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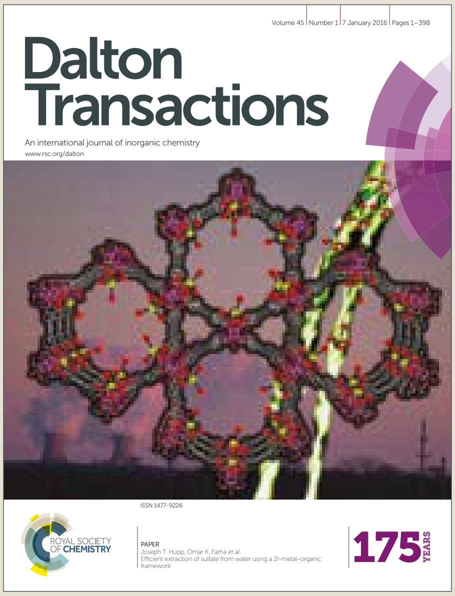

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ARTICLE

Selective hydrogenolysis of C-O bonds in lignin model compounds by Pd-Ni bimetallic nanoparticles in ionic liquids

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The β-O-4 and α-O-4 linkages can be selectively cleaved by Pd-Ni bimetallic nanoparticles in ionic liquids using hydrogen gas as the hydrogen donor under ambient pressure and neutral conditions. No hydrogenation of benzene ring takes place in the catalytic system. A obvious improvement in activity is found compared with single nickel and palladium catalysts based on the results of experiments and characterization. After the reaction, the catalytic system still stays in reactor by simple extraction, which can be reused without further treatment.

Introduction

Lignin is the only large-volume renewable polyaromatic feedstock, which is a potential alternatives to fossil fuels for the production of fuels and chemicals in the near future.[1] However, the current strategy including hydrolysis, reduction, oxidation and microbe for the degradation of lignin into value-added products is inefficient,[2] so it is typically viewed as a waste stream in current biorefinery processes. Inspired by the structure of lignin which is mainly bonded through several types of C_{aryl}-O linkages,[1,2j] selective hydrogenolysis of C-O bonds, especially β-O-4 linkages has become one of the most significant and challenging accesses for the utilization of lignin.[3]

Compared with other metals, nickle catalysts show excellent selectivity in the cleavage of the C_{aryl}-O ether linkages.[4] A series of powerful and high-selective nickel catalysts have been disclosed to selective hydrogenolysis of aryl ethers.[5] Meanwhile, palladium catalysts can selective activation of the C_{aryl}-O bonds,[6] and the cleavage of β-O-4 linkages *via* hydrogen transfer is also achieved by these catalysts.[7] Therefore, we reason that the Pd-Ni bimetallic nanoparticles (BMNPs) are more powerful and higher selective catalysts for the hydrogenolysis of lignin than single Ni and Pd catalyst, because they usually show a combination of properties associated with two different metals and performance superior to their monometallic counterparts due to a phenomenon collectively referred as synergistic effects.[8]

Several nickle based BMNPs have been prepared for the cleavage of β-O-4 linkage,[9] in which the combination of nickle and other noble metals can obvious improve the yields and selectivity of hydrogenolysis. More recently, our group has designed a efficient Pd-Ni BMNPs for the hydrogenolysis of β-O-4 linkages,[10] however, α-O-4 linkages fails to be cleaved, and the hydrogenation of arenols cannot be suppressed in the presence of H_2. On the other hand, ionic liquids (ILs) as green solvents are not only more effective at lignin dissolution than other solvents,[2i,11] but also suitable medias for the generation and stabilisation of metal nanoparticles (MNPs),[12] in which the reaction medium with MNPs can be reused directly by simple extraction or distillation. A few reports have developed several metal NPs in ILs for the selective reductive cleavage of C–O and HDO.[13]

Based on these results, we envisage to explore a Pd-Ni BMNPs in ILs for the selective hydrogenolysis of C-O bonds. Herein, a facile and stable Pd-Ni BMNPs in [bmim]OTf is introduced by which the β-O-4 and α-O-4 linkages can be cleave selectively, moreover no hydrogenation of arene occurs. To the best of our knowledge, there is the first example on selective hydrogenolysis of C-O bonds by Pd-Ni BMNPs in ILs.

