A Smart Heterogeneous Catalyst for Efficient, Chemo- and Stereoselective Hydrogenation of 3-Hexyn-1-ol

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Abstract: We examine the easy preparation of mono- and bi-metallic heterogeneous catalysts with low Pd and Cu contents on alumina and provide a detailed study of many reaction parameters in the catalyzed selective semihydrogenation of 3-hexyn-1-ol to (Z)-3-hexen-1-ol, a very important fragrance with an herbaceous note. In particular, two different protocols of Pd catalyst preparation, substrate/catalyst molar ratio, the effect of time and temperature, introduction of some additives to the reaction mixture, and the nature of the solvent were investigated. These factors are not independent variables. The results show that it is possible to control the reaction outcome to obtain the target (Z)-alkenol using different experimental conditions. The best result, as an appropriate compromise between conversion and selectivity, may be obtained by working with a very high substrate/catalyst molar ratio (>6000/1), with one type of Pd catalyst, in a short time (about 150 min) at 60 °C.

Keywords: heterogeneous catalyst; selective hydrogenation; alkyne; (Z)-alkene; fragrance

1. Introduction

The selective hydrogenation of unsaturated substrates is a powerful tool for the preparation of both bulk and fine chemicals [1–3]. The design of an efficient catalyst to obtain a high chemo- and/or stereo-selectivity without loss of catalytic activity is often still a challenge. Homogeneous catalysts are more selective than heterogeneous ones due to the steric and electronic effects of the ligands, but heterogeneous catalysts are preferable from an industrial point of view as they can be easily separated and reused. For this reason, metals supported on charcoal, zeolites, or oxides, such as SiO₂ or Al₂O₃, are largely employed and the selectivity strongly depends on the adsorption strength and configuration of both reactants and intermediates on the surface of the catalyst, which in turn is determined by the electronic and geometric structures of the active sites [4,5]. As a result, the preparation process of the catalyst plays a fundamental role. An interesting aspect of selectivity is the semihydrogenation of alkynes to alkenes with strong relevance for industrial applications [6–26]. Chemoselectivity is important for internal alkynes, but it is not the only parameter to consider: another crucial aspect for producing (Z) or (E) isomers is stereoselectivity. This underlines that a subsequent isomerization from (Z) to (E) isomers may occur in the reaction mixture being catalyzed by the same heterogeneous metallic species. In this work, we focused on the selective reduction of 3-hexyn-1-ol (I) to produce mostly the corresponding (Z)-3-hexen-1-ol [(Z)-II] [27–29] (Scheme 1).
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Scheme 1. Hydrogenation of 3-hexyn-1-ol (I).

Compound (Z)-(II) is found in various natural essential oils and aroma-active volatiles, and it is currently used in many perfumes because of its powerful, fresh, green, grassy, and herbaceous notes [27,30,31]. With this aim, we prepared two heterogeneous 0.25% Pd/Al2O3 catalysts (Cat 1 and Cat 1*), following a general smart methodology developed in our laboratory to prepare low metal content heterogeneous catalysts on alumina [32,33]. The preparation of these two catalysts differs only in the addition of alumina: in the case of Cat 1, it was introduced as a solid into the reaction mixture containing the colloidal reduced metal in cyclopentyl methyl ether (CPME); for Cat 1*, the reaction mixture containing the colloidal reduced metal was added to a suspension of alumina in CPME. Some publications claim there is an advantage to using bimetallic catalysts, in particular catalysts containing Pd and Cu, for the semi-hydrogenation of alkenes (20,21,23,26). As a result, we decided to explore for the first time the synthesis of a bimetallic catalyst (0.156% Cu, 0.075% Pd)/Al2O3 (Cat 2) using a one-pot protocol, where regents were placed all together in the reactor. Here, we present the results obtained by investigating the influence of numerous reaction parameters, such as catalyst preparation protocol, amount of catalyst, temperature, reaction time, presence of some additives, and nature of the solvent in the semihydrogenation of I in the effort to identify suitable conditions to maximize both substrate I conversion and selectivity to (Z)-(II).

