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Research analysis and progress of niobium based catalysts in lignin depolymerization

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Abstract: **lignin is a three-dimensional macromolecular compound composed of phenylpropane structural units connected by C-C bond and C-O bond. Due to its inert structure and the complexity of functional groups, lignin has become the most difficult material to depolymerize in biomass. Catalytic hydrodeoxygenation technology can depolymerize lignin into high value-added small molecular compounds. With energy depletion and environmental pollution, there is an urgent need to find a renewable resource to provide energy and materials needed in production and life. Lignin is a large amount of renewable resources that can provide aromatic rings in nature. It is an important part of biomass and has great economic value. This paper mainly discusses the research progress and application of niobium based catalysts in the depolymerization of lignin. Niobium based catalysts have unique acidity, excellent thermal stability and water resistance. They are widely used in dehydration, hydrogenolysis, hydrolysis, esterification and alkylation.**

Keywords: **Lignin niobium based catalyst niobium based; Hydrodeoxidation**

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1.Introduction

As the only renewable resource containing carbon in nature, biomass has a structure similar to traditional fossil resources and can be transformed into different forms of fuel. It widely exists in nature and is an inexhaustible natural renewable resource. Biomass is a three-dimensional network structure composed of cellulose (30% ~ 40%), hemicellulose (20% ~ 30%) and lignin (15% ~ 30%) [3]. Cellulose and hemicellulose have been widely used in the past decade, while the utilization rate of lignin is only 5%, and more than 95% of lignin is used for emission or combustion [4]. With the development of society and the improvement of industrial level, human beings have great interest in coal, oil The demand for non renewable energy such as natural gas is growing day by day, and the massive consumption of fossil resources has led to problems such as energy depletion and environmental pollution [1]. In order to alleviate such problems, countries all over the world attach importance to the development and utilization of renewable resources in order to replace traditional fossil energy with renewable resources to provide chemicals and energy needed for human production and life [2].

This has not only caused water and air pollution, but also caused a great waste of resources. Lignin is the most abundant source of aromatics in nature. Transforming lignin into high value-added small molecular compounds can not only alleviate environmental problems, but also effectively utilize renewable biomass resources and realize sustainable development strategy. A series of porous acid catalysts, especially transition metal oxide porous catalysts, have been widely studied. Among them, niobium phosphate porous material is a very important water-resistant catalyst. It has unique acidic characteristics, adjustable acid site density and high thermal stability. It has excellent catalytic activity for the depolymerization reaction system of lignin. This paper mainly discusses the research progress of niobium based catalysts in lignin depolymerization [5]. Platinum group metals are one of the important catalyst materials in the field of catalysis because their d electron orbitals are not filled, their surfaces are easy to adsorb reactants, and their adsorption strength is moderate, which is conducive to the formation of intermediate “active compounds”, and have high catalytic activity. At the same time, they also have comprehensive excellent characteristics such as high temperature resistance, oxidation resistance and corrosion resistance. Noble metal catalysts are mainly platinum group metals, mainly including supported heterogeneous catalysts with platinum (PT), palladium (PD), ruthenium (RU), rhodium (RH), iridium (IR), osmium (OS) and various homogeneous catalysts composed of platinum group metal inorganic compounds or organic metal complexes. At the same time, it plays an important role in the fields of noble metal catalysts, no combustion, environmental protection, and so on.

2.Background

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2.1. Research Value

Lignin, also known as lignin, is crosslinked with cellulose and hemicellulose through covalent bond and hydrogen bond to form the main structure of plants. Its content accounts for about 15% ~ 30% of the dry weight of ligneous biomass. It is regarded as the most abundant non petroleum resource of renewable aryl compounds in nature [6], and has great potential in the preparation of fuels and aromatic chemicals. Figure 1 shows some structural fragments of lignin. It can be seen that lignin is composed of phenylpropane structural unit through 1 / 3c-o bond （β- O-4、 α- O-4, 4-5 keys, etc.) and 2 / 3c-c keys （β- 1、 α- 1. Natural phenolic random polymers with three-dimensional network structure connected by 5-5 ‘) bonds have a variety of functional groups in their structural units, such as phenolic hydroxyl, ester hydroxyl, methoxy and carbonyl, which makes lignin show different chemical activities in different chemical reactions such as oxidation, reduction, polymerization and decomposition. Due to the structural complexity, diversity of functional groups and high stability of lignin, it has become the most difficult component to depolymerize in biomass. In recent ten years, many fields have made in-depth exploration on lignin depolymerization in the direction of homogeneous catalysis and made some progress. The structure and content of lignin are significantly different due to different extraction conditions, extraction locations and plant types. It is generally believed that lignin structure contains carbon, hydrogen, oxygen, nitrogen and sulfur, and its basic units are p-hydroxyphenylpropane (H), guaiacyl propane (g) and syringyl propane (s).

