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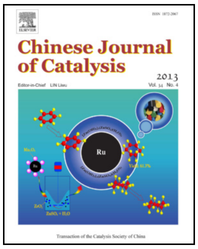

Communication

Hydrogenation and cleavage of the C–O bonds in the lignin model compound phenethyl phenyl ether over a nickel-based catalyst

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ABSTRACT

Phenethyl phenyl ether (PPE) was selected as a typical lignin model compound and hydrogenated and cleaved over two readily accessible nickel-based catalysts, which could be easily separated from the product mixture. The results revealed that the reduction of the nickel catalyst with gaseous hydrogen produced a species capable of achieving higher activity towards C–O–C bond cleavage compared to the Ru/C and Pd/C catalysts. The selectivity of the C–O–C bond cleavage over the Ni/C catalyst was 85%, and higher than the corresponding values in the Ru/C (40%) and Pd/C (69%) systems. Using the carbothermal reduction method for the production of the Ni/C-C catalyst, the conversion and selectivity levels reached 99%, with 40% of the benzene rings in PPE being reserved. In comparison, no benzene ring containing products wer observed over the noble metal catalysts. This difference was attributed to the interaction between the carbon support and the nickel nanoparticles.

Aromatic compounds are important bulk chemicals in the petroleum oil industry, with the majority of these compounds being produced from fossil fuels such as petroleum, coal and natural gas. The production of aromatic compounds from fossil fuels, however, represents a non-sustainable and challenging supply chain, because of the dwindling supplies of fossil fuels and their nonrenewable properties. The development new of methods for the production of aromatic compounds from renewable biomass resources is therefore of critical importance.

Lignin is a three-dimensional natural polymer, which serves as a glue to adhere cellulose and hemicelluloses and provide strength to plants. The basic unit of lignin is phenylpropane, with these units being connected to each other via C–O–C bonds (accounting for 2/3–3/4 of all linkages) and C–C bonds (accounting for 1/4–1/3 of all linkages). Aromatic compounds could be obtained from lignin if a suitable method was developed to exploit this natural resource. For example, the development of techniques for the selective cleavage of the C–O–C bonds without disrupting the benzene rings would provide some useful aromatic compounds. The efficient use of lignin to produce aromatic compounds therefore represents a potentially sustainable route to aromatic materials.

In light of complex structure and composition of native lignin, methods for investigating C–O bond cleavage in lignin model compounds and studying the associated cleavage rules have been widely studied. In the majority of cases, research has focused on cleaving the C–O bonds of lignin model compounds using homogeneous catalysis. For example, Toste's group [1]

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developed a series of vanadium–oxo complexes and applied them to the non-oxidative cleavage of the C–O bonds of dimeric lignin model compounds to give aryl enones with 95% conversion. Hansen's group [2–4] also studied a vanadium complex catalyzed lignin model oxidation reaction, and reported that the C–O and C–C bonds could be selectively cleaved by changing the ligand involved in the catalysis [5]. The use of hydrogenation as another potential method for the conversion of lignin has also been the subject of considerable attention. Hartwig's group [6] recently reported the use of a nickel carbene complex as an effective catalyst for the hydrogenolysis of the aryl ether bonds in several lignin model compounds in the presence of the organic base NaO^{t}Bu, achieving 99% conversion. Bergman's group [7] reported the use of a ruthenium xantphos catalyst for the cleavage of the C–O bond of a lignin model compound using transfer hydrogenation with a 62%–98% conversion.

There are several advantages associated with the use of homogeneous catalysts, including their high catalytic performance and controllable activities. The main limitations of using homogenous catalysts, however, including difficulties associated with their separation and recycling. In contrast, heterogeneous catalysts can be easily separated from reaction mixtures and reused. The choice of conversion method is also an important factor in determining the efficiency of the lignin conversion. For example, the oxidation reactions of lignin can exhibit relative poor selectivity towards the oxidation of the C–O and C–C bonds, resulting in the over oxidation of lignin and damage to the benzene ring [8]. In contrast, the hydrogenation reactions of lignin can cleave of C–O bonds selectively and reserve benzene ring. These reactions therefore provide good atomic economy with low levels of hydrogen consumption. In our previous studies, we developed a method of the hydrogenation of lignosulfonate into aromatic compounds with 60% conversion and 70%–95% selectivity [9]. These results demonstrated that nickel not only has a high level of activity for C–O bond cleavage but that it also possesses a propensity towards the preservation of the benzene ring. To further investigate the C–O bond hydrocracking and gaining C–O cleavage rule, we prepared a series of carbon supported nickel catalysts and studied the hydrocracking behavior of a lignin model compound over the nickel catalysts.

