



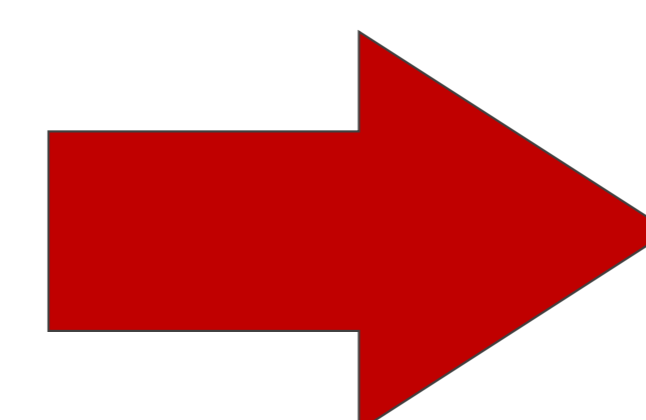
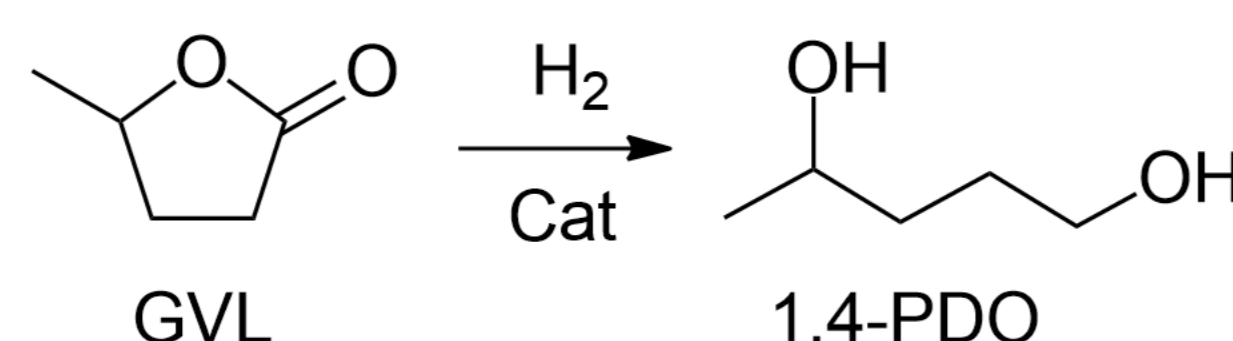
INTRODUCTION

Biomass-waste valorisation and the use of sustainable processes are pillars of green chemistry. Several lactones can be obtained from cellulosic biomass, in particular γ -valerolactone. This can be upgraded towards alcohols and amines that are ubiquitous in today's chemical industry, in particular in polymer production.

