

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

Kang-kang Sun, Guo-ping Lu*, Jia-wei Zhang, Chun Cai

Chemical Engineering College, Nanjing University of Science & Technology, Nanjing, Jiangsu
210094, P. R. China

* Corresponding Author E-mail: glu@njust.edu.cn

1 The yields of all products and the conversions of all reactions.....	2
2 ICP-MS results of Pd₁Ni₇ BMNPs in [bmim]OTf.....	3
3 TEM results of Pd-Ni BMNPs in [bmim]OTf.....	3
4 Pd 3d XPS images.....	6
5 NMR Studies.....	6
6 Synthesis of substrates.....	7
References.....	8

1 The yields of all products and the conversions of all reactions

Table S1 Optimization reaction conditions.^a

entry	IL	T (°C)	catalyst	conversion (%) ^b	yield (%) ^b	
					2a	4a
1	[hmim]NTf ₂	100	Pd ₁ Ni ₄	37	25	12
2	[hmim]Br	100	Pd ₁ Ni ₄	14	12	2
3	[hmim]HSO ₄	100	Pd ₁ Ni ₄	18	13	5
4	[hmim]BF ₄	100	Pd ₁ Ni ₄	30	14	16
5	[hmim]OAc	100	Pd ₁ Ni ₄	0	0	0
6	[bmim]OTf	100	Pd ₁ Ni ₄	74	70	4
7	[bupy]BF ₄	100	Pd ₁ Ni ₄	7	7	0
8	[pmpip]NTf ₂	100	Pd ₁ Ni ₄	0	0	0
9 ^c	[bsmim]OTf	100	Pd ₁ Ni ₄	74	72	2
10	[bmim]OTf	100	Pd ₁ Fe ₄	1	<1	<1
11	[bmim]OTf	100	Pd ₁ Cu ₄	2	2	<1
12	[bmim]OTf	100	Pd ₁ Co ₄	44	39	5
13	[bmim]OTf	100	Pd ₁ Zn ₄	0	0	0
14	[bmim]OTf	100	Pd ₁ Sn ₄	0	0	0
15	[bmim]OTf	100	Ir ₁ Ni ₄	0	0	0
16	[bmim]OTf	100	Ru ₁ Ni ₄	0	0	0
17	[bmim]OTf	100	Au ₁ Ni ₄	0	0	0
18	[bmim]OTf	80	Pd ₁ Ni ₄	24	17	7
19	[bmim]OTf	120	Pd ₁ Ni ₄	79	78	1
20	[bmim]OTf	130	Pd ₁ Ni ₄	89	87	2
21	[bmim]OTf	160	Pd ₁ Ni ₄	100	91	9
22	[bmim]OTf	130	Pd ^d	13	13	0
23	[bmim]OTf	130	Ni ^e	0	0	0
24	[bmim]OTf	130	Pd ^d +Ni ^e	15	15	0
25	[bmim]OTf	130	Pd ₁ Ni ₁	12	9	3
26	[bmim]OTf	130	Pd ₁ Ni ₂	73	73	0
27	[bmim]OTf	130	Pd ₁ Ni ₆	93	93	0
28	[bmim]OTf	130	Pd ₁ Ni ₇	99, 99 ^f , 79 ^g	99, 98 ^f , 76 ^g	0, 1 ^f , 3 ^g
29	[bmim]OTf	130	Pd ₁ Ni ₈	98	98	0

^a Conditions: Catalyst 5 mol% (the amount of palladium in the catalyst), IL 1.0 mL, **1a** 0.5 mmol, H₂ 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.

Table S2 The hydrogenolysis of β -O-4 linkages by Pd-Ni BMNPs in [bmim]OTf.^a

Reaction scheme: $\text{Ar}^1\text{-CH(OH)-CH}_2\text{-O-Ar}^2$ (1) $\xrightarrow[\text{[bmim]OTf}]{\text{Pd}_1\text{Ni}_7 \text{ BMNPs}}$ $\text{Ar}^2\text{-OH}$ (2) + $\text{Ar}^1\text{-CH(OH)-CH}_3$ (3) + $\text{Ar}^1\text{-CH}_2\text{-CH}_2\text{-OAr}^2$ (4)