Nickel supported on activated carbon catalysts (Ni/C) were prepared by the incipient-wetness impregnation method and further reduced by hydrogen (denoted as Ni/C-H) or by the carbothermal reduction (denoted as Ni/C-C) method [10,11]. The nickel metal loading in these catalysts was set as 10 wt %. The catalyst precursors were typically prepared as follows: nickel nitrate (II) hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 2.76 g) was added to water (8.0 ml) in a beaker. The solution was stirred for 30 min to give an impregnation stock solution. Activated carbon (5.0 g, water absorption capacity 1.8 ml/g) was added to this solution and the beaker was then covered with a culture dish to keep the sample wet for 24 h. The sample was then dried at 120 °C overnight before being milled (80 mesh). The Ni/C-H catalyst was reduced in a horizontal furnace in a H_2 flow (30 ml/min). The reduction temperature reached 400 °C in 60 min and was maintained at 400 °C for 2 h. The Ni/C-C catalyst was reduced in a horizontal furnace in a N_2 flow (30 ml/min) at 450 °C for 2 h. The Ru/C (5 wt%) and Pd/C (5 wt%) catalysts used in this study were purchased from Aladdin Reagent Co. Ltd (Shanghai, China).

The phenethyl phenyl ether (PPE) reactant was synthesized from phenol and 1-bromo-2-phenylethane using the Williamson ether synthesis method [12]. Briefly, powdered caustic soda (18.0 g) was added to a solution of phenol (47.0 g) in benzene (200 g), and the resulting mixture was heated to 95 °C. 1-Bromo-2-phenylethane (46.0 g) was then added, and the resulting mixture was stirred for 12 h at 95 °C. Upon completion of the reaction, the mixture was cooled, and washed and extracted with water and benzene, respectively. The solvent was then removed in vacuo to give the crude PPE product, which was purified by column chromatography. The purity of the final PPE product was great than 99.6% (determined by GC), and its structure was confirmed by ^{1}H NMR analysis and mass spectroscopy. The PPE hydrocracking reaction was carried out in 75 ml autoclave under 2 MPa of hydrogen pressure. The reaction products were qualified by gas chromatography-MS (GC-MS) (Agilent 6890 N GC/5973 MS, SE-54 column) and quantified by GC (Agilent 7890, FID detector, HP-5 column, 30 m × 0.25 mm × 0.32 mm)

In our recent report, a nickel precursor supported on activated carbon was completely reduced to the nickel nanoparticles (d = 20 nm) at 400 °C [11]. However, the exact nickel reduction temperature of the carbothermal reduction method is not clear. As a result, we attempted to reduce the Ni/C precursor using the carbothermal method in N_2 at temperatures of 300, 400, and 450 °C. The Ni/C products obtained in each case were characterized by X-ray diffraction (XRD) analysis (see Fig. 1). The curves B and C in Figure 1 represent the Ni/C treated at 400 and 300 °C, respectively. The peaks positioned at 2θ = 37°, 43°, and 63° were assigned to NiO (PDF 47-1049), suggesting that nickel nitrate decomposed to NiO, which was reduced no further by the carbon when the reduction temperature was below 400 °C. When the Ni/C precursor was reduced at a temperature of 450 °C, however, the XRD pattern of the Ni catalyst was different to those for the samples treated at 400 °C (curve B) and 300 °C (curve C). The XRD pattern of the sample heated

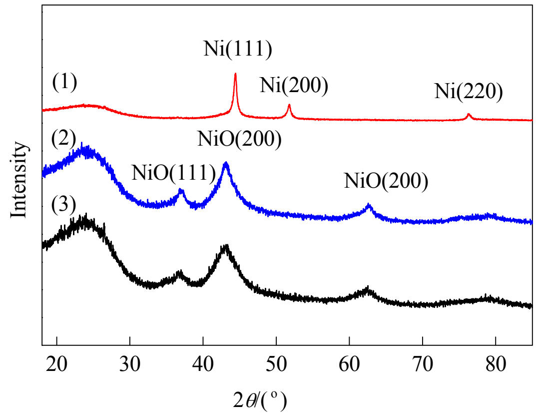


Fig. 1. XRD patterns of the Ni/C catalyst reduced using the carbothermal method in N_2 at 450 °C (1), 400 °C (2), and 300 °C (3).

