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# Chemoselective flow hydrogenation of $\alpha, \beta$ – unsaturated aldehyde with nano-nickel

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#### Abstract

Herein, it is presented a novel catalytic system for the continuous-flow chemoselective hydrogenation of  $\alpha,\beta$  – unsaturated aldehydes used in the production of high-value cosmetics and pharmaceuticals precursors. The reaction was catalyzed by nano-nickel particles grafted on polymeric support, synthesized via a simple, adaptable and green methodology. The system was highly active and very selective to C=C bond saturation.

**Keywords:** hydrogenation in flow, nano-nickel catalyst, resin supported catalyst, selective hydrogenation of  $\alpha,\beta$  – unsaturated aldehydes

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#### 1. Introduction

Catalytic hydrogenation is undoubtedly the most important method for the reduction of organic compounds. The process versatility and green credentials make it an attractive and adoptable strategy for the reduction of a plethora of organic compounds in high yields. In the fine chemical industry, catalytic hydrogenations are performed majorly in batch conditions [1], even if continuous flow is often preferred [2]. The use of flow simultaneously process profitability and continuous improves green credentials since it improves reaction atom efficiency, decreases energy costs, affords simplified large-scale synthesis (scalability) and handling of various substrates in workup and sequence with the same catalyst [3]. Flow methodology has been adopted for a multitude of purposes including organic synthesis [4], biological transformation [5], substitution [6], and conversion reactions [7].

Herein, it is presented a catalytic methodology for the chemoselective hydrogenation of  $\alpha,\beta$  – unsaturated aldehydes in flow with heterogeneous nano-nickel and hydrogen, as catalyst and reducing agent, respectively. The catalyst was prepared via a green route and could be used directly in the reaction. Selective hydrogenation of  $\alpha,\beta$  – valuable unsaturated aldehydes is a promising strategy for the synthesis of intermediates for the pharmaceutical and fine chemical industries. The strategy implies selective hydrogenation of only one of the functionalities (C=C or C=O) but not both. For instance the selective hydrogenation of cinnamaldehyde (CA) yields the formation hydrocinnamaldehyde (HCA) or cinnamyl alcohol (COL) of either (Scheme **S1**, supporting information (SI)). COL is an important intermediate in cosmetics production and HCA is applied in HIV treatment [8], while the fully hydrogenated product (no selective path) has no industrial application.

Selective hydrogenation of CA has been widely investigated as model reaction. Most of the reported studies relate to catalysts using supported precious metals [9]. There is a visible tendency towards development of catalysts composed of more cost-efficient materials, namely transition metals. Monometallic catalysts based on transition metals based on copper [10], silver [11], or nickel [12-19] were found also active in C=C bond selective hydrogenation. However, most of the studies on CA selective hydrogenation over nickel catalysts were performed under stationary (batch) conditions and corroborate the above-mentioned trend

[12-19], as given in **Table S1** where Ni based catalysts CA hydrogenation chemoselective performance in assembled [12-19].

High-pressure flow hydrogenations impose several demands in respect to catalyst design, among them the need for large nominal size particles (low surface area support) and high dispersion of the nano-active phase. Polymeric matrices used as supports can be modified to allow grafting of nanomaterials post-synthetically, thus enabling the development of monodispersed nanoscale active phases in low loading, while keeping relatively large nominal particle sizes for the catalyst support in order to minimize pressure drop and thus energy consumption.

#### 2. Experimental section

#### 2.1. Catalyst synthesis

Catalyst (NiTSNH<sub>2</sub>) preparation involved two steps, namely, synthesis of nickel nanoparticles (NPs) and subsequent grafting on polymeric support. Nickel NPs were obtained by chemical reduction of nickel (II) acetylacetonate with NaBH<sub>4</sub> (reducing agent) and trioctylphosphine oxide (TOPO) (capping agent). TOPO regulates growth and prevents nickel NPs agglomeration. After centrifuging and washing, the NPs were immobilized on amino groups terminated resin (Tentagel-S-NH<sub>2</sub>, BET surface area 152  $m^2/g$  and pore volume of 0.13  $cm^3/g$ ) with a nominal size of 90  $\mu$ m. The metal loading was found to be 0.7 wt.% by atomic adsorption spectroscopy (AAS) and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OPS). Note that the synthesis was carried out at room temperature, in argon atmosphere with ethanol, as solvent, which confers the process a high degree of scalability. Additionally, the polymeric resin has expands upon contact with polar solvents, increasing functional groups exposure and consequently increase in metal loading [20].

