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ARTICLE

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Catalytic transfer hydrogenation of 4-O-5 models in lignin-derived compounds to cycloalkanes over Ni-based catalysts

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Abstract

There is an urgent need to develop a selective hydrogenolysis of C_{aryl}-O bonds in lignin to produce valued-added chemicals and fuels. Recently, hydrogen has been used in the hydrogenation reaction, which hides inevitable danger and is not economical. Therefore, isopropanol, as a hydrogen-donor solvent, is employed for aryl ether hydrogenolysis in lignin models over nickel supported on a carbon nanotube (CNT). Except for aromatic ether (4-O-5), the Ni/CNT catalyst is also found to be suitable for alkyl-aryl ether (α-O-4 and β-O-4) cleavage in control experiments. The physicochemical characterizations were carried out by means of H_2-temperature-programmed reduction, X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy analyses. The catalyst can be magnetically recovered and efficiently reused for five consecutive recycling tests in the transfer hydrogenation of aromatic ethers. A mechanism study indicated that the hydrogenolysis cleavage of the ether bond is the first step in the reaction process, and hydrogenation of aromatic rings is only a successive step in which phenol and benzene are intermediate states and are then further hydrogenated. Furthermore, it has been demonstrated that aryl groups play an important role in the hydrogenation of phenol in the competitive catalytic hydrogenation reaction of phenol.

KEYWORDS
aromatic ether bonds, catalytic transfer hydrogenation, isopropanol, lignin, Ni/CNT

1 | INTRODUCTION

Upgrading biomass to obtain value-added fuels, energies, and chemicals has been recognized as a green and novel approach to the use of renewable carbon resources, complementing the traditional chemical industry that heavily depended on fossil fuels.[1–4] In comparison, biomass contains peer carbon, and the use of biomass will not aggravate greenhouse pollution. Lignocellulosic biomass, especially lignin, has received great attention as it can be potentially utilized to produce functionalized aromatic and cycloalkane derivatives.[5–7] Owing to the complex natural aromatic three-dimensional network structure, it is difficult to achieve the depolymerization of lignin into small-molecule compounds.[8,9] As is well known, a variety of ether bonds is present in the lignin, containing

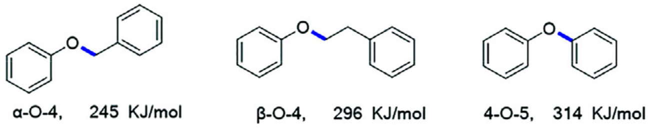


FIGURE 1 The dissociation energies of different types of C-O bonds in lignin

β-O-4, α-O-4, and 4-O-5.[10] Among these types of ether bonds, α-O-4 is the most vigorous, while 4-O-5 is the most robust,[11] resulting in more challenges in the cleavage of the 4-O-5 ether bond (Figure 1).

Thus, selective cleavage of these ether bonds is of great significance for the valorization of lignin and its derived compounds. In the past decades, noble metal and nonnoble metal catalysts (i.e., Ni,[12] Cu,[13] Pt,[14] Ru,[15] Pd[16]) have been widely investigated for the hydrogenolysis of the above substrates. For example, Gao et al reported a heterogeneous catalyst Ni/C that showed satisfying conversion for cleaving the aromatic ether bond of 4-O-5 linkage under very demanding conditions (high temperature, long reaction time, excessive use of moisture-sensitive base, and 1 bar H_2) with 86.5% of cyclohexanol and 86.5% of benzene.[17] To overcome the shortcomings, Hua et al explored the first work on the transfer hydrogenolytic cleavage of diphenyl ether over Ru/C using *i*PrOH as the hydrogen resource (avoiding the use of H_2) under relatively milder conditions (120°C and 10 hr) compared to Gao et al.[18] However, some cases still added sodium *tert*-butoxide to give impetus to the reaction. Although sodium *tert*-butoxide has the ability to promote the efficiency of the catalytic transfer hydrogenation, its recyclability is still a difficult problem that needs to be dealt with. Therefore, Ru/Hydroxyapatite was designed to achieve an efficient cleavage of aromatic ether bonds in the absence of moisture-sensitive bases from the same group.[19] Although noble metal catalysts have been proven to have a strong ability to transfer hydrogen, which has the advantage in the hydrogenolysis to the aromatic ether bonds, the hydrogenation of aromatic rings occurs and leads to a poor selectivity toward cycloalkanes. Hence, the exploration of novel and efficient catalysts is still ongoing.[20,21]

Catalytic transfer hydrogenation shows an efficient and green alternative for hydrogen in sustainable catalysis, in that hydrogen donor molecules such as isopropanol can be easily obtained from renewable resources.[22,23] Furthermore, the use of hydrogen donor molecules can reduce security risks and cut the costs associated with the transportation and storage of hydrogen. Hence, the application of catalytic transfer hydrogenation in lignin depolymerization and ether bond cleavage have been known as efficient and novel alternatives to traditional hydrogenolysis procedures.[24] So far, various research groups have successfully achieved the efficient transfer hydrogenolysis of lignin and model molecule conversion to value-added chemicals containing aromatics and cycloalkanes.[25,26]