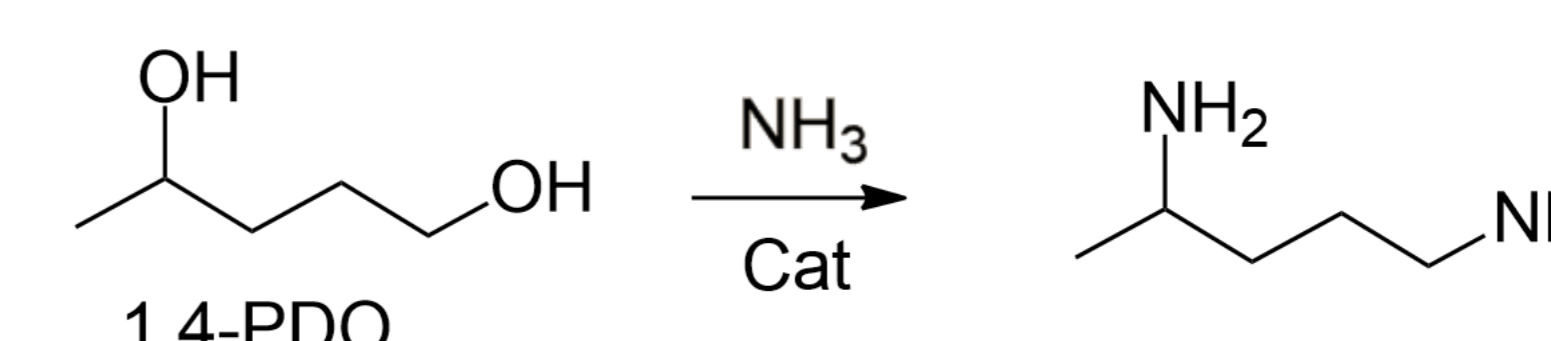


GOALS

Hydrogenation of biomass-derived lactones to diols



Amination of diols to give diamines or alcoholamines



GOALS

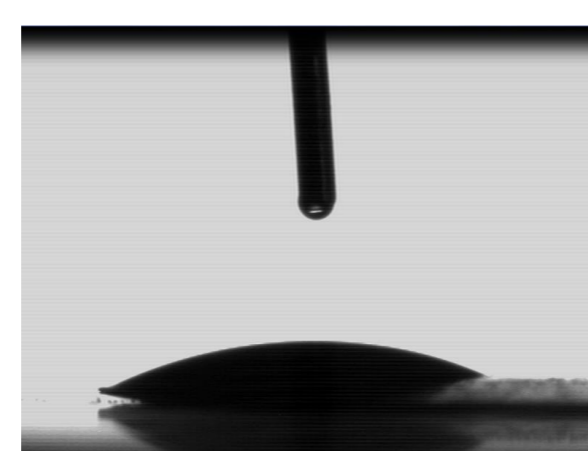


HYDROGENATION

CATALYST PREPARATION

A slightly hydrophilic (SiO₂ A) and a more hydrophilic (SiO₂ B) silica were chosen to prepare the catalysts.

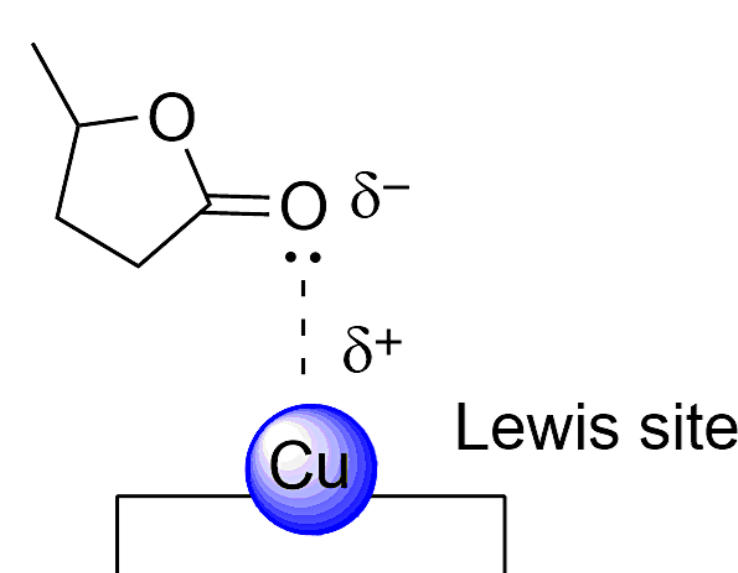
Wettability properties were evaluated through contact angle and silanol density (by TGA analysis) measurements.



