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Supported Pd nanoparticle catalysts with high activities and selectivities in liquid-phase furfural hydrogenation

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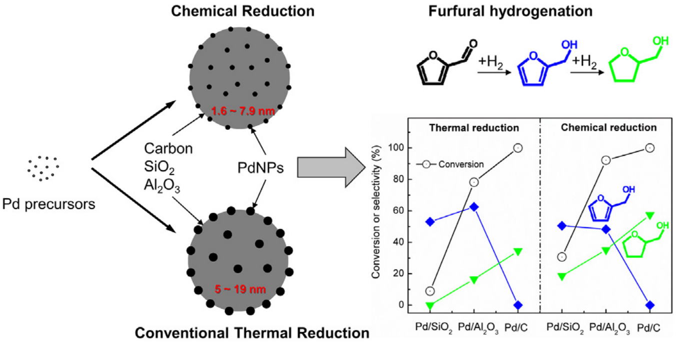
GRAPHICAL ABSTRACT



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ABSTRACT

Highly dispersed and ultrafine Pd nanoparticles (NPs) deposited on carbon, silica, and alumina supports were prepared by chemical reduction (CR) using sodium borohydride, in the presence of trisodium citrate as a stabilizer. For comparison, supported Pd catalysts were also prepared through impregnation followed by thermal reduction (TR) and capillary inclusion of the colloidal Pd NPs (CI). The activities and selectivities of the prepared catalysts were evaluated in the liquid-phase furfural (FAL) hydrogenation reaction under 20 bar H_2 at 180 °C. Under these conditions, FAL was converted via two distinct pathways to produce either furan via decarbonylation or furfuryl alcohol (FA) via aldehyde hydrogenation. Subsequently, furan and FA were converted to tetrahydrofuran and tetrahydrofurfuryl alcohol (THFA), respectively, via ring hydrogenation. 2-Methylfuran was also produced from the hydration of FAL. To verify the efficiency of the preparation methods, the size of the Pd NPs, the degree of metal dispersion, and the type of supports were correlated with the catalytic conversions and selectivities of FAL hydrogenation. It was confirmed that the 5 wt% Pd/C catalysts possessed highly dispersed

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Abbreviations: BF-STEM, bright field scanning TEM; CI, capillary inclusion; CR, chemical reduction; DI, deionized; FA, furfuryl alcohol; FAL, furfural; FFT, fast Fourier transform; HRTEM, high-resolution transmission electron microscopy; GC, gas chromatography; HAADF-STEM, high-angle annular dark-field scanning TEM; ICP-AES, inductively coupled plasma-atomic emission spectrometry; MF, 2-methylfuran; NP, nanoparticle; FID, flame ionization detector; TEM, transmission electron microscopy; THF, tetrahydrofuran; THFA, tetrahydrofurfuryl alcohol; TR, thermal reduction; XRD, X-ray diffraction

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small Pd NPs with large metallic Pd surface areas, which resulted in high conversions and selectivities towards THFA in the FAL hydrogenation reaction compared to conventional supported catalysts.

