



Short communication

# Electrodeposited Re-promoted Ni foams as a catalyst for the dry reforming of methane



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## ARTICLE INFO

## Article history:

Received 11 October 2015

Received in revised form 2 December 2015

Accepted 15 December 2015

Available online 17 December 2015

## Keywords:

Methane reforming

Electrodeposition

Metal foams

## ABSTRACT

The dry reforming of methane (DRM) utilizes carbon dioxide (CO<sub>2</sub>) as the oxidizing agent in order to produce synthesis gas. Catalyst deactivation via coking, oxidation, and sintering has stymied the industrialization of catalysts for the DRM. Here, we utilized electrodeposition followed by de-alloying in order to synthesize metal alloy foams (5 m<sup>2</sup>/g). Through this process we have created the first electrodeposited DRM catalyst capable of converting more than 10,000 mL/g·h at near-equilibrium conversion. Rhenium promotion was observed over the entire temperature range studied (700–800 °C), with the most dramatic enhancement at 700 °C. After 50 h of reaction, no significant accumulation of carbonaceous deposits were detected, making electrodeposited structures a viable candidate for stable methane conversion catalysts.

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## 1. Introduction

Significant attention has been given over the last 20 years towards the dry reforming of methane (DRM). Typically, methane is reformed with steam as the oxidizing agent (Eq. (1)); however, such high H<sub>2</sub>:CO ratios are undesirable for downstream processing into long-chain hydrocarbons such as synthetic liquid fuels via Fischer–Tropsch synthesis [1]. The DRM (Eq. (2)) utilizes carbon dioxide (CO<sub>2</sub>) as the oxidizing agent in order to decrease the H<sub>2</sub>:CO ratio from 3:1 to 1:1 as shown below.



The primary factor preventing the industrialization of the DRM is the lack of catalyst materials resistant to deactivation [2]. In the case of supported catalyst, deactivation primarily occurs through carbon deposition [3], oxidation [4], or sintering of active sites [5]. Therefore, DRM catalyst materials resistant to these forms of deactivation are highly desirable.

The vast majority of DRM studies focus their attention on supported catalysts where active metallic phases (typically, alloys of noble metals with Ni, Fe, and/or Co) are distributed about metal-oxide nanoparticles [6]. While such materials have the advantage of providing large surface areas (BET surface areas typically between 20 and 200 m<sup>2</sup>/g), they can exhibit large pressure drops and poor heat transfer compared to conductive structured catalysts. This can be particularly devastating for highly endothermic (including DRM, ΔH<sup>0</sup> = +247 kJ/mol) [2] and exothermic reactions, as temperature

gradients will inevitably form. Nevertheless, structured catalysts such as metallic gauzes and foams can be designed to offer a low flow resistance, short diffusion distances, and higher thermal conductivities compared to porous ceramic supports [7]. The design of highly active metallic foam catalysts, such as the materials described in this work, may therefore compromise between the need for specific surface area and effective heat and mass transfer.

Previous efforts to design structured wire catalysts for methane reforming either required the presence of steam at high pressures and temperatures [8] or low gas-hourly space velocities [9] in order to achieve high conversion or stable performance. In this work, we show that low-level rhenium alloying (0.5–1.5 at.%) can lead to high and stable DRM activity at large space velocities at atmospheric pressure. While rhenium is currently used in various fuel reforming applications, only a handful of studies have investigated its capacity to catalyze or promote DRM [10–12]. Despite rhenium's coke-resistant properties, these reports cite the volatility [13] and high operating temperatures [14] as drawbacks for its use. Here, the favorable reducibility of bulk metallic phases (by comparison to nanopowder supported phases which can show low reducibility due to stabilization [15]) is exploited to design a material where rhenium promotion of DRM is stable at lower temperatures. Furthermore, the procedure described here only requires low levels of Re, making our method much more viable for future industrial applications.

## 2. Experimental

## 2.1. Catalyst preparation

Stainless steel type 316 gauze (325 mesh woven from 36-μm diameter wires) was provided by Alfa Aesar. The nominal chemical

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composition of the wire material was 67.5 wt% Fe, 17 wt% Cr, 13 wt% Ni, and 2.5 wt% Mo, as provided by the manufacturer. The gauze was laser-cut into circular samples (dia 14 mm). The cut samples were cleaned by sonication for 15 min in 32 vol% HCl in DI water. The sonicated samples were rinsed and sonicated for another 15 min in DI water.

## 2.2. Electrodeposition

The electroplating bath was prepared using 180 mM nickel sulfate and 180 mM citric acid, and was adjusted to pH  $5 \pm 0.1$  using 5 M sodium hydroxide. Rhenium-alloyed samples were fabricated using the same bath, but with the addition of up to 3 mM ammonium perrhenate. Electrodeposition of pure Ni and Ni–Re alloys onto the stainless steel gauze was done by immersing the gauze sample into the proper electrolyte fixed between two platinum gauze (52 mesh) counter electrodes spaced 1 cm away on either side. Electrodeposition was carried out in a jacketed electrochemical cell with a magnetic stir-bar connected to a heated bath recirculator set to 60 °C. Electrochemical measurement and control was through Princeton Applied Research 263A Potentiostat/Galvanostat. The electrodeposition was galvanostatic at a current density of 40 mA/cm<sup>2</sup> for 800–1100 s, as required to deposit a 10- $\mu$ m layer (~36 mg).

