



How to increase the selectivity of Pd-based catalyst in alkynol hydrogenation: Effect of second metal



Artur Yarulin^a, Igor Yuranov^a, Fernando Cárdenas-Lizana^{a,1},
Duncan T.L. Alexander^b, Lioubov Kiwi-Minsker^{a,*}

^a Group of Catalytic Reaction Engineering (GGRC), École Polytechnique Fédérale de Lausanne, EPFL-SB-ISIC-GGRC, Station 6, CH-1015 Lausanne, Switzerland

^b Interdisciplinary Centre for Electron Microscopy (CIME), École Polytechnique Fédérale de Lausanne, EPFL-SB-CIME, Station 12, CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:

Received 6 December 2013

Received in revised form 24 February 2014

Accepted 1 April 2014

Available online 13 April 2014

Keywords:

Partial hydrogenation

Dehydroisophytol

Isophytol

Pd nanoparticles

Sintered metal fibers

ZnO

Pd-Cu

Pd-Ag

ABSTRACT

The development of selective Pd-based catalyst for *semi*-hydrogenation of dehydroisophytol (DIP), a C₂₀-alkynol, is reported. A series of *unsupported* mono- (Pd) and bimetallic (Pd-M) nanoparticles (NPs) with Pd/M molar ratios of 1.5–5.0 (M = Ag or Cu) were examined as model systems. The Pd-Ag and Pd-Cu NPs with controlled crystal sizes of ~3.3 nm were prepared by Ag (Cu) electroless deposition on pre-formed poly(N-vinyl-2-pyrrolidone)-stabilized Pd⁰ colloids. Bimetallic Pd-Ag NPs adopted a core (Pd)-shell (Ag) structure whereas a mixed alloy was attained in the Pd-Cu nanocrystals. A (partial) Pd surface segregation induced by reaction with H₂ was in evidence for the Pd-Ag NPs. A significant increase in selectivity up to 97% (at X_{DIP} = 99%) to the target alkenol was demonstrated following the incorporation of a second metal. This result is attributed to the dilution of the surface Pd-sites by Ag (Cu) and a modification of the Pd electronic properties. Pd-Ag NPs, having shown the highest selectivity, were further deposited on a structured support based on sintered metal fibers (SMF) coated with ZnO. The improved selectivity achieved over the unsupported Pd-Ag colloidal NPs was retained over the structured catalytic system. The bimetallic Pd_{5.0}Ag/ZnO/SMF (S_{IP} = 93%) demonstrated a drastic increase in IP selectivity relative to the monometallic Pd/ZnO/SMF (S_{IP} = 78%) and state-of-the-art Lindlar catalyst (S_{IP} = 62%) at DIP conversion ≥99% with the stable activity during 50 h, suggesting catalyst feasibility for selective *semi*-hydrogenation of long chain alkynols with important applications in the manufacture of vitamins and fine chemicals.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The selective *semi*-hydrogenation of long-chain (≥C₂₀) alkynols (to the correspondent alkenol) is an important reaction in fine chemistry with a prominent example in 3,7,11,15-tetramethyl-1-hexadecyn-3-ol (dehydroisophytol (DIP), C₂₀ alkynol) hydrogenation to 3,7,11,15-tetramethyl-1-hexadecen-3-ol (isophytol (IP)). IP is an intermediate in the industrial synthesis of vitamin E [1,2] with an estimated annual worldwide production of >30 × 10³ tonnes [3]. Pd is typically the metal of choice to catalyze DIP → IP hydrogenation due to its high activity combined with high

selectivity to the target alkenol [4]. Nevertheless, the formation of an undesired overhydrogenation product (alkanol) is also promoted over Pd catalysts [5], particularly at high conversions; typical IP selectivities being in the 80–93% range [6,7]. One of the approaches to enhance the olefin yield is the addition of modifiers to the reaction mixture (*reaction modifiers*) or incorporation in the catalyst structure (*catalyst modifiers*) [8]. These modifiers induce variations in the Pd electronic (e.g. charge transfer) and/or geometric (e.g. separation of Pd surface sites) properties that impact on the selectivity response [4,9]. Up to 100% IP selectivity was achieved using *reaction modifiers* such as S-, N- and/or O-containing compounds (e.g. quinoline, 2,2'-ethylenedioxydiethanol, 2,2'-ethylenedithiodiethanol, 3,6-dithia-1,8-octanediol) and metal salts (Mn²⁺, Pb²⁺) [4,8,10–12]. However, the incorporation of these *reaction modifiers* translates into additional costs due to the requirement of separation and treatment steps before disposal [13]. These costly and environmentally harmful processes can be fully circumvented by an alternative approach based on *catalyst modification*.

