Catalysis: a Tool for the Decarbonization of the Chemical Industry

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The global greenhouse gas (GHG) emissions increased by 1.1% from 2021 to reach 50.6 billion metric tonnes (Gt) of CO_2-equivalent (CO_2-eq) in 2022, and the chemical industry contributed 4% of the total emissions. It is urgent to find alternatives to existing processes that minimize industrial CO_2 emissions to the atmosphere, and innovations in catalysis and catalytic reactors are one of the most promising paths to mitigate these adverse environmental effects. Among efforts in the decarbonization of the chemical industry, two are of primary interest to this thesis: new catalytic processes based on renewable feedstocks, and the substitution of industrial endothermic (heat-consuming) reactions for exothermic alternatives.

The second and third chapters of this thesis discuss the synthesis of 4,4'-dimethylbiphenyl (4,4'-DMBP), a promising platform chemical intermediate for producing polymers, plasticizers, and metal-organic frameworks. 4,4'-DMBP is conventionally produced from petrochemical feedstocks, but this process suffers from low regioselectivity (~50%) given that there are six possible isomers with similar physical properties. A sustainable two-step process to produce 4,4'-DMBP using biomass-derived 2-methylfuran (2-MF) and ethylene is proposed and demonstrated with high chemoselectivity and regioselectivity. The first step is the oxidative coupling of 2-MF to form 5,5'-dimethylbifuran (5,5'-DMBF) through a homogeneous palladium-catalyzed reaction. In the second step, ethylene is added to 5,5'-DMBF via a tandem Diels-Alder cycloaddition and dehydration reaction under a heterogeneous acid catalyst. This alternative provides an entirely renewable path to 4,4'-DMBP synthesis. A techno-economic analysis (TEA) and life-cycle assessment (LCA) of this process were developed to evaluate the feasibility. These results demonstrate a novel pathway for producing valuable and sustainable biphenyl chemical products.

The fourth chapter discusses the oxidative dehydrogenation of ethane (ODHE) over boron-containing chabazite (B-CHA). Ethylene production is the second largest source of GHG emissions in the chemical industry, because of its scale and because steam cracking, today's dominant production method, is an endothermic process that needs high temperatures to achieve high conversion. ODHE is a promising substitute because of its exothermic properties. However, the overoxidation of alkane and alkene is a problem that has yet to be overcome. ODHE over B-CHA is developed and high ethylene selectivity is obtained, with 86% and 73% selectivity at 21% and 42% conversion respectively. Unlike common catalysts that deactivate over time in the stability test, B-CHA shows a higher final ethane conversion than the initial conversion. One-dimensional ^{11}B magic angle spinning (1D ^{11}B MAS) nuclear magnetic resonance (NMR) and two-dimensional ^{11}B multiple quantum MAS (2D ^{11}B MQMAS) NMR spectroscopy were used to investigate this unexpected behavior to study the boron species evolution during the reaction. The spectroscopic results show that the deboronation of framework boron sites increases the ODHE activity. These results demonstrate that microporous environments of the B-CHA catalyst can be engineered to control the reaction, which could benefit olefin production. Other measures to further improve the ODHE activity over B-CHA, including steaming effects, were also

investigated to achieve a higher ethane conversion while maintaining the high ethylene selectivity.