2. Results and Discussion

The preparation of these 0.25% Pd/Al2O3 catalysts, as described in the experimental section, is simple, requiring no special equipment or energy-intensive reactions. It is characterized by the absence or limited amount of water in the reaction mixture, unlike the procedures commonly used to prepare supported metal catalysts [5,28]. Our protocol is affected by the type of alumina used as support [33] and has a good reproducibility. The catalysts, if stored under controlled conditions to avoid unwanted contact with humidity and air, maintain a good stability over time. In the laboratory, we have always adopted a two-pot protocol to prepare the Pd catalysts; however, here, we decided to explore a different order of the addition of alumina with the aim to improve the homogeneity of the catalyst and to reduce possible variability effects. A preliminary investigation of the structure of two catalyst samples, prepared with these two procedures, was performed by SEM analysis (Figures S1–S5). In the Cat 1* sample, the average metal particle size was significantly smaller (<100 nm) compared with those of Cat 1 (where bigger metal particles up to 200 nm were present), and a better distribution occurred. As preliminary work, we also explored the outcome of the simpler one-pot procedure, inspired by the Rh/Al2O3 industrial protocol [34], but we only have a limited number of results for the Pd catalyst at present, which calls for a more detailed study, but this did not affect the present work. The bimetallic catalyst (0.156% Cu, 0.075% Pd)/Al2O3 was prepared using the one-pot procedure, requiring more drastic conditions to achieve the reduction of both metals.

The main results obtained with our catalysts (Figure 1, Figures 3–6; Tables S1, S3–S6) and, for comparison, with a commercial one specifically claimed for this application [28] (Figure 2; Table S2), are reported and discussed. The amount of all compounds in the reaction mixture, denoted as the area percentage, was determined at different reaction times by GC analysis using pure compounds as references. Stereoselectivity was calculated as: \(((Z)-(II))/[(Z)-(II) + (E)-(II)]\).
Figure 1. Hydrogenation of (I) catalyzed by Cat 1. Preliminary investigation. Substrate (I) = 138.4 mg (1.41 mmol); (I)/Pd (mol) = 500; pH$_2$ = 0.1 MPa; Solvent = i-propanol (10 mL); T = 25 °C. a Area percentage determined by GC analysis.

A first set of experiments (Figure 1; Table S1) was carried out using Cat 1 in i-propanol at 0.1 MPa of H$_2$. This catalyst showed very high activity, even at room temperature, and very short reaction times using a substrate/Pd molar ratio = 500/1. Given the same experimental conditions, its activity is surprisingly much higher than that of a commercial benchmark catalyst [28] (Figure 2; Table S2). Unfortunately, at total conversion after 90 min, only 64% of (Z)-(II) formed, as 19.4% of (E)-(II) and 19.6% of hexanol (III) were also produced (Figure 1; Table S1, Run 1 [90]).

To better control of the reaction, we explored the use of some additives, as t dopants may modulate the activity and selectivity of heterogeneous catalysts, too. In particular, the Pd Lindlar catalyst, generally used in semihydrogenation of alkenes, is characterized by the presence of lead acetate or lead oxide and/or quinoline as poisons [6,21]. In previous works that we carried out on two-phase aqueous organic solvent reactions, we found that ammonium acetate, a very hygroscopic reagent, was a generous gift of No-
was not obtained at all or was produced in a very limited amount (Figure 3A; Table S3, Run 1 [180, 210]).

