

Plant-mediated synthesis of ZnO supported Ni-Pd alloy catalyst for the selective hydrogenation of 1, 3-butadiene

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ABSTRACT

We report the green synthesis of ZnO supported Ni-Pd alloy nanoparticles for the gas-phase selective hydrogenation of 1, 3- butadiene. The supported catalysts were synthesized through a simple bio-reduction route using Cinnamomum Camphora leaf extract. X-ray diffraction, scanning and transmission electron microscopy and energy dispersed X-ray were used to characterize and verify the nature of the catalysts. The results showed that the Ni-Pd alloy particles were 3.2 ± 0.7 , 3.4 ± 0.3 and 3.8 ± 0.6 nm for Ni₁Pd₁, Ni₁Pd₃ and Ni₃Pd₁ respectively. FTIR analysis revealed that stretching vibration bands such as C-H,-C=C-, O-H, -C-O- O remained on the surface acting as stabilizer. The influence of some reaction variables, such as type of S-Pd bimetallic catalyst, type of metal oxide support and reaction temperature, on the hydrogenation activity and selectivity towards total butene (trans-2-butene, 1-butene and cis-2butene) is investigated. The bioreduction supported catalysts showed excellent catalytic activity and selectivity to butene in the selective hydrogenation of 1,3 butadiene. The calculated total butene selectivity was above 80% for all supported S₁-Pd₁ catalyst compared to 46.92 % for monometallic Pd/ZnO catalyst. In addition, the Ni₁-Pd₁/ZnO catalyst presented the best butene yield 88.90 % which was 1.9 times that of Pd/ZnO catalyst. Moreover, it maintained stability over a 10 h durability experiment.

Keywords: Zinc Oxide supported catalyst; Selective hydrogenation; Biosynthesis; Ni-Pd alloy

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1. Introduction

Hydrogenation of 1, 3-butadiene is an important industrial process used for the purification of butene streams to obtain butene (*trans*-2-butene, 1-butene and *cis*-2-butene), generated from cracking naphtha or gas oil.¹ Among which 1-butene is most desired for making polyethylene with butane considered a by-product. The suppressing butane formation and the isomerization of 1-butene to attain the desired product is a challenging task.

Palladium catalyst supported on various inorganic materials has proven to be efficient in the hydrogenation of dienes and unsaturated hydrocarbons. However, the process is limited by the generation of large amounts of by-products due to double bond and geometric isomerization reducing the overall yield and quality of the desired products. Due to the demand of high purity products, the attainment of even a slight improvement in the selectivity of the desired products is of significant importance. Over the past few decades tremendous research effort from both industry and academia towards improving the selectivity of desired products has been carried out. Among these, alloying Pd with a second metal and the selecting of an appropriate support has shown to improve the selectivity. Several metals including Ag, Au, Sn, Ni etc. acting as modifiers improves selectivity and helps prevent "green oil formation" which is reported as the causative agent for catalyst deactivation.²

In a previous work, El Kolli co-workers prepared Au-Pd on alumina and titania oxide using three different methods and showed that their surface composition depended on the preparation method. In addition, the alloyed catalyst had superior performances over their monometallic counterparts for hydrogenation of butadiene in the presence of excess propene.³ It was also observed that, co-deposition-precipitation (DP) method produced smaller uniform and reproducible Au/Pd particles which also outperformed their counterparts produced using co-impregnation in excess of solution (IES) in hydrogenation of 1,3- butadiene.^{2d} In addition, Pattamakomsan and co-workers reported a remarkable improvement in both activity and selectivity in the gas-phase hydrogenation of 1, 3-butadiene over Pd–Sn catalyst supported on mixed phase θ/α -(MA) and pure α -alumina (AA) catalyst.^{2b}

Furthermore, Hou and co-workers showed from modeled (density functional theory (DFT) calculations, temperature-programmed desorption (TPD) and experimental work that asproduced Ni-Pd/ γ -Al₂O₃ outperformed their monometallic ones in both activity and selectivity to butene.⁴ In addition, they observed that the Ni-Pd bimetallic bond formation on the γ -Al₂O₃was very small (only 1.4) and this could be improved by utilizing other metal supports. In a related work using different supports for Ni-Pd bimetallic catalyst, Hou and co-workers observed that different supports had no significant influence on hydrogenation activity except Pd-Ni/CeO₂ catalyst which showed a slightly lower activity. On the contrary, they showed marked difference is the selectivity to total butene which was attributed to strong metal-support (SMSI) interaction, oxygen defects, geometric and electronic properties.⁵

Moreover, Pt-Ni bimetallic catalyst supported on TiO_2 and γ -Al₂O₃ showed different results for hydrogenation of 1, 3-butadiene, with the former support performing lower than the later due to structural stability of the catalyst caused by the support.⁶ In another study, Primet and co-workers observed that the acidic properties of the support affected the selectivity to butene and butene

distribution. ⁷ Basic supports were more selective to butene and promoted 1-butene formation. The above reports thus motivate research into the attainment of a suitable synthesis protocol and the identification of other alternative metal oxide supports to the conventional utilized ones for industrial application.

