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Efficient method for the conversion of agricultural waste into sugar alcohols over supported bimetallic catalysts

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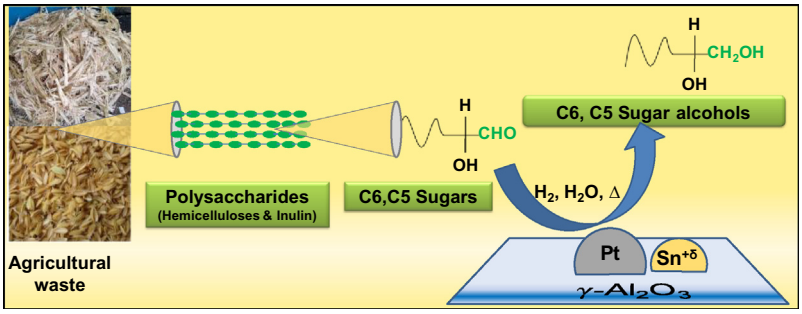
HIGHLIGHTS

- Developed one pot method for converting mono- and polysaccharides to sugar alcohols.
- Complete characterization of agricultural wastes was done by TAPPI and ICP method.
- Pt–Sn bimetallic catalyst is used to improve the yields of sugar alcohols.
- Variety of substrates are used for sugar alcohols production.
- Catalyst is active in wide range of reaction condition and recyclable.

GRAPHICAL ABSTRACT



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ABSTRACT

Promoter effect of Sn in the PtSn/γ-Al_2O_3 (AL) and PtSn/C bimetallic catalysts is studied for the conversion of variety of substrates such as, C5 sugars (xylose, arabinose), C6 sugars (glucose, fructose, galactose), hemicelluloses (xylan, arabinogalactan), inulin and agricultural wastes (bagasse, rice husk, wheat straw) into sugar alcohols (sorbitol, mannitol, xylitol, arabitol, galactitol). In all the reactions, PtSn/AL showed enhanced yields of sugar alcohols by 1.5–3 times than Pt/AL. Compared to C, AL supported bimetallic catalysts showed prominent enhancement in the yields of sugar alcohols. Bimetallic catalysts characterized by X-ray diffraction study revealed the stability of catalyst and absence of alloy formation thereby indicating that Pt and Sn are present as individual particles in PtSn/AL. The TEM analysis also confirmed stability of the catalysts and XPS study disclosed formation of electron deficient Sn species which helps in polarizing carbonyl bond to achieve enhanced hydrogenation activity.

1. Introduction

Because of obvious drawbacks such as fluctuating costs, geo-political issues, and heterogeneous distribution around the world associated with the use of fossil feedstocks (crude oil, coal, natural gas, etc.), it has become necessary to look for alternate feedstocks. In view of this, biomass which is renewable and available in abundance can be useful, particularly to synthesize the chemicals. In the last couple of years, lignocellulosic biomass consisting of three main components, cellulose (ca. 50%), hemicellulose (ca. 30%) and lignin (ca. 20%) is considered as an excellent feedstock for the chemicals synthesis because of no food value attached to it. While, cellulose is a homopolysaccharide made up of glucose; hemicelluloses are of various types and based on their composition are named as, xylan (polysaccharide of xylose), arabinogalactan (arabinose, galactose), glucomannan (glucose, mannose), etc. Lignin, whose primary function is to protect the cell wall from microbial attacks is highly branched, complex polymer made up of aromatic monomers. Besides cellulose and hemicelluloses, inulin is another frequently occurring polysaccharide in the plants which is mainly composed of fructose. The conversions of these

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polysaccharides into wide range of industrially important chemicals such as, glucose, fructose, xylose, arabinose, 5-hydroxymethylfurfural (HMF), furfural, glycols, etc. has been reported in the literature (Rinaldi and Schüth, 2009; Kim and Lee, 1988; Sahu and Dhepe, 2012; Wang and Zhang, 2013). One of the imperative classes of the biomass derived chemicals is sugar alcohols. Polysaccharides (cellulose, hemicellulose, inulin, etc.) are typically hydrolyzed using acidic catalysts into corresponding monomer sugars and these sugars can further undergo hydrogenation reactions in the presence of supported metal catalysts to yield sugar alcohols. Several reports claim, the development of one pot method for the conversion of cellulose and glucose into sugar alcohols (sorbitol and mannitol) over supported metal catalysts (Tathod et al., 2014; Dhepe and Fukuoka, 2007). However, compared to this, very few reports show conversion of hemicelluloses, inulin and agricultural wastes into sugar alcohols using heterogeneous catalysts. It is reported that conversion of hemicelluloses like xylan, arabinogalactan, arabinan into sugar alcohols i.e. xylitol, arabitol, galactitol, etc. is possible over Ru/C and Ru/MCM-48 catalysts (Yi and Zhang, 2012; Kusema et al., 2012; Guha et al., 2011). Hydrolysis of inulin using acidic zeolite LZ-M-8 to yield fructose (Abasaeed and Lee, 1995) and its further conversion into sugar alcohol (mannitol + sorbitol) using Ru/C catalyst is also shown (Heinen et al., 2001). Nevertheless, only handful of reports discuss the use of untreated agricultural wastes instead of isolated polysaccharide, in the production of sugars and furans (Dhepe and Sahu, 2010; Sahu and Dhepe, 2012). Conversion of bagasse and beet fibers to yield sugar alcohols has been reported in the recent past (Yi and Zhang, 2012; Guha et al., 2011). The development of 'Biofine' and 'Mascal' methods is known for the efficient conversion of lignocellulosic biomass into levulinic acid and ethyl levulinate in the presence of mineral acids (H_2SO_4, HCl) and organic solvents (ethanol, dichloroethane) (Hayes et al., 2008; Mascal and Nikitin, 2010). However, use of corrosive acids and highly volatile and halogenated solvents may hamper its commercial applications. It is estimated that India produces ca. 342 MMT of sugarcane, ca. 158 MMT of rice and ca. 86 MMT of wheat per annum and the production of these crops is increasing along the years (Food and Agriculture Organization of the United Nations; http://faostat3.fao.org/faostat-ateway/go/to/download/Q/QC/E). Considering this, huge amounts of agricultural wastes (bagasse, rice husk, wheat straw, etc.) generated from these crops, which are typically lignocellulosic materials can be used for the production of chemicals and particularly, in the production of sugar alcohols. Nonetheless, development of efficient catalytic methods to achieve better yields for sugar alcohols formation from variety of substrates like monomer sugars, polysaccharides (hemicelluloses, inulin, etc.) and agricultural wastes is essential.

