



# **On-the-fly** Catalyst Accretion and Screening in Chemoselective Flow Hydrogenation

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Herein, it is reported an *on-the-fly* accretion/reaction protocol to evaluate the structure-performance relationship in the chemoselective flow citral hydrogenation over Ni-based catalysts. Based on the methodology one was able to determine Ni nanoparticles ideal average size (ca. 9 nm), in a rapid and facile manner. The methodology offers a simple workflow, costeffective and adaptable strategy for process intensification and optimization.

The last decade witnessed the gaining in importance of continuous flow processing, as means to improve process sustainability and intensification. Application of continuous flow microreactors offers several benefits, such as reduction of mass and heat transfer, minimization of by-products formation and solvent usage, thus providing an environmentally and economically efficient technology for fine chemicals production comparatively to batch reactions.<sup>[1,2]</sup> Additionally, flow technology affords versatile and integrated (multi-step) reaction configurations that simplifies complex synthesis protocols<sup>[3]</sup> and speeds-up optimization of catalytically mediated processes.<sup>[4,5]</sup> The multi-step processing in catalysis entails either i) directing the reactant flow through consecutively assembled constituents, such as multiple catalyst beds, membranes or heaters<sup>[6,7]</sup> or ii) perform different steps of the process on a catalyst bed by sequential introduction of different components, such as reactants, modifiers or regeneration agents.<sup>[8]</sup>

Herein, we report a noble workflow for *on-the-fly* catalyst metal nanoparticles morphology modification and assess its causality in liquid-phase flow hydrogenation catalysis, providing

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.201800581 a simple and cost-effective strategy for process intensification.<sup>[9]</sup> The strategy is schematically represented in Scheme 1, and was verified for the chemoselective citral hydrogenation over Nibased catalysts. In these proof-of-concept experiments, the methodology was used to establish the effect of nominal particles size in the catalytic output. The best catalytic performances were attained with Ni particles with ca. 9 nm in size; however, the selectivity strongly depends on temperature and pressure.

The parent catalyst NiTSNH<sub>2</sub> was prepared in a two-step, namely chemical reduction of metal precursor (nickel acetylacetonate) followed by Ni nanoparticles (NPs) grafting onto amino terminated polymeric resin.<sup>[10]</sup> Particle size modification was attained via chemical reduction of Ni<sup>2+</sup> ions on the parent catalyst. The accretion process consisted of an on-the-fly continuous procedure where Ni<sup>2+</sup> ions in aqueous solution were passed through the parent catalytic bed under reducing atmosphere (H-Cube Pro™ microreactor at 40 bar H<sub>2</sub>, 100 °C and variable time). The materials were subsequently flashed with ethanol to remove ions excess and tested in the chemoselective hydrogenation of citral. A series of three modified materials have been synthesized and labelled as mod15-NiTSNH<sub>2</sub>, mod60-NiTSNH<sub>2</sub> and mod105-NiTSNH<sub>2</sub>, which corresponds to 15, 60 and 105 minutes of exposition time (Table 1), respectively. Metal loading of all nickel catalysts was estimated via atomic absorption spectroscopy and inductively coupled plasma - optical emission spectroscopy and found to as follows: 0.7 wt.% for parent, 1.0 wt% for mod15-NiTSNH<sub>2</sub>, 3.0 wt% for mod60-NiTSNH<sub>2</sub> and 4.9 wt% for mod105-NiTSNH<sub>2</sub>.

X-ray diffraction (XRD) was performed to estimate the nickel crystallite size (Figure 1, and Table 1). The parent NITSNH<sub>2</sub> did not exhibit discernible peaks associated to nickel, indicative of



**Scheme 1.** Schematic representation of the on-the-fly methodology applicable for process intensification and optimization.

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Table 1. M	letal	particle	size	of	Ni	catalysts	before	and	after	modificatio	br
and metal	cont	ent.									

Catalyst	Modificatior time [min]	n Crystallite size (XRD), [nm]	NPs size (TEM) [nm]	Metal content (AAS) [at.%]
NITSNH <sub>2</sub>	-	-	3-4	0.7
mod15- NiTSNI	H <sub>2</sub> 15	5	7	1.00
mod60- NiTSNI	H <sub>2</sub> 60	9	9	3.0
mod105- NiTSN	NH₂ 105	12	14	4.9



Figure 1. XRD patterns of parent  $\mathsf{NiTSNH}_2$  material and catalysts after modification.

small Ni NPs. This was confirmed by transmission electron microscopy (TEM), which revealed that the parent catalyst has Ni NPs with sizes of 3–4 nm (Figure 2, and Table 1). The emergence of reflections corresponded to nickel metal confirmed the proposed procedure effectiveness to increase particle nominal size. Structural analysis revealed that the longer exposure times yield peaks with sharper linewidths, indicative of bigger NPs. Analysis of the linewidths with Scherrer equation enabled estimation of Ni crystallite size after



Figure 2. TEM images of parent and modified catalysts.

