ISGC 2022

N°404 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Refining lignin to mono-aromatics over brominated metallic catalysts

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PURPOSE OF THE ABSTRACT

Refining lignin to mono-aromatics over brominated metallic catalysts

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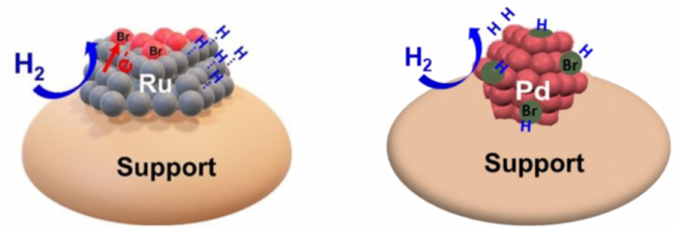
As a major waste of lignocellulosic biomass industry, lignin, the most abundant source of aromatic building blocks in nature, possesses great potential to produce sustainable mono-aromatics. The obtained mono-aromatics could be used as solvents, polymers, dyes, and pharmaceuticals etc. However, the base-free valorization of lignin via cleavage of inter-aromatic C-C/C-O linkages without side hydrogenation of aromatic rings is of great challenge.

Recently, we found a new strategy by modification of the supported Pd catalysts with iodine and bromide to perform extremely selective reductive esterification and hydrodeoxygenation of biomass-derived furan reagents [1,2]. In this contribution, we put forward this method to Ru catalyst for the transformation of diphenyl ether model compound and lignin to aromatic molecules [3].

The Br modified Ru and Pd catalysts were obtained by pretreatment of supported catalysts with benzene bromide under a hydrogen atmosphere (Figure 1). Multiple characterization techniques of HRTEM, XAS, XPS, CO/Pyridine FTIR and indicate the distinct siting of Br atoms on metals. As illustrated in Figure 1, for Ru catalyst, Br atoms prefer to deposit on the terrace sites of Ru nanoparticles resulting in deactivation of these sites without effect on the corner and edge sites. While Br-Pd in-situ generates Bronsted acid sites by heterolytic dissociation of hydrogen.
To test our materials, we firstly conduct the conversion of diphenyl ether (DPE), which represents the lignin model molecule containing robust 4-O-5 linkage [3]. We found commercially available Ru/C modified with Br atoms enabled transformation of DPE to benzene and phenol predominately (90.3% yield) via selective cleavage of C-O bonds. However, the parent Ru/C catalyst only produces hydrogenation products. Thus, Br selectively poisons the terrace site over Ru nanoparticles by Br, which are active in the hydrogenation of aromatic rings, while the active sites on the edges and corners remain available and provide higher intrinsic activity in the C-O bond cleavage.

Furthermore, the above Br-Ru/C, and bimetallic Br-(Ru+Pd)/C afforded increased selectivity to mono-aromatics than Ru/C without Br modifications during the refining of real lignin (Figure 2). The coupling of remaining defective Ru sites for hydrogenolysis and in-situ formed Bronsted acid sites on Pd catalyst contribute to the selective activation of C-O and C-C bonds in lignin without hydrogenation of aromatic rings in the products during lignin depolymerization. In short, this novel strategy opens an efficient way to promote the production of mono-aromatics from lignin valorization.

FIGURES



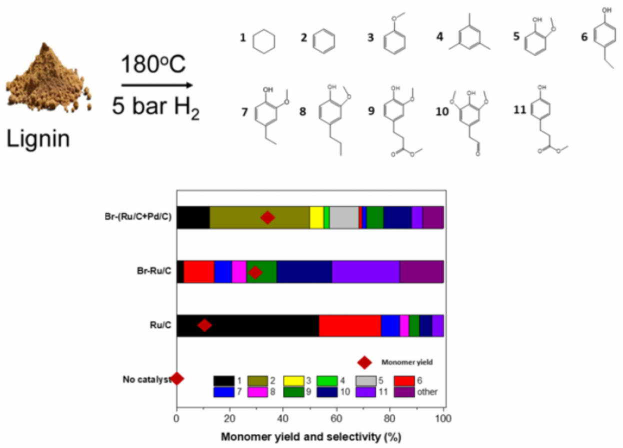


FIGURE 1

Illustration of the process of pretreatment of metals with benzene bromide and structure of Br modified Ru and Pd catalysts.

For Br-Ru catalyst, Br atoms prefer to deposit on the terrace sites of Ru nanoparticles resulting in deactivation of these sites without effect on the corner and edge sites. While Br-Pd generates Bronsted acid sites by heterolytic dissociation of H2.

FIGURE 2

Conversion of lignin into aromatics over Ru/C, Br-Ru/C and Br-(Ru/C+Pd/C) catalysts.

Br-Ru/C and bimetallic Br-(Ru+Pd)/C afforded increased selectivity to mono-aromatics than Ru/C without Br modifications during the refining of real lignin.

KEYWORDS

Lignin valorization | Mono-aromatics | Ru catalyst | Halogen modification

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