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Self-hydrogen transfer hydrogenolysis of β -O-4 linkages in lignin catalyzed by MIL-100(Fe) supported Pd-Ni BMNPs

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A MIL-100(Fe) supported Pd-Ni BMNPs catalyst has been fabricated, the catalyst exhibits superior catalytic performance toward intramolecular transfer hydrogenolysis of lignin model compounds and organosolv lignin. Alcoholic groups ($C_{\alpha}H$ -OH) of lignin were exploited as the hydrogen source, selectively cleavage of β -O-4 linkages in lignin was realized without extra hydrogen donor. This protocol was suitable for organosolv lignin as well as model compounds, several phenols and functionalized acetophenones were detected when treated extract lignin under our system. The catalyst exhibits outstanding catalytic stability during the reaction process, which can be ascribed to the porous structure and strong water stability of MIL-100(Fe). The excellent catalytic performance of Pd₁Ni₄/MIL-100(Fe) highlights the "synergistic effect" between the BMNPs and the functional synergy between MNPs and MOFs, and our work shows the bright future of BMNPs and MOF in catalysts' development for sustainable chemistry.

Introduction

Increasing global awareness of the diminishing fossil energy reserves and global efforts to reduce greenhouse gas emissions have accelerated the study about utilization of renewable biomass for sustainable development.¹⁻³ Nowadays, more than 10% of the world's primary energy is biomass, and it is the fourth largest source of energy in the world (following oil, coal, and natural gas).⁴ Lignocellulose is the most abundant form of biomass as well as a promising renewable organic resource with abundant supplies, which was expected to replace fossil resources in the production of carbon based fuels.^{3,5} Lignin, one of the three main constituents of lignocellulosic biomass as well as the only large volume renewable feedstock that comprises aromatics on the earth, has the potential to supplement or replace coal or crude oil as the source of arenes.^{1, 6-9} However, current utilization process of lignin is still not gratifying

since lignin has mainly been burned to supply energy and recover pulping chemicals in the operation of paper mills,^{2, 10} further studies on getting higher value from lignin in an economic way are still necessary due to the requirements of green and sustainable society.^{8, 11}

Lignin is a natural amorphous polymer, which can be viewed as a disordered polymer of phenylpropanolic units linked by ether (e.g., α -O-4, β -O-4, and 4-O-5) and C-C (β - β , β -5, and 5–5) bonds, among those linkages, the β -O-4 linkages comprise approximately 50% of native lignin linkages.^{1, 12, 13} Since depolymerization is a critical step for the lignin utilization process because it could provide a source of low-molecular-mass feedstocks suitable for downstream processing, much attention has been focused on the dissociation of the relatively weaker β -O-4 linkages due to their high abundance in lignin.^{10, 14} State-of-the-art strategies for β -O-4 dissociation linkages can be broadly classified into oxidation,¹⁵⁻¹⁹ hydrolysis^{11, 20, 21} and hydrotreating,²²⁻²⁴ amongst those different strategies, hydrotreating process is regarded as the most promising options.²⁵ Nevertheless, hydrotreating processes often operate under high hydrogen pressures and high temperatures, which easily leads to dearomatization and deoxygenation of lignin.^{26, 27} In recent breakthroughs, catalytic cleavage of C-O linkages through hydrogen transfer reactions were also made, reductively cleaves lignin utilizing isopropyl alcohol,²⁸ HCOONH₄²⁹ and hydrosilanes³⁰ as mild hydrogen donor represents another excellent options for lignin depolymerization.³¹ In fact, there are a plethora of alcohol moieties in the natural lignin, which could act as the hydrogen source for the C-O linkage cleavage reaction, and this provide a potential atom economic method for lignin depolymerization without adding external hydrogen donor.^{2, 9}

Ellman and coworkers reported a redox neutral C-O bond cleavage reaction of β -O-4 model compounds using RuH₂(CO)(PPh₃)₃ as the catalyst and xantphos as the ligand, the reaction was completed within 2h, affording phenolic and functionalized acetophenone products with high selectivity, but the ruthenium precursor was inexchangable, only RuH₂(PPh₃)₄ showing significant activity catalyst and the catalyst recyclability is problematic.³² Moreover, Samec and coworkers reported the first heterogeneous C-O bond cleavage under redox-neutral reaction conditions,

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commercial available Pd/C was applied as the catalyst, the reaction could proceed under air, but catalytic amounts of NaBH₄ must be added in the reaction.³³ Those outstanding works laid the road map for the utilization of intramolecular hydrogen for the C-O linkage of lignin, and inspired us to plough deeper in this area.