This result showed that by reducing the activity of Cat 1 with this cheap and benign dopant mixture, it was possible to improve the fine tuning of chemo- and stereoselectivity. When the same reaction was carried out in the presence of the sole NH$_4$Cl or sole CH$_3$COONa·3H$_2$O, the activity of the catalyst was enhanced, but both chemo- and stereoselectivity were lowered, especially with the former additive (Figure 3B; Table S3 ls, Run 2). Interestingly, by working with the latter dopant, it was possible to obtain the (Z)-isomer in quantitative yield by limiting the conversion to 60%. Additionally, in this case, an enhancement of the reaction time resulted in complete conversion, although it was achieved at the expense of selectivity (Figure 3C; Table S3, Run 3). By comparing these results with those obtained using the same reaction conditions in the absence of any additive, we assert that sodium acetate might exert a positive effect in terms of selectivity to (Z)-(II) while maintaining a comparable activity.

To verify the possible influence of the solvent in this reaction, we performed some comparative hydrogenation experiments in CPME, the solvent used for the preparation of the catalyst, (Figure 4A; Table S4) and in i-propanol (Figure 4B; Table S4). The reaction in CPME was carried out at 25 °C, while that of i-PrOH was carried out at 60 °C.
Even if, surprisingly, the activity of the catalyst was very high in CPME with a good selectivity, it was not possible to remove it completely from (Z)-(II) by distillation. For this reason, i-propanol remains the solvent of choice for this application. However, CPME might be useful for the hydrogenation of other substrates that are characterized by a higher boiling point and it may be possible to use the catalyst without drying it.

Through the use of Cat 1*, it was possible to work with a much higher substrate/Pd molar ratio (6000/1–10,000/1; TOF = 2260–2400 h\(^{-1}\)) and to obtain promising results in terms of both conversion and selectivity to the target compound (Z)-(II) (Figure 5B–D,G; Table S5, Runs 2,3,6). We think that the higher activity may be related to the smaller particle sizes of the metal and to the better homogeneity of Cat 1* as shown by SEM analysis. If we compare Figure 5B,C corresponding to Table S5 (Runs 2 and 3 at 120 min, respectively), it is possible to deduce that the procedure is reproducible (±5%). Furthermore, the catalyst of Figure 5D (Table S5, Run 3) was recycled twice after a pre-treatment with 0.1 MPa of hydrogen for 2 h at 60 °C (Figure 5E,F; Table S5, Runs 4 and 5). A lower level of activity was observed when stopping the reaction at the same time, but, in our opinion, it was likely due to an unwanted small loss of catalyst during the catalyst separation and reuse rather than a metal leaching in the organic phase; to confirm the absence of traces of leached metal, after the separation of Cat1*, a sample of 1-undecene was added to the organic phase and the mixture was treated at 80 °C under 5 MPa of H\(_2\) for 6 h, but undecane was not detected.
Finally, we explored the synthesis of a bimetallic catalyst, (0.156% Cu, 0.075% Pd)/Al₂O₃, to reduce the amount of precious metal, on the basis of numerous literature reports [13,20,21,23], which suggested a positive effect when using a catalyst containing both Pd and Cu. As better described in the experimental section, the catalyst was prepared using the simplified one-pot procedure, and Cat 2 was used in the hydrogenation of I. The preliminary data described in Figure 6 and Table S6 point out, as expected, a much lower catalytic activity with respect to that of Cat 1 (Figure 1; Table S1), but a slightly improved selectivity that requires further studies to be confirmed. Unfortunately, it was not possible to recycle this catalyst because its activity was lost completely after the work-up and any attempt to regenerate it through a pre-treatment with hydrogen failed.

Figure 5. Hydrogenation of (I) catalyzed by Cat 2. Substrate I = 172.7 mg (1.76 mmol); (I)/Cu,Pd (mol) = 500; pH₂ = 0.1 MPa; Solvent = i-propanol (10 mL); T = 40 °C. a Area percentage determined by GC analysis.

