Preparation and Catalytic Hydrodechlorination Property of Nano Bimetallic Catalyst Pd–Ni/γAl₂O₃–SiO₂

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Abstract: Pd–Ni bimetallic catalyst supported on a composite carrier of γAl₂O₃ and SiO₂ was prepared by chemical precipitation methodology enhanced with an ultrasonic wave. In the present paper, the influence of dispersant, carrier, ultrasonic time and intensity on the dechlorination property of the catalysts obtained are investigated. The appearance, morphology and structure of the prepared catalysts were characterized using X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), N₂ adsorption–desorption isotherm and X-ray photoelectron spectroscopy spectrometer (XPS). The chemical composition of active gradients in the catalysts was tested with inductively coupled plasma-atomic emission spectrometry (ICP-AES). The metal dispersion and mean particle size of the metallic phase of the prepared catalysts were also determined with CO chemisorption. Results indicate that a nano bimetal Pd–Ni catalyst on an average particle size of 2.45 nm with a distribution range of 1–7 nm supported on a composite carrier of γAl₂O₃ and SiO₂ can be effectively prepared, and that the chlorine content of shellac dechlorinated with the obtained catalyst is 0.18 wt%, which is lower than that reported in the previous literature, indicating the perfect dechlorination property of the catalyst.

Keywords: bimetallic catalyst; ultrasonic enhancement; catalytic hydrodechlorination; nanomaterials

1. Introduction

Most chlorine-containing organics have high thermal and chemical stability, which are not easy to be decomposed or biodegraded in natural conditions. Moreover, strong toxicity and carcinogenicity contained in the chlorine-containing organics are easy to be enriched in organisms of humans and cattle through food cycling and pose threats to human health and the safety of the natural environment [1]. Bleaching agent containing chlorine is often used in the modification process of seedlac, a natural product, resulting in the binding of chlorine contained in bleached shellac, which becomes a chlorine-containing organic, not only affecting the physical and chemical properties of the product, but also limiting its application in the food and pharmaceutical industries [2–4]. How to eliminate the chlorine contained in the bleached shellac has eventually become a hotspot for chemists in the domain of lac products.

In recent years, the removal of chlorine by the catalytic hydrodechlorination (HDC) process from organics containing chlorine has been a hotspot of research in the fields of environmental management and fine chemical engineering [5–8]. The research results show that Pd is an active component of an effective HDC catalyst, and the bimetallic catalyst modified by the second metal (e.g., Ni and Ru) and metal oxides (e.g., NiO and CeO₂) shows higher catalytic activity and stability [9–13]. In addition to reducing the cost of the catalyst, the pore size distribution and specific surface area of the catalyst carrier can be improved. The interaction between Pd and Ni and the stability resulting from bimetals enhance the catalytic activity of Pd [14,15]. Simagina et al. used a Pd–Ni/Ç bimetallic catalyst for HDC hexachlorobenzene [16]. A small amount of Pd was added into Ni to generate a Pd-Ni alloy
on the surface of the catalyst. Śrebowata et al. studied the Pd–Ni/C catalyst HDC of 1, 2-dichloroethane; the results show that when the temperature is below 230 °C, the double metal Pd–Ni/C catalyst has a stable dichlorination (DC) performance [17]. Studies by Liao et al. show that the bimetallic catalyst with Pd-Ni as the active ingredient was added into the solution after lac bleaching with hydrogen, and the chlorine added to the lac molecule ring terpene acid was replaced by hydrogen in the process of bleaching modification, thus obtaining the low-chlorine bleached shellac with 0.44% of chlorine mass fraction [18].