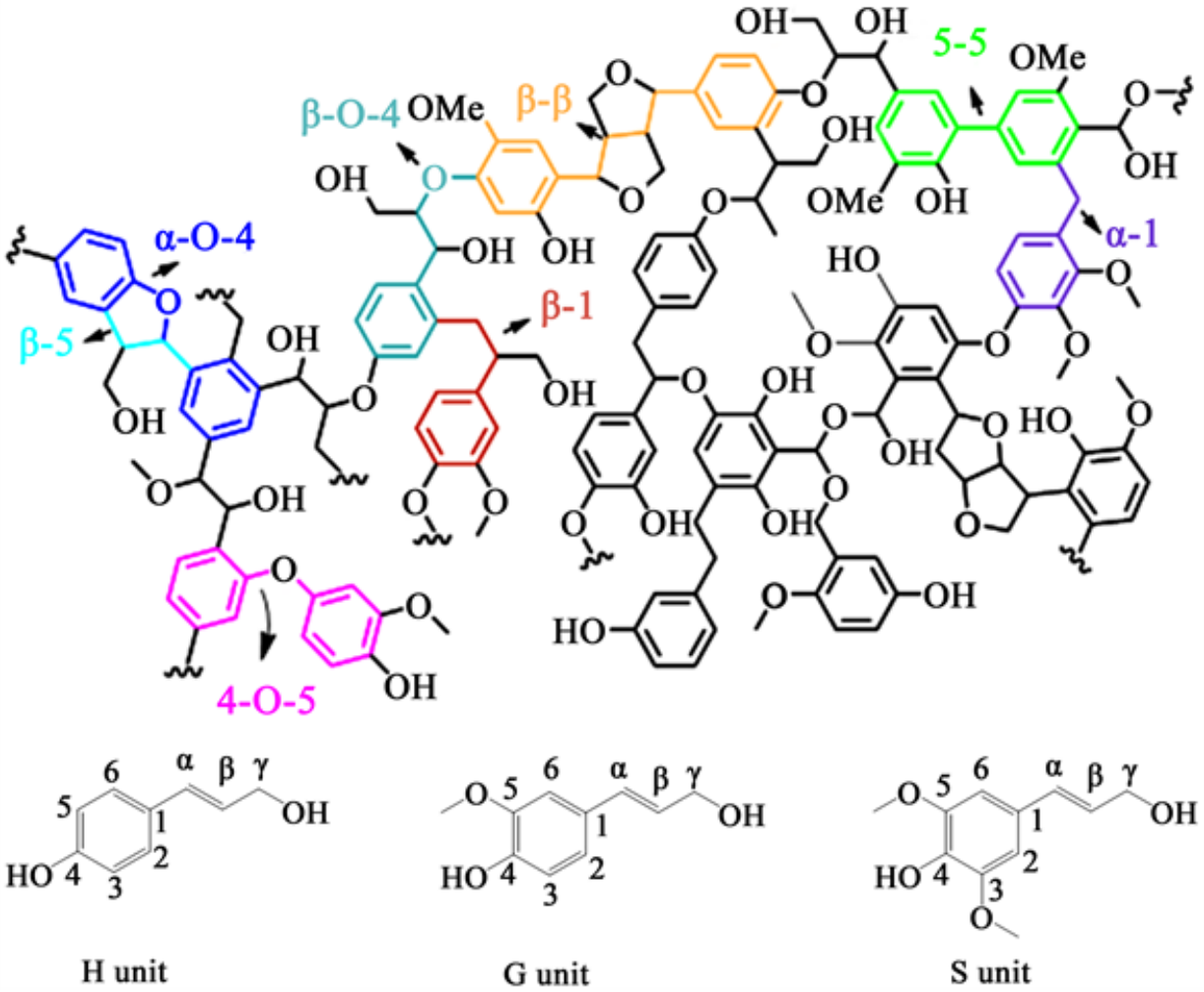

Figure 1. Structure and basic structural units of lignin
Figure 1 Lignin structure and its basic structural unit diagram

