

Zr doped Ni/CeO₂ prepared by Flame spray pyrolysis for CO₂ methanation

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1. Introduction

Utilization of CO₂ by converting it into CH₄ is sought because it reduces CO₂ emission to the environment and stores H₂ produced by renewable energies. So far, for this reaction, Ru supported on CeO₂ is one of the most active catalyst but its utilization is limited due to the cost of Ru. Alternatively, Ni has attracted the interest but it suffers from the low activity at low temperature (< 250 °C) compared to Ru catalysts. To address the issue, high Ni loading with keeping the size small is promising approach for maximizing the Ni surface area. Here, we successfully prepared highly-loaded NiO (60 wt% as Ni) on CeO₂ nanoparticles by flame spray pyrolysis (FSP). Furthermore, the effect of Zr doping to the Ni/CeO₂ catalyst for CO₂ methanation was investigated.

2. Experimental

Ni (60wt%) supported on Ce_{1-x}Zr_xO₂ (x = 0 and 0.1) was prepared by an FSP reactor [1]. Appropriate amount of Ni (II) acetate tetrahydrate (Wako, purity > 98.0%), Zr 2-ethylhexanoate in mineral spirits (Wako, 11.7-12.3% as Zr) and Ce (III) 2-ethylhexanoate, 49% in 2-ethylhexanoic acid (Alfa Aesar, Ce: 12%) were mixed with a mixture (1: 1) of 2-ethylhexanoic acid (Sigma-Aldrich, purity > 99%): methanol (Wako, Reagent Grade) to be the total metal concentration (Ni + Zr + Ce) of 0.2 M. The precursor solution was fed to the two-fluid spray nozzle at 3 mL min⁻¹, dispersed to a fine spray by 5 L_{STP} min⁻¹ of O₂ dispersant (technical grade). The spray was evaporated and combusted by a premixed CH₄/O₂ plot flame (1.5 L_{STP} min⁻¹/3.2 L_{STP} min⁻¹) to form particles. The particles were collected on a glass-fiber filter by a vacuum pump (Busch SV1040C). Also, 20 and 60 wt% of Ni was deposited on FSP-made pure CeO₂ by an impregnation method. Before the characterization and activity tests, all the catalysts were reduced in 5% H₂-Ar at 500 °C for 1 h.

Catalytic activity was evaluated using a fixed bed reactor. The catalyst (100 mg) and SiC powder (400 mg) were filled into a quartz tube (inner/outer diameters of 6/8 mm). The catalyst was reduced at 500 °C for 1 h in 5% H₂-Ar (100 mL_{STP} min⁻¹), and subsequently, a reactant gas (CO₂/H₂/N₂ = 1/4/1) was fed to the catalyst at 60 mL_{STP} min⁻¹. The composition of the product was measured by a gas chromatograph equipped with a thermal conductivity detector.

3. Results and discussion

PXRD pattern of all the catalysts shows the peaks of fluorite CeO₂ at 28° and 33°. In the absence of Zr, the peak positions were identical while the Zr doping

shifts the peaks to the higher diffraction angle. Additionally, the peaks of monoclinic and tetragonal ZrO₂ were not detected. These facts indicate the preferable Zr doping to the CeO₂ lattice. EDX mapping (not shown) exhibited the size of Ni in FSP-made 60Ni/CeO₂ and 60Ni/Ce_{0.9}Zr_{0.1}O₂ was small (10-20 nm), despite the high Ni content (60 wt%).

Figure 2 shows the activity of FSP-made and wet-made catalysts for CO₂ methanation. The conversion of FSP-made 60Ni/CeO₂ was higher than that of wet-made ones. Notably, the Zr doing by FSP significantly enhanced the catalytic activity. In addition, by-product (CO) was not detected for all the tests. In conclusion, highly active and selective catalyst was developed by simultaneously achieving high Ni content (60wt%), small Ni size (10-20 nm) and Zr doping to CeO₂ by FSP.

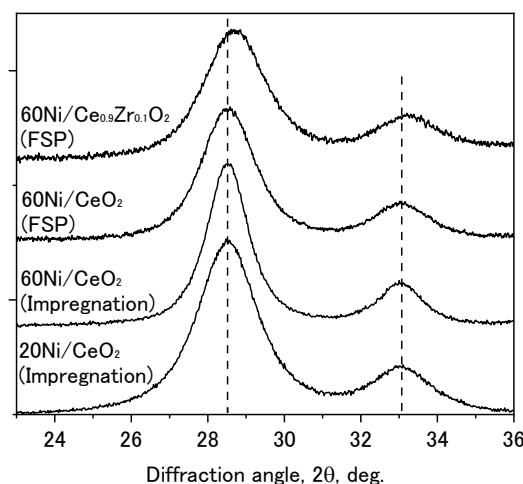


Fig. 1 PXRD patterns of FSP-made Ni/Ce_{1-x}Zr_xO₂ and wet-made Ni/CeO₂ particles

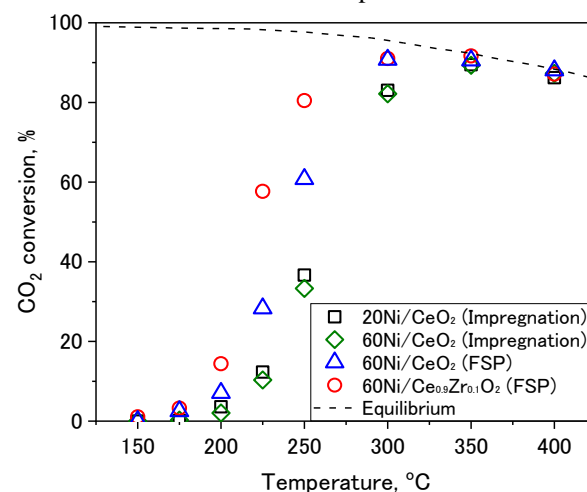


Fig. 2 Catalytic activity of FSP-made and wet-made catalysts for CO₂ methanation.

References

1. Fujiwara, K.; Tada, S.; Homma, T.; Sasaki, H.; Nishijima, M.; Kikuchi, R., *AIChE J.* **2019**, 65, e16717.