Our previously work has demonstrated that bimetallic nanoparticles (BMNPs) show extraordinary catalytic performance in _ hydrogenolysis of lignin due to their unique electronic states and structural conformations,^{34,} and this lead us to explore BMNPs as a ____ potential catalyst in the redox-neutral C-O linkage dissociation reaction.³⁵⁻³⁷ Recently, porous metalorganic frameworks (MOFs) was emerged as a class of very promising catalyst matrix due to it's high surface area, porosity, and chemical tenability, 41, 42 and it was reported that functional synergy between MNPs and MOFs can effectively synergize their respective multiple advantages, resulting boost in catalytic performance.^{41, 43-45} Since catalyst carrier is reported to be another key factor determining the hydrodeoxygenation activity of catalysts,³⁸⁻⁴⁰ we decide to explore the application of MOFs as catalyst carrier in the lignin depolymerization reaction. Herein, MIL-100(Fe) was chosen as the catalyst support for the BMNPs due to it's highly porous structure, water stability and strong lewis acid, which was reported to promote the O-H bond cleavage.^{42, 46} Several supported BMNPs were screened for intramolecular hydrogen transfer C-O cleavage of lignin model compounds, the Pd1Ni4/MIL-100(Fe) catalyst shown the optimal catalytic performance, highlighting a gratifying synergistic effects between BMNPs and MOF.⁴¹ The lignin model compounds were transformed into corresponding phenols and functionalized acetophenones in 6 h without adding extra hydrogen source, and little molecules were also obtained when organosolv lignin were treated in our system. The catalytic system exhibits a broad [a] Reaction conditions: 1a (0.2mmol), catalyst (4 mol %, based on Pd), 1mL substrate scope as well as excellent stability during the reaction process, no significant loss in catalytic performance was observed when the catalyst was recycled for five times.

Results and discussion

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At the initial stage of our study, 2-Phenoxy-1-phenethanol (1a) was selected as the model substrate to optimize the condition for unsupported Pd₁Ni₄ BMNPs catalyze hydrolytic cleavage of β -O-4 bonds, but the substrate was clearly cleaved into phenol and acetophenone in a contrast experiment in the absence of hydrogen gas (Table 1, entry 1). Considering that a small amount of 2phenoxy-1-phenylethanone (4a) was detected as the by-product, we proposed that C-O bond cleavage may proceed via an intramolecular hydrogen transfer way. Then, we turn to explore the reaction conditions for self-hydrogen transfer hydrogenolysis of β -O-4 linkages. Firstly, to verify the indispensable role of the catalyst, the reaction was allowed to perform without a catalyst, no aimed products was detected (entry 2). Contrast experiments using monometallic nanoparticles as the catalyst were carried out, Pd NPs show moderate activity and selectivity for this reaction (entry 3), the dehydrogenation product 4a was the main by-product. Together with our previous work,³⁴ we could say that alloying Ni with Pd can improve the utilization efficiency of the molecular hydrogen and speed up the hydrogenolysis process due to the electronic effects.

No reaction happened when using Ni NPs as the catalyst (entry 4), and this indicates that Pd was the main active for this reaction. Table 1. Optimization for the reaction conditions.

