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Solid base supported metal catalysts for the oxidation and hydrogenation of sugars

Anup Tathod, Tanushree Kane, E.S. Sanil, Paresh L. Dhepe*

Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India

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ABSTRACT

Pt impregnated on γ-Al_2O_3 (acidic support) and hydrotalcite (basic support) catalysts were synthesized, characterized and used in the oxidation and hydrogenation reactions of C5 and C6 sugars. In the absence of homogeneous base, 83% yield for gluconic acid; an oxidation product of glucose can be achieved over Pt/hydrotalcite (HT) catalyst at 50 °C under atmospheric oxygen pressure. Similarly, 57% yield for xylonic acid, an oxidation product of xylose is also possible over Pt/HT catalyst. Hydrogenation of glucose conducted using Pt/γ-Al_2O_3 + HT catalytic system showed 68% sugar alcohols (sorbitol + mannitol) formation. The 82% yield for C5 sugar alcohols (xylitol + arabitol) was obtained by subjecting xylose to hydrogenation over Pt/γ-Al_2O_3 + HT at 60 °C. UV analysis helped to establish the fact that under alkaline conditions sugars prefer to remain in open chain form in the solution and thus exposes —CHO group which further undergoes oxidation and hydrogenation reactions to yield acids and alcohols.

1. Introduction

The requirement for alternate resources for obtaining chemicals which are presently derived from non-renewable (in short cycle), fossil feedstocks have attracted researchers across the world to work on the renewable resource, viz., biomass. Among biomass non-edible to humans, lignocellulosic materials (cellulose, hemicelluloses, and lignin), which can be derived from agricultural wastes have dominated the research domain for chemical synthesis. In an acidic medium, cellulose undergoes hydrolysis reaction to yield glucose which upon further dehydrocyclization gives 5-hydroxymethyl furfural (HMF). Similarly, hemicelluloses (xylans) can yield xylose, arabinose and furfural under the acidic conditions. Once these sugars and furans are obtained, those can act as platform chemicals to synthesize value added chemicals by undergoing oxidation (acids), hydrogenation (sugar alcohols), isomerization, hydrogenolysis (glycols), and reforming (alkanes, hydrogen) reactions.

Glucose, derived from cellulose is used as a food additive but it can also be converted to many useful chemicals such as ethanol (fermentation) [1], sorbitol and mannitol (hydrogenation) [2,3], 5-hydroxymethyl furfural (dehydrocyclization) [4], hydrogen (hydrogenolysis/cracking/reforming) [5–7] and gluconic and glucaric acid (oxidation) [8–12]. Gluconic acid has many diverse industrial applications such as, biodegradable chelating agent, water soluble cleansing agent, an ingredient for concrete and as an intermediate in the food and pharmaceutical industries [13]. Calcium gluconate is used as a detoxifying agent after exposure to HF [14]. Gluconic acid has an annual estimated market of 6×10^4 ton and on industrial scale is currently prepared by fermentation of glucose by *Aspergillus niger* [10,15]. However, fermentation method has many drawbacks such as slow reaction rate and disposal of dead microbes and excretory substances of microbes [16,17]. To overcome these drawbacks, replacement of enzymes with heterogeneous catalysts is a viable option.

There have been few reports on the aerobic oxidation of glucose to gluconic acid carried over supported transition metals catalysts including Pd, Pt, Rh and Au supported on various supports like TiO_2, Al_2O_3 and activated carbon (AC) [8,10,11,18–27]. Among those, gold catalysts have been extensively studied by various research groups [10,18,19,23–27]. It is claimed that gold nanoparticles (NP) supported on activated carbon show good catalytic activity in the oxidation of glucose to gluconic acid done at 50 °C [22]. Another report claims better turnover frequency (TOF) values per surface Au atom of 45 s^{-1} at 50 °C, pH 9.0 and 56 s^{-1} at 50 °C, pH 9.5 in the case of gold catalyst supported on ZrO_2 [28]. In most of these studies metals suffer from over oxidation and thus they eventually deactivate [22–24,27]. Study on particle size effect shows that rate of reaction is inversely proportional to Au size indicating that reaction is structure-sensitive. In Au/C catalyst, Au with 1.9 nm particle size gives maximum yield [29]. It is also observed that these metals undergo sintering during the reaction and thus drop in activity is reported [30]. Moreover, in all these reactions, homogeneous base (1–20 equiv.) is used to maintain the reaction solution pH between