Results and discussion

The hydrogenolysis of C-O bonds performance of Pd-Ni BMNPs were investigated *via* selecting **1a** as the model substrate (Table 1). Various Pd-Ni BMNPs in different ILs were prepared for the hydrogenolysis of **1a** (entries 1-9). Only [bmim]OTf and [bsmim]OTf provided moderate yields (entries 6, 9). However the obviously aggregation of NPs was observed during the reaction in [bsmim]OTf, so [bmim]OTf was selected for the further studies. Other types BMNPs in [bmim]OTf were also applied in the reaction, but no satisfactory result was observed (entry 10-17). The temperature was also optimized, and 130 °C was the best option. Pd NPs results in a poor yield, and no reaction occurred catalyzed by Ni NPs (entries 22, 23). Moreover, a simple mixture of Pd and Ni NPs did not lead to a obvious increase in catalytic activity (entry 24), which verified the roles of the synergistic effects in BMNPs.

A higher ratio of nickel in BMNPs lead to a more active catalyst when the total loading of palladium is held constant in

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Electronic Supplementary Information (ESI) available: More experimental, details, ICP and TEM data and NMR studies. See DOI: 10.1039/x0xx00000x

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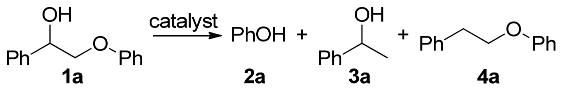
Table 1 Optimization reaction conditions.[a]



entry	IL	T (°C)	catalyst	yield (%)[b]	
				2a	**4a**
1	[hmim]NTf$_2$	100	Pd$_1$Ni$_4$	25	12
2	[hmim]Br	100	Pd$_1$Ni$_4$	12	2
3	[hmim]HSO$_4$	100	Pd$_1$Ni$_4$	13	5
4	[hmim]BF$_4$	100	Pd$_1$Ni$_4$	14	16
5	[hmim]OAc	100	Pd$_1$Ni$_4$	0	0
6	[bmim]OTf	100	Pd$_1$Ni$_4$	70	4
7	[bupy]BF$_4$	100	Pd$_1$Ni$_4$	7	0
8	[pmpip]NTf$_2$	100	Pd$_1$Ni$_4$	0	0
9[c]	[bsmim]OTf	100	Pd$_1$Ni$_4$	72	2
10	[bmim]OTf	100	Pd$_1$Fe$_4$	<1	<1
11	[bmim]OTf	100	Pd$_1$Cu$_4$	2	<1
12	[bmim]OTf	100	Pd$_1$Co$_4$	39	5
13	[bmim]OTf	100	Pd$_1$Zn$_4$	0	0
14	[bmim]OTf	100	Pd$_1$Sn$_4$	0	0
15	[bmim]OTf	100	Ir$_1$Ni$_4$	0	0
16	[bmim]OTf	100	Ru$_1$Ni$_4$	0	0
17	[bmim]OTf	100	Au$_1$Ni$_4$	0	0
18	[bmim]OTf	80	Pd$_1$Ni$_4$	17	7
19	[bmim]OTf	120	Pd$_1$Ni$_4$	78	1
20	[bmim]OTf	130	Pd$_1$Ni$_4$	87	2
21	[bmim]OTf	160	Pd$_1$Ni$_4$	91	9
22	[bmim]OTf	130	Pd[d]	13	0
23	[bmim]OTf	130	Ni[e]	0	0
24	[bmim]OTf	130	Pd[d]+Ni[e]	15	0
25	[bmim]OTf	130	Pd$_1$Ni$_1$	9	3
26	[bmim]OTf	130	Pd$_1$Ni$_2$	73	0
27	[bmim]OTf	130	Pd$_1$Ni$_6$	93	0
28	[bmim]OTf	130	Pd$_1$Ni$_7$	99, 98[f], 76[g]	0, 1[f], 3[g]
29	[bmim]OTf	130	Pd$_1$Ni$_8$	98	0

