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Hydrogenolysis of Alkaline Lignin Catalyzed by Metal Complex and Triphenyl Phosphine

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Abstract: The catalytic hydrogenolysis of alkaline lignin has been carried out by metal complex and PPh_3, such as Pd, Ni. When the catalyst precursors were $Ni(OAc)_2$ and $NiCl_2$, the catalytic activities were not as good as that of $Pd(OAc)_2$ and $PdCl_2$. The products were characterized by viscosity measurement and thermal gravimetric analysis. The molecular weight of soluble components reduced obviously. Reaction conditions such as temperature, time, solvent, catalyst precursor and catalyst loading were optimized. The optimal reaction conditions were as follows, lignin(0.5000 g); $PdCl_2$(0.0809 g); PPh_3(0.2322 g); temperature 150 ℃, time 15h, 1,2-dichloroethane and ethanol as medium, the volume ratio of 2 : 1.

Key words: $PdCl_2$; $Pd(OAc)_2$; PPh_3; lignin; hydrogenolysis

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Biomass as the only renewable resources, which can be transformed into liquid fuels, has attracted more and more attention with the dwindling of fossil energy. In a narrow sense, biomass mainly refers to straw and tree and lignocellulose during the agroforestry production process in addition to grain, fruit, of which characteristic is renewable, low pollution and widely distributed. Lignocellulosic biomass is constituted of 20% ~30% of lignin, 40% ~50% of cellulose, and 25% ~35% of hemi-cellulose[1-2]. Lignin is natural biomass polymer, which content is next to cellulose. Lignin is produced extensively as a co-product during the process of bioethanol preparation and in paper pulp enterprises[3-4]. Currently, the amount of lignin on earth is about 300 Gt, however, about 95% lignin is directly discharged into rivers or burned. Only small amount of lignin is utilized[5]. Lignin is a three-dimensional amorphous polymer consisting of methoxylated phenyl-propane structures, including p-coumaryl, coniferyl, and sinapyl alcohol. The linkages between them include β-O-4, β-β, β-1 and 4-O-5, of which the β-O-4 linkage is dominant[6-7]. Lignin has potential application value to synthesis of functional polymer, high value-added fine chemicals, and biofuel by chemical modification such as hydrogenation, oxygen, pyrolysis and grafting copolymerization, etc[8-9].

Heterogeneous catalysts were frequently used in the procedure of hydrocracking lignin. American patent US4731491[10] described that phenols were prepared by hydrogenolysis of lignin, which reaction conditions were as follow, temperature 376 ~425 ℃; time 1 h; pressure 5 ~15 MPa; FeS as catalyst. Yan[11] reported that hydrogenation of lignin can be catalyzed by Pt/C to synthesize dimers and monomers, which the conversion of the reaction was 42%, and the reaction conditions were as follows, temperature 200 ℃, time 4 h, pressure 4 MPa. And then, Pd/C catalyst was used in hydrocracking of lignin at 300 ℃ over 0.5 ~2 h, which products were alkanes and methanol. It has been demonstrated that C—O bond cleavage of lignin can be realized by several conventional heterogeneous hydrogenation catalysts such as platinum, palladium, nickel, and homogeneous catalysts such as ruthenium, rhodium, and borane with iodine. When $RuCl(PPh_3)_3$ was used, the solubility of the hydrogenated

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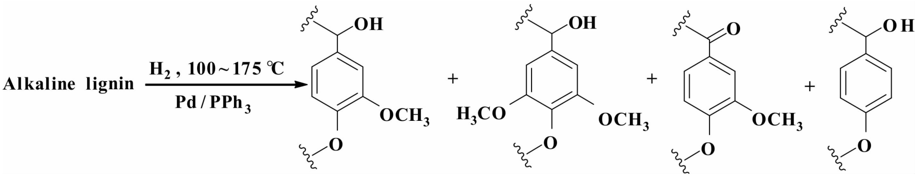
lignin in ethanol increased to 96.4%, resulting in nearly complete dissolution. At the same condition, when heterogeneous catalyst Co/Mo was used, the solubility was up to 54.3%. The solubility was 76.5% in the presence of Pt/C[12]. Zhao[13] investigated to the hydrogenolysis of lignin catalized by $NaBH_4/I_2$. The results showed that the molecular weight of lignin become smaller compared with lignin raw material.

However, there are still some problems in these reactions, for example, high temperature and pressure, long reaction time. In this work, Pd/PPh_3 as catalyst is applied in hydrogenolysis of alkaline lignin for the first time, and the high catalytic activity was obtained under low temperature and pressure.

