Hydrogen generation from hydrous hydrazine over Ni/CeO$_2$ catalysts prepared by solution combustion synthesis

Wooram Kang, Arvind Varma*

Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907, USA

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ABSTRACT

Hydrous hydrazine is a promising hydrogen carrier for fuel cell vehicles owing to its high hydrogen content (8.0 wt% for N$_2$H$_4$·H$_2$O), low cost and stable liquid state at ambient temperature. The development of cost effective catalysts with high activity and 100% selectivity for hydrogen generation under mild conditions, however, is a significant challenge for its practical use. In this work, a series of Ni/CeO$_2$ catalysts were prepared by solution combustion synthesis (SCS), varying the SCS parameters in terms of ratio of precursor oxidizers (nickel nitrate and ammonium cerium nitrate), fuel-to-oxidizer ratio (0.5–3) and fuel type (hydrous hydrazine and glycine). These parameters influence the combustion behavior and, in turn, the physicochemical properties of catalysts such as crystallinity, Ni particle size, surface area and pore size as well as formation of Ni−O−Ce solid solution. The reaction mechanism for the SCS process is discussed. The tailored 6 wt% Ni/CeO$_2$ catalyst synthesized with fuel-to-oxidizer ratio 2 and hydrous hydrazine fuel, exhibited 100% selectivity for hydrogen generation and good activity with a TOF value 34.0 h^{-1} at 50 °C, which is the highest catalytic performance among all prior reported catalysts containing Ni alone.

1. Introduction

Hydrogen is a promising energy carrier since its gravimetric energy density (120 MJ/kg) is higher than conventional hydrocarbon fuels such as gasoline and diesel, with the added benefit that its combustion product, water, is environmentally benign. Hydrogen, however, is the lightest gas, hence it has poor volumetric energy density (0.01 MJ/L at STP), which presents significant difficulty in storing large quantity of hydrogen for vehicle and portable applications. Accordingly, finding an efficient hydrogen storage material is among the main challenges for the development of on-board hydrogen storage applications. Over the past decades, various hydrogen storage materials (sorbents, metal hydrides, chemical hydrides) have been investigated extensively [1]. None of these materials, however, have been demonstrated to meet practical requirements such as volumetric and gravimetric hydrogen capacities, handling pressure and temperature, regeneration of spent product and cost [1,2].

Hydrous hydrazine such as hydrazine monohydrate (N$_2$H$_4$·H$_2$O) is a promising but not well explored hydrogen carrier for storage and transportation applications owing to its high hydrogen content (8.0 wt %), low material cost and capability of generating hydrogen at room temperature [3,4]. In particular, its stable liquid state over a wide range of temperature (221–393 K) presents advantages for easy recharging

and potential availability of current infrastructure for liquid fuels. In addition, generation of only nitrogen as byproduct obviates the need for on-board collection for spent fuel regeneration.

Basically, hydrogen can be generated from hydrazine decomposition which proceeds by two different reaction pathways: the complete decomposition [N$_2$H$_4$ (l) → N$_2$ (g) + 2H$_2$ (g)] and the incomplete decomposition [3N$_2$H$_4$ (l) → 4NH$_3$ (g) + N$_2$ (g)]. Notably, since only the complete decomposition leads to hydrogen generation and even small amount of ammonia as byproduct is poison for hydrogen fuel cells [5,6], the development of efficient and selective catalysts, which enhance the complete decomposition and simultaneously suppress the incomplete decomposition, is important. Towards this aim, many catalysts containing noble (Ir, Rh, Pd and Pt) and transition metals (Ni, Fe, Co and Cu) have been investigated for efficient catalytic decomposition of hydrous hydrazine [7–14]. Among these, Ni-based catalysts exhibit superior catalytic activity and selectivity for hydrogen generation. Recent studies also show that the use of metal oxides (Al$_2$O$_3$, CeO$_2$, La$_2$O$_3$ and MnO$_2$) as supports significantly enhances catalyst performance by providing high metal surface area and strong metal-support interaction [15–22].