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	1a	2a	3a	4a	
Entry	Catalyst	Tem. (°C)	Conversion (%) ^b	2 or 3 (%) ^b	4(%) ^b
1	Pd ₁ Ni ₄	130	100	95	5
2	No Catalyst	130	0		
3	Pd	130	75	60	40
4 ^c	Ni	130	0		
5	Pd ₁ Ni ₂	130	95	83	17
6	Pd ₁ Ni ₆	130	97	98	2
7	Pd ₁ Ni ₈	130	100	96	4
8	Pd_1Co_4	130	81	98	2
9	Pd ₁ Fe ₄	130	100	80	20
10	Pd ₁ Cu ₄	130	~5		100
11	Ru ₁ Ni ₄	130	49	82	18
12	Pd ₁ Ni ₄	80	0		
13	Pd ₁ Ni ₄	100	0		
14	Pd ₁ Ni ₄	115	30	40	60
15	Pd ₁ Ni ₄	150	100	>95	<5
16 ^d	Pd ₁ Ni ₄	130	80	90 ^e	10
17	$Pd_1Ni_4/g-C_3N_4$	130	<5		
18	Pd ₁ Ni ₄ /WO ₃	130	~99	>95	<5
19	Pd ₁ Ni ₄ @MIL-100(Fe)	130	78	91	9
20	Pd ₁ Ni ₄ /MIL-100(Fe)	130	~99	>95	<5
21	Pd/MIL-100(Fe)	130	77	71	29

 H_2O , the reaction mixture was stirred under argon for 6 h. [b] Yields and selectivity were determined by GC and GC-MS. [c] 1.6 mol % Ni nanoparticles was applied as the catalyst. [d] The reaction was proceed under air. [e] The produced acetophenone was totally transformed into benzoic acid.

Compositions of the BMNPs were reported to be vital for catalytic efficiency, BMNPs with different metal ratio (entries 5-7) and constituent (entries 8-11) were prepared and tested in this reaction. Keeping the Pd content of the BMNPs still, BMNPs with higher Ni contents show better activity and selectivity for the hydrogen transfer reaction, and 1:4 was emerged to be the most suitable Pd/Ni ratio. Besides, alloying Pd with Co can improve the selectivity to some extent, but the conversion of the substrate is moderate (entry 8). However, when Pd₁Fe₄ BMNPs was employed as the catalyst, the substrate was equivalently transformed but the selectivity was moderate (entry 9). Interestingly, decreased catalytic activity was observed when Pd was alloyed with Cu (entry 10). Ru₁Ni₄ BMNPs was also tested in this reaction, but the catalytic efficiency was far inferior to Pd₁Ni₄ BMNPs (entry 11). Primary attempts to lower the reaction temperature show that the reaction do not happen when the temperature was lower than 100 °C (entries 12-14), and the BMNPs still show excellent catalytic activity at higher temperature (entry 15). Interestingly, the reaction can also proceed under air, except that the produced acetophenone was totally transformed into benzoic acid (entry 16).

Since the recycle process of the unsupported Pd-Ni BMNPs is

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not easy to handle, we than attempt to immobilized the BMNPs on different matrices. Initially, graphitic carbon nitride $(g-C_3N_4)$ was selected as the support due to it's excellent stability and metal immobilization ability,⁴⁷ but no reaction was observed when $Pd_1Ni_4/g-C_3N_4$ was applied as the catalyst (entry 17), and we think this may be owing to the extremely strong coordination between g-C₃N₄ and metal nanoparticles. Then, we try to use tungsten oxide as the support, as it was reported that dissociation of H₂ can happen at the interface of metal NPs and tungsten oxide.48 The catalytic activity and selectivity of Pd₁Ni₄/WO₃ catalyst for the transformation of model compound 1a were found to be quite outstanding (entry 18), however, at the following substrate scope stage, the Pd₁Ni₄/WO₃ catalyst do not show excellent functional group tolerance. Finally, MIL-100(Fe) was chosen as the matrix in our system because of it's high chemical stability and water stability,^{46,49} moreover, it was reported that the O-H bond cleavage is promoted with the assistance of the Lewis acid activity metal center of the MIL-100(Fe).⁴² The MIL-100(Fe) encapsulated Pd₁Ni₄ BMNPs (Pd₁Ni₄@MIL-100(Fe), preformed Pd-Ni BMNPs was used as nucleation centers for subsequent MIL-100(Fe) growth) and Pd₁Ni₄ BMNPs immobilized on MIL-100(Fe) (Pd₁Ni₄/MIL-100(Fe), prepared by a impregnation-reduction method) were prepared and tested in our reaction system, both the catalytic activity and selectivity of Pd₁Ni₄/MIL-100(Fe) are better than Pd₁Ni₄@MIL-100(Fe) (entry 19 vs entry 20). Notably, when Pd₁Ni₄@MIL-100(Fe) was applied as the catalyst, ethylbenzene was detected as the by-product after the reaction, because BMNPs was covered by a layer of MIL-100(Fe), a part of the produced acetophenone was trapped in the micropore of MIL-100(Fe) and may not release from the catalyst surface on time, so the absorbed acetophenone may be further reduced into ethylbenzene. What's more, Pd/MIL-100(Fe) was also employed as a catalyst in our system, the conversion of the substrate is similar to unsupported Pd NPs, but the selectivity is relatively better, and this stress the importance of MIL-100(Fe) in the catalysis.



