Palladium-nanoparticles on end-functionalized poly(lactic acid)-based stereocomplexes for the chemoselective cinnamaldehyde hydrogenation: Effect of the end-group

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ABSTRACT

Differently carboxylic acid end-functionalized poly(lactic acid) (PLA)-based stereocomplexes were used as polymer support to stabilize Pd-nanoparticles (NPs) generated by the metal vapor synthesis technique. The dispersion of Pd was strongly dependent on the end-group present in the polymer structure, as shown by HRTEM measurements. 2,2′-Bipyridine- and pyridine-based stereocomplexes showed high metal dispersion (i.e. well-separated Pd-NP size of 2.0 ± 0.6 nm), whereas stereocomplexes bearing benzyl and carboxylic acid end groups exhibited strong Pd-NPs aggregation. The heterogenous catalysts were employed to chemoselectively hydrogenate the C=C double bond in cinnamaldehyde, showing for Pd-NPs, stabilized by the 2,2′-bipyridine-modified polymer support, the best performance in terms of chemoselectivity (99%) and recyclability in THF solution. Even under bulk cinnamaldehyde hydrogenation conditions, chemoselectivity for 3-phenylpropanal of 90% at 88% conversion was obtained.

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1. Introduction

The selective hydrogenation of the C=C double bond in α,β-unsaturated carbonyl compounds is an important organic transformation leading to the saturated counterparts which are widely applied in synthetic and pharmaceutical chemistry [1–3]. Metallic palladium embedded in a carbon support is generally used to catalyze the latter substrate conversion, which is not always chemoselective [4–7]. The support, which functions as macroligand, notably influences the electron density of the surface atoms of the Pd nanoparticles (NPs), thus allowing to promote a specific chemoselectivity. The graphitic structure of carbon, for instance, increases the charge density on the NP-surface [8]. As a consequence, the binding energy of the C=C bond in α,β-unsaturated carbonyl compounds decreases due to repulsive four-electron interactions, whereas the C=O bond hydrogenation is fostered by the favored back-bonding interaction of the Pd-NPs with the π*CO-orbital [8].

Alternatively to carbon supports, organic polymers [9,10], such as polyamines [11] and polyketones [12], endowed with functional groups that interact with the metal-NPs' surface, have shown to be a promising alternative support material for metal Pd-NPs, used in the hydrogenation of the structure-sensitive cinnamaldehyde to 3-phenylpropanal. Chemoselectivity in the range between 84% and 88% has been observed with the latter catalysts [11,12].

Recently we introduced the stereocomplex of 2,2′-bipyridine-functionalized poly(lactic acid) PLA as organic support for Pd-NPs, which selectively catalyzed the partial hydrogenation of phenylacetylene and diphenylacetylene [13]. The stereocomplex, which is formed upon hydrogen bond interactions between l- and d-PLA [14], is much more resistant against hydrolytic [15,16] and thermal degradation [17] compared to l- or d-PLA.

Herein we report the synthesis of differently end-functionalized PLA-based stereocomplexes, which were subsequently employed to stabilize Pd-NPs generated by metal vapor synthesis (MVS) technique [18,19]. The obtained heterogeneous polymer-based

catalysts were used in the chemoselective C=C double bond hydrogenation of cinnamaldehyde to 3-phenylpropanal. Pd-NP dispersion and chemoselectivity of the catalytic reactions were notably influenced by the nature of the end-group present in the polymer back bond.

2. Experimental

2.1. Materials and apparatus

Tin octanoate (Sn(Oct)$_2$) 4-hydroxymethylpyridine, benzylalcohol, 4-methyl-4′-(hydroxymethyl)-2,2′-bipyridine and l-lactide and d-lactide were purchased from Aldrich. l-lactide and d-lactide were sublimated before utilization and stored thereafter at 4 °C under nitrogen atmosphere. Solvents such as n-hexane, CHCl$_3$, CDCl$_3$ and HPLC-grade THF were purchased from Aldrich and used without further purification. Mesitylene and n-hexene were purified by conventional methods, distilled and stored under nitrogen. The co-condensation of palladium and the appropriate solvent was carried out in a previously described static reactor [18,20].

^{1}H NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer, measuring at 300.13 MHz, while ^{13}C{^{1}H} NMR spectra were obtained with a Bruker Avance DRX-400 spectrometer, acquiring at 100.62 MHz.

ATR-IR spectra were recorded on a Shimadzu model IR-Affinity apparatus, equipped with a Golden Gate single reflection diamond ATR accessory.

Gel-Permeation Chromatography (GPC) was carried out with a Waters Binary HPLC 1525 pump, a manual injector with a six way valve and a 200 μL loop, three Shodex KF-802, KF-803 and KF-804 columns connected in series (length: 300 mm each, inner diameter: 8.0 mm, 24,500 theoretical plates, exclusion limit for polystyrene (PS) up to 400,000 g mol^{-1}; a refraction index (RI) detector (Optilab T-rEXTM, Wyatt Technology) and a UV detector (Waters mod. 2489)). HPLC-grade THF with a water content of maximal 0.1 vol% was used as eluent at a constant flow of 1.0 mL min^{-1}, keeping the columns at 30.0 °C with a thermostat. The GPC system was calibrated using PS as standard. Samples were prepared by dissolving 5.0 mg of analyte in 1.0 mL of eluent. The obtained solution was filtered through a 0.2 μm PTFE filter and injected.

