

# Development of Nickel Catalysts using Spinel Type Oxides for Dry Reforming of Methane

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In this study, dry reforming of methane (DRM),  $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ , has been focused on as heat recovery from the exhaust of solid oxide fuel cells (SOFCs). This reaction is expected to simplify the fuel processing in the SOFC system because it can utilize heat and  $\text{CO}_2$  from the fuel cell stack and proceed without the presence of water vapor in high concentrations, which can remove a steam generator in the system. Nickel catalysts have been widely accepted as cost-effective and active catalysts for DRM reaction, but, when compared with steam reforming of methane, the DRM reaction is vulnerable to carbon deposition on nickel which leads to deactivation of the catalyst. To overcome this shortcoming, number of support materials have been investigated. It is known that basicity of support materials as well as a redox cycle of support materials can suppress carbon deposition efficiently.<sup>1</sup> Magnesium aluminate,  $\text{MgAl}_2\text{O}_4$  has been utilized as a basic support for above reason. Additionally,  $\text{MgAl}_2\text{O}_4$ , which is classified as spinel-type oxides, has been adapted as a support of Ni catalyst for dry reforming because of its high surface area and thermal stability.<sup>2,3</sup> However, enhancement of activity and durability are still desired. In this research,  $\text{MgAl}_2\text{O}_4$  substituted with nickel in the A site ( $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ ) is prepared, and their activity and durability in DRM reaction were tested. Fig. 1 summarizes  $\text{CH}_4$  conversion over the Ni catalysts prepared via different methods, namely, impregnation (Sup), Pechini method (Spi\_pec), and coprecipitation (Spi\_cop). The order of the activity is Spi\_pec > Sup > Spi\_cop. When the reaction temperature was 800°C, the difference in the activity was small, but the difference was expanded as the temperature was decreased. The Spi\_pec catalyst maintained its activity at low

temperatures. Next, durability tests at a constant temperature were conducted for the Spi\_pec catalyst. It was found that the Spi\_pec catalyst exhibited excellent activity for DRM reaction and stability even under severe condition where carbon deposition is thermodynamically expected. In temperature programmed oxidation analysis of the spent catalysts, a quite small amount of  $\text{CO}_2$  was detected, which indicates that a slight amount of carbon was deposited on the catalyst during the reaction. Consequently, it can be considered that the carbonaceous species as intermediate species were promptly removed from the catalyst surface during the DRM reaction.

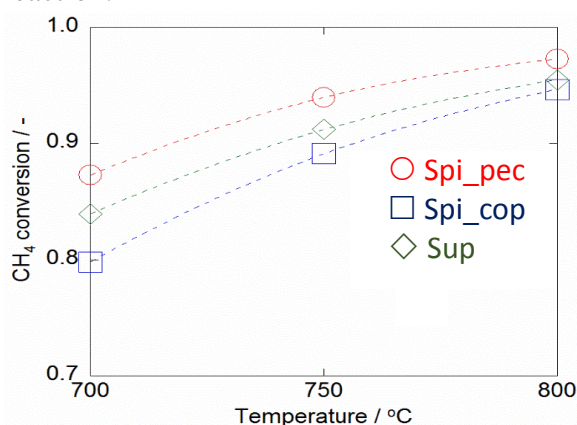


Fig. 1  $\text{CH}_4$  conversion in DRM reaction.

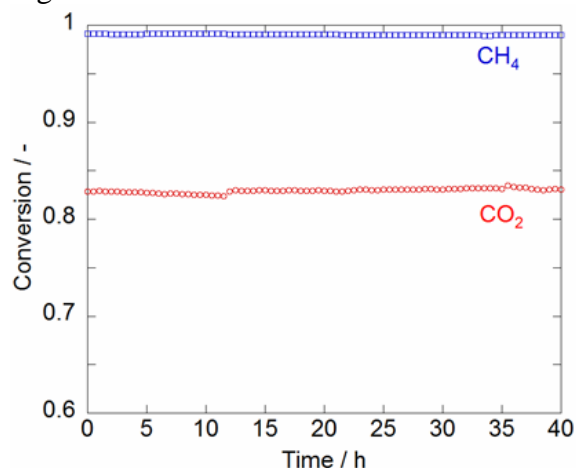


Fig. 2 Durability test in DRM reaction ( $\text{CH}_4/\text{CO}_2/\text{H}_2\text{O} = 1/1.34/0.9$ )

## REFERENCES

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