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Catalytic conversion of vanillic acid to catechol by palladium acetate/bis(aminomethyl)-*nido*-dicarba-undecaborane (11) system

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ABSTRACT

The vanillic acid was converted to catechol using a catalyst system of $PdAc_2/[Na]^+[7,8\text{-bis(aminomethyl)-}$*nido*$\text{-}C_2B_9H_{10}]$. The 90.3% yield of catechol was achieved from vanillic acid in 4 h using the system at 240 °C. The reaction was also compared using catalyst system of $PdAc_2$/TMEDA (*N,N,N′,N′*-tetramethylethylenediamine), $PdAc_2$/dppe (1,2-bis(diphenylphosphine)ethane) and Pd/AC (activated carbon) under the same conditions. The product, catechol, was characterized by ^1H and ^{13}C NMR spectra and its yield was determined by a high-performance liquid chromatography (HPLC).

1. Introduction

Catechol is a naturally occurring chemical, which can be isolated directly from several plants including beech wood and mimosa catechu [1–4]. Synthetic catechol is commercially available and, currently, it has been used as a precursor to pesticides, flavors and fragrances [5–7]. It has also been used as a common building block in organic synthesis to prepare pharmaceutical compounds [5–7]. For industrial use, the catechol is prepared by (1) the hydrolysis of *ortho*-halogen-substituted phenols or ortho dihalobenzenes under suitable conditions with hot aqueous basic solutions; (2) the dehydroxylation of salicyaldehyde using hydrogen peroxide; (3) the replacement of sulfonic groups by alkali fusion, and (4) the hydroxylation of phenol using hydrogen peroxide [5,8,9]. However, these methods have some inherent limitations of considerably lower product yields and the use of highly corrosive reagents. On the other hand, all direct synthetic approaches involve fossil fuels as the original starting materials. Fossil fuels have been used as one of the essential chemical resources for many centuries. Considering the depletion of fossil fuels and increased environmental pollution because of their rapid consumption, the discovery of green and sustainable chemical and energy resources is therefore warranted.

The biomass is well recognized as a sustainable source of fuels and chemicals [10–12]. In case of chemical production using biomass, new processes need to be developed to produce high value-added chemicals and fuel additives. Lignin is increasingly drawing attention as a suitable renewable resource to produce aromatic chemicals, particularly phenolic compounds. For example, phenolics comprising mainly vanillic acid, syringic acid and vanillin have been produced from organosolv beech wood lignin in a reasonable yield of 33% [13,14]. In addition, separation and purification technology has been well developed for biomass conversion processes and >99 wt% of the phenolics can be recovered [13–17]. Producing catechol from lignin is a relatively straightforward process, and thus more efforts are warranted for this potentially promising technology. Lignin can be depolymerized by oxidation or reduction reactions to generate the aromatics, and the major products are methoxyl group-functionalized phenolics, such as phenol, guaiacol and vanillic acid [18–20]. A deep oxidation depolymerization of lignin often produces phenolic acids, including vanillic acid [13,21]. We have already demonstrated that lignin-based sources can produce terephthalic acid by a cascade fix-bed

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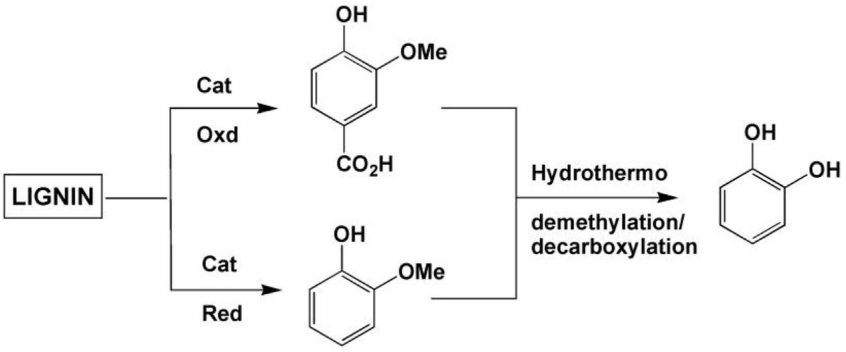
process including hydrogenation demethylation and carboxylation reactions [22]. Accordingly, the vanillic acid and syringic acid were converted to terephthalic acid in two steps *via* an intermediate of *p*-hydroxybenzoic acid. In this work, the methoxyl group-functionalized phenolics, such as vanillic acid, were used as model compounds to demonstrate this concept as illustrated in Scheme 1.

