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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 were observed over the noble metal catalysts. This difference was attributed to the interaction between the carbon support and the nickel nanoparticles.

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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 NaOtBu, 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 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 ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 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 ^1H 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 $\times$ 0.25 mm $\times$ 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 $2\theta = 37^\circ$, 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 $2\theta = 44^\circ$, 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.

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 derivatives, 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 derivatives 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-

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

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 H₂ provided a good performance towards C–O bond cleavage, the PPE molecule was completely hydrogenated 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 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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Ni基催化剂上木质素模型化合物苯基苯乙醚C–O键的加氢裂解

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摘要: 研究了Ni基催化剂上木质素模型化合物苯基苯乙醚中C–O–C键加氢裂解性能。结果表明, Ni/C催化剂显示出优异的加氢裂

解能力, 苯基苯乙醚的转化率达到99%以上. Ni/C催化剂的还原方法对裂解选择性有重要影响; 氢气还原制备的Ni/C-H催化剂上, C–O–C键裂解选择性为85%. Ru/C和Pd/C催化剂上裂解选择性分别为40%和69%. 采用碳热还原方法制备的Ni/C-C催化剂, 可以实现高选择性加氢和裂解, C–O–C键裂解选择性达到99%以上, 其中芳烃化合物收率为44%. 这可能与镍组分和载体碳之间的相互作用有关.

关键词: 木质素模型化合物; 苯基苯乙醚; 加氢裂解; 镍基催化剂; 芳香化合物

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石油、煤和天然气等化石资源是液体燃料和化学品的主要原料来源, 其中芳香族化合物在石油化工行业中占有重要地位. 但是, 储量有限和不可再生使得化石资源的可持续稳定供应面临着极大挑战. 开发和利用可再生的生物质资源, 制备芳香族化合物具有重要的意义.

木质素是生物质的主要成分之一, 是植物体经光合作用获得的含大量苯环结构的天然聚合物. 木质素的基本结构单元为苯丙烷结构, 是天然芳香化合物的来源之一. 木质素的基本结构单元间的连接方式主要为C–O–C键(占2/3~3/4), 其次为C–C键(占1/4~1/3). 通过催化加氢裂解的方法, 使得木质素的C–O–C键裂解并保留苯环, 可获取具有重要用途的芳香化合物. 因此, 高效合理利用木质素资源制备芳香化合物, 是一条可持续发展和具有挑战性的途径之一.

木质素的组成和结构非常复杂, 通过研究组成结构简单的木质素模型化合物分子的裂解, 获取基本的化学键断裂信息, 是木质素直接催化转化利用的重要途径和策略, 受到了国内外的广泛关注. 目前的研究工作大多集中于均相裂解催化剂的设计和开发. Toste课题组^[1]发展了一种均相钒氧(V=O)络合物的氧化裂解催化剂, 通过调变催化剂的配体属性, 可将95%的模型化合物氧化转化为愈创木酚和愈创木酚烯酮衍生物. Hanson课题组^[2~4]也对均相钒配合物催化剂上氧化裂解模型化合物进行了研究, 通过调变钒基催化剂的配体, 可选择性氧化裂解模型化合物的C–C键或C–O键, 得到2,6-二甲氧基苯醌或愈创木酚烯酮衍生物^[5]. 另外, 采取加氢方式来研究模型化合物中醚键裂解也受到极大重视. Hartwig课题组^[6]采用氢解的方式, 以Ni碳烯卡宾络合物为催化剂, 在有机碱NaO^tBu的作用下高效氢解二苯醚等模型化合物中的C–O–C键, 转化率>99%, 同时可保留底物中的苯环. Bergman课题组^[7]以RuH₂(CO)(PPh₃)₃为催化剂, 4,5-双二苯基膦-9,9-二甲基氧杂蒽(Xantphos)为配体, 研究了2-苯甲氧基-1-苯乙醇及其衍生物中C–O–C键的加

氢裂解, 裂解产物的分离收率为62%~98%.

均相催化剂的活性较高, 且配体可调, 但催化剂分离和循环使用不便; 而多相催化剂则可弥补这些不足. 此外, 氧化降解对底物分子的C–O键和C–C键断键的选择性较低, 容易造成过度氧化, 导致芳香环基本结构的破坏^[8]. 采用选择加氢裂解的方式, 选择裂解C–O–C键, 同时保留苯环结构, 具有较高的原子经济性和较低的氢气消耗. 在前期研究中, 本课题组报道了Ni基催化剂上木质素磺酸盐的加氢裂解过程, 木质素磺酸盐转化率达到60%, 酚类产物的选择性达到70%~95%^[9]. 结果表明, Ni基多相催化剂可选择性加氢裂解木质素中的C–O–C键, 而且在该过程中大量的苯环得以保留, 表现出优异的选择裂解C–O–C键和保留苯环的能力. 生物质催化气化相关研究亦表明, Ni基催化剂具有较好的C–O–C键断裂能力. 为进一步研究木质素中C–O–C键选择加氢裂解规律, 本文采用负载型Ni基催化剂, 对木质素模型化合物苯基苯乙醚的选择加氢裂解过程进行研究.

