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ARTICLE TYPE

Free-radical conversion of lignin model compound catalyzed by Pd/C

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Abstract Efficent cleavage of C-O bond in lignin and its model compounds is of great importance for transfomation of lignin into fuel and value-added chemicals. In this work, we explored the transformation of lignin model compound benzyl phenyl ether(BPE) at 150^{o}C using Pd/C as the catalyst in argon atmosphere in the presence of Na_2CO_3 and N-methyl-2-pyrrolidone(NMP). The effects of different reaction parameters such as the amounts of Pd/C, Na_2CO_3 and NMP as well as reaction time were investigated. It was found that Pd/C played a key role for the conversion of BPE. At the same time, Na_2CO_3 and NMP also promote the transformation effectively. The yields of phenol and toluene reached 71.6% and 50.4%, respectively. Analytic results of electron paramagnetic resonance (EPR) indicated that reaction proceeded through free-radical reaction mechinsm. Control experiments indicated that direct pyrolysis of BPE was the main route to generate the target products.

Keywords: depolymerization, benzyl phenyl ether, lignin, free-radical

1.Introduction

Transformation of lignocellulosic biomass into high value-added chemicals has attracted much attention in recent years.[1,2] As a main component of lignocellulosic biomass, lignin is considered to be the unique renewable aromatic resource.[3] Selective cleavage of the chemical bonds is the major challenge for converting lignin into liquid fuels or value-added chemicals. Currently, depolymerization reactions of lignin can be mainly divided into cracking,[4] hydrolysis reactions,[5] catalytic reduction reactions,[6] and catalytic oxidation reactions.[7] In the oxidation reactions, both preventing deep oxidation and enhancing the yield of target products are crucial. During reductive depolymerization, extra hydrogen resource is necessary and keeping the aromatic structure is difficult. Thus, hydrolysis or cracking reaction of lignin in inert atmosphere are desirable methods to obtain aromatic compounds.

Due to the structural complexity and variability, model compounds with different linkages like β-O-4, α-O-4, and 4-O-5 are selected to disclose selective cleavage of the chemical bonds in lignin valorization.[8] Among various lignin model compounds, benzyl phenyl ether (BPE) has been widely employed for studying the transformation of the α-O-4 bond in lignin.[9] It was reported that BPE could be transformed into phenol, bezene and toluene with the yields of 45.8%, 6.6% and 2.4% under nitrogen atmosphere with Pd/$Cs_xH_{3.0-x}PW_{12}O_{40}$ as the catalyst at the temperature of 200 ^{o}C.[10] In high temperature water (250 ^{o}C), BPE was hydrolyzed and the selectivities of phenol and benzyl alcohol were 76.1% and 83.9%, respectively.[11] When hydrolytic cracking of BPE was conducted under 175 ^{o}C using $In(OTf)_3$ as the catalyst, the yields of phenol and benzyl alcohol were 60% and 50%, respectively.[12] BPE was equally cleaved into phenol and benzyl alcohol in water at 250 ^{o}C. Under the selected conditions, the conversion increased linearly to 31% as a function of time up to 110 min, and the yields of phenol and benzyl alcohol synchronously increased to around 13%.[13] It was reported that with the assistance of microwave irradiation, BPE could be transformed into phenol, benzyl alcohol, 2-benzylphenol, 4-benzyphenol, benzyl ethyl ether, benzyl ether in acidic ionic liquid under 180 ^{o}C for 10 minutes. The yields of phenol and benzyl alcohol were 35.3% and 4%, respectively.[14] Thus, exploration for the cleavage of phenyl benzyl ether under mild conditions in inert atmosphere with high yield is highly desireble.

The non-catalyzed pyrolysis of BPE has been extensively investigated in the past. Usually, BPE can be pyrolyzed by the cleavage of C-O bond at $T \geq 275$ °C to produce benzyl and phenoxy radicals[15] and then hydrogen abstracted from BPE or from an added hydrogen donor can combine these radicals and produce toluene and phenol as dominant products. However, recombination of the incipient radicals through coupling at phenoxy ring carbons has also been detected. It was reported[16] that Pd/Al_2O_3 can adsorb H· free radical and promote the formation of alkyl and aromatic free radical intermediates as detected by EPR on the catalyst surface. Thus, it is possible to carry out the pyrolysis of BPE catalyzed by metal catalysts under mild conditions.