Entry	Ar ¹	Ar ²	Conversion (%) ^b	Yield (%) ^b	
				2	4
1	Ph	Ph	100	>99	<1
2	Ph	2,6-dimethylphenyl	99	87	12
3	Ph	3,5-dimethoxyphenyl	100	98	2
4	Ph	2,6-dimethoxyphenyl	99	95	4
5	4-MeOC ₆ H ₅	2,6-dimethoxyphenyl	93	58	35
6	4-MeOC ₆ H ₅	Ph	74	46	28
7	3-MeOC ₆ H ₅	2-MeOC ₆ H ₅	76	73	3
8	3-MeOC ₆ H ₅	2,6-dimethoxyphenyl	91	85	6

^a Conditions: **1** 0.5 mmol, Pd₁Ni₇ BMNPs 4 mol% (the amount of palladium in the catalyst), [bmim]OTf 1 mL, H₂ 1 atm, 130 °C, 16 h. ^b GC yields with dodecane as the internal standard.

Only products **2**, **3** and **4** was found in all reactions (Table S1 and S2), so the yields of **2** are the same as the yields of **3**. The reaction conversions are the sum of the yields of **2** and **4**.

2 ICP-MS results of Pd₁Ni₇ BMNPs in [bmim]OTf

Table S3 ICP-MS analysis of the as prepared Pd₁Ni₇ in [bmim]OTf.

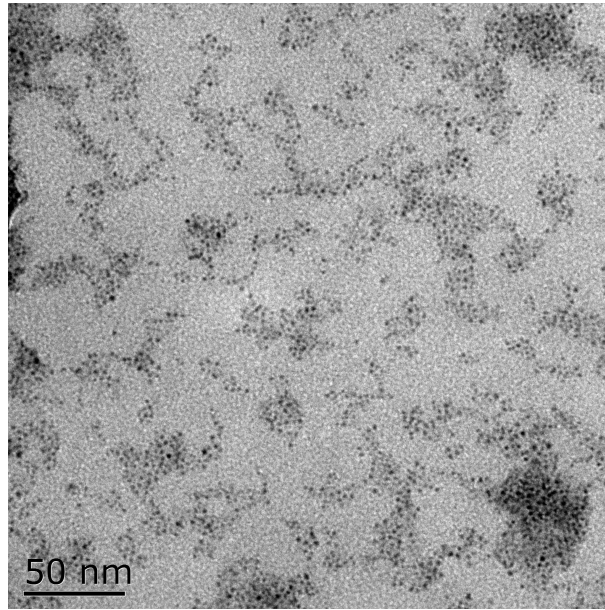
Nanoparticles	Metal Content (g/kg)		Molar Ratio (%)	
	Pd	Ni	Pd	Ni
Pd ₁ Ni ₇	19.81	81.98	12.03	87.97

3 TEM results of Pd-Ni BMNPs in [bmim]OTf

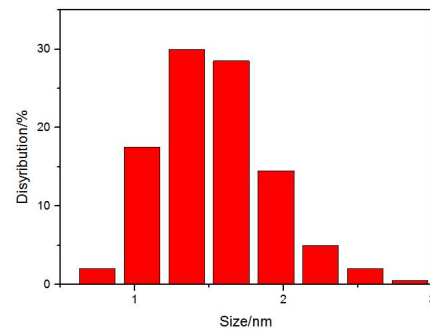
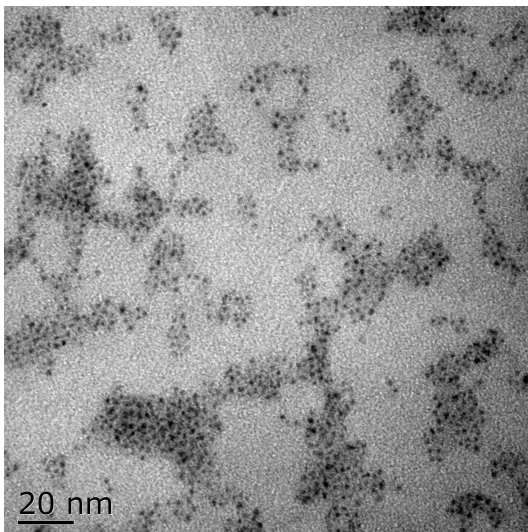
Sample preparation and NP characterization:

The NPs were isolated by adding acetone and then centrifugation (2600 rpm) for 15 minutes. After that it was washed with ethanol (3 × 8 mL). The final solution was ultrasonic for 20 min. An ethanol suspension of nanoparticles was deposited on a copper grid coated by a carbon film and then used in transmission electron microscopy (TEM) measurements. The mean sizes of NPs in this study were determined by TEM of randomly selected areas and based on at least 200 particles.

