Journal of CO_2 Utilization 24 (2018) 328–333

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Selective hydrodeoxygenation of lignin β-O-4 model compounds and aromatic ketones promoted by palladium chloride with acidic CO_2/MeOH system

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ARTICLE INFO

Keywords:
Carbon dioxide
In situ acid
Lignin
Palladium
Hydrodeoxygenation

ABSTRACT

Selective hydrogenolysis is a crucial challenge for lignin valorization. A $PdCl_2$-catalyzed hydrogenolysis of C—OH bond of various lignin β-O-4 alcohol model compounds was developed for preparation of corresponding phenethoxybenzene in 78–98% isolated yield. Notably, the introduction of low-pressure CO_2 (1 MPa) remarkably improves the reaction efficiency and selectivity of phenethoxybenzene. Neither over-reduction of aromatic ring nor further debenzylation was detected. This is understandable that the *in situ* methylcarbonic acid generated from CO_2 and methanol acts as an acidic catalyst and enhances the leaving ability of hydroxyl group of β-O-4 alcohols. Besides, the present $PdCl_2$/CO_2/MeOH catalyst system proved to be effective for reductive cleavage of C—O bonds of β-O-4 ketones, producing ethylbenzenes accompanied with phenols in high yields. Furthermore, this protocol could also be extended to selective hydrodeoxygenation of the carbonyl group to methylene in aromatic ketones. As a sound reaction medium, such *in situ* CO_2/MeOH acidic system could be inherently neutralized by depressurizing CO_2, providing feature advantages for simple post-processing and none waste disposal.

1. Introduction

One of the promising ways to sustainably supplying energy, materials and chemicals could be the efficient utilization of renewable carbon resources e.g. lignin biomass. As one of the most abundant biomass, lignin accounts for 15–30 wt % of lignocellulosic biomass and could be regarded as an ideal source of aromatic compounds [1]. However, efficient and selective conversion of lignin faces great challenge due to the three-dimensionally amorphous structure of this robust biopolymer. Most researches have focused on splitting the most recurring β-O-4 alkyl–aryl ether linkage that mirrors the representative linkages in lignin.

In targeting the valorization of lignin, various methodologies including reduction [2], oxidation [3], solvolysis [4], hydrolysis [5] are developed. Among a number of pathways for lignin valorization, hydrogenolysis is one of the most prevalent strategies because it enables the conversion of oxygen-rich lignin to a set of deoxygenated fuels and chemicals. Importantly, methods that enable selective cleavage of carbon-carbon or carbon-heteroatom bonds (OH, OR, *etc.*) in lignin to well-defined chemicals are highly desired. In this regards, hydrodeoxygenation (HDO) is regarded as the most important process in bio-oil up-grading to produce hydrocarbons [6]. Selective hydrodeoxygenation of the lignin-derived monomers has been successfully achieved by combining metal catalyst (e.g. Pd, Pt, Rh, Ru) and acid (H_3PO_4, HCOOH, CH_3COOH, $–SO_3H$, and –OH) in an aqueous phase or ionic liquids [7]. Metal-catalyzed hydrogenation and acid-catalyzed hydrolysis were also supposed to work cooperatively during the reaction. Solid acids, such as Nafion/SiO_2, zeolite (HZSM-5), have also been reported as a replacement of mineral acids, thus facilitating the depolymerization of oxygen-rich lignin [8].

Recently, direct investigation on the reactivity of the oxidized lignin model compounds (β-O-4 ketones) has been reported with varying degrees of success (Scheme 1). Several groups have studied the effective deconstruction of β-O-4 ketone model compounds to acetophenone, esters, acids and phenol [9]. The oxidation of α-C—OH of β-O-4 alcohol to β-O-4 ketone could decrease the C—O bond energy, thus facilitating subsequent C—O bond cleavage of the β-O-4 linkage [10]. Stahl and coworkers described a formic acid-induced depolymerization of oxidized lignin to aromatics that results in more than 60% yield of low molecular-mass aromatics [9a]. Besides, catalytic reductive C–O bond

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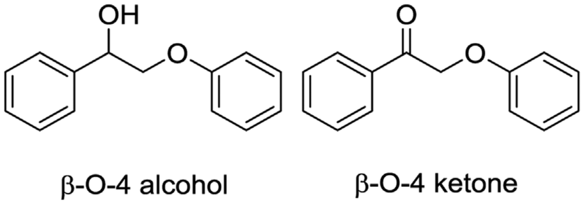
https://doi.org/10.1016/j.jcou.2018.01.019
Received 17 December 2017; Received in revised form 13 January 2018; Accepted 24 January 2018



Scheme 1. Representative structures of β-O-4-linked model compounds.

cleavage promoted by photocatalyst, such as $[Ir(ppy)_2(dtbbpy)]PF_6$ [9b–c] or carbazolic copolymers (CzCPs) [9d] in the presence of formic acid and DIPEA have also been described.

Since the lignin reduction in the presence of acid is a well-known process, replacing mineral acids with environmentally benign process may allow for an increase in reaction efficiency as well as offer environmental benefits. As well-known, the utilization of carbon dioxide as a C1 building block for the production of chemical products has attracted much attention [11]. Besides, as a kind of weak acidic reaction medium, *in situ* acidic system involving CO_2 *i.e.* CO_2/H_2O or CO_2/ROH has been applied in organic synthesis, providing numerous advantages such as adjustable acidity, self-neutralization and simple post-processing compared with traditional strong acidic system from the viewpoint of green chemistry and clean technology [12]. Interestingly, such *in situ* acids can act as efficient reaction media for the hydrogenolysis of benzylic alcohols via a Pd/C catalyst [13]. As a consequence, we envisaged that selective hydrogenolysis of lignin β-O-4 model compounds would be reasonable in *in situ* acidic CO_2/ROH system to form deoxygenated products.