Herein, we conducted the decomposition of BPE using commercial Pd/C as the catalyst with Na_2CO_3 and NMP in argon atmosphere. It was demonstrated that BPE could be transformed into phenol and toluene with little amount of bezene. Under the temperature of 150 ^{o}C with reaction time of 3 hours, the yields of phenol and toluene reached 71.6% and 50.4%, respectively. Further investigations showed that Pd/C catalyzed the free-radical reaction, especially in the presence of Na_2CO_3 and NMP.

2. Experimental section

2.1 Chemicals

BPE, Pd/C(5 wt% Pd), 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), N-methyl-2-pyrrolidone(NMP), N-tert-butyl-a-

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phenylnitrone (PBN) and Na_2CO_3 were purchased from Alfa Aesar. Dichloromethane, $PdCl_2$, active carbon, NaOH, $NaHCO_3$, pyrrole, cyclopentanone, cyclohexylamine and biphenyl were provided by Beijing Chemical Reagents Company. Hydroxyapatite (HAP) was obtained from Aldrich and used as received. Argon and H_2 were provided from Beijing Analytical Instrument Factory and their purity was >99.99%.

2.2 Preparation of Pd/HAP catalysts

We choose Pd/HAP as the comparative catalyst in order to detect whether the carbon from Pd/C reacted with water to produce the hydrogen. The metal Pd catalyst supported on HAP was prepared by the ion exchange method.[17] In a typical procedure, 0.5 g HAP was dispersed in 150 mL double deionized water under vigorous stirring for 2 h. Then a certain amount of $PdCl_2$ aqueous solution was added into the HAP suspension. After being stirred for 2 h at room temperature, the slurry was heated and refluxed at 100 °C for 12 h. The obtained solid was collected by filtration and washed with deionized water until the Cl^- was not detectable. The as-prepared Pd/HAP catalyst was obtained after dryed under vacuum at 60 °C overnight and reduced in pure H_2 (99.99%, 60 $cm^3 \cdot min^{-1}$) at 300 °C for 1 h.

2.3 Catalyst characterization

The X-ray diffraction (XRD) patterns were collected on a D/Max 2500 V/PC X-ray diffractometer with high intensity Cu Kα (40 kV, 200 mA) radiation. The high-resolution transmission electron microscopy (HRTEM) observation was carried out on JEM 2011 at an accelerating voltage of 200 kV.

2.4 Catalytic measurements

The reactions were conducted in a 8 mL reactor made of 316 stainless steel. In a typical experiment, desired amount of BPE, Pd/C, Na_2CO_3, NMP and water were loaded into the reactor. The reactor was placed in the pre-heated furnace of desired temperature and the air was removed under vaccum, then argon of ambient pressure was charged into the reactor and the stirrer was started. After a suitable reaction time, the reactor was cooled in ice water. The products were extracted with dichloromethane and analyzed by gas chromatograph (GC) using a HP 4890 GC equipped with a flame ionization detector (FID), and biphenyl was used as the internal standard. Identification of the products was carried out using a GC-MS (SHIMADZU-QP2010) and by comparing the retention times to respective standards in the GC traces. The yields are calculated as the moles of products formed divided by the moles of the reactant initially loaded into the reactor.

2.5 Procedures of spin trap in our reaction system

In the experiment, desired amounts of Pd/C, Na_2CO_3, NMP, lignin model compound, water and PBN were added in the reactor. The air of the reactor was removed under vacuum and the reactor was placed in the preheated furnace of the desired temperature, then argon was charged into the reactor to 0.1 MPa and the stirrer of the reactor was started. After 60 min, the reactor was opened, a suitable amount of reaction solution was taken out, and the EPR spectrum was recorded using a Bruker ER 300 EPR spectrometer operating at X-band with a TM 110 cavity using a quartz flat cell. The microwave frequency was measured with an EIP Model 575 microwave counter (EIP Microwave, Inc., San Jose, CA). Spectra were recorded at ambient temperature (25℃).