Transmission electron microscopy (TEM) images of the modified catalysts, presented in Figure 2 and Table 1, revealed that Ni NPs of spherical shape, with average sizes of 7, 9 and 14 nm for modification: mod15-NiTSNH<sub>2</sub>, mod60-NiTSNH<sub>2</sub> and mod105-NiTSNH<sub>2</sub>, respectively. The EDX-mapping of mod15-NiTSNH<sub>2</sub>, mod60-NiTSNH<sub>2</sub> and mod105-NiTSNH<sub>2</sub> can be found in supporting information (SI), Figure S1. The small divergence between XRD analysis and TEM images has easily explained the fact that XRD detects solely the crystalline part of the NPs whereas TEM measures the entire NPs. Note that, surface termination is always amorphous in nature, and thus it does not contribute to XRD signal.

X-ray absorption spectroscopy (XAS) around Ni K-edge (8340 eV) measurements were performed to determine the chemical state of Ni NPs. The experiments were performed on a state-of-the-art laboratory von Hamos spectrometer. Figure 3 shows an example of a XAS spectrum and its deconvolution using as reference the spectra reported elsewhere.<sup>[11]</sup> The other measurements can be found in supporting information (SI), Figure S2-3. All the measured spectra were fitted with only two components, namely Ni<sup>0</sup> and Ni<sub>2</sub>O<sub>3</sub> (Ni<sup>3+</sup>), in other words, there was no evidence of NiO (Ni<sup>2+</sup>). The presence of Ni<sup>3+</sup> was also confirmed by X-ray photoelectron spectroscopy (XPS). However, the vacuum conditions seem to affect the component ratio and therefore such analysis was done only using XAS data.

Figure 4 shows the percentage of Ni<sup>0</sup> and Ni<sup>3+</sup> as a function of modification time. It is clear that increase in modification time (aka increase in average particles size) resulted in a significant decrease in Ni<sup>3+</sup> component. Moreover, addition of small amounts of NaBH<sub>4</sub> to sample during measurement resulted in a small increase of Ni<sup>0</sup> contribution. The results suggest that Ni<sup>3+</sup> component is located primarily at the surface and is the product of surface passivation with atmospheric air. Since the parent catalyst was pre-reduced in 40 bar of H<sub>2</sub> at 100 °C, it is reasonable to assume that only Ni<sup>0</sup> phase (active phase) is present during reaction.

The effectiveness of the presented methodology, as an *on-the-fly* modifier of catalytic output was verified with citral flow hydrogenation. Citral hydrogenation has several possible reaction pathways presented in Scheme 2.<sup>[12]</sup>

Hydrogenation reactions were performed straight after modification in the same flow micro-reactor under different conditions of temperature (65–100 °C) and H<sub>2</sub> pressure (10–60 bar). Prior the reaction catalyst bed was flashed with solvent at 40 bar H<sub>2</sub>, to reduce the superficially oxidized metal atoms (Ni<sup>3+</sup>). Figure 5 shows the effect of reaction parameters in the substrate conversion with the parent catalyst. The general trend is that conversion is promoted with the increase of H<sub>2</sub> pressure and reaction temperature, which is epitomized by the observation that the best conversion (ca. 98.6%) was attained at 100 °C and 60 bar. Similar results were obtained with the modified catalysts (see SI Figure S4–6).

Catalyst selectivity is also strongly dependent on reaction conditions. In the competitive carbonyl and conjugated alkenyl



Figure 3. XAS spectrum and spectral deconvolution of (top panel)  $NiTSNH_2$  and (bottom panel) mod60-  $NiTSNH_2$  measured in ethanol.



Figure 4. Relative contribution of  $\rm Ni^0$  and  $\rm Ni^{3+}$  species to the XAS spectrum as a function of modification treatment time.

