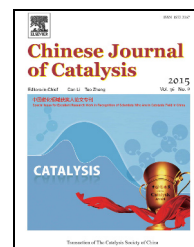


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Minireview (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

Porous carbon in catalytic transformation of cellulose



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ABSTRACT

The application of porous carbon in catalytic transformation of cellulose has received considerable interest owing to increasing energy and environmental pressures. In this mini-review, we first outline the featured properties of porous carbon in catalytic cellulose transformation in terms of porosities and surface functionalities. An interconnected hierarchical structure and enrichment of mesopores are highly desired for reactant, intermediate, and product diffusion; while hydrophilic surfaces are favored in aqueous phase transformation and certain acidic oxygen functionalities play a role of acid sites as well as enhancing the adsorption of feedstock *via* 1,4-glycosidic bonds. We then summarize specific reactions in cellulose transformation in the order of hydrolysis and hydrolytic hydrogenation. In the hydrolysis of cellulose, porous carbon is generally used as a solid acid by taking advantage of its enriched oxygen functionalities, while in the hydrolytic hydrogenation, carbon serves as the support of bifunctional catalysts with active acidic sites. Finally, the synthesis and potential application of specific novel porous carbon materials, such as heteroatom-modified porous carbon and mesoporous carbon composites, are highlighted.

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1. Introduction

Because biomass is the only renewable organic carbon resource in nature, its conversion into value-added products stimulates tremendous interest [1–4]. With particular regard to current energy and environmental pressures, catalytic biomass conversion offers many opportunities in energy substitution and chemical production, and is considered an efficient, environmental benign, and high atom economy “green” process. To avoid conflict between the food and fuel industries, inedible lignocellulose, which comprises cellulose, hemicellulose, and lignin, is broadly accepted as a biomass resource for the production of fuels and chemicals. In lignocellulose, cellulose ((40–50) wt.%) acts like a scaffold to maintain the structural stability of plants; hemicellulose ((16–33) wt.%) acts like a string that binds the cellulose fibers, and lignin ((15–30) wt.%)

acts like cement to harden the structure [5–7]. Of all these components, cellulose is the most abundant biomass with a huge global production of up to 70 billion tons/year [6]; its structure comprises numerous hydroxyl groups making it an ideal feedstock for the manufacture of industrially important products. Therefore, in this mini-review we have focused only on the catalytic transformation of cellulose; further information on the conversion of lignin and other feedstocks can be found in other recent publications [8,9].

Owing to its abundant intra- and inter-molecular hydrogen bonds, cellulose is intrinsically resistant to the cleavage of its β -1,4-glycosidic bonds, and pretreatments to disassemble the supramolecular cellulose structure are usually required for the subsequent catalytic transformation process [2,4,10]. Even so, the diffusion of the degraded polymeric cellulose and its accessibility to active sites are still substantially conditioned by the

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structure and porosity of the catalyst support. The sole presence of micropores imposes diffusion limitations and slow mass transport to and from active sites located within the micropores, which represents the major drawback in cellulose conversions by zeolites. Therefore, the design and application of hierarchical porous materials comprising meso- and micropores is highly desirable [10]. However, long-channeling pores are generally disfavored in biomass conversion owing to concerns about pore blockage and bulky molecule diffusion [11,12]. On the other hand, since the transformation of cellulose into fuels is an O/C ratio reduction process, excess oxygen must be removed in the aqueous phase at high temperatures and/or high pressures, and hydrothermal stability is, therefore, another crucial requirement of the catalyst and its support [2,4,10].

In view of its diversified porosity, high hydrothermal stability, and large surface area, activated carbon is considered one of the most promising candidates in catalytic cellulose transformation [2,13]. In addition, its tunable surface polarity and hydrophilicity/hydrophobicity, and its resistant to acidic and basic media endow carbon with unique advantages in both academic research and industrial applications. Furthermore, advances in nanocarbon technology have enabled the controllable tailoring of the pore structure and surface functionalities of porous carbon [14–16], and thus provided a possibility to clear the role porous carbon playing and allowed a rational design of new catalysts for cellulose transformation. To more clearly depict its function, we opt to highlight the properties of porous carbon first, and then to discuss most of the recently reported examples of catalytic cellulose transformation involving porous carbon. At the end of this paper, provisional conclusions and take-home messages will be provided.

2. Properties of porous carbon in catalytic cellulose transformation

2.1. Porosities

Porosity in activated carbon is created during the carbonization of an organic macromolecular precursor. The removal of small molecules brings distortions within the structure and

hence forms micropores of < 2 nm. Because the heat treatment temperature is usually below 1000 °C, the graphitization level of activated carbon is relatively low. Although the porosity structure models are controversial [17], it is widely accepted that activated carbon comprises three pore categories with regard to size (macro-, meso-, and micropores), while micro-sized pores are dominant (> 0.2 cm³/g) and account for most of its internal surface area (> 400 m²/g). Therefore, diffusion limitation and accessibility to active sites become important issues when employing activated carbon as the catalyst support. A particular concern in liquid phase cellulose transformation, apart from the large size of the reactants, is that multilayer of solvent are found to form in the pores *via* sequential diffusion, and the accumulation of such solvents is considered to be the major cause of catalyst deactivation [18]. Activated carbon, which has much less uniformity of pore size and shape, is perhaps more easily blocked and more strongly affected by the diffusion limitations. Generally, pretreatment of activated carbon, such as by oxidation or sulfonation, can provide larger, more irregular pores, though the function of activation is usually claimed for surface chemistry modification.

With the development of material science, the concise control of meso-structure and morphology becomes possible. Typically, phenolic resin, furfural resin, glucose, and some biomass-derived precursors are able to act as the carbon source, and they endow the obtained mesoporous carbon a similar texture to that of activated carbon. A soft or hard templating strategy has been used to form mesopores of 2–10 nm diameter with ordered/disordered 2D/3D pore structures. Moreover, to optimize the mass transport network, macropore-sized templates have also been introduced to the synthesis system to obtain hierarchical structured porous carbon. In principle, a highly interconnected hierarchical structure will improve the diffusion of the reactant as well as its accessibility to active sites.

2.2. Surface functionalities

Cellulose transformation is a solid-solid interaction at the initial stages of the process, and adsorption of the feed cellulose and desorption of the product depend strongly on the hydro-



Tao Zhang (Dalian Institute of Chemical Physics, Chinese Academy of Science) **received the Catalysis Award for Young Scientists in 2008**, which was presented by The Catalysis Society of China. Professor Tao Zhang received his Ph.D. degree from Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, in 1989, and he joined the same institute and was promoted to full professor in 1995. He did postdoctoral research with Prof. Frank Berry at Birmingham University in 1990. Prof. Zhang was an invited professor at University of Poitiers (France) in 2006–2007, and he has been a guest professor at University of Namur (Belgium) since 2011. He is currently the director of DICP (since 2007). Prof. Zhang has also received several research awards, including the Distinguished Award of Chinese Academy of Sciences (2010), Zhou Guangzhao Foundation Award for Applied Science (2009), National Award of Technology Invention (2008, 2006, 2005). He was selected as an academican of the Chinese Academy of Sciences. In the past decades, Prof. Zhang has successfully designed a great number of nano and subnano metallic catalysts for applications in energy conversion and environmental control. His research interests include (1) Design and synthesis of nano- and subnano catalytic materials; (2) utilization of biomass for production of chemicals.

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