3. Results and discussion

3.1 Catalyst characterization

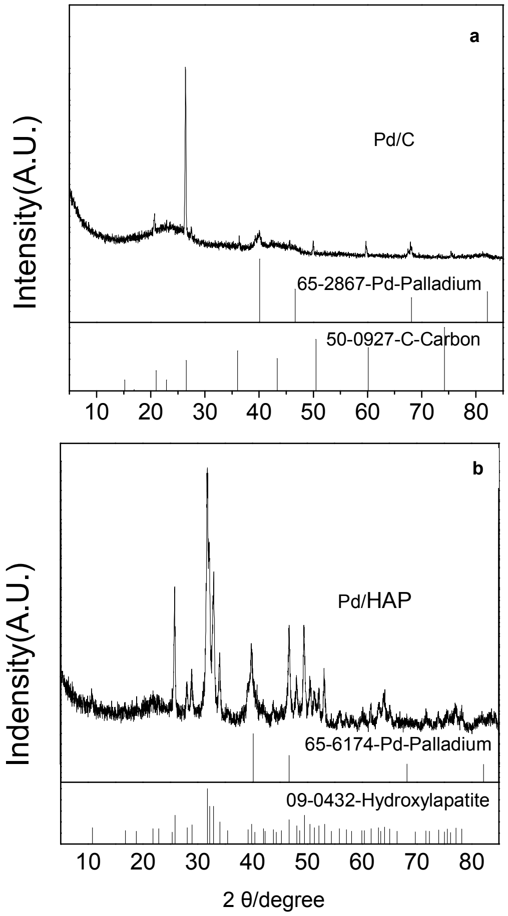

Figure 1. XRD patterns of the Pd/C(a) and Pd/HAP(b)

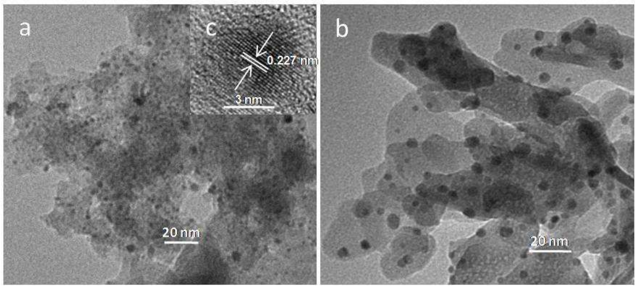

Figure 2. TEM images of the Pd/C(a), Pd/HAP(b) catalysts and the insert of Fig. 2a is HRTEM image of a typical Pd particle in Pd/C (c)

In the decompositon reaction of BPE, Pd/C were used as the catalyst. Meanwhile, We choose Pd/HAP as the comparative

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catalyst in order to detect whether the carbon from Pd/C reacted with water to produce the hydrogen. Both Pd/C and Pd/HAP were characterized by XRD and TEM to get the information for the composition and morphology of catalysts.

It can be known from Fig. 1a that the XRD patterns of the metal Pd particles and carbon are consistent with that in the JCPDS database. Likewise, the XRD patterns of HAP and metal Pd agree with that in the JCPDS database (Fig. 1b). All these data show that the catalysts have definite crystalline structures. The TEM images of the Pd/C and Pd/HAP are shown in Figure 2. The diameters of Pd particles in the catalyst Pd/C and Pd/HAP were in the ranges of 2-5 nm and 6-8 nm, respectively. The lattice fringes with d = 0.227 nm from the Pd (111) plane in Pd/C are clearly visible from the HRTEM image (Fig. 2c). In addition, the surface area and porosity of Pd/C and Pd/HAP are determined by N_2 adsorption-desorption method and listed in the supporting information (Table S1).

3.2 Conversion of BPE

We carried out the reaction of BPE in different catalytic systems, and the results are provided in Table 1. BPE could not be transformed in water or Na_2CO_3 or NMP alone at 150 ^{o}C for 3 hours in Ar atmsphare (entries 1-3). In the presence of catalyst Pd/C (entry 4), the conversion of BPE was 27.8% and the yields of phenol and toluene were 17.4% and 3.7%, respectively. In additon, the results show that Na_2CO_3 or NMP favored the formation of toluene (entries 5 and 6). In the presence of both Na_2CO_3 and NMP, the conersion reached 98.8% and the yields of phenol and toluene were 71.6% and 50.4%, respectively(entry 7).