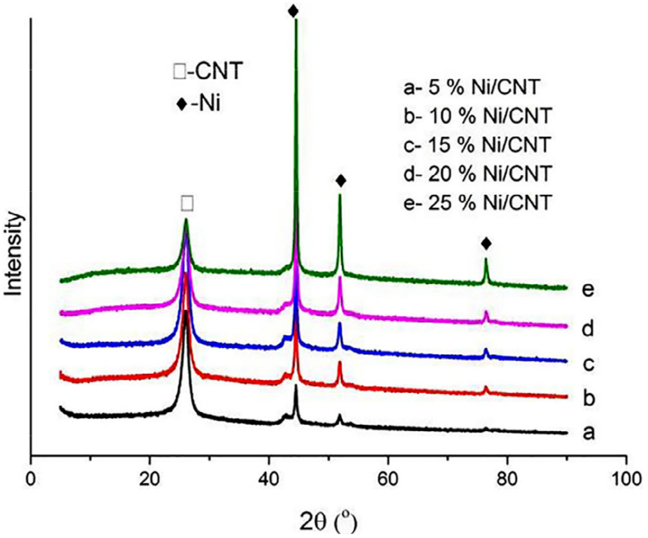


FIGURE 2 XRD of Ni/CNT catalysts with different proportions. (a) 5% Ni/CNT, (b) 10% Ni/CNT, (c) 15% Ni/CNT, (d) 20% Ni/CNT, and (e) 25% Ni/CNT

Carbon nanotubes (CNTs) are interesting materials for carrying out chemical reactions in confined spaces, and several organic reactions have been conducted widely.[27–29] In this paper, CNT-supported nickel was developed by a simple and economic impregnation method to test its catalytic performance in the hydrogenolysis of aromatic compounds in *i*PrOH in the absence of hydrogen. We initially chose diphenyl ether as the model molecule to optimize the hydrogenolysis reaction over a 20% Ni/CNT catalyst. Then, the catalyst was also found to be efficient in the transformation of other diphenyl ether derivatives to corresponding cycloalkanes and cyclic alcohols. All of the catalysts studied were characterized by H_2-temperature-programmed reduction (TPR), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses, and the mechanism was proposed at the end.

2 | RESULTS AND DISCUSSION

2.1 | Catalyst characterization

Figure 2 shows the XRD patterns of the Ni/CNT catalyst with different metal proportions, including 5% Ni/CNT, 10% Ni/CNT, 15% Ni/CNT, 20% Ni/CNT, and 25% Ni/CNT catalysts, in the system for the hydrogenolysis of diphenyl ether. The peak at 26.5° could be assigned to the diffraction peaks of the (002) planes of the graphitelike tube wall of the CNT.[30–32] Apart from the CNT feature, the presence of metallic Ni in the reduced Ni/CNT catalyst was clearly demonstrated. As could be clearly seen from the XRD results, only one kind of Ni-based phase was observed for the Ni/CNT catalyst. Peaks at 44.5°, 51.9°, and 76.4° could be assigned to the diffraction of the (111), (200), and (220) planes of metallic Ni,[33] indicating that only metallic nickel species were observed in reduced Ni/CNT catalysts.

As shown in Figure 3, all Ni/CNT catalysts exhibit a wide peak in the temperature range of 400–700°C, which would be assigned to the CNTs' methanation process. Methanation occurs in the case of the reduction process, starting at 390°C and ending at about 800°C.[34,35] It can be seen from TPR profiles of the Ni/CNT catalysts that a peak occurs at 100–200°C, which could most likely be attributed to H_2 consumption of bulk NiO particles. The amount of superficial NiO species increased when the Ni-loading amount increased from 5 to 25%. To some extent, a higher temperature is required for the reduction of more NiO particles.

XPS detection was carried out to test the composition of the optimal Ni/CNT catalyst (20% Ni/CNT), and the absorption peaks were identified for C, O, and Ni. As we can clearly see in Figure 4, binding energies at 852.9 and 856.3 eV were observed for 20% Ni/CNT, which corresponded to Ni^0 (2p3/2) and Ni^{2+} (2p3/2), respectively. The binding energies at 872.3 and 874.8 eV corresponded to the main lines of Ni^0 (2p1/2) and Ni^{2+} (2p1/2), respectively. It could be seen that a small amount of metallic Ni was oxidized before or during the XPS testing, which contributed to the understanding of Ni^{2+} detection in the XPS spectra.

