Value-added Chemicals from Biomass by Heterogeneous Catalysis

In the contemporary debate on resource utilisation, biomass has been discussed as an alternative carbon source to fossil reserves in order to reduce the emission of CO2 to the atmosphere. The replacement or supplement of oil based transportation fuels through biomass based conversion has already been implemented. Subject on chemical production has received less attention. This thesis describes and evaluates the quest for an alternative conversion route, based on a biomass feedstock and employing a heterogeneous catalyst capable of converting the feedstock, to a value-added chemical. The project work to fulfill the above objective has been conducted with a multi-disciplinary approach ranging from fundamental catalyst research, through experiments, characterisation and process evaluation to market analysis. The motivation herein is sought in the assets of sustainable resource utilisation obtained for such a process and the hypothesis that process feasibility in comparison with the conventional synthesis gas based technologies may further be attainable, taking advantage of the conservation of chemical C-C bonds in biomass based feedstocks. With ethanol as one example of a biomass based feedstock, having retained one C-C bond originating from the biomass precursor, the aspects of utilising heterogeneous catalysis for its conversion to value added chemicals is investigated. Through a simple analysis of known, but not industrialised catalytic routes, the direct conversion of ethanol to acetic acid product is identified to show good perspectives. The nesting of a useful catalyst and an effective process is crucial to the potential of the overall process innovation. In a pre-screening study, a group of Cu based catalysts active in the conversion have been identified. Considering the freedom to operate, the prospects of process development are further identified through process calculations based on the experimental evidence attained, theory and the process elements described in literature (primarily patent-related). The protection of the process inventions made in relation to this is sought through the filing of three patent applications. The most important contributions of this thesis are reflected in the eventual conclusion that an ethanol to acetic acid process and a related catalyst, both subject to further development, are identified. The understanding of the catalytic behaviour of down-selected catalysts, Cu spinel (CuAl2O4) and Cu/SiO2, is obtained through characterisation as well as activity, selectivity and stability studies in appropriately developed experimental setups. Through numerous characterisation analyses (XAFS, XRPD, SEM, TEM, TPR, carbon analysis etc.) the rapid deactivation of the Cu spinel catalyst may be concluded to be attributed to the formation of high molecular carbonaceous compounds covering the catalytic surface, being catalysed by acidic alumina sites present during and after catalyst activation. This theory explains several phenomena observed for this catalyst. The Cu/SiO2 catalyst, having an inert support, shows far higher robustness to process variations, but immediately exhibits a too low activity from an industrial angle. Several means of improving its activity are elucidated. For example an activity dependence on the Cu crystal size is indicated by the comparison of the activity and XRPD analyses obtained for crushed and whole catalyst pellets. Empirical kinetic models, in good agreement with the experimental data obtained for the Cu/SiO2 catalyst, are developed in order to support the establishment of an improved economic evaluation of the investigated process. Extrapolation of the derived model to the industrial pressure regime indicates a satisfactory activity. The Cu/SiO2 catalyst is further able to withstand partly oxidative dehydrogenation conditions, allowing for immense process improvements. Finally, the ethanol to acetic acid process is put into a broader context, by reviewing the methods used in this work, the market influence on its fate, the conclusions and suggested improvements listed. Eventually, with an outlook on some alternative process possibilities, my recommendations are given under the consideration of the initial project objective. The results of the thesis, taking one example of biomass conversion, show that the utilisation of biomass in the production of chemicals by heterogeneous catalysis is promising from a technical point of view. But risks of market price excursions dominated by fossil based chemicals further set a criterion of a solid economic margin. Therefore, under market considerations other alternatives are to be investigated. In addition to the technical conclusions it appears that a multi-disciplinary approach to process innovation is advantageous.

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