

“Bimetallic Co-NM Catalysts for the Direct Amination of Alcohols”

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Synthetic amines are important building blocks in the chemical industry, serving as intermediates in the manufacture of agrochemicals, surfactants, polymers, water treatment reagents, pharmaceuticals, solvents and dyes. Among the existing technologies for amine synthesis, the direct amination of alcohols with ammonia stands out as an atom-efficient and environmentally benign route, since water is generated as the sole by-product. This process offers the added advantage of being potentially compatible with biorefineries, which are expected to supply a large portfolio of alcohols. In this context, a main challenge is to avoid over-alkylation of the substrate with the produced amines, resulting in equilibrium mixtures of primary, secondary and tertiary amines.

In a first step, we combined first-principles calculations, scaling relations, kinetic simulations and catalysis experiments to unveil the key factors governing the activity and selectivity of metal catalysts for this reaction. We show that the loss of selectivity towards primary amines is linked to a surface-mediated C-N bond coupling between two N-containing intermediates: CH_3NH and CH_2NH . The barrier for this step is low enough to compete with the main surface hydrogenation reactions and can be used as a descriptor for selectivity. The combination of activity and selectivity maps using the C and O adsorption energies as descriptors is used for the computational screening of 348 dilute bimetallic catalysts. Among the best theoretical candidates, $\text{Co}_{98.5}\text{Ag}_{1.5}$ and $\text{Co}_{98.5}\text{Ru}_{1.5}$ (5 wt% Co) were identified as the most promising catalysts from experiments.

Next, we optimized the preparation of CoRu and CoAg catalysts for the synthesis of octylamine from the reaction of 1-octanol with NH_3 . The impregnation protocol was found to be critical with the best results being obtained for sequentially impregnated Ag-Co and co-impregnated Co(Ru) catalysts. Further optimization of the Ag and Ru metal loading led to two formulations affording a comparable activity to that of an Al_2O_3 -supported catalyst containing 2.4 times more Co. At optimized conditions, the best formulation (5wt.%Co, 3 atom%Ag) afforded 90% conversion and 78% yield to 1-octylamine in the gas-phase amination reaction of 1-octanol with NH_3 at 200 °C using 21 equiv. of NH_3 compared to 1-octanol.

We studied the kinetics of the direct gas-phase amination reaction of 1-octanol with NH_3 over Ag-Co/ Al_2O_3 . An exhaustive experimental dataset was acquired on a Flowrence unit using a full factorial experimental design, covering the effect and interactions of 1-octanol, NH_3 and H_2 partial pressures in the temperature range 160-180 °C. An apparent *zero* order was obtained for both reactants (1-octanol and NH_3), addressing alcohol dehydrogenation as rate-determining step of the overall catalytic process. A non-trivial positive effect of the exogenous H_2 pressure was observed on the 1-octanol conversion, also favoring the formation of the secondary amine. To unveil the promoting role of H_2 on the reaction rate, a comprehensive kinetic modeling study was carried out. Based on the observed experimental trends, various kinetic models were proposed relying on an *in situ* catalytic deactivation-regeneration mechanism of the catalyst surface. Upon statistical discrimination, a robust kinetic model could be obtained, pointing out the adsorbed octylimine intermediate as the most plausible source of deactivation. The kinetic model affords an optimal excellent description of the observed experimental trends at both low and high 1-octanol conversion and provides a sound mechanistic explanation accounting for the unexpected role of H_2 in alcohol amination reactions.