# Cerium Oxide Promoted Nickel Nanoparticles Deposited on $Al_2O_3$ by Atomic Layer Deposition for Reforming of Methane with Carbon Dioxide

**Baitang Jin [1], Zeyu Shang [1], Shiguang Li [2], and Xinhua Liang [1,*]**

*[1] Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology*

*[2] Gas Technology Institute*

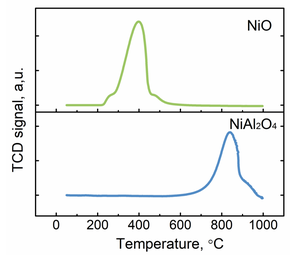
## Objectives

- To improve the catalytic activity of $Ni/Al_2O_3$ for dry reforming of methane (DRM).
- To decrease carbon formation on catalyst during DRM.

## Problems to Solve

- ALD-prepared $Ni/Al_2O_3$ contains a large amount of spinel $NiAl_2O_4$.
- Low reducibility of $NiAl_2O_4$–rich catalyst leads to low utilization of Ni.
- Carbon deposition originated from side reactions causes the deactivation.
- High temperature leads to the sintering of Ni nanoparticles during reaction.

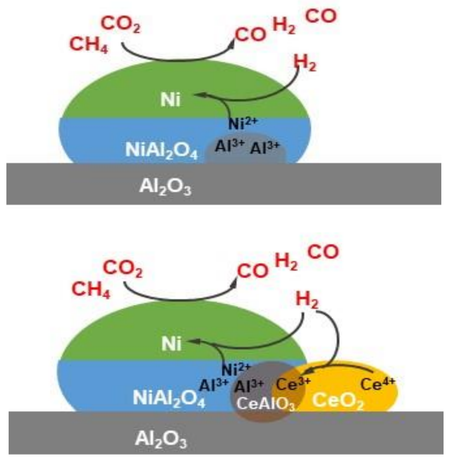
$\alpha$-$Al_2O_3$ support




$NiAl_2O_4$ with low reducibility

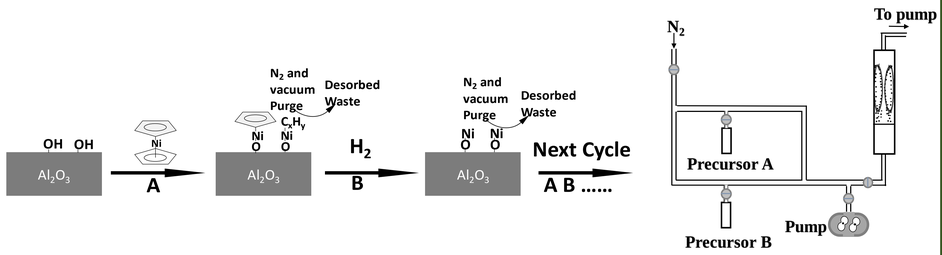
## Approach

- Catalysts were activated at 850 °C where the $NiAl_2O_4$ could be gradually reduced by $H_2$ to release Ni.
- $CeO_2$ promoter was applied to improve the reducibility of the ALD-prepared $Ni/Al_2O_3$ for better activity and to enhance $CO_2$ activity for less carbon deposition.



