

One-pot Conversion of Cellulose and Furfural into Fuels and Valuable Chemicals Using Ir-ReO_x-based Catalysts

著者	LIU SIBAO
学位授与機関	Tohoku University
学位授与番号	11301甲第16999号
URL	http://hdl.handle.net/10097/64354

氏名	りゅう し ほう 劉 斯 宝
研究科, 専攻の名称	東北大学大学院工学研究科 (博士課程) 応用化学 専攻
学位論文題目	One-pot Conversion of Cellulose and Furfural into Fuels and Valuable Chemicals Using Ir-ReO _x -based Catalysts (Ir-ReO _x 系触媒を用いたセルロース及びフルフラールの燃料または高付加価値化学品へのワンポット変換)
論文審査委員	主査 東北大学教授 富重 圭一 東北大学教授 正田晋一郎 東北大学教授 Richard Lee Smith Jr.

論文内容要約

[Chapter 1: Introduction]

Decreasing fossil resources supplies, increasing energy demand and global warming issues provide incentives to conversion of renewable biomass into high-quality transportation fuels and valuable chemical feedstocks. Among various biomass resources, non-edible lignocellulosic biomass is the most abundant, of which cellulose and hemicellulose account for over 70%. Furfural can be produced by hydration + dehydration of hemicellulose on an industrial scale and it is regarded as an important biomass feedstock. Efficient utilization of these feedstocks can give fuels and valuable chemicals such as alkanes, mono-alcohols and diols. However, these feedstocks contain large amount of oxygen. Efficient deoxygenation of these feedstocks by catalytic hydrotreating is a good method. Ir-ReO_x/SiO₂ catalyst, reported by the author's group, was effective in hydrogenolysis of sorbitol to *n*-hexane and tetrahydrofurfuryl alcohol (THFA) into 1,5-pentanediol (1,5-PeD). However, production of sorbitol and THFA, which are the intermediate substrates, needs additional synthesis steps from cellulose and furfural, respectively and this could cause efficiency problems and economic problems. To overcome these problems, this thesis focuses on the study of development of one-pot process for efficient conversion of cellulose, furfural, and related biomass materials into fuels and valuable chemicals over Ir-ReO_x based catalysts.

[Chapter 2 and 3: One-pot conversion of cellulose to *n*-hexane or hexanols over Ir-ReO_x/SiO₂ catalyst combined with acids]

Cellulose, the major constituent (40~50%) of lignocellulose, is composed of glucose units linked by β-1,4 glycosidic bonds and a lot of hydrogen bonds. Its robust crystalline structure hinders the efficient transformation of cellulose. Recently, there have been numerous researches on conversion of cellulose into polyols, such as hexitols, isosorbide, and ethylene glycol by hydrogenation or hydrogenolysis routes. However, it is still urgent to find other new products, such as *n*-hexane or hexanols, from cellulose in the bio-refinery

scheme. Although Ir-ReO_x/SiO₂ combined with HZSM-5 was active in production of *n*-hexane from sorbitol, the production of sorbitol needs steps of the hydrolysis and hydrogenation of cellulose. Therefore, in the present study, Ir-ReO_x/SiO₂ catalysts combined with different acids were used for one-pot conversion of cellulose into *n*-hexane or hexanol in biphasic reaction system (*n*-alkane + H₂O). When Ir-ReO_x/SiO₂ catalyst was combined with HZSM-5, it showed good performance in production of *n*-hexane from cellulose. The yield of *n*-hexane reached 83% from ball-milled cellulose (463 K, H₂ 6 MPa, 12 h) and 78% from microcrystalline cellulose (483 K, H₂ 6 MPa, 24 h). When Ir-ReO_x/SiO₂ catalyst was combined with H₂SO₄, high yield (60%) of hexanols could be obtained from cellulose (413 K, H₂ 10 MPa, 24 h). The key for the production of hexanols were: mechanocatalytic depolymerization of cellulose with the aid of H₂SO₄ before hydrogenolysis, lower reaction temperature and the use of sufficient organic solvent (*n*-decane) which extracted the produced hexanols. The transformation of cellulose to *n*-hexane or hexanol consists of the hydrolysis of cellulose to glucose via water-soluble oligosaccharides, hydrogenation of glucose to sorbitol and the successive hydrogenolysis of sorbitol to *n*-hexane or hexanol. Ir-ReO_x/SiO₂ catalyst promotes hydrogenation and hydrogenolysis steps. HZSM-5 or H₂SO₄ enhanced hydrolysis rate of cellulose in hot water and C-O bond hydrogenolysis activity of Ir-ReO_x/SiO₂ catalyst.