Table 1 Depolymerization of BPE at different conditions[a]

Entry	Catalyst	Conversion,%	Phenol,%	Toluene,%
1	H_2O	0	0	0
2	Na_2CO_3	0	0	0
3	NMP	0	0	0
4	Pd/C	27.8	17.4	3.7
5	Pd/C+Na_2CO_3	30	13.9	9.4
6	Pd/C+NMP	31.5	12.2	9.18
7	Pd/C+Na_2CO_3+NMP	98.8	71.6	50.4
8	Pd/HAP+Na_2CO_3+NMP	99	64.6	35.8
9	Pd/HAP+C+Na_2CO_3+NMP	69.2	37.8	26.3
10	Pd/C+NaOH+NMP	100	0	34.6
11	Pd/C+$NaHCO_3$+NMP	51.9	17.8	18.5
12	Pd/C+Na_2CO_3+ pyrrole	28.8	13.8	15.8
13	Pd/C+Na_2CO_3+ cyclopentanone	8.2	7.2	7.4
14	Pd/C+Na_2CO_3+NMP +TEMPO	73.5	47	26.4

a. Reaction conditions: BPE 0.05 g, Pd/C 0.025 g, Pd/HAP 0.025 g, Na_2CO_3 0.4 g, NaOH 0.4 g, $NaHCO_3$ 0.4 g, NMP 0.05 g, pyrrole 0.05 g, cyclopentanone 0.4 g, TEMPO 0.015 g, H_2O 2 g, Ar 0.1 MPa, reaction temperature 150 ^{o}C, reaction time 3 hrs, volume of the reactor 8 mL.

In order to investigate whether the carbon from Pd/C reacted with water to produce the hydrogen, we also used the Pd/HAP as the catalyst to conduct the transfprmation of BPE(entry 8). Similarly, the converstion and the yields of the target products were high, indicating that the metal Pd played the main role to promote the reaction. Meantime, as active carbon was added into the reaction system at the condition of entry 8, the conversion and yields decreased and no other products were detected(entry 9), which showed that active carbon could not react with water providing the hydrogen for this transformation.

Considering the roles of alkaline for depolymerization of lignin,[18] we chose other two inorganic alkalines to conduct the reaction. When strong alkaline NaOH was added into the reaction system (entry 10), the conversion reached 100% but phenol was partly degraded. On the other hand, both conversion and yields decreased as $NaHCO_3$ was used (entry 11) due to its weak alkalinity.

Because NMP could promote the depolymerazation of BPE, we also investigated the role of the two functional groups of NMP through adding pyrrole and cyclopentanone to replace NMP. Comparing entries 12 and 4, we found that pyrrole promoted the formation of toluene. It can be known from the results of entries 4 and 13 that cyclopentanone played minor role in the transformation of BPE. Based on the above, we can deduce that the functional group containing nitrogen benefits to the reaction. In additon, free radical quenching agent TEMPO was added into the reactor (entry 14) and both conversion and yields decrease, indicating that depolymerazation of BPE was governed by the free-radical reaction mechanism.

Further, we tested the lignin β-O-4 model compound 2-phenoxyacetophenone using our catalytic system at the condition of Entry 7 in Table 1. It was shown that the model compound could be transformed into acetophenone and phenol. The conversion could reach 77.7%, and the yields of acetophenone and phenol were 20.1% and 14.7%, respectively, indicating that the system can promote the transformation of lignin β-O-4 model compounds but the selectivity of target products is not high.

3.3 Effects of reaction parameters

The effects of reaction parametes were further studied using the catalyst Pd/C. From the experimental results in Table 1, we know that the metal Pd played the decisive role for depolymerization of BPE in our reaction system. The dependence of the transformation of BPE on the amounts of Pd/C is shown in Fig. 3. The conversion increased as the loading amount of Pd/C was changed from 0~0.025 g, and the conversion approached 100% at the loading of 0.025 g. The yields of phenol and toluene increased firstly and decreased after the amount of Pd/C exceeded 0.025 g. Generally, increasing amount of active components is favorable to the conversion of reactants. But for free-radical reactions like the depolymerization of BPE, too many catalytic sites promote the formation of free radicals fastly. Thus, the linkage of different free radicals would produce high molecular compounds thereby leading to the decrease of the yields of target products. So, the yields decreased as the amount of Pd/C exceeded 0.025 g.