* Corresponding author. Tel.: +41 21 693 3182; fax: +41 41 216936091.

E-mail addresses: artur.yarulin@epfl.ch (A. Yarulin), igor.iouranov@epfl.ch (I. Yuranov), lioubov.kiwi-minsker@epfl.ch (F. Cárdenas-Lizana), duncan.alexander@epfl.ch (L. Kiwi-Minsker).

¹ Present address: Institute of Mechanical, Process and Energy Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK

Bimetallic nanoparticles (NPs) are known to improve catalytic performance relative to the monometallic counter partners in $C\equiv C$ hydrogenation [14]. In particular, increased olefin selectivities (up to 99%) have been reported in the hydrogenation of short chain ($\leq C_{14}$) alkynols over Ag^0 [15], Cu^0 [16,17], and Zn^0 -modified [12] Pd catalysts, although there is a dearth in the literature focused on the application of bimetallic systems for the *semi*-hydrogenation of alkynols with longer hydrocarbon chain. Bimetallic NPs can be regarded as a more sustainable catalytic alternative relative to the toxic lead-containing Lindlar catalyst commonly employed for alkynol hydrogenations at industrial level [3,10–12].

The physical and chemical properties of bimetallic NPs strongly depend on the distribution of both metals within the crystal nanostructure [18–20] which, in turn, impacts on hydrogenation catalytic response [21]. The structure of bimetallic NPs is affected by a number of parameters, such as preparation technique (e.g. sequential and simultaneous reduction methods lead to the formation of $Ag_{core}Pd_{shell}$ and Ag-Pd alloy NPs, respectively [21]), the difference in atomic radii [22], surface energies [23] and/or relative amount of both metals [24,25], NP size [26], type of support [13,27], and/or reaction environment (e.g. modified surface composition of Pt-Co, Rh-Pd and Pt-Pd bimetallic NPs in the presence of CO, NO, O_2 , H_2 due to surface catalyst restructuring [28,29]).

In terms of rational catalyst design, colloidal NPs represent a valuable model systems to understand the nature of the catalytic systems and optimize bimetallic catalysts [30,31] although there is a requirement of their subsequent deposition onto a support for industrial implementation. In this respect, a ZnO-based support is a promising candidate due to its ability to form an intermetallic PdZn phase upon interaction with Pd NPs under hydrogen which prevents metal leaching into the reacting mixture improving catalyst stability [32].

Herein, we report the results on the development of a stable and highly selective catalytic system for DIP (as a model molecule bearing a long-chain) *semi*-hydrogenation. We adopted the methodology of using colloidal (Pd, Pd-Ag and Pd-Cu) NPs with controlled size and composition for direct correlation with catalytic performance. Catalytic response was rationalized by characterizing catalysts using scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDX).

2. Experimental

2.1. Materials

Poly(N-vinyl-2-pyrrolidone) (PVP, Sigma Aldrich; $M_w \sim 50,000$), palladium (II) chloride anhydrous (Sigma Aldrich; $\geq 95.0\%$), sodium chloride (Fluka; $\geq 99.5\%$), ethanol (Sigma Aldrich; 99.8%), L-ascorbic acid (Sigma Aldrich; 99.0%), zinc acetate dihydrate (Fluka; $\geq 99.5\%$), monoethanolamine (Fluka; $\geq 99.0\%$), 3-hydroxybutynone (acetoin, mixture of monomer and dimer; Fluka; $\geq 97.0\%$), hydrazine hydrate (Fluka; 24–26% in water), potassium dicyanoargentate (I) (Sigma Aldrich; 99.9%), copper (II) formate (Sigma Aldrich; 97.0%), DIP (DSM Nutritional Products; $\geq 95\%$) were used as received without further purification. H_2 and N_2 were of ultra-high purity (Carbagas; $\geq 99.99\%$). FeCrAl-alloy sintered metal fibers (SMF; Cr 20%, Al 5%, Y >1%, other elements ca. 1–2%, Fe balance) were purchased from Bekaert SA (Belgium).

2.2. Support preparation

SMF panels were treated in boiling toluene for 0.5 h (to remove grease [33]), dried (at room temperature in air) and oxidized (in air) at 973 K for 3 h in order to improve adhesion of ZnO [32]. Finally they were cooled down to the room temperature.

