

Ethanol Dehydrogenation Mechanism on CuNi Catalysts for Hydrogen Production

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ABSTRACT

Ethanol dehydrogenation mechanism was investigated over catalysts containing Cu and Ni metals prepared by solution combustion synthesis. In situ DRIFTS studies were conducted on individual metals (Cu and Ni) as well as on CuNi alloy to understand the metal-metal interaction in bimetallic systems and their implications on reaction pathway. The catalyst synthesis parameters (such as fuel to oxidizer ratio, combustion temperature) were monitored and correlated with the synthesized materials properties. The amount of fuel content in the combustion solution was found to greatly affect the phase and microstructure of the synthesized catalysts. A change in reaction pathway was clearly observed over Cu and Ni catalysts. Cu mainly favors synthesis of acetaldehyde and acetate whereas Ni and CuNi both showed more tendency towards methane and carbon monoxide formation.

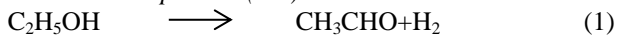
Keywords: solution combustion synthesis, Cu Ni catalysts, ethanol hydrogen production, DRIFTS studies, reaction mechanism

1 INTRODUCTION

Hydrogen is required in many chemical and industrial processes, particularly for clean energy generation. Advancement in fuel cell technology has further increased the demand of pure hydrogen leading the research for alternative and renewable sources of hydrogen. Fuel cell energy production based on hydrogen technology avoids CO₂ emissions and generates only water vapor as byproducts along with producing clean energy [1-6]. There are numerous sources and techniques for hydrogen generation [2, 5-11], however renewable hydrocarbons are seen as future source of hydrogen with minimal carbon footprint. Recent research trends indicate that low molecular weight alcohols such as methanol and ethanol can be extracted from corn stover and other biomass derived products [12]. In this paper we use ethanol as a source of hydrogen and investigate reaction mechanism leading to hydrogen production on two transition metal catalysts; namely Cu and Ni. There are mainly three routes of hydrogen production from ethanol, which are: steam reforming, partial oxidation, and dehydrogenation or

decomposition [6]. The stoichiometric equations are presented below for the sake of convenience.

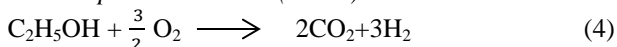
Ethanol decomposition(ED)



Ethanol steam reforming (ESR)

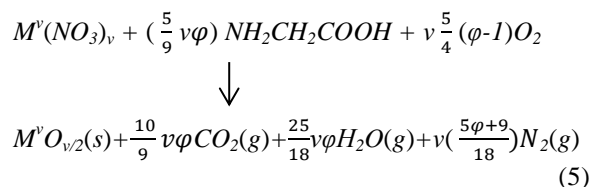


Ethanol partial oxidation(EPOx)



Here, we focus only on ethanol decomposition reaction as it is relatively less studied as compared to ESR and EPOx. Nickel and copper based catalysts are selected to be studied on the basis of primary screening of literature reported active catalysts for ethanol hydrogen production [1, 3, 5, 13]. The catalyst nanopowders are synthesized using solution combustion synthesis technique (SCS) as concisely explained in the next section.

Solution combustion synthesis (SCS) is an economical, simple, fast and energy efficient method for the synthesis of variety of nanomaterials with high surface area and uniform properties [1-5, 8, 14-19]. This method is primarily used for metal-oxides synthesis, however, recent studies do indicate that metals can be synthesized by properly tuning the synthesis parameters [14, 17]. In SCS method, a homogeneous mixture consisting of metal nitrates (metal precursor) and a fuel (reducing agent) is dissolved in water to get a solution which is heated over the hot plate heater to initiate the combustion process. The redox reaction between the reducing agent (fuel e.g.: glycine, cellulose, citric acid, glucose, urea, hydrazine) and oxidizing agent (metal nitrate) provide the energy for the combustion [14, 17]. The stoichiometric reaction for the synthesis of metal nanoparticles using SCS technique can be described as follows.



Where M is the metal with valency v . The value ϕ known as fuel/oxidizer ratio determine the oxidation state of the metal in the output. $\phi > 1$ is fuel rich condition, $\phi < 1$ is fuel lean condition and $\phi = 1$ is the stoichiometric condition with no need of atmospheric oxygen for fuel oxidation.