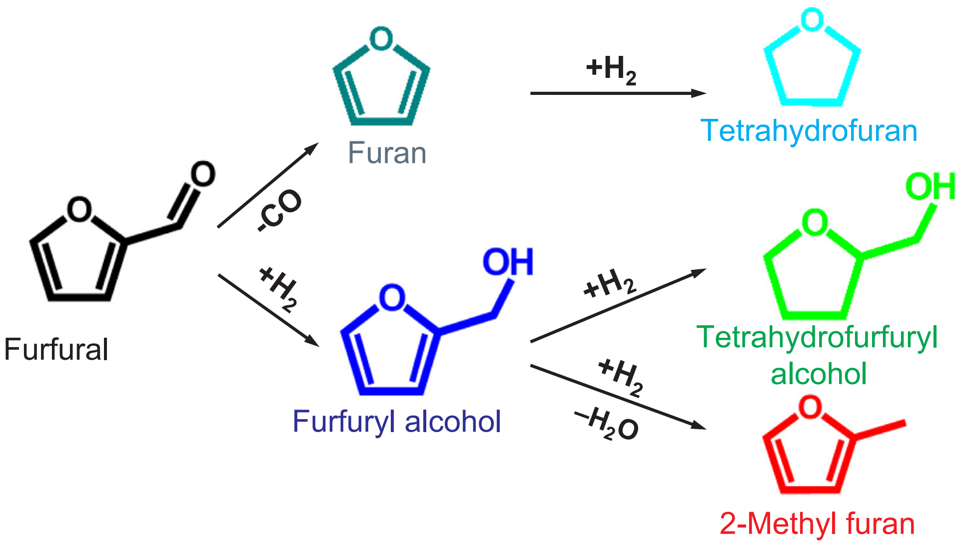
1. Introduction

In the field of heterogeneous catalysis, significant attention has been paid to enhancing catalytic properties by the highly dispersed deposition of an active metal onto a support [1–3]. To minimize the consumption of precious metals and achieve the desired high dispersion, the preparation of small (i.e., nanometer or atomic scale) metal particles is of particular interest. Indeed, the recent development of nanochemistry offers efficient ways to load small nanoparticles (NPs) onto high surface area supports [4–6]. However, the organic capping molecules stabilize colloidal NPs must be removed to maximize the number of active sites on the NP surfaces [7,8]. Although the use of harsh washing conditions and high-temperature treatment methods has been applied to eliminate these organic molecules, the resulting colloidal NPs tend to be a poor alternative to existing supported catalysts prepared by general impregnation methods, due to the trace amount of organics [9,10]. As such, the development of an efficient preparation method to produce a highly dispersed active species on a support with a large specific surface area is of particular importance.

With the increasing demand for eco-friendly products and the associated replacement of petroleum-based chemicals, the interest in biomass conversion has also increased [11–15]. As unsaturated oxygenate species are abundant in decomposed biomass components, the catalytic conversion of biomass derivatives, such as heterocyclic molecules containing alcohol or aldehyde moieties, is important not only for the energy industry but also to improve the fundamental understanding of various catalytic processes [16–24]. In this case, furfural (FAL) was selected as a model compound [22,23], as it can be catalytically converted into furan, tetrahydrofuran (THF), 2-methylfuran (MF), furfuryl alcohol (FA), and tetrahydrofurfuryl alcohol (THFA) through the reaction pathways shown in Scheme 1. In furfural hydrogenation, production of FA has been most intensively studied, because FA can be used as a potential fuel/fuel additive or solvent for the production of resins [25]. On the other hand, THFA is widely used as an environmentally benign solvent, because it is degradable, less toxic, and more stable than unsaturated furan compounds. Furthermore, it is used as a feedstock for the preparation of 1,5-pentanediols which have applications in mono esters and polyurethane manufacturing [26–28]. Therefore, needs for the production of THFA from furfural are gradually increasing.

To date, several catalysts have been employed for the selective hydrogenation of FAL, with its liquid-phase hydrogenation being carried out using supported metal catalysts based on copper chromite, Cu, Ni, Mo, Co, Pt, Rh, Re, and Pd [29–37]. The products obtained following the chemical transformation of FAL on such transition metal catalysts are mainly determined by the affinity of the reaction intermediates towards the metal itself. For example, FAL undergoes hydrogenation to FA on weakly-binding Cu catalysts through carbonyl adsorption [29,30], whereas "flat" adsorption through the furan ring is anticipated on Pd catalysts [31–32,38]. In addition, the Pd-catalyzed FAL hydrogenation demonstrated competition between the aldehyde hydrogenation and decarbonylation pathways upon variation in the reaction conditions and the specific characteristics of the Pd catalyst. Indeed, FAL undergoes selective hydrogenation to MF and THFA over Pd catalysts at low temperatures in the aqueous phase [39,40], while at higher temperatures, decarbonylation to furan is favored [31–32,40–43]. Recent results have also revealed that the activity and product selectivity are also affected by the size of NPs and the type of support employed [35–36,44–46].

Herein, we report preparation ways of supported catalysts composed of well-dispersed Pd NPs immobilized on a range of supports. The chemical reduction (CR), impregnation followed by thermal reduction (TR), and capillary inclusion of the Pd NPs (CI) were used for the preparation of the Pd NP catalysts [6]. To verify the efficiency of these methods in varying both the size of the Pd NPs and the degree of metal dispersion, the use of three different supports (i.e., carbon, SiO_2, and Al_2O_3) were examined and the resulting supported catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 physisorption, CO chemisorption, and inductively coupled plasma-atomic emission spectrometry (ICP-AES) techniques. Finally, liquid-phase FAL hydrogenation was conducted over the as-prepared Pd catalysts to determine the effect of the Pd catalyst structure on the catalytic activity and selectivity. We found higher performances in the production of THFA over highly dispersed Pd/C catalysts which were prepared by chemical reduction method than over conventional supported catalysts with larger Pd particles. The hydrogenation of FAL



Scheme 1. Reaction pathways and corresponding products of the liquid-phase furfural hydrogenation reaction.