

Synthetic and Kinetic Study of Ni/ZrO₂-coated Wires for the Electrified Steam Reforming of Methane

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Highlights

- Successfully coated Ni-ZrO₂ onto highly curved FeCrAl heating elements
- Uniform Ni distribution and high thermal stability were achieved on coated wires
- CO₂ inhibition is quantified and analyzed
- Reaction scheme involving hydroxyl and carboxyl intermediates proposed and verified

Introduction:

Hydrogen production methods in commercial use today include steam methane reforming, partial oxidation, and auto-thermal reforming, with steam methane reforming (SMR) technology contributing to 95% of overall global hydrogen production. Current SMR technology is highly carbon-intensive, and results in 9.7 kg of CO₂ emissions per kg of H₂ produced. A potential solution that can help mitigate CO₂ emissions is the use of electrically/resistively heated reactors for replacing conventional SMR reactors with compact, modular reactors that can allow for decarbonization of H₂ production. Specifically, parallel wire configurations enable uniform current distribution and high thermal efficiencies. [1]

The catalytic structure developed must be thermally stable with sufficient activity under joule heating conditions, especially during fast start-up and shut-down procedures. Challenges in synthesizing an efficient catalyst coated heating element include preparation of a homogenous catalyst slurry (without phase separation) with suitable viscosity for deposition, strong adhesion with the heating element, and avoiding the agglomeration of active metal for efficient catalyst activity. In the current work, we overcome these challenges to successfully synthesize FeCrAl-coated wire catalysts by optimizing pH, slurry viscosity, and ballmilling time for Ni-ZrO₂ catalysts, and the addition of binders in the case of Ni-Al₂O₃. Ni-ZrO₂ exhibited uniform distribution of active nickel and good hydrothermal stability.

However, intrinsic kinetics for steam methane reforming have been mainly reported on traditional catalysts like Ni-MgAl₂O₄ and Ni-Al₂O₃, but not on Ni-ZrO₂ catalysts that seem to be more amenable for electrification applications. For instance, Wismann et al. use 'k_{as}' – a single kinetic parameter from a study by Xu and Froment's on Ni-MgAl₂O₄, despite the fact that they use a Ni-ZrO₂ catalyst. [2] We address herein this gap in the literature and elucidate the effect of this change in support identity on SMR mechanism and kinetics. Our results point to crucial differences versus conventional Ni-Al₂O₃ catalysts that are necessary to account for in order to accurately model and scale up electrified reactors for SMR applications.

Methods:

The first step in the coating process was thermal pre-treatment (i.e. calcination) of FeCrAl wires (1mm) for 16 hours in a muffle furnace under an air flow of 0.8 lit/min at 900°C using a ramp rate of 2.7 °C/min. The calcined FeCrAl wires were dip-coated into the prepared Ni-ZrO₂ slurry, and the residual liquid blown off using compressed air. The dip-coated wires were then dried in oven at 100°C for an hour, followed by calcination at 500°C for 4 hours. Scanning electron microscopy (SEM) images of coated FeCrAl wires were measured on a JEOL JSM 6400 scanning electron microscope at an acceleration voltage of 20 kV and surface elemental compositions with EDAX spectrometer attached to the SEM. 10 wt% Ni/ZrO₂ coated catalyst was tested in a fixed bed continuous flow reactor operated at atmospheric pressure and at 500-600°C. Pre-reduction in a stream of 57 vol% H₂ in N₂ for 90min through catalyst bed at 500 °C was carried out prior to reaction runs. The effluent was monitored using an online Gas chromatograph equipped with an FID. To take the deactivation rate into account, prior to each reaction condition, reference condition is carried out to assess the decrease in number of active sites and accordingly data points are corrected by dividing with fraction of active sites available.

