

Hydroaminomethylation in Supercritical Ammonia

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Hydroaminomethylation reaction is an important route for the synthesis of amines from olefins in a one pot reaction using carbon monoxide, hydrogen and ammonia in the presence of transition metal catalysts and suitable ligands. The reaction runs via aldehyde and imine intermediates in the liquid phase, i.e. a biphasic reaction system is present. Mostly, the reaction is carried out under conditions that are used generally for metal catalysed hydroformylation of olefins ($p = 80\text{-}130$ bar, $T = 100\text{-}300$ °C).

However, control of product selectivity is a crucial goal because a consecutive reaction of the desired primary amines leads to secondary and tertiary products that should be avoided. The topic of this work is to shift the reaction to the supercritical state to enable a homogeneous reaction mixture that could beneficially support the formation of primary reaction products.

The contribution presents various examples for thermodynamic properties of hydroaminomethylation reaction carried out by using model olefins ($C_5\text{-}C_{12}$ olefins were selected) as well as product mixtures (amines, aldehydes and unconverted olefin). Furthermore, selected results of catalytic tests in separate autoclaves and dependencies of catalytic performance from reaction parameters will be shown.

Thermodynamic measurements of various hydroaminomethylation reactant or product mixtures were carried out in a high-pressure set-up containing an optical cell. This apparatus enables the observation of cloud points of different mixtures at temperatures and pressures up to 180 °C and 300 bar. The apparatus consists of gas (CO , H_2) and liquids (NH_3) metering systems, the optical cell with sapphire windows and a video recording equipment.

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