GC analyses were performed with a Shimadzu 2010 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) VF-WAXms capillary column.

GC–MS analyses were performed with a Shimadzu QP5000 apparatus, equipped with a 30 m (0.32 mm i.d., 0.50 μm film thickness) CP-WAX 52CB WCOT-fused silica column.

High resolution transmission electron microscopy (HRTEM) analyses of the supported Pd-NPs were carried out with a ZEISS LIBRA 200FE HRTEM instrument, equipped with a FEG source operating at 200 kV, in column second-generation omega filter for energy selective spectroscopy (EELS) and energy selective imaging (ESI), HAADF STEM facility, EDS probe for chemical analysis, integrated tomographic HW and SW. The samples were dispersed by sonication in a 1:1 solvent mixture of isopropanol/CHCl$_3$ and a drop of the obtained solution was deposited on a holey-carbon film supported on a copper TEM grid of 300 mesh. Histograms of the particle size distribution were obtained by counting at least 500 particles. The mean particle diameter (d_m) was calculated by using the formula $d_m = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i.

Inductively coupled plasma–optical emission spectrometry (ICP–OES) was carried out with an iCAP 6200 Duo upgrade, Thermofisher instrument. A sample (0.5 mL) of Pd-solvated metal atoms (SMA) solution was heated over a heating plate in a porcelain crucible in the presence of aqua regia (2.0 mL) for six times followed by dissolving the solid residue in 0.5 M aqueous HCl.

Powder X-ray diffraction (PXRD) experiments were carried out at room temperature with a PANalytical X'PERT PRO powder diffractometer, employing Cu Kα (λ = 1.5418 Å) radiation and a parabolic MPD-mirror. Diffractograms were acquired in the 2Θ range from 5.0° to 80.0°, applying a step size of 0.1050° and a counting time of 441 s.

Thermogravimetric (TG) analyses were carried out under nitrogen atmosphere using a Seiko EXSTAR 7200 TG/DTA instrument. TG spectra were collected on samples of 5–10 mg in the temperature range from 30 to 700 °C (N$_2$ flow = 200 mL/min) with a heating rate of 10 °C/min. The onset temperature of degradation (T_{onset}) is defined as the temperature that corresponds to a mass loss of 5%. The rate inflection temperature for the different degradation steps was extracted from derivative TG (DTG) curves.

X-ray photoelectron spectroscopy (XPS) analyses were performed in a UHV chamber equipped with an X-ray source (nonmonochromatized Mg Kα source, 1253.6 eV) and an hemispherical analyzer by VSW mounting a 16-channel detector. The X-ray source, mounted at 54.44° with respect to the analyzer, was operated at a power of 100 W (10 kV and 10 mA). The analyzer has been equipped with a differential pumping stage in order to operate up to a pressure of 5×10^{-8} mbar. XPS spectra were measured at normal emission with a fixed pass energy of 22 eV for the high resolution Pd3d region spectra and 44 eV in the survey scans. All spectra were referenced to the C1s peak due to adventitious carbon at 284.5 eV. The inelastic background in the spectra was subtracted by means of the Shirley method [21]. Data analysis was based on a standard method for deconvolution using mixed Gaussian and Lorentzian line shapes for each component in the spectra.

Environmental scanning electron microscopy (ESEM) analyses were carried out on a FEI ESEM QUANTA 200 apparatus with a tungsten source using a gaseous secondary electron detector (GSED) with a 500 μm aperture. The images were collected with a magnification of 3000×, applying 6 kV, a chamber pressure of 3 Torr and a working distance of 7.0 mm.

2.2. Synthesis of end-functionalized macroligands l-PLA^R and d-PLA^R

A general synthetic procedure for the synthesis of l-PLA^R and d-PLA^R (R = 4-methyl-4′-(hydroxymethyl)-2,2′-bipyridine (BiPy), 4-(hydroxymethyl)-pyridine (Py) and benzyl (Bn)) is described as follows. In a Schlenk tube, l-lactide (d-lactide) (4.00 g, 28.00 mmol) was heated at 135 °C under a nitrogen atmosphere in the presence of Sn(Oct)$_2$ (56.3 mg, 0.139 mmol) and ROH (0.400 mmol) for 3 h. Afterward, the reaction mixture was allowed to cool to room temperature and residual crystalline l- or d-lactide (ca. 1.0%), which sublimated during reaction, was removed mechanically from the Schlenk tube. The crude reaction product was then dissolved in CHCl$_3$ (20.0 mL) and precipitated upon addition of n-hexane (30.0 mL), giving an off-white solid powder, which was separated from solution by filtration, washed several times with n-hexane and dried by vacuum at room temperature for 12 h.

In case R = H (i.e. carboxylic acid end group) the synthetic protocol was modified as follows. To a two necked flask was added l-lactide (d-lactide) (2.50 g, 18.00 mmol), Sn(Oct)$_2$ (90.00 mg, 0.222 mmol), water (5.00 μL, 0.270 mmol) and anhydrous toluene (20.0 mL) (i.e. in order to control the amount of water present in the reaction mixture). The reaction mixture was then refluxed under a nitrogen atmosphere for 24 h. Afterward, the obtained solution was cooled to room temperature causing the precipitation of a white solid. The crude product was dissolved in CH$_2$CL$_2$ (20.0 mL), passed through a paper filter and to the clear solution