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The role of shape selectivity in catalytic fast pyrolysis of lignin with zeolite catalysts

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ABSTRACT

Catalytic fast pyrolysis (CFP) of lignin with four different zeolite catalysts was investigated to determine the role of shape selectivity of zeolites in CFP. These zeolites included ZSM-5, mordenite, beta, and Y zeolites, which have various crystallographically determined static pore sizes between 5.6 and 7.6 Å. The molecular dimensions of pyrolysis products, including lignin-derived oxygenates and aromatics, were calculated using quantum chemical computations. The effective pore sizes of the four zeolites at 650 °C were then determined by analyzing the molecular size and conversion behavior of the pyrolysis products in CFP. Results suggest that thermal distortion of the zeolite pore structure under high-temperature conditions of CFP effectively enlarge the crystallographically determined pore sizes of the zeolites by 2.5–3.4 Å. Therefore, many lignin-derived oxygenates with a molecular size considerably larger than the static pore size were able to enter the pores of the zeolites and become effectively converted in our CFP tests. Bulkier monolignols derived from syringyl lignin, however, could not be effectively converted by ZSM-5 and mordenite zeolites due to size exclusion or pore blockage. Among the four zeolites, ZSM-5 produced the highest aromatic yield, followed in order by beta, mordenite, and Y zeolites. Beta and Y zeolites were the most effective catalysts for deoxygenating lignin-derived oxygenates. This analysis indicates that for CFP of softwood, ZSM-5 is the optimal catalyst because it can achieve satisfactory deoxygenation and aromatic production simultaneously, whereas for hardwood feedstock, beta zeolite may be used to convert bulky oxygenates derived from syringyl lignin.

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1. Introduction

Catalytic fast pyrolysis (CFP) is a promising technology that can convert solid lignocellulosic materials directly into gasoline-range liquid fuels such as aromatic hydrocarbons [1]. During CFP processes, biomass is fast pyrolyzed in the presence of zeolite catalysts. The primary pyrolysis products of biomass, which are predominantly oxygenated species (e.g., alcohols, aldehydes, phenolics, etc.), are then further catalytically converted to hydrocarbons within the framework of zeolite catalyst, while the oxygen in the biomass feedstock is largely removed as CO, CO₂, and H₂O [2]. High degrees of deoxygenation are generally desired in the CFP of biomass, as any remaining oxygen content decreases the energy density of fuel product and can cause aging and corrosion during storage and combustion [3].

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Zeolite catalysts play a vital role in CFP processes because they dictate chemical compositions and yields of final products [1,4–6]. The surface chemistry and pore structures of zeolites are the most important properties that influence the conversion process [2,7–10]. Specifically, several researchers have indicated that Brönsted acid sites are the active catalytic sites for cracking, deoxygenation, coking, and aromatization reactions [2,7-9]. Although Brönsted acid sites exist on both the external and internal surfaces of zeolites, chemical reactions catalyzed by crystalline zeolites have been thought to occur mainly within the internal pores of zeolites because the external surface usually accounts for negligible or minor fractions of surface area for zeolites [11,12]. The conversion of biomass-derived oxygenates to aromatics in CFP, then, would be largely dependent on whether or not these compounds can enter, form in, and diffuse out of the pores of zeolite (i.e., reactant, transition state, and product shape selectivity, respectively). This is determined by the dimensions of molecules relative to the pore size and internal pore space of zeolites. And thus, the pore structure of zeolites can strongly affect the conversion process via shape selective catalysis [10].

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