Various chemical and physical preparative means have been utilized to prepare bimetallic nanomaterials for target applications with commercially obtained conventional oxide supports (γ -Al₂O₃, TiO₂, SiO₂, CeO₂, and ZrO₂). These methods usually involve the reduction of metals precursors using reducing agents and then the as-produced nanomaterials are stabilized with organic, dendrimers or polymers. After which they are affixed unto the supports and the stabilizers removed through calcinations. These methods have the advantages of morphological control of the resulting nanomaterials and can produce large amounts of nanomaterials. However, they require complex and tedious operations conditions, costly substrates, high temperatures and surfactants or stabilizers (PVP, CTAB etc.) and non-biodegradable materials.

These drawbacks can be circumvented using biogenic means which is proven to be environmentally benign, less costly and uses less sophisticated equipment.⁸ Our group in a previous work studied the hydrogenation of 1, 3- butadiene using biosynthesized Ag-Pd/ γ -Al₂O₃ catalyst.⁹ In this present study, we report the green synthesis of Ni-Pd alloy nanoparticles of sizes 3~6 nm affixed onto biosynthesized zinc oxide (ZnO) support as efficient catalyst for the hydrogenation of 1, 3-butadiene using *Cinnamomum camphora* (*C. camphora*) leaf extract as reducing and stabilizing agent. In addition, we studied the effects of different metal oxide support, temperature and type of S-Pd bimetallic catalyst, where S= Au, Ag, Ni on catalytic performance and selectivity to butene.

2. Experimental section

2.1. Materials and methods

Cinnamomum camphora leaves (C. *Camphora*), as in our previous work¹⁰ was obtained from Xiamen Peony Fragrance Co Ltd, washed several times with DI water, dried and crushed into fine powder. Zinc nitrate hexahydrate Zn $(NO_3)_2.6H_2O$, Nickel (II) nitrate hexahydrate (Ni $(NO_3)_2.6H_2O$), Ascorbic Acid (AA) was purchased from Sangon Biotech (Shanghai) Co., Ltd. Palladium nitrate Pd $(NO_3)_2$, and all other commercial supports (P25 TiO₂, referred to as TiO₂ in this work and SiO₂) used were obtained from Sinopharm Chemical Reagent Co. Ltd., and used as received without purification. Deionized (DI) water was employed throughout the work.

2.2. Synthesis of the Ni-Pd Alloy Nanoparticles and the ZnO, CuO support

The water extraction method was used to obtain the *C. camphora* leaf extract. 1 g of the leaf powder was dissolved in 100 mL DI water, placed in an oil bath rotating at 160 rpm with the aid of a magnetic stirrer, at 60 °C for 6 hr. Then the resulting mixture was filtered through a 0.8 μ m membrane to obtain the plant extract. To synthesize the Ni-Pd alloy nanoparticles, 1 mL of 10 mM, Pd(NO₃)₂ and (Ni(NO₃)₂.6H₂O) solution (molar ratio 1:1) was added to a 150 mL round bottom flask and the volume adjusted to 40 mL with DI water. The flask was then placed in a preheated oil bath at 90 °C, 1000 rpm for 10 min. After which, 10 mL of the *C. camphora* leaf extract was added to the mixture under vigorous stirring for 20 min. Different Ni-Pd alloy nanoparticles varying molar ratios were obtained by changing the ratio of the precursor solutions

(3:1, 1:1 and 1:3). Monometallic Pd and Ni nanoparticles were prepared for comparison using the same process by using only Pd (NO₃)₂ or (Ni (NO₃)₂.6H₂O) respectively. The ZnO and CuO supports used were prepared as in our previous works with little adjustments.¹⁰⁻¹¹ In a typical synthesis of ZnO and CuO, 30 ml of 0.2 mol/L Zn (NO₃)₂.6H₂O and 0.1 mol/L of Cu(NO₃)₂.3H₂O solutions were added to 10 and 20 mL of *C. camphora* leaf extract respectively in a 150 mL round bottom flask and kept at room temperature to age for 1 h. After, the respective mixtures were dried in the oven at 80 °C for 10 h and then annealed at 450 °C 4 h. The obtained metal oxides were milled using a lab mortar and pistil and then sieved with a 50 mm mesh and stored for further use.

2.3. Catalyst synthesis

To obtain the supported catalyst, bimetallic and monometallic Ni-Pd nanoparticles were affixed onto the metal oxide supports through electrostatic attraction: typically 0.5 g of the support was added to the as-prepared Ni-Pd colloidal suspension at room temperature and pH was adjusted depending on the isoelectric points of the metal oxides.¹² After stirring for 1 h, the mixture was filtered and vacuum dried at 150 °C for 10 h to obtain the catalyst which were labeled Ni_xPd_y/M. Where x, y and M are the molar ratios of Ni, Pd and support respectively. For comparison, Au₁Pd₁ and Ag₁Pd₁/ZnO catalyst using the same procedures as above and three Ni₁Pd₁/TiO₂ catalysts, synthesized using conventional impregnation or/and annealing at 450 °C, and chemical reduction with AA.