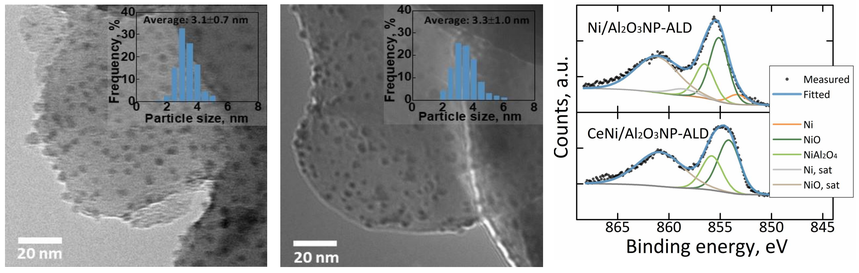

## Catalyst Preparation

### Ni-Atomic Layer Deposition (ALD)



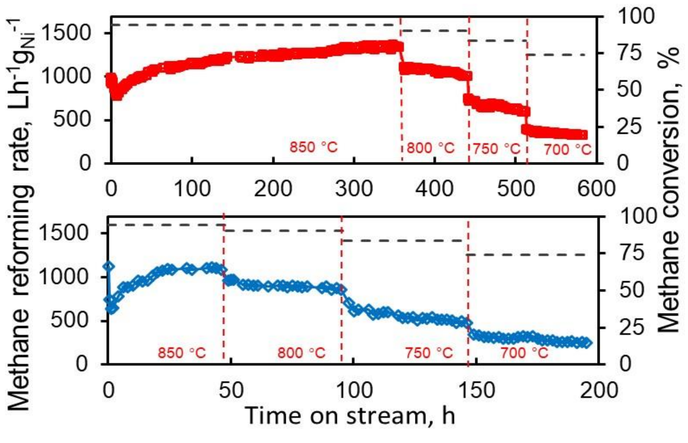

### $CeO_2$-Incipient Wetness (IW)

$Ni/Al_2O_3$ NPs catalysts → Soaked in $Ce(NO)_3$ solution → Dried → Calcined at 500 °C → $CeO_2$-$Ni/Al_2O_3$ NPs catalysts



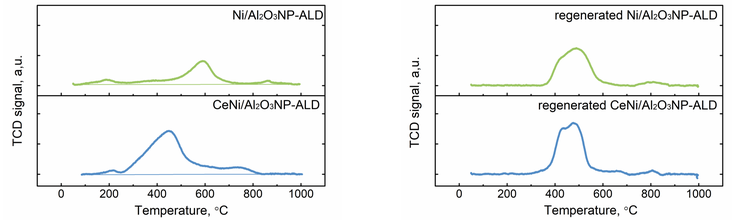

TEM and XPS of fresh $Ni/Al_2O_3$ and $CeO_2$-promoted $Ni/Al_2O_3$ catalysts

## Catalytic Performance



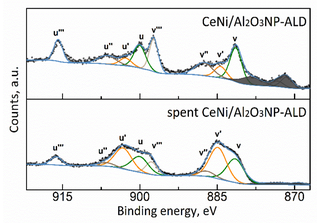

Catalytic performance of pristine and $CeO_2$-promoted nanoparticle supported catalysts

## Characterizations

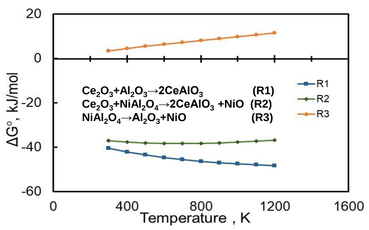



TPR of fresh catalysts and regenerated catalysts

- Gradual reduction of $NiAl_2O_4$ results in activation of catalyst.
- $CeO_2$ can improve the reducibility of $Ni/Al_2O_3$, especially for $NiAl_2O_4$.

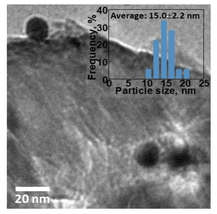



XPS Ce 3d of fresh and spent $CeO_2$-promoted $Ni/Al_2O_3$catalyst

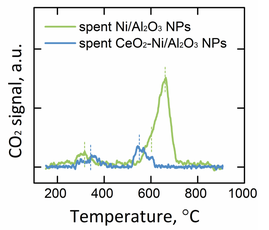



Gibbs free energy analysis of solid reaction during DRM

- Ce(IV) was reduced to Ce(III) during DRM.
- Formation of $CeAlO_3$ assisted the reduction of $NiAl_2O_4$.




TEM of spent $Ni/Al_2O_3$ and $CeO_2$ promoted $Ni/Al_2O_3$ catalysts




TPO of spent catalysts

- The introduced $CeO_2$ improved the reducibility of $NiAl_2O_4$ and prolonged the activation of the catalyst during reaction.

## Conclusions

- $CeO_2$ improved the reducibility of $NiAl_2O_4$ via formation of $CeAlO_3$ and released more Ni during DRM (longer activation time).
- $CeO_2$ enhanced the $CO_2$ activity in coke gasification and decreased carbon formation.
- $CeO_2$ stabilized Ni nanoparticles from sintering.

This work is supported by the U.S. Department of Energy (Contract Number DE-FE0029760).