The effect of reaction time on the transformation of BPE is shown in Fig. 4. The conversion increased with reaction time and

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reached 100% at 3 hrs. The yields of phenol and toluene increased with reaction time and reached a maximum at 3 hours. Before 3 hours, BPE was transformed continuously and the yields of target products also increased with the reaction time. After 3 hours, BPE was consumed completely and different radicals in the system would interact with each other, leading to the formation of by-products. Therefore, too long reaction time were favarable to the occurrence of side reactions. After optimum reaction time, more phenoxy and benzyl radicals was consumed by other radicals in the reaction system. So, the yield of phenol and toluene decreased with reaction time after the maximum.

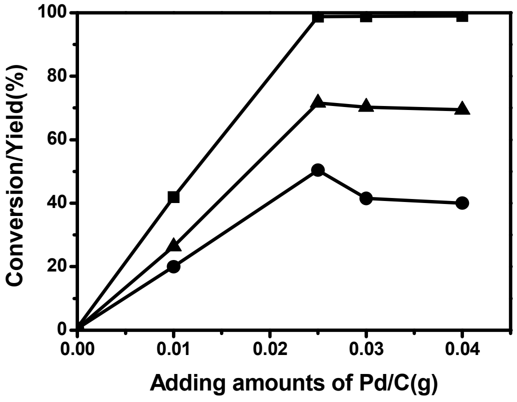

Fig. 3. Effects of amount of Pd/C on depolymerization of BPE. (■) conversion of depolymerization of BPE, (▲) yield of phenol, (●) yield of toluene. Reaction conditions: BPE 0.05 g, Na_2CO_3 0.4 g, NMP 0.05 g, H_2O 2 g, Ar 0.1 MPa, reaction temperature 150 °C, reaction time 3 hrs, volume of the reactor 8 mL.

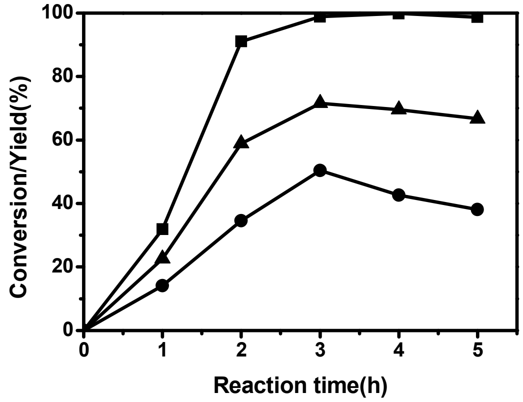

Fig. 4. Effects of reaction time on depolymerization of BPE. (■) conversion of depolymerization of BPE, (▲) yield of phenol, (●) yield of toluene. Reaction conditions: BPE 0.05 g, Na_2CO_3 0.4 g, Pd/C 0.025 g, NMP 0.05 g, H_2O 2g, Ar 0.1 MPa, reaction temperature 150 °C, volume of the reactor 8 mL.

Fig. 5 shows the dependence of the conversion of the BPE and yields of the products on the amount of Na_2CO_3 loaded in the reaction. When the amount of the Na_2CO_3 increased from 0 to 0.4 g, and the conversion increased firstly and then reached the platform because the reactant could be converted completely. The maximum yields could be observed when the amount of the Na_2CO_3 was 0.4 g. The reaction can proceed by hydrolysis and pyrolysis pathways.[14] It was reported that Na_2CO_3 aqueous solution has a strong inhibiting effect on BPE hydrolysis.[19] Thus, with the increasing amount of Na_2CO_3, the yields of toluene, dimers and trimers were enhanced and the formation of the hydrolysis products phenol and benzyl alcohol was remarkably reduced. The presence of the metal ion leads to the formation of a cation–BPE adduct,[19] in which the ether bond is polarized and, therefore, more prone to be heterolytically cleaved. On the other hand, the alkalinity of carbonate can accelerate hydrogen abstraction. It should also be noted that the relatively large fraction of high molecular weight compounds could likely serve as source of hydrogen. Unfortunately, the yields of target products decreased after the amount of Na_2CO_3 exceeded 0.4 g due to the formation of dimers and trimers.