2.4. Characterization of the Ni-Pd Alloy nanoparticles

Transmission electron microscopy (TEM), Energy dispersed X-ray (EDX) and selected area (electron) diffraction (SAED) examinations were conducted on an electron microscope (Tecnai F30, FEI; Netherlands) with an accelerating voltage of 300 kV. Diameter measurements of the as-produced Ni-Pd NPs were done as in our previous report.¹³ XRD investigation of the dried samples was done on an X-ray crystallography (Phillips; Netherlands) provided with Cu K α radiation (40 kV, 30 mA). FT-IR measurements were carried out on Nicolet 6700 spectrophotometer (Thermo Nicolet, U.S.A). Brunauer-Emmett-Teller (BET) analysis was conducted using a Micromeritics Tristar 3020 system. H₂-TPR profiles for the as-prepared catalyst were measured using a Micromeritics Autochem II 2920 instrument. Atomic absorption spectroscopy (AAS) analysis of Ni (II) and Pd (II) ions in the solutions before and Ni and Pd in the obtained samples were conducted using (AAS Pgeneral, China).

Pulse CO and H₂ chemisorption were conducted on ASAP 2020 (Micromeritics) as in a previous report.¹⁴ Briefly, chemisorption uptakes of adsorbates (H₂ and CO) on catalysts were measured on a Micromeritics ASAP 2020 (M+C) analyzer using the static volumetric method. A measured amount of catalyst (minimum of 500 mg) sample was reduced under a flow of high-purity dihydrogen at 573 K for 2 h and then evacuated for 1 h to ensure the complete removal of chemisorbed species. Under a precisely controlled temperature of 308 K, an initial isotherm was measured in a pressure range of 100–600 Torr. A 30 min evacuation at 308 K was conducted to remove the reversibly adsorbed adsorbate molecules on the catalyst surface prior to measuring a repetitive isotherm under the same conditions as the initial one. The difference between the

initial and repetitive isotherms reflects the uptake of the irreversibly chemisorbed adsorbates on catalysts. The test was program such that the H_2 chemisorption test preceded the CO chemisorption test.

2.5. Catalyst activity test

The gas phase hydrogenation of 1, 3- butadiene using the Ni_x-Pd_y/M catalysts were carried out at 35 °C in a fixed bed reactor (diameter 1 cm) under atmospheric pressure using a reactant concentration of 2.12%, 4.28% and (93.6%) of 1,3- butadiene, H₂ and N₂ respectively. 50 mg of the catalyst was placed into the reactor and the reactor effluent was analyzed every 20 min for 4 h using a gas chromatograph (GC) having an Al₂O₃ column and a FID detector. The output conversion of 1, 3- butadiene and the corresponding selectivity to total butene (*cis*-2-butene *trans*-2-butene, and 1-butene) or its by-product butane were determined from their corresponding GC peaks. The metal loadings of all catalyst were controlled at 1 wt. % and the results represent an average of four tests. The overall yield was calculated as in our previous studies using the formula below.

3. Results and discussions

3.1. Characterizations of Ni-Pd/ZnO catalysts

3.1.1. TEM, HRTEM and SAED Analyses

The structural properties of the as-produced bimetallic nanostructures were investigated using low resolution TEM. TEM images of the bimetallic and their monometallic counterparts are shown in Fig.1.The size of the Pd NPs is 2.8 ± 0.4 nm and the Ni NPs is 4.7 ± 0.6 (Fig.1A and E). The sizes of the bimetallic alloy Ni-Pd NPs were 3.2 ± 0.8 nm, 3.4 ± 0.7 nm and 3.8 ± 0.3 nm corresponding to Ni/Pd of initial molar ratios of 1:1, 1:3, 3:1 respectively (Fig.1B, C and D). From Fig.3F (plot of average particle size of the as-produced nanostructures against the Pd molar fractions), it is observed that, the average particle size decreases linearly with increasing palladium amount.

The High-resolution TEM (HRTEM) and SAED patterns of the bimetallic NPs are presented in Figure S1, Supporting Information. The HRTEM shows that the as-produced bimetallic NPs are made up of clear crystallographic orientations in different directions which are confirmed by its SAED results. In addition, the results shows that the Ni-Pd alloy NPs are presented by dominant (111) facets. Moreover, an interplanar distance of 0.21 nm is observed for a single Ni-Pd NP which lies between the *d*-spacing of Ni (0.204 nm) and Pd (0.225 nm) and corresponds to the face centered cubic Ni (111) and Pd (111). The typical SAED pattern shows four Bragg diffractions of (111), (200), (220) and (311).



Figure 1. TEM images and diameter distribution histograms of the biogenic Ni-Pd NPs with molar ratios (B) 1:1, (C) 1:3, and (D) 3:1; and their monometallic NPs (A) Pd and (E) Ni; and (F) plot of average diameter distribution vs Pd molar ratio

