



# Development of catalysts for hydrogen production through the integration of steam reforming of methane and high temperature water gas shift



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## ABSTRACT

There is great concern about the increasing demand for energy with respect to carbon emissions, but hydrogen (H<sub>2</sub>), a clean fuel, could help alleviate this concern. The replacement of fossil fuels with H<sub>2</sub> is cost prohibitive, but integration of SRM (steam reforming of methane) and WGS (water gas shift) could greatly decrease production costs. A composite catalyst of nickel, cerium, zirconium, and zinc was designed to provide activity in both the SRM and WGS reactions. The catalysts were characterized by a variety of techniques including BET (Brunauer Emmett Teller), TEM (transmission electron microscopy), SEM (scanning electron microscopy), TGA (thermogravimetric analysis), and XRD (X-ray diffraction). It was found that the addition of zinc decreased the surface area, and therefore activity of the SRM reaction, although it increased WGS activity as observed by improved carbon dioxide selectivity and H<sub>2</sub> production. Zinc also increased resistance to carbon deposition. Additionally, aging of precipitates during catalyst synthesis improved stability. A Ce/Zr/Zn catalyst doped with 10% Ni and aged for 2 h was found to have a final conversion of nearly 20% at 650 °C, and high CO<sub>2</sub> selectivity around 55%. This catalyst is an important step in the emerging field of low temperature SRM, a field that could lead to a reduction in carbon emissions.

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## 1. Introduction

Hydrogen (H<sub>2</sub>) is becoming an important clean fuel, and due to the increasing concerns over carbon emissions [1–4] research focused on its production has also increased [5–7]. Until sustainable renewable methods are developed, providing a more viable, efficient, and reliable hydrogen product, SRM (steam reforming of methane) and WGS (water gas shift) reactions based on fossil fuels will remain the major H<sub>2</sub> production technology [8–11]. These reactions are important for an emerging hydrogen economy and the implementation and distribution of hydrogen to consumers. In typical hydrogen production, the first step is SRM performed in a high temperature reactor (~1000 °C), where methane (CH<sub>4</sub>) and steam are used to produce H<sub>2</sub> and carbon monoxide (CO), a mixture called syngas [12]. Syngas is valuable as a feedstock for

Fischer–Tropsch synthesis and the production of many chemicals including ammonia and methanol [13,14]. The SRM reaction [15] is shown as R1.



While many feedstocks can be used for reforming, methane is preferred for hydrogen production as it has high hydrogen to carbon ratio and lower byproduct formation compared to other starting materials.

In separate reactors, the subsequent WGS steps take place during which CO and steam are converted to produce additional hydrogen and CO<sub>2</sub>, as shown as R2. This WGS step is used to increase the H<sub>2</sub> to CO ratio for the production of hydrogen [16].



The complete conversion of CO to CO<sub>2</sub> at high temperatures is impossible without product removal due to equilibrium constraints [17]. This necessitates that the WGS reaction be done in two reactors, a HTSR (high temperature shift reactor) and a LTSR (low

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temperature shift reactor). The HTSR converts CO equivalent to the equilibrium, followed by the LTSR which often converts the remaining CO [18]. Due to the use of syngas in the aforementioned industries, the formation of CO<sub>2</sub> in steam reforming has been selected against [19]. However, for the production of hydrogen, this should be encouraged to allow for smaller WGS reactors thereby lowering the overall cost.

In an effort to lower hydrogen production costs, integration of SRM and WGS using a composite catalyst is an attractive choice. When both SRM and WGS proceed simultaneously, the overall reaction becomes R3.



Reaction conditions for the integrated reactor need to satisfy the requirements for both SRM and WGS. At higher pressures SRM is highly suppressed, but conversion linearly increases with temperature [20]. Traditional SRM temperatures would be too high to allow for more than a small conversion of CO through WGS, though new catalysts capable of low temperature SRM have been found [21,22]. Under these low temperature conditions, conversion of CO to CO<sub>2</sub> through WGS would also be possible, thus a composite catalyst for both SRM and WGS with these characteristics could be used for hydrogen production. If high CO conversion could be achieved in the integrated reactor, then the use of a single downstream low temperature WGS reactor could become a viable option. This would dramatically decrease the cost of the production of hydrogen from fossil fuels. The combination of WGS and SRM has been attempted [22–27], although no catalyst has been found with high activity for both reactions, high stability, efficient operation at lower temperatures, and a low steam to carbon ratio (S/C).

