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Catalytic hydrogenation of aromatic rings catalyzed by Pd/NiO†

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Cite this: *RSC Adv.*, 2014, **4**, 2729

Received 5th October 2013
Accepted 14th November 2013

DOI: 10.1039/c3ra45600e

www.rsc.org/advances

A simple and efficient heterogeneous palladium catalyst was prepared for aromatic ring hydrogenation. The catalyst was prepared by a reduction-deposition method and exhibited high activity and selectivity for the hydrogenation of a variety of substituted aromatic compounds to the corresponding cyclohexane and cyclohexanol derivatives with up to 99% yields. The catalyst was characterized by BET, TEM, XRD, XPS and ICP. Meanwhile the reusability of the catalyst was investigated, and it can be reused for several runs without significant deactivation.

Cyclohexane derivatives are important moieties in a variety of organic compounds, such as diesel fuels,[1] natural products and pharmaceuticals.[2] Normally cyclohexane derivatives can be obtained through two ways, *i.e.* the modification of cyclohexane and the hydrogenation of aromatic rings. Clearly, the method through the modification of cyclohexane is very difficult and thus catalytic hydrogenation of aromatic rings becomes the main route to synthesize substituted cyclohexane because it is a simple, convenient and sustainable method and the full hydrogenation of arenes and phenols represents an important industrial transformation, especially for low aromatic diesel fuels.[1,3] Moreover, the hydrogenation of phenols to alcohols plays an important role in paper production[4,5] and the production of fuels from biomass.[6] In most cases, the hydrogenation of aromatic rings is performed by using heterogeneous catalysts such as supported Rh, Pt, Ru, Pd, Co and Ni[2–4,7–18] due to the ease of separation and reusability of the catalysts. It is well known that supported Rh catalysts are generally more active than other catalysts. Recently, Sajiki *et al.*[2] reported an efficient arene hydrogenation system based on the use of Rh/C catalyst. In his study, a wide variety of arenes were hydrogenated to the corresponding cyclohexane and cyclohexanol derivatives in good yields, but the reusability of the catalyst was poor. Rhodium on graphite (Rh/Gr, C24Rh) was described as an active catalyst for the hydrogenation of carbocyclic and heterocyclic aromatic compounds, too.[10] Although the experimental conditions are mild enough, the selectivity needs to be improved. According to the former reports, the catalytic activity for hydrogenation of aromatic rings decreases in the order Rh > Ru > Pt > Ni > Pd > Co.[18] Moreover, among these catalysts, Ru, Ni or Pd catalysts are commonly chosen owing to their high thermal stability. Nagashima *et al.*[11] investigated the complete hydrogenation of aromatic rings over Ru/CNFs. Among those Ru/CNFs, Ru/CNF-p showed excellent catalytic activity towards the hydrogenation of benzene derivatives and pyridine at 100 °C under 30 atm hydrogen pressure. A new method was developed for the hydrogenation of phenol and its derivatives under microwave irradiation.[17] Zhao *et al.* found that phenol was transformed efficiently to cyclohexanone with >98% yield under microwave irradiation. However, the species of the phenols are limited. Therefore, the development of clean and economic catalyst system for the hydrogenation of aromatic rings is still desirable. Here an active Pd/NiO catalyst was prepared for the hydrogenation of aromatic rings. It exhibited good generality to various aromatic compounds and the yields of the hydrogenated products were high enough.

The Pd/NiO catalyst was prepared by reduction-deposition method using nickel oxide as support, ethanol as reducing agent and polyvinyl pyrrolidone (PVP) as surfactant.[19] The TEM images of Pd/NiO are presented in Fig. 1 to illustrate the Pd particle dispersion and catalyst morphology. The TEM results revealed that the Pd nanoparticles have an average diameter of 5.2 nm and dispersed on NiO homogeneously, and the Pd (111) crystal lattice can be observed from Fig. 1(d).

The diffraction patterns of NiO and Pd/NiO were presented in Fig. S1.† If compared the NiO support with the Pd/NiO catalyst, it can be seen that the peaks related to NiO phases were similar and three weak Pd peaks were observable. The appearance of the Pd diffraction peaks indicated that the Pd particles possess relatively good crystallinity, which is in accordance with the TEM results.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra45600e

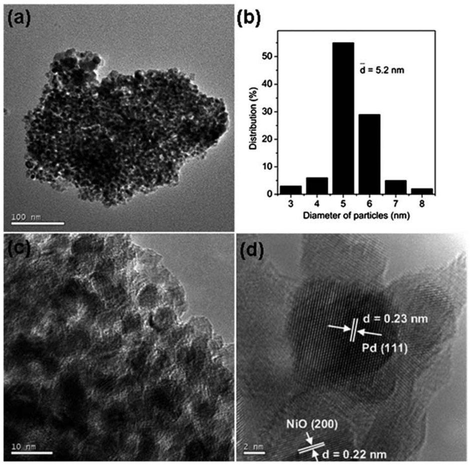
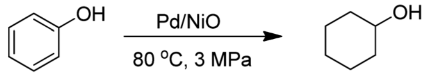


Fig. 1 TEM images of Pd/NiO (a and c), particles distribution (b), and HR-TEM (d).