3.1.2. STEM and EDX Elemental Analyses

Scanning TEM (STEM) and energy dispersed X-ray Spectroscopy (EDX) were done to study the elemental distribution of the Ni-Pd NPs. Figure 2 show the STEM images of the Ni-Pd NPs with different initial molar ratios. The colored mapping Ni (brown Figure 2B, E and H) and Pd (yellow Figure 2C, F and I) shows that, as-produced nanostructures contained Ni and Pd. However, due to poor resolution the images were not very clear. Therefore, EDX analysis was

conducted to further confirm their alloy nature. Typical EDX image of Ni_3Pd_1 NPs is showed in Figure S2. Three peaks are observed for Pd, Ni and P probably from the plant extract. The atomic percentage concentrations of the Ni-Pd solutions were estimated by AAS analysis of the solutions before and Ni-Pd NPs after reaction, the results are shown in Figure S2 B and tabulated in Table S1. It the case of Ni₁-Pd₁ and Ni₁-Pd₃, though, the calculated atomic percentages deviated by about \pm 5 %, the Ni: Pd ratios were close to the nominal ones. However, in the case of Ni₃-Pd₁, the estimated ratio was about 1.6:1 which we attribute to the inability of *C.camphora* to completely reduce the Ni(II) to Ni(0) under the current reaction time. It is known that, Pd(II) can easily be reduced to Pd(0) compared to Ni(II) due to the differences in their reduction potentials, the amount of leaf extract was not enough to totally reduce Ni in the case of Ni₃-Pd₁.¹⁵ The observation agrees with our previous work using alfalfa leaf extract to synthesize Ni NPs, it was observed that, by increasing the amount of leaf extract used, more Ni(II) were reduced to Ni(0) and the particle sizes became larger.^{15b} Furthermore, the calculated atomic percentages from the AAS analysis were similar to the atomic percentage concentrations from EDX analysis Table S1 without considering element P.



Figure 2. STEM images of the Ni-Pd bimetallic nanoparticles of molar ratio ratios (A) 1:1 (D) 1:3 and (G) 3:1and their corresponding EDX elemental maps Ni (B, E and H) and Pd (C, F and I) concentrations

3.1.3. XRD Analysis

XRD patterns of the bio-reduced bimetallic Ni-Pd NPs and their monometallic counterparts are presented in Figure 3. The bimetallic Ni-Pd NP showed diffraction peaks at 42.1, 41.6 and 41.0 ° respectively corresponding to samples with initial molar ratio 3:1,1:1 and 1:3 respectively. These peaks coincide with the (111) diffraction peak values between pure Ni (pdf2 card no: 01-089-7128) and Pd (pdf2 card no: 01-087-0635) affirming the formation of an alloy structure. Moreover, there is a gradual peak shift towards pure Ni with increasing Ni content.



Figure 3. XRD patterns of the monometallic (I) Pd NPs (V) Ni NPs and bimetallic Ni-Pd NPs with initial molar ratio of (I) 1:3 (II) 1:1 and (IV) 3:1

3.1.4. XPS and DRUV-vis spectra Analyses

XPS analyses of the S-Pd NPs and the supported catalysts were conducted to check their electronic state and composition. The XPS results for Ni-Pd NPs are shown in Figure 4; the binding energy $2p_{3/2}$ at about 853.3 eV Figure 4A corresponds to the Ni (0) component while that of $3d_{5/2}$ at about 335 eV Figure 4B corresponds to Pd (0). From the results, it is observed that as Pd content increases, the binding energies shifts to higher energy levels (Figure 4B). For example the Pd (0) $3d_{5/2}$ for metallic Pd were 335.50, 335.53 and 335.60 eV corresponding to Ni-Pd NPs of molar ratios 3:1, 1:1 and 1:3 respectively. The Ni (0) $2p_{3/2}$ also shows similar shifts in binding energies with increasing Ni content. In addition, a satellite peak is observed around 859.7 eV in all Ni-Pd samples probably due to the partial oxidation of Ni during the drying process. The shits show possible changes in the electronic properties of the two metals. The binding energies are summarized in Table S2 supporting information. The XPS data was used to estimate the atomic percentage concentration of the Ni-Pd alloy NPs from the major peaks. The results are shown in Table S3. The major peaks observed were Ni 2p, Pd 3d, C1s and O1s. The results agreed with those from the AAS and EDX analysis.

A similar phenomenon is observed when the Ni-Pd, Ag-Pd and Au-Pd NPs were immobilized on to the various supports Figure 5. In our previous work, we observed a shift in the XPS spectra of Ag after anchoring it onto CeO₂ support,¹⁶ which we attributed to the changes in their Fermi energy levels as a result of interactions between the Ag nanoparticles and the CeO₂ support. This is in agreement with other reports in literature.¹⁷ Habibi et.al observed a marked shift to a lower binding energy from the XPS of metallic Ag (3d_{5/2} at 368.1 eV) compared to as-prepared Ag-ZnO NPs (367.7 eV). And thus to a large extent, the supports surfaces were reduced by the different S-Pd alloy NPs and they presented possible (SMIS). The binding energies of all six catalysts are summarized in Table S4. From the table it is observed that, all the binding energies of the metals shifted to higher energy levels. According to literature, the positive shift could be as a result of change in particle size, chemical or charge effects.¹⁸ However, from the TEM images of the S-Pd alloy supported catalyst (Figure S3) we can rule out effect of particle size since no obvious change in particle size is observed. Therefore the shifts of binding energies to higher values are attributed to charge and chemical effects and partially to the possible interactions between the biomolecules from the leaf extract and the supported catalyst. In the case of Au-Pd/ZnO catalyst compared to bimetallic Au-Pd, the 4f_{7/2} is not observed probably due to its overlap with the Zn 3p binding energy level Figure 5 E.