As indicated in equation (5), metal oxides are synthesized readily in a single step, and if an appropriate value of ϕ is chosen, metallic powders could also be synthesized instead of metal-oxides. The synthesized nanoparticles are ready for catalytic applications and they do not need further treatments (e.g. calcination; as they are already crystalline with energy of calcination coming from exothermic combustion reaction itself).

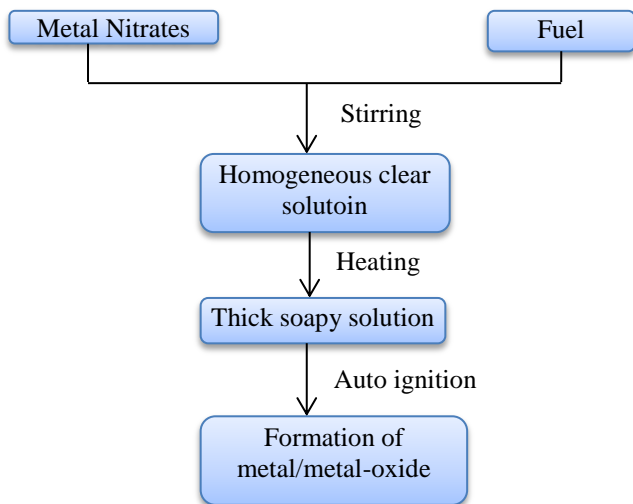


Figure 1: Steps for the synthesis of metal/metal-oxide nanopowders using solution combustion synthesis.

2 EXPERIMENTAL

Nanoparticles of copper, nickel and bimetallic CuNi were synthesized using metal precursors copper nitrate hydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; nickel nitrate hydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; and glycine ($\text{C}_2\text{H}_5\text{NO}_2$) as fuel. A schematic of the synthesis process is presented in Fig. 1. The precursors were mixed together and dissolved in deionized water and kept there for a fixed amount of time (approx. 1 hr) to obtain a uniform and clear solution. The quantity of precursors used are based on the stoichiometric equation (5) with a ϕ of 0.5. The desired amounts of precursors were calculated to obtain an output product of 1.5 g (of oxides) and those were mixed in 75 ml of water in 200 ml capacity beaker. Thus prepared solution was heated over a hot plate heater at 200°C in air at atmospheric pressure until all the water gets evaporated and the mixture reaches to its ignition temperature. Once ignition started, the combustion wave moves from one end to the other end of the beaker producing nanopowders in the beaker. As indicated in our previous publications, this value of $\phi = 0.5$ is suitable for metal oxides preparation rather than reduced

metals [14, 17]. Nonetheless, we continued with this value for individual metals synthesis as choosing a lower ϕ value results in higher surface area in SCS [19]. These catalysts were further reduced in hydrogen flow before being used for ethanol decomposition reaction. This way if there is any metal oxide it would eventually be reduced to its metallic form before ethanol is passed over the catalyst bed. However for bimetallic CuNi synthesis a value of $\phi = 1.75$ was chosen to ensure bimetal formation. A lower ϕ value will result in individual metal oxides synthesis, which upon reduction may not result in a homogeneous distribution of CuNi bimetallic phase throughout the sample and instead phase segregation with larger volumes of individual Cu and Ni nanoparticles could be obtained. $\phi = 1.75$ is reported to give predominantly CuNi bimetallic phase [17, 19] and further phase segregation is less likely to take place upon reduction/activation of catalyst in hydrogen flow before conducting ethanol decomposition studies.

The synthesized catalysts are further characterized by various methods (e.g. XRD, BET, SEM, TEM etc.) as indicated elsewhere [13]. The nanoparticles were characterized before and after the reaction to understand the effect of reaction on nanoparticles microstructure, porosity etc. The detailed characterization, including DRIFTS studies can be found in reference [13] and only a summary is presented here for comparison purpose. Crystalline phase measurements and calculations were performed using Rigaku MiniFlexII Desktop X-ray powder diffractometer. The wavelength of the X-ray source was 0.154056 nm (Cu- $K\alpha$ radiation) and the scan range used for the analysis was $10 - 90$ degrees. SEM morphological studies were conducted with Nova Nano 450 (FEI, 200 kx magnification) SEM. The equipment is capable of doing EDS for elemental analysis of the synthesized materials. A high resolution transmission electron microscopy (HRTEM, TECNAI G2 F20, FEI) was used for the particle size identification of the derived nanopowders.

