Journal of Catalysis 311 (2014) 212–220

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Green semi-hydrogenation of alkynes by Pd@borate monolith catalysts under continuous flow

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ARTICLE INFO

Article history:
Received 11 September 2013
Revised 11 November 2013
Accepted 30 November 2013
Available online 31 December 2013

Keywords:
Unconventional monoliths
Alkynes semi-hydrogenation
Borate polymers
Palladium nanoparticles
Continuous flow

ABSTRACT

Palladium nanoparticles were immobilized onto an unconventional polymeric borate macroporous monolith and the resulting mesoreactor (i.d. 3 mm, length 25 mm) used in liquid-phase catalytic semi-hydrogenation reaction of substituted alkynes under continuous flow. The catalytic system showed excellent efficiency, both in terms of activity and selectivity, and long-term stability under mild reaction conditions (methanol, room temperature, 1.5 bar H_2 max), with no need of additives. Particularly, the leaf alcohol *cis*-3-hexen-1-ol was for the first time obtained with selectivity comparable to that of the industrial batch process. The performance of the catalyst is discussed and compared with those of the analogous batch and industrial processes.

1. Introduction

Fine-chemicals production *via* continuous flow of a liquid-phase over-structured heterogeneous catalysts is receiving increasing interest due to the need of greener technologies [1,2] in an industrial sector blemished by the highest E-factors [3–5], while contributing to most of the EU chemicals trade market [6]. Indeed, compared to conventional batch systems, catalysis under continuous flow provides considerable benefits in terms of efficiency, purification, safety, waste emission, automation, space and energy consumption [7–10]. Particularly, monolithic reactors may be extremely useful in the synthesis of fine-chemicals because of the improved mass and heat transfer, lower pressure drop, uniform residence times distribution, with respect to packed-bed setups [11,12]. To this purpose, *true monoliths* [13], either from inorganic [14–18] and organic materials [19–24], featured by uniformly distributed meso and/or macropores, and not to be confused with conventional foams or honeycombs with millimeter size cavities [25,26], have been used to support catalytically active species. Due to the simpler synthetic procedures compared to the parent inorganic materials, these unconventional polymer-based monoliths were the first to demonstrate the utility of monoliths in the fine-chemicals production [27,28]. However, issues have still to be solved concerning chemical stability, shrinking phenomena and back pressure evolution at high flow rate due to limited porosity, which adversely affect the performance of polymeric monoliths as catalysts support [29,30].

Among organic polymers, ion-exchange resins are particularly suited to engineer single-site heterogeneous catalysts [31], either immobilized metal nanoparticles (MNPs) [32,33] or molecular complexes [34,35], due to several favorable features [36]:

- low manufacture costs,
- possibility to be obtained with diverse functionalities, porosities and morphologies,
- ease of handling,
- satisfactory chemical, mechanical, and thermal resistance,
- ability to stabilize MNPs due to the dual effect of charged functional groups (electrostatic stabilization) [37] and porosity (steric stabilization) [38,39],
- effective and easy catalyst anchoring *via* non-covalent linkage [40,41],
- versatility in terms of accessible reactions.

Despite the above advantages, very few polymeric ion-exchange monoliths were described so far, and mostly limited to chromatographic applications. Examples include sulfonated resins obtained either by removal of water from water-in-oil styrene-DVB emulsions followed by post functionalization [42], or by sulfonation of preformed poly(styrene-*co*-DVB) and poly(GMA-*co*-EDMA) monoliths in capillary silica columns [43–45], and quaternary

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Abbreviations: DVB, divinylbenzene; GMA, glycidyl methacrylate; EDMA, ethylene glycol dimethacrylate; PEGDA, polyethylene glycol diacrylate.

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http://dx.doi.org/10.1016/j.jcat.2013.11.027

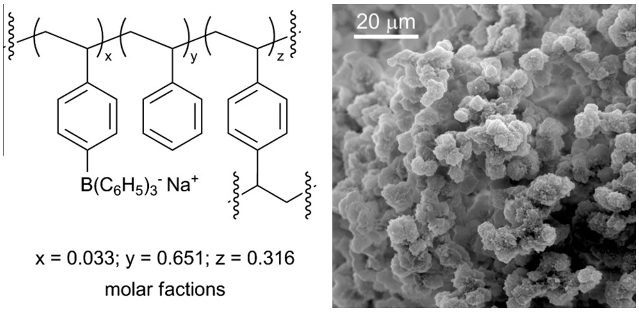

Fig. 1. Sketch of composition (left) and representative SEM image (1600 magnifications, right) of MonoBor.

ammonium polymers prepared by amine treatment [46] or by copolymerization of 2-(acryloyloxy)ethyl trimethylammonium chloride and PEGDA [47].

We recently reported the synthesis and characterization of a macroporous polymeric monolith, hereinafter called MonoBor (Fig. 1), in which cation-exchange tetraphenylborate anions are incorporated in a highly cross-linked styrene–divinylbenzene matrix [48]. A striking feature of this material is its reproducible, isotropic microstructure based on a ‘rigid’ skeleton of ca. 6 μm thickness forming a narrow size distribution of interconnected flow-through pores of 10 μm size, corresponding to a BET surface area of 9.72 $m^2\,g^{-1}$, which guarantees a very low flow resistance and a high mechanical stability. The chemical and thermal resistance of the polymer was demonstrated up to 350 °C. The monolith was easily obtained *in situ* within the walls of a commercial glass column resistant up to 1200 psi pressure, so as to provide a monolithic mesoreactor (i.d. 3 mm, length 25 mm) perfectly suited for use in synthetic applications under continuous flow [49]. The exchange ability of the monolith was demonstrated and the anchoring of cationic metal complexes was successfully achieved to give a uniform metal distribution within the solid support.