Results and Discussion:

SEM images of the Ni-ZrO₂ coated wire cross section (**Figure 1-a**) evidence a relatively uniform coating of thickness between 8-12 μm on the wire surface, with minimal to no exposure of the bare wire surface. The uniformity of the coating and the distribution of nickel were further assessed using SEM-EDX mapping (**Figure 1-b**). A highly uniform distribution of nickel was obtained, and the weight % of nickel was found to be 12.7% -- close to the target value (15 wt%). Ball milling and pH adjustment of Ni-ZrO₂ catalyst slurry in the range between 3.5 and 4 helped tune the zeta potential of the slurry, resulting in favorable washcoat adhesion and uniformity. Ni-Al₂O₃ coated wires, on the other hand, exhibited significantly less uniform 'Ni' dispersion, suggesting either agglomeration of nickel within the alumina particles, or a non-uniform distribution of the washcoat. A possible reason for this could be the higher viscosity of the catalyst slurry resulting from the addition of binders for the case of Ni/Al₂O₃, but not Ni/ZrO₂. (**Figure 1c**)

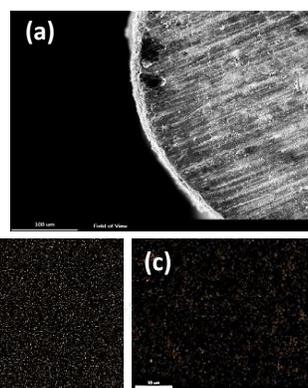


Figure 1: (a) SEM image of cross-section of Ni-ZrO₂ coated FeCrAl wire (b) SEM-EDX Map of Ni particles on Ni-ZrO₂ and (c) Ni-Al₂O₃ coats.

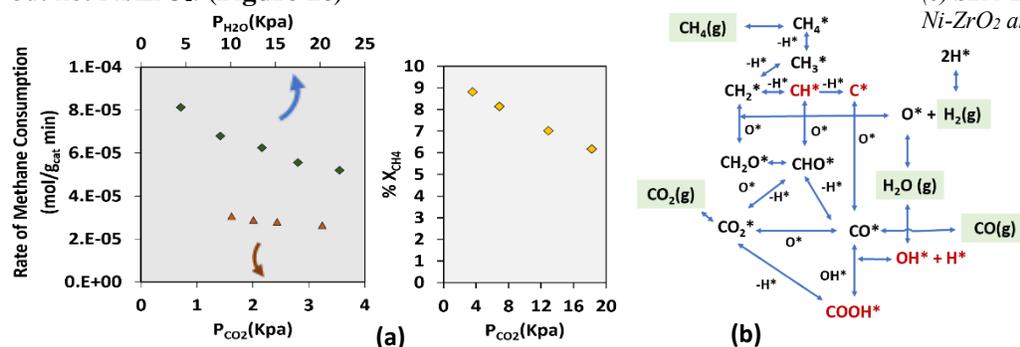


Figure 2: (a) Rates of methane consumption in dry and steam reforming reactions(left); Effect of carbon dioxide concentration on methane conversion(right) (b) Proposed SMR reaction scheme

In the presence of steam, surface hydroxyl species form on Ni/ZrO₂ through the interaction of water with the ZrO₂ support, unlike the case of Ni/Al₂O₃ catalysts.[3] CO₂ can be formed through the oxidation of CO* or via decomposition of COOH* species formed from hydroxyl species. **Figure 2-a(left)** compares steam and dry reforming rates on Ni/ZrO₂. Despite the fact that the partial pressure range of CO₂ is lower than that of steam, methane consumption rates are of the same order of magnitude, suggesting a considerable influence of CO₂ concentration during Ni/ZrO₂-mediated SMR. Large coverages of COOH* or CO* species also explain the negative effect of CO₂ feed concentration on methane conversion (**Figure 2-a(right)**) and are consistent with the mechanistic scheme proposed in our work involving hydroxyls and carboxyl-mediated pathways (**Figure 2-b**). A detailed kinetic model that accounts for all these steps and explains the entirety of the differential and integral SMR kinetic data is presented.

Conclusions:

Ni-ZrO₂ catalysts exhibit better adhesion and uniformity compared to conventional catalysts when coated onto curved substrates for joule heating applications. Kinetic analysis of Ni-ZrO₂ coated SMR catalysts reveals significant CO₂ inhibition and dry reforming under SMR conditions, both of which can be quantitatively analyzed by considering hydroxyl and carboxyl formation pathways. These results point to differences between ZrO₂ and Al₂O₃ supports that are critical to consider for electrified SMR applications.

References

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