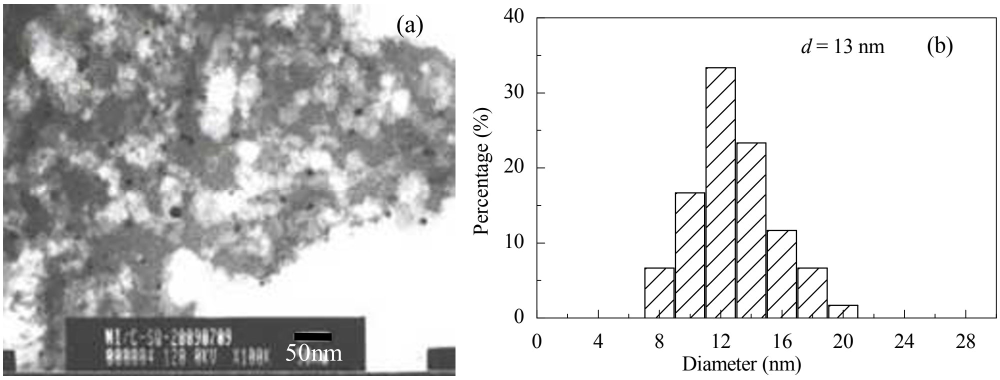


Fig. 2. TEM image (a) and Ni particle size distribution (b) of the Ni/C catalyst carbothermally reduced at 450 °C.

at 450 °C contained new diffraction peaks at $2\theta = 44°$, 52°, and 76°, which were assigned to metal Ni (PDF 3-65-2865). This result suggested that the nickel nitrate had been reduced by the carbon support at 450 °C.

A TEM image of the Ni/C-C material reduced at 450 °C is shown in Fig. 2. The average size of the nickel nanoparticles within this material was found to be 12 nm (calculated from 120 particles), which was smaller than that of the Ni/C-H sample (20 nm) [11]. In the carbothermal reduction method, the activated carbon not only served as a support but also acted as a reducing agent upon which nickel nitrate was reduced to nickel metal at 450 °C (see Fig. 1 (1) and (2)). During the carbothermal process, the nickel nitrate was initially decomposed to NiO. Further increases in the temperature led to the reduction of the NiO to nickel particles by the carbon support at the nickel-carbon interface, with some of the carbon being simultaneously oxidized to CO_x [13,14]. During the reduction process, these CO_x species were effectively swept away by the flow of N_2 through the system. The consumption of carbon species during Ni reduction resulted in the formation of a concave hole in the carbon surface (Fig. 3) which was supported by the results of BET analysis. The BET result showed that a mesopore with a 7–15 nm pore size was present following the completion of the carbothermal reduction process. The presence of the concave hole allowed the Ni nanoparticles to burrow into the surface and become partially embedded in the carbon matrix. The nickel nanoparticles did not grow into larger particles because of the restriction effect imposed by the concave hole. As a result, the diameter of the nickel particles in Ni/C-C material (d = 13 nm) were smaller than those in the Ni/C-H material (d = 20 nm). This reduction method created many Ni-carbon point contacts and consequently formed a surface with close contacts between the nickel and the carbon support, as illustrated in Fig. 3. The occurrence of such close surface contact plays an important role in enhancing nickel-carbon interactions, and can potentially result in enhanced catalytic activity.

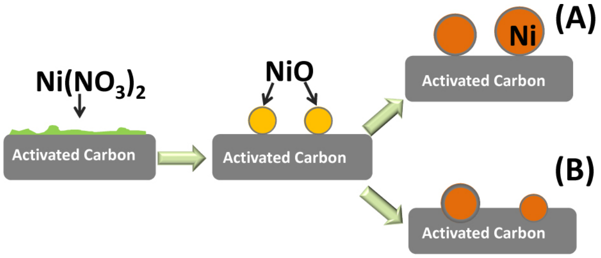
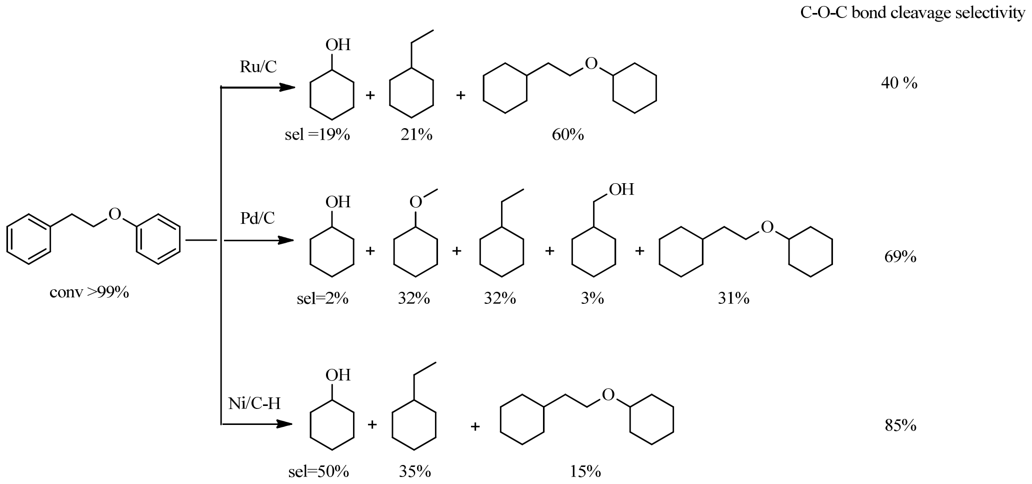