#### 2.2. Catalyst characterization

Fourier-transformed Infrared (FT-IR) spectra were recorded with Nicolet 380 FT-IR spectrometer in the region of 4000 – 500 cm<sup>-1</sup> using KBr pellets. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a PHI 5000 VersaProbe<sup>TM</sup> (ULVAC-PHI) scanning ESCA Microprobe using monochromatic Al-K $\alpha$  radiation (hv = 1486.6 eV) from an X-ray source operating at 100 µm spot size, 25 W power and 15 kV acceleration voltage.

High resolution (HR) XPS spectra were collected with a hemispherical analyzer at a pass energy of 23.5 eV, an energy step size of 0.1 eV and a photoelectron take off angle of 45  $^{\circ}$  with respect to the surface.

Powder X-ray diffraction (PXRD) measurements were performed employing Bragg-Brentano configuration. This type of arrangement was provided using PANalytical Empyrean diffraction platform, powered at 40 kV  $\times$  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 step size of 0.008 ° and counting time 60 s/step.

High-resolution transmission electron microscopy (HRTEM) was performed on a FEI Titan Cubed at 300 kV accelerating voltage. Before measurement the catalyst sample was dispersed in pure methanol via ultrasonification. 300 mesh copper grid with holey carbon film was immersed in the obtained suspension of the catalyst. No plasmacleaning was applied. Scanning electron microscopy (SEM) was carried out on a FEI Nova NanoSEM microscope.

Energy dispersive X-ray fluorescence analysis (EDXRF) was carried out using MiniPal 4 equipment from PANalytical Co., with an Rh-tube and silicon drift detector (resolution 145 eV). EDXRF method was used to gain information on the elemental composition of liquid samples after catalytic experiments.

#### 2.3. Catalytic tests

Continuous-flow hydrogenation of CA was chosen as model reaction to evaluate catalytic performance. Note that this is to our knowledge the first application of the selective hydrogenation of  $\alpha,\beta$  – unsaturated aldehydes carried out in flow with nanonickel. Catalytic tests were carried out in continuous-flow micro-reactor (ThalesNano H-Cube Pro<sup>TM</sup>) that provides isothermal and isobaric conditions within 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 continuous flow of hydrogen and CA 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 CA ethanol solution was flown through cartridge with 0.5 mL min<sup>-1</sup>, which results in supplying 2.5 µmol of CA per minute (3.2 µmol of prenal per minute). The optimal reaction conditions were selected according to generation of the highest amount of desired C=C hydrogenation product. Thus, the reactions were carried out at

100 °C and 40 bar with CA and at 85 °C and 60 bar with prenal. The residence time (defined as bed volume/flow rate) was calculated to be 6 min. Since the resin support swells due to the interaction with the solvent, the catalytic experiments were initiated after exposing materials to the solvent for 1 h. This procedure ensured that the samples were stable in respect to support swelling. After attaining stable condition, samples were collected at the outlet of the reactor every 30 min for 3 h 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.

#### 3. Results and discussion

Changes in the  $-NH_2$  terminal groups, monitored by FT-IR spectroscopy, were used to to confirm Ni NPs grafting to resin [21]. **Figure 1** shows the primary amine -NHstretching (3200-3800 cm<sup>-1</sup>) and bending (1550-1700 cm<sup>-1</sup>) regions. The pristine resin shows bands at 3470 and 1650 cm<sup>-1</sup>, assigned to primary amine [22]. The addition of Ni NPs decreased the bands intensity and induced a small shift of the -NH stretching band to lower wavenumber (3447 cm<sup>-1</sup>), corroborating the idea that the Ni NPs are covalently linked via the  $-NH_2$  terminal groups. PXRD (**Figure 2**) and SEM (**Fig. S1**, **SI**) revealed that the polymer is unaltered upon loading of metal NPs, indicative of only surface modification. The absence of new diffraction peaks in the PXRD and discernible small particles in the SEM suggests that Ni NPs are smaller in size than 5 nm.

