

production, and the resistance of carbon deposition can also be improved, indicating that metal Ce is a suitable additive. Mg additive can restrain the formation of crystalline carbon on the surface of Ni-Al catalyst. Much lower heat-treating temperature or impregnation by step in preparation can obtain more effective active sites for Ni-Mg-Al catalyst. Moreover, Mg additive can improve the catalytic activity and hydrothermal stability of Ni-Al catalyst. As to the Ni catalyst loaded on rutile TiO₂ prepared by sol-gel process, Ni crystals with much higher dispersity can be achieved by lowering the heat-treating temperature, which provide more active sites and promote the C-C bond breaking of biomass under hydrothermal conditions as well as water gas shift reaction and methanation reaction, thus improving the conversion efficiency of biomass. The thermodynamic analysis was performed with Aspen Plus V7.3.2. The thermodynamic models was built using the P-R equation of state and the MHV2 mixing rule to predict the gas yields in the hydrothermal gasification process. Hydrothermal gasification of biomass and its model compounds was theoretically analyzed. The equilibrium state of hydrothermal gasification reaction was obtained by calculating the gas production under certain temperature and pressure, which points out the direction and limitation of hydrothermal gasification reaction.

Key Words: Hydrogen production; Hydrothermal gasification; Biomass; Catalyst; Thermodynamic model

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草本能源植物培育及催化制备先进液体燃料

马隆龙 刘琪英

(中国科学院广州能源研究所)

摘要: 研究前两年围绕3个关键科学问题开展, 取得的进展如下: (1) 针对关键科学问题1, 围绕解析能源高粱等能源植物物质组成和结构, 能源物质生物合成及抗逆相关基因的功能和作用机制开展研究, 提出了高粱等能源植物中次生细胞壁生物合成调控网络的解析机理; 阐明了抗逆性相关基因的功能和作用机制; 建立了检测技术平台以及种质遗传多样性的评价体系与方法。(2) 针对关键科学问题2, 揭示了生物质大分子水热解聚为糖类衍生物的反应机理及产物选择性调控规律; 深入解析了酸/碱处理木质素的结构特征, 构建了碱溶出木质素过程的动力学模型; 提出了微波在木质素氧化与液化解聚过程中的协同促进机制, 获得较高的单酚收率。(3) 针对关键科学问题3, 围绕解聚产物制氢、糖类衍生物制液体烃类/含氧燃料和酚类衍生物制液体烃燃料, 进行了深入系统地研究。根据Gibbs自由能最小化原理建立了模拟流程, 阐明了葡萄糖水溶液的水热气化模型与反应途径。设计制备了高效的Ni/CeO₂-Al₂O₃和Ni/TiO₂催化剂, 并对其结构与化学性质进行深入分析, 该类催化剂在葡萄糖水热制氢反应中的产氢率超过90%, 具有较好的稳定性。首次发现了mdtB基因对细菌的抗逆性、生长速率和产氢速率具有重要的影响。创制了强化水相传质与相转移的微液膜反应体系, 实现糖类衍生物一步高效转化为平台化合物HMF与C5/C6糖醇; 研制了高水热稳定的功能化纳米碳及金属酸性盐催化体系, 提高了选择性断键性能; 研制了高效过渡金属/介孔-微孔固体复合催化体系, 揭示了糖醇水相催化合成液体烃燃料的转化机理与产物控制规律; 初步建立了糖类衍生物水相催化合成液体烃类燃料的中试验证系统。发展了多种新型的催化剂体系, 可协同转化纤维素和半纤维素, 实现了糖类衍生物到平台分子(糠醛, HMF和乙酰丙酸)的高效转化, 揭示了上述转化过程的反应机理与产物控制机制; 设计制备了新型双功能加氢催化剂, 研究了水相平台分子HMF加氢氢解为含氧化合物2,5-二甲基呋喃的反应机理、选择性控制规律; 制备了高效的氧化催化剂K-OMS-2, 阐明了该催化剂上HMF到2,5-呋喃二甲醛的转化规律。发展了从酸水残渣中提取甜高粱木质素的方法, 并对其结构进行了表征; 在实验室合成了木质素二聚体模型; 制备了高效负载型金属催化剂体系, 研究了木质素低聚物解聚反应和酚类衍生物制备液体烃的反应机理; 发展了含钒杂多酸在水/醇混合溶剂体系中催化氧化解聚木质素, 获得了含有芳香醛类化合物, 研究了Aldol缩合、频哪醇偶联和傅克反应的增碳反应机理, 通过催化剂加氢脱氧, 实现了由木质素制取C13-C17的液态烃类燃料。

关键词: 能源植物 培育 化学催化 先进燃料 基础研究

Advanced Liquid Fuel Production by Herbage Energy Plant Breeding and Catalytic Transformation

Ma Longlong Liu Qiying

(Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences)

