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Catalytic C–O bond cleavage in a β -O-4 lignin model through intermolecular hydrogen transfer



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ARTICLE INFO	A B S T R A C T
Keywords:	A base-free and redox neutral approach for the selective breaking of arvl ether bond (C–O) contained by a lignin
Redox-neutral	model compound mimicking a β -O-4 linkage is reported. A palladium loaded metal-organic framework (MOF)
Hydrogenolysis	was used as a catalyst for this purpose. The reaction proceeds through dehydrogenation of henzylic alcohol
Lignin model	was used as a cataryst for this purpose. The relation protected information and purpose and the second seco
Heterogeneous catalysis	the reaction to take place.

1. Introduction

Lignocellulosic biomass composed of cellulose, hemicellulose and lignin, is the most abundant, cheap, and inexpensive renewable organic resource that can potentially replace the fossil feedstocks in the sustainable production of fuels and carbon-based chemicals [1–4]. Lignin comprises 25-30% of the total biomass and is considered as one of the renewable feedstocks for the sustainable production of value-added aromatic chemicals [5-7] and materials [8]. However, as compared to other lignocelluloses (cellulose and hemicellulose), this biopolymer has been underutilized to its maximum potential for energy production, for instance, as a boiler fuel to generate heat in paper and pulp industries [3,9]. This is mainly because of recalcitrant nature of C-O bonds and recondensation reactions of highly reactive degraded-products that render depolymerization of lignin quite challenging [10]. Lignin depolymerization, however, is considered as an entry point towards the valorization of lignin to obtain low-molecular-weight compounds (lignin platform compounds), which can be chemically modified into carbon-containing chemicals and fuels [11,12]. Thereby deconstruction of lignin via C–O bond cleavage utilizing catalytic depolymerization [6] of lignin via hydrogenation [13], hydrogenolysis [14], and catalytic transfer hydrogenolysis (CTH) [15,16] has been utilized which provide low-yield of ill-defined products. However, these approaches require a base to proceed at an appreciable rate.

Studies show that oxidation of benzylic hydroxyl group contained by the most abundant motif (a β -O-4 linkage) of lignin, reduces the bond

dissociation energy of C-O bond from 69.2 kcal/mol to 55.9 kcal/mol [17]. So obtained oxidized lignin has been shown to provide high yield (60 wt%) of low molecular weight products [18]. However oxidation of lignin required in the first step of aforementioned approach in the presence of green and inexpensive oxidants and reusable catalysts has not been achieved yet [19,20]. Dehydrogenation of benzylic alcohol at Cα of β-O-4 linkage to obtain oxidized lignin is another attractive strategy that doesn't require any external oxidant [21]. Recently, several groups have reported a number of heterogeneous [22,23 24 25 26 16 27] and homogeneous [28 29 23] catalysts operating under mild and redox-neutral conditions and regardless of the progress, a heterogeneous catalyst for completely redox-neutral cleavage of C-O bonds in β -O-4 linkages in model compounds as well as in native lignin is still desirable. In this work, we report a complete redox-neutral cleavage of C-O bond in β-O-4 lignin model compounds using a reusable Metal-Organic Framework (MOF) integrated with palladium nanoparticles (NPs) labeled as Pd@MOF. MOFs has emerged as a promising class of template material because of their high surface area, ordered pores, tunable pore window and inherent host-guest chemistry [30]. The synergistic effect between the metal NPs and MOFs matrix is reported to promote the performance of a catalyst [31]. Herein, MIL-101-Cr [32] was selected as a catalyst support due to its high crystallinity, stability in water, thermal stability and Lewis acidity which may promote the cleavage of O-H bonds [33].

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Scheme 1. Synthesis of β -O-4 model compounds 4a-e.

2. Experimental

2.1. Synthesis of MIL-101 (Cr)

MIL-101-Cr was synthesized by following a procedure reported in literature [34]. Typically, Cr(NO₃)₃·9H₂O (2.50 mmol, 1 g), terephthalic acid (2.50 mmol, 0.415 g), and concentrated HCl (12 M, 0.25 mL) were dissolved in deionized (DI) water (25 mL). The resulting solution was placed in a Teflon-lined stainless-steel autoclave reactor and heated at 200 °C for 12 h. After the autoclave reactor was cooled down to room temperature, green precipitates were separated by centrifugation (5000 rpm, 20 min) and washed with hot DMF to remove unreacted organic linker. The synthesized MOF was activated in ethanol at 80 °C for 12 h. Finally, the MOFs was separated by centrifugation and dried overnight at 80 °C in a vacuum oven.