This study is focused for the first time on a non-conventional one-step method, namely solution combustion synthesis (SCS), as the preparation method of cost effective metal catalysts supported on metal

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oxide for decomposition of hydrous hydrazine. SCS is a self-sustained process where the main source of energy is the combustion reaction between a metal oxidizer and a fuel. In general, since the combustion reaction is completed within a short time, various products (e.g., metals, metal oxides, alloys and sulfides) can be obtained simply and rapidly [23]. Also, the mixing of precursors in aqueous solution at the molecular level and the generation of gaseous byproducts during combustion allow the formation of nanoscale powders with uniform composition and high metal dispersion. It has been noted that physical properties of the resulting products depend strongly on combustion characteristics which are mainly determined by the synthesis parameters such as the nature of fuel, metal oxidizer, and fuel-to-oxidizer ratio [24–31]. Although many prior studies used SCS to prepare metal or metal oxides for various applications, there are relatively few reports describing the quantitative effects of synthesis parameters on the physical and catalytic properties of catalysts.

In this work, Ni/CeO$_2$ catalysts, as a representative of metal catalysts supported on metal oxide, are prepared by SCS in a one-step process by varying the synthesis parameters to develop efficient catalysts for decomposition of hydrous hydrazine. The characterization and testing of the Ni/CeO$_2$ catalysts were conducted to understand the effects of the synthesis parameters on the SCS process and its correlation with the physical and catalytic properties. Finally, the catalytic performance of the Ni/CeO$_2$ prepared by SCS was compared with that of catalysts prepared by different prior methods.

2. Experimental

2.1. Catalyst preparation

The SCS was used for preparation of all the studied catalysts in this work. In a typical experiment, stoichiometric amount of nickel nitrate hexahydrate [Ni(NO$_3$)$_2$·6H$_2$O, Alfa Aesar, 98%] and cerium ammonium nitrate [(NH$_4$)$_2$Ce(NO$_3$)$_6$, Alfa Aesar, 98 + %] as metal oxidizers were dissolved in a minimum amount of distilled water and then added to hydrous hydrazine (N$_2$H$_4$·H$_2$O, Alfa Aesar, 99 + %) or glycine (NH$_2$CH$_2$COOH, Alfa Aesar, 99.5%) as fuel. The amounts of metal oxidizers were determined to prepare catalysts with different nickel loading (3–68 wt%). The Ni contents of the catalysts were determined by atomic absorption spectroscopy (Table S1). The amount of fuel was adjusted by the fuel-to-oxidizer ratio, ϕ and four values (0.5–3) were selected to investigate the effect of ϕ on the SCS behavior and properties of the resulting products. After thorough mixing of the obtained solution, the mixture was heated over a hot plate to induce the self-sustained combustion. Typically, after dehydration of the aqueous precursor solution, ignition occurred, leading to combustion along with large gas evolution. During combustion, the temperature abruptly increased to a maximum value, followed by rapid cooling due to gas evolution and heat loss to the surroundings (Fig. 1). The temperature change during combustion was monitored using an R-type thermocouple (tip diameter 0.125 mm) and the combustion behavior was also monitored by video recording. After cooling to room temperature, the resulting powders were calcined in air at 400 °C for 4 h and then treated at 400 °C for 1 h in a flow of 10 vol% hydrogen, balance argon, to reduce NiO to Ni. All the prepared catalysts are designated as x wt% Ni/CeO$_2$-y-z, where 'x' is the wt% of Ni present in the catalyst, 'y' is the type of fuel and 'z' is the ϕ value. For example, 6 wt% Ni/CeO$_2$-HH-2 denotes a Ni/CeO$_2$ catalyst with 5.8 wt% Ni loading, prepared with hydrous hydrazine as fuel and $\phi = 2$.