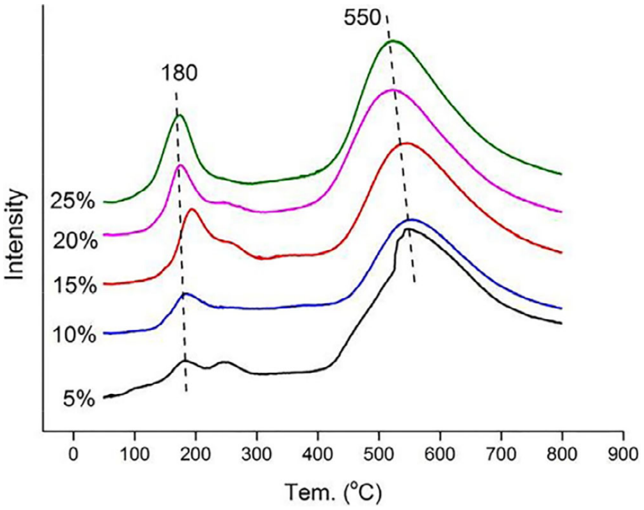


FIGURE 3 TPR of Ni/CNT catalyst with different proportions. 5% Ni/CNT ~ 25% Ni/CNT

As can be seen in Figure 5, most Ni particles were displayed uniformly outside the CNT. However, the Ni particle size and its distribution varied from each other, mainly owing to the loading amount of Ni on the surface of the CNT. We selected the optimal catalyst in our catalytic system (20% Ni/CNT catalyst) as an example. Ni particles were nearly evenly distributed on the surface of the CNTs in Figure 5a, while aggregation of nickel metal occurred when the loading amounts increased to 25% Ni/CNT (Figure 5b). Taken together, nanoparticle Ni on the surface of a CNT demonstrated an excellent activity in the catalytic transfer hydrogenation of diphenyl ether.

2.2 | Optimization of the reaction condition

Transfer hydrogenolysis of diphenyl ether, a model molecule of the 4-O-5-type linkage in lignin, is of great

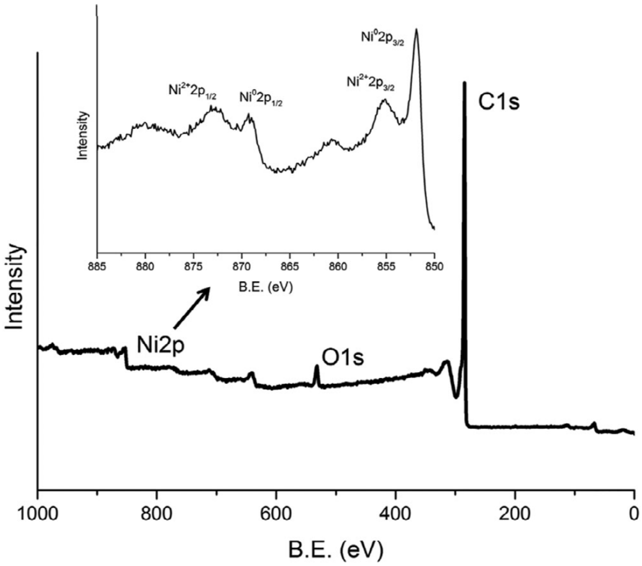


FIGURE 4 XPS of the 20% Ni/CNT catalyst

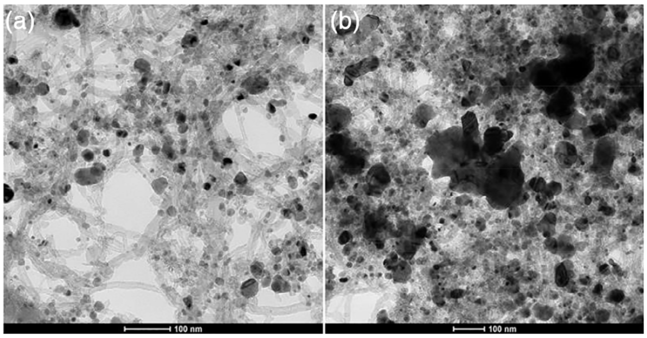
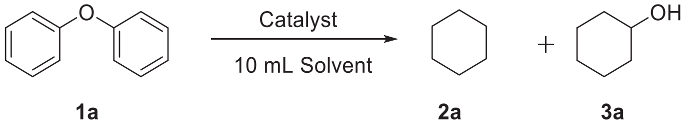


FIGURE 5 TEM of the 20% Ni/CNT catalyst (a) and 25% Ni/CNT catalyst (b)

TABLE 1 Optimization of different catalysts for the hydrogenolysis of diphenol ether **1a**[a]



Entry	Catalyst	Solvent	T. (°C)/t. (h)	Con. (%)[b]	Yield (%)[b] 2a	Yield (%)[b] 3a
1	None	*i*PrOH	240/4	0	0	0
2	CNT	*i*PrOH	240/4	8	<5	<5
3	20% Ni/CNT	*i*PrOH	240/4	100	88	82
4	15% Ni/CNT	*i*PrOH	240/4	100	72	60
5	10% Ni/CNT	*i*PrOH	240/4	95	70	58
6	5% Ni/CNT	*i*PrOH	240/4	90	68	54
7	20% Fe/CNT	*i*PrOH	240/4	<5	<5	<5
8	20% Co/CNT	*i*PrOH	240/4	28	16	12
9	20% Mo/CNT	*i*PrOH	240/4	22	8	6
10	20% Ce/CNT	*i*PrOH	240/4	<5	<5	<5

Abbreviations: Con, conversion; t, reaction time; T, reaction temperature.