Figure 6. Hydrogenation of (I) catalyzed by a commercial catalyst. [BASF (catalyst code 543136) 0.6% Pd/C]. Substrate (I) = 138.4 mg (1.41 mmol); (I)/Pd (mol) = 500; pH₂ = 0.1 MPa; Solvent = i-propanol (10 mL); T = 25 °C. a Area percentage determined by GC analysis.
3. Materials and Methods

3.1. General

3-hexyn-1-ol, cyclopentyl methyl ether (CPME), trioctyl amine (TOA), ammonium chloride, sodium acetate trihydrate, palladium chloride, cuprous chloride, and isopropanol (i-PrOH) were Aldrich products (St. Louis, MO, USA). γ-Al₂O₃ was a generous gift of Chimet S.P.A (Badia al Pino (AR), Italy). Catalyst 0.6% Pd/C (543136) was a generous gift of BASF. (Z)- and (E)-3-hexen-1-ol, as reference compounds, were a generous gift of Novachem Aromatici S.r.l. (Gallarate (VA), Italy). The amounts of Pd and Cu contained in these catalysts were determined using a Perkin Elmer Analyst 100 spectrometer equipped with a single-element hollow cathode lamp. SEM analyses were carried out using a TM3000 Hitachi instrument coupled with a Swift ED 3000 (Oxford Instruments, Abingdon, UK).

GC analyses were carried out on an Agilent 6850A gas chromatograph (FFAP column 30 m × 0.25 mm × 0.25 μm; low 0.7 mL/min, pressure 0.689 bar; 100 °C × 5 min, followed by a heating rate of 0.5 °C/min up to 240 °C and further 19 min; retention time: (III) 7.10 min, (E)-(II) 7.50 min, (Z)-(II) 8.10 min, (I) 13.10 min. GC-MS analyses were performed using an Agilent Technologies 7820A GC System coupled with quadrupole mass spectrometer Agilent Technologies 5977B MSD (HP-5MS column 30 m × 0.25 mm × 0.25 μm).

In the Figures (tables in Supplementary Materials), the amount of compounds in the final mixture is reported as the area percentage. Conversion is based on the amount of starting material observed in the final mixture. The area percentage corresponds to the real amount of the compounds in the mixture, using pure standards. Stereoselectivity was calculated as: (Z)-(II)/[(Z)-(II) + (E)-(II)].

3.2. Preparation of Cat 1 and Cat 1*

In a Schlenk tube, 25 mg (0.15 mmol) of PdCl₂ and 0.22 mL (0.50 mmol) of TOA were stirred under nitrogen in 5 mL of CPME. The Schlenk tube was transferred into a 150 mL stainless steel autoclave, pressurized with 0.1 MPa of H₂ and stirred for 24 h at 25 °C. Then, the residual gas was released and the reaction mixture was transferred into a 50 mL double-neck jacket round-bottom flask. CPME (10 mL) and γ-Al₂O₃ (5 g) were added and the stirred mixture was maintained under a hydrogen atmosphere at room temperature. After 24 h, the mixture was filtered, washed several times with CPME, and dried in vacuo. A sample was analyzed to determine the amount of palladium in the catalyst: 0.25%.

The preparation of Cat 1* was similar, but after the first phase, the solution was transferred, under an inert atmosphere, into a 50 mL double-neck jacket round-bottom flask that already contained alumina and CPME. The resulting mixture was finally stirred for 24 h at 25 °C under hydrogen atmosphere and then worked as above.

3.3. Preparation of Cat 2

In a Schlenk tube, 7.5 mg (0.0423 mmol) of PdCl₂, 16.4 mg (0.1652 mmol) of CuCl, 0.22 mL (0.50 mmol) of TOA, and 5 g of γ-Al₂O₃ were stirred under nitrogen in 10 mL of CPME. The Schlenk tube was transferred into a 150 mL stainless steel autoclave, pressurized with 2.5 MPa of H₂ and stirred for 24 h at 100 °C. Then, the residual gas was released and the reaction mixture was filtered, washed several times with CPME, and dried in vacuo. A sample was analyzed to determine the amount of palladium and copper in the catalyist: 0.075% (Pd) and 0.156% (Cu).

