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### Hydrogen Production via Ethanol Decomposition over Bimetallic Catalyst

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Bimetallic catalyst shows distinct physical and chemical properties differ from its monometallic catalyst due to the high synergy between the monometals. Bimetals of transition metals shows different applications in the field of catalysis, batteries and solar energy conversion etc. CuCo bimetallic catalysts are excellent candidate for the applications in the field of heterogeneous catalysis, solid state sensor, energy storage devices, and lithium-ion batteries. With the increase in fuel cell application, need of H<sub>2</sub> source also rises. H<sub>2</sub> can be extracted from the hydrogen rich precursors of light alcohol such as methanol and ethanol that can be produced from corn stover, starch containing materials and other biomass byproducts. Ethanol is low toxic and easy handling renewable source for H<sub>2</sub> production for fuel cell applications and the production of ethanol is environmentally sustainable. Transition metal possess high C-C cleavage bond which is an indispensable property in ethanol conversion. Steam reforming, partial oxidation, dehydrogenation and decomposition are the main routes for the hydrogen generation from ethanol. Out of these, decomposition technique is a low temperature process and suitable for small scale fuel cell applications e.g. charging cell phones, computers etc. We follow decomposition route for H<sub>2</sub> production along with other necessary byproducts. Bimetallic CuCo catalyst shows good performance during ethanol decomposition for hydrogen production in the temperature range of 50°C–400°C. Various physical and chemical techniques (such as thermal method, precipitation methods, pyrolysis process, sonochemical method, polyol method, microwave irradiation, sol-gel process, combustion method etc.) have been reported for the synthesis of different morphological structures of bimetallic nanoparticles. In this work we are following combustion synthesis method to prepare cobalt catalysts which have been reported to be active for ethanol-hydrogen production. This work focuses primarily on understanding the reaction mechanism leading to various products using in situ DRIFTS studies. Combustion synthesis was opted for synthesis due to various advantages such as low energy requirement, single step, fast and economic synthesis process as it does not require expensive equipment. In Solution Combustion Synthesis (SCS) the precursors were mixed to form a homogenous solution and heated it over the hotplate heater to initiate the combustion process which resulted in the synthesis of nanoparticles with uniform properties. Typically, it consist

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a redox reaction of the homogeneous mixture of metal nitrate (oxidizing agent) and oxygen containing fuels (reducing agent) such as glycine, urea, glucose, citric acid etc. The reaction between  $\text{NH}_3$  and  $\text{HNO}_3$  released during decomposition of glycine and metal nitrate respectively produces the energy required for single step combustion synthesis. At higher value of  $\phi$ , the reactive medium generates  $\text{H}_2$  rich reducing environment to convert metal oxide to metallic form. Bimetallic CuCo were synthesized from the aqueous solution of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ ) in solution combustion synthesis (SCS) method using a fuel to oxidizer ratio of  $\phi$  0.5, 1, 1.75 and 2.5. The amount of precursors was calculated based on the synthesis of 1.5 g product in the output. These precursors were mixed in 75 ml of water and stir continuously for 1 hr to form a homogenous mixture. The solution was heated over a hot plate heater until all the water got evaporated. Once it reaches the ignition temperature, the combustion reaction started locally at one point and then spread inside the beaker. The resulted powder was grinded using a mortar and pestle to get a uniform powder to be used for catalytic investigations. Synthesized particles were characterized using XRD, SEM and TEM. Ethanol decomposition over bimetallic CuCo were conducted using in situ diffuse reflectance infrared fourier transform spectroscopy (DRIFT) study under  $\text{N}_2$  flow at different temperatures (50, 100, 200, 300, 400°C). Temperature-time profile of CuCo shows an increase in combustion temperature with increase in fuel ratio with maximum temperature at  $\phi = 1$  (stoichiometric ratio) and after that it decreases. The XRD shows the presence of copper-cobalt component in their oxidized states. Theoretical studies shows increase in particle size with maximum flame temperature. Crystalline size calculation using Scherrer formula shows the same trend in particle size calculation as in Table 1. SEM of as-synthesized nanoparticles of cobalt oxide at different molar ratios from 0.5 to 2.5 in SCS mode shows the nanoparticles of high porosity that are randomly distributed as well as agglomerated. Mostly this high porosity is due to the escaping of excess gases during combustion process. Also the EDS results are in consistent with the XRD results showing higher amount of oxide in the synthesized CuCo compound. TEM image in Fig. 1 also shows agglomeration that is common in solution combustion mode with non-uniform sized particles. Copper-cobalt oxide synthesized using combustion technique has been reduced to pure nanocrystal by passing hydrogen in the reaction chamber at 300°C. An FTIR spectrum at 50 and 100°C shows the presence of adsorbed ethanol and ethoxy species over the reduced catalyst. IR band at  $3669\text{ cm}^{-1}$  indicates the presence of OH from adsorbed ethanol on the catalyst surface. At higher temperature the molecularly adsorbed ethoxy species is converted into acetate species along with the presence of carbonate species. After increasing the temperature from 200°C the intensity  $\text{CO}_2$  band at  $2335\text{--}2367\text{ cm}^{-1}$  is evident. At this temperature the acetate species are dehydrogenated to acetaldehyde and other intermediate species. Strong acetate band of  $1760\text{ cm}^{-1}$  above 200°C could be due to the transformation of acetaldehyde formed by the dehydrogenation of ethanol to either ethyl acetate or acetic acid though the nucleophilic reaction of ethoxy or hydroxyl species with the surface aldehyde. The presence of IR band between  $2830\text{--}2695\text{ cm}^{-1}$  shows the presence of aldehyde group in the decomposition reaction. At higher temperature, the presence of carbonate species is evident with the carbonate layer formation from SEM and TEM images. This carbon layer at higher temperature hinders the action of catalyst in ethanol decomposition reaction.

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