In addition, the different oxide supports may present different surface oxygen vacancies when the S-Pd alloy NPs are immobilized on the supports which could affect their possible catalytic performance. A further study of their O1s XPS spectra could provide more information. The asymmetric O1s XPS spectra of ZnO can be deconvoluted into three distinct peaks, oxygen species in the lattice (O_L) at 530.0 eV, oxygen vacancies O_V at 531.28 eV and dissociated or chemisorbed oxygen O_C at 532.36 eV, Figure 6. ^{17, 19} The O1s of TiO₂ also show three similar peaks however, most of the peaks shifted to lower binding energies compared to the ZnO, probably due to interactions with the residual organic groups. While that of SiO₂ shows only (O_V and O_L) and CuO (O_L and O_C). The intensity and number of oxygen defects were similar on the TiO₂ and ZnO support, suggesting they may have more surface oxygen defects compare to SiO₂ and CuO.



Figure 4. XPS spectra of the Ni-Pd NPs

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DRUV-vis spectra analysis of the supported Ni-Pd catalysts is shown in Figure S4. The ZnO and TiO₂ show absorbance below 400 nm, while the supported catalyst shows slight red shifts to higher absorbance to indicate the incorporation of the S-Pd NPs. Usually Ag displaces absorption plasmon at about 420 nm while that of Au shows around 560 nm. ^{16, 20} However, the observation is not marked since Pd in bimetallic nanoparticles usually suppresses the surface absorption plasmon of Au, and Ag.^{9, 21}



Figure 5. Comparison of the XPS spectra of the supported S-Pd catalysts and their corresponding bimetallic NPs



Figure 6. The XPS spectra of the supports (A) ZnO (B) TiO₂ (C) SiO₂ and (D) CuO showing the O1s region

3.1.5. FTIR Analysis

FTIR absorption spectra of the different supported Ni₁-Pd₁ catalyst after reaction, and the plant extract before reaction are shown in Figure S5. The spectrum (Figure S5 I) shows several clear bands at 1059, 1109, 1245, 1384, 1735, 2852, 2921 and 3426 cm⁻¹ within the region of 1000 to 4000 cm⁻¹. The peaks around 1245 and 1059 cm⁻¹ are ascribed to the C–O stretching vibration from cyclic compounds and hydroxyl in carbohydrate respectively. Those centered at 1319 and 2921cm⁻¹ are due to C–H bending and stretching vibration in alkanes. Moreover, the broad peak at 3426 cm⁻¹ can be attributed to the stretching vibration of (N-H group) in amides found in proteins. The peak at 1109 cm^{-1} is attributed to the -C-O- groups of polyols like flavonoids, polysaccharides and terpenoids in the plant biomass. In addition the absorption peak at 1634 cm^{-1} can be assigned to -C=C- stretch vibration. After the reaction, the bands at 1059 shits to 1053 in II and 1051 cm⁻¹ in III while it disappeared completely in IV and V. In addition, the bands at 1245, 1319, and 1731 cm⁻¹ in Figure S5 I disappeared completely from Figure S5 II-V. The FTIR analysis shows that, interactions occurred between all the catalyst and biomolecules from the leaf extract. Therefore, from the FTIR analysis it is speculated that, the biomolecules mostly streaching vibration bands from C-H,-C=C-, O-H, -C-O- O that remained on the supported Ni-Pd catalysts after the bio-reaction acted as stabilizers.

3.2. Catalytic Activity Evaluation

The possible hydrogenation routes of 1, 3-butadiene using S-Pd/M catalyst is shown in scheme 1 below. The process involves the hydrogenation and isomerization of 1, 3- butadiene over Pd supported metal catalyst with butene (trans-2-butene, 1-butene and cis-2-butene) as the desired reaction product and butane a by-product. Modifying the electronic and structural properties of Pd by alloving with other metals tunes its selectivity toward butane. The average catalytic performance of the as-produced mono and bimetallic Ni-Pd/ZnO catalysts in the selective hydrogenation of 1, 3-butadiene at 35 °C after 4 h of reaction is summarized in Table S5, and plotted in Figure 7. Ni/ZnO catalyst is almost inactive in 1, 3- hydrogenation achieving a very low conversion of 2.54 \pm 0.5 % compared to 100 % conversion for the Pd/ZnO catalyst. However, it showed high selectivity to cis-2-butene, a low selectivity to 1-butane and no selectivity towards *trans-2*-butene and butane. In addition, a marked improvement in both selectivity towards butene and conversion is observed using the bimetallic Ni-Pd/ZnO catalysts. Specifically, the conversion of 1, 3- butadiene was 98.8 ± 0.2 % for Ni₁-Pd₁/ZnO catalyst and 100% for both Ni₁-Pd₃/ZnO and Ni₃-Pd₁/ZnO catalyst. In terms of selectivity towards total butene (trans-2-butene, 1-butene and cis-2-butene), the Ni₁-Pd₁/ZnO catalyst recorded the highest selectivity of about 90.0 \pm 0.4 % and 40.7 \pm 0.8 % for single 1-butene with an overall calculated yield of 88.9 \pm 2%. And thus, alloying with Ni in the case of Ni₁-Pd₁/ZnO could prevent full hydrogenation while increasing selectivity to butene. Table S6 presents six catalytic performance assessment of the Ni₁-Pd₁/ZnO catalyst, the last four were considered in calculating the average performance.

