SYNTHESIS OF TAILORED HIERARCHICAL ZSM-5 ZEOLITES AND AGGREGATES FOR THE CATALYTIC PYROLYSIS OF BIOMASS

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Catalytic fast pyrolysis (CFP) is a one-step process for the conversion of lignocellulosic biomass into valuable chemicals and a deoxygenated liquid energy carrier (bio-oil) with improved properties compared to bio-oil from conventional fast pyrolysis. In the process, the vapors produced from the thermal decomposition of biomass react on the surface of a heterogeneous catalyst and are deoxygenated, cracked and converted into more desirable products. Many materials have been investigated as candidate catalysts for CFP, with the most commonly studied one being the ZSM-5 zeolite. ZSM-5 has been found to be a very effective catalyst due to its high acidity and unique micropore structure that is very shape selective for the production of monoaromatic hydrocarbons and the minimization of unwanted coke.

However, bulky oxygenates and oligomers that are formed form the thermal decomposition of biomass cannot diffuse into the micropores of the ZSM-5 and can only react on the limited external surface area of the catalyst. For this reason, the purely micropore structure of the ZSM-5 may not be optimal for the CFP of biomass and recently, there is increasing interest for hierarchical mesoporous zeolites as candidate catalysts for the process. These materials combine the high acidity and shape selectivity of the zeolite microporous structure with the enhanced accessibility that is provided by a secondary mesoporous network. The desilication of conventional zeolites is reportedly one of the most effective, versatile and easily scalable methods available to synthesize hierarchical zeolites. Hierarchical zeolites synthesized via desilication have been tested for the CFP of biomass in small-scale reactors by several groups. Provided that desilication was carried out at mild conditions, these materials performed better in terms of activity and desirable product formation. At more severe desilication conditions, the performance of the materials deteriorated, most likely due to a collapse of the zeolite structure, macropore formation and severe loss of microporosity and shape-selectivity.

In this work, the mild desilication (0.2M NaOH aqueous solution) of a microporous ZSM-5 catalyst (Si/Al = 40) was carried out at variable temperatures (50, 65 and 80 °C) and contact times (15, 30 and 45 min). The aim was the controlled formation of mesopores in the ZSM-5 catalyst with minimal loss of the micropore structure in order to increase accessibility and preserve shape selectivity, properties that are desirable for the CFP of biomass. Desilication at 50 °C was found to be effective for the increase of the total and external surface area of the zeolite to levels comparable or higher to those achieved at the higher and more commonly used temperatures of 65 °C and 80 °C, provided enough contact time was allowed (≥ 30 min). Moreover, desilication at the lower temperature of 50 °C resulted in a zeolite with a markedly narrower mesopore size distribution, between 2-20 nm, compared to desilication at 65 °C or 80 °C where wider mesopore size distributions were observed (2-40 nm), as well as some macropore formation (> 50 nm). The smaller mesopore sizes achieved with desilication at 50 °C may prove to be beneficial for biomass CFP, in which shape-selectivity plays a crucial role to inhibit the formation undesirable byproducts, such as coke. A simple laboratory procedure was developed to prepare the most interesting hierarchical zeolite samples into aggregates with a binder (bentonite) in order to carry out catalyst screening studies in medium-scale fluidized bed reactors with wood biomass. The prepared aggregates were also characterized in depth to identify any interactions between the zeolite and the binder phases.

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References