Thermogravimetric analysis (TGA) shows that the polymer is thermally stable up to approximately 300°C, which appreciably higher than temperatures used in the catalyst synthesis and chemoselective hydrogenation reactions.

HRTEM analysis showed that nickel exists in agglomerated form either on polymer surface or inside pores (**Figure 3**), which impedes easy recognition of single beads. Nevertheless, a large majority of NPs is significantly lower than 10 nm, as presented in the **Figure 3a**, where NPs are in size 3-4 nm. Moreover, crystallites above 20 nm were seldom spotted. Material features, such as presence of polymeric matrix and NPs agglomeration, increase sample thickness above transmission limitation, making reliable assessment that concentration/occurrence frequency are straitened.

XPS was carried out to determine the oxidation state of the grafted NPs. Figure 4 shows Ni 2p region fitted using constrains for area intensity, full maximum half width and doublet energy separation tabulated in the NIST database. Sample charging was corrected using C 1s  $sp^3$  signal (284.6 eV). The dominant signal of Ni  $2p_{3/2}$  located at 856.1 eV relates to Ni(OH)<sub>2</sub>. The value is roughly 0.2 eV higher than the one reported in literature [23], which is a clear indication for the presence of nanoparticles. Previous reports revealed that the binding energy shifts to higher energies when sample is in a form of small nanoparticles [24]. The peak at 860.4 eV is ascribed to metallic Ni shake-up satellite. There is a peak at low biding energy (852.9 eV) related to Ni<sup>0</sup> [25], which is also slightly shifted to higher energies corroborating presence of nanoparticles [24].

**Figure 5** shows catalyst activity in CA hydrogenation and selectivity to the saturated aldehyde (desired product). The catalyst displays stable performance, with activities related to 80% conversion of reagent and selectivity to the desired product at around 93 % after 12h of continuous reaction. It should be noticed here that only negligible deactivation was observed during this long – term experiment. The study was expanded to another molecule, prenal, with similar outcome (**Table 1**), namely high selectivity (95%) to prenal C=C saturation, as desired product from an industrial point of view. Note that resin without the catalyst was not active in any of the reported reactions. Finally, the observed high selectivity towards C=C hydrogenation product and nearly perfect carbon balance obtained suggests that C-C and C-O bond cleavage does not occur in a significant extent in the reaction conditions used.

XRF analysis for the samples of post-reaction solutions did not show any amount of nickel within the detection limit, i.e., no detectable metal leaching. There was also no observable change in the PXRD pattern (**Figure 2**) and HR-TEM (**Fig. S2, SI**) of the catalyst after reaction, suggesting high stability of the Ni NPs and resin. Finally, the XPS show no evidence for change in the oxidation state of the Ni NPs. These findings imply that the minor deactivation observed is related to blocking of reactive sites by substrate and/or product, as corroborated by the appearance in the spent catalyst of two small contributions accounting to about ca. 5% of the XPS C 1s signal (**Fig. S3, SI**) ascribed to C=O (287.4 eV).

Considering current state-of-the-art (**Table S1, SI**) the current strategy is economically more competitive since it employs nearly tenfold less metal than what has been previously reported [12-19]. Moreover, CA hydrogenation is usually carried out in

batch reactor instead of flow (desired mode) and at higher temperatures and pressures [12-19] than those used in the present work. Physicochemical characterization of spent catalyst (XRD, XPS, HRTEM) indicates that the catalyst is stable because there were not observable changes in the structure and morphology of Ni NPs grafted on the resin (**Figs. 2-4**) due to reaction.