* Corresponding author. Tel.: +91 20 25902024; fax: +91 20 25902633.
E-mail address: pl.dhepe@ncl.res.in (P.L. Dhepe).

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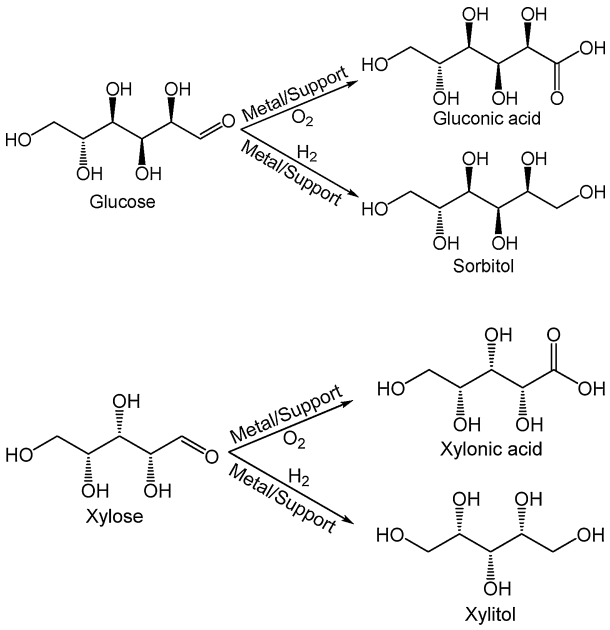

Scheme 1. Conversion of sugars to corresponding acids and sugar alcohols.

9 and 11. The increase in pH (>11) typically leads to degradation reactions and hence it is required to charge the homogeneous base in continuous mode to maintain the pH [22]. Additionally, handling of corrosive homogeneous base is also a major problem. It is known that glucose oxidation carried out in a media other than alkaline is a very slow process. Under acidic conditions, AC supported Au–Pt bimetallic catalysts show 64% conversion and turnover frequency (TOF) of 295 h^{-1} [8]. Most of the reports use high pressures of oxygen in the reactions. There are only few reports available in the literature on the oxidation of xylose to xylonic acid using heterogeneous catalysts [31]. Electro-catalytic oxidation of xylose to xylonic acid using Au and Pt electrodes in alkaline medium is known [32].

To avoid the use of homogeneous base and to develop a method which is environmentally friendly and harmless, we have employed Pt-supported on solid acid and basic supports. In this paper, we report the liquid phase aerobic oxidation of glucose to gluconic acid (Scheme 1) using Pt/hydrotalcites (HT). To compare the results we have also carried out reactions with Pt/γ-Al_2O_3 catalysts with the addition of homogeneous base (Na_2CO_3) and solid base (HT). Oxidation of xylose to xylonic acid is also performed.

In the US DOE report, sugar alcohols, sorbitol and xylitol obtained by hydrogenation of glucose and xylose, respectively are named among the 12 value added chemicals obtained from biomass [33]. These sugar alcohols are low calorie sweeteners and find application in oral hygiene products. Sorbitol is used as humectant and utilization of xylitol is known in cosmetics and pharmaceutical industries. Moreover, sugar alcohols have non-diabetes and anti-caries properties because of low amount of lactic acid formation [34,35]. Recently, exploitation of sorbitol for the production of hydrogen and C5, C6 hydrocarbons has been investigated [6,36]. Additionally, a spectrum of other functional chemicals such as, 1,4-sorbitan, sorbose, isosorbide, glycols, lactic acid, vitamin C etc. are produced from sugar alcohols [37,38]. Due to widespread applications of sugar alcohols demand for those is increasing day by day [39,40].