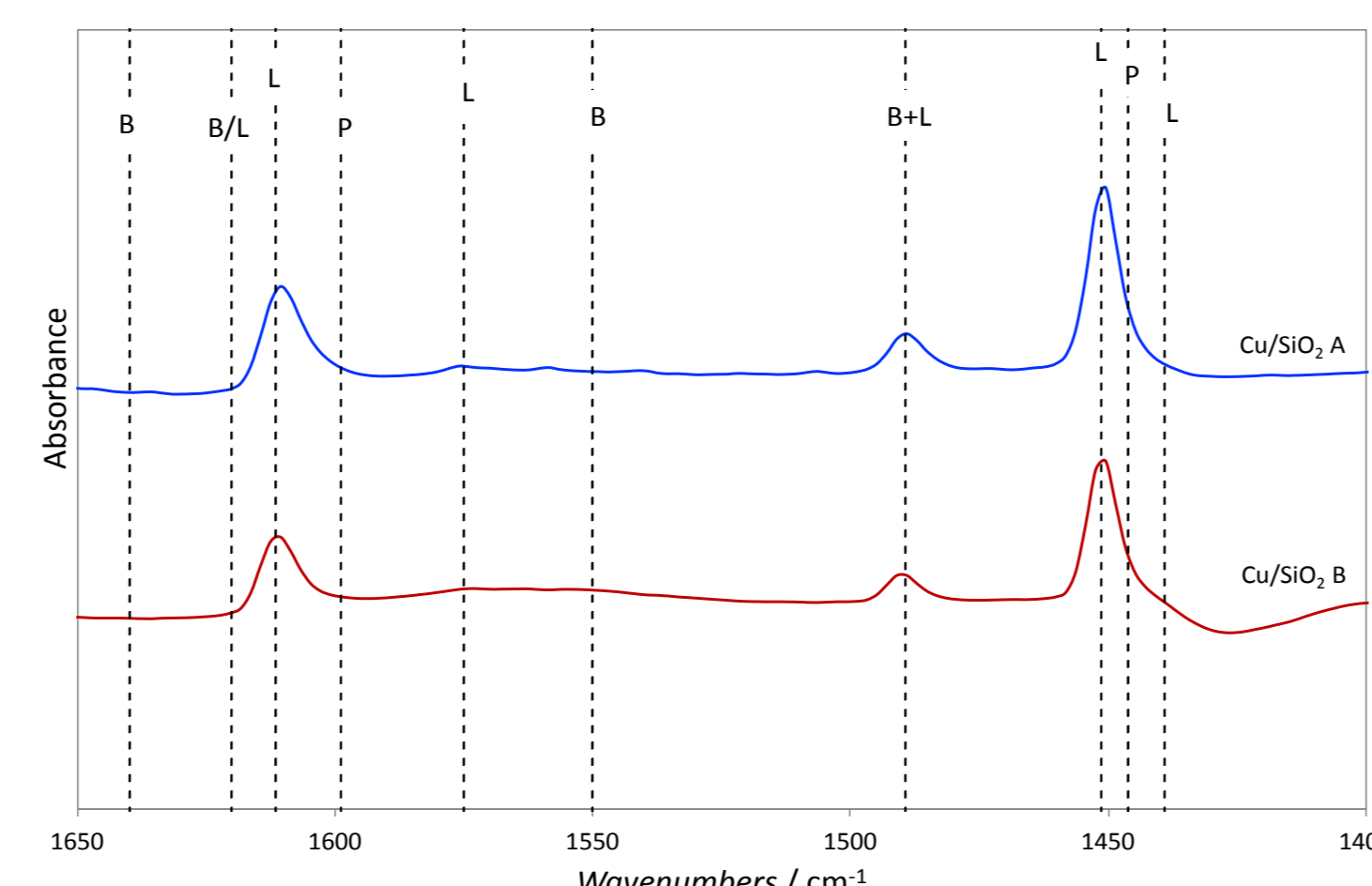
	Silanol density (mmol _{OH} g ⁻¹)	Contact Angle (θ)
SiO ₂ A	3.1	25°
SiO ₂ B	6.6	19°

Copper was deposited using the Chemisorption Hydrolysis as method¹ obtaining CuO/SiO₂ A and CuO/SiO₂ B (Cu loading of 16%) samples.

CATALYST ACIDITY



FT-IR spectra of pyridine adsorbed on Cu/SiO₂ A and Cu/SiO₂ B exhibit the presence of only Lewis acidic sites with a slightly higher amount on Cu/SiO₂ A (0.18 mmol_{py}/g_{cat}) respect to Cu/SiO₂ B (0.15 mmol_{py}/g_{cat}).

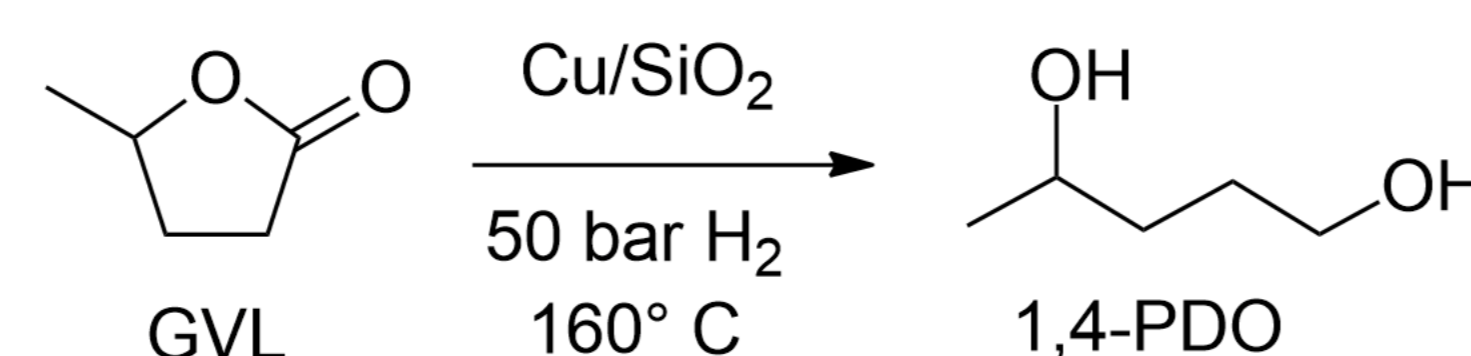


Effective acidity² was measured in the reaction solvent CPME and dioxane. CuO/SiO₂ A shows a much lower amount of strong acidic sites in CPME compared to dioxane.