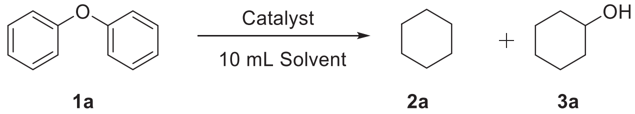
[a] Reaction conditions: **1a** (500 mg), Catalyst (50 mg), Solvent (10 ml).

[b] The conversion and yields were determined by GC/MS with n-dodecane as the internal standard.

importance and is also a challenging step for the valorization of lignin owing to the high stability of the diaryl ether bonds, compared to alkyl-aryl ether bonds (Figure 1). Hence, diphenyl ether was chosen as a model molecule to explore the transfer hydrogenolysis with isopropanol as the hydrogen resource. Various catalysts were screened to show the catalytic activity for the transfer hydrogenolysis of diphenyl ether at 240°C within a reaction time of 4 hr. No reaction was determined in the absence of any catalysts and when employing a solo CNT as the catalyst, which presented a poor conversion of diphenyl ether (Table 1, entries 1–2). The highest conversion (up to 100%) was achieved with the Ni/CNT catalyst in *i*PrOH after 4 hr, while the corresponding yields of cyclohexane and cyclohexanol varied with the different loading amounts of nickel over CNT. The 5% Ni/CNT exhibited a perfect conversion of diphenyl ether, but only 68 and 54% yields of cyclohexane and cyclohexanol were obtained, respectively. Further analysis by Gas Chromatography/Mass Spectroscopy (GC/MS) demonstrated that aromatic chemicals, including benzene and phenol, were detected with very low yields. When the loading amounts of nickel over the CNT were gradually increased from 5 to 20% at an interval of 5%, the change of cyclohexane and cyclohexanol yields presented the same trend, and in the end, the 20% Ni/CNT catalyst was the most suitable catalyst to yield 88% cyclohexane and 82% cyclohexanol (Table 1, entries 3–6). In comparison, different metal-supported catalysts (i.e., 20% Fe/CNT, 20% Mo/CNT, 20% Co/CNT, and 20% Ce/CNT) were also synthesized to investigate the catalytic performance during the hydrogenolysis of diphenyl ether. However, it was disappointing to find that Fe, Mo, Co, and Ce showed poor performance on the hydrogenolysis of the 4-O-5 model compound, and large amounts of diphenyl ether were recovered (Table 1, entries 7–10). In summary, the combination of nickel and CNT played a highly important role in the hydrogenolysis of diphenyl ether to produce cyclohexane and cyclohexanol in *i*PrOH at 240°C with a reaction time of 4 hr.

In addition, the effect of time and temperature on the hydrogenolysis of diphenyl ether was explored subsequently. As was presented in Table 2, the conversion of diphenyl ether was nearly up to 100%, and yields of cyclohexane and cyclohexanol had no change (up to 80%) within the error range when the reaction time increased from 2 to 6 hr in intervals of 2 hr, which indicated that time played an unimportant role in the reaction process at a temperature of 240°C (Table 2, entries 1–3). Hence, temperature was another key factor to the hydrogenolysis of 4-O-5 model compounds. The conversion was found to be completely achieved at 100% when the temperature remained over 210°C. When the temperature decreased from 210°C to 190°C, the yields of cyclohexane and cyclohexanol decreased, which was because part of the diphenyl ether is recovered, and generated benzene and phenol were detected in the reaction process (Table 2, entries 4–8).

TABLE 2 Optimization of time and temperature for the hydrogenolysis of diphenol ether **1a**[a]



Entry	Catalyst	Solvent	T. (°C)/t. (h)	Con. (%)[b]	Yield (%)[b] 2a	3a
1	20% Ni/CNT	*i*PrOH	240/2	100	85	82
2	20% Ni/CNT	*i*PrOH	240/4	100	88	82
3	20% Ni/CNT	*i*PrOH	240/6	100	80	78
4	20% Ni/CNT	*i*PrOH	230/4	100	83	79
5	20% Ni/CNT	*i*PrOH	220/4	100	84	81
6	20% Ni/CNT	*i*PrOH	210/4	100	88	82
7	20% Ni/CNT	*i*PrOH	200/4	78	56	52
8	20% Ni/CNT	*i*PrOH	190/4	56	42	38

Abbreviations: Con, conversion; t, reaction time; T, reaction temperature.

