REFORMATION OF BIOETHANOL TO LIQUID HYDROCARBON USING GREEN SYNTHESIZED MGO-ZNO, MGO-CUO CATALYSTS IN SINGLE REACTOR CATALYSIS

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Introduction:

With increased demand for energy, stringent environmental regulations, and continued depletion of fossil feedstock, alternative and renewable energy resources have attracted increased interest in recent research. Due to its renewable nature with low CO_2 emission, biomass has been recognized as one of the most viable resources to produce biofuels, such as ethanol, which can be readily integrated into the infrastructure of the current end-user. Ethanol conversion to hydrocarbons with a focus on nanocomposites as a catalysts and fundamental understanding of conversion of ethanol to higher hydrocarbons. Green approach for the preparation of nanocomposite found an increasing attention because of the increasing need to make up environmentally benign technologies.

Currently, bio ethanol accounts for almost 90% of global biofuel production. Driven by the latest innovations, world ethanol production is increasing rapidly and anticipated to reach more than 30 billion gallons in 2017.Blending gasoline with bioethanol is compatible to conventional infrastructures (e.g., combustion engine) and has been mandated to substitute part of fossil fuels for transportation. However, this blending is only limited to 5−10 vol % in the U.S.A. Based on energy independence and security act (EISA) of 2008, annual ethanol production in the U.S. will go beyond the blending wall around 2014.

On the other hand, higher blending ratios and even ethanol-enriched fuels are not likely to be widely practiced, due to the concerns about fuel economy and potential side effects on the conventional end user (e.g. combustion engine). Therefore, it is anticipated that the excess ethanol will become available as a platform molecule for the production of value-added chemicals in the near future.

Objectives:

- Bio-ethanol is one of the alternative fuels that is obtained from biomass. The efficiency of ethanol as a fuel, however, is limited due to its relatively high oxygen content.
- Lowering of the oxygen content (=hydroxyl content) by conversion of ethanol to 1-

butanol or highly branched hydrocarbons may solve this problem.

- The aim is to design and develop new materials that can be used to carry out mild transfer hydrogenation of intermediates in cascade aldol condensation reactions.
- Dehydrogenation of bioethanol in the first step yields that may react in an aldol condensation to form 3-hydroxybutanal.
- Dehydration and hydrogenation of 3-hydroxybutanal may result in the formation of butyraldehyde or 1-butanol.
- We propose to use MgO-ZnO, MgO-CuO composites in single catalyst reactor for this reaction.
- Synthesis of MgO-ZnO and MgO-CuO composites and their characterization.
- Using synthesized composites, 3-hydroxybutanal acetaldehyde can be converted into butyraldehyde or 1-butanol.
- Further Aldol condensation of the butanal may result in higher hydrocarbons.

Methodology:

Synthesis of plant extract:

The Rudanti fruit was grinded to fine powder. To this fruit powder, a known quantity of double distilled water was added and the mixture was heated in Microwave oven for 10 minutes to get a concentrated solution. Filtered it with the help of Whatman filter paper and stored it in refrigerator for further use.

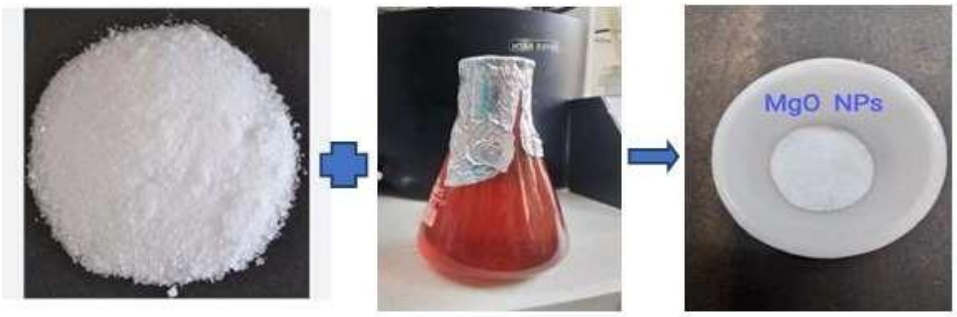
Biosynthesis of ZnO nanoparticles:

0.1 M solution of Zn(NO3)2.6H2O (5.94g in 200mL distilled water) of and 50mL Rudanti fruit extract were mixed in 500 mL two necked flask. The reaction mixture was stirred at 80^{o}C for 4 hr, after being cooled to room temperature the ZnO nanoparticles were collected by centrifugation (4000rpm) and calcinated at 600^{o}C for 5 hr.

