_2 + C$

(3) $CeO_2 + \delta C \rightarrow CeO_{2-\delta} + \delta CO$

(4) $CeO_{2-\delta} + \delta CO_2 \rightarrow CeO_2 + \delta CO$

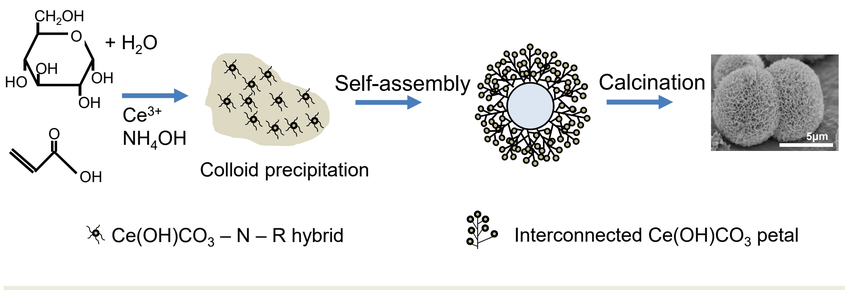
EXPERIMENTAL

Preparation of flowerlike-CeO_2 powder (Ce(F))

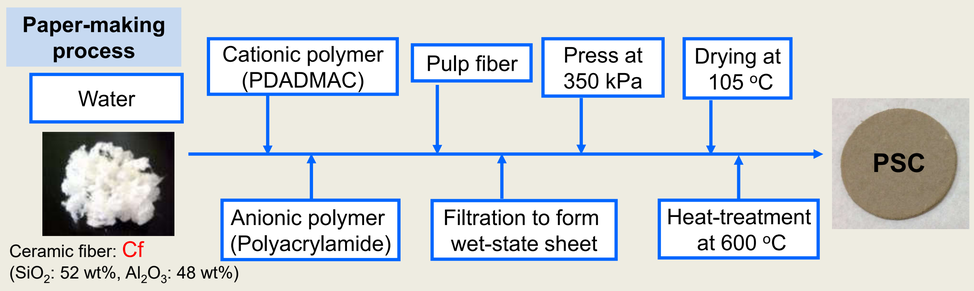
Ingredients in the Precursor Solution for Hydrothermal Synthesis Aiming at Producing Flowerlike-CeO_2 Powder (Ce(F)).

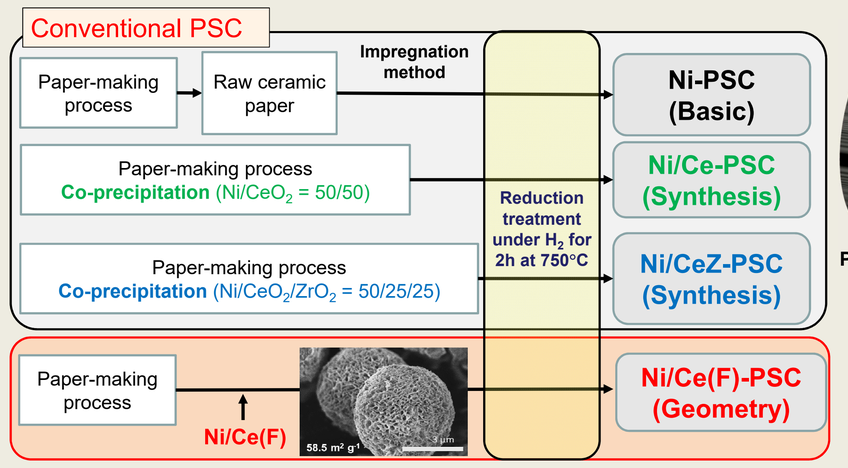
Sample	Glucose (mol)	Acrylic acid (mol)	25 wt% NH_4OH (mL)
a	0.0150	0.0225	4.4
b	0.0150	0.0225	5.5
c	0.0150	0.0225	6.6
d	0.0150	0.0225	7.7
e	0.0075	0.0225	6.6
f	0.0150	0.0150	6.6
g	0.0150	0.0300	6.6

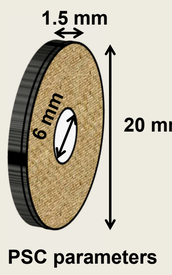
Formation of flowerlike ceria Ce(F)