[a] Reaction conditions: **1a** (500 mg), Catalyst (50 mg), Solvent (10 ml).

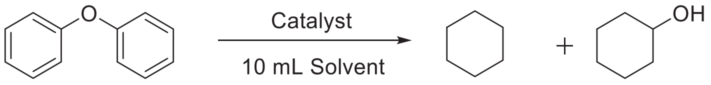
[b] The conversion and yields were determined by GC/MS with n-dodecane as the internal standard.

With the optimal catalyst, temperature, and reaction time (20% Ni/CNT, 210°C and 4 hr) in hand, the reaction conditions for the hydrogenolysis of diphenyl ether are still being researched. It was found that solvents played a crucial role in the depolymerization of lignin based on chemical properties of different solvents. Hence, polar solvents (i.e., *i*PrOH, methanol, ethanol, dioxane, H_2O, and THF) and apolar solvents (i.e., *n*-hexane and cyclohexane) were chosen in the Ni/CNT-catalyzed hydrogenolysis of the 4-O-5 model compound. Apolar solvents were expected to present poor activities for the hydrogenolysis of diphenyl ether, resulting in 100% recovery in the starting substrate and no corresponding products detected in the reaction process (Table 3, entries 1–2). Hydrogen-donor solvents (*i*PrOH, methanol, and ethanol) were believed to favor the ether bond hydrogenolysis reaction in lignin. However, almost no reaction was unexpectedly detected in the Ni/CNT-catalyzed hydrogenolysis reaction when methanol and ethanol were assessed as solvents, while *i*PrOH showed a highly efficient activity in the transformation of diphenyl ether to yield 88% cyclohexane and 82% cyclohexanol (Table 3, entries 3–5). This is probably because the secondary alcohol isopropanol could give higher activity than those primary alcohols[33]; 24% yield of cyclohexane and 20% yield of cyclohexanol were obtained in tetrahydrofuran (THF) under the catalytic system, which indicated that THF had a poor ability to convert diphenyl ether to expected products (Table 3, entries 7). As an environmentally friendly nature resource, water has been employed in a variety of chemical reactions. In spite of the 41% conversion of diphenyl ether, relatively lower yields of cyclohexane (22%) and cyclohexanol (16%) were achieved. Taking all the factors into consideration, the optimal reaction condition was finally described (20% Ni/CNT, 210°C, 4 hr, *i*PrOH).

2.3 | Scope of the substrates

Encouraged by the satisfactory results above, further study on the catalytic activity of five 4-O-5 model compounds, one α-O-4 dimer, and two β-O-4 dimers over 20% Ni/CNT were investigated under the optimal reaction conditions. As was shown in Table 4, the dominant products in the first five reactions were cyclohexane and cyclohexanol derivatives, which suggested that the hydrogenolysis of diphenyl ether derivatives occurred. Diphenyl ether could be completely transferred to yield cyclohexane (88%) and cyclohexanol (82%) (Table 4, entries 1), while the substrates containing different substituent groups could be transferred to different corresponding products over 20% Ni/CNT. In these cases, the conversions and yields diminished, indicating that the steric hindrance played a significant factor in this reaction. When diphenyl ethers were substituted with methyl and hydroxyl groups on the *para*-position, 100% conversion of substrates was achieved, and the yields of corresponding cycloalkanes and cyclic alcohols were relatively higher (Table 4, entries 2–3). In comparison (entries 2 and 3), only one side methyl-substituted diphenyl ether was employed in our reaction process. Although 1-methyl-3-phenoxybenzene was fully consumed, small amounts of cyclohexane (50%) and 3-methylcyclohexan-1-ol (43%) were achieved, which

TABLE 3 Optimization of different solvents for the hydrogenolysis of diphenol ether **1a**[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	T. (°C)/t. (h)	Con. (%)[b]	Yield (%)[b] 2a	Yield (%)[b] 3a
1	20% Ni/CNT	*n*-hexane	210/4	0	0	0
2	20% Ni/CNT	Cyclohexane	210/4	0	0	0
3	20% Ni/CNT	*i*PrOH	210/4	100	88	82
4	20% Ni/CNT	Methanol	210/4	0	0	0
5	20% Ni/CNT	Ethanol	210/4	0	0	0
6	20% Ni/CNT	Dioxane	210/4	0	0	0
7	20% Ni/CNT	THF	210/4	31	24	20
8	20% Ni/CNT	H_2O	210/4	41	22	16

Abbreviations: Con, conversion; t, reaction time; T, reaction temperature.

[a] Reaction conditions: **1a** (500 mg), Catalyst (50 mg), Solvent (10 ml).

