

Short communication

A novel nano-palladium catalyst for continuous-flow chemoselective hydrogenation reactions



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ABSTRACT

Herein, we report a catalyst composed of palladium nanoparticles immobilized on polymeric resin for chemoselective hydrogenation reactions under flow conditions. The catalyst exhibits high activity and selectivity towards hydrogenation of C=C double bond, as confirmed in the hydrogenation of 2-heptene and 6-methyl-5-hepten-2-one.

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1. Introduction

The pharmaceutical and chemical industries typically use stoichiometric amounts of reagents in their processes, which diminish processes greenness and competitiveness due to the large amounts of waste generated. Hence, scientists have been intensively looking for the alternative ways of the pharmaceuticals and fine chemicals synthesis, which is in agreement with the twelve principles of green chemistry, which often entails the use of catalysis in flow mode [1]. Catalytic hydrogenation is widely used method for the reduction of organic compounds to high value chemicals or precursors [2]. However, in the fine chemical and pharmaceutical industries, hydrogenations must be chemoselective because their common substrates, such as unsaturated ketones, aldehydes or esters, often possess several hydrogenable functionalities but the desired product requires that only a specific functionality be hydrogenated, depending on their end-use [3,4]. Noble metals, such as palladium, are highly active hydrogenation catalysts, operating at mild reaction conditions. Palladium is routinely used to hydrogenate C=C bonds [5], but the systems are often non-selective and lose effectiveness with the increase of hydrogenable functionalities in the molecule [3]. Poisoning of the catalyst with, for example lead, accomplishes desired

selectivity; such is the case of the Lindlar catalyst commonly used in industry [6,7]. The demand for palladium catalysts able of performing chemoselective hydrogenation of organic compounds is a current topic of research and a continuous industrial pursue.

Herein, a novel palladium catalyst composed of nano-Pd grafted on polymeric resin is reported, which can be used in chemoselective hydrogenation of the substances containing C=C and C=O bonds under flow and with hydrogen as reducing agent. The catalysts exhibit very high activity and selectivity towards C=C bonds hydrogenation.

2. Experimental part

2.1. Synthesis of the catalyst

Palladium nanoparticles (Pd NPs) were prepared by chemical reduction via two-step synthesis method. In the first step, palladium(II) acetylacetonate was dissolved in ethanol and mixed with trioctylphosphine oxide (TOPO) to prevent agglomeration. Subsequently, NaBH₄ was added and the final solution was mixing under argon atmosphere and at room temperature. The formed Pd NPs were centrifuged and washed with ethanol and hexane and subsequently grafted on polymer terminated by amino group (TentaGel-S-NH₂) with bead size of 90 μm and pore volume of 0.13 cm³/g, which can be used directly for flow applications. The resulting catalyst, labeled as PdTSNH₂, was dried over the night at temperature of 90 °C.

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2.2. Physicochemical characterization

Elemental analysis was performed by atomic absorption spectrometry (AAS) and inductively coupled plasma - optical emission spectrometry (ICP-OES). The Pd loading was found to be 2.16 wt%.

Fourier-transformed Infrared (FTIR) spectra were recorded with Nicolet 380 FTIR spectrometer in the region of 4000–500 cm^{-1} using KBr pellets.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a PHI 5000 VersaProbe™ (ULVAC-PHI) scanning ESCA Microprobe using monochromatic Al-K α radiation ($h\nu = 1486.6 \text{ eV}$) from an X-ray source operating at 100 μm spot size, 25 W power and 15 kV acceleration voltage.

The high resolution (HR) XPS spectra were collected with a hemispherical analyzer at the pass energy of 23.5 eV, the energy step size of 0.1 eV and the photoelectron take off angle of 45° with respect to the surface. CasaXPS software was used to evaluate the XPS data. Deconvolution of XPS spectra were performed using a Shirley background and a Gaussian peak shape. The binding energies (BE) of all detected spectra were calibrated with respect to the BE of carbon $\text{sp}^3 \text{C} 1\text{s}$ at 285 eV [8]. 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 α radiation. Data were collected in range of $2\theta = 5\text{--}95^\circ$, with step size of 0.008° and counting time 60 s/step.

2.3. Chemoselective hydrogenation reactions

Catalytic hydrogenation of 2-heptene and 6-methyl-5-heptene-2-one was investigated in continuous-flow system – ThalesNano™ H-Cube Pro. 0.15 g of the TSNH₂ or PdTSNH₂ was placed in the stainless-steel cartridge (CatCart@70, 4 mm i.d.), which was subsequently connected to the apparatus (Scheme 1) [9]. The hydrogen was generated in situ via electrolysis of water.