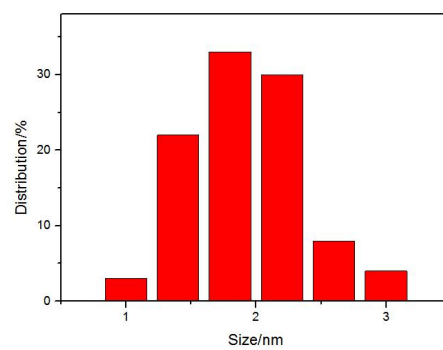
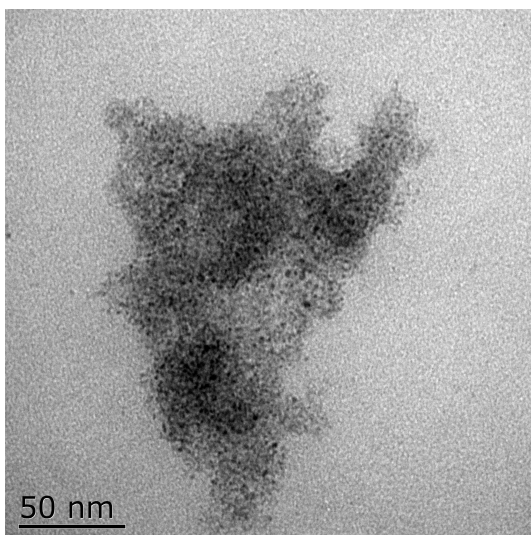
TEM images



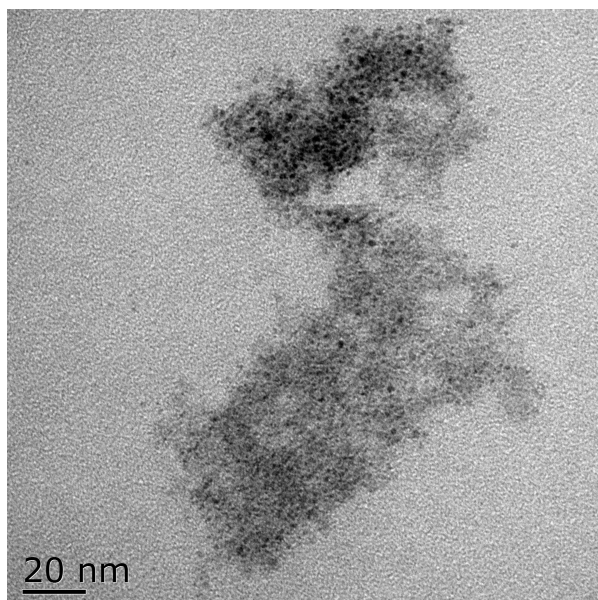
(a)



(b)



(c)



(d)