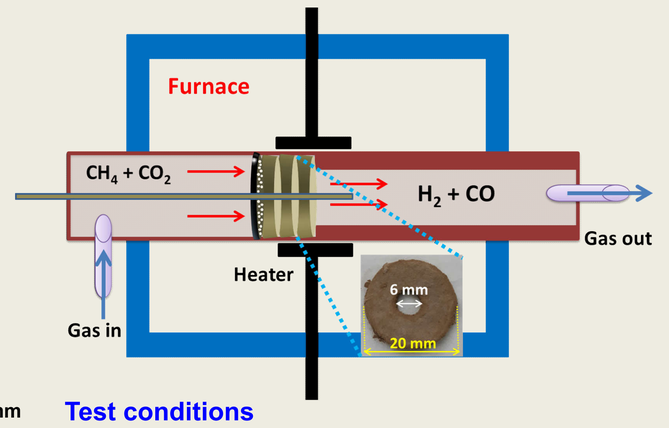
Preparation of paper-structured catalysts (PSCs)







Dry reforming (DRM) tests with PSCs



Test conditions

- Temperature: 750 °C
- Fuel composition: CH_4:CO_2 :N_2 = 1:1:1
- Total flow rate: 60 mL min^{-1}
- Gas hourly space velocity (GHSV): ~2500 h^{-1}

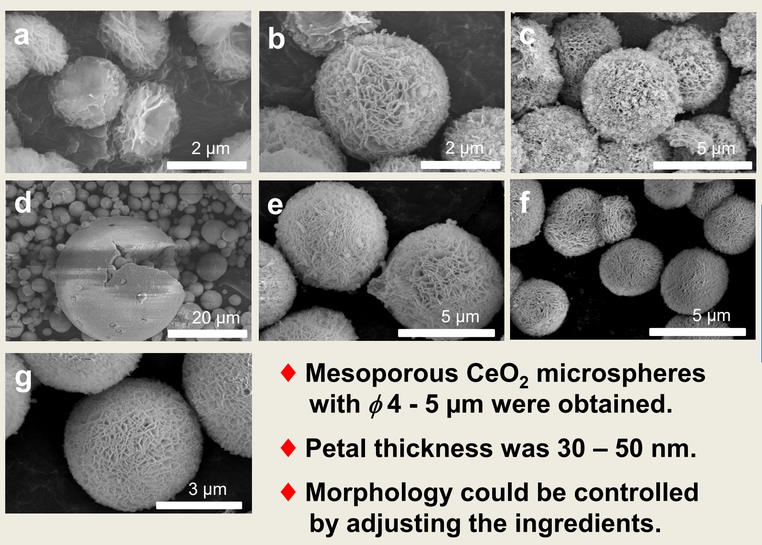
Reformate composition was analyzed every 0.5 h using gas chromatography (GC-20B; Shimadzu, Japan).

Methane conversion (%)

= [CH_4 convert]/ [CH_4 in] *100%

RESULTS AND DISCUSSION

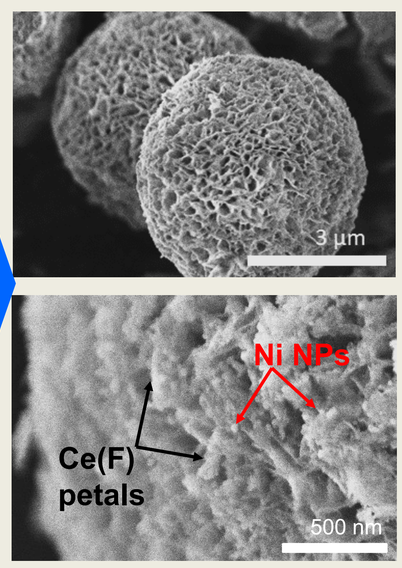
Morphologies of Ce(F)

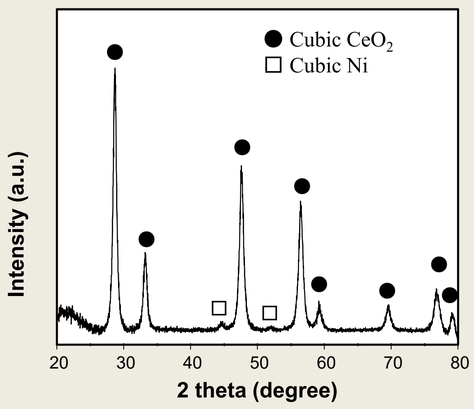


- Mesoporous CeO_2 microspheres with ϕ 4 - 5 μm were obtained.
- Petal thickness was 30 – 50 nm.
- Morphology could be controlled by adjusting the ingredients.