Sugar alcohols, sorbitol and xylitol are named in the list of "top value added chemicals obtained from biomass" prepared by US DOE, which underlines the significance of these sugar alcohols. Sugar alcohols are extensively used as low calorie sweeteners and find application in oral hygiene products. Sorbitol is used in humectants and applications of xylitol are well known in the cosmetics and pharmaceutical industries (Mikkola and Salmi, 2001). Researchers have also investigated the possibility of the production of hydrogen from sugar alcohols using supported metal catalysts (Davda and Dumesic, 2004). Furthermore, conversion of sugar alcohols into chemicals such as 1,4-sorbitan, sorbose, isosorbide, glycols, lactic acid, vitamin C, etc. has been studied (Sun and Liu, 2011; De Wulf et al., 2000). Mannitol is used clinically for its osmotic diuretic properties and in the treatment of cerebral oedema (Shawkat et al., 2012). Because of the wide range of applications of sugar alcohols in various industries, demand for those is increasing incessantly (Yadav et al., 2012). Considering the importance of sugar alcohols, conversion of sugars and polysaccharides into sugar alcohols using supported metal catalysts is studied comprehensively and among all the supported metal catalysts, Pt and Ru based catalysts are shown to perform much better and hence are used quite often (Yi and Zhang, 2012; Yadav et al., 2012).

It is well known that in the hydrogenation reactions, the activity of the supported metal catalysts can be enhanced by the addition of promoter metal(s). Generally, along with Pt and Ru metals, promoters such as Ga, Fe and Sn are combined since they have a tendency to remain in electron deficient state which helps in achieving higher carbonyl group hydrogenation activity by way of polarizing the carbonyl group (Marinelli et al., 1995). However, among all the bimetallic catalysts known for hydrogenation, Pt–Sn bimetallic catalytic system is interesting in regards with understanding the effects of concentration of promoter, metal-promoter interaction, metal-support interaction and mechanistic studies (Torres et al., 1999; Homs et al., 2001).

Herein, the synthesis of Pt–Sn bimetallic catalysts and comparison of their activities with monometallic Pt catalysts in the conversion of wide range of substrates like C5 sugars (xylose and arabinose), C6 sugars (glucose, galactose and fructose), hemicelluloses (xylan and arabinogalactan), inulin and agricultural wastes (bagasse, rice husk and wheat straw) to yield sugar alcohols (sorbitol, mannitol, xylitol, arabitol, etc.) is reported.

2. Methods

For details on materials and characterization techniques please refer Supplementary data.

2.1. Catalyst preparation

The supported metal catalysts were prepared by co-impregnation method using γ-Al_2O_3 (AL) and Carbon black pearl-BP2000 (C) supports.

Prior to catalyst preparation, supports were evacuated at 150 °C for 6 h under vacuum (−700 Torr). As per the requirement of wt% loading of metal, quantities of metal precursor solutions (10 wt% aqueous solution of $Pt(NH_3)_4(NO_3)_2$ and $SnCl_2{\cdot}2H_2O$ solution in 3 M HCl) were drop wise added under stirring to the support (suspended in water). Mixture was stirred for 16 h at room temperature (30 °C). Next, solvent was removed by rotary vacuum evaporator and obtained powder was then dried at 60 °C for 12 h in oven and at 150 °C for 3 h under vacuum. In case where AL is used as support, completely dried powder was subjected to calcination (at 400 °C for 2 h in a flow of oxygen, 20 mL/min) and reduction (in a hydrogen flow, 20 mL/min at 400 °C for 2 h). Catalysts in which C (carbon) is used as a support, were directly reduced without calcination (in a hydrogen flow, 20 mL/min at 400 °C for 2 h). Pt/AL, PtSn/AL, Pt/C and PtSn/C catalysts were prepared by keeping Pt loading of 2 wt% and Sn loading of 0.25 wt% i.e. Pt(2)/AL (2 wt% Pt/γ-Al_2O_3), Pt(2)Sn(0.25)/AL (2 wt% Pt-0.25 wt% Sn/γ-Al_2O_3), Pt(2)/C (2 wt% Pt/Carbon) and Pt(2)Sn(0.25)/C (2 wt% Pt-0.25 wt% Sn/Carbon). Other than these catalysts, acidified-Pt(2)/AL catalyst (2 wt% Pt/γ-Al_2O_3 acidified by adding HCl during synthesis) was prepared. In a typical synthesis process, aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (quantity according to 2 wt% loading of Pt) and 3 M HCl (quantity equals to the quantity of 3 M HCl used to prepare Pt(2)Sn(0.25)/AL) were added to AL and the mixture was stirred for 16 h. Rest of the catalyst preparation procedure was same as explained above.

2.2. Catalytic test

All the catalytic reactions were carried out in a batch mode autoclave with a 50 mL capacity (Amar Equipments, India). In all

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