Abstract: With aiming to the three key scientific issues, this project conducted the production advanced liquid fuels from biomass, and the development is listed as follows: (1) So as to the first key scientific issue, this project conducted the investigation on the component and construction, and the function and mechanism of the stress-inducible gene during biosynthesis of energy plant such as energy sorghum. The net mediation mechanism of secondary cell wall formation in energy sorghum by biosynthesis was elucidated. The measurement platform and evaluation system for the genetic diversity of plasm germ was established. (2) For the second key scientific issue, this project clarified the depolymerization mechanism and product controlling pathway of biomass macro-molecules

in hydrothermal condition. The structure properties of acid/alkali treated lignin were explained and the dynamical model of the alkali dissolved lignin was built. For obtaining the yield of high phenolic monomers, the cooperative promotion mechanism of lignin depolymerization by oxidation and liquifaction was investigated under microwave irradiation. (3) For the third key scientific issue, the study focused on the H₂ production by decomposed products of biomass, the liquid alkane fuels and oxygen contained fuels from sugar derivatives by catalysis, and the liquid alkane fuels by phenol derivatives. The stimulated process was established based on the principle of Gibbs energy minimization and the hydrothermal gasification model and conversion pathway of glucose aqueous solution. The catalysts contained Ni/CeO₂-Al₂O₃ and Ni/TiO₂ were prepared, characterized and their performance was tested in H₂ production by glucose aqueous solution, which obtained the H₂ yield of more than 90% and good catalytic stability. For the first time, we found that the mdtB gene significantly affects the stress resistance and growth rate of the fungus, and thus influences the H₂ production rate. The mass transfer enhanced micro-liquid layer system was developed to achieve high yielded HMF and alditol by one-pot conversion of sugar derivatives and the effective catalysts included functionalized nano-carbon and metal sulfates and phosphates were designed to the selective cracking of bonds in sugar derivatives. To obtain the high yield of liquid alkanes from sorbitol conversion in aqueous phase, the highly active metal supported on micro-/meso-porous zeolite was fabricated and the detailed reaction mechanism and pathway for products formation were researched. The pilot scaled apparatus for liquid alkanes production from sugar derivatives has been built up on the basis of scientific investigation in lab. To achieve the simultaneous conversion of cellulose and hemi-cellulose to platform (furfural, HMF and levulinic acid, etc.), the new catalysts were developed and the formation mechanism and product controlling pathway was clarified. The effective dual functionalized catalyst and K-OMS-2 catalyst were prepared and their performance was evaluated in hydrogenation of HMF to 2,5-dimethyl furan and partial oxidation of HMF to furan-2,5-di-aldehyde, respectively. We developed the new method for obtaining lignin from the residue produced by acid-hydrolysis of sweet sorghum. The structure of the lignin was characterized in detail. For better understanding the decomposed mechanism of real lignin, we synthesized dimer models of lignin in lab. We prepared the supported metal catalysts for hydrodeoxygenation of lignin derived oligo-mers and phenolic derivatives to liquid alkanes and the detailed mechanism was investigated. The vanadium contained heteropolyacids was prepared to achieve oxidative decomposition of lignin to aromatic aldehydes in alcohol-water system. The C-C coupling mechanism for Aldol condensation, Pinacol coupling and Friedel-Crafts alkylation of phenol derivatives was studied, followed by hydrodeoxygenation to C13-C17 alkanes by supported metal catalysts.

Key Words: Energy plant; Breeding; Chemical catalysis; Advanced fuel; Basic research

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生物大分子的解聚研究

邱学青

(华南理工大学)

摘要: 为了充分研究生物大分子的解聚机理, 课题组对纤维素水解的关键影响因素、纤维素、半纤维素水解机理、木质素解聚方式和表征、木质素模型化合物的制备等关键科学问题进行了探讨。借助SEM、BET、XRD研究手段, 研究了半纤维素的水解、纤维素的结晶度、聚合度对纤维素水解的影响规律; 借助TEM、EDXA-SEM和Raman等分析手段, 从超微尺度入手, 追踪解聚过程中木质素、半纤维素和纤维素在细胞壁中的分布变化。结果表明, 半纤维素被水解移除后, 生物质表面孔洞增多, 孔隙率、总孔容增大, 从而促进了纤维素的水解; 相比于聚合度而言, 晶型结构对水解的影响更大。在酸性环境下, 木质素在细胞壁各层间发生迁移, 而在碱性环境中木质素会直接脱离。同时, 该课题开展了在微波协同下的木质素催化氧化解聚及液化解聚, 并通过比较了不同的氧化剂的种类对解聚产物单苯环物质收率的影响, 并通过液质联用, 高压液相色谱等手段对解聚产物进行定性和定量分析。结果表明, 微波协同下在相对较低的温度和压力下获得单苯环化合物的收率可达到15.2%。为了对木质素的解聚机理进行进一步的研究, 该课题合成了包含 α -o-4, β -o-4和 β -5键的木质素模型物三聚体和四聚体, 并通过气质联用色谱和核磁共振色质谱等手段进行分析和表征。木质素模型物的合成为后续的木质素解聚机理奠定基础, 并为木质素解聚为单酚类化合物的高收率目标提供参考。

关键词: 解聚机理 纤维素 木质素 模型物

Depolymerization of Biomacromolecules

Qiu Xueqing

(South China University of Technology)

Abstract: For the purpose of investigation of the depolymerization mechanism of biomass macromolecule, some key scientific issues were explored, including important factors responsible for the hydrolysis of cellulose, depolymerization mechanism of hemicelluloses and cellulose, characterization of degraded products of lignin, and preparation of model compounds of lignin. The distribution of lignin,