♦ Ce(F)g with the highest surface area: of 78.8 m^2 g^{-1} was the best.

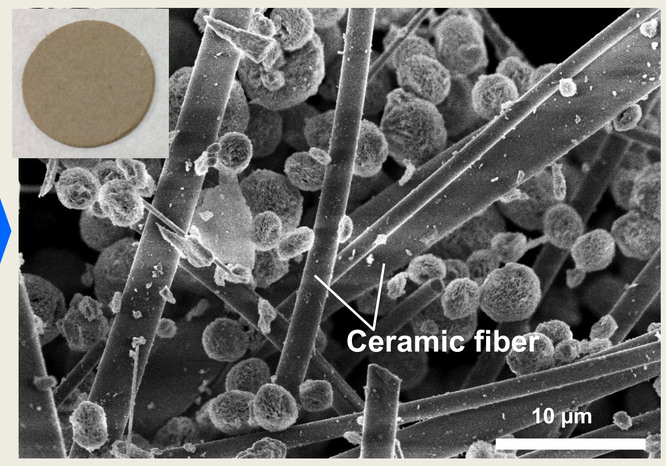
Ce(F)g after Ni loading





- Ni-loaded Ce(F) (Ni/Ce(F)g) was formed.
- Morphology was remained even after catalyst loading.
- Ni/Ce(F)g had the specific surface area of 58.5 m^2 g^{-1}.

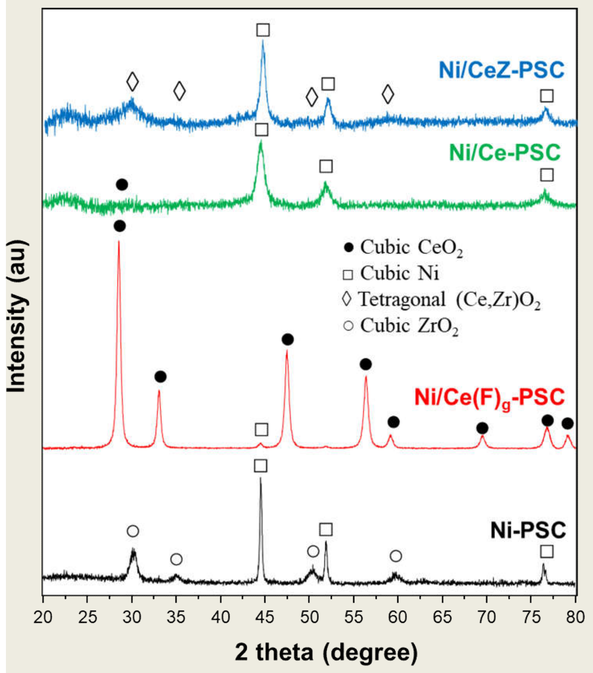
$Ni/Ce(F)_g$ in fiber network ($Ni/Ce(F)_g$ -PSC)



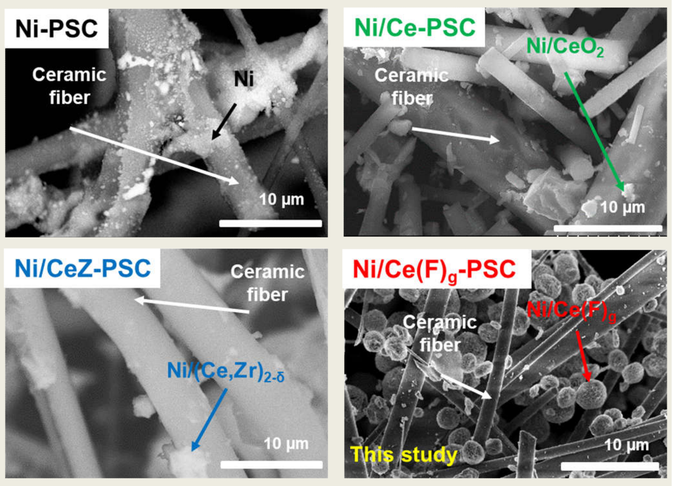
♦ $Ni/Ce(F)_g$ was formed into a catalyst-sheet for the application to DIR-SOFC.