Table 1 Reaction conditions optimization for the hydrogenation of phenol[a]



1a 2a

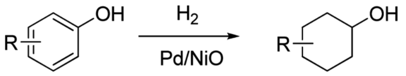
Entry	Solvents	t/h	Yield/%[b]
1	MeOH	12	33
2	EtOH	12	41
3	EtOAc	12	Trace
4	THF	12	Trace
5	DCM	12	Trace
6	i-PrOH	12	92
7	*n*-Hexane	12	95
8	i-PrOH	4	53
9	*n*-Hexane	4	87

[a] *Reaction conditions*: 1 mmol phenol, 50 mg Pd/NiO (2 wt%), 2 mL solvent, 3 MPa H_2, 80 °C. [b] GC yield determined by GC-FID using biphenyl as standard material.

XPS study of Pd/NiO was performed to determine the chemical state of Pd nanoparticles. The Pd_{3d} XPS spectra were shown in Fig S2.† It can be seen that the peaks of Pd_{3d} are consisted of more than one contribution. Thus, the Pd_{3d} lines were de-convoluted to two peaks with the least-squares fitting routine using the Gauss functions. The Pd_{3d} signal of the catalyst showed a maximum at 335.2 eV, which agrees with the binding energy of metallic Pd. The small peak around 337.5 eV is attributed to PdOx, which was not strange because the catalyst was reduced by ethanol at r.t., and calcined at 100 °C in air.[20,21]

By applying phenol hydrogenation as model reaction, the influence of solvents and also the reaction time on the reaction were investigated (Table 1). The results revealed that the reaction was solvent dependent. Moderate yields were obtained if the reactions were performed in MeOH and EtOH while almost no reaction occurred if EtOAc, THF and DCM were used (entries 1–5). To our delight, 92–95% yields were obtained if using n-

Table 2 Hydrogenation of phenol derivatives[a]



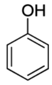
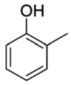
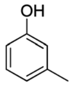
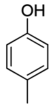
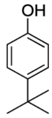
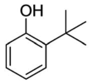
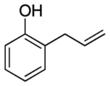
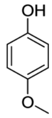
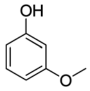
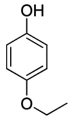
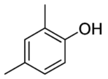
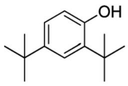
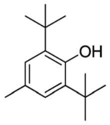
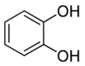
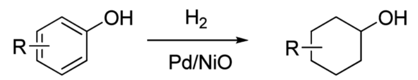
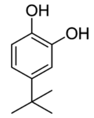
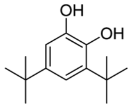
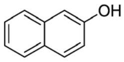
Entry	Substrate	T/°C	t/h	P/MPa	Yield/%[b]
1[c]		80	4	3	87
2[c]		80	10	1	98
3[c]		80	10	1	89
4[c]		80	10	1	>99
5		100	8	3	98
6[c]		100	8	3	92
7[c]		100	16	3	98
8		80	10	1	99
9[c]		80	10	2	98
10[c]		80	10	3	99
11		130	10	5	90
12[c]		130	10	5	87
13[d]		130	12	5	84
14		80	10	3	82

Table 2 (*Contd.*)



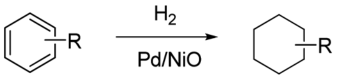
Entry	Substrate	T/°C	t/h	P/MPa	Yield/%[b]
15		130	12	3	90
16		150	24	5	85
17		120	24	3	92

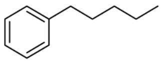
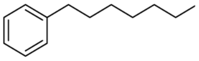
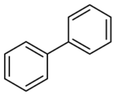
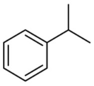
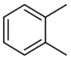
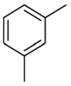
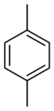
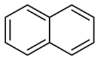
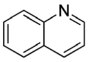
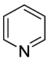
[a] *Reaction conditions*: 1 mmol substrate, 2 mL *n*-hexane, 50 mg catalyst (2 wt%). [b] Isolated yield. [c] GC yield determined by GC-FID using biphenyl as standard material. [d] The product was 2,6-di-*tert*-butyl-4-methylcyclohexanone.

hexane or i-PrOH as solvent (entries 6–7). Moreover, better result was obtained in n-hexane than in i-PrOH when the reaction time was reduced to 4 h (Entries 8 and 9). Therefore, *n*-hexane was used for the next study.