4 Pd 3d XPS images

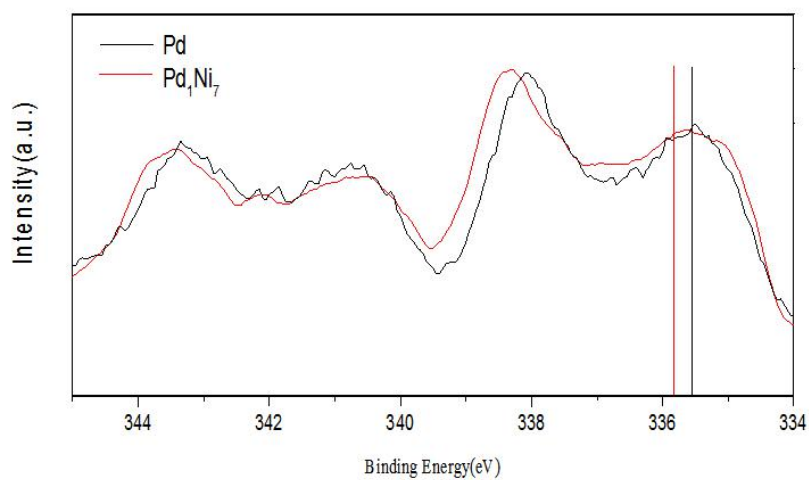


Fig. S1 Pd 3d XPS of Pd NPs and Pd₁Ni₇ BMNPs in [bmim]OTf

5 NMR Studies

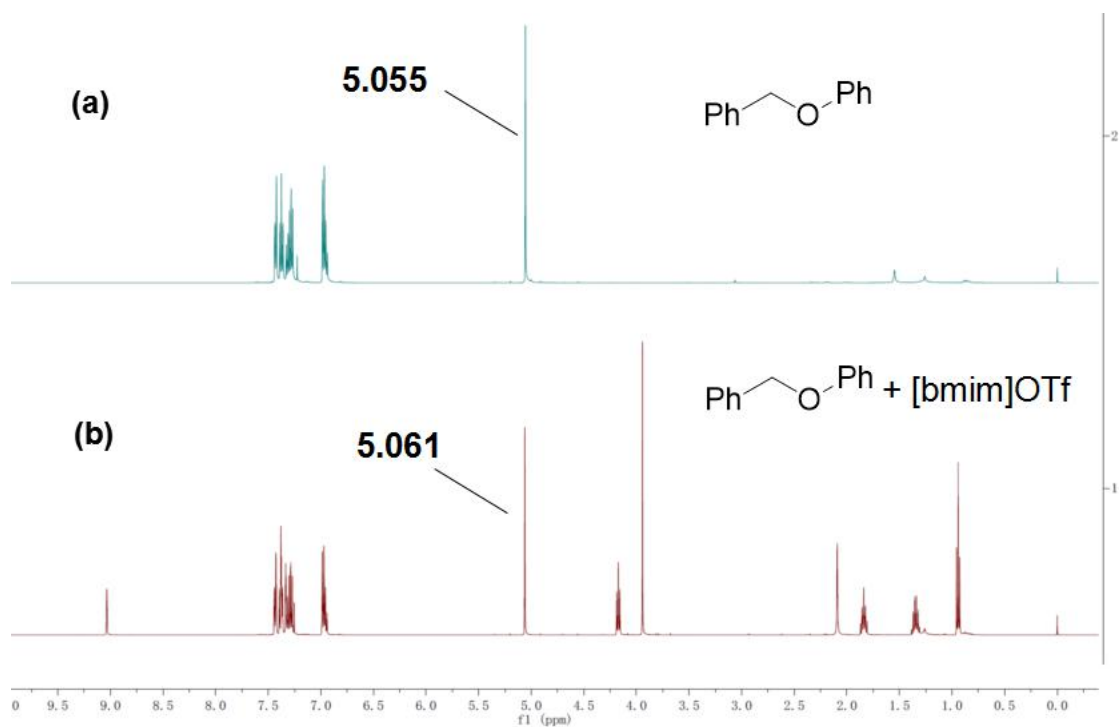
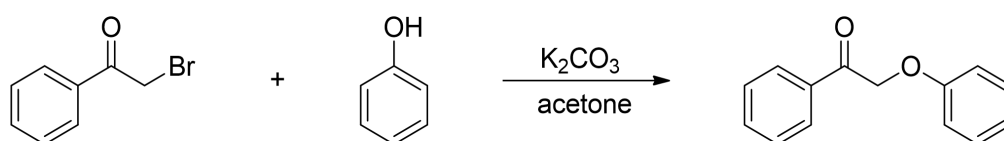


Fig. S2 NMR spectra of (a) (benzyloxy)benzene, (b) (benzyloxy)benzene + [bmim]OTf.

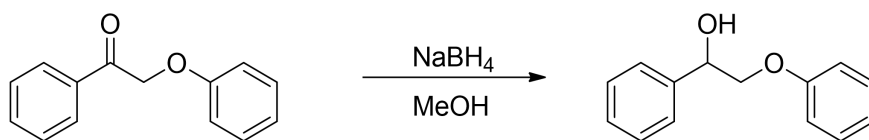
The proton in methylene of (benzyloxy)benzene shifts from 5.055 to 5.061 in the presence of [bmim]OTf. The results indicates that the acidic of methylene is enhanced by IL that can be explained by the non-covalent interactions between IL and (benzyloxy)benzene.^[1] Therefore, [bmim]OTf play a similar role as the electron-withdraw groups in Ar¹ ring, which can decrease the BDE of the C-O bond.^[2]

6 Synthesis of substrates

The typical procedures for the synthesis of 1^[3]