The ethanol decomposition studies on the combustion synthesized catalysts were performed using in situ Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique. FTIR equipment from Thermo Scientific (Thermo Nicolet 6700 FTIR) with a reaction chamber (Harrick, HVC) along with an optical assembly of praying mantis was used to carry out the DRIFTS study. The sample was first activated under hydrogen flow to convert metal oxides (if any) to metallic phase. The activation part was done by placing the sample in the reaction chamber and heating it to 300°C in H_2 (100 scfm) atmosphere. Once the activation is completed in an hour, the hydrogen flow was replaced by N_2 to purge over the chamber and collect the background spectrum at various temperature values planned for this study. Ethanol was passed over the catalyst with N_2 as carrier gas through an ethanol bubbler at designated temperature values between 50°C and 400°C , and the spectra was collected with 256 scans between $700\text{-}4000\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} .

3 RESULTS AND DISCUSSION

The DRIFTS studies on ethanol decomposition reaction was performed to understand the reaction mechanisms on three catalysts (Cu, Ni and CuNi bimetallic) synthesized by SCS techniques. These catalysts were characterized by XRD, SEM, TEM before the reaction to study the effect of synthesis parameters on the synthesized phase, microstructure, particle size and porosity of nanopowders. After ethanol decomposition studies, the catalyst materials properties are expected to change due to thermal sintering and/or possible deposition of carbon on the surface. So the spent catalysts were characterized to observe these differences arising due to reaction. The details of all these characterizations along with reaction mechanism study can be found in our recent publication [13], nonetheless the results are summarized here for the sake of completion.

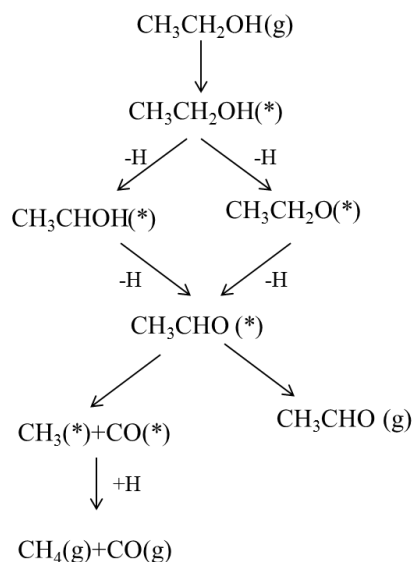


Figure 2: Summary of proposed ethanol decomposition mechanism on Cu, Ni and CuNi surface

Fig. 2 shows the hypothesized mechanism for ethanol decomposition reaction on Cu surface (Fig. 2, right side) leading towards hydrogen and acetaldehyde formation. This reaction pathway is based on the vibrational frequencies of the surface adsorbed species as well as the gaseous phase products [13]. Gas phase ethanol adsorbs on the surface and proceeds towards the formation of aldehyde intermediate via two pathways; one being ethoxy ($\text{CH}_3\text{CH}_2\text{O}(\ast)$) intermediate and the other one being 1-hydroxyethyl intermediate ($\text{CH}_3\text{CHOH}(\ast)$). The possibility of both the intermediates is there as O–H vibrational frequency does not disappear completely. This frequency could be due to unreacted ethanol (in the gas phase) or 1-hydroxyethyl species, but it is difficult to separate them because of overlapping peaks. The same observations were made in

case of Ni and CuNi catalysts (Fig. 2, left side). Once the aldehyde intermediate is formed, it is found to be more stable on Cu as compared to Ni surface. On Cu surface, the aldehyde intermediate easily desorbs forming gaseous acetaldehyde as the temperature is increased. However, the aldehyde peak was not so strong on Ni surface and further increase in temperature led to methane and carbon monoxide formation as indicated by the pathway in Fig. 2 (left side). Similar observations were made on CuNi bimetallic catalyst generating methane and carbon monoxide at higher temperature. This behavior in bimetallic system (CuNi) could be due to phase segregation in catalyst upon exposure to ethanol. In this case perhaps more aldehyde intermediates are formed on Cu sites, but they quickly migrate to Ni sites leading to methane and carbon monoxide production as compared to gaseous acetaldehyde formation on Cu catalyst.

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