Herein we describe the immobilization of palladium nanoparticles onto MonoBor and the use of the corresponding monolithic reactor (Pd@MonoBor) in the catalytic partial hydrogenation reaction of alkynes under continuous flow. Choice of palladium NPs was motivated by their known versatility as catalysts, so as to be often used to investigate the effect of the support on the catalyst efficiency [50], and by the method we recently developed for the effective and environmentally friendly immobilization of PdNPs onto monolithic supports [15]. The hydrogenation reaction of substituted alkynes was selected because of its high significance as probe of catalyst chemo-, stereo- and regio-selectivity, and because it is the technology currently adopted for the large-scale production of several important fine-chemicals, including pharmaceuticals, fragrances and food ingredients [51].

2. Experimental section

2.1. 1. Materials and methods

All reaction and manipulations were performed under nitrogen by using standard Schlenk techniques, unless otherwise stated. Tetrahydrofurane was distilled from sodium-benzophenone prior of use. The MonoBor monolith was prepared as previously described into a commercial Omnifit Labware Glass Column (3.0 i.d. × 25 length mm) equipped with 0.2 μm PE frit to ensure an optimum flow distribution [48]. All the other reagents were commercial products and were used as received without further purification. Palladium on activated charcoal (5 wt.%) was obtained from Aldrich. ESEM (Environmental Scanning Electron Microscopy) measurements were performed on a FEI Quanta 200 microscope operating at 25 keV accelerating voltage in the low-vacuum mode (1 torr) and equipped with an EDAX Energy Dispersive X-ray Spectrometer (EDS). X-ray maps were acquired on the same instrument using a 512 × 400 matrix, 100 μs dwell time and 25 keV accelerating voltage. TEM (Transmission Electron Microscopy) analyses were performed using a CM12 PHILIPS instrument at 120 keV accelerating voltage. The sample preparation was carried out by dispersing the grinded resin into about 1 mL of ethanol and treating the solution in an ultrasonic bath for 30 min. Successively, a drop of solution was deposited onto a carbon coated Cu TEM grid and the solvent left to evaporate. XRD (X-ray Diffraction) patterns were recorded with a PANanalytical XPERT PRO powder diffractometer, employing CuKα radiation ($\lambda = 1.54187$ Å), a parabolic MPD-mirror and a solid state detector (PIXcel). The samples were prepared on a silicon wafer (zero background) that was rotating (0.5 rotations per second) during acquisition. All XRD patterns were acquired at room temperature in a 2θ range from 30° to 55°, applying a step size of 0.0263° and a counting time of 295.29 s. TGA analyses were performed with a Seiko EXSTAR TG/DTA 7200 thermogravimetric analyzer. The metal content in the supported catalysts was determined by Atomic Absorption Spectrometry (AAS) using a ANALYST200 spectrometer. Each sample (50–100 mg) was treated in a microwave-heated digestion bomb (Milestone, MLS-200, 20 min @ 220 °C) with concentrated HNO_3 (1.5 mL), 98% H_2SO_4 (2 mL), and 0.5 mL of H_2O_2 30%. After filtration, the solutions were analyzed. The content of metal leached in the solutions recovered after catalysis was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Varian 720ES instrument at a sensitivity of 500 ppb. The solutions were analyzed directly after 1:5 dilution in 0.1 M hydrochloric acid. GC-analyses were performed on a Shimadzu GC 2010 gas chromatograph equipped with flame ionization detector and a 30 m (0.25 mm ID., 0.25 μm FT) SPB-1 Supelco or a 30 m (0.25 mm ID, 0.25 μm FT) VF-WAXms fused silica capillary column. GC–MS analyses were performed on a Shimadzu QP5000 apparatus equipped with a SPB-1 Supelco fused silica capillary column or on a Shimadzu GC–MS 2010 apparatus equipped with a 30.0 m (0.32 mm ID) WCOT-Fused silica CP-Wax 52 CB capillary column. Reactions under a controlled pressure of hydrogen were performed using a H_2 generator Parker H2PEM-260. Reactions under continuous flow were carried out using a reactor system constructed at Istituto di Chimica dei Composti OrganoMetallici, Sesto Fiorentino (Italy). The system was designed to allow for a simultaneous flow of substrate solution and hydrogen gas (up to 40 bar pressure). The reactor was completely inert, as all wet parts were made of PEEK, PFA or PFTE. A constant flow of substrate solution was regulated by an Alltech® model 426 HPLC pump in PEEK. A constant flow of hydrogen gas was adjusted, and its pressure monitored, by a BRONKHORST flow controller and pressure meter, respectively. The concurrent flows of gas and liquid were driven through a T-shaped PEEK mixer to ensure efficient gas dispersion. The mixed hydrogen-substrate solution stream was introduced in the reactor through a 6-port Rheodyne switching valve in PEEK. The system was equipped with a temperature controller. At the outlet of the reactor, the product solution was collected for GC analysis and the excess amount of the hydrogen gas released to the atmospheric pressure. The reaction products were unequivocally identified by the GC retention times, mass and NMR spectra of those of authentic specimens.

2.2. Synthesis of Pd@MonoBor

A solution of $Pd(NO_3)_2$ in THF (0.025 M) was flowed through a MonoBor monolithic column (3.0 i.d. × 25 length mm, ca. 30 mg dry material) at 0.5 mL min^{-1} for 3 h using an HPLC pump and an