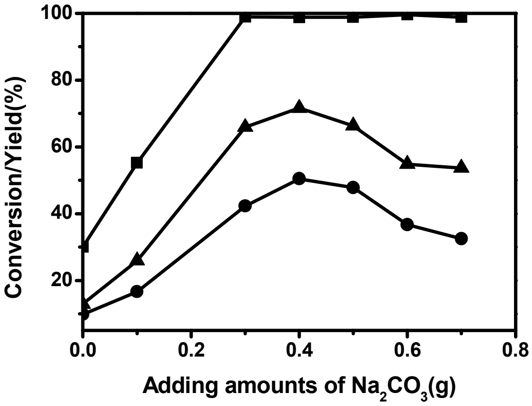

Fig. 5. Effect of amount of Na_2CO_3 on depolymerization of BPE. (■) conversion of BPE, (▲) yield of phenol, (●) yield of toluene. Reaction conditions: BPE 0.05 g, Pd/C 0.025 g, NMP 0.05 g, H_2O 2g, Ar 0.1 MPa, reaction temperature 150 °C, reaction time 3 hrs, volume of the reactor 8 mL.

Fig. 6 shows the dependence of conversion of BPE and yields of the products on the amount of NMP used in the reaction. When the amount of NMP increased from 0 to 0.04 g the BPE cound be converted completely. The maximum yield could be observed when the amount of NMP was 0.04 g. As we know, NMP may be produced through the reaction of γ-butyrrolactone and methylamine and the reaction is a reversible chemical reaction. Therefore, when NMP and water exists in the same reactor under relative high temperature, certain amount of methylamine can be produced. The alkalinity of amines can accelerate the depolymerization of BPE through enhancing hydrogen abstraction. In order to verify this hypothasis, we replaced NMP with cyclohexylamine and found that the depolymerization of BPE also proceeded smoothly. So, addition of NMP is helpful to the transformation of BPE. Just like Na_2CO_3, too much NMP would lead to the formation of by-products and the yields of the traget products decreased.

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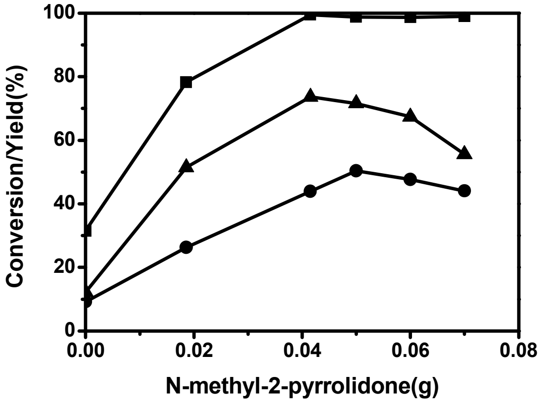


Fig. 6. Effects of amount of NMP on depolymerization of BPE. (■) conversion of depolymerization of BPE, (▲) yield of phenol, (●) yield of toluene. Reaction conditions: BPE 0.05 g, Na_2CO_3 0.4 g, Pd/C 0.025 g, H_2O 2g, Ar 0.1 MPa, reaction temperature 150 °C, reaction time 3 hrs, volume of the reactor 8 mL.

3.4 Reaction mechanism

As we know, EPR is the most direct and effective way to detect the existence of free radicals. In this work, we carried out the EPR study with PBN as the the spin trap. The EPR spectrum is showed in Figure 7. The g-value obtained from the spectrum was 2.004±0.002 for BPE, which is corresponding with the value reported in the literature.[20] Considering the structure and reaction pathway of the α-O-4 dimeric model compounds, the peaks in the spectrum are ascribed mainly to the carbon-centered benzyl radical and oxygen-centered phenoxy radical. It has been reported that the g-value of phenoxy radical[21] ranges from 2.0040 to 2.0053 and benzyl radical[22] is 2.0030. Further, we know that the hyperfine parameter a_N is 1.62 mT, which reveals the existence of free radical containing carbon center. Therefore, it can be deduced that the transformation of BPE proceeds by a free-radical mechnism.

