# $CO_2$ Assisted Primary Amine Isolation and Catalyst Recycling in the Homogeneously Catalyzed Nitrile Hydrogenation and Alcohol Amination

B. Rienhoff, N. Oppenberg, F. Zolthoff, D. Vogt, T. Seidensticker
TU Dortmund University, Laboratory of Industrial Chemistry, Germany

## Abstract

Primary amines are of significant value as intermediates in the chemical industry. On an industrial scale, they are produced through nitrile hydrogenation with molecular hydrogen or by the conversion of alcohols with ammonia. These processes frequently yield secondary and tertiary amine side products, which necessitate energy-intensive rectification processes for separation.
Homogeneous catalysis presents a promising alternative for selective primary amine synthesis. However, it introduces challenges related to catalyst recovery during downstream processing. To address this issue, we developed a novel approach that leverages the reaction of primary amines with $CO_2$ to form ammonium carbamate species (Figure 1). This reversible and waste-free salt formation enables the selective crystallization of the target product from non-polar reaction solutions, followed by solid-liquid separation via filtration. The free amine is recovered from the carbamate salt through thermal $CO_2$ removal, while the homogeneous catalyst remains dissolved in the filtrate for direct reuse in subsequent reaction cycles.

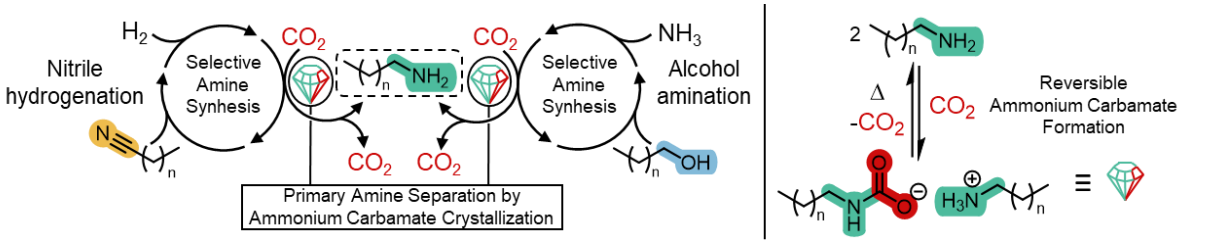


*Figure 1: Illustration of the primary amine product isolation and catalyst recycling in the homogeneously catalyzed nitrile hydrogenation and alcohol amination by ammonium carbamate crystallization.*

This strategy successfully achieved efficient product isolation with minimal catalyst losses in homogeneously catalyzed nitrile hydrogenation and alcohol amination reactions. Catalyst recycling was demonstrated exceeding five successive cycles for both systems, thereby emphasizing the robustness of this method. Furthermore, due to the distinctive ammonium carbamate solubilities of primary, secondary and tertiary amine species this method demonstrates additional potential in the purification of primary amines from amine mixtures.