Sorbitol (annual production: 6.5×10^5 ton) and xylitol (annual production: 2.4×10^4 ton) are commercially prepared by hydrogenation of glucose and xylose using (Raney) nickel catalyst [41,42]. However, catalyst deactivation is a major problem in these reactions [43–45]. Efforts have been taken to rise above the disadvantages associated with nickel based catalysts by synthesizing Fe, Mo, Sn, Cr promoted nickel, and nickel supported on ZrO_2, TiO_2 and ZrO_2/TiO_2 catalysts [3,43]. Hydrogenation of glucose over supported metal catalysts has been extensively studied by the researchers in the last few decades [2,46–50]. Ru catalysts are expansively used for the glucose hydrogenation, but the catalysts are observed to be deactivating during the continuous use [51]. Typically, neutral (AC, SiO_2) [2,46,47] or mildly acidic (Al_2O_3) [3] supports have been used in the study. Enzymatic conversion of glucose is another route for the production of sorbitol but enzymes, soluble in water are difficult to separate after use and hence intricate to recycle [52]. Xylose hydrogenation using supported metal catalysts and enzymes is well known [39,53–58]. It is shown that hydrogenation of xylose is possible over Ru/C catalyst [59]. Recently, it is reported that the reduced Ni/Cu/Al hydrotalcite catalyst at 125 °C and 30 bar H_2 pressure can convert glucose to yield ca.70% sorbitol [60].

In the current work we have studied glucose and xylose hydrogenation using Pt supported on acidic, γ-Al_2O_3 and basic, HT supports under mild reaction conditions (Scheme 1). Good yield and selectivity has been achieved at optimum reaction conditions.

Even though solid base catalysts have been used in several industries, extensive catalytic studies on them are scanty compared to the solid acid catalysts [61]. Application of homogeneous bases in reactions such as isomerization, addition, alkylation and cyclization is well documented. But the homogeneous nature makes their separation and recycling very tricky. Beside this, use of homogeneous bases makes the overall process corrosive and most of the times it needs to be added in the stoichiometric amount. On the other hand solid bases are easily separable from reaction mixture, safe to handle and can be recycled. In recent past, solid base catalysts such as, basic zeolites, hydrotalcites, apatites, chrysotile, sepiolite, basic metal oxides like MgO, CaO and mixed oxide like SiO_2-MgO, SiO_2-CaO, Al_2O_3-MgO, etc. have been used instead of homogeneous bases [61–67]. It is understood that in solid base catalysts like metal oxides, surface O^{2-} species form the Lewis base site [61,64].

Hydrotalcites (HT) are anionic clays having a double layered structure with OH^- and HCO_3^- groups. They have the general formula, $[Me^{2+}_{1-x}Me^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$ and naturally occurring hydrotalcite is hydroxycarbonate of magnesium and aluminum having formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$. They are known to show catalytic activity in numerous base catalyzed reactions such as, aldol condensation, Knoevenagel and transesterification [68–70]. HT supported metal catalysts are applied in the oxidation reactions of alcohols [71]. This class of catalysts shows applications in chemical synthesis, in isomerization reactions and as additive in polymer and in medicine [72–74]. Layered double hydroxides of Mg and Fe have been used in catalysis; water purification and anion exchange [75–77]. Basic nature of hydrotalcites has been studied extensively to use them in few other reactions [78,79].

In this work, our aim of using basic support like HT is to shun the use of homogeneous base in oxidation reactions and to make the overall process environmentally benign and safe. It is thought that properties pertaining to strong interaction between metal and basic support may help us in achieving higher activities in oxidation and hydrogenation reactions.

2. Experimental

2.1. Materials

Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) was purchased from Merck, India (99%), Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) was purchased from Thomas Baker, Germany.