

# Hydrogen production with a solar steam–methanol reformer and colloid nanocatalyst

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## **ABSTRACT**

In the present study a small steam–methanol reformer with a colloid nanocatalyst is utilized to produce hydrogen. Radiation from a focused continuous green light laser (514 nm wavelength) is used to provide the energy for steam–methanol reforming. Nanocatalyst particles, fabricated by using pulsed laser ablation technology, result in a highly active catalyst with high surface to volume ratio. A small novel reformer fabricated with a borosilicate capillary is employed to increase the local temperature of the reformer and thereby increase hydrogen production. The hydrogen production output efficiency is determined and a value of 5% is achieved. Experiments using concentrated solar simulator light as the radiation source are also carried out. The results show that hydrogen production by solar steam–methanol colloid nanocatalyst reforming is both feasible and promising.

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# 1. Introduction

Producing hydrogen for generating electrical power with fuel cell systems is of great importance. Hydrogen fuel cells generally have high efficiency because they directly convert chemical energy to electricity [\[1\]](#page--1-0) which leads to a reduction in pollution, cost and fuel waste. A common method for producing hydrogen is steam reforming where hydrogen is produced from the catalytic conversion of water and hydrocarbon mixtures. Methanol is an appropriate fuel for steam reforming because of its relatively high theoretical conversion efficiency, low conversion temperature, and small byproduct production, e.g. carbon monoxide, compared to other hydrocarbon fuels such as ethanol, methane and gasoline [\[2,3\]](#page--1-0).

Conventional steam–methanol reformers utilizing catalyst structures with characteristic lengths, e.g. catalyst particle size or catalytic wall coating thickness, of micrometers have been extensively studied [\[4–6\].](#page--1-0) The effective heat and mass transport in microreformers yield higher methanol conversion efficiencies than in large scale reformers. In addition, microreformers can be integrated into small and portable fuel cell systems. Studies of micro-steam–methanol reformers reformers of advanced thermofluidic designs, for example, internally heated reformers, have been carried out [\[7,8\]](#page--1-0) to improve the reforming system efficiency.

Energy for the endothermic steam–methanol reforming reactions in a reformer is often provided by electrical resistive heating or integrating the reformer with a fuel combustor.

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Using concentrated solar energy to provide energy for the steam–methanol reformer has the advantage of increasing the overall fuel to electricity efficiency and reducing the  $CO<sub>2</sub>$ emission [\[9\].](#page--1-0)

To further increase the hydrogen production and thereby increase the reformer efficiency, nano-structured catalytic reformers have been investigated. Pfeifer et al. [\[10\]](#page--1-0) fabricated and tested a steam–methanol reformer with microchannels coated with nanocatalytic particles. Their experimental results showed that the conversion efficiency can be enhanced, especially at low reforming temperature, by utilizing nanocatalytic particle coatings. Lee et al. [\[11\]](#page--1-0) used pulsed laser ablation (PLA) technology to generate nanocatalytic particles in liquid methanol environments. They then mixed the nanocatalyst methanol colloid with water and irradiated the solution with a pulsed laser. Their results showed that a significant amount of hydrogen can be produced from this photothermal reforming system which uses photon energy to induce the endothermic steam–methanol reaction. To assess solar energy utilization of this nanocatalytic reformer, a photon energy source that has power and wavelength(s) comparable to solar radiation should be utilized.

In the present study, the photon energy input is from a focused continuous green light laser (514 nm wavelength) and is applied to the nanocatalytic colloid prepared by a method similar to that used by Lee et al. [\[11\].](#page--1-0) To improve the hydrogen production rate and hence to increase the hydrogen production output efficiency (equation [\(8\)](#page--1-0)), a novel reforming system that uses borosilicate capillaries is fabricated and tested.

## 2. Catalyst preparation

### 2.1. Experiment apparatus

Nanocatalytic particles were prepared by using pulsed laser ablation (PLA) technology similar to that used by Lee et al. [\[11\].](#page--1-0) Bulk BASF F3-01 (CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>) catalyst pellets were ground and sieved to an average size of approximately  $75 \mu m$  and loaded in a glass vial with a v-shaped bottom. The vial was then filled with methanol. The final particle concentration of the catalyst colloid is determined by the amount of catalyst and methanol filled in the vial. The vial was then placed on a holder that allows the pulsed laser to irradiate the particles from the bottom (cf. Fig. 1). A Nd:YAG pulsed laser (Continuum® Surelite II-10), 10 Hz frequency, with a pulse width of 4–6 ns and wavelength 532 nm, is applied. The 5 mm diameter laser beam is slightly focused to about 3 mm to cover the entire cross-sectional area of the bottom of the vial.

A small plume of fine particles inside the clear methanol liquid was observed immediately after the lasing was initiated. The solution soon became dark brown in color indicating efficient nanoparticle fabrication. The large particles in the solution fall to the bottom of the vial and are directly exposed to the laser light. This circulation increases the ablation efficiency of the particles because the laser energy is received directly by the larger particles and is not attenuated by the smaller particles that are present in the solution.



Fig. 1 – Experimental setup for nanocatalyst particle fabrication.

## 2.2. Impact of pulsed laser energy

The initial concentration of microparticle loading in the methanol solution is 10 mg of catalyst in 2 ml of methanol. Three pulsed laser energies, 10, 20 and 30 mJ, irradiate the particles for 1 h. A small portion of the resulting colloid was deposited on a silicon wafer and measured by using scanning electronic microscopy (SEM). Fig. 2(a) –(b) show SEM photographs of particles. Particles fabricated by using 10 mJ laser energy are mostly non-spherical with a characteristic size of approximately 1  $\mu$ m (cf. Fig. 2(a)). Particle size distributions for particles fabricated using 20 and 30 mJ laser energies can be



Fig. 2 – SEM photographs of catalyst particles fabricated by pulsed laser ablation. (a): 10 mJ pulse energy. (b): 20 mJ pulse energy.

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