Low loading of well-exposed active nano-Ni phase (0.7 wt.%) indicates high catalytic performance in studied reaction (Fig. 5 and Table 1), where excellent stability is obtained after 12 h of continuous reaction. The specific nature of resin support eliminates diffusion restrictions and provides uninhibited access to the metal phase. As a result, hydrogenated molecules approach the metal surface in a position imposed by electronic interactions with the active phase. The strength of steric interactions is inflected by the exposure of different metal crystal faces in the Ni clusters and nanoparticles. More corrugated Ni(110) pattern (Fig. 3) causes weaker repulsion with  $\alpha$ ,  $\beta$ comparison to flat (111) unsaturated carbonyls in surface. easing simultaneous adsorption of both unsaturated bonds ( $\eta_4$  geometry). When either alkenyl and carbonyl bonds are adsorbed via  $\pi$ -d mode the alkenyl hydrogenation is preferred due to kinetic selectivity of the reaction is reasons [26]. Thus, shifted towards formation of unsaturated aldehyde. Moreover, the results may imply that the electronic structure of chosen metal modulated by the nanosize influences adsorption of the present substrates via steric repulsion between C=C bond and small Ni NPs, which also assists its selective saturation [27].

#### 4. Conclusions

In summary, we reported to our knowledge the first nano-nickel catalyst active in selective hydrogenation of  $\alpha,\beta$  – unsaturated aldehydes in continuous flow mode. The presented results show that nano-nickel immobilized on polymeric resin selectively converts  $\alpha,\beta$  – unsaturated aldehydes to saturated aldehyde with molecular hydrogen, i.e., system is selective to C=C hydrogenation. The catalyst was prepared with a two-step procedure, which enables control of size and shape of the particles and leads to high loading active phase into a ready-to-use support. Well-exposed metal phase on polymeric resin provides unrestricted access to the metal surface and eliminates diffusion restrictions and clogging of the reactor.

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Figures captions

Figure 1. FT-IR spectra depicting the characteristic primary amine  $-NH_2$  vibrations for polymeric resin before (*blue*) and after (*red*) grafting with the Ni NPs.

**Figure 2.** PXRD patterns for polymeric resin before (*blue*) and , NiTSNH<sub>2</sub> as prepared after (*red*) grafting with the Ni NPs and spent- NiTSNH<sub>2</sub> (green).

Figure 3. HRTEM overall view (a) and magnification of the selected area with FFT image insert (b) showing Ni NPs in the polymer matrix. The crystal structure was identified as nickel ffc, a=3.52 Å

Figure 4. XPS of nickel catalyst after preparation and after catalyst reaction. Narrow scan of Ni 2p region.

Figure 5. Catalytic activity of the nano-nickel catalyst in the chemoselective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde.

**Table 1.** Summary of the catalytic activities and selectivity for chemoselective hydrogenation of  $\alpha,\beta$  – unsaturated aldehydes after 3h.





Figure 2







Figure 5

#### Table 1

| Substrate      | Activity,<br>μmol min <sup>-1</sup> | Conv., % | Selectivity, %    |                   |                        |      |        |                                    |                 |
|----------------|-------------------------------------|----------|-------------------|-------------------|------------------------|------|--------|------------------------------------|-----------------|
|                |                                     |          | C=C<br>saturation | C=O<br>saturation | Complete<br>saturation | т, ℃ | p, bar | Flow rate,<br>mL min <sup>-1</sup> | Reaction scheme |
| cinnamaldehyde | 2.3                                 | 87       | 93                | -                 | 7                      | 100  | 40     | 0.5                                |                 |
| prenal         | 1.2                                 | 37       | 95                | -                 | 5                      | 85   | 60     | 0.5                                | +H2, 0.7NiTSNH2 |
|                |                                     |          | PT                | EV                | Y                      |      |        |                                    |                 |

### Graphical abstract



#### Highlights

- Ready-to-use Ni NPs immobilized on resin catalyst for flow hydrogenation ٠
- Simple, adaptable and green methodology for catalyst synthesis •
- High selectivity towards unsaturated aldehyde •
- Low metal loading •
- High catalytic performance •

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