$Zn(NO_3)_2.6H_2O$ Rudanti fruit extract ZnO NPs

Biosynthesis of MgO nanoparticles:

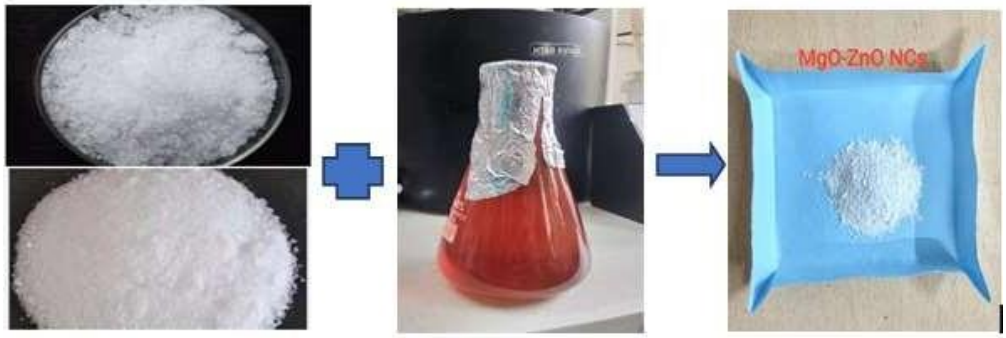
0.1M of Mg (NO3)2.6H2O (5.12g in 200 mL) and 50mL Rudanti fruit extract were mixed in 500mL two necked flask. The reaction mixture was stirred at 80°C for 4 hr, after being cooled to room temperature the MgO nanoparticles were collected by centrifugation (4000rpm) and calcinated at 600°C for 5 hr.



$Mg(NO_3)_2.6H_2O$ Rudanti fruit extract MgO NPs

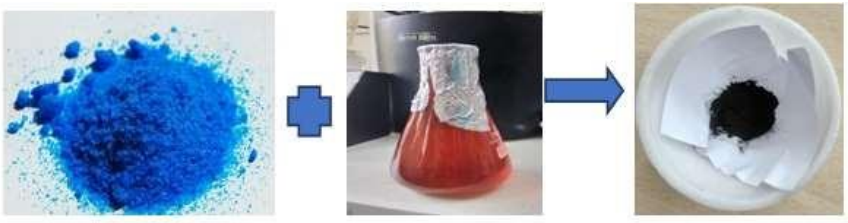
Biosynthesis of MgO-ZnO nanocomposite:

0.1M of Mg(NO3)2.6H2O (5.12g in 200 mL distilled water) and 50 mL Rudanti fruit extract were mixed in 500mL two necked flask. Kept for stirring continuously at 85°C for 1 hr. After that add 0.1M of Zn(NO3)2.6H2O (5.94g in 200 mL distilled water) to above solution, after being cooled to room temperature the MgO-ZnO nanocomposites were collected by centrifugation (4000rpm) and calcinated at 600°C for 5 hr.



Biosynthesis of CuO Nanoparticle:

0.1M of of Cu(NO3)2.3H2O (4.83g in 200mL distilled water) and 50 mL Rudanti plant extract were mixed in two necked flask. Kept for stirring. The reaction mixture was stirred at 80°C for 4 hr, after being cooled to room temperature the CuO nanoparticles were collected by centrifugation (46000rpm) and calcinated at 600°C for 5 hr.



$Cu(NO3)_2.3H_2O$ Rudanti plant extracts CuO NPs

Results:

Uv-visible spectra:

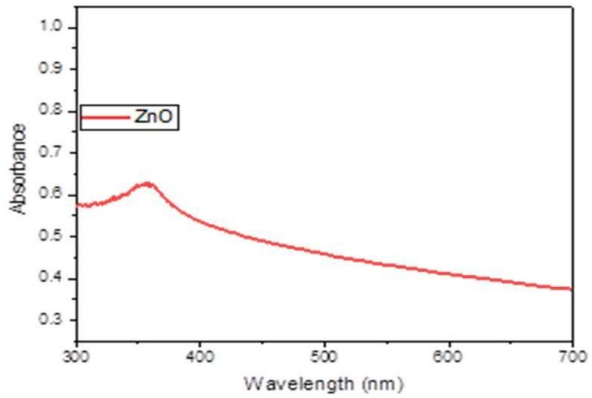


Fig.1.UV-vis spectral analysis of ZnO nanoparticle

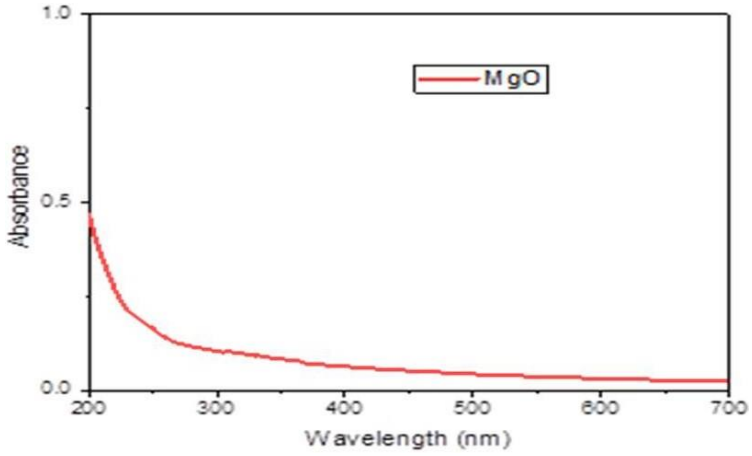


Fig.2.UV-vis spectral analysis of MgO nanoparticle

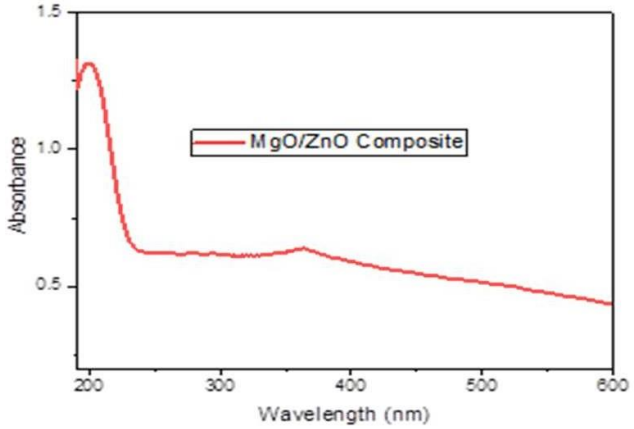


Fig.3.UV-vis spectral analysis of MgO/ZnO nanocomposite

UV-vis spectra of magnesium oxide, zinc oxide and magnesium-zinc oxide composite measurements were taken in the wavelength range of 200 to 700 nm as shown in the above figures. From fig.1 the absorption spectra of ZnO nanoparticle exhibited

characteristic absorption peak at 357 nm and fig.2 shows the absorption spectra of MgO nanoparticle exhibited characteristic absorption at 244 nm. However, equal proportions of magnesium nitrate and zinc nitrates leads to increase absorbance and the peak were spotted at 200 nm and 360nm in case of MgO/ZnO-NCs (1:1) sample. It was found at the equal concentration of magnesium nitrate and zinc nitrate leads to the formation of more and aggregated MgO/ZnO- NCs, which could be observed as intense spectral peaks in the absorption spectrum of MgO/ZnO-NCs.

XRD:

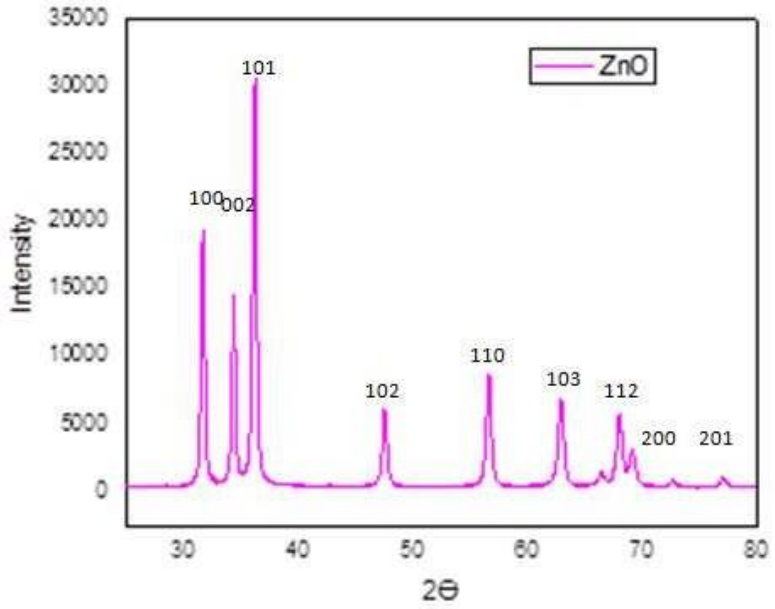


Fig.4. XRD analysis of ZnO nanoparticle

The study of XRD is ideal for the prepared nanoparticles and nanocomposites structural analysis. In case of ZnO NPs light yellow colored powder obtained and revealed several peaks at 2Θ values =31.74º, 34.39º,36.27º,47.47º,56.67º,62.86º,66.18º, 67.91ºand 72.57º for ZnO NPs which corresponds to the 100, 002, 101, 102,110, 103, 200, 112 and 201 occurrence of some weak peaks may be due to the residuals acquired from the synthesis process. No other strong peaks were detected in XRD pattern.

Innovation:

During the last past years ethanol conversion to hydrocarbons has been extensively studied over a variety of heterogeneous catalyst including Alumina, zeolites, transition metal oxides and heteropoly acids. Now we are trying to convert ethanol to hydrocarbons by using nanocomposites as catalyst through green synthesis. The idea of converting ethanol to hydrocarbons by using nanocomposite by green synthesis method is more efficient and ecofriendly. Here we are using Rudanti as a plant extract which is medicinal as well as it is found to be easy to prepared Nanocomposites and also it gives more yield.

Scope:

The depleting fossil fuel resources and the increased availability of bioethanol conversion have made ethanol a platform molecule for the production of value-added chemicals as well as the fuel in the near future. However, ethanol fuel from green synthesis is more environment friendly. The efficiency of ethanol as a fuel, however, is limited due to its relatively high oxygen content. Lowering of the oxygen content (=hydroxyl content) by conversion of ethanol to 1-butanol or highly branched hydrocarbons may solve this problem.