To calculate the adiabatic temperature for a given SCS condition and compare to the experimentally measured maximum temperature, thermodynamic calculations were conducted using the "Thermo" software package, which is based on the minimization of thermodynamic potential and includes properties of more than 2500 compounds [32]. The combustion reactions between metal oxidizers and fuel [Eq. (1) for hydrous hydrazine and Eq. (2) for glycine] considered for the
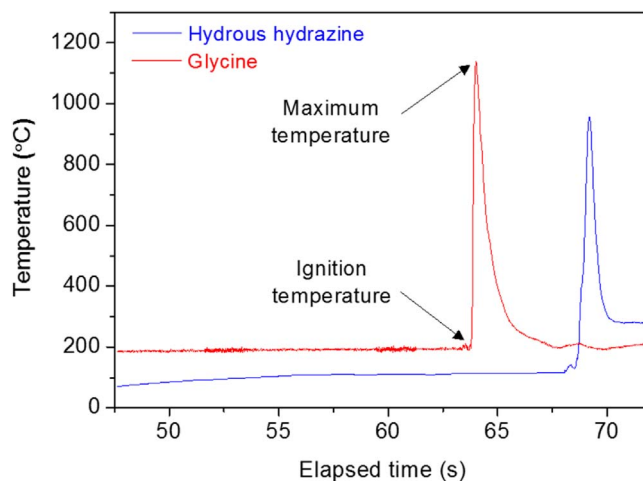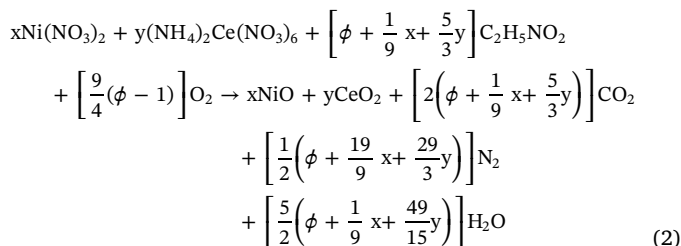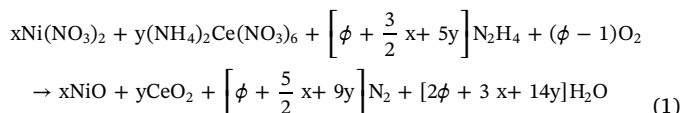

Fig. 1. Temperature-time profiles for SCS in hydrous hydrazine and glycine fuel systems.

thermodynamic calculations are shown below:

$$xNi(NO_3)_2 + y(NH_4)_2Ce(NO_3)_6 + \left[\phi + \frac{3}{2}x + 5y\right]N_2H_4 + (\phi - 1)O_2$$

$$\rightarrow xNiO + yCeO_2 + \left[\phi + \frac{5}{2}x + 9y\right]N_2 + [2\phi + 3x + 14y]H_2O \tag{1}$$

$$xNi(NO_3)_2 + y(NH_4)_2Ce(NO_3)_6 + \left[\phi + \frac{1}{9}x + \frac{5}{3}y\right]C_2H_5NO_2$$

$$+ \left[\frac{9}{4}(\phi - 1)\right]O_2 \rightarrow xNiO + yCeO_2 + \left[2\left(\phi + \frac{1}{9}x + \frac{5}{3}y\right)\right]CO_2$$

$$+ \left[\frac{1}{2}\left(\phi + \frac{19}{9}x + \frac{29}{3}y\right)\right]N_2$$

$$+ \left[\frac{5}{2}\left(\phi + \frac{1}{9}x + \frac{49}{15}y\right)\right]H_2O \tag{2}$$

where x and y are the number of moles of Ni and Ce, respectively. The number of moles of evolved gases per mole of product was calculated based on Eqs. (1) and (2).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained using Rigaku SmartLab X-Ray Diffractometer with CuKα radiation (λ = 0.1541 nm) and a power 40 kV × 40 mA. The intensity data were collected by step-scanning over the range 20°–80° with a step of 0.02°. The specific surface area, total pore volume and average pore size of the catalysts were measured in a Quantachrome Autosorb by N$_2$ adsorption-desorption analysis using the multi-point BET method and BJH model. Prior to each measurement, the sample was degassed at 250 °C for overnight. The microstructure of samples was determined using a transmission electron microscope (TEM, FEI Tecnai G2 20). To prepare the TEM samples, the powder catalyst was first dispersed in water by ultrasound and then deposited on a copper grid coated with a holey carbon film. The mean particle size of Ni in catalysts was determined from the XRD patterns by the Scherrer equation and confirmed with TEM pictures. The Ni loading in the catalysts was measured using atomic absorption spectroscopy (AAS) on a PerkinElmer AAnalyst 300. The H$_2$ temperature programmed reduction (H$_2$-TPR) experiments were carried out with 200 mg NiO/CeO$_2$ sample packed in a stainless-steel column, using a Gow-Mac Model 20 thermal conductivity detector. Prior to TPR studies, N$_2$ gas was passed at 200 °C for 1 h to pretreat the sample and then cooled to room temperature. A 10 vol% H$_2$/N$_2$ mixture as reducing gas was flowed until the baseline of TCD signal became stable and then the sample temperature was increased at a constant 10 °C/min rate from room temperature to 700 °C. The amount of H$_2$ consumption as a