Studies on the preparation of Pd–Ni bimetallic catalysts mainly focus on single carriers, such as ZrO₂, γAl₂O₃, and active carbon, a small amount of research reports on composite carriers [19–21], and, moreover, the preparation methods used are mainly of impregnation and chemical precipitation [22,23]. While the latter method is performed, the catalyst with a large specific surface area can be obtained due to strong the interaction and reaction between the supporting metal and the carrier [24]. The chemical precipitation enhanced with the ultrasonic wave, a novel methodology, is employed in the present study for the preparation of the nano Pd–Ni bimetallic catalyst supported on the composite carrier consisting of γAl₂O₃ and SiO₂. Not only were the influence of the parameters, such as the pH value, ultrasonic wave, deposition temperature, carrier, and the dosage of dispersants on the dichlorination (DC) performance of the catalyst for chlorine removal in bleached shellac by catalytic hydrogenation investigated, but the morphology characteristics and structure of the prepared catalyst were also characterized.

2. Results and Discussion

2.1. The Influence of the Preparation Conditions on the DC Properties of the Catalyst

2.1.1. The Influence of the Ultrasonic Sound

The precursors for the preparation of catalysts were obtained at the same conditions of precipitation under a stirring speed of 500 r/min for 1 h at 40 °C, when the dis-persant with an amount of 3 wt% to the mass of the carrier at pH 11.5 was added, fol-lowed by dispersal under the different parameters with respect to the ultrasonic sound. Afterwards, the catalysts with a Pd mass fraction of 1.0 wt% and mass ratio 1:1 of Pd to Ni supported on the carrier composited with γAl₂O₃ and SiO₂ with a mass ratio of 1:1 were prepared using the precursors. The time duration of the ultrasound emission was in pulse mode at 50%, whose irradiation period was one half of the active time, and the apparatus was silent in one half of the pulse [25]. The influence of ultrasonic time and ultrasonic power density [26] on DC performance of the catalyst prepared shown in Figure 1 (see Supplementary Materials for detailed data).

![Figure 1](image-url)  
Figure 1. Influence of ultrasonic time at 60% intensity (a) and ultrasonic power density at 5 min (b) on the catalytic DC property.

It can be observed from Figure 1 that the DC performance of the catalyst obtained without or with ultrasonic dispersion at different times is different. The catalyst prepared
by dispersion with ultrasonic sound for 5 min with power reaching 60% (ultrasonic output power: 720 W) has a good DC performance.

The hydroxide of the active component should be thoroughly deposited and homologically distributed, grown on the carrier for obtaining the precursor to further prepare the Pd–Ni/γAl₂O₃–SiO₂ bimetallic catalyst, which requires sufficient crystal nuclei. Under the action of the ultrasonic wave, bubbles produced in the reaction system continuously vibrated. When the sound pressure of the ultrasonic wave reaches a certain value, this leads to the dynamic process of the crystal growth and collapse, resulting in the cavitation phenomenon and providing a large number of ultrafine crystal nuclei with the energy required for growth and increasing the nucleation rate. Under normal circumstances, the phenomenon in which particles continuously reunite occurs at the growth stage of the crystal nucleus, inducing a larger particle size and un-uniform distribution of active components. On the contrary, with respect to the conditions dispersed by the ultrasonic sound, a large number of bubbles produced a strong shock, destroying the surface adsorption force between the particles and leading to the decomposition of the hydrogen bond, with the result that the particles separated from each other and effectively prevented the particles from uniting [27–29], thus resulting in the further preparation of the catalyst with a good DC performance. Additionally, in the duration of the pulse, the thickness of the diffusion layer can be effectively reduced and the nucleation rate becomes faster with the increase in the intensity of the ultrasonic wave, and then the grain size can be reduced. However, when the intensity of the ultrasonic wave exceeds a certain value, the grain size of the particles increases instead of decreasing, thus reducing the DC performance of the catalyst [30].