## 2.3. Catalyst testing assembly

Catalysts were placed inside a 12-mm ID quartz tube ( $L = 60$  mm, OD = 15 mm) in the isothermal zone of an Electrotherm tube furnace. The temperature of the isothermal zone was changed using the integrated controller on the furnace chassis. The temperature of the catalyst was measured using a K-type thermocouple. In order to prevent reaction on the thermocouple surface, we placed the thermocouple on the outside of the tube at the lateral position of the catalyst. A separate experiment utilizing 2 K-type thermocouples was conducted to measure the differential temperature between the catalyst surface and the outer thermocouple. All temperatures reported in this report refer to the temperature of the catalyst. The reaction mixture was created by mixing argon, carbon dioxide, and methane using Alicat mass flow controllers (MFCs). The mixture had a molar CO<sub>2</sub>:CH<sub>4</sub>:Ar ratio of 1:1:8. Mixing occurred at atmospheric pressure prior to delivery into the furnace. No significant pressure drop was observed across the loaded quartz tube owing to the low flow resistance provided by the foam catalyst. After the furnace, the converted gas was sent through trace-heated (110 °C) tubing to an SRI gas chromatograph fitted with Molecular Sieve 13X and Hysep C columns. The GC contained two thermal conductivity detectors (TCDs) and a methanizer-flame ionization detector (FID). Hydrogen was quantified using a TCD with a nitrogen carrier, CO, CO<sub>2</sub>, and CH<sub>4</sub> were quantified using the methanizer-FID, and O<sub>2</sub>, N<sub>2</sub> were measured using a TCD with a helium carrier.

## 2.4. Sample transfer

In order to prepare our samples for ex-situ analysis, the reactor was purged and cooled in an argon environment in order to prevent unwanted oxidation of our catalyst between the reactor and the XRD analysis. Furthermore, samples were stored in a desiccated vacuum chamber. We cannot completely rule out the possibility of oxidation during the transfer process, however, these processes were present in both the pre- and post-reaction XRD spectra. Furthermore, the most abundant phase of rhenium was completely absent from the pre-reaction XRD spectra. Therefore, despite the reality of oxidation during the transfer process, we find the XRD analysis to give a meaningful and reliable description of our material.

## 3. Results and discussion

Fig. 1 shows that the coating displays a mesoscale colony surface morphology as is typical of Ni-based electrodeposits at 40 mA/cm<sup>2</sup>. Such morphology was observed in Ni and Ni-alloy electrodeposits whenever the applied current density exceeded the mass-transport limiting current density [16].

Elemental mapping of the cross-section of the precursor Ni–Re layer (Fig. 2A) reveals that the Re-content is highest at the interface between the stainless steel substrate and the coating (14 at.%) and lowest at the outer surface (5 at.%) due to the depletion of the perrhenate ion in the electrolyte during electrodeposition. To form the final catalyst material, the Ni–Re- and Ni-coated gauzes were then calcined at 900 °C in a 10<sup>-1</sup> Torr vacuum for 16 h, during which time the volatile nickel oxide (NiO) and rhenium oxide (Re<sub>2</sub>O<sub>7</sub>) were partially removed from the coating, transforming the catalyst deposit from a compact layer into a metal foam (BET surface area of 5.1 cm<sup>2</sup>/g; pore volume of 0.012 cm<sup>3</sup>/g), also shown in Fig. 1. Furthermore, the mass lost in the calcination step was approximately 17%.

Elemental dot maps of the post-reaction catalyst (Fig. 2B) show the outward diffusion of both iron and chromium into the catalyst foam layer. The diffusion of iron into the catalyst foam layer is significant because iron, while not very active for methane reforming, has been shown to prevent the accumulation of carbonaceous deposits [17]. Furthermore, a significant amount of chromium segregated to the stainless steel surface, typical effect found in austenitic stainless steels at elevated temperatures [18]. The level of outward diffusion of iron and chromium into the catalyst layer was not found to be impacted by the presence of Re. The atomic Re-content of the final catalyst material ranged from 1.5 at.% at the stainless steel interface to 0.5 at.% at the outer surface of the foam (from XPS). Cross-sectional analysis also revealed that the porosity of the catalyst layer was greatest adjacent to the steel gauze support and dropped off towards the outer surface. While still containing pores, the catalyst layer near the outer surface was more compact as

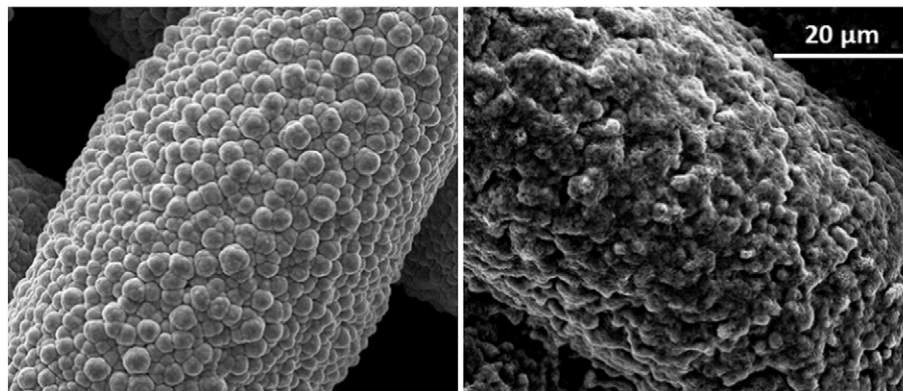


Fig. 1. SEM images of the Ni–Re catalyst precursor surface morphology as-deposited (left) and post-reaction (right). Scale bar shown is for both images.

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