The hydrogenation of 6-methyl-5-hepten-2-one and 2-heptene was carried out in ethanol under different reaction conditions (at temperature range between 25 and 100 °C and at pressure range of 10–60 bar). Additionally, we were able to adjusting the flow rate of our reactants in range of 0.3–1 mL/min. Follow our experimental data 0.5 mL/min was chosen as the best flow rate. Afterwards the best parameters of the temperature and pressure were selected for five hours experiment. Hence, hydrogenation of 2-heptene was carried out at the temperature of 65 °C and with hydrogen pressure of 10 bar, hydrogenation of 6-methyl-5-hepten-2-one was carried out at temperature of 85 °C and with hydrogen pressure of 10 bar. Products were collected into the vial and next

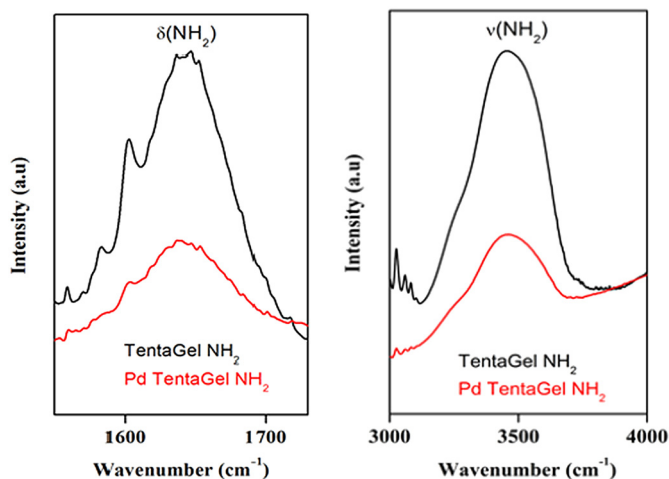


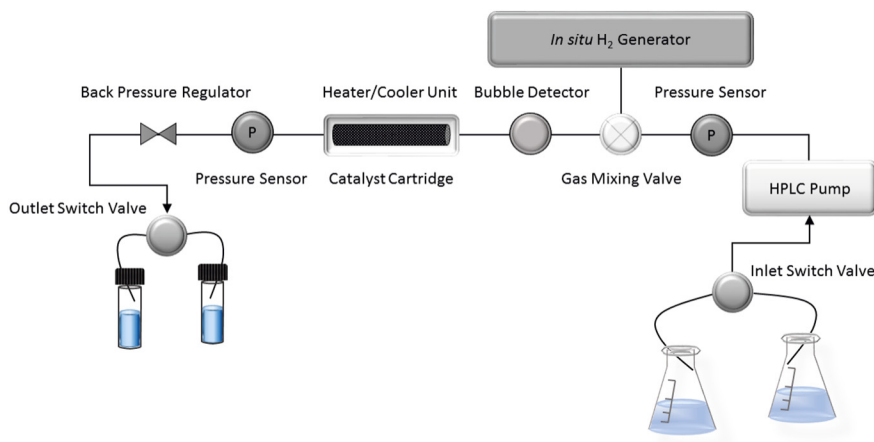
Fig. 1. FT-IR spectra for polymeric resin before and after grafting with the Pd NPs.

analyzed by GC chromatograph Bruker 456GC equipped with FID detector. Blank experiment with TSNH₂ did not show any catalytic activity in hydrogenation either 2-heptene or 6-methyl-5-hepten-2-one.

3. Results and discussion

Comparison of selected vibrational bands in the IR spectrum of the free resin and the catalyst confirmed that Pd NPs are grafted on the resin (Fig. 1). In the IR spectrum of TSNH₂ characteristic broad bands at the range of 3200–3800 cm^{-1} (with maximum at 3470 cm^{-1}) and at the range of 1550–1700 cm^{-1} (max. 1647 cm^{-1}), correspond to the $\nu(\text{NH})$ and $\delta(\text{NH})$ vibrations of primary amine, respectively [10]. Changes in the bands wavenumber and intensity in these regions of the catalyst spectrum are consistent with the presence of Pd NPs covalently-bonded through the $-\text{NH}_2$ functional groups of the resin. Furthermore, the formation of covalent bond between the resin and Pd NPs is confirmed by shift towards lower wavenumber ($\Delta = 6 \text{ cm}^{-1}$) and in a decrease in intensity of the $\nu(\text{CN})$ stretching band in the spectrum of the catalyst. Additionally, data obtained from FT-IR spectra revealed that structure of polymeric resins had not been changed.

The PXRD of TSNH₂ and PdTSNH₂ (Fig. 2) indicate that two-step synthesis method did not affect the crystallinity of the polymeric resin, when comparing resin main diffraction peaks at $2\theta = 19.1, 23.3, 26.4^\circ$, what is in agreement with previous report [11]. Addition of Pd NPs resulted in the appearance new diffraction peak at $2\theta = 40.1^\circ$ associated to Pd (111) [12]. Pd NPs crystallite size was estimated to be 4 nm from line broadening. Moreover XRD results for spent catalysts did not



Scheme 1. Schematic draw of the H-Cube Pro reactor by Thales Nanotechnology Inc., Hungary [9].

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