负载型镍基催化剂前体采用等体积浸渍法制备, 然后分别通过氢气和碳热法进行还原, 得到的催化剂分别标记为Ni/C-H和Ni/C-C^[10,11]. 其中Ni负载量均为10%. 将2.76 g Ni(NO₃)₂·6H₂O, 溶于8.0 ml去离子水中, 搅拌30 min使之充分溶解, 之后加入5.0 g活性炭(比表面积为1318 m²/g, 吸水率为1.8 ml/g), 并充分搅匀. 在室温下浸渍24 h. 后再于120 °C干燥12 h, 取出后碾磨过80目筛, 得到催化剂前体. 催化剂前体在H₂中于400 °C还原3 h, 即得到Ni/C-H样品. 在N₂中, 于450 °C处理2 h, 即得到Ni/C-C样品. 作为参照催化剂的5%Ru/C和5%Pd/C购于阿拉丁试剂公司.

以苯酚和2-溴代苯乙烷为起始原料, 采用Williamson法合成反应底物苯基苯乙醚^[12]. N₂保护下在150 ml苯溶剂中加入47.0 g苯酚搅拌, 待苯酚完全溶解后加入片状NaOH(18.0 g)搅拌, 所得混合物在油浴中加热至95 °C, 再加入β-溴代苯乙烷(46.0 g), 在95 °C搅拌反应

12 h. 反应结束后, 混合物经去离子水洗涤、无水硫酸钠干燥、旋转蒸发溶剂后, 得到淡黄色油状粗产物, 再以乙酸乙酯和石油醚的混合溶剂($V/V = 1/10$)经硅胶柱分离纯化得到苯基苯乙醚产物(色谱纯度 $>99.6\%$), ^1H NMR和MS表明, 合成产物为苯基苯乙醚^[12]. 催化加氢裂解反应在75 ml高压反应釜中进行. 反应产物采用GC-MS (Agilent 6890 N GC/5973 MS, SE-54 色谱柱)定性, 加氢转化率和裂解选择性采用GC面积归一法计算(Agilent 7890型气相色谱, FID检测器, HP-5 色谱柱, 30 m $\times$ 0.25 mm $\times$ 0.32 mm).

我们最近的研究表明^[11], 对于Ni/C-H催化剂, 在400 °C时Ni物种可以完全被 H_2 还原为金属态(粒径 $d = 20$ nm). 为了研究碳热处理温度对镍还原的影响, 将Ni/C催化剂前体在 N_2 下分别经300, 400, 450 °C处理, 所得Ni/C-C催化剂的物相结构如图1所示. 可以看出, 经400和300 °C碳热处理后的Ni样品在 $2\theta = 37^\circ$, 43° 和 63° 处出现衍射峰归属为NiO(PDF 47-1049), 表明在400 °C以下碳热处理时, Ni物种由硝酸镍转变为NiO, 而未发生Ni组分的还原. 进一步将处理温度升至450 °C时, 所得样品在 $2\theta = 44^\circ$, 52° 和 76° 处出现金属Ni的衍射峰(PDF 3-65-2865), 此时NiO物相消失. 这表明450 °C的碳热处理使催化剂前体由NiO还原为金属态Ni.

图2为经碳热还原后的Ni/C-C催化剂的TEM照片. 测得Ni粒子的粒径约为13 nm; 而Ni/C-H样品的Ni粒径为20 nm^[11]. 在碳热还原方法中, 活性炭不仅起到载体作用, 而且在450 °C下可将NiO还原为Ni粒子. 该过程可以理解(见图3): 在 N_2 气氛下加热催化剂前驱体时, 随着温度的升高, 镍盐首先受热分解为NiO, 经过较高温度碳热还原后, NiO物种进一步被还原成为Ni粒子, 而部分碳载体则被氧化为气态的 CO_x ^[13,14]. 在碳热还原过程中, Ni粒子周围的碳载体上出现有大量凹穴和孔隙结构(见图2(a)), 这可能归因于碳载体在还原Ni物种过程中, 自身被氧化生成 CO_x 物种, 并脱离催化剂体系而形成该结构. 孔径测试表明, 碳热还原后的Ni/C催化剂出现了新孔(7~15 nm). 另外, 对于落在碳载体凹穴中的Ni粒子而言, 凹穴的存在对Ni粒子有物理空间上的限制, 避免Ni粒子的长大. 这可能是导致碳热还原的Ni粒子粒径小于Ni/C-H样品的主要原因.

我们对Ni/C-H, Ni/C-C, Ru/C和Pd/C催化剂上苯基苯乙醚中C–O–C键加氢裂解进行了研究. 反应在75 ml反应釜中进行, 将原料(0.167 mmol)溶于10 ml甲醇, 同时加入25 mg的催化剂, 在150 °C和2 MPa条件下反应2 h.