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Figure 5. Dependence of reaction conditions on citral hydrogenation conversion, tested over parent catalyst.

bond hydrogenation, the presented Ni-based catalysts exhibit higher appetency towards C=C bond saturation located near the C=O group (Figure 6), i.e., formation of citronellal, which at low pressure (10 bar) is the only product formed. Note that citronellal is one of the desired products from citral hydrogenation because it is an insect repellent, in particular against mosquitoes,<sup>[13]</sup> and strong antifungal qualities.<sup>[14]</sup>

At 20 bar H<sub>2</sub> pressure, the main product at low temperature is citronellol (saturation of one of the C=C and the C=O) with values close to 100% at 65 °C. However, at 100 °C, the selectivity reverts back to citronellal formation. Similar results are obtained at 40 bar pressure but in this case, the selectivity switches back to C=C bond saturation at 85 °C. Finally, at 60 bar pressure, the selectivity is mainly to citronellal but the increase of temperature induces some C=O hydrogenation. Note that citronellol is a valuable commodity used in the production of perfumes, insect repellent<sup>[15]</sup> and mite attractant.<sup>[16]</sup> Citronellol complexation is also used in the production of the raw material rose oxide.<sup>[17]</sup>

In general, adsorption of  $\alpha,\beta$  – unsaturated aldehydes on nickel surface occurs via di –  $\delta_{CC}$   $\eta_2$  and/or di –  $\pi$   $\eta_2$  ( $\eta_4$ ). The former case considers adsorption via d- $\delta$  interactions with carbon atoms of alkenyl bond in  $\alpha$  position while the latter involves  $\pi$  electrons from both carbonyl and conjugated alkenyl bonds. Irrespective of which abovementioned adsorption mode occurs the C=C adsorption dominates, thus explaining the



Figure 6. Conversion in function of reaction conditions, tested over parent catalyst.





Scheme 2. Possible pathways of citral hydrogenation. A – conjugated alkenyl bond hydrogenation; B – carbonyl bond hydrogenation; C – isolated alkenyl bond hydrogenation

preference for this hydrogenation. In the case of citral, there are two C=C bonds, and clearly, the one located near the C=O group is the one that gets hydrogenated, which seems to be related to less steric hindrance when compared with the other bond. The increase in catalytic activity enables subsequent hydrogenations in the catalytic bed, namely saturation of the remaining C=C or the C=O. In our case, the second hydrogenation occurs solely on the C=O bond, which is significantly more accessible and reaction conditions are propitious to its conversion to the alcohol form (higher temperature and pressure). However, if the pressure and temperature are too high the molecule does not stay adsorb long enough to get further hydrogenated, consisting with the Sabatier principle. Influence of Ni NPs size on catalytic behavior was performed after *on-the-fly* modification of the parent catalyst. The presented methodology relies on catalyst modification followed by a catalytic reaction performed in situ after washing. The sequence can be conducted repeatedly with varied accretion time. Here, it is reported a three-step alternate introduction of modification agent and reactant solution. Thus, every modification step changes the Ni NPs size whereas consecutive hydrogenation reaction allows monitoring catalytic behavior after those changes. The results are shown in Figures 7 and 8.

It is clear from the analysis of Figures 7 and 8 that the studied reaction is structure-sensitive in terms of nanoparticles size both in terms of product distribution and reaction yield.



Figure 7. Citral hydrogenation chemoselective behaviour of the tested catalysts.

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Figure 8. Influence of Ni nanoparticles size on catalytic performance in citral hydrogenation at 40 bar  $H_2$  pressure.

The best catalytic performance was obtained with the catalyst containing an average particle size of ca. 9 nm and 3.0 wt% of Ni loading. The dependence with particle size follows volcano plot behavior. Catalysts with particles size >9 nm are less active, especially at a higher temperature, due to the reduction of active surface area. While, smaller nanoparticles are less active due to 'self-poisoning' from substrate and/or product caused by stronger bond formation with catalytic surface.<sup>[18]</sup>

The selectivity is also affected by particle accretion. Generally, larger particles favor the formation of citronellal. However, the trend deranged when particles become too large (above 9 nm), resulting in an increase in the formation of citronellol. Reasons for changes in selectivity with smaller and larger particles differ. In the case of smaller particles, selectivity drop relates once again to 'self-poisoning', while drop in selectivity with larger particles (> 9 nm) are probably caused by steric hindrance.<sup>[19]</sup>

Citral hydrogenation is predominantly performed in batch mode with noble metals, such as Pt and Pd,<sup>[20]</sup> which are often doped with other metals to enhance selectivity.<sup>[21]</sup> Citral hydrogenation over Ni catalysts results in the formation of the conjugated alkenyl product. A recent study<sup>[22]</sup> showed that Ni NPs (~ 5 nm) supported on carbon is able to produce citronellal with 50% of selectivity at 100 °C and 10 bar. Selectivity can be further increased to 90% if the reaction temperature and H<sub>2</sub> pressure are increased to 200 °C and 30 bar, respectively.<sup>[23]</sup>

It should be mentioned that catalysts were found to be stable on stream for at least 300 min (in SI Figure S7–8), both in respect to activity and selectivity.

In conclusion, we reported an innovative *on-the-fly* protocol to assess structure-activity relationships. The presented approach enabled us to optimize catalytic performance by changing catalysts morphology and/or reaction parameters, permitting control of product formation. The methodology offers a simple workflow, cost-effective and adaptable strategy for process intensification and optimization.