A homogeneous ZnO film was prepared by sol-gel method [32]. Monoethanolamine (18.3 g) and acetoin (12.8 g) – solubility enhancement additives that prevent ZnO crystallization in solution before deposition [32] – were dissolved in iso-propanol ($1 \times 10^3 \text{ cm}^3$) and 65.8 g of zinc acetate dihydrate were added to the solution under continuous stirring. The SMF panels underwent a three-step procedure based on (i) dipping (into the ZnO precursor solution), (ii) drying in air at room temperature (0.5 h) and (iii) calcination in air at 873 K for 0.5 h. This multistep procedure was repeated 6 times to deposit ca. 5 wt.% ZnO. The coated SMFs were post-annealed in air at 1173 K for 15 min to promote ZnO crystallization [32].

2.3. Preparation of mono- and bimetallic nanoparticles

A series of PVP-stabilized NPs were prepared by colloidal technique [34]. Pd NPs were synthesized by heating (363 K) an aqueous solution (30 cm^3) containing PVP ($5.0 \times 10^{-3} \text{ mol}$) and ascorbic acid ($8.5 \times 10^{-4} \text{ mol}$) as stabilizing and reducing agents, respectively. An aqueous Na_2PdCl_4 solution ($1.0 \times 10^{-4} \text{ mol cm}^{-3}$; PVP/Pd molar ratio = 10), prepared by dissolving $PdCl_2$ and NaCl in water (Pd/Na molar ratio = 0.5), was added to the PVP-containing solution and the mixture was stirred for 3 h at 363 K. The instantaneous dark coloration of the solution after the Pd precursor was added indicated the formation of Pd^0 NPs [35]. The NPs stabilized by PVP were separated from the solution via flocculation with acetone (1/3, v/v solution/acetone), rinsed thoroughly with acetone (3 times), centrifuged and redispersed in water attaining ca. 0.4 wt.% Pd in the final solution.

Ag NPs as reference nanocatalysts were prepared by colloidal methodology following the procedure described in detail elsewhere [21]. Briefly, $AgNO_3$ ($2.3 \times 10^{-4} \text{ mol}$) and PVP ($2.3 \times 10^{-3} \text{ mol}$) were dissolved in 30 cm^3 of ethylene glycol under stirring. The solution was slowly heated in a $100 \text{ cm}^3 \text{ min}^{-1} N_2$ flow at 7 K min^{-1} up to 393 K and was held at this temperature for 30 min to obtain colloidal Ag NPs, which were subjected to the post-treatment procedure as described above.

A catalytic electroless deposition method [36] was used for the preparation of a series of bimetallic Pd-Ag and Pd-Cu NPs (denoted in this work as Pd_xM with x defined as the Pd/M molar ratio = 5.0, 3.5, 2.0 and 1.5) where Pd acts as a catalyst for the Ag and Cu reductive deposition. A calculated amount of the second metal precursor (potassium dicyanoargentate (I) or copper (II) formate) was added to the prepared PVP-stabilized Pd^0 colloidal solution. In the case of Pd-Ag system, ca. 0.3 cm^3 of hydrazine hydrate (ca. 25% in water) as a reducing agent was added to the solution whereas the Cu precursor already contains intrinsic reducing agent – formate. The mixture was subsequently stirred for 3 h at room temperature to promote the formation of bimetallic NPs.

The obtained metal NPs were deposited by impregnation of the pre-synthesized colloidal dispersion on the 5%ZnO/SMF support followed by air-drying. The procedure was repeated twice to attain 0.2 wt.% of Pd on the support. In order to ensure the anchoring of the metal NPs on the support, the PVP was removed from the particle surface by air calcination at 873 K [37] and the catalyst was then activated in H_2 flow (10% in Ar, total flow $450 \text{ cm}^3 \text{ min}^{-1}$) at 573 K (heating 5 K min^{-1}) for 2 h.

2.4. Catalyst characterization

The metal (Pd, Cu and Ag) content in the synthesized colloidal solutions and powdered Lindlar catalyst was measured by atomic absorption spectroscopy (AAS) using a Shimadzu AA-6650 spectrometer with an air-acetylene flame from the diluted solutions in aqua regia (2/3, v/v HNO_3/HCl).

Download English Version:

<https://daneshyari.com/en/article/39687>

Download Persian Version:

<https://daneshyari.com/article/39687>

[Daneshyari.com](https://daneshyari.com)