[Chapter 4: One-pot conversion of hemicellulose (xylan) over Ir-ReO_x/SiO₂ combined with acids]

Utilization of hemicellulose, the second major constituent (20~40%) of lignocellulose, could bridge C5 chemistry. However, since now, direct reduction of hemicellulose into fuels and chemicals has gained few attentions. Regarding both cellulose and hemicellulose are polysaccharides, in this study, one-pot transformation of hemicellulose (xylan) into *n*-pentane, pentanols or xylitol was performed using a similar catalyst system to that used in cellulose conversion, by simply adjusting the reaction temperature, amounts of organic solvent and reaction time. 70% yield of *n*-pentane can be produced by using Ir-ReO_x/SiO₂ combined with HZSM-5 + H₂SO₄ in biphasic solvent system (4 ml *n*-dodecane + 9.5 ml H₂O) at 463 K for 24 h. 32% yield of pentanols can be produced by using Ir-ReO_x/SiO₂ combined with H₂SO₄ in biphasic solvent system (20 ml *n*-dodecane + 9.5 ml H₂O) at 413 K for 144 h. 79% yield of xylitol can be produced by using Ir-ReO_x/SiO₂ combined with H₂SO₄ in aqueous phase at 413 K for 12 h. The addition of H₂SO₄ not only neutralized the residual alkali of xylan, but also mitigated the negative effect of mineral ions and humins on the catalytic performance.

[Chapter 5: Conversion of sorbitol over Pt-modified Ir-ReO_x/SiO₂ catalyst without external hydrogen]

In most researches on biomass conversion by hydrotreating, expensive external high pressure hydrogen was used and this could lead to safety and economic problems. To lower the dependence of external hydrogen,

this study showed a one-pot process where in-situ aqueous phase reforming of sorbitol produced hydrogen for the subsequent hydrogenolysis of sorbitol to gasoline-ranged products over a new multifunctional Pt-modified Ir-ReO_x/SiO₂ catalyst system with biphasic solvent (*n*-decane + H₂O). Good yield (42%) of gasoline-ranged products was obtained including C5-C6 alkanes and C2-C6 mono-functionalized compounds such as ketones, alcohols, cyclic ethers and carboxylic acids. The addition of HZSM-5 promoted the formation of C5-C6 alkanes. The catalyst structure and reaction mechanism were proposed.

[Chapter 6 and 7: One-pot conversion of furfural into 1,5-pentanediol over Pd- and Rh-modified Ir-ReO_x/SiO₂ catalysts]

Conversion of furfural into 1,5-PeD with hydrogen is a promising way for the utilization of furfural, because 1,5-PeD can be used as a monomer of polyesters and polyurethanes. At present, very limited yield (<35%) of 1,5-PeD can be obtained by Pt-Li/Co₂AlO₄ or Co/TiO₂ catalysts according to the literature. Although Ir-ReO_x/SiO₂ catalyst was effective in C-O hydrogenolysis of THFA into 1,5-PeD and selective hydrogenation of furfural into furfuryl alcohol, it is inert in the hydrogenation of furan ring. Moreover, furfural and furfuryl alcohol is easily polymerized in aqueous phase, especially at high temperature. To overcome these problems, in this study, two new bifunctional catalysts, namely Pd- and Rh-modified Ir-ReO_x/SiO₂ catalysts and a new catalytic process with two-step controlled temperature reaction were developed for one-pot conversion of furfural into 1,5-PeD with high yield. The maximum yield of 1,5-PeD could reach 78% from diluted furfural (10 wt%) and 71% from concentrated furfural (50 wt%) could be obtained over Rh(0.66 wt%)-Ir-ReO_x/SiO₂. Characterization results indicated that the Pd-Ir-ReO_x/SiO₂ catalyst consisted of ReO_x-modified Pd metal particles and ReO_x-modified Ir metal particles while Rh-Ir-ReO_x/SiO₂ catalyst showed the structure of Ir-Rh alloy particles partially covered with ReO_x species. The lower-temperature reaction step was very crucial for the total hydrogenation of furfural into THFA intermediate, which was converted to 1,5-PeD by hydrogenolysis during the high temperature step. Rh-Ir-ReO_x/SiO₂ showed lower activity in hydrogenation of furfural to THFA intermediate at low temperature step while higher hydrogenolysis activity for THFA to 1,5-PeD at the high temperature step than those of Pd-Ir-ReO_x/SiO₂. Long reaction time at the low temperature step is necessary to obtain good 1,5-PeD yield over Rh-Ir-ReO_x/SiO₂ in two-step reaction of furfural.

[Chapter 8: Conclusion]

Efficient conversion of biomass into fuels and chemicals is crucial for the construction of a sustainable society. One-pot process is very effective for conversion of cellulose, hemicellulose, furfural and sorbitol into fuels and chemicals including alkanes, mono-alcohols and diols in high yields by using Ir-ReO_x/SiO₂ catalyst combined

with different acids or noble metal modified Ir-ReO_x/SiO₂ catalyst. The development of multifunctional catalyst system and feasible catalytic process is very important for implementing the one-pot process. The one-pot method that combined several successive chemical reactions would be a promising strategy for the conversion of biomass related materials or even raw lignocellulosic biomass with high efficiency. The concept of designing novel system with multifunctional catalyst, multi-phase solvents and/or multi-temperature steps reaction process could contribute to the development of feasible one-pot process for biomass conversion.