The addition of Pd greatly enhanced the conversion efficiency of 1,3- butadiene and the selectivity to butene compared to the monomettalic Ni/ZnO catalyst proving Pd is the main active constituent for the reaction. The observed marked improvement of the bimetallic Ni₁Pd₁/ZnO catalyst over their monometallic counterparts is attributed to the catalyst composition, modification of the electronic and structural properties of Pd and the enhance bimetallic-support interaction (Ni-Pd bimetallic bonding) as support by the XPS analysis above (Figure 5). As mentioned above, the enhancement in both catalytic performance and selectivity to butene in the hydrogenation of 1, 3- butadiene on bimetallic catalyst over monometallic Pd has been proven from both experimental and DFT calculations.^{2b, 4, 22} The present works thus confirms this trend using biosynthesized Ni-Pd bimetallic catalyst on a less conventional biosynthesized ZnO as support.

For comparison, Ni₁-Pd₁/TiO₂ catalyst prepared by impregnation, impregnation and subsequent calcinations at 450 °C and chemical reduction using 1 mL of 1 mol/L, ascorbic acid as reductant are shown in Table S5. Compared to the plant-mediated synthesis in our current work, the Ni-Pd/TiO₂ synthesized using impregnation were very selective towards total butene with a selectivity of about 99 \pm 0.1 and 71.6 \pm 3 % for single 1-butene, nevertheless, it showed low conversion of about 10 %. After annealing at 450 °C, no obvious change in activity was observed. However, the distribution of selectivity towards total butene changed, for example selectivity to single 1-butene reduced from 71.6 \pm 3 to 45.3 \pm 4 % while that of single *cis*-2-butene increased from 16.1 \pm 0.3 to 33.37 \pm 5 %. When it was reduced with ascorbic acid, a conversion of 100 % was observed, with a drop in the total selectivity to butene to about 44.8 \pm 1 and 22.8 \pm 4 % for single 1-butene respectively. The observation highlights the importance of preparation conditions of catalyst in the selective hydrogenation of 1,3 butadiene. Moreover, the Ni₁-Pd₁/ZnO showed good reusability performance (Table S 7), with about 73 \pm 5% conversion and 95 \pm 2 and 52 \pm 4% selectivity towards total butene and single 1-butene

respectively after a week. A gradual increase in the selectivity to total butene from 90.0 ± 0.4 to 95 ± 2 was accompanied with a drop in the conversion of 1,3 butadiene from 98.8 ± 0.2 to about $73 \pm 5\%$.



Scheme.1 Possible reaction routes for 1, 3- butadiene



Figure 7. A plot of the catalytic performance of the Ni-Pd/ZnO catalyst and their monometallic counterparts in 1, 3-hydrogenation

Table 1.	Physical	properties	of the	different	supported	Ni/Pd	catalyst
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Sample	$S_{BET}(m^2g^{-1})^a$	Pore Volume ^b (cm^3g^{-1})
ZnO	22.0	0.16
TiO ₂	52.0	0.73
SiO ₂	1.0	0.04
CuO	18.0	0.07
Ni ₁ Pd ₁	4.0	0.02
Ni ₁ Pd ₁ /ZnO	25.0	0.14
Ni ₁ Pd ₁ / TiO ₂	50.0	0.46
Ni_1Pd_1/SiO_2	2.00	0.03
Ni ₁ Pd ₁ /CuO	15.0	0.05

a. The BET surface area is determined by the BET method using the adsorption data in the relative pressure (P/P_0) b. BJH Adsorption cumulative volume of pores

Catalyst	Average Particle size (ANPs)	Metal Dispersion from CO chemisorptions (%)	CO-Uptake (µmol/g)	H2-Uptake (µmol/g)	CO uptake/ANPs
Ni ₁ Pd ₁ /ZnO	3.6	7.2	8.4	6.5	2.0
Ni ₁ Pd ₁ /TiO ₂	2.6	20.4	7.0	2.5	2.8
Ni ₁ Pd ₁ /SiO ₂	3.2	3.4	3.6	2.0	1.1
Ni ₁ Pd ₁ /CuO	2.9	54.0	32.4	14.1	11.2
Au ₁ Pd ₁ /ZnO	4.1	3.9	7.1	6.5	1.7
Ag ₁ Pd ₁ /ZnO	4.5	3.6	9.9	5.7	2.2

Table 2. Summary of the metal dispersion, average particle sizes and CO and H_2 uptake values of the supported Ni/Pd catalyst

3.2. 1. Effect of metal oxide support on the Catalytic Activity

TiO₂, SiO₂ and CuO were selected to compare the effects of different supports on the catalytic activity. The biosynthesized Ni-Pd bimetallic catalysts supported on different supports were evaluated in the selective hydrogenation 1, 3- butadiene and the results are shown in Table S8 and plotted in Figure 8. The average 1, 3- butadiene conversion over a 4 h period at 35 °C in order of maximum activity was as follows TiO₂ (100 %), ZnO (98.8 ± 0.2 %), CuO (63.3 ± 2 %) and SiO₂ (44.0 ± 3 %). In terms of average calculated yield, the Ni₁-Pd₁ bimetallic catalyst supported on ZnO presented the best yield about 88.9 ± 2 % and TiO₂ recorded a yield of 80.5 ± 3%, followed by CuO (53.9 ± 1%) and SiO₂ (41.3 ± 2 %) respectively. Thus the hydrogenation activity was close in the case of ZnO and TiO₂ support but very wide for SiO₂ and CuO.