2.2 Present situation of this test

Lignin depolymerization (LDP) is the key to lignin appreciation. A variety of functional groups and aromatic

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structures in its molecular structure provide raw materials for small molecular aromatic compounds. According to different depolymerization environments, depolymerization methods can be divided into oxidation environment, reduction environment and non reduction environment. At present, the common methods of lignin depolymerization include hydrolysis, pyrolysis, alcoholysis, hydrogenolysis, oxidation, reduction, hydrodeoxygenation, etc. the products include more than 400 compounds such as alcohols, phenols, ethers, aldehydes, ketones, esters, acids, furans, branched alkanes and cycloalkanes. In addition, the different types and sources of lignin will also affect the depolymerization effect and product distribution, which has guiding significance for the depolymerization method. This paper mainly discusses the catalysts used for CO catalytic oxidation, from three aspects: metal oxide catalysts, noble metal catalysts and single-atom catalysts. Metal oxide catalysts have a cer-tain catalytic activity for CO oxidation, but the catalytic activity is low; compared with metal oxide catalysts, noble metal catalysts have better catalytic activity, but the metal utilization rate is low, resulting in waste of resources. The emergence of single-atom catalysts effectively solves the above problems and provides a basis for the efficient CO oxidation reaction.

Because lignin is a high polymer connected by C-C bond and C-O bond, the complex structure and the uncertainty in the preparation of lignin bring great difficulties to the depolymerization and transformation of lignin. Therefore, in order to simplify the reaction process and study the reaction mechanism, lignin model compounds are usually used to study the transformation process of lignin. Common monomer lignin model compounds include phenol, guaiacol, purple eugenol and so on; Common phenolic dimer model compounds include diphenyl ether, benzylphenyl ether, phenoxyethylbenzene and so on. Phenolic dimers belong to aromatic ethers and have two basic aromatic units. Their structure is similar to lignin. It is easier to speculate the reaction path of catalytic depolymerization in experimental operation. The most common bond type in phenolic dimers is β- O-4, followed by α- O-4 and 4-5 key types. However, the price of noble metals in noble metal catalysts is relatively expensive, and the atomic utilization of noble metals is not high. Monatomic catalyst can effectively improve the atomic utilization of precious metals, and can effectively catalyze CO oxidation at low temperature. In short, the development of high-efficiency, economic and high-temperature resistant CO catalytic oxidation catalysts is the future development trend and research hotspot in this field.Although metal oxide catalysts can improve the activity of CO oxidation reaction to a certain extent, the utilization rate of metals is not high and the catalytic efficiency is not particularly ideal. Noble metal catalysts make up for the low metal utilization of metal oxide catalysts, and greatly improve the activity of CO oxidation reaction.

2.3Test results

Niobium based catalysts have unique acidity and high stability. They can be used in batch reactors or fixed bed reactors for hundreds of hours. They are widely used in heterogeneous catalytic reactions. Precious metals and niobium can be easily recovered from deactivated catalysts through water and hydrofluoric acid, which further improves their potential. Niobium phosphate is an important water-resistant solid acid with adjustable acid site density and high hydrothermal stability. Figure 2 shows the source of surface acidity of common phosphate solid acids. In the process of lignin depolymerization, solid acid catalyst has very excellent catalytic activity for the breaking of C-O bond in its structure and the removal of oxygen-containing functional groups. However, in this process, water as substrate or product will poison and inactivate the acid site on the surface of solid acid. Therefore, the development of water-resistant solid acid catalysis is of great significance for lignin depolymerization. As an early transition metal, niobium has a high abundance in the crust, similar to cobalt and lithium, but lower than molybdenum and tungsten.