3.4. Hydrogenation of 3-hexyn-1-ol (I)

All the hydrogenation reactions were carried out following a procedure similar to the procedure described below for the hydrogenation of I catalyzed by Cat 1 in i-propanol. Experimental details (different solvents, catalysts, substrate to metal molar ratios, reaction temperatures and times) are reported in Tables S1–S6.

A total of 100 mg of Cat 1 (0.25% Pd/Al₂O₃) and 10 mL of i-propanol were introduced under nitrogen in a three-necked round-bottom flask. Then, 138.4 mg (1.41 mmol) of I was introduced in the flask via a syringe and the mixture, vigorously stirred by a magnetic
stirrer, and maintained under 0.1 MPa of hydrogen at 20 °C. Samples were analyzed at different times by GC and GC-MS to check the course of the reaction. The amounts of (Z)-(II) and (E)-(II) were determined by comparison with the corresponding standards.

4. Conclusions
This study showed a useful application of an easily prepared and smart heterogeneous catalyst containing very low amounts of catalytic metallic species: the selective semihydrogenation of an internal alkyne to a (Z)-alkene, which should find wide applicability. In particular, many factors that may affect the outcome of the reaction were investigated in the context of an important industrial case, the hydrogenation of 3-hexyn-1-ol to (Z)-3-hexen-1-ol, a fragrance having a multi-ton market in the world. It was possible to obtain a good balance between reactivity and selectivity, with performance comparable or usually superior to those of known available catalysts.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/1/14/s1, Figure S1: title, Table S1: title, Video S1: title. Tables S1–S6; Figures S1–S5: SEM of Cat1 0.25% Pd/Al2O3 (100 magnifications), Figure S4: SEM of Cat 1* 0.25% Pd/Al2O3 (100,000 magnification), and Figure S5: SEM of Cat1* 0.25% Pd/Al2O3 (250,000 magnification).