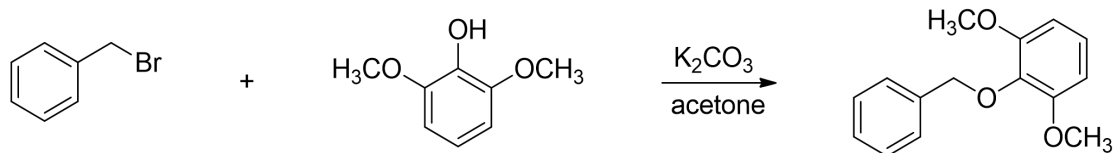
A 250 mL round bottom flask equipped with a reflux condenser and a dropping funnel was charged with phenol (0.520 g, 5.5 mmol) and K₂CO₃ (1.040 g, 7.6 mmol) in acetone (50 mL) and stirred at RT. To this solution, 2-bromoacetophenone (1.000 g, 5.0 mmol) in acetone (50 mL) was added dropwise over 30 min at RT. The resulting suspension was stirred at reflux for 6 h, after the suspension was filtered and concentrated in *vacuo*. The crude product was purified by recrystallization from petroleum ether to give 2-phenoxy-1-phenylethanone as a white solid (1.050 g, 4.9 mmol) in 98% yield.



A round bottom flask was charged with 2-phenoxy-1-phenylethanone (1.7 g, 8.0 mmol) and methanol (60 mL). Sodium borohydride (0.33 g, 8.8 mmol) was added to the solution in small portions at 25 °C. After stirring for 4h, the suspension was quenched with saturated aqueous NH₄Cl (150 mL), followed by the addition of ethyl acetate (150 mL). After separation, the organic phase was washed with H₂O (2 x 100 mL), dried over MgSO₄, filtered and the solvent was evaporated under vacuum. The

crude product was purified by recrystallization from petroleum ether to give a white crystalline in 96% yield, whose purity and structure are further confirmed by GC-MS.

The typical procedures for the synthesis of **5**^[4,5]



A 250 mL round bottom flask equipped with a reflux condenser and a dropping funnel was charged with 2,6-Dimethoxyphenol (0.848 g, 5.5 mmol) and K₂CO₃ (1.040 g, 7.6 mmol) in acetone (50 mL) and stirred at RT. To this solution, Benzyl bromide (0.855 g, 5.0 mmol) in acetone (50 mL) was added dropwise over 30 min at RT. The resulting suspension was stirred at reflux for 6 h, after the suspension was filtered and concentrated in *vacuo*. The crude product was added to ethyl acetate (50 ml) and washed with solution of Sodium hydroxide (3×50 mL), dried over MgSO₄, filtered and the solvent was evaporated under vacuum to give the pure product with 85% yield, whose purity and structure are further confirmed by GC-MS.

Other substrates including **4a**, **8-10**, **12** are prepared according to the literature procedures.^[5]

References

- (1) Sarkar, A.; Roy, S. R.; Chakraborti, A. K., Ionic liquid catalysed reaction of thiols with [small alpha],[small beta]-unsaturated carbonyl compounds-remarkable influence of the C-2 hydrogen and the anion. *Chemical Communications* **2011**, 47 (15), 4538-4540.
- (2) Kim, S.; Chmely, S. C.; Nimlos, M. R.; Bomble, Y. J.; Foust, T. D.; Paton, R. S.; Beckham, G. T., Computational Study of Bond Dissociation Enthalpies for a Large Range of Native and Modified Lignins. *The Journal of Physical Chemistry Letters* **2011**, 2 (22), 2846-2852.
- (3) Zhang, J.-w.; Cai, Y.; Lu, G.-p.; Cai, C., Facile and selective hydrogenolysis of [small beta]-O-4 linkages in lignin catalyzed by Pd-Ni bimetallic nanoparticles supported on ZrO₂. *Green Chemistry* **2016**, 18 (23), 6229-6235.

(4) Sergeev, A. G.; Hartwig, J. F., Selective, Nickel-Catalyzed Hydrogenolysis of Aryl Ethers. *Science* **2011**, 332 (6028), 439-443.

(5) Galkin, M. V.; Dahlstrand, C.; Samec, J. S. M., Mild and Robust Redox-Neutral Pd/C-Catalyzed Lignol β -O-4' Bond Cleavage Through a Low-Energy-Barrier Pathway. *ChemSusChem* **2015**, 8 (13), 2187-2192.