2.2. Synthesis of Pd@MOF

Palladium nanoparticles (NPs) were encapsulated into the MOFs using well established double solvent approach [35]. In this method, *n*hexane and water waere used as hydrophobic and hydrophilic solvents respectively. For 3 wt% metal loading, 300 mg of activated MOFs was dispersed in *n*-hexane (60 mL), the resultant mixture was sonicated for 20 min until it became homogenous and stirred for additional 2 h. An aqueous solution (0.4 mL) of K₂PdCl₄ (0.084 mmol, 35 mg) was dropwise added over 20 min under constant and vigorous stirring which was continued for 6 h. The volume of water containing metal salt must be less than or equals to pore volume of MOFs so that it could easily be absorbed within hydrophilic pores. The product was separated through centrifugation and dried overnight at 100 °C in a vacuum oven. Overwhelming reduction (OWR) approach using an aqueous solution of NaBH₄ was used to reduce Pd(II) in the MOFs. In a typical experiment, freshly prepared (0.6 M) aqueous NaBH₄ solution (5 mL) was added to Pd(II)/MOF dispersion under continuous stirring, which resulted in the generation of catalysts as a dark-colored suspension. The synthesized materials were separated by centrifugation and dried overnight at 80 $^\circ C$ in a vacuum oven.

2.3. Synthesis of β -O-4' lignin model compounds

2.3.1. General method of synthesis of 2-phenoxy-1-phenylethanol (2a)

Lignin model substrates were synthesized according to a modified procedure reported in the literature (Scheme 1) [36]. A 100-mL round bottom flask, equipped with a reflux condenser and magnetic stirrer, was charged with phenol (**2a-e**, 12 mmol) and K_2CO_3 (15 mmol) in acetone (50 mL). 2-Bromoacetophenone (1, 10 mmol, 1.99 g) in 50 mL acetone was then added dropwise into the reaction mixture with constant stirring at room temperature. While stirring, the suspension was refluxed for 6 h. After complete consumption of **1** (TLC monitoring), the reaction mixture was filtered to remove K_2CO_3 and the filtrate was

concentrated in *vacuo*. The resulting solid was recrystallized in hot petroleum ether to obtain phenoxyphenylethanones (**3a-e**) in excellent (\sim 90%) yields

2.3.2. General method for the synthesis of β -O-4 model compounds

Phenoxyphenylethanones (**3a-e**, 10-mmol) were dissolved in a mixture of THF/water (5:1) (25 mL) and NaBH₄ (0.74g, 20 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 5 h. Afterward, aqueous NH₄Cl solution (30 mL) was added to quench the excess NaBH₄ in the reaction. The mixture was filtered directly into a separatory funnel containing ethyl acetate to extract the product (3×30 mL). Combinned ethyl acetate layer was washed with water and dried over MgSO₄. Finally, the extract was concentrated in *vacuo* to obtain an off-white solid product.

2.3.3. 2-phenoxy-1-phenylethanol (4a):(85% yield)

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.46 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 5.3 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 5.13 (dd, J = 8.8, 3.0 Hz, 1H), 4.11 (dd, J = 9.5, 3.1 Hz, 1H), 4.02 (t, J = 9.2 Hz, 1H).

2.3.4. 2-(2-methoxyphenoxy)-1-phenylethanol (4b), (80% Yield)

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.44 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.07–6.98 (m, 1H), 6.95–6.92 (m, 2H), 6.91–6.88 (m, 1H), 5.11 (dd, J = 9.4, 2.8 Hz, 1H), 4.19 (dd, J = 10.0, 2.8 Hz, 1H), 3.98 (t, J = 9.8 Hz, 1H), 3.88 (s, 3H).

2.3.5. 2-(4-methoxyphenoxy)-1-phenylethanol (4c): (83% Yield)

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.46 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 9.3 Hz, 2H), 6.84 (d, J = 9.3 Hz, 2H), 5.10 (dd, J = 8.8, 3.1 Hz, 1H), 4.07 (dd, J = 9.7, 3.1 Hz, 1H), 3.97 (t, J = 9.5, 9.2 Hz, 1H), 3.78 (s, 3H).

2.3.6. 2-(2,6-dimethoxyphenoxy)-1-phenylethanol (4d) (75% Yield)

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.39 (d, J = 7.6 Hz, 2H), δ: 7.34 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.04 (t, J = 8.4 Hz, 1H), 6.61 (d, J = 8.4 Hz, 2H), 4.96 (dd, J = 9.9, 2.5 Hz, 1H), 4.44 (dd, J = 10.9, 2.6 Hz, 1H), 3.72 (t, J = 10.4 Hz, 1H), 3.88 (s, 6H).