[a] Conditions: Catalyst 5 mol% (the amount of palladium in the catalyst), IL 1.0 mL, **1a** 0.5 mmol, H_2 1 atm, 12 h. [b] GC yields with dodecane as the internal standard. Only products **2a**, **3a** and **4a** was found in the reaction, so the yield of **2a** is the same as the yield of **3a**. [c] The obviously aggregation of NPs was observed during the reaction. [d] 5 mol% Pd NPs was used. [e] 20 mol% Ni NPs was used. [f] 4 mol% of palladium in the catalyst was used. [g] 3 mol% of of palladium in the catalyst was used.

the reaction at 5 mol% (entries 20, 25-29), and a Pd/Ni molar ratio of 1/7 was found to be optimal presumably owing to the enhancement of hydrogen storage capacity.[9] The Pd$_1$Ni$_7$ BMNPs was detected by the inductively coupled plasma mass spectrometry (ICP-MS) (see ESI, Table S3), which confirmed that the Pd/Ni ratio was consistent with the designed composition of the Pd$_1$Ni$_7$ BMNPs. The excellent yield was also afforded when the amount of palladium in BMNPs could be dropped to 4 mol% (entry 28).

Encouraged by these remarkable results, further investigations on the morphologies of the catalyst were made. Pd$_1$Ni$_7$ NPs were separated from [bmim]OTf by centrifugation, which was suspended in ethanol, deposited on a copper grid coated by a carbon film and then used in transmission electron microscopy (TEM) measurements. As shown in Fig. 1, the as prepared Pd-Ni BMNPs are well-proportioned, anomalously spherical, and the average size of the NPs is about 1.5 nm and 2.0 nm for the freshly prepared and 4 cycle-samples, respectively. Nevertheless, Pd-Ni BMNPs are aggregated obviously after reusing four times (Fig. 1c, 1d).

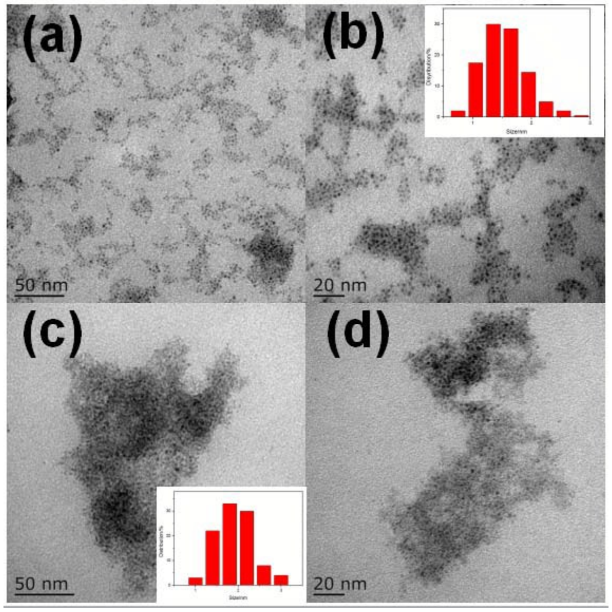


Fig. 1 TEM images of (a) (b) freshly prepared Pd$_1$Ni$_7$ BMNPs in [bmim]OTf (c) (d) Pd$_1$Ni$_7$ BMNPs after 4 cycles. The inset images show the size distribution of Pd-Ni BMNPs.

Furthermore, X-ray photoelectron spectrum (XPS) was also carried out to evaluate the surface composition and electronic state of the Pd-Ni bimetallic catalyst. The XPS results indicate that the ratio of the surface concentration between Pd and Ni is 0.22, which is higher than the results determined by ICP-MS (Table S3 in ESI), so the structure of Pd-Ni BMNPS is mixed alloy, on the surface of which Pd mainly distributes. The hydrogen transfer ability of Pd is weakened due to the surrounded Ni atoms in BMNPs, which makes great contributions to the inhibition in hydrogenation selectivity (geometric effects).[14] Because nickel can be easily oxidized to oxide and hydroxide when exposed to oxygen and moisture in air, the Ni spectral feature of the catalyst consists of metallic Ni as well as Ni oxide and hydroxide, which may segregate its terrace zones, thus preventing benzene ring coordination and hydrogenation.[9c]

