



Combustion synthesis of copper–nickel catalysts for hydrogen production from ethanol



A. Kumar^{a,b,*}, A. Cross^b, K. Manukyan^b, R.R. Bhosale^a, L.J.P. van den Broeke^a, J.T. Miller^c,
A.S. Mukasyan^b, E.E. Wolf^{b,*}

^a Department of Chemical Engineering, Qatar University, Doha, Qatar

^b Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN, USA

^c Chemical Sciences Div., Argonne National Laboratory, Argonne, IL, USA

HIGHLIGHTS

- Active catalysts of Cu and Ni were synthesized using combustion synthesis methods.
- Ethanol decomposition activity and hydrogen selectivity were investigated.
- Bimetallic catalysts were characterized by in situ X-ray absorption spectroscopy (XAS).

ARTICLE INFO

Article history:

Available online 19 January 2015

Keywords:

Solution combustion synthesis
Nickel copper catalysts
Hydrogen production
Ethanol decomposition
XANES analysis

ABSTRACT

Cu and Ni based catalysts were synthesized using solution combustion synthesis method. The catalytic activity and hydrogen selectivity were investigated for ethanol decomposition reaction. The amount of fuel content in the combustion solution was found to greatly affect the phase and the microstructure of the synthesized catalyst. In situ X-ray absorption spectroscopy (XAS) studies were carried out to study the reduction of the catalyst containing mixed oxides of copper and nickel. The reduced catalyst was further subjected to an oxidizing environment to collect the in situ XAS data during the oxidation of the catalyst. These investigations show that the catalyst oxidation state changes rapidly in the first few minutes of the pretreatment process and then gradually slows down.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

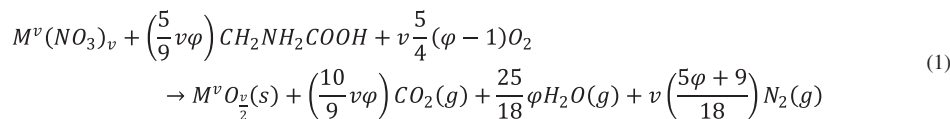
1.1. Combustion synthesis

Combustion synthesis (CS) being an economical and energy efficient synthesis process has been recently used for the synthesis of a wide variety of materials [1,2]. The conventional CS system contains a reactive mixture of solid powders which are compressed to form pellets. These pellets can be ignited locally to initiate a reaction that can propagate layer by layer converting the initial mixture into final products. This mode of combustion is referred as self-propagating high temperature synthesis (SHS) mode of CS. The reactive pellet can also be combusted almost simultaneously throughout the entire volume by heating the pellets uniformly,

which is termed as volume combustion synthesis (VCS) mode of CS. The conventional solid–solid combustion was recently extended to flame synthesis [3], and solution combustion synthesis (SCS) [4] methods to synthesize variety of nanomaterials. The SCS method uses water soluble precursors which are dissolved in water to achieve molecular level mixing. This mixing is expected to generate products with uniform properties. A beaker containing precursor's solution and a hot plate heater are the only required equipment for synthesizing nanopowders using SCS method. Due to the ability of SCS for synthesizing nanopowders in a short period of time (approx. 30 min.) it is being applied in various areas such as pigments, catalysis, electronic and magnetic materials, drug delivery, etc. [1,2,5]. SCS mixture is composed of metal nitrates and fuels (e.g. glycine, urea, etc.) which are dissolved in water. This solution is heated over a hot plate heater, and after the evaporation of water the CS reaction takes place according to the scheme suggested in Eq. (1):

* Corresponding authors at: Department of Chemical Engineering, Qatar University, Doha, Qatar (A. Kumar).

E-mail addresses: akumar@qu.edu.qa (A. Kumar), ewolf@nd.edu (E.E. Wolf).



Scheme 1. Combustion synthesis reaction.

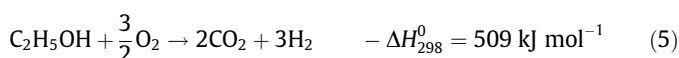
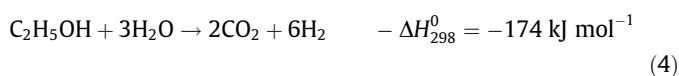
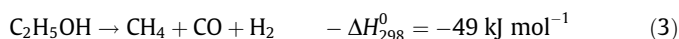
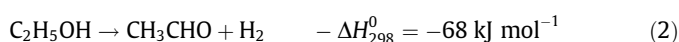
where M^v is a v -valent metal. The parameter φ , the fuel to oxidizer ratio, is defined such that $\varphi = 1$ corresponds to a stoichiometric oxygen concentration, meaning that the initial mixture does not require atmospheric oxygen for complete oxidation of the fuel, while $\varphi > 1$ (<1) implies fuel-rich (or lean) conditions.