### **Experimental Section**

#### **Catalyst Preparation**

The catalyst was prepared by chemical reduction of Ni(acac)<sub>2</sub> 0,001 mol with NaBH<sub>4</sub> (molar ratio 1:2) at room temperature and under Ar atmosphere. The synthesis was performed in presence of trioctylphosphine oxide in 65 ml of ethanol. After reduction, black Ni NPs were immobilized onto commercially available resin Tentagel-S-NH<sub>2</sub> at room temperature and constant stirring.

#### **Catalyst Characterization**

**XRD measurements:** XRD measurements were performed employing Bragg-Brentano configuration. This type of arrangement was provided using PANalytical Empyrean diffraction platform, powered at 40 kV×40 mA and equipped with a vertical goniometer, with theta-theta geometry using Ni-filtered Cu K $\alpha$  radiation. Data were collected in the range of  $2\theta = 5-95^{\circ}$ , with a step size of 0.008° and counting time 60 s/step.

**TEM experiments:** TEM experiments were performed on the electron microscope Titan G2 60–300 kV (FEI, Japan) equipped with EDAX EDS (energy dispersive X-ray spectroscopy) detector. Microscopic studies of the catalysts were performed at an accelerating voltage of the electron beam equal to 300 kV. The samples were prepared by their dispersing in pure alcohol using an ultrasonic cleaner and putting a drop of this suspension on carbon films on copper grids.

XAS measurements: X-ray absorption spectroscopy measurements were done at ambient conditions by means of a laboratory in-air experimental setup consisting of an X-ray source, NiTSNH<sub>2</sub> sample and a crystal X-ray spectrometer of the von Hamos geometry. The source used was XOS X-Beam Superflux PF X-ray tube operated at the voltage of 40 kV and the current of 0.9 mA and equipped with a focusing optics. The polychromatic incident X-ray beam of about 3° divergence penetrated the sample placed in the beam focal point through a spot with the nominal size of 100 µm. The transmitted radiation was diffracted by a cylindrically bent Si(440) crystal of 25 cm-radius of curvature at the Bragg angle of 65.2° and registered by an Andor Newton CCD camera with front-illuminated  $1024 \times 256$  matrix of 26  $\mu$ m-sized pixels. The pressure in the camera's interior was decreased to 10<sup>-7</sup> mbar and the sensor was cooled down to -40 °C with the thermoelectric cooler built in the device. The camera's entrance was sealed with 250  $\mu\text{m-thick}$  Be window.

**XPS measurements:** The chemical composition of the Ni catalysts was examined using photoelectron spectroscopy (Microlab 350 – Thermo Electron). The chemical state of surface species was identified using the high energy resolution spherical sector analyzer of the spectrometer (SSA). XPS spectra were excited using AlK<sub>α</sub> (hv = 1486.6 eV) radiation as a source. The high-resolution spectra were recorded using 40 eV pass energy with the step 0.1 eV. A Shirley background subtraction was made to obtain the XPS signal intensity. The peaks were fitted using an asymmetric Gaussian/ Lorentzian mixed function. The binding energies measured were corrected in reference to the energy of C 1s peak at 284.5 eV. Advantage-based data system software (Version 5.97) was used for data processing.

Elemental analysis was performed by atomic absorption spectrometry (AAS).



#### **Catalytic Test**

Catalytic tests were performed in continuous-flow micro-reactor (ThalesNano H-Cube Pro<sup>TM</sup>) that provides isothermal and isobaric conditions within the operational range of pressure and temperature up to 100 bar and 150 °C. The catalyst (150 mg) was placed in a stainless steel cartridge (70 mm CatCart®) that enables a continuous flow of hydrogen and citral solution through the catalyst bed. The hydrogen was generated in situ via electrolysis of water and then supplied to the reaction medium. The 0.05 M citral ethanol solution was flown through the cartridge with 0.5 mLmin<sup>-1</sup>.The residence time (defined as bed volume/flow rate) was calculated to be 6 min. After attaining stable condition, samples were collected at the outlet of the reactor and analyzed by Bruker Scion 456-GC gas chromatograph equipped with FID Analyzed compounds were separated with non-polar BP-5 0.25  $\mu$ m (5% phenyl/95% dimethyl polysiloxane) column.

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### **Conflict of Interest**

The authors declare no conflict of interest.

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## COMMUNICATIONS

**Catalysis & Go!** A potential farreaching methodology to vary nanoparticles morphology and assess its causality in liquid-phase flow hydrogenations is reported. The protocol provides a platform for on-the-fly investigation of structure-activity relationships and optimization of metal nanocatalysts catalytic performance.



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