Scheme 1. Control experiments to illustrate the reaction mechanism.

Argon, H₂O, 130 °C

To study the reaction mechanism, several mechanism verification experiments were conducted (Scheme 1). If dehydrogenation product 4a was used as the substrate, no reaction occurred under the same reaction condition (Eq. 1), and this favor our initial speculation about this mechanism. Isotope labeling

experiment was also performed to track the flow of H in the substrate, when 1a' was used as the substrate, deuterium was found in acetophenone after reaction (Eq. 2). Furthermore, to verify whether the solvent participate in the reaction or not, D₂O was applied as a solvent in this reaction, and we found almost no deuterium atom was detected in our produced acetophenone (Eq. 3). Finally, no reaction was proceed when 1j was applied as the substrate, which highlights the importance of $C_{\alpha}H$ -OH groups in this reaction. According to those results, a schematic pathway was proposed. As shown in Scheme S1 (SI), the reaction starts with a reversible dehydrogenation of 1 to generate 4 and chemically adsorbed hydrogen ("hydrogen pool") on BMNPs.^{33, 50} To trap the hydrogen, the reaction system was linked with a tube equipped with cyclooctene and a catalytic amount of Pd/C to trap the hydrogen, and cyclooctane was detected after the reaction, although the amount is low, we think the result proved the existence of the "hydrogen pool" in our reaction system. The dehydro-genation ketone 4 is in fast equilibrium with its enol tautomer, which absorbs to BMNPs to generate intermediate 5.²⁹ Then, atomic hydrogen on BMNPs surfaces may insert into the β -O-4 linkage, leading to ether bond cleavage.



Fig. 1 (a) (b) (c) TEM images of the $Pd_1Ni_4/MIL-100(Fe)$ catalyst. (d) size distribution of Pd₁Ni₄ BMNPs. The inlet image of (b) was the

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Morphologies of the Pd1Ni4/MIL-100(Fe) were directly observed by transmission electron microscopy (TEM). As shown in Fig.1, the anomalously spherical BMNPs were encapsulated in the micropores of MIL-100(Fe), this kind of structure can effectively prevent BMNPs from aggregating, guaranteeing an excellent stability of the catalyst. Beside, size of the BMNPs was mainly distributed between 2~3nm, the ultrafine BMNPs provides more contact opportunities between the active sites and substrates, which means higher catalytic efficiency. What's more, the representative high-resolution TEM (HRTEM) image shows the BMNPs have clear crystalline fringe patterns and the lattice fringes align parallel to each other, besides, the lattice distance is measured to be 0.21 nm, which could be assigned to the d-spacing for the (111) plane of Pd-Ni alloy.⁵¹

HRTEM image of the BMNPs.