The above scheme, (Eq. (1)), suggests the generation of a significant amount of gaseous products along with the metal oxide as the only solid product. The amount of gases can be controlled by controlling the type and amount of fuel used in the synthesis process. These gases, while escaping, generate porosity in the synthesized material which can be optimized to give high surface area. Recent publications [6–9] indicate that controlling the fuel content (i.e. the parameter φ) during SCS process also affects the phase of the solid component synthesized. The parameter φ can be optimized to synthesize pure metals and bimetal nano-powders as well. Experimental conditions and a reaction pathway for the synthesis of pure Ni, Cu metals and CuNi bimetal using SCS can be found in our previous publications [8–10]. The SCS technique can further be modified to synthesize nanomaterials by impregnating the solution on a thin media (e.g. cellulose paper, carbon nanotubes or graphite sheet, etc.) or on a porous support to decrease the energy density for CS, and increase the cooling rate of the products formed [11–14]. The CS reaction in a thin layer with relatively low temperature and fast cooling rate generates a unique microstructure of the products with fine particles and high surface area suitable for catalytic applications [12–14].

In this study we used combustion synthesis to synthesize metallic Ni, Cu and bimetallic CuNi catalysts. We studied the catalytic activity and hydrogen selectivity of these catalysts for ethanol decomposition reaction along with the in situ X-ray absorption spectroscopic (XAS) study on the reduction and oxidation of CuO–NiO and CuNi catalysts respectively. A brief review on ethanol reforming is presented below to describe the choice of Cu and Ni components for ethanol decomposition catalyst.

1.2. Ethanol reforming

Ethanol is being considered as an attractive renewable source for hydrogen production for fuel cell related applications. This route for energy production from ethanol is seen as a potentially carbon neutral energy pathway as there are substantial active research efforts on producing ethanol from corn stover [15] and other biomass byproducts [16]. The carbon dioxide produced during hydrogen generation from ethanol is recycled back into the production of carbohydrates and biomass products by natural photosynthesis process making the entire cycle a carbon zero energy cycle. Following reaction schemes show the routes for hydrogen generation from ethanol and the corresponding heat of reaction are as follows:



The heat of reaction clearly indicate that except ethanol partial oxidation (Eq. (5)), all other reactions are endothermic and require an external energy source. Ethanol decomposition (Eq. (2)) and ethanol dehydrogenation (Eq. (3)) reactions require less energy compared to ethanol steam reforming (Eq. (4)), which is a highly endothermic reaction involving high temperature and external steam supply to sustain the reaction. A comprehensive review on the catalyst used for ethanol reforming reaction is described in our previous publications [10,17,18]. On the basis of literature results described previously [10,17] we found that Ni and Cu are among the active catalysts for low temperature ethanol reforming reactions. We selected these metals to study the less explored ethanol decomposition reaction, as compared to ethanol steam reforming, using combustion based techniques for synthesizing catalysts. We also report the effect of fuel to oxidizer ratio on the combustion synthesis temperature and synthesized catalyst phases.

2. Experimental

2.1. Catalyst synthesis

A mixture of metal nitrates (Alfa Aesar) $M^v(NO_3)_v \cdot xH_2O$ (where $Me = Ni, Cu$) and glycine ($C_2H_5NO_2$, as fuel) were dissolved in water to prepare a 75 ml of active solution for volume combustion synthesis (VCS). The molar ratios of the fuel to metal nitrates were adjusted according to Scheme 1 to synthesize lab scale amounts (1.5–3 g) of catalysts sufficient for catalytic activity and characterization measurements. The homogeneous aqueous solution of metal nitrates and fuel is heated over a hot plate until the solution reaches a temperature known as ignition temperature after the evaporation of water. Once ignited, the reaction proceeds very fast, which can lead to either an explosive combustion mode or to the SHS mode inside the beaker itself. The fuel/oxidizer ratio φ was varied from 0.5 to 2 to study the effect of φ on combustion synthesis temperature. A φ value of 1.75 was selected for further studies to produce a reduced bimetallic NiCu phase. The $\varphi = 1.75$ is the optimized value reported in our earlier publications for the production of pure metallic Ni nanoparticles using combustion synthesis [8]. After synthesis, the resulting powders were milled using a planetary ball mill (Retsch PM 100) at 650 rpm for 2 min to get a mixture with uniform particle size. The ratio of catalyst sample and milling balls was kept at 1:2 in all the cases. The time temperature profile during combustion synthesis was recorded using a high speed data recorder (Omega, OMB-DAQ-3000).

2.2. Catalyst characterization

Multiple techniques were used to characterize the Ni, Cu and CuNi catalysts. XRD was used to identify the bulk phases present in the catalyst, while the morphology of the powders was imaged by high resolution SEM. XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) experiments were conducted in Argonne National Laboratory (ANL) in order to determine oxidation states of Ni, and Cu during catalyst reduction and oxidation conditions.

2.2.1. XRD, SEM measurements

XRD measurements were carried out in air at room temperature using a X-ray diffractometer (Scintag Inc) with Cu-K α radiation of

Download English Version:

<https://daneshyari.com/en/article/146153>

Download Persian Version:

<https://daneshyari.com/article/146153>

[Daneshyari.com](https://daneshyari.com)