



Towards industrial furfural conversion: Selectivity and stability of palladium and platinum catalysts under continuous flow regime

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ARTICLE INFO

Keywords:

Furfural
Hydrogenation
Continuous flow
Selectivity
Stability

ABSTRACT

Furfural is an important biorefinery platform chemical, derived from hemicelluloses which represent an important fraction of lignocellulosic biomass feedstocks and waste streams originating from them. Recently, promising results have been reported on the hydrogenation of furfural, although the selectivity still may be improved. Most of these studies dealt with batch hydrogenation, however, hydrogenation in continuous flow is preferable for industrial applications. In this work, we compare the conversion, selectivity and stability on-stream in continuous flow regime of lab-synthesized and commercial palladium and platinum catalysts.

1. Introduction

The global population could reach and even exceed 9 billion by 2050 [1]. The use of sustainable feedstocks to meet the growing global energy demand and to reduce the use of fossil resources is now a highly imminent challenge for the research community, and a challenge to be adopted in currently existing industrial refineries or to be designed in future biorefinery plants. The largest part of the current fossil derived petroleum refining is used for fuels production. Still, an important part of petroleum is used for the production of bulk chemicals and materials. Today, the use of alternative biomass feedstocks (or waste streams derived from them) has become a widely reported research area. Considering the complexity and the recalcitrance of biomass, many works focused on the transformation of biomass derived platform molecules to fuels and high-added value chemicals. For example, C5 sugars are key representative compounds of the hemicellulose fraction of lignocellulose, which can be converted to valuable platform molecules and subsequently valorized into high-added value products [2]. Furfural (F) is an important platform chemical, which can be obtained via dehydration under mild conditions from xylose, a typical C5 sugar.

Furfural can undergo reactions typical for aldehydes like acetalization, acylation, aldol and Knoevenagel condensations, reduction to alcohols, reductive amination to amines, decarbonylation, oxidation to carboxylic acids and Grignard reactions. Besides, the furan ring can be subjected to alkylation, hydrogenation, oxidation, halogenations and nitration reactions. Due to the electron-withdrawing effect of the carbonyl group, the furan ring is less susceptible to hydrolytic ring cleavage and Diels-Alder cycloaddition reactions. Therefore, furfural is considered to be an attractive platform chemical for the production of a

wide range of chemicals, e.g. solvents (tetrahydrofuran), plastics (in particular, polyamides), resins via furfuryl alcohol and fuel additives (methylfuran, methyl-tetrahydrofuran, valerate esters, ethylfurfuryl and ethyltetrahydrofurfuryl ethers and C10–C15 coupling products) [2]. Around 60–70% of the global furfural production is converted to furfuryl alcohol [2,3]. It is widely reported that furfural can be further transformed into various compounds by hydrogenation, such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF). Most of these reactions were performed in batch conditions [4–8] with noble or transition metals based catalysts, while only a few of them were performed in continuous flow [7,9]. Especially, these reactions were performed using only either lab-synthesized or commercial catalysts, with a simple comparison of existing results obtained under different conditions. Regarding to the advantages of flow chemistry, such as faster, safer reactions and easy scale-up, it would be interesting to give a comparison of catalytic performance of both lab-synthesized and commercial catalysts under same reaction conditions in continuous flow system. Previous work from our group has provided insights into the reaction pathway comparing noble metal and transition metal catalysts (Scheme 1), showing favorable results for Pd based catalysts [9]. The mechanism of furfural conversion on palladium catalysts was also studied by other researchers based on density functional theory (DFT) [10].

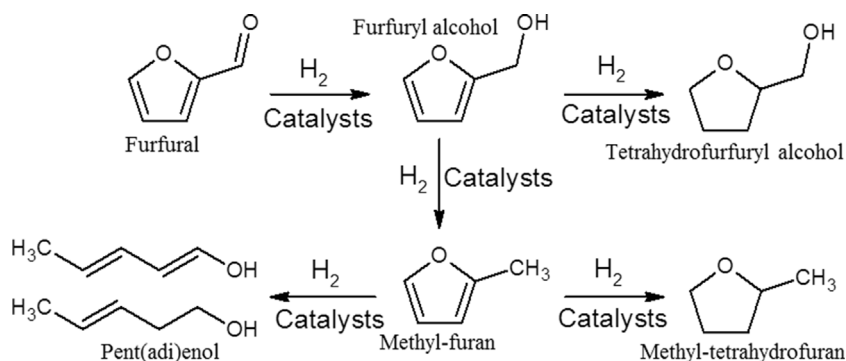
Despite the excellent conversion and selectivity of Pd catalysts, adding magnetic properties to the catalyst would be preferable for catalyst recovery through applying an external magnetic field, which would result in a more straightforward and cost-effective separation method as compared with conventional methods, as illustrated in previous reports [11–14]. Magnetically separable Pd based nanocomposite

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<http://dx.doi.org/10.1016/j.cattod.2017.07.011>

Received 7 May 2017; Received in revised form 4 July 2017; Accepted 8 July 2017
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Scheme 1. Reaction pathway in the catalytic furfural hydrogenation using heterogeneous catalysts.

materials have shown good catalytic activities before in different organic synthesis, such as oxidation and C–C coupling [15–18]. Interestingly, temperature and pressure were reported to have significant positive effects to the reaction [19]. In previous work in our group on continuous flow furfural hydrogenation with hydrogen gas, relatively mild conditions were used (90 °C, 50 bar, 0.3 mL min⁻¹) [9]. In continuation of our previous work, we employ a lower catalyst loading, but at higher temperature and longer residence time, using both lab-synthesized and commercial catalysts to provide a comparison in terms of activity and stability. This study on hydroconversion of furfural attempts to further progress towards the industrial valorization of hemicellulose derived compounds in lignocellulosic biomass.