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Fig. 2 XPS spectrum of the as-prepared $Pd_1Ni_4/MIL-100(Fe)$ catalyst: (a) Pd 3d region (b) Ni 2p region

To ascertain the detail surface chemical states of the samples, XPS measurements were performed. Well-defined peaks corresponding to Pd and Ni species both can be detected, the doublet in **Fig. 2a** with binding energies of 335.2 (Pd $3d_{5/2}$) and 340.5 eV (Pd $3d_{3/2}$) can be assigned to metallic Pd⁰, while the another doublets at 338.1 eV and 342.8 eV are ascribed to the +2 oxidation state of Pd, indicating that oxidation was happened during the characterization process. Besides, as shown in **Fig. 2b**, the Ni species on the surface of the catalyst was consist of metallic Ni as well as Ni oxide and hydroxide, indicating that surface nickel can be easily oxidized to oxide and hydroxide when exposed to oxygen and moisture in air. In addition, the Ni/Pd ratio contents on the catalyst surface determined by XPS was 3.36, almost equivalent to the results determined by ICP (Ni/Pd=3.55, **SI, Table S1**), showing that the Pd–Ni BMNPs in our catalyst is in a random homogeneous alloy form.



Fig. 3 Recycling of the ${\rm Pd_1Ni_4}/{\rm MIL-100}({\rm Fe})$ catalyst in the self-hydrogen transfer hydrogenolysis of C-O linkage in 1a

Once the optimal reaction conditions were established, we turn to investigate the recyclability of the Pd₁Ni₄/MIL-100(Fe) catalyst. Upon completion of the reaction, the catalyst was separated from the reaction mixture by filtration, the catalyst was washed with water and EtOH, dried under vacuum and then directly reused in the next cycle under the same conditions (Fig. 3). The BMNP catalyst could be reused up to five times without losing its activity, the size of the BMNPs after recycle experiments was distribute between 2~5 nm (SI, Fig. S2), no obvious agglomeration was observed. About 20% dropping in selectivity was observed when the catalyst was used for four times, the major by products found was the dehydrogenation product 4a. And we propose that the main reason for the dropping in catalytic selectivity may come from the catalyst loss during the recycled process, so 5% of the catalyst was added to make up the mechanical loss of the catalyst at the fifth cycle of the catalyst, and the catalytic performance of the catalyst almost recover to the initial level. ICP analysis of the reaction solution after the reaction indicated that about 2.1% of the

total Pd and 3.4% of the total Ni was lost during one cycle, which support our proposition that the catalyst amount may influence the selectivity of the reaction.

Table 2. Pd1Ni₄/MIL-100(Fe) catalyzed β -O-4 cleavage of various lignin models.^a

	он	R ³			ОН			
			Pd ₁ Ni	₄ /MIL-100(Fe)			
۲ 1		R ⁴	H ₂ O, 6h					
R∸ 1a-h					R² 2a-h	3a-h		
	Entry	1	R ¹	R ²	R³	R ⁴	Yield [%] ^b	
	1	1a	н	Н	Н	н	>95	
	2	1b	н	н	н	OMe	~99	
	3 ^c	1c	н	OMe	OMe	OMe	84	
	4 ^c	1d	н	OMe	н	OMe	87	
	5 ^d	1e	OMe	н	н	н	91	
	6 ^c	1f	OMe	н	н	OMe	>95	
	7 ^d	1g	OMe	н	OMe	OMe	81	
	8 ^d	1h	Me	н	н	н	93	

^{*a*} Reaction conditions: 0.5 mmol of substrate, 4 mol% Pd₁Ni₄/MIL-100(Fe) catalyst (based on palladium), 2 mL H₂O, the reaction mixture was stirred at 130 °C under argon atmosphere for 6 h. ^{*b*} Yields were determined by GC and GC-MS. ^{*c*} The reaction temperature was 150 °C ^{*d*}The reaction temperature was 180 °C.