[b] The conversion and yields were determined by GC/MS with n-dodecane as the internal standard.

suggested that the symmetrical structure with substituent groups was beneficial to the hydrogenolysis of 4-O-5 lignin-derived compounds under the Ni/CNT-catalyzed system (Table 4, entries 4). In addition to the diphenyl phenol derivatives, this catalytic system was also well suited for aryl-alkyl ether, in which phenyl methyl ether could be transferred to cyclohexanol with a yield of 62% (Table 4, entry 5).

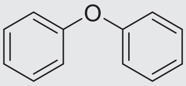
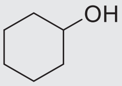
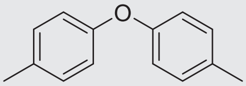
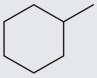
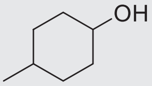
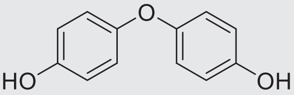
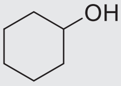
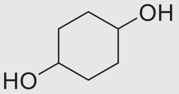
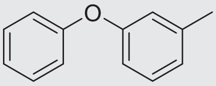
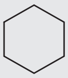
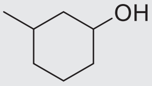
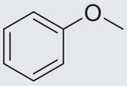
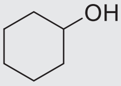
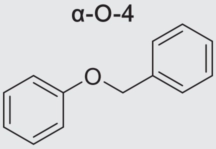
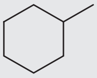
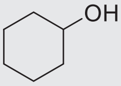
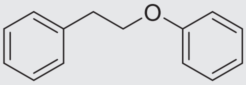
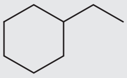
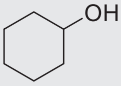
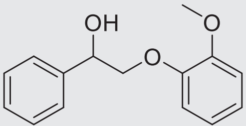
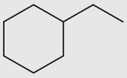
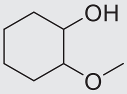
Moreover, an experiment involving the conversion of one α-O-4 model compound was also investigated (Table 4, entry 6). It was gratifying to find that benzyl phenol ether underwent selective carbon–oxygen bond cleavage and hydrogenolysis of aromatic rings over the treatment with the 20% Ni/CNT catalyst, and there was no negative effect on the conversion and yield during the reaction process. As the β-O-4 bond is predominant in the lignin structure, phenethoxybenzene and 2-(2-methoxyphenoxy)-1-phenylethan-1-ol were chosen to investigate the catalytic activity of Ni/CNT, and the perfect performance on the catalytic transfer hydrogenation system is shown in Table 4. When methoxy substitution of the O-terminus aryl ring led to a decreased yield of 2-methoxycyclohexan-1-ol (45%), compared to no substituent group on the O-terminus aryl ring (Table 4, entries 7–8), it was worth noting that almost no aromatic compounds were observed, indicating that the Ni/CNT catalyst demonstrated the perfect ability to hydrocrack the carbon–oxygen bond and dearomatize the benzene rings in one step. The results above proved that Ni/CNT was highly efficient for the catalytic transfer hydrogenation of a variety of diphenyl ether derivatives.

In comparison with entries 1, 6, and 7 in Table 4, an interesting phenomenon was discovered: Even though the yields of corresponding cycloalkanes were up to 60%, the yields of cyclic alcohols varied (entry 1 > entry 6 > entry 7). Hence, a competitive catalytic hydrogenation reaction was carried out, in which we mixed phenol with benzene, toluene, and ethylbenzene in an equimolar feed composition to simulate the catalytic hydrogenation of diphenyl ether, phenyl methyl ether, and phenyl ethyl under the optimal conditions. At the same time, a blank experiment including solo phenol hydrogenation was tested. As is demonstrated in Figure 6, the hydrogenation yields of cyclohexanol decreased by degrees in the presence of benzene, methylbenzene, and ethylbenzene. So, the addition of different aromatic chemicals contributed to an impairment of phenol hydrogenation activity. Related coordination chemistry of benzene and toluene on nickel (111), (110), and (100) surfaces has already been reported in previous literature.[36]

2.4 | Possible reaction mechanism and the recycling of catalyst

Comprehending the reaction pathway is of great importance for the valorization of lignin to produce value-added chemicals. In general, we proposed two possible reaction pathways for the hydrogenolysis of diphenyl ether. In the first potential pathway (pathway one in Figure 7, red one), benzene and phenol were directly obtained from the cleavage of an aromatic ether bond in which the formation of a coordinative bond between the

TABLE 4 Cleavage of various 4-O-5, α-O-4, and β-O-5 model compounds over 20% Ni/CNT[a]

Entry	Substrate	T(°C)/t(h) [b]	Conversion [b]	Yield [b]	
	4-O-5				
1	 **1a**	210/4	100	 88	 82
2	 **1b**	210/4	100	 70	 61
3	 **1c**	210/4	100	 67	 62
4	 **1d**	210/4	100	 50	 43
5	 **1e**	210/4	100	 62	—
	α-O-4				
6	 **1f**	210/4	100	 62	 60
	β-O-4				
7	 **1g**	210/4	100	 65	 51
8	 **1h**	210/4	100	 66	 45

Abbreviations: t, reaction time; T, reaction temperature.