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References
1. Blaser, H.U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. Selective Hydrogenation for Fine Chemicals: Recent Trends and New Developments. Adv. Synth. Catal. 2003, 345, 103–151. [CrossRef]
2. Vilé, G.; Albani, D.; Almora-Barrios, N.; López, N.; Pérez-Ramirez, J. Advances in the Design of Nanostructured Catalysts for Selective Hydrogenation. ChemCatChem 2016, 8, 21–33. [CrossRef]
3. Zhang, L.; Zhou, M.; Wang, A.; Zhang, T. Selective Hydrogenation over Supported Metal Catalysts: From Nanoparticles to Single Atoms. Chem. Rev. 2020, 120, 683–733. [CrossRef] [PubMed]
4. Campanati, M.; Fornasari, G.; Vaccari, A. Fundamentals in the preparation of heterogeneous catalysts. Catal. Today 2003, 77, 299–314. [CrossRef]
5. Munnik, P.; de Jongh, P.E.; de Jong, K.P. Recent Developments in the Synthesis of Supported Catalysts. Chem. Rev. 2015, 115, 6687–6718. [CrossRef]
6. Lindlar, H. Ein neuer Katalysator für selektive Hydrierungen. Helv. Chim. Acta 1952, 35, 446–450. [CrossRef]
7. Molnár, Á.; Sárkány, A.; Varga, M. Hydrogenation of carbon–carbon multiple bonds: Chemo-, regio- and stereo-selectivity. J. Mol. Catal. 2001, 173, 185–221. [CrossRef]
8. Anderson, J.A.; Mellor, J.; Wells, R.P.K. Pd catalysed hexyne hydrogenation modified by Bi and by Pb. J. Catal. 2009, 261, 208–216. [CrossRef]
9. Maccarrone, M.J.; Lederhosa, C.R.; Torresa, G.; Betti, C.; Coloma-Pascual, F.; Quiroga, M.E.; Yori, J.C. Partial hydrogenation of alkyne hydrogenations. J. Mol. Catal. 2013, 384, 27–32. [CrossRef] [PubMed]
10. Crespo-Quesada, M.; Cárdenas-Lizana, F.; Dessimoz, A.-L.; Kiwi-Minsker, L. Modern Trends in Catalysis and Process Design for Alkyne Hydrogenations. ACS Catal. 2012, 2, 1773–1786. [CrossRef]
11. Wite, P.T.; Boland, S.; Kirby, F.; van Maanen, R.; Bleeker, B.F.; de Winter, D.A.M.; Post, J.A.; Geus, J.W.; Berben, P.H. NanoSelect Pd Catalysts: What Causes the High Selectivity of These Supported Colloidal Catalysts in Alkyne Semi—Hydrogenation? ChemCatChem 2013, 5, 582–587. [CrossRef]
12. Mitsudome, T.; Takahashi, Y.; Ichikawa, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Metal–Ligand Core–Shell Nanocomposite Catalysts for the Selective Semihydrogenation of Alkenes. Angew. Chem. Int. Ed. 2013, 52, 1481–1485. [CrossRef] [PubMed]
13. Yarulin, A.; Yurlov, L.; Cárdenas-Lizana, F.; Alexander, D.T.L.; Kiwi-Minsker, L. How to increase the selectivity of Pd-based catalyst in alkynyl hydrogenation: Effect of second metal. Appl. Catal. A Gen. 2014, 478, 186–193. [CrossRef]
14. Vile, G.; Almira-Barrios, N.; Mitchell, S.; López, N.; Pérez-Ramirez, J. From the Lindlar Catalyst to Supported Ligand-Modified Palladium Nanoparticles: Selectivity Patterns and Accessibility Constraints in the Continuous-Flow Three-Phase Hydrogenation of Acetylenic Compounds. Chem. Eur. J. 2014, 20, 5926–5937. [CrossRef] [PubMed]
15. Fedorov, A.; Liu, H.J.; Lo, H.K.; Copéret, C. Silica-Supported Cu Nanoparticle Catalysts for Alkyne Semihydrogenation: Effect of Ligands on Rates and Selectivity. J. Am. Chem. Soc. 2016, 138, 16502–16507. [CrossRef]
16. Lu, Y.; Feng, X.; Takale, B.S.; Yamamoto, Y.; Zhang, W.; Bao, M. Highly Selective Semihydrogenation of Alkynes to Alkenes by Using an Unsupported Nanoporous Palladium Catalyst: No Leaching of Palladium into the Reaction Mixture. ACS Catal. 2017, 7, 8296–8303. [CrossRef]

17. Delgado, J.A.; Benkirane, O.; Claver, C.; Curulla-Ferré, D.; Godard, C. Advances in the preparation of highly selective nanocatalysts for the semi-hydrogenation of alkynes using colloidal approaches. Dalton Trans. 2017, 46, 12381–12403. [CrossRef]

18. Ibben, A.O.; Kansal, S.K. The Reduction of Alkynes Over Pd-Based Catalyst Materials—A Pathway to Chemical Synthesis. J. Chem. Eng. Process Technol. 2018, 19, 7544–7549. [CrossRef]

19. Maazaoui, R.; Abderrahim, R.; ChemLa, F.; Ferreira, F.; Perez-Luna, A.; Jackowski, O. Catalytic Chemoselective and Stereoselective Semihydrogenation of Alkynes to E-Alkenes Using the Combination of Pd Catalyst and ZnI2. Org. Lett. 2018, 20, 10656–10667. [CrossRef]

20. Markov, P.V.; Bragina, G.O.; Baeva, G.N.; Rassolov, A.V.; Mashkovsky, I.S.; Stakheev, A.Y. Highly Selective Pd–Cu/α-Al2O3 Catalysts for Liquid-Phase Hydrogenation: The Influence of the Pd: Cu Ratio on the Structure and Catalytic Characteristics. Kinet. Catal. 2018, 59, 601–609. [CrossRef]