2.3.7. 2-(4-methylphenoxy)-1-phenylethanol (4d) (77% Yield)

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.46 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 5.12 (dd, J = 8.9, 3.0 Hz, 1H), 4.09 (dd, J = 9.6, 3.0 Hz, 1H), 3.98 (t, J = 9.3, 1H), 2.29 (s, 3H).

2.4. Catalytic reaction

In general procedure for redox neutral C–O bond cleavage in 4a, a reaction tube (Schlenk Flask) charged with a magnetic stirrer bar and catalyst (20 mg) was used. The reaction tube was evacuated and refilled



Fig. 1. SEM images of (pristine MOF (a) and Pd-loaded MOF (b). EDX elemental maps of a Pd-loaded MOF (c) are shown in (d-f). PXRD diffraction patterns of the MOFs are shown in (g) along with a simulated pattern.

 Table 1

 Solvent screening for the redox-neutral C–O bond cleavage.

	он о –	Catalyst					
4a			5a	2a		3a	
Sr.	Catalyst	Solvent	Tem.	Conv.	Yield (%)		
#			(°C)	(%)	5a	2a	3a
1	Pd@MOF	EtOH	120	18	_	_	>99
2	Pd@MOF	MeCN	120	0	-	-	-
3	Pd@MOF	H_2O	120	56	39	39	61
4	Pd@MOF	Dioxane	120	5	-	-	>99
5	Pd@MOF	Xylene	120	0	-	-	-
6	Pd@MOF	Diglyme	120	0	-	_	_
7	Pd@MOF	THF	120	0	-	-	-
8	MIL-101	EtOH/	120	0	-	-	-
	(Cr)	H_2O					
9	Pd@MOF	EtOH/	120	>99	>99	>99	<1
		H_2O					
10	No catalyst	EtOH/	120	0	-	-	-
	-	H_2O					

Reaction conditions: substrate (0.1 mmol), catalyst (2.8 mol% based on Pd), solvent (10 mL each). The reaction tube was purged with nitrogen and the reaction mixture was stirred under nitrogen atmosphere for 6 h.

with nitrogen gas (three times). Lignin model substrate 4a (0.1 mmol, 21 mg) and ethanol/water (1:1, 10 mL) was added in the reaction tube under a continuous flow of nitrogen. The reaction mixture was refluxed at 120 $^{\circ}$ C in an oil bath for 6 h. After cooling the reaction mixture to room temperature, it was centrifuged to separate the catalyst. The products were extracted with DCM or ethyl acetate (30 mL). The extract was concentrated under reduced pressure and analyzed with GC–MS.

3. Results and discussions

To achieve homogeneously dispersed and cavity-fit Pd NPs into the cages of MOFs, we employed a double solvent approach (DSA) [37] in which two solvents, water (hydrophilic) in small amount and *n*-hexane (hydrophobic) in large amount are used (experimental section). The presence of *n*-hexane in excess over-spreads the external surface of MOFs, ensuring the diffusion of aqueous Pd-salt into the pores through capillary action.

Surface morphology and crystal size of as-prepared catalyst was analyzed through scanning electron microscopy (SEM). SEM image of pristine MOF (MIL-101-Cr) revealed octahedral shape of crystals with an average size of 2 μ m and a rather broad size distribution. A few rod-like crystals spotted at different places (Fig. 1a) that might correspond to MIL-88B geometry [38]. The morphology of the MOFs remained intact even after the loading of Pd NPs (3 wt%) as indicated in SEM images in

Fig. 1b. Incorporation of Pd within the MOF crystals was confirmed through Energy Dispersive X-ray (EDX) analysis. EDX elemental maps of a MOF crystal (Fig. 1c) are presented in Fig. 1d-f that confirm the successful incorporation and uniform distribution of Pd within the MOF.

Crystallinity of pristine and Pd@MOF was also analyzed by Powder X-Ray diffraction (PXRD) analysis (Fig. 1g). In diffraction patterns of pristine MOF, peaks at of 8.5°, 9.1°, 10.3°, 16.5°, and 18° (2 θ) matched closely with the simulated patterns of MIL-101. No significant change in diffraction pattern was observed upon the incorporation of Pd within the MOF and the peaks matched well with the simulated patterns of MIL-101. An extra peak, however, at 28.3° (2 θ) was observed in the diffractogram Pd@MOF which could not be explained.