As illustrated in Fig. 2b, the peaks located at 335.8 eV and 340.7 eV can be assigned to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$, which confirmed the formation of the Pd-Ni alloy in the BMNPs.[15] The other doublet at 338.3 eV and 343.2 eV is ascribed to the +2 oxidation state of Pd.[8e,16] The 3d$_{5/2}$ binding energy of Pd shifted from 335.6 eV in the Pd catalysts to 335.8 eV in Pd-Ni BMNPs (see Fig. S1 in ESI), indicating electron transfer from Pd to Ni[9,10,17] that creates more electron-rich Ni sites. The electron-rich Ni center may spur the conversion from H• to H$^-$, which significantly speeds up the hydrogenolysis process (electronic effects).[9b] Based on experimental and XPS results, it can be purposed that Ni and Pd promote the participation of each other in the hydrogenolysis reaction through the formation of alloy NPs.

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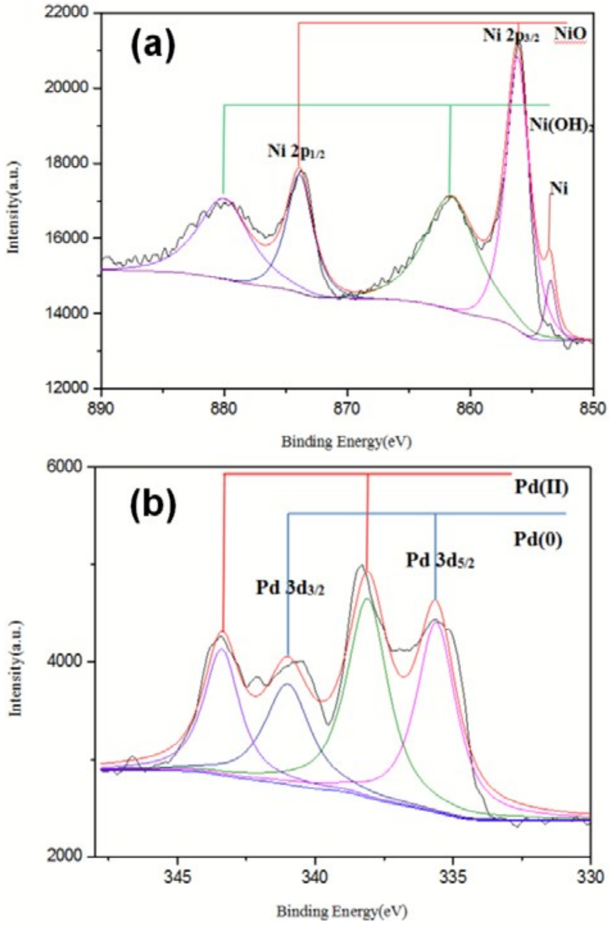
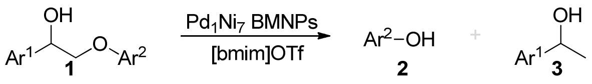


Fig. 2 XPS spectrum of Pi$_1$Ni$_7$ BMNPs: (a) Ni 2p region (b) Pd 3d region.

With the optimized conditions in hands, a series of β-O-4 lignin model compounds were selected to investigate the β-O-4 bond cleavage in more detail (Table 2). Introducing methyl or methoxyl group in Ar^2 ring have no obvious influence in the reaction in all cases, while a evident decrease of yield was observed in the cases of Ar^1 with methoxyl group (entries 5-8) owing to the increased BDE of the β-O-4 linkage and the yield of undesired products **4** (See Table S2 in ESI).[18] Only products **2**, **3** and **4** was found in all reactions (Table 2), so the yields of **2** are the same as the yields of **3**. The α-O-4 lignin model compounds have more reactive than the β-O-4 ones (Table 3), and the hydrogenolysis can be achieved at 100 °C. The methoxyl group on Ar^1 ring can inhibit the process (entries 5, 6), while a electron-withdraw group (nitro group) on Ar^1 ring enhance the transformation (entry 7). In all cases, no hydrogenation product or other byproduct was detected (Table 2 and 3). Only products **6** and **7** was found in all reactions (Table 3), so the yields of **6** are the same as the yields of **7**.