2. Experimental

2.1. Reagents

Chemicals were purchased from Sigma-Aldrich [Pluronic P123, tetraethyl orthosilicate, palladium (II) acetate, tetraammineplatinum (II) chloride hydrate, iron nitrate nanohydrate, furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, aluminum isopropoxide], Panreac [37% HCl, ethanol] and Merk [Fe(NO₃)₃·9H₂O] respectively. All chemicals were used as purchased in the experiments without any further purification.

2.2. Synthesis of SBA-15 and Al-SBA15

SBA-15 silica was prepared according to the procedure reported by Bonardet et al. [20]. More specific, Pluronic P123 surfactant (8.0 g) was dissolved into a solution of deionized water (260 mL) and HCl (12 M, 40 mL) under vigorous stirring at 40 °C for 2 h. Subsequently, 7 g of tetraethyl orthosilicate (TEOS) were added dropwise to the above solution. The mixture was stirred at 40 °C for 24 h, followed by hydrothermal treatment at 100 °C for 48 h in an oven. The liquid phase was removed by filtration and the obtained white solid was dried at 60 °C. The template was removed by calcination at 600 °C for 8 h. The Al-SBA support was synthesized using a modification of the protocol previously reported by our group [21]. After filtration and drying dried at RT, the solid was calcined under nitrogen atmosphere at 600 °C for 2 h and then in air for an additional 6 h.

2.3. Synthesis of Cu-Pd/Al-SBA-15

The continuous flow deposition of palladium oxide nanoparticles on Al-SBA-15 was performed under a series of conditions using a recently reported innovative continuous setup [22]. A stainless-steel reactor was packed with Al-SBA-15 support set between two plugs of quartz wool to prevent the solid support to move in the reactor upon pumping in the flow of the metal precursor feed solution. Separately, a 0.5 wt% Pd solution in ethanol was prepared using palladium (II) acetate as Pd precursor. The solution was filtered off prior to flow through the system

to avoid the presence of any undissolved metal precursor. The system started with pumping a solution of pure ethanol (0.5 mL min⁻¹, 5 min) through the catalyst bed to wet the support. The temperature of the reactor was then set to 150 °C and the feed was changed to the 0.5 wt% Pd solution. The incorporation was conducted under optimized flow rates (0.5 mL min⁻¹) and circulation time (15 min). At the end of the process, the feed was again switched to ethanol which was pumped through the Pd-incorporated catalyst to remove physisorbed/unreacted Pd species on the catalyst. The resulting Pd/Al-SBA-15 was recovered from the reactor and calcined at 400 °C for 4 h under air. Following, the Cu nanoparticles were supported on Pd/Al-SBA-15 material by a mechanochemical protocol using a planetary ball mill (Retsch 100) under previously reported optimized conditions (350 rpm, 10 min) [23] yielding the Cu-Pd/Al-SBA-15 bimetallic catalyst after calcination at 400 °C for 4 h in air.

2.4. Synthesis of (Pd,Pt)/SBA-15

Pd/SBA-15 and Pt/SBA-15 materials were synthesized following a previously reported mechanochemical protocol for the straightforward preparation of the supported metal nanoparticles on SBA–aluminosilicates [23]. The appropriate amount of Pd and Pt precursor (palladium (II) acetate and tetraammineplatinum (II) chloride hydrate, respectively) to reach the theoretical Pd and Pt contents of 2 wt% Pd and Pt, respectively. The pattern SBA-15 and precursor were milled together in a planetary ball mill (Retsch 100) under previously reported optimized conditions (350 rpm, 10 min) [23]. Upon incorporation of the metal, the sample was calcined at 400 °C (4 h, in air). The obtained materials were highly reproducible from batch to batch.

2.5. Synthesis of Pd/MAGSNC

5% Pd/MAGSNC was synthesized using a mechanochemical method according to the protocol reported previously by our group [24]. In detail, 0.5 g synthesized SBA-15 was grinded with 1.34 g Fe(NO₃)₃·9H₂O, 0.25 mL propionic acid and an appropriate amount of the palladium precursor [Pd(Ac)₂] in a Retsch PM-100 planetary ball mill (18 10 mm stainless steel balls, 10 min, 350 rpm) to reach a theoretical 5 wt% Pd loading. The nanocomposite was slowly heated (1 °C min⁻¹) to 300 °C under air and kept at 300 °C for an additional 30 min.

2.6. Continuous flow hydrogenation

The hydrogenation of furfural was performed in a H-Cube Pro apparatus (ThalesNano, see Fig. S1 in the Supporting information (SI)). Both lab-synthesized and commercial catalysts (ca. 100 mg) were packed in CatCart cartridges, a stainless-steel tube with length of 70 mm and inner diameter 4 mm. The synthesized SBA catalysts based were swollen upon absorbing solvent; therefore, the SBA supported catalysts were first diluted with celite at 1:1 mass ratio prior to package. A feedstock solution of 0.2 M furfural in ethyl acetate (EA) was

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