Structure of prepared PSCs

XRD patterns after reduction



Dispersions of catalysts in the fiber network



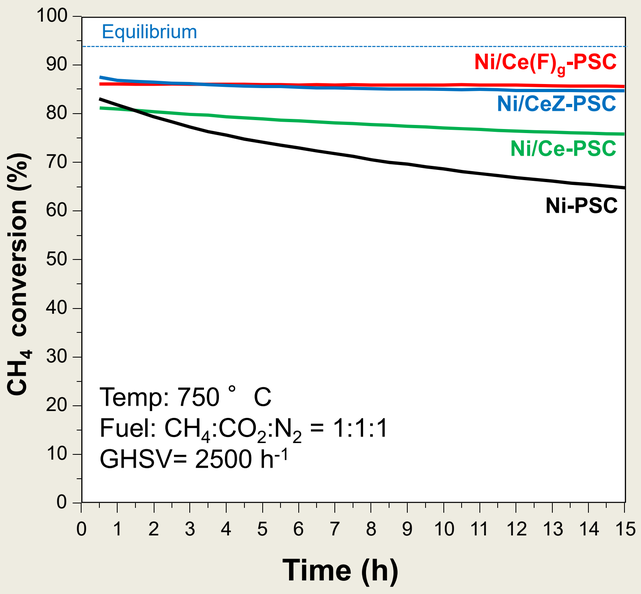
S_{BET}, Ni loading and Ni Crystallite Size (D_{Ni})

	S_{BET} (m^2 g^{-1})	Ni loading (wt%)	D_{Ni}* (nm)
Ni-PSC	5.8	12	58
$Ni/Ce(F)_g$-PSC	32	3	16.8
Ni/Ce-PSC	10.1	4.3	9.1
Ni/CeZ-PSC	24	6.1	13

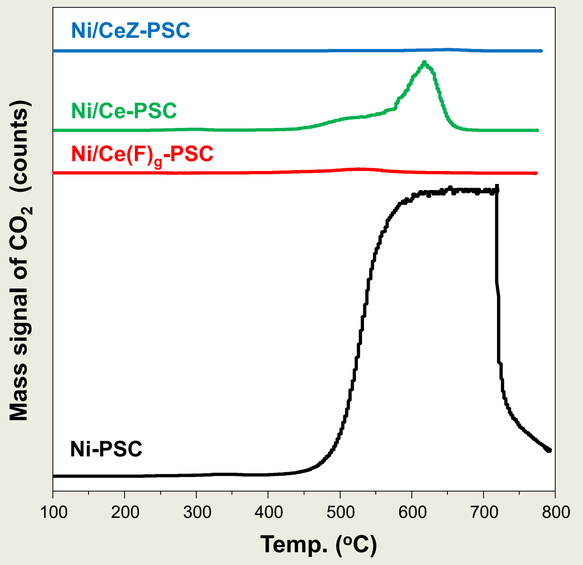
*estimated with Scherrer equation from XRD patterns

Dry reforming test

CH_4 conversion



TPO profiles after 15 h DRM test



Catalytic performance

Ni-PSC < Ni/Ce-PSC < Ni/CeZ-PSC ≈ $Ni/Ce(F)_g$-PSC

Coking tolerant!

SUMMARY

♦ Coking-tolerant paper-structured catalyst (PSC) for the dry reforming of methane (DRM) was studied.

♦ $Ni/Ce(F)_g$-PSC exhibited excellent catalytic performance comparable to the conventional best PSC (Ni-loaded $Ce_{0.4}Zr_{0.6}O_2$ (CeZ)-dispersed PSC prepared by co-precipitation (on paper synthesis)).

→ The flowerlike ceria-zirconia solid solution should be synthesized to further increase the catalytic performance.