1 Experimental

Representation reaction process was as follows (scheme 1), lignin (0.5000 g), palladium salt (0.0809 g), and PPh_3 (0.2322 g) were dissolved in 15 mL medium. The solution was introduced into 50 mL autoclave and the closed reactor was then purged several times with nitrogen and 4 MPa of hydrogen at room temperature. The reaction was carried out at a certain temperature and time. After completing reaction, the reaction mixture was filtered. The residue was the insoluble component. The filtrate was concentrated by reduced distillation at 45 ℃, and the soluble component was obtained.



Scheme 1 The hydrogenolysis of alkaline lignin catalyzed by complex Pd/PPh_3

2 Results and Discussion

Influences of reactive conditions such astemperature, time, solvent, catalyst precursor and catalyst loading were investigated (Table 1). The soluble components percentage of hydrogenated lignin in dichloroethane and ethanol are summarized. The blank experimental at 150 ℃ was showed in brackets. The percentage of soluble component increased from 35.5% to 75.8% catalyzed by complex Pd/PPh_3 compared with blank experimental (Entry 3). The hydrogenolysis reactions of alkaline lignin were performed at 100, 125, 150 and 175 ℃ for 15 h respectively. The percentages of soluble components were 75.8 % at 150 ℃ and 59.2% at 175 ℃ (Entries 3, 4). It was possible that the condensation of lignin aromatic rings took place and the hydrocracking of lignin was incomplete at low temperature. The reaction times were studied for 5, 10, 15 and 20 h at 150 ℃ respectively. The optimum reaction time was 15 h. If the reaction time was too short, the hydrocracking of alkaline lignin occured incompletely. The condensation of hydrogenated lignin might take place when the time was too long. The reaction medium was optimized, such as dichloroethane, ethanol and their mixture (Entries 3, 8 ~ 10). When the volume ratio of dichloroethane and ethanol was 2 : 1, the percentage of soluble component was higher. The various catalyst precursors were studied (Entries, 11 ~ 14). The catalytic activity of $Pd(OAc)_2$ was better than that of $PdCl_2$. This was due to the better solubility of $Pd(OAc)_2$, meanwhile, $Pd(OAc)_2$ and PPh_3 readily formed complex. When the catalyst precursors were $Ni(OAc)_2$ and $NiCl_2$, the catalytic activities were not as good as that of $Pd(OAc)_2$ and $PdCl_2$. The dosage of $PdCl_2$ was investigated (Entries 3, 10). The percentage of soluble components decreased with reducing the dosage of $PdCl_2$.

Alkaline lignin is water-soluble and is purchased from Sigma-Aldrich, of which weight average molecular weight (Mw) is $9.0\times10^3 \sim 1.0\times10^4$ g mol^{-1}. The weight average molecular weight of soluble component was 5.0×10^2 g mol^{-1}. Obviously, the Mw of hydrogenated lignin decreased. Thus, the cleavage of β-O-4 bond, might take place during the procedure of hydrogenolysis of alkaline lignin.

Table 1 Effect of different reaction conditions on solubility

Entry	Temperature /℃	Time /h	Medium	Catalyst Precursors	Soluble fraction /%	Relative viscosity
1	100	15	Dichloroethane and ethanol	$PdCl_2$	36.5	1.030
2	125	15	Dichloroethane and ethanol	$PdCl_2$	65.1	
3[a]	150	15	Dichloroethane and ethanol	$PdCl_2$	75.8(35.5)	1.084
4	175	15	Dichloroethane and ethanol	$PdCl_2$	59.2	1.044
5	150	5	Dichloroethane and ethanol	$PdCl_2$	33.1	
6	150	10	Dichloroethane and ethanol	$PdCl_2$	67.4	
7	150	20	Dichloroethane and ethanol	$PdCl_2$	37.5	
8[a]	150	15	Ethanol	$PdCl_2$	50.1(4.8)	
9[a]	150	15	Dichloroethane	$PdCl_2$	29.7(17.7)	
10[b]	150	15	Dichloroethane and ethanol	$PdCl_2$	55.6	
11[c]	150	15	Dichloroethane and ethanol	$PdCl_2$	61.0	
12[c]	150	15	Dichloroethane and ethanol	$Pd(OAc)_2$	62.7	
13	150	15	Dichloroethane and ethanol	$Ni(OAc)_2$	42.7	
14	150	15	Dichloroethane and ethanol	$NiCl_2$	37.4	

a: the data of brackets are blank runs, that is no catalyst in reaction process.

b: dichloroethane and ethanol as solvents, the volume ratio of 4:1, other volume ratio of 2:1;

c: the loading of catalyst are the same, which are half of others.