[a] Reaction conditions: **1a–1h** (500 mg), Catalyst (50 mg), *i*PrOH (10 ml).

[b] The conversion and yields were determined by GC/MS with n-dodecane as the internal standard.

phenoxide group and nickel (oxidative addition step) was subsequently hydrogenated in the presence of *i*PrOH. After this, the produced benzene and phenol were further hydrogenated to afford cyclohexane and cyclohexanol.

On the other hand, intermediate product cyclohexyl phenyl ether was hydrogenated from diphenyl ether by active hydrogen. Owing to the dissociation energy of the C(sp^2)-O bond being higher than the C(sp^3)-O bond, the generated cyclohexyl phenyl ether above could easily be transformed to cyclohexane and phenol. Subsequently, phenol was hydrogenated to cyclohexanol under our reaction system. However, only cyclohexane, cyclohexanol, benzene, and phenol were observed in the reaction process. Hence, pathway one could be regarded as the dominate reaction pathway.

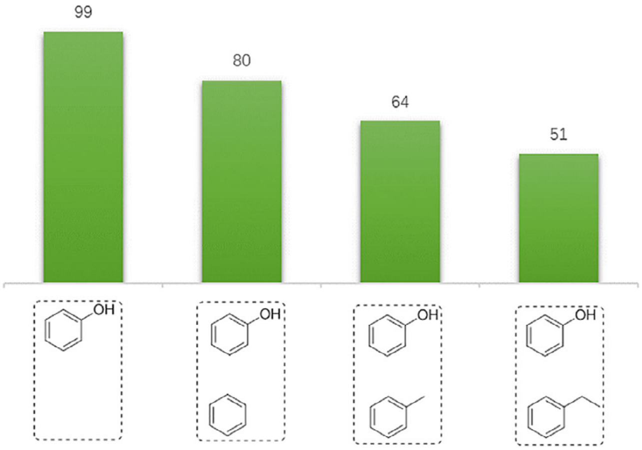


FIGURE 6 The competitive catalytic hydrogenation reaction of phenol with different aromatics at equimolar mixture under the optimal reaction condition (20% Ni/CNT, 210°C, 4 hr, *i*PrOH)

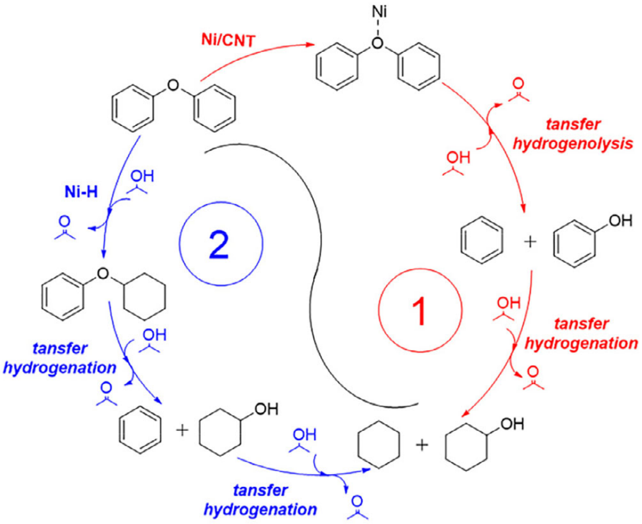


FIGURE 7 Possible pathways of the catalytic transfer hydrogenation of diphenyl ether over Ni/CNT

Finally, the recyclability of the 20% Ni/CNT catalyst, based on successive recycling tests at 210°C for 4 hr, was subsequently explored using diphenyl ether conversion as the model reaction. The 20% Ni/CNT retained its activity after five consecutive runs, and minor changes in product selectivity was observed, giving prominence to the good stability of the catalyst. Except for this, the catalyst could be recovered by a magnet and could be used in the next run after simple processing (washing with *i*PrOH and drying at 105°C) (Figure 8).