The metal dispersion, average particle sizes and CO uptake of the supported Ni-Pd catalyst are presented in Table 2 above. The CO uptake values are similar in the case of ZnO and TiO₂ but very high in the case of CuO and low in the case of SiO₂. The Ni₁Pd₁/CuO catalyst recorded the highest metal dispersion (54%), followed by Ni₁Pd₁/TiO₂ (20 %), Ni₁Pd₁/ZnO (7.2 %) and Ni₁Pd₁/SiO₂ (3.4 %). Hydrogenation activity of 1, 3 butadiene is reported to strongly depend on Pd metal dispersion while 1-butene selectivity is insensitive to dispersion.²³ Moreover, hydrogenation activity is reported to decrease when dispersion is higher than 20% and is similar at dispersions 20 % and lower regardless of metal oxide support type. Hou et al also observed that Pd-Ni/CeO₂ with a higher metal dispersion resulted in a lower TOF compared to Pd-Ni bimetallic supported on (γ -Al₂O₃, TiO₂, SiO₂ and ZrO₂) with lower dispersion.⁵ The higher metal dispersion 54 % recorded for the Ni₁Pd₁/CuO catalyst causes the significant reduction in hydrogenation activity. The observation can be ascribed to less exposed active sites on the Ni-Pd bimetallic surface²³ and the strong binding of 1,3 butadiene on the Ni-Pd bimetallic catalyst due to electronic effect.²⁴ In the case of the Ni₁Pd₁/SiO₂ catalyst the low CO uptake is not surprising since a small surface area of $(2 \text{ m}^2/\text{g})$ could affect dispersion. Moreover, the O1s XPS analysis revealed that, the Ni-Pd supported on TiO₂ and ZnO possessed more oxygen defects compared to SiO₂ and CuO this could be a possible attribute to the high hydrogenation activity in the case of the former supports. However, further studies are needed to support this claim and since interpretation is yet to be reported in literature we take notice of the results and plan to carry out further studies.

Comparing the selectivity to total butene the biosynthesized Ni₁-Pd₁ bimetallic catalyst supported on SiO₂ recorded the highest selectivity 93.6 \pm 2 %, followed by ZnO with a selectivity of about 90 \pm 0.4 %, then CuO 85.17 \pm 1 % with TiO₂ recording the lowest 80.5 \pm 3%. It is worth nothing that the selectivity to total butene was above 80 % for all bimetallic supported catalyst compared to 46.9 \pm 2 % for monometallic Pd/ZnO catalyst. And there was a slight reduction in the selectivity at 100 % conversion of 1, 3- butadiene. Furthermore, in the case of selectivity to single 1-butene the trend was as follows SiO₂, TiO₂, CuO and ZnO. As mentioned above selectivity to butene is independent on metal dispersion. Therefore factors such as metal dispersion and particle size can be ruled out since the Ni-Pd bimetallic catalysts are of similar size 2.6 ~ 3.6 nm.

The apparent difference in the selectivity towards total butene and to a large extent single 1butene on the dissimilar supports is attributed to their composition, the nature of the supports and their interaction with the biosynthesized bimetallic catalyst. Strong metal-support interaction was inferred from the ability of the oxide to suppress the chemisorption of H₂ onto the metal. SMSI has been shown to occur when small metal particles are dispersed on metal oxide supports.²⁵ Kang et.al reported that the selectivity to butene isomers in the hydrogenation of 1, 3 butadiene increases when Cu was added to Pd/CeO₂ to form Cu-Pd/CeO₂ catalyst.²⁶ The bimetallic Cu-Pd/CeO₂ could suppress the extent of SMIS effect by reducing the amount of chemisorb H₂. Previous reports showed that, all the supports (SiO₂, TiO₂, CuO and ZnO) used in the present study present SMIS effect when reduced at higher temperature.²⁷ However, alloying as well as preparation conditions could reduce the required reduction temperature for SMIS to occur on catalyst.^{26, 28} H₂-TPR profiles of the catalyst Figure S6, shows several peaks between 80 to 850 °C which we attribute to different Pd, Ni, Pd-Ni, Ni-Pd and leaf extract biomolecules interactions with the support. Therefore, possible SMIS effect on the catalyst affected the selectivity to total butene and 1-butene.

In addition, different supports may affect the geometric and electronic properties of the supported Ni-Pd catalyst as observed from the different shifts in binding energies (Figure 5 XPS results).



Figure 8. Catalytic performance of the Ni-Pd bimetallic catalyst on different supports in 1, 3- butadiene hydrogenation

Moreover, the O1s region (Figure 6) of the supports show different levels of oxygen defects existed on the different supports. The SiO_2 oxide support with the least oxygen defects showed the best selectivity while TiO_2 with the highest level of oxygen effect presented the worst selectivity to total butene. This suggests a correlation between 1,3 hydrogenation activities, butene selectivity and the oxygen defects of the supports.

