Advancing Sustainable Ethanol Production: An Experimental and Kinetic Exploration of the Integrated Synthesis of Cellulose to Ethanol through a Cascade of Reactions

Ambereen A. Niaze[1*], Sreedevi Upadhyayula[1], Mahendra Sunkara[2]
[1] *Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi-110016, India*
[2]*Department of Chemical Engineering, University of Louisville, Louisville, KY 40292, USA*
[*]*ambreen.niazi9@gmail.com (corresponding author)*

Highlights

- Chemocatalytic process allows quick and effective transformation of cellulose to ethanol
- Metal sites provide the hydrogenolysis/hydrogenation reaction by O-H formation and C-OH cleavage
- The rate-determining step is the conversion of glycolaldehyde to ethylene glycol

1. Introduction

The Ministry of New and Renewable Energy (MNRE) in India has initiated several programs to promote effective ways of utilizing biomass energy to boost the country's economy [1]. In order to improve the effective use of biomass resources, the initiative for biomass power and cogeneration has adopted the use of bagasse-based cogeneration and biomass power generation in sugar mills. Because of its remarkable characteristics, including its high-octane number, low cetane number, and significant heat of vaporization, bioethanol is considered as a desirable biofuel [2]. In addition, the increased biofuel production, in particular bioethanol, satisfies the criteria of the energy demand. These criteria include the fuel's ability to be blended with gasoline and diesel, as well as standards for low-carbon fuels.

Several routes have been employed to produce ethanol, such as biochemical and thermochemical routes, yet biochemical routes have its own limitations [3], the thermochemical methods like chemocatalytic method able to tune the reaction pathway possibly avoiding CO_2 formation to achieve high atom efficiency. In particular, chemocatalytic conversion provides techniques for multifunctional catalysts that reduce side reactions caused by an intermediate product while facilitating cascade reactions that lead to a desired product. Furthermore, the nanowires (NWs) appeared to be very stable, influencing the growing industry and potentially lowering the cost of the process. This work is primarily concerned with the elucidation of reaction mechanisms and the understanding of bond functionality in which the presence of Bronsted acid from tungsten-based catalysts and Bronsted base from hot compressed water (HCW) collectively participate in combination with NWs supported metal catalysts for the conversion of cellulose to C_2 alcohols.

2. Methods

In this work, metal oxide nanowires (TiO_2 and WO_3) were synthesized using a plasma-assisted method and metal nanoparticles (Pt and Ru) were impregnated on the as-synthesized nanowires (NWs). In a high-pressure slurry batch reactor, reactions were carried out to obtain the optimal conditions for the desired product. The catalysts were characterized to reveal the catalysts-activity relationship. Various analytical techniques were used to quantify the liquid and gaseous products collected after the reactions.

3. Results and discussion

The direct conversion of cellulose to C_2-C_3 alcohols using tungsten-based co-catalysts was enhanced even at low temperatures. X-ray photoelectrons spectroscopy (XPS) and Raman analysis show the oxygen vacancy (Ov) enrichment on the surface of Pt/TiO_2 in presence of tungsten co-catalysts which improved their catalytic activity. The role of metallic platinum (Pt^o) was also investigated and found to have a linear relationship with the activity as follows: $H_2WO_4 > (NH_4)_6H_2W_{12}O_{40}.xH_2O > H_3PW_{12}O_{40}$. Maximum yields of 32.33% and 51.52% of ethanol and propane-2-ol at optimum temperatures of 220°C and 250°C, respectively, were obtained with H_2WO_4. Catalytic reaction performed using tandem catalytic system gives a high ethanol yield of 25.56%, which is low as compared to an integrated catalytic system. Based on the experimental results, the reaction pathway is proposed which elaborates the activation and cleavage of specific C-C and C-O bonds.

Moreover, the dual functionality of tungsten oxide (WO_3) nanorods as support and co-catalyst was also studied, enhances the catalytic behaviour, and the promotional study of W was studied for delivering a high yield of ethanol to 43.98% under optimum reaction conditions. The cellulose conversion was calculated to be 98.5%. The XPS study reveals the oxidation state of WO_3 employing the change in catalytic activity before and after the addition of co-catalysts. The electron-deficient state of the metallic component (Ru^o) is favorable for H_2 adsorption on the surface, producing more active hydrogen species and thus promoting hydrogenation. As a result of these electronic understandings of Ru^o and W, the reason for the higher activity of these nano synthesized Ru/WO_3 compared to WO_3 was concluded. Furthermore, a series of characterizations were performed to reveal the catalysts-activity relationship. The bond functionality was also investigated by performing reactions with various reactants under the same reaction conditions. Moreover, the proposed reaction network was simplified to perform the kinetic study for integrated synthesis of cellulose to ethanol by using the combination of catalysts in a kinetically controlled regime. The model is developed for the first order kinetics and validated with experimental data.

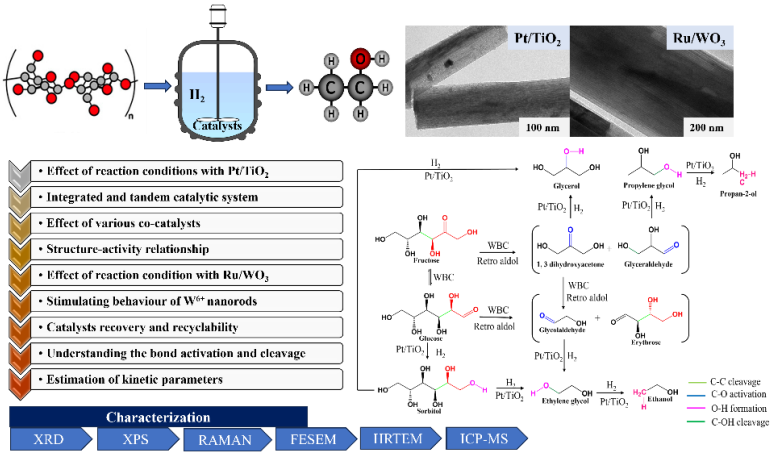

Figure 1. Overview of the work performed

4. Conclusions

Characterization and activity test suggested that the synergistic effect of W^{6+} and Ru^o facilitate the formation of ethanol whereas, Bronsted acid sites from W-based catalysts and Bronsted base from hot compressed water (HCW) collectively participate in the hydrolysis of cellulose and C-C cleavage of glucose to ethanol via selective hydrogenolysis of C-OH. This research will provide an accurate understanding of the mechanism and kinetic correlation of the integrated cellulose-to-ethanol synthesis, paving the way for feasible uses of sustainable ethanol production.

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Keywords

Chemocatalytic, Ethanol, Integrated system, Nanorods