It has been known that there has a certain relationship between molecular weight and viscosity of polymer. The viscosity of polymer decreases with decreasing molecular weight. The soluble components were dissolved into dichloroethane and ethanol (2 : 1, v/v), of which concentrations were 0.2、1.0 and 10.0 mg/mL respectively. When the concentration was 0.2 mg/mL, the viscosity was almost the same as that of solvent. The viscosity of solution was more than that of solvent at 10.0 mg/mL (Entries 1, 3 and 4). This results indicated that the molecular weight of soluble components were lower.

The cleavage of methyl-aryl ether bond is just below 400 ℃. Decompostion or condensation of aromatic ring is probable to take place at 400 ~ 600 ℃. All the lignin fractions exhibit similar thermograms, indicating an equal thermal stability of the lignins[14]. The insoluble component was characterized by thermal gravimetric analysis (Fig. 1). Two weight loss start point at 151.5 ℃ and 262.5 ℃ were obviously seen, 10% weight loss appeared at 163 ℃. When the temperature ascended to 269 ℃, the weight loss reached 30.0%. The weight loss increased significantly to 62.3% at 500 ℃.

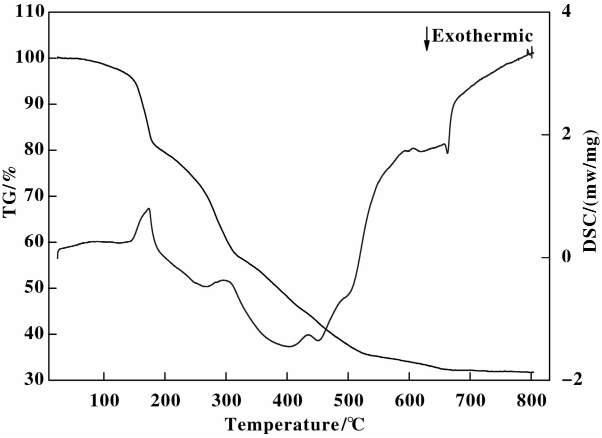


Fig. 1 The thermogram of insoluble components

3 Conclusion

In summary, the hydrogenolysis of alkaline lignin was catalyzed by complex Pd/PPh_3 and Ni/PPh_3. The catalytic activity of palladium salt was better than that of nickel salt. The products included soluble and insoluble components. After reaction, the soluble components of hydrognetated lignin obviously increased from 35.5% to 75.8%. The weight average molecular weight of hydrogenated lignin evidently reduced. The cleavage of *β-O*-4 bond may take place during the procedure of hydrogenolysis of alkaline lignin. The reac-

tion conditons were optimized. The optimum reaction conditions were as follows, 0.5000 g of lignin, 0.0809 g of $PdCl_2$, 0.2322 g of PPh_3, dichloroethane and ethanol mixtures as medium, the hydrogen pressure 4MPa, temperature 150 ℃, time 15 h. The price of Pd/PPh_3 is much lower than that of $RhCl(PPh_3)_3$ and $RuCl(PPh_3)_3$, and the catalytic activity of Pd/PPh_3 is almost the same as them.

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金属配合物和三苯基膦催化加氢裂解碱木质素

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摘　要: 分别以配合物 Pd/PPh_3 和 Ni/PPh_3 为催化剂, 二氯乙烷和乙醇的混合物为介质, 非均相催化加氢裂解木质素, 产物分为溶解组份和不溶解组份, 反应后溶解组份明显增加; 当催化剂前体为 $Ni(OAc)_2$ 和 $NiCl_2$ 时, 催化活性没有 $Pd(OAc)_2$ 和 $PdCl_2$ 的高; 对产物进行粘度测试、热重分析和分子量测定, 溶解组份分子量大幅降低; 考察反应温度、时间、溶剂、催化剂前体及其用量对催化活性的影响, 得到较优化的反应条件: 木质素 0.5000 g, 氯化钯 0.0809 g, 三苯基膦 0.2322 g, 温度 150 ℃, 时间 15 h, 介质为 1,2-二氯乙烷和乙醇的混合物, 体积比为 2∶1.

关键词: 氯化钯; 醋酸钯; 三苯基磷; 碱木质素; 加氢裂解