The catalytic hydrogenation of phenol derivatives with different substituents was tested over Pd/NiO catalyst to examine the scope and limitations, and the results were shown in Table 2. Phenol was converted to cyclohexanol with 87% yields (entry 1). The mono-substituted phenols were hydrogenated smoothly to the corresponding cyclohexanol derivatives with up to 99% yields (Entries 2–10). The presence of functional groups such as methyl, *tert*-butyl, allyl and methoxyl did not influence the hydrogenation reactions. The di-substituted and tri-substituted phenols were also investigated, and they were hydrogenated to the corresponding substituted cyclohexanol with excellent yields (entries 11–12). However, relatively higher temperature, pressure and longer reaction time were needed in order to gain good yields due to the steric hindrance. In the extremity, 2,6-di-*tert*-butyl cyclohexanone was obtained with 84% yield when 2,6-di-*tert*-butylphenol was employed (entry 13). That means the greater steric hindrance influences the reaction pathway. In addition, we explored the Pd/NiO-catalyzed hydrogenation of catechol and its derivatives (entries 14–16). Fortunately, catechol and substituted catechols were completely hydrogenated to the corresponding cyclohexanediol and its derivatives in good yields. β-naphthol was hydrogenated to decahydro-β-naphthol with 92% yield, too (entry 17).

Table 3 Hydrogenation of benzene derivatives[a]



Entry	Substrate	T/°C	t/h	Yield/%[b]
1		140	24	94
2		140	24	90
3		130	24	92
4[c]		130	24	84
5[c,d]		130	30	91
6[c,d]		130	28	93
7[c,d]		130	26	87
8		150	36	93
9		120	24	93
10[c]		150	24	80

[a] *Reaction conditions*: 1 mmol substrate, 2 mL *n*-hexane, 5 MPa, 50 mg catalyst (2 wt%). [b] Isolated yield. [c] GC yield determined by GC-FID using biphenyl as standard material. [d] 5 MPa.

The hydrogenation of benzene derivatives was further investigated, and the results were shown in Table 3. Clearly, Pd/NiO showed high catalytic activity on the hydrogenation of alkyl benzenes and the yields were 92–94% (entries 1 and 2). Biphenyl and cumene were successfully converted into the corresponding cyclohexane derivatives with excellent yields (entries 3 and 4). Moreover, the catalytic hydrogenation of disubstituted benzenes could occur under lower temperature if compared to mono-substituted benzenes (entries 5–7). The catalytic hydrogenation of naphthalene was also realized using Pd/NiO as catalyst and 93% yield was obtained (entry 8). Furthermore, heteroaromatic compounds were reduced to the corresponding heterocyclic compounds with 80–93% yields (entries 9 and 10). However, the main product in the hydrogenation of quinoline was tetrahydroquinoline. In one word, the hydrogenation of alkylbenzene and biphenyl, as well as naphthalene, can be realized with good to excellent yields.

In order to investigate the stability of the Pd/NiO catalyst, the reusability experiment was performed. As the results shown in Fig. 2, the catalyst was used for five cycles in the hydrogenation of phenol and 81% yield was maintained at the 5th run, which suggested that the catalyst was very stable during the reaction. According to ICP-AES analysis, the palladium loading only decreased from 2.1 wt% to 2.0 wt%, which also confirmed the stability of the catalyst.

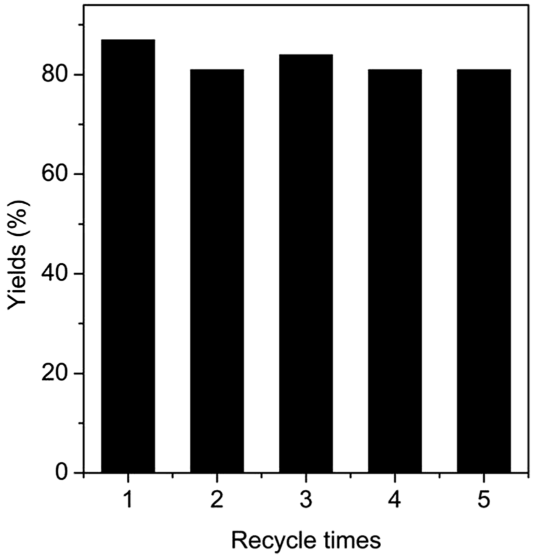


Fig. 2 The reusability test of Pd/NiO in phenol hydrogenation.

In conclusion, we have introduced a simple and practical Pd/NiO catalyst for the catalytic hydrogenation of aromatic rings. Benzene and phenol derivatives with different structures can be hydrogenated into the corresponding cyclohexane and cyclohexanol derivatives with good to excellent yields. In addition, this Pd/NiO showed excellent reusability and maintained stable for at least 5 runs.

Acknowledgements

Financial support was provided by the National Natural Science Foundation of China (21303228 and 21073208).

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