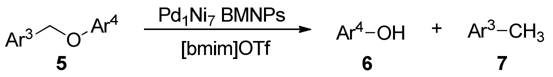
Table 2 The hydrogenolyisis of β-O-4 linkages by Pd-Ni BMNPs in [bmim]OTf.[a]



Entry	Ar^1	Ar^2	Yield (%)^b
1	Ph	Ph	>99
2	Ph	2,6-dimethylphenyl	87
3	Ph	3,5-dimethoxyphenyl	98
4	Ph	2,6-dimethoxyphenyl	95
5	4-MeOC$_6$H$_5$	2,6-dimethoxyphenyl	58
6	4-MeOC$_6$H$_5$	Ph	46
7	3-MeOC$_6$H$_5$	2-MeOC$_6$H$_5$	73
8	3-MeOC$_6$H$_5$	2,6-dimethoxyphenyl	85

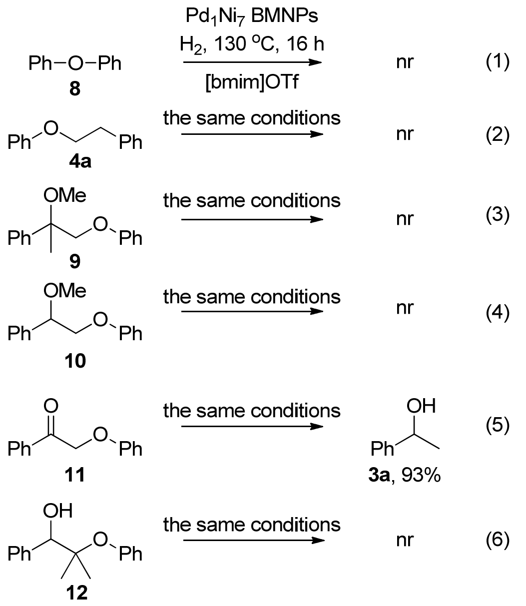
[a] Conditions: **1** 0.5 mmol, Pd$_1$Ni$_7$ BMNPs 4 mol% (the amount of palladium in the catalyst), [bmim]OTf 1 mL, H$_2$ 1 atm, 130 °C, 16 h. [b] GC yields of **2** with dodecane as the internal standard**.**

Table 3 The hydrogenolyisis of α-O-4 linkages by Pd-Ni BMNPs in [bmim]OTf.[a]



Entry	Ar^3	Ar^4	Yield (%)^b
1	Ph	Ph	83
2	Ph	2,6-dimethylphenyl	89
3	Ph	2,6-dimethoxyphenyl	98
4	Ph	3,5-dimethoxyphenyl	95
5	4-MeO	2,6-dimethoxyphenyl	62^c
6	3-MeO	2,6-dimethoxyphenyl	71^c
7	4-O$_2$N	2,6-dimethoxyphenyl	>99^{d,e}

[a] Conditions: **1** 0.5 mmol, Pd$_1$Ni$_7$ BMNPs 4 mol% (the amount of palladium in the catalyst), [bmim]OTf 1 mL, H$_2$ 1 atm, 100 °C, 16 h. [b] GC yields of **6** with dodecane as the internal standard. [c] 130 °C. [d] 80 °C. [e] *p*-toluidine and 2,6-dimethoxyphenol were obtained as the final products.



Scheme 1 Control experiments. Conditions: aryl ether 0.5 mmol, Pd$_1$Ni$_7$ BMNPs 4 mol% (the amount of palladium in the catalyst), [bmim]OTf 1 mL, H$_2$ 1 atm, 130 °C, 16 h; GC yields.