3 | EXPERIMENTAL

3.1 | Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) was purchased from Aladdin Industrial Inc. Shanghai, China; the CNT was provided by Sigma-Aldrich; diphenyl ether (>99.99%), 4,4′-oxybis(methylbenzene) (>99.99%), dimethyl 4,4′-oxydibenzoate (>99.99%), 4,4′-oxydiphenol (>99.99%), 1-methyl-3-phenoxybenzene (>99.99%), anisole (>99.99%), 9H-xanthene (>99.99%), (benzyloxy) benzene (>99.99%), and all the solvents were obtained from commercial sources and used without further purification. 2-phenoxy-1-phenylethan-1-ol and 2-(2-methoxyphenoxy)-1-phenylethan-1-ol were synthesized according to literature method.[37]

3.2 | General procedure for Ni/CNT-catalyzed DPE

In a typical catalytic reaction, 500 mg of diphenyl ether (DPE) or another derivate, 50 mg of catalyst, and 10 ml

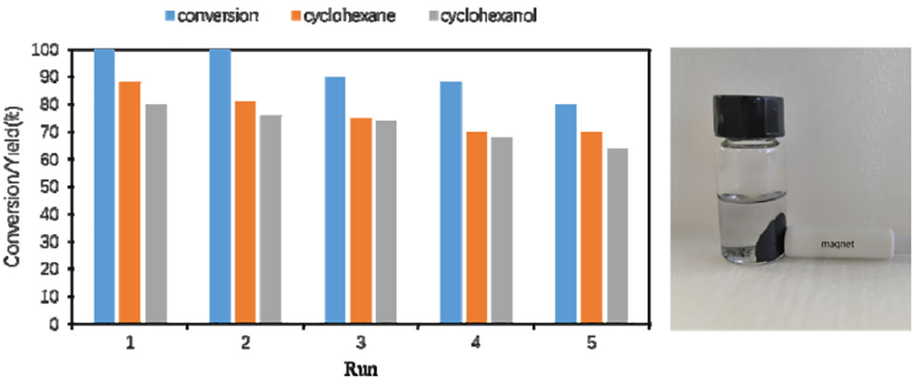


FIGURE 8 The recycling runs for Ni/CNT catalyst in the catalytic transfer hydrogenation and magnetic recovery of Ni/CNT catalyst

of isopropanol were placed in a stainless Parr autoclave (25 ml), and any trace of air present in the reactor was eliminated by fluxing H_2 (99.99%) thrice. The reactions were subsequently conducted at the desired temperature and stirred (600 rpm). At the end of the reaction, the reactor was cooled to room temperature, and the pressure was released; the mixture was filtered to collect the catalyst; and the filtrate was analyzed by the gas chromatograph/mass spectrometer using the n-dodecane as an internal standard. The collected catalyst was washed with isopropanol thrice and dried at 100°C to explore the cycle test under the optimal reaction condition. The conversion and product yield in the liquid phase were, respectively, calculated according to the following formulas:

$$\text{Conversion} = \frac{\text{model of DPE reacted}}{\text{total mole of DPE}} \times 100\%$$

$$\text{Yied of cyclohexane} \frac{\text{model of cyclohexane}}{\text{total mole of DPE}} \times 100\%$$

$$\text{Yied of cyclohexane} \frac{\text{model of cyclohexane}}{\text{total mole of DPE}} \times 100\%$$

3.3 | Catalyst preparation

In a typical process, the 20% Ni/CNT catalyst was prepared by impregnating the CNT (2 g) with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (1.5 g) in 30 ml of deionized water. Then, the suspension was stirred for 24 hr at room temperature to ensure high dispersion. Subsequently, the suspension was dried at 110°C for 5 hr, and the obtained solid sample was calcined in a furnace at 500°C for 5 hr. The desired 20% Ni/CNT catalyst was finally achieved after reducing at 500°C for 3 hr under hydrogen flow. Different M/CNT catalysts (i.e., Fe/CNT, Mo/CNT, Co/CNT, and Ce/CNT) were synthesized by the same method.

3.4 | Catalyst characterization

XPS was carried out on an ESCALAB-250 (Thermo-VG Scientific) spectrometer with an Al Kα (1,486.6 eV) irradiation source. Powder XRD was performed on a Bruker D8 Advance X-ray powder diffractometer. TEM images were collected using a TEM Tecnai G2 20. TPR profiles of the catalysts were obtained with GC-1690 equipped with a TCD detector.

4 | CONCLUSION

We described a mild and efficient strategy, which proceeded through the selective cleavage of aromatic ether bonds and a hydrogenolysis of aromatic rings. The Ni/CNT catalyst not only exhibited the perfect ability to catalyze the transfer hydrogenolytic cleavage of aromatic ether bonds in various compounds, employing *i*PrOH as a hydrogen resource, but also could be easily recovered magnetically from the reaction process for the next five recycling tests. The competitive catalytic hydrogenation reaction indicated that the yields of cyclic alcohols in the transfer hydrogenolysis of diphenyl ether, benzyl phenol ether, and phenethoxybenzene were deeply affected by the nature of the aryl groups, in which the more arene derivatives substituted, the lower yields of cyclohexane achieved. The circular diagram of the mechanism provided two pathways to form cycloalkanes and cyclic alcohols, and the main pathway can be concluded as follows: direct cleavage of aromatic ether bonds and dearomatization subsequently. This work may inspire more research on the depolymerization of real lignin using nonnoble metal catalysts in the absence of hydrogen.

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