With the robust reaction condition in hand, we then turn to evaluate the scope of this protocol, a range of starting materials were explored (Table 2). Gratifyingly, no passive influence on the yield was observed when a methoxy group was introduced at R^3 or R^4 position (**Table 2. entry 2**). However, embarrassment occurred when there were several methoxy groups at R^2 , R^3 , R^4 position, satisfied reaction results were obtained only when the reaction was performed at 150 °C when 1c and 1d were used as the starting material (entries 3-4). The temperature was increased to 180 °C to finish the reaction when 1e was chosen as the substrate (entry 5). Moreover, introducing another methoxy group at R⁴ position of **1e** leads to an enhancement in reaction activity of the substrate, C-O linkage of $\mathbf{1f}$ was equivalently cleaved at 150 $^{\circ}$ C (entry 6). It's worth noting that at the same reaction condition, only minor 1f was transformed into corresponding product when using Pd₁Ni₄/WO₃ as the catalyst, and we think that the difference in catalytic performance may result from the gas enrichment function^{44, 52} of MOFs and the electron transfer effect⁴⁵ between the guest BMNPs and MOFs. Even with an electron donating group at R¹ position, excellent yields were also obtained at 180 °C (entries 7-8). Together with bumpy substrate scope process, we could conclude that electron donating groups at R¹ or R² position may hamper the reaction process, while substitutes at R³ or R⁴ position do not have huge impact on the reaction process. As to the electronic effects of the reaction, we proposed that an electron donating group at R^{\perp} or R^2 may lower the acidity of benzyl, which means that hydrogen release process from the model compound was suppressed. To verify whether the γ -C affects the cleavage of β -O-4 bond, 2-(2methoxyphenoxy)-1-phenylpropane-1,3-diol (1i), whose structure is closer to the true structure of lignin, was prepared and test in our

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system. About 81% yields was obtained at 180 °C for 6h, the main products was identified as 2-methoxyphenol and propiophenone.

Finally, our reaction system was also attempted in the cleavage of organosolv lignin extracted from birch sawdust, organosolv lignin extracted by the similar procedure was reported to contain a high proportion of β -O-4 linkages.¹⁵ 1wt% Pd₁Ni₄/MIL-100(Fe) was applied as the catalyst, the reaction was proceed under argon atmosphere at 180 °C for 6h. After reaction was completed, the catalyst was removed by filtration and the reaction solution was extract with ethyl acetate, the organic layer was analyzed by GC and GC-MS. As shown in the GC-MS spectrum of the depolymerization products (SI, Fig. S1), the GC-MS spectrum of the lignin depolymerization product, several phenols and functionalized acetophenones like guaiacol and 4-methoxyaceto-phenone were obtained, and about 17% monomer yield was obtained after depolymerization, those results clearly confirm that our reaction system was also applicable for real lignin depolymerization.

Conclusions

In summary, Pd-Ni BMNPs immobilized on MIL-100(Fe) was fabricated, which was proven to be highly effective for the selfhydrogen transfer hydrogenolysis of β -O-4 linkage in lignin. Water was used as the green solvent, the dehydrogenation and hydrogenolysis reaction are happened at the same time using alcoholic groups in lignin as the hydrogen donor, offering a more economical choice for large-scale operations of the lignin depolymerization. The Pd₁Ni₄/MIL-100(Fe) catalyst show outstanding stability during the reaction process, no obviously decrease in catalytic activity was observed after 5 cycles. Excellent stability of the catalyst was due to the extraordinary water stability and porous structure of the MIL-100(Fe), the BMNPs was encapsulated into the micropores of MIL-100(Fe), no obvious agglomeration was observed although the reaction was proceed under relatively high temperature. Catalytic cooperation between a MIL-100(Fe) host and guest BMNPs together with synergistic effects of BMNPs include

(i) The BMNPs was encapsulated in the micropores of MIL-100(Fe), preventing the BMNPs from agglomeration, guaranteeing a satisfying catalytic recyclability.

(ii) The electron transfer between Pd and Ni in BMNPs together with the interfacial electron transfer effect between BMNPs and MIL-100(Fe) would result in more electron rich center, which may spur the conversion from H^{\bullet} to H^{-} in the "hydrogen pool", thus boosting the catalytic efficiency.

(iii) MIL-100(Fe) can cooperate with BMNPs to promote the O-H bond cleavage, forming a "hydrogen pool", which could be utilized in the following hydrogenolysis process.

(iv) MIL-100(Fe) can enrich the hydrogen molecules around the active sites to certain degree, which may greatly speed up the hydrogenolysis process.

The excellent catalytic performance of BMNPs/MIL-100(Fe) in our work validate the natural advantages of BMNPs and MOFs, and we believe BMNPs/MOFs has a very bright future in the catalysis field.

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