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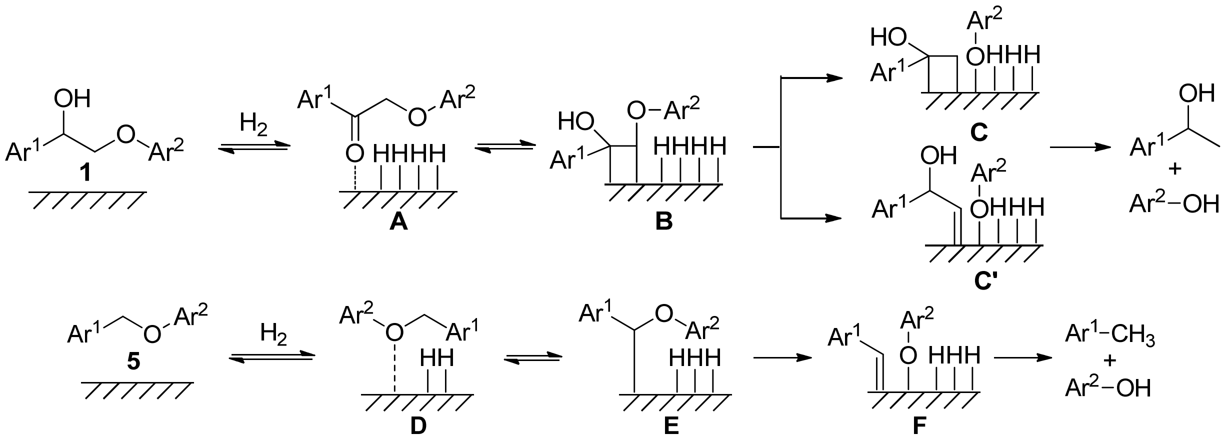

Fig. 3 Proposed mechanisms for the hydrogenolysis of β-O-4 and α-O-4 linkages. Pd_1Ni_7 BMNPs are depicted by surface for clarity.

Further experiments were also performed to investigate the tentative pathway for the hydrogenolysis. Aryl ethers **4a, 8-10**, **12** failed to be cleaved under optimized conditions (eq. 1-4,6), and the hydrogenolysis of **11** proceeded smoothly to afford a excellent yield of **3a** (eq. 5). Based on these results, it can be concluded that (1) the hydrogens at α and β positions of β-O-4 ethanolaryl ethers and the HO-substituted α-carbon are necessary for the reaction; (2) **11** may be a intermediate of the hydrogenolysis.[7a,7c]

Although the detailed mechanism of this reaction remains to be elucidated, a tentative pathway for the hydrogenolysis of C-O bonds by Pd-Ni BMNPs was illustrated in Fig. 3. For the β-O-4 linkages, the reaction starts with a reversible dehydrogenation of **1** and chemically adsorbed hydrogen on catalyst to generate intermediate **A**,[7a,7c] which can be transformed to **B** by further absorbing to BMNPs. According to the Horiuti-Polanyi-type mechanism,[19] the atomic hydrogen may insert into either the α or β position of intermediate **B**. Therefore, two intermediates **C** and **C'** are yielded following inserting metal to the C-O bond. Reductive elimination of aryloxide and enol equivalent (**C**) or carbene (**C'**) lead to the final products. For the α-O-4 linkages, the benzylic C-H can be activated by the catalyst to form **E**. Then, metal inserts to the C-O bond to produce **F**. The hydorgenolysis products are obtained though the reductive elimination of **F**. The [bmim]OTf may also enhance the reaction by the non-covalent interaction,[20] which may play a similar role as the electron-withdraw groups in Ar^1 ring to enhance the acidic of methylene of **5** (See ESI, Fig. S2).

Finally, studies were also conducted to assess the potential for recycling of the reaction medium, and the reaction of **1a** was selected as the model reaction. After completion of reaction, the product underwent in-flask extraction with minimum amounts of an organic solvent (ethyl ether). The IL phase with BMNPs can be reused directly in the next run. The process could be repeated 4 times without an obvious change in yields (Fig. 4). The inactivation of the catalyst may be caused by the aggregation of the NPs after each reaction (Fig. 1c,1d). The loss of NPs in each run may be another main reason as well.