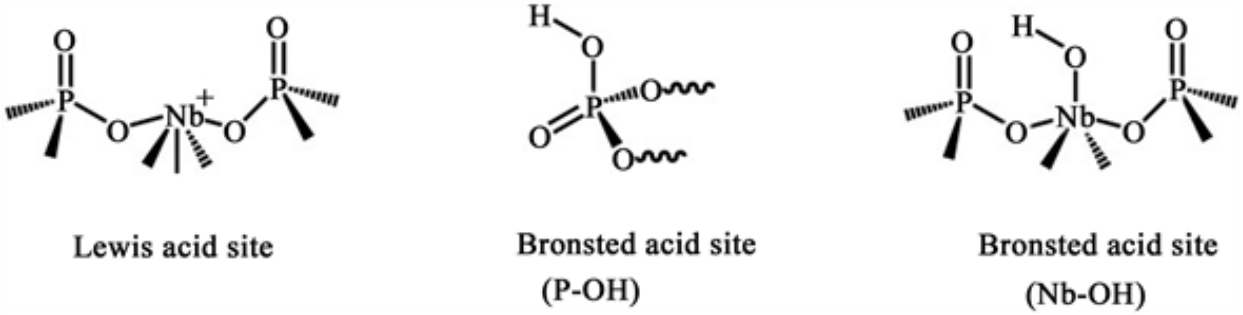

Figure 2. Schematic diagram of surface acidity of niobium phosphate

Figure 2 Schematic diagram of surface acidity of niobium phosphate

In 2018, the catalytic activity of different sizes of metal Ru loaded on nbopo4 for the hydrodeoxygenation of

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lignin was explored. The research showed that the hydrolytic activity of C-O bond was different for Ru particles with different sizes. In 2017, a new hydrodeoxygenation reaction system of lignin was reported. Using Ru / Nb2O5 as catalyst, organic lignin was depolymerized and selectively hydrodeoxygenated into aromatic hydrocarbons in one pot. When birch lignin was used as substrate, the yield of C7-C9 monomer hydrocarbons was close to the theoretical yield of monomers contained in lignin, and the selectivity of aromatic hydrocarbons was as high as 71%. Ru / Nb2O5 catalyst showed excellent catalytic activity and aromatic hydrocarbon selectivity in lignin hydrodeoxygenation, which was attributed to the synergy between nbox species and Ru metals.

3.Conclusion

In noble metal catalysts, not only noble metals will interact with the support, but also noble metals and other metals will interact with each other. In 2010, Xu et al. [25] studied PD Au nano alloy catalyst with silica as carrier to catalyze low-temperature CO oxidation. Except for pure metals, these materials always show two-phase separation to form palladium rich or gold rich materials. The results show that the performance of pd4au1 catalyst for CO oxidation is the best. This catalyst is a mixture of pd90au10 (72.5 at.%) and pd31au69 (27.5 at.%). It has excellent catalytic activity at 300 K and is more stable than pure gold catalyst. For catalysts with PD as the main material (PD: Au = 16:1; 8:1; 4:1), palladium rich alloy components usually exist in the form of hollow spheres or rings, while gold rich crystals are usually multi twin crystals. X-ray diffraction (XRD) shows that the solubility limit of gold in palladium crystal is 12 at.%, PD is more soluble in Au (~ 31 at.%), which is consistent with X-ray photoelectron spectroscopy (XPS), which reveals that Au in PD rich alloys is mainly concentrated on the alloy surface. At the same time, alloying electronic modification of PD and Au elements can change the core energy levels of pd3d and au4f and promote the charge transfer between PD and Au, which is conducive to the adsorption of Co.

The depolymerization of lignin to produce renewable high value-added chemicals has received more and more attention from industry and academia. The depolymerization of lignin will be the key to the development of biorefinery technology in the future. The synthesis of niobium based catalysts and their application in lignin depolymerization are a new and potential method for the production of high value-added monocyclic aromatic compounds. Niobium based catalyst can depolymerize lignin efficiently under mild conditions without high-pressure hydrogenation and other reaction conditions. It has important scientific significance and practical application prospect for the preparation of liquid alkane fuels and aromatic chemicals from lignin. The key in the research of lignin depolymerization is the development and utilization of catalysts. It is very important to prepare multifunctional catalysts with strong anti deactivation activity, high selectivity, cheaper and recyclable through some emerging preparation methods

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