3.2.2. Effect of type of supported S-Pd bimetallic on catalytic activity

The nature of bimetallic catalyst in terms of electronic state, synergistic effect, and alloy formation could affect both activity and selectivity in hydrogenation reactions. Two different biosynthesized Pd bimetallic catalyst (Ag₁Pd₁ and Au₁Pd₁) supported on ZnO (sizes between 3.6 ~ 4.5 nm) were investigated in the hydrogenation of 1, 3- butadiene and compared to the Ni₁Pd₁/ZnO catalyst (Figure 9A). The results are also tabulated in Table S 9. Compared to monometallic Pd, Au, Ni and Ag are all inactive for 1, 3- hydrogenation.

However, they show 100 % selectivity to total butene as to $46.9 \pm 2\%$ for Pd. Addition of Pd increased their respective conversions drastically to 98.8 ± 0.2 , 96.2 ± 0.8 , and $95.9 \pm 0.6 \%$ for Ni₁Pd₁, Au₁Pd₁ and Ag₁Pd₁ respectively. And thus the bimetallic catalysts irrespective of composition had almost similar conversions slightly lower than the biosynthesized monometallic Pd/ZnO catalyst. In addition, they exhibited higher selectivity over monometallic Pd. The ZnO supported Ni₁Pd₁ and Au₁Pd₁ catalyst showed the highest selectivity towards total butene about 90 %, (3.54 %) slightly higher than the Ag₁Pd₁/ZnO catalyst (86.5 %). Nonetheless, the Au₁Pd₁ /ZnO.

The observed higher selectivity to butene species for the bimetallic catalysts over monometallic Pd is ascribed to synergistic effect of the alloy in hydrogenation. Moreover, the adding of the second metal (Ni, Au and Ag) could increase selectivity to butene by favoring isomerization and subduing complete hydrogenation.²⁹ In addition, the observed difference in selectivity to total butene of the Ag₁Pd₁/ZnO catalyst compared to Ni₁Pd₁, and Au₁Pd₁/ZnO catalysts is as a result composition and to a large extent Ag₁-Pd₁ bonding with ZnO.



Figure 9. Catalytic performance of different S-Pd bimetallic catalyst on ZnO supports in 1, 3- butadiene hydrogenation

3.2.3. Effect of reaction temperature on catalytic activity

The catalytic performance of the Ni-Pd/ZnO catalyst at different reaction temperature (25 to 50 °C) is plotted in Figure 10 and the results over a 4 h is tabulated in Table S 10. Butane selectivity increased linearly with increasing temperature while selectivity to total butene decreased. The selectivity to 1-butene is observed to linearly decrease with increasing temperature while *Trans-2*-butene and *cis-2*-butene present an initial increase in selectivity from 25 to 35 °C and then decreases rapidly after 35 °C Figure 10 A.

Figure 10 B compares 1,3 butadiene conversion and yield against temperature. It is observed that, 1,3 butadiene conversion increases markedly from 59.6 % at 25 °C to 90.8 % at 30 °C then to 98.8 % at 35 °C then stabilizes to 100 % with increasing temperature. The calculated yield Figure 10 B shows an initial linear increase from 57.0 % at 25 °C to a maximum of 88.9 % at 35 °C, and then it decreases rapidly to 29.5 % at 50 °C. As reaction temperature increase from 25 to 50 °C, conversion of 1,3 butadiene and butane selectivity increased. This implied higher temperature promoted hydrogenation of 1,3 butadiene to butane and inhibited isomerization to obtain butene species.



Figure 10. Effect of reaction temperature on catalytic Activity (A) selectivity to butane and butene (B) conversion and yield of 1, 3butadiene

3.2.4. Catalyst stability

The durability of the catalyst was tested at 35 °C within a time on stream of 10 h. Figure 11 plots the selectivity to butene and conversion of 1,3- butadiene versus reaction time. As can be seen no apparent loss in both the selectivity to total butane and conversion of butadiene is observed over the 10 h period. Thus the biosynthesized Ni₁-Pd₁/ZnO catalyst possessed desired stability and excellent catalytic activity.



Figure11.Time on stream plot of conversion of 1, 3- butadiene and butene selectivity over the biosynthesized Ni₁-Pd₁/ZnO catalyst

4. Conclusion

In conclusion, vapor phase selective hydrogenation of 1,3-butadiene was studied on different biosynthesized S-Pd/M catalysts using *Cinnamomum Camphora* leaf extract as reducing and stabilizing agent. The process is simple, inexpensive and environmentally-friendly. Comparative

studies using different S-Pd bimetallic catalysts, and metal oxide supports were carried out. The bimetallic Ni₁-Pd₁/ZnO catalyst exhibited excellent selective hydrogenation of 1,3-butadiene with an overall butene yield of 88.93 compared to 46.92 % for Pd/ZnO which we attributed to the bimetallic synergistic effect. The effect of different support was more significant on hydrogenation activity and selectivity to total butene than S-Pd bimetallic composition. The chemical properties of the support, oxygen defects and strong metal-support (SMSI) interaction are assigned to be possible reasons for the marked difference is both hydrogenation performance and selectivity to butene. TiO₂ with the highest oxygen defect presented the maximum 1,3-butadiene conversions (100 %) while the highest butene selectivity was observed on the SiO₂ with the least number of oxygen defect. Finally, it was observed that, 1,3-butadiene conversion increased as reaction temperature increased and inhibited butene selectivity. The total 1-butene selectivity reduced from a maximum of 55.47 % at 25 °C to about 14.75 % at 50 °C.

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