加氢裂解苯基苯乙醚反应选择性采取将产物归一为六元环后的产物色谱峰面积与苯基苯乙醚色谱峰面积的2倍的百分比来确定, 即产物裂解选择性=(所有单苯环产物色谱峰面积之和+所有环己基类产物色谱峰面积之和)/(苯基苯乙醚色谱峰面积 $\times 2$) $\times 100\%$; 产物分布=所有单苯环类产物色谱峰面积之和/(所有单苯环类产物色谱峰面积之和+苯基苯乙醚苯环完全加氢产物色谱峰面积 $\times 2$) $\times 100\%$. 考虑到苯基苯乙醚含有两个苯环, 其苯环量在计算中需乘以2. 反应结果如图式1所示. 可以看出, 在该反应条件下, 这三种催化剂皆表现出较高的催化加氢活性, 转化率均在99%以上, 反应的物料平衡在96%以上, 反应后对上层气体检测表明, 没有小分子烷、醇、醚等产物生成. 但是, 不同的催化剂在加氢裂解过程中表现出显著不同的C–O–C键裂解选择性.

Ru/C催化剂主要发生苯环加氢, 而不是C–O–C键的裂解. 原料中C–O–C键裂解选择性只有40%, 即使在裂解产物中, 也生成了苯环的加氢产物环己醇(19%)和乙基环己烷(21%). 相同条件下, Pd/C催化剂的裂解选择性为69%, 表明Pd/C催化剂具有更高的裂解C–O–C键能力. 在Pd/C催化反应中生成了32%的乙基环己烷, 这可能与Pd有较强的加氢脱氧能力有关^[15]. 而对于Ni/C-H催化剂, 原料转化率达到99%以上, 得到的产物为环己醇和乙基环己烷, C–O–C键的裂解选择性达到85%. 结果表明, 与Ru/C和Pd/C催化剂相比, Ni/C催化剂具有更高的加氢裂解C–O–C键的能力, 与文献[16,17]结果一致.

虽然Ni/C-H催化剂上可以实现选择加氢断裂C–O–C键, 但反应物中的苯环几乎完全转化为环己基类加氢产物, 从而消耗大量 H_2 . 研究发现, 碳热还原法制得的Ni/C-C催化剂不但可实现C–O–C键的选择裂解, 而且可抑制苯环加氢产物. 结果见图式2. 可以看出, 在相同的反应条件下, Ni/C-C催化剂可以将底物完全转化, 产物几乎全部为C–O–C键裂解的产物, 裂解选择性达到100%, 表明该催化剂对C–O–C键的优异选择性. 此外, 产物中有44%的苯环未被加氢, 表明该催化剂不仅可以控制苯环的加氢深度和选择性.

为了区别于传统的均相催化剂, 对该催化剂的分离过程进行研究. 本文采用外加磁场方法, 实现了与反应物分离, 如图4所示.

研究表明, 金属组分的粒径对反应活性有重要影响, 一般认为其加氢活性随着催化剂活性组分粒径的减小而增大^[18,19]. 与Ni/C-C催化剂相比, Ni/C-H表现出非选择性的苯环加氢能力, 这可能与氢气还原和碳热还原的

模式不同有关.

对于Ni/C-H催化剂, 400°C时H₂将NiO还原为Ni金属粒子, 载体碳几乎不参与还原, 生成的Ni粒子与碳载体接触不紧密(见图3), 相互作用可能较弱; 而碳热还原过程是在NiO被碳还原并进一步深入碳因氧化而产生的凹穴, 形成了一种紧密接触的嵌入式结构, 如图3所示. 活性炭载体表面存在有石墨烯层结构; 在Ni(0)与碳载体紧密接触的部位, Ni(0)与石墨烯层可以发生紧密接触, 从而使得石墨烯层p_z轨道的 π 电子与Ni金属的d带电子杂化, 通过共价键作用, 能够增加电子的流动性^[20–22]. 因此, Ni/C-C催化剂中的Ni粒子通过嵌入碳载体, 彼此之间紧密接触, 可形成镍-碳的强相互作用; 且由于石墨烯层的富电子性, Ni金属表面可能带上部分负电荷.

另一方面, 苯加氢活性与金属表面的缺电子性质相关^[23–25], 即在负载型催化剂中, 载体的作用可使金属表

面表现出一定的缺电子性能, 并促进苯加氢反应的发生. 在本文中, 对于Ni/C-C催化剂, 通过其与碳组分的强相互作用, 活性炭的石墨烯层的 π 电子通过杂化作用可部分转移给镍的d轨道, 使金属镍表现出富电子效应, 从而降低苯加氢的活性, 因此抑制了苯环加氢. 原料加氢产物中有40%的苯环未被加氢, 使产物中保留有较多的苯环结构.

综上所述, 通过调变催化剂的制备方法, 得到了碳热还原方法制备Ni/C-C催化剂, 在木质素模型化合物苯基苯乙醚加氢裂解的反应中表现出优异的催化活性和醚键裂解选择性. 这可能与金属镍组分和碳载体之间的相互作用有关. 该催化剂可控制苯环加氢的深度, 有利于减少反应中H₂的消耗, 提高芳香化合物选择性. 该结果对于深入认识醚键加氢和裂解规律, 设计木质素选择加氢裂解催化剂, 具有重要的参考价值.