# Oxidative amidation with heterogeneous copper based catalysts

# Amidation oxydante avec des catalyseurs hétérogènes à base de cuivre

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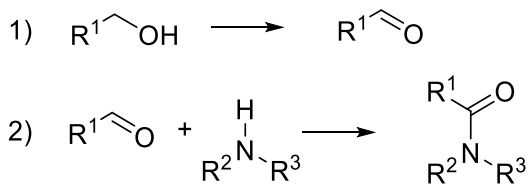
**Context:** Amides are important chemicals employed in pharmaceuticals and agrochemicals industries. The standard production route involves the conversion of carboxylic acid with stoichiometric reagents but the associated production of large quantity of toxic byproducts represent serious drawbacks. Therefore there has been recent interest on the development of more efficient and sustainable catalytic methods for the synthesis of amide.[1] While most of the literature focus on homogeneous catalysis,[2] only one publication report the use of heterogeneous catalyst for the oxidative amidation of alcohol.[3]

**Project:** The project aims at developing heterogeneous catalysts for oxidative amidation of reactions. This transformation occurs in two steps, first the oxidation of the alcohol generates the associated aldehyde (1), which is then converted to the amide (2). These reactions can be conducted in batch or semi-batch reactor, under either inert atmosphere (i.e. oxidative dehydrogenation reaction) or air.




Copper supported on oxide (e.g. $ZrO_2$) catalysts are known to be active for the oxidation of alcohol.[4] For this reaction, the activity of the catalyst increases with a decrease in particle size. However the synthesis of small nanoparticles of Cu on oxides is challenging. Indeed the use of traditional methods such as impregnation with reduction under $H_2$ generates particles in the range of 10-30 nm.[4] Therefore it is necessary to develop preparation methods in order to obtain small (< 5 nm) and well dispersed particles of copper. Next to impregnation, other traditional methods (e.g. deposition-precipitation) will be tested. Alternatively, nanoparticles of copper stabilized by polymers can be synthesized before being deposited on the support. Colloidal methods (with PVA or PVP as stabilizer and $NaBH_4$ as reducing agent)[5] will be used before addressing eventually the use of organometallic and polyols methods,[6] which have only been evaluated for the synthesis of nanoparticles. All these aspects represent one of the main objective of this project: reaching an affordable method for preparing well dispersed copper-based catalysts.

Once prepared and characterized, the catalysts will be tested first for the alcohol oxidation before being evaluated for the second step. The last reaction requires optimization of the conditions (temperature, solvent, nature of the atmosphere). Depending on the results, other metal supported catalysts will also be screened. Alternatively, bimetallic catalysts will be synthesized and developed, particularly for the one-step oxidative amidation of alcohols.

The study will focus first on benzyl alcohol and piperidine. Then other biobased molecules will be

tested, including vanillic alcohol and cinnamic alcohol.

**Skills:** Heterogeneous catalysis: synthesis and characterization of catalysts (XRD), reaction in liquid phase, analysis (GC-FID, NMR).

**Profile of the candidate:** Candidates should hold a Master of Chemistry degree with at least 5 months internship in a research or industrial laboratory. Speaking basic French is required. Send a CV and recommendation letter(s) to Dr. N. Perret before 01-04-2021.

**References**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