INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student	:	Yedla Santosh Kumar
Roll Number	:	146107018
Programme of Study	:	Ph.D.

Thesis Title: Modified Zeolites and Titania Catalysts for the Conversion of Carbohydrates to 5-Hydroxymethylfurfural

Name of Thesis Supervisor(s)	:	Dr. Nageswara Rao Peela, Prof. Animes Kumar Golder
Thesis Submitted to the Department/ Center	:	Chemical Engineering Department
Date of completion of Thesis Viva-Voce Exam	:	19-09-2019
Key words for description of Thesis Work	:	Biomass; Carbohydrates; Value-added products; Heterogeneous catalysts; Cellulose; Glucose; Fructose; Zeolite catalysts; Titania catalysts; Brønsted acidity; Lewis acidity; Catalysts modifications; Ionic liquids; Choline chloride; 1-Butyl-3-methylimidazolium bromide; Bio-inspired doping; Metal doping; Phosphorus doping; 5-Hydroxymethylfurfural production; High conversion; High yield; Enhanced selectivity

SHORT ABSTRACT

The replacement of the fossil fuels with renewable sources to produce fuels and value-added chemicals is essential due to the quick depletion of fossil sources and also to meet the stringent environmental regulations. Biomass is known to be the best renewable resource because of the presence of the carbon atom in its chemical structure. Biomass consists of cellulose, hemicellulose, and lignin as its constituent biopolymers molecules. Cellulose is a polymer of glucose and these glucose molecules are bonded together with β (1→4) glycosidic bonds. So, it makes this polymer hard to break. The production of 5-Hydroxymethylfurfural (5-HMF) from the cellulose-based carbohydrates is probably one of the promising pathways for the utilization of such renewable resources for the formation of value-added chemicals because 5-HMF has many potential applications in chemical, solvent, biofuel, polymer, and pharmaceutical industries. 5-HMF could be produced with high yields from fructose, with moderate yields from glucose and with low yields from cellulose. A higher yield of 5-HMF from cellulose substrate is necessary for the industrial viability of the process.

Various homogeneous and heterogeneous catalysts have been developed for the conversion of carbohydrates to 5-HMF with high and low to moderate yields, respectively. However, homogeneous catalysts are difficult to separate out for reuse and end up with the generation of a huge quantity waste material. Alternatively, an ionic liquid (i.e. choline chloride and [BMIM]Br) encapsulated zeolites could catalyze the reactions with a high yield of 5-HMF and the catalyst separation is much easier than the homogeneous catalytic system. To the best of our knowledge, there are no reports in the open literature on the utilization of IL (either choline chloride or [BMIM]Br) encapsulated zeolites for the conversion of carbohydrates to 5-HMF. Moreover, the interactions of ILs with zeolites are not well established in the literature. In this doctoral thesis, ILs (choline chloride and [BMIM]Br) encapsulated zeolites and Ag-, Cu-, P-doped titania catalysts are prepared using an impregnation, ship-in-a-bottle, and bio-inspired methods, respectively. These catalysts are well-characterized and tested for the carbohydrates conversion to 5-HMF. In all the catalyst tests, a biphasic system with methyl isobutyl ketone (MIBK) as an extraction phase is used. NaCl is used as a salting-out agent to enhance the partition coefficient between the aqueous (reaction) and the organic (extraction) phases. The effects of variation of operating conditions (temperature, reaction time, substrate concentration) are studied in detail.

Bare zeolites for the carbohydrates conversion to 5-HMF: At the beginning of this study, the conversion of cellulose, glucose, and fructose to 5-HMF over selected 10- and 12-membered bare zeolites, namely, HY, HBeta, HMOR, and HZSM5 is investigated. The catalysts are characterized using powder X-ray diffraction (p-XRD), N_2-sorption experiments, Field emission transmission electron microscopy (FETEM), Pyridine Fourier transformed infrared spectroscopy (Py-FTIR), and Ammonia temperature programmed desorption (NH_3-TPD). Among the catalysts tested, HBeta showed the highest 5-HMF yield of 94% with a fructose conversion of 98%. The highest yield to 5-HMF obtained with the glucose is 51.5% (at 72.9% conversion), respectively, at 180°C. HBeta showed an excellent stability with no signs of deactivation even after reuse of the same catalysts up to 5 cycles.