Sample	Effective Acidity (mmol _{PEA} g _{cat} ⁻¹)			
	CPME		Dioxane	
	Total sites	Strong sites	Total sites	Strong sites
CuO/SiO ₂ A	0.11	0.025	0.09	0.03
CuO/SiO ₂ B	0.17	0.16	0.06	0.03

The very low amount of strong acidic site in CPME with a pure Lewis acidity may account for the high selectivity to 1,4-PDO observed for Cu/SiO₂ A. Moreover, it seems that an unfavourable interaction of the 1,4-PDO product with the less hydrophilic catalyst surface may lower the chance of secondary reactions.

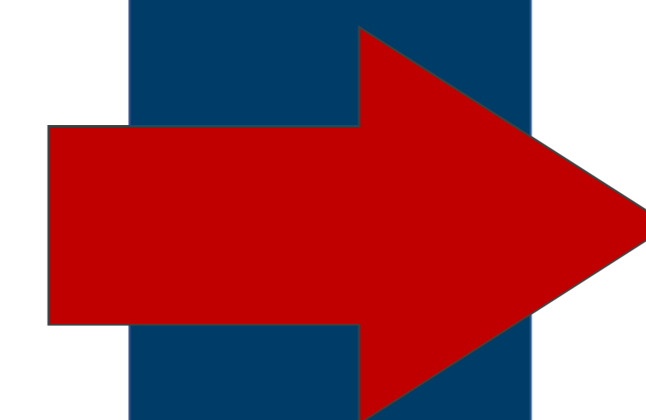
CATALYTIC TEST



Catalysts are pre-reduced under hydrogen before each reactions.

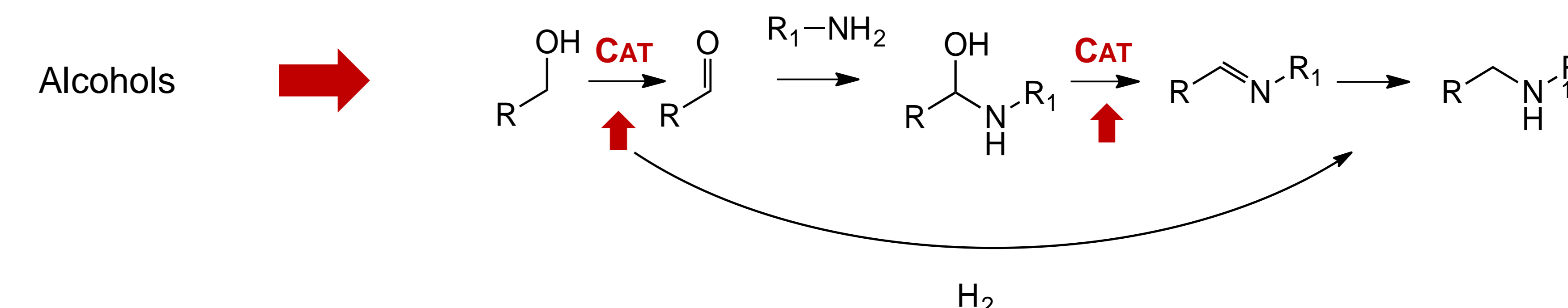
	Solvent	Conversion (%)	Selectivity (%)
Cu/SiO ₂ A	Dioxane	49	81
Cu/SiO ₂ B	Dioxane	57	80
Cu/SiO ₂ A	CPME	80	98
Cu/SiO ₂ B	CPME	57	82

The results exhibit that the choice of the support and solvent has a pivotal role in increasing the reaction yield towards 1,4-PDO.



