Engineered Cellulose Nanomaterial Systems for Biomass Upgrading Catalysis

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Cellulose nanomaterials (CNMs) are advanced bioproducts which are well positioned to take hold as new high-value products of the forestry and pulp industries. These elementary building blocks of cellulose have remarkable uses in numerous forms: as liquid crystals, hydrogels, foams, films, aerogels, and composite additives. Their ability to form structured porous materials like aerogels and an expansive suite of chemical modifications offer unique opportunities in catalysis. Co-located organic acid and base surface species on heterogeneous supports, typically studied in silane-modified silicas, can function as enzyme-inspired cooperatively catalytic active sites. This thesis aims to expand the capabilities of cellulose nanomaterials as catalysts toward heterogeneous organocatalysis and to investigate potential advantages of alternative supports in this area. CNM-based acid–base organocatalysts are developed with a straightforward chemical functionalization approach utilizing TEMPO-mediated oxidation and amide coupling. Modified cellulose nanocrystals (CNCs) are demonstrated to be effective cooperative catalysts for aldol condensation reactions. The acid–base surface chemistry is analyzed in detail and optimized for catalyst performance. Biomass-derived furans are upgraded with catalyzed aldol condensation reactions, and CNCs are favorably compared to silica-supported organocatalysts. Finally, cross-linked cellulose nanofibril aerogel catalysts are synthesized and highlighted as a promising example for CNM-based catalyst materials for use in continuous flow reactions.