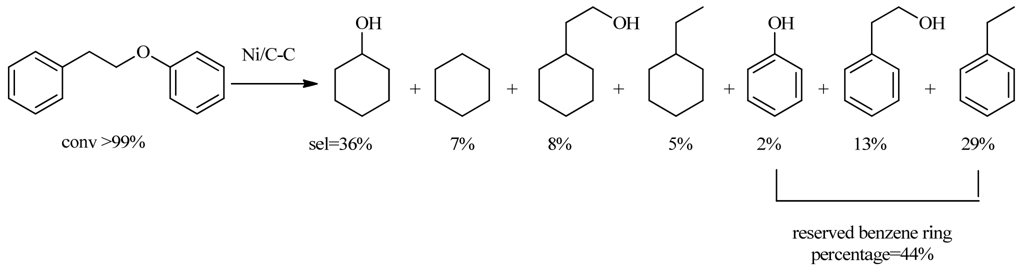
Fig. 3. Representation of the Ni/C catalyst reduced by H_2 (A) and activated carbon (B), respectively.

We initially conducted hydrogenation and cleavage reactions of the PPE over different catalysts, including Pd/C, Ru/C and Ni/C-H, and compared the hydrogenation and cleavage abilities of the different catalysts towards the C–O bonds in PPE. The reactions were carried out in a 75 ml autoclave. Briefly, a portion of the catalyst (25 mg) was added to a solution of the PPE (0.167 mmol) in methanol (10 ml), and the resulting mixture was stirred at 150 °C under 2 MPa of H_2 pressure for 2 h. The reaction was then quenched and analyzed by GC-MS and GC. The results are shown in Scheme 1. The material balance of PPE in all of these runs was found to be 96%. No small alkane, alcohol or ether compounds were detected in the reaction gas according to analysis by MS. The Pd/C, Ru/C and Ni/C-H catalysts exhibited high levels of activity towards the conversion of PPE, providing conversions in excess of 99%. The three different catalysts, however, showed different selectivities towards the C–O bond cleavage.

For the Ru/C catalyst, all of the products were found to be saturated cyclohexane derivates, such as cyclohexanol (19%), ethylcyclohexane (21%), and the fully hydrogenated PPE product (60%). The C–O cleavage selectivity of PPE at full conversion over the Ru/C catalyst was only 40%. Based on the product distribution, it was concluded that the major reaction involved in this reaction was the hydrogenation of the benzene rings rather than C–O bond cleavage. This result indicated that the hydrogenation of the benzene rings was preferred to the cleavage of the C–O bond over the Ru/C catalyst. PPE was also converted to cyclohexane derivates over the Pd/C catalyst but with a higher selectivity towards C–O bond cleavage (69%). Ethylcyclohexane (32%) was observed as one of the major products formed from the hydrogenation reaction of PPE over Pd/C. The occurrence of this product was attributed to palladium's hydrodeoxygenation ability [15]. For the Ni/C-H catalyst, PPE was converted to cyclohexanol (50%) and ethylcyclohexane (35%) with >99% conversion and 85% C–O cleavage selectivity. The selectivity result obtained for the Ni/C-H catalyst was higher than those of the Ru/C and Pd/C catalysts, sug-



Scheme 1. Hydrogenation and cleavage of phenethyl phenyl ether over Ru/C, Pd/C and Ni/C-H catalysts.



Scheme 2. Hydrogenation and cleavage of phenethyl phenyl ether over Ni/C-C catalyst.

gesting that Ni had a pronounced ability to cleave C–O bonds, which was consistent with similar reports from the literature [16,17].