21. Da Silva, F.P.; Fiorio, J.L.; Gonçalves, R.V.; Teixeira-Neto, E.; Rossi, L.M. Synergic Effect of Copper and Palladium for Selective Hydrogenation of Alkynes. Ind. Eng. Chem. 2018, 57, 16209–16216. [CrossRef]

22. Swamy, K.K.C.; Reddy, A.S.; Sandeep, K.; Kalyani, A. Advances in chemoselective and/or stereoselective semihydrogenation of alkynes. Tetrahedron Lett. 2018, 59, 419–429. [CrossRef]

23. Buxaderas, E.; Volpe, M.A.; Radivoy, G. Selective Semi-Hydrogenation of Terminal Alkynes Promoted by Bimetallic Cu-Pd Nanoparticles. Synthesis 2019, 51, 1466–1472. [CrossRef]

24. Wei, Z.; Yao, Z.; Zhou, Q.; Zhuang, G.; Zhong, X.; Deng, S.; Li, X.; Wang, J. Optimizing Alkyne Hydrogenation Performance of Pd on Carbon in Situ Decorated with Oxygen-Deficient TiO2 by Integrating the Reaction and Diffusion. ACS Catal. 2019, 9, 10656–10667. [CrossRef]

25. Guan, Q.; Zhang, J.; He, L.; Miao, R.; Shi, Y.; Ning, P. Selective Hydrogenation of Acetylene to Ethylene over the Surface of Sub-2 nm Pd Nanoparticles in Miscanthus sinensis-Derived Microporous Carbon Tubes. ACS Sustain. Chem. Eng. 2020, 8, 11638–11648. [CrossRef]

26. Spee, M.P.R.; Boersma, J.; Meijs, M.D.; Slagt, M.Q.; van Koten, G.; Geus, J.W. Highly active and selective precious metal catalysts by use of the reduction-deposition method. Stud. Surf. Sci. Catal. 2010, 175, 135–143. [CrossRef]

27. Stoll, M.; Rouvè, A. Synthèse du cis-β, γ-hexénol (hexénol naturel). Helv. Chim. Acta 1938, 21, 1542–1547. [CrossRef]

28. Witte, P.T.; de Groen, M.; de Rooij, R.M.; Bakermans, P.; Donkervoort, H.G.; Berben, P.H.; Geus, J.W. Highly active and selective precious metal catalysts by use of the reduction-deposition method. Stud. Surf. Sci. Catal. 2010, 175, 135–143. [CrossRef]

29. Liguori, F.; Barbaro, P. Green semi-hydrogenation of alkynes by Pd@borate monolith catalysts under continuous flow. J. Catal. 2014, 311, 212–220. [CrossRef]

30. Steinhaus, M.; Sinuco, D.; Polster, J.; Osorio, C.; Schiebert, P. Characterization of the Key Aroma Compounds in Pink Guava (Psidium guajava L.) by Means of Aroma Re-engineering Experiments and Omission Tests. J. Agric. Food Chem. 2009, 57, 2882–2888. [CrossRef]

31. (Z)-hex-3-en-1-ol. Available online: http://www.thegoodscentscompany.com/data/rw1005932.html (accessed on 22 December 2020).

32. Tassini, R.; La Sorella, G.; Montin, D.; Paganelli, S.; Bardi, F.; Piccolo, O. Sintesi sostenibili con CO. La Chimica e l’Industria 2012, 94, 157.

33. Piccolo, O.; Verrazzani, A. US 7087548, (Chemi SpA). 2006. Available online: https://worldwide.espacenet.com/publicationDetails/originalDocument?FT=D&date=20060808&DB=EPODOC&locale=en_EP&CC=US&NR=7087548B2&KC=B2&ND=4 (accessed on 22 December 2020).