We have firstly applied the CO_2-expanded methanol medium for highly selective hydrogenolysis of two kinds of lignin β-O-4 model compounds via a homogeneous $PdCl_2$ catalysis (Scheme Scheme 2). The hydrogenolysis of C—OH bond of various β-O-4 alcohols performs well to afford a series of phenethoxybenzenes in excellent yields with high chemoselectivity when CO_2 is introduced as a tunable reagent. This is probably due to the methylcarbonic acid *in situ* generated from CO_2 and methanol protonates hydroxyl group and enhances its leaving ability [14]. Over reduction of the aromatic ring and further debenzylation is hampered, therefore maintaining the aromaticity and decreasing in hydrogen consumption. Phenethoxybenzene is a kind of promising source of phenol for fine chemicals synthesis, and ethylbenzene for polymer and fuel industry [15]. Intriguingly, as to the hydrogenolysis of β-O-4 ketones, the present $PdCl_2/CO_2$/MeOH catalyst system is proved to be effective for reductive cleavage of C–O bonds, producing ethylbenzenes accompanied with phenols in high yields. In addition, the hydrodeoxygenation of various aromatic ketones also work well, which is an important transformation in organic synthesis as well as bio-oil upgrading to fuels and high-value chemicals [16].

2. Experimental

2.1. Materials and methods

Lignin β-O-4 model compounds were synthesized by reacting 2′-bromoacetophenones with phenols according to the published procedures [17]. The aromatic ketones and transition metal catalysts were purchased from Alfa Aesar China Co., Ltd and Aladdin Reagent Inc. All the other reagents were obtained commercially from Tianjin Guangfu Fine Chemical Research Institute and used without further purification except for the alcohols, which were distilled prior to use. ^{1}H NMR spectra were recorded on a Bruker 400 spectrometer in $CDCl_3$ and $CDCl_3$ (7.26 ppm) was used as internal reference, ^{13}C NMR spectra were recorded at 100.6 MHz in $CDCl_3$ and $CDCl_3$ (77.0 ppm) was used as internal reference. GC-MS data were collected on Finnigan HP G1800 A. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-50, 30 m × 0.25 μm) using a flame ionization detector.

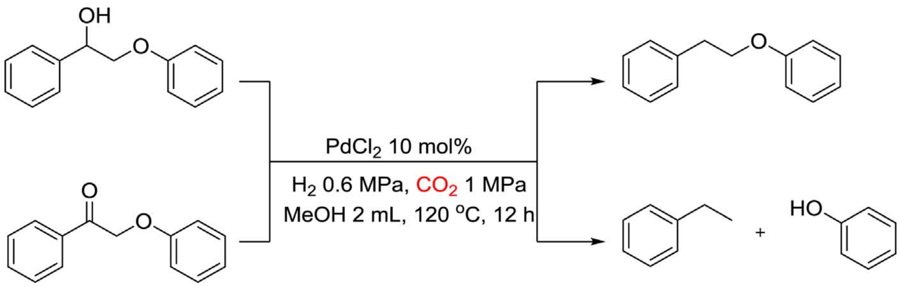
2.2. General procedure for hydrogenolysis of lignin β-O-4 model compound

A mixture of 2-phenoxy-1-phenylethanol (0.5 mmol, 0.1071 g), $PdCl_2$ (10 mol%, 8.9 mg), MeOH (2 mL) were placed in a 50 mL stainless steel autoclave equipped with an inner glass tube in room temperature. CO_2 (1 MPa) and H_2 (0.6 MPa) were subsequently introduced into the autoclave and the system was heated under the predetermined reaction temperature for 25 min to reach the equilibration. The mixture was stirred continuously for the desired reaction time. After cooling, products were then diluted by ethyl acetate and analysed by GC and ^{1}H NMR. The residue was purified by column chromatography on silica gel (200–300 mesh, eluting with n-hexane/ethyl acetate from 50:1 to 10:1) to afford the desired product. The isolated products were further identified with NMR spectra and GC-MS.

3. Results and discussion

3.1. Optimization conditions

We began our investigation using 2-phenoxy-1-phenylethanol (**1a**), a common lignin β-O-4 alcohol model compound, as the substrate at 120 °C for 12 h to validate our hypothesis. Table 1 summarizes the results about catalysts and solvents screening under the given pressure. Initially, the reaction performed in the presence of 10 mol% $PdCl_2$ in 2 mL H_2O, giving 47% yield of phenethoxybenzene (**2a**) in the absence of CO_2 (entry 1). However, 13% yield of ethylbenzene and 7% yield of phenol were detected, indicating the cleavage of the C—O bond in aryl ether also took place. Interestingly, the reaction under 7 MPa CO_2 gave nearly doubled **2a** yield with 96% product selectivity (entry 2 *vs.* 1). This is presumably because the *in situ* formed acid from H_2O and CO_2 could provide an acidic environment, resulting in facile formation of a better leaving group ($–OH_2^+$) from hydroxyl group. In addition, the CO_2-expanded methanol could also increase the solubility of hydrogen and improve the mass transfer of the reaction system. Subsequently, $PdBr_2$ and $Pd(OAc)_2$ were examined respectively. However, lower activity with poorer chemoselectivity was observed compared to $PdCl_2$ (entries 3–4 *vs* 2). Pd^{II}-catalyzed reduction reactions are likely to undergo the reduction via the intermediacy of Pd°. The H–X reductive elimination pathway may be more favored when an anion is chloride in comparison with bromide and carboxylate. Heterogeneous metal



Scheme 2. Hydrogenolysis of lignin β-O-4 model compound in *in situ* acidic CO_2/MeOH system.