Choline chloride (ChCl) encapsulated zeolites for the carbohydrates conversion to 5-HMF: In the second study, a bio-based IL, ChCl is encapsulated successfully onto HMOR, HZSM5, HBeta, NaY, and HY using an impregnation method and they are then tested for the conversion cellulose, glucose, and fructose to 5-HMF. The XRD analysis indicates the change in electron density around the zeolite pore walls. A stronger interaction of methylene carbons (N-CH_2-) in ChCl with HZSM5 is observed in ^{13}C solid-state (SS) NMR spectra. This study obtains a good 5-HMF yield of 49 (selectivity, 83%) and 55% from glucose and cellulose over ChCl/HMOR and ChCl/HY, respectively, at the optimized reaction conditions of 180°C, 1 h, substrate:catalyst ratio 3 w/w, and substrate concentration 10 wt%. The activity of the zeolites (HZSM5) with moderate silica-to-alumina ratios (SAR) is found to be enhanced by the encapsulation of ChCl due to a stronger interaction between ChCl and the zeolite as depicted from SS NMR spectra. However, this effect is negligible for the zeolites either with a low or high SAR. Similar to bare zeolites, ChCl encapsulated HZSM5 is stable and reusable up to the 5^{th} cycle tested in this study.

[BMIM]Br encapsulated zeolites for the carbohydrates conversion to 5-HMF: This study focuses on the modifications of bares zeolites using a second IL, namely, 1-Butyl-3-methylimidazolium bromide ([BMIM]Br) in a ship-in-a-bottle method. The higher temperature required for the decomposition of [BMIM]Br in zeolites as compared to that required for the bulk [BMIM]Br indicate a stronger interaction of [BMIM]Br with the zeolite. It is found that [BMIM]Br interacts more strongly with the H-form zeolite as compared to that with Na-form zeolite. ^{27}Al SS NMR reveals that the HMOR loses its extra-framework Al with the [BMIM]Br encapsulation. The SAR increases and Na/Al ratio decreases with the incorporation of [BMIM]Br, as depicted from the EDX analysis. The decrease in Na/Al ratio indicates that some of the Na^+ cations are replaced with the $[BMIM]^+$ cations during its encapsulation into the zeolite pores. The total surface area, micropore area, and the micropore volume of the zeolites are also decreased with the encapsulation of [BMIM]Br. The modified catalysts exhibit significant improvements in the conversions of carbohydrates to 5-HMF compared to the bare zeolite counterparts. At the optimal reaction conditions (180°C, substrate:catalyst ratio 3 w/w and substrate concentration 10 wt%), [BMIM]Br/NaY exhibits the highest 5-HMF yields of 80 (1 h), 62 (2 h), and 59% (3 h reaction time) with fructose, glucose, and cellulose, respectively. Moreover, these catalysts are recyclable for the production of 5-HMF with a moderate decrease in its activity till the second reuse run.

Bio-inspired Ag-, Cu- and P-doping on TiO_2 for glucose conversion to 5-HMF: Instead of zeolites as the supports, this work also explores a new bio-inspired pathway to functionalize TiO_2, a semiconductor support of amphoteric in nature. A combination of noble metal (Ag), transition metal (Cu), and inorganic (P, phosphorous) dopants are tested. The plant-based analytes present in *S. edule* extract successfully dope Ag, Cu, and P into the lattice structure of TiO_2 as evidenced from the XRD and HRTEM analyses. The surface area of the doped catalysts is found to be decreased as accordance with the lattice strain calculation. Among the catalysts, P/TiO_2 showed the highest 5-HMF yield of 50% at 81% glucose conversion at a slightly higher reaction temperature of 190°C compared to the IL encapsulated zeolite catalysts.

Upon overall comparison of the performance of the catalysts developed in this study, it could be inferred that the highest yield of 5-HMF is observed over [BMIM]Br encapsulated NaY catalyst with 62 and 59% yield from the glucose and cellulose substrates, respectively. Whereas, ChCl encapsulated HMOR catalyst showed the highest yield of 5-HMF from fructose and the highest selectivity to 5-HMF (83%) from the glucose substrate. The catalysts particularly, [BMIM]Br/NaY and ChCl/HMOR developed in this work outperformed the catalysts reported in many earlier studies for the production of 5-HMF from carbohydrate-based substrates.