Experimental

General

All chemical reagents are obtained from commercial suppliers and used without further purification. GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120 kv. X-ray photoelectron spectroscopy (XPS) were performed on a ESCALAB 250Xi spectrometer, using a Al Kα X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV. 1H NMR spectra are recorded on an AVANCE III 500 Bruker spectrometer operating at 500 MHz in $CDCl_3$.

Synthesis of Pd_1Ni_7 BMNPs in [bmim]OTf

$Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and $Ni(OAc)_2$ (24.7 mg, 0.14 mmol) in 500 μL methanol was stirred at room temperature for 20 min. Then the solution was added into [bmim]OTf (1.0 mL). The reaction mixture was stirred at room temperature. After 10 min, methanol were then removed under reduced pressure (0.1

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bar) at 35 °C for 30 min using a rotary evaporator, followed by the addition of 60 μL of $NaBH_4$ (12.0 mg, 0.32 mmol) solution in water (The operations was carried out under N_2 atmosphere), which was prepared immediately before use. The formation of a deep black solution indicated the formation of metal nanoparticles, the mixture was further stirred for 2 h.

General procedures for the catalytic reactions

Lignin model compounds 0.5 mmol was added into the catalytic system ([bmim]OTf with Pd_1Ni_7 BMNPs) equipped with a magnetic stirrer, then the H_2 was induced (H_2 was provided using a hydrogen balloon. Removing the air from the reactorwith Ar before this operation). Subsequently, the reactor was placed into a preheated oil bath at 100 ºC or 130 ºC and stirred for 16 h. After the reaction completion, the reactor was quenched to ambient temperature using cooling water, Then, organic components are extracted with diethyl ether repeatedly until no more product present in the bottom IL residue (determined by 1H NMR). The obtained residue was analyzed by GC/MS or GC.

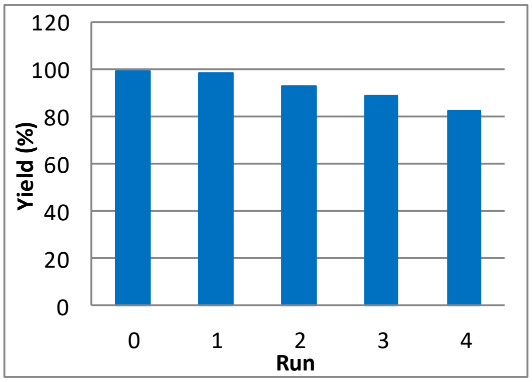

Fig. 4 Catalyst recycling studies

Recycling catalytic system

After reaction completion, the mixture was then extracted with diethyl ether (3×1 mL). The organic layer was collected and removed in *vacuo* to afford the crude products, which was analyzed by GC/MS or GC. The IL phase sperated by extraction could be reused in the next run directly. To the recovered IL phase with Pd_1Ni_7 BMNPs, **1a** 0.5 mmol was added. Then, the H_2 was induced (H_2 was provided using a hydrogen balloon. Removing the air from the reactor with Ar was required before this operation) at room temperature. Subsequently, the reactor was placed into a preheated oil bath at 100 ºC or 130 ºC and stirred for 16 h. The extraction cycle was then repeated for the separation of crude products and catalytic system.

Conclusions

In summary, we have prepared a stable Pd-Ni BMNPs in [bmim]OTf, which proves to be an efficient catalyst for the hydrogenolysis of β-O-4 and α-O-4 linkages with high selectivity. Compared with single nickle and palladium catalysts, the Pd-Ni bimetallic catalyst has a superior activity enhancement owing to the synergistic effects based on experimental and characterization results. Tentative mechanisms for the hydrogenolysis of β-O-4 and α-O-4 linkagesby the catalyst are also proposed according to the results of control experiments. Moreover, the ionic liquid with Pd-Ni BMNPs remains in the reactor after simple extraction, and can be reused several times without further treatment.

Acknowledgements

We gratefully acknowledge the Natural Science Foundation of China (21402093) and Jiangsu (BK20140776) and Chinese Post-doctoral Science Foundation (2016T90465, 2015M571761) for financial support. This work is a project funded by the Priority Academic Program development of Jiangsu Higher Education Institution.

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DOI: 10.1039/C7DT02498C

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