Ce, Zr, Zn, and Ni were the four elements chosen to compose the catalyst for this work. Ce was chosen as it shows promise in many applications as a catalyst support and promoter [14], partially attributed to its high OSC (oxygen storage capacity) which is integral to the SRM reaction [28]. Zr was chosen as it increases the OSC of Ce supports [28] and has been shown to increase stability of Ni catalysts [29]. Zn has a high propensity to increase the CO<sub>2</sub> selectivity, and Ni is used as an inexpensive alternative to noble metals since it has fair activity for both reactions. All four elements have been proven to have activity in both SRM and WGS [30]. Due to this crossover in activity, a composite catalyst including these four elements was designed to convert a large percentage of CH<sub>4</sub> and to have high selectivity towards CO<sub>2</sub>. Ni is susceptible to carbon deposition [31,32], which is often one of the largest causes of deactivation in both SRM and WGS catalysis. It has been shown that nickel crystal size greatly effects carbon deposition with smaller crystals being more resistant [33]. Due to nickel's affinity for coking, the desired catalyst must also reduce the activity in two coking reactions, CO disproportionation and CH<sub>4</sub> decomposition, shown as R4 and R5 respectively [34].



The catalysts evaluated in this work are prepared with Ce:Zr at a 4 to 1 ratio as ratios in the range of three to four times the Ce loading compared to Zr have been shown to have higher activity for SRM; however this ratio is not optimized for this reaction system [28,35,36]. Zn is loaded between 0 and 40 wt% of the total Ce/Zr mixture to increase the WGS activity. Finally, nickel is doped as 5, 10 or 15 wt% of the metal, and while the best methane reforming is found on Ni/Ce/Zr catalysts with 15% Ni, higher CO<sub>2</sub> production is found at lower nickel concentrations [37]. This research was designed to progress the field of integrated SRM and WGS, and the

development of new catalysts is the most important step towards the realization of this goal.

## 2. Experiments

### 2.1. Catalyst preparation

A series of catalysts were prepared by co-precipitation in predetermined ratios of zirconium (IV) oxynitrate hydrate (99%, Sigma–Aldrich), zinc nitrate hexahydrate (98%, Sigma–Aldrich), and ammonium cerium (IV) nitrate, (99%, Fluka). For co-precipitation of the mixed nitrates, 400 ml of deionized (DI) water was stirred at 600 RPM and heated to 60 °C where it was kept until the nitrates dissolved. The pH was then raised to 9.0 using liquid ammonium hydroxide (28.97%, Fisher Scientific), to create the desired precipitate. After filtering and washing with DI water to remove excess ions, the resulting precipitate was allowed to dry overnight and subsequently calcined at 500 °C in dry air for 1 h. The catalyst was then sieved to obtain particles no larger than 125 μm in diameter (sieve No. 120). Nickel (II) nitrate (99%, Sigma–Aldrich) was deposited by incipient wetness impregnation at 5, 10, or 15 wt% of the total metal content, followed by additional drying and 1 h calcination in dry air at 500 °C. All catalysts were prepared with the desirable ratio of 4 to 1 for Ce to Zr. Due to this unchanging ratio, the catalysts will be denoted only by their Zn and Ni content to delineate between them. For example, the catalyst containing no Zn, precipitated with 80% Ce, 20% Zr, and 0% Zn, and doped with 15 wt% Ni is denoted as 0Zn15Ni. The catalyst 20Zn10Ni was used to investigate the effect of precipitate aging for times of 0, 1, and 2 h. Aged catalysts are prepared using precipitation conditions previously described with the addition of aging in the mother liquor at 60 °C and a pH of 9.0 for the desired time prior to filtering and washing. Aged catalysts are prefixed with 1A or 2A to denote an aging time of one or two h, respectively. Calculated weight percentages for all catalysts are shown in Table 1.

### 2.2. Catalyst characterization

Elemental analysis was performed with a PerkinElmer ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) to

**Table 1**  
Calculated compositions of catalysts in weight percentage.

Catalyst	Ce (wt%)	Zr (wt%)	Zn (wt%)	Ni (wt%)
0Zn0Ni	80	20	0	0
10Zn0Ni	72.7	18.2	9.1	0
20Zn0Ni	66.7	16.7	16.7	0
30Zn0Ni	61.5	15.4	23.1	0
40Zn0Ni	57.1	14.3	28.6	0
0Zn5Ni	76.2	19.0	0	4.8
10Zn5Ni	69.3	17.3	8.7	4.8
20Zn5Ni	63.5	15.9	15.9	4.8
30Zn5Ni	58.6	14.7	22.0	4.8
40Zn5Ni	54.4	13.6	27.2	4.8
0Zn10Ni	72.7	18.2	0	9.1
10Zn10Ni	66.1	16.5	8.3	9.1
20Zn10Ni	60.6	15.2	15.2	9.1
30Zn10Ni	55.9	14.0	21.0	9.1
40Zn10Ni	51.9	13.0	26.0	9.1
0Zn15Ni	69.6	17.4	0	13.0
10Zn15Ni	63.2	15.8	7.9	13.0
20Zn15Ni	58.0	14.5	14.5	13.0
30Zn15Ni	53.5	13.4	20.1	13.0
40Zn15Ni	49.7	12.4	24.8	13.0

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