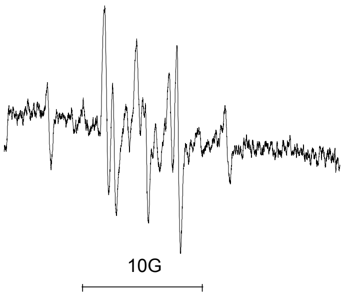
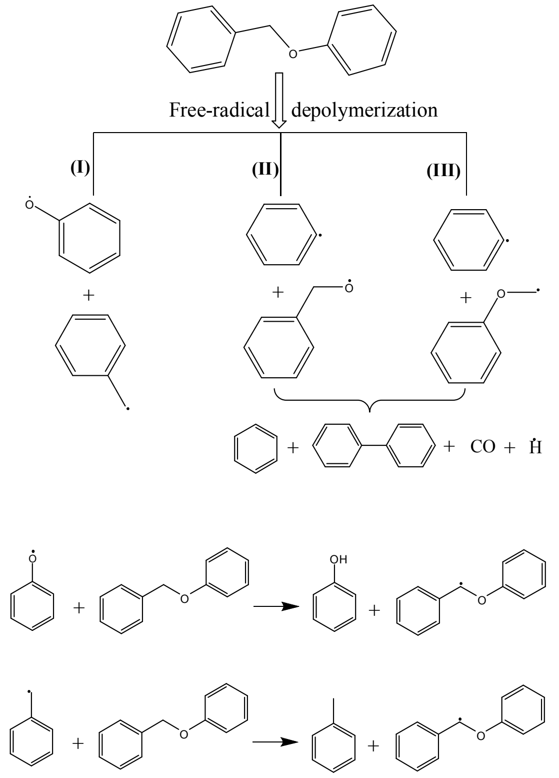


Fig. 6. EPR spectrum of the reaction mixture containing PBN at 25°C



Scheme 1. Possible pathways of depolymerization of lignin model compound BPE.

Depolymeration of BPE often involves hydrolysis and pyrolysis pathways.[14] During the hydrolysis process of BPE, phenol and benzyl alcohol are the main products. For the pyrolysis pathway, BPE can be decomposed into phenol and toluene. In our experimental results, the main products were not benzyl alcohol and phenol but phenol and toluene, which means that the depolymeration of BPE in our reaction system may be via the pyrolysis pathway. Further, when TEMPO was added into the reaction system, both conversion and yields of the target products decreased, which showed that the decomposition of BPE was carried out via the free-radical pyrolysis. In addition, the results of entries 2 and 4 in Table 1 suggest that Pd/C can accelarate the reaction, but Na_2CO_3 aqueous solution alone can not promote the reaction. Thus, based on our experimental results and the related chemical aknowlage we can infer that the free-radical depolymerazation took place in our reaction system.

In order to explore the pyrolysis pathway of BPE, we analyzed the final liquid products by GC-MS and the products contained phenol, toluene, benzene. As the carbon balance of the total liquid products was less than 100%, which indicated that polymerization might occur just like reported in the literature 14. The gasoues product detected was mainly carbon monoxide.

On the basis of the results discussed above, we propose possible pathways for the depolymerization of BPE, which is showed in scheme **1**. There are three possible pathways existing in our reaction system. As a main pathway(**I**), BPE is firstly cracked into phenoxy and benzyl radicals. These two radicals can react with BPE to form phenol, toluene and PhOCH•Ph radical.[23] In the pathway **II**, BPE can be cleaved into benzyloxy radical

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and phenyl radical. For the pathway **III**, BPE can be depolymerized into phenoxymethyl radical and phenyl radical. And then, benzyloxy and phenoxymethyl radicals can be further decomposed into phenyl radical, carbon monoxide and hydrogen radical.[24] Next, hydrogen radical from pathway **I and II** may combine with PhOCH•Ph radical to form BPE or PhOCH•Ph radical combines with other radicals or itself to produce heavier products.[25] Thus, the products containing bezene, biphenyl, carbon monoxide and other high molecular weight compounds can be formed through the linkage of different radicals.

4. Conclusions

We have carried out the depolymerization of BPE into phenol and toluene using Pd/C as the catalyst with and without Na_2CO_3 and NMP in argon atmosphere. The reaction is governed by a free-radical pathway. In our reaction system, as a main pathway, BPE is cracked into phenoxy and benzyl radicals. Pd/C can catalyze the reaction, and Na_2CO_3 and NMP can enhance the transformation. There is a maximum in each of the yield *vs* reaction time curve, yield *vs* Pd/C amount curve, yield *vs* amount Na_2CO_3 curve, and yield *vs* NMP amount curve because the combination of different free radicals can be further taken place. At the optimized reaction conditions, the yields of phenol and toluene can reach 1.6% and 50.4%, respectively. We believe that the interesting results of this work will trigger more researches on exploring new and green methods for the catalytic valorization of lignin.

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Notes and references

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