Although the Ni/C-H reduced by H_2 provided a good performance towards C–O bond cleavage, the PPE molecule was completely hydrogenation to the corresponding cyclohexyl products. To retain the benzene rings in the products, we prepared the Ni/C-C catalyst which was reduced by the carbothermal method, and applied it to the PPE reaction. As showed in Scheme 2, the hydrocracking of the PPE model molecule occurred with >99% conversion and >99% C–O bond selectivity over the Ni/C-C catalyst, demonstrating that the Ni/C-C catalyst showed an excellent performance towards C–O bond cleavage. Furthermore, aromatic compounds accounted for 44% of the final products, indicating that that the Ni/C-C catalyst favored the preservation of the benzene rings in the PPE.

Compared with traditional homogeneous catalysts, the Ni/C-C catalyst could be easily separated from the product mixture using a magnetic field (Fig. 4).

It is well known that the size of the nanoparticles in a catalyst has a significant effect on the reaction activity. Generally, the smaller the nanoparticles in a catalyst, the higher the activity of the catalyst [18,19]. For the nickel-catalyzed benzene hydrogenation reaction, the Ni/C-C catalyst (d = 13 nm) hydrogenated 56% of the benzene rings in the PPE (retained 44% of the benzene rings in the product), whereas the Ni/C-H catalyst (d = 20 nm) hydrogenated >99% of the benzene rings. These results suggested that the larger nickel size provided a higher level of hydrogen activity, which was in direct contradiction of the general rule provided above. The fact that the capacity of the Ni catalysts to facilitate benzene hydrogenation decreased with a reduction in the size of the nickel nanoparticles suggested that the benzene hydrogenation reaction was governed by factor other than the size effect.

During the reduction of the Ni/C-H catalyst, nickel nitrite was reduced by hydrogen at 400 °C. The activated carbon served as an intact support and was not involved in the reduction process. Thus, the nickel-carbon interaction in this case was weak (see Fig. 3). In the carbothermal reduction method, however, the nickel nanoparticles became semi-embedded in the carbon support because of the consumption of carbon at the nickel-carbon interface. This structure led to an increase in

Fig. 4. Photograph of the Ni/C-C catalyst separated by a magnet following the reaction.

Graphical Abstract

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Hydrogenation and cleavage of the C–O bonds in the lignin model compound phenethyl phenyl ether over a nickel-based catalyst

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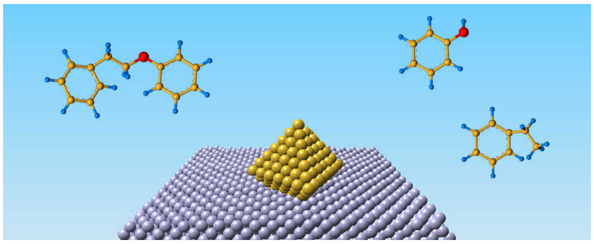
The C–O bond in the lignin model compound, phenethyl phenyl ether, was successfully hydrogenated and cleaved over a nickel-based catalyst, which had been prepared using the carbothermal reduction method.



the level of nickel-carbon interaction. Furthermore, the surface structure of the carbon was a graphene in which the π electrons were delocalized. Based on the close interaction between the carbon and nickel atoms, the π electrons in Pz orbitals of the carbon could become hybridized with the d electrons of the nickel, leading to an increase in the electron mobility [20–22], which may result in the nickel bearing a negative charge.

It is generally believed that reaction activity of benzene hydrogenation is proportional to the amount of positive charges on surfaces of metal nanoparticles [23–25]. For supported catalysts, this positive charge is predominantly formed as a consequence of the strong interactions between the metal and the support. In the Ni/C-C catalyst, the Pz π electrons of the carbon surface could have become hybridized with the nickel d orbitals and subsequently donated to nickel, resulting in negatively charged nickel nanoparticles, which could lead to a decrease in the benzene hydrogenation activity. The benzene ring would therefore be preserved in the products, as observed, accounting for the 44% of aromatic compounds in the final products following the hydrocracking of PPE over the Ni/C-C catalyst.

In summary, the lignin model compound phenethyl phenyl ether was effectively hydrocracked over a nickel-based catalyst. The Ni/C-C catalyst was produced by reduction using the carbothermal method, and exhibited high levels of activity and C–O bond selectivity. Compared with the noble catalysts, the Ni/C-C catalyst showed better benzene ring selectivity, with the difference being attributed to the strong nickel-carbon interactions in the catalyst. These results provide a better understanding of the C–O bond hydrocracking rule and will be useful for the design of new high performance catalysts.

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