Pd@MOF was tested in redox-neutral cleavage of aryl ether bonds in lignin model compounds. For screening experiments, the compound PhCH(OH)CH₂-OPh (**4a**) containing β –O-4' ether linkage to generate phenol (**2a**) and aryl-ketone (**3a**) was used.

The reactions were performed without adding any base or external hydrogen source in order to demonstrate the utilization of intramolecular hydrogen that promote the cleavage of C-O bonds (Table 1). When reaction was performed in EtOH only 18% conversion to 3a along with cleaved products 2a and 3a was observed (entry 1). No conversion of the substrate was observed in acetonitrile (entry 2), dioxane (entry 4), xylene (entry 5), diglyme (entry 6) and THF (entry 7). However, H₂O showed significantly higher conversion, with the 39% yield of aimed products, respectively (entry 3). Pristine MOF was unable to convert the substrate either (entry 8) which shows the role of Pd in promoting both dehydrogenation and C-O bond cleavage reactions. Surprisingly, with the mixture of H₂O and EtOH (1:1) compound 4a was almost quantitatively converted into desired products 5a and 2a with negligible amount of 3a (entry 9). Keeping in mind the detection of small amount of 3a, we hypothesized that cleavage of C-O bond in 4a may proceed through a Pd-catalyzed dehydrogenation of C_{α} -OH bond followed by cleavage of C₀-O bond via intramolecular hydrogen transfer. To prove this hypothesis firstly, the reactions were conducted without a catalyst and with pristine MOF (with no Pd NPs), but the substrate remained unchanged and no desired products were observed (entry 9-10). To further demonstrate the mechanism, several other reactions were conducted with the same reaction conditions. Performing the reaction with 3a as substrate favored our hypothesis because the formation of 5a and 2a was not observed. In order to omit the possibility of dissolved oxygen that might facilitate dehydrogenation, the reaction was performed in completely deaerated solvent. The dissolved oxygen was removed with argon purging for half an hour. The results were incredibly good with complete conversion into desired products indicating the dissolved oxygen playing no role in this reaction.

The experiments were performed to screen the best temperature conditions for the redox-neutral cleavage of C–O bond (Table S1). The reactions carried out at 30 °C,60 °C and 90 °C lead to no conversion. The reaction performed at 120 °C within 2 h offered excellent yield of aimed

Table 2

Redox-neutral cleavage of C–O bond in methoxy-substituted $\beta\text{--}O\text{--}4'$ ether linkages.



Reaction conditions: Substrate (0.1 mmol), catalyst (2.8 mol% based on Pd) and solvent (10 mL, 1:1). The reaction tube was purged with nitrogen and the reaction mixture was stirred under nitrogen atmosphere for 6 h.

products. To reveal the time screening or time resolved conversion six different sample were taken hourly from the reaction mixture, which was heated at 120 °C. After complete workup, these samples were analyzed with GCMS to determine the conversion of **4a** into products. Except the first sample taken after 1 h, **4a** was not detected in any of the sample, indicating its complete conversion.

With the optimized reaction conditions, the catalyst was employed for the redox-neutral cleavage of C–O bond in β -O-4 ether linkages substituted with methoxy groups at various aryl positions. (Table 2). The substrates in which the methoxy group was introduced at R₄ and R₅ positions were completely converted into corresponding phenol and aryl ketone in excellent yields (entry 2–3). Delightfully, methoxy groups present at R₃ position did not influenced the conversion, with the same reaction conditions excellent yield of the products was achieved (entry 4). The electron-donating methoxy groups did not produce any passive effect on the performance of catalyst. The substrate having relatively poor electron donating group at R₄ position was also converted into cleaved products with excellent yields (entry 5).

We also checked the reuse of the catalysts for five successive runs. The catalysts provided high conversion (>99%) and yield (above 94%) with minor loss in the activity (Fig. S1).

4. Conclusions

We have demonstrated a complete redox-neutral C–O bond cleavage in lignin model compounds without utilizing any base and external hydrogen source. Pd NPs encapsulated in MIL-101-Cr show selective breaking of C–O bonds in a series of β –O-4 lignin model compounds. The studies revealed that, C–O bond cleavage occurred through a simultaneous dehydrogenation of side-chain alcoholic groups and intramolecular hydrogen transfer reaction and therefore doesn't require any external hydrogen. Our catalyst is reusable and offers a broad substrate scope.

CRediT authorship contribution statement

Muhammad Ahsan Usman: Investigation. Maham Naeem: Investigation. Muhammad Saeed: Resources, Conceptualization. Muhammad Zaheer: Conceptualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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