2. Results and discussion

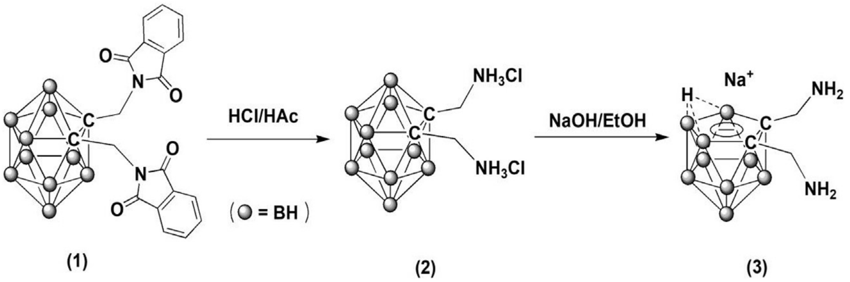
It has been reported that methoxyl-functionalized phenols, derived from lignin resources, can undergo demethylation to form the corresponding arenes [23–29]. However, there are very limited reports associated with demethylation of the methoxyl-functionalized phenols to produce catechol. Nevertheless, to improve the valorization from lignin, it is necessary to use a process that does not require the addition of hydrogen. In this work, the phenolic compounds are prepared by a catalytic hydrothermal demethylation reaction in aqueous media. The vanillic acid and guaiacol were selected as the model compounds to investigate the catalytic conversion to produce catechol. Palladium acetate has been widely used in organic synthesis as an efficient catalyst and, therefore it was used as the catalyst for the hydrothermal conversion reported here. On the other hand, carborane-based multidentate ligand, sodium salt of [7,8-bis(aminomethyl)-*nido*-$C_2B_9H_{10}$] anion, was prepared and used as a catalyst component because of its stability in both the acidic and basic media [30]. For comparison, the reactions were also investigated with catalyst systems of $PdAc_2$/TMEDA, $PdAc_2$/dppe and Pd/AC under the same conditions.

The ligand, $[Na]^+$[7,8-bis(aminomethyl)-*nido*-$C_2B_9H_{10}]^-$, was prepared according to the reaction pathway shown in Scheme 2. The precursor (**1**), 1,2-bis(phthalimidomethyl)-1,2-dicarda-*closo*-dodecaborane (12), was prepared according to the procedure published elsewhere [31]. After deprotection and acidification of the functional moiety with hydrochloric acid, the resulting bis(aminomethyl)-*ortho*-carboranyl hydrochloride, $[1,2\text{-}(NH_3CH_2)_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}]^{2+}[Cl^-]_2$ (**2**), was obtained in 81% yield. Compound **2** was reacted further with sodium ethoxide in ethanol to produce the corresponding sodium compound (**3**), $[Na]^+[7,8\text{-}(NH_2CH_2)_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$, in 75% yield as a colorless salt. Compounds **2** and **3** showed the typical infrared absorptions of methylene and amine functional groups in the IR spectra, as well as the B-H group in the ^{1}H NMR spectra measured in the solvent of D_2O and DMSO-d_6, respectively as presented in Fig. 1. Compound **2** showed NMR peaks of CH_2 at $\delta = 4.38$ ppm and of BH at a range of 1.10–2.90 ppm, respectively; whereas the NMR spectrum of **3** exhibited two types of BH peaks at −0.80–3.20 ppm and −2.90 ~ −2.20 ppm for cage BH and bridge BH, respectively. The presence of NMR peak of bridge BH in **3** confirmed the successful decapitation of **2**. The chemical shifts of CH_2 groups attached to the carborane cage shifted to higher field from 4.38 ppm to 3.10 and 2.92 ppm. The NH groups showed broad resonances at a range of 4.80–7.60 ppm due to the H-D interaction. The ^{13}C NMR spectra exhibited the peaks for methylene groups and for carbons of the polyhedral carborane cage at 39.72 (CH_2), 74.13 (C_{cage}) ppm for **2**; and 35.21(CH_2), 54.93 (C_{cage}) ppm for **3**, respectively, in methanol-d_4. The resonances of both CH_2 and cage carbons shifted to higher field. The ^{11}B NMR spectra showed peaks at −5.42 (4B) and −12.77 (6B) ppm for **2**, and -11.36 (3B), −19.44 (4B), −37.51(1B), −39.70 (1B) ppm for **3** in methanol-d_4, respectively. The peaks of −37.51, −39.70 ppm are as a result of the decapitation of *closo*-carborane cage **2**. Unfortunately, our attempts to grow single crystals of these compounds were not successful. The FT-IR spectra also exhibited strong absorption peaks at 2520 cm^{-1} and 2519 cm^{-1} for **2** and **3**, respectively, which are attributed to B-H stretching modes of vibrations (ν_{BH}).

Defunctionalization of phenolic compounds, vanillic acid, guaiacol and syringic acid, to produce the catechol and pyrogallol was carried out in a Parr reactor using a solvent mixture of water and DMA (v/v = 1:2) at 240 °C. The reactions were not conducted



Scheme 1. Synthesis of catechol from lignin through phenolics.



Scheme 2. Synthesis of the sodium salt of bis(aminomethyl)-*nido*-carborane anion.

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