AMINATION

HYDROGEN BORROWING MECHANISM

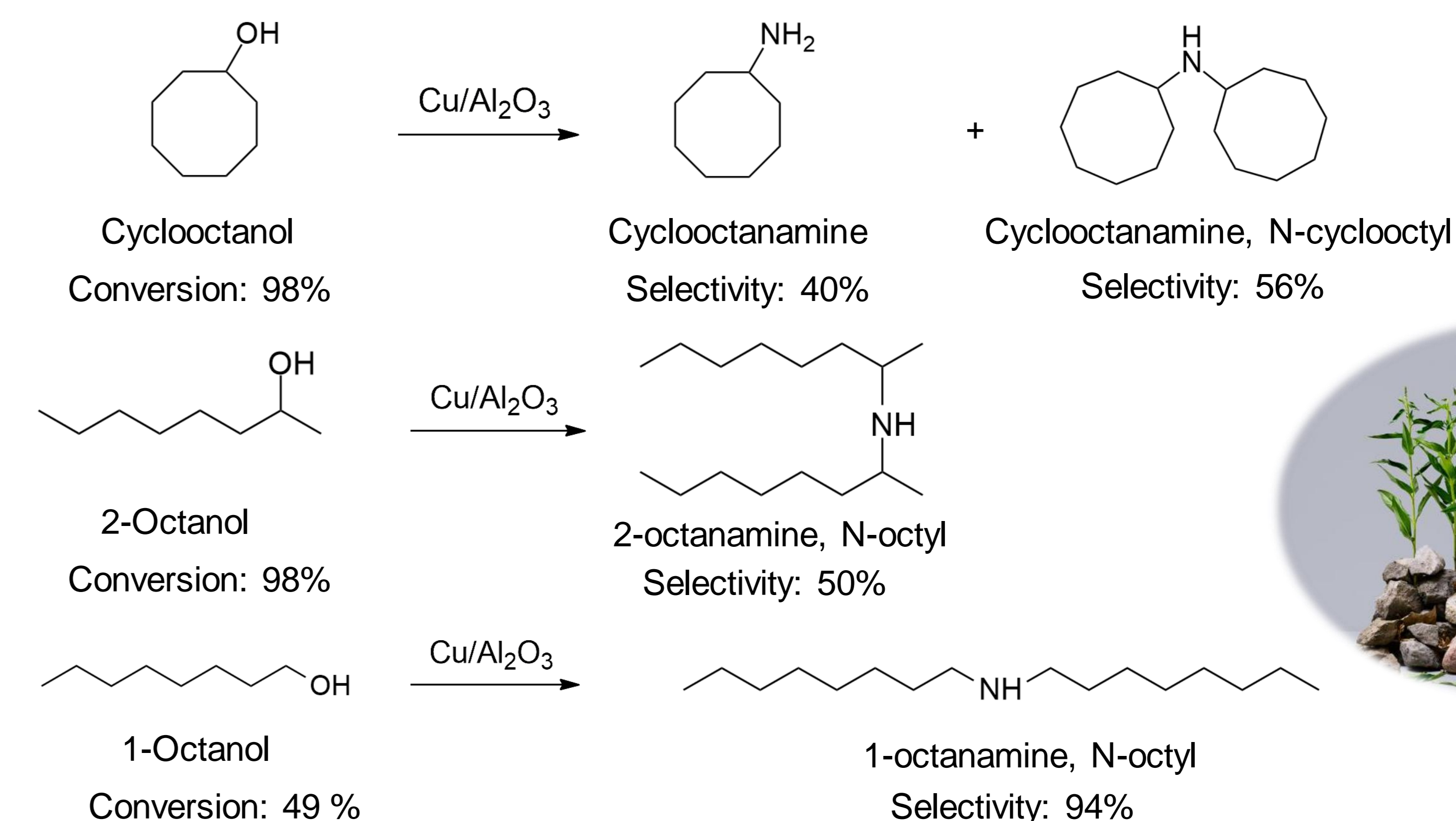


CATALYTIC RESULTS

Amination of alcohols with ammonia can be achieved with this strategy using copper catalyst supported on Al₂O₃ prepared with CH method at 16% copper loading.

Reaction conditions: T = 180° C, t = 2 h, P(NH₃) = 3 bar, P(H₂) = 10 bar

Different monoalcohols were tested initially to understand the reaction mechanism such as 1-octanol, 2-octanol, cyclooctanol namely a primary, a secondary and a cyclic alcohol.



The formation of the primary amine was found only in the case of the cyclic alcohol. The dehydrogenation product was observed in all reactions.

In the future, the reaction mechanisms will be clarified to improve selectivity toward primary amine.

REFERENCES

- [1] F. Zaccheria, N. Scotti, M. Marelli, R. Psaro, N. Ravasio, *Dalt. Trans.*, 2013 42 (5), 1319–1328
[2] P. Carniti, A. Gervasini, M. Marzo *Catal. Today* 2010, 152 (1–4), 42–47.