Continuously operated hydroaminomethylation in advanced multiphase systems for efficient recycling

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Abstract

The development of sustainable processes is an ongoing challenge in the chemical industry. In an integrated approach, we combine highly selective homogeneous catalysis with efficient catalyst recycling and product separation and purification. As a means for process intensification, our group developed various thermomorphic multiphase systems (TMS) to reach these objectives. Such a TMS makes use of a temperature-dependent miscibility gap to carry out reactions under monophasic conditions at elevated reaction temperature, avoiding liquid-liquid mass transport limitations. Cooling after reaction leads to the formation of two phases. One phase containing the product and the other phase containing the valuable homogenous catalyst in its active form, which can directly be reused. We successfully applied a TMS consisting of methanol and dodecane for the continuous hydroaminomethylation (HAM) of various longer chain alkenes using molecular hydrogen and CO. We were able to achieve a stable catalyst recycling in a continuously operated miniplant and switch the substrates on stream, highlighting the robustness of this system. However, in these conventional TMS, the apolar product phase contains large amounts of the apolar solvent *n*-dodecane, thus, after decantation still requiring energy-intensive downstream processing.

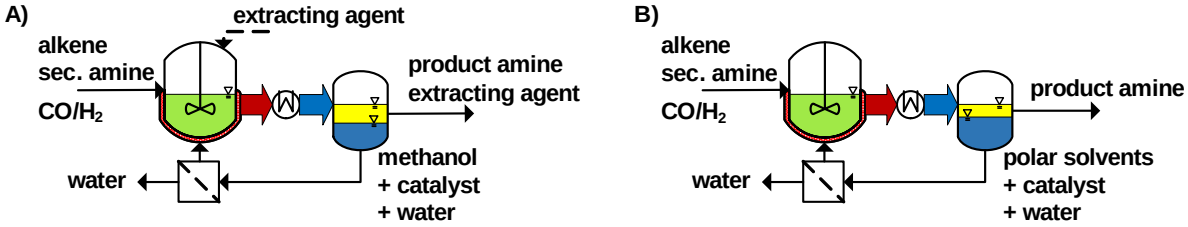

Figure 1: Process flowsheet of continuous hydroaminomethylation in conventional TMS with the nonpolar extracting agent *n*-dodecane **A)** and newly developed TMS without extracting agent **B)**.

Here, we report on a newly developed generation of TMSs that fully omit the use of nonpolar extracting agents to significantly reduce the efforts for product purification. To this end, the composition of green polar solvents is tailored such that the reaction proceeds without mass transport limitation, and an almost solvent-free product phase is formed after cooling. Very successful hydroaminomethylation of 1-decene with diethylamine in a continuously operated miniplant will be presented. In addition, we included an in-situ removal of the by-product water *via* an organic solvent nanofiltration (ONF) membrane. With this approach, we were able to maintain consistent process conditions for over 90 hours with reaction yields to the tertiary amine of up to 79%, providing reliable information about the stability of the novel solvent systems, the homogeneous catalyst and the overall process.