2.1.2. The Influence of the Carrier

The catalysts with a Pd mass fraction of 1.0 wt% and mass ratio 1:1 of Pd to Ni supported on different kinds of carriers were prepared with the precursors obtained during the conditions of precipitation under a stirring speed of 500 r/min for 1 h at pH 11.5 and 40 °C, and the amount of dispersant of 3 wt%, after dispersal with ultrasonic sound for 5 min at 60% intensity (ultrasonic output power: 720 W). The influence of carrier on DC performance of the prepared catalyst is shown in Figure 2 (see Supplementary Materials for detailed data), which indicates that the catalytic DC performance of the catalyst supported on the composite carrier is better than that of the single carrier, and that the catalytic DC performance of the catalyst supported on the carrier fraction γAl₂O₃ and SiO₂ of 1:1 is better than other proportions.

![Figure 2. Influence of the carrier mass ratio on the catalytic DC property.](image)

γAl₂O₃ has a smaller average particle size and higher activity, which enhances the DC performance of the Pd–Ni bimetallic catalyst. SiO₂ can adsorb more active metals on the surface and internal structure of the catalyst due to its larger internal pores and larger specific surface area, which can help to improve the catalytic activity of the catalyst.
Therefore, the mass content ratio of γ-Al₂O₃ and SiO₂ in the carrier has a key effect on the particle size and the DC of the Pd–Ni/γ-Al₂O₃–SiO₂ bimetallic catalyst.

2.1.3. The Influence of the Pd–Ni Ratio

For the purpose of investigating the influence of the mass ratio of Pd to Ni, the catalysts with a different mass ratio of Pd to Ni that supported the carrier compositied with γ-Al₂O₃ and SiO₂ with a mass ratio of 1:1 were prepared using different precursors obtained in the conditions of precipitation under a stirring speed of 500 r/min for 1 h at pH 11.5 and 40 °C and the amount of dispersant of 3 wt%, after being dispersed with ultrasonic sound for 5 min at 60% intensity (ultrasonic output power: 720 W). The metal dispersion and mean particle size of the metallic phase of the prepared catalysts are listed in Table 1. Accordingly, the experimental results for the DC of the catalysts are presented in Table 2, which indicates that the catalyst introduced with the second-phase metal Ni to form the bimetal with the active component of Pd has a high DC performance, and the DC performance of the catalyst supported by the composite carrier is higher than that of the single carrier, while the Pd–Ni ratio is 1:1, being consistent with the results reported in the literature [10,14,16].

Table 1. Metal dispersion (D, %) and mean particle size (\(\bar{d}_i\), nm) of the metallic phase of the prepared catalyst.

| Catalyst | STEM \(\bar{d}_i\) | CO Chemisorption D \(\bar{d}_i\) |
|----------|---------------------|-------------------------------|
| Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 2.45 ± 0.75 | 34.21 |
| Pd–Ni/γ-Al₂O₃ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 4.91 ± 1.25 | 30.46 |
| Pd–Ni/SiO₂ (m(Pd):m(Ni) = 1:1, ω(Ni) 1.0 wt%) | 3.57 ± 1.02 | 28.34 |
| Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 5:1, ω(Pd) 1.0 wt%) | 3.72 ± 1.08 | 23.61 |
| Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 2:1, ω(Pd) 1.0 wt%) | 3.65 ± 1.15 | 27.43 |
| Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 5:4, ω(Pd) 1.0 wt%) | 2.60 ± 0.95 | 32.25 |
| Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 5:6, ω(Pd) 1.0 wt%) | 2.65 ± 0.85 | 33.40 |

Table 2. Experimental results of catalytic HDC for shellac by the prepared catalyst.

| Item | Catalyst Type | Chlorine/wt% |
|------|---------------|--------------|
| Raw material | | 1.95 |
| Dechlorinated shellac | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 0.18 |
| Dechlorinated shellac | Pd/γ-Al₂O₃–SiO₂ (ω(Pd) 1.0 wt%) | 0.45 |
| Dechlorinated shellac | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 5:1, ω(Pd) 1.0 wt%) | 0.42 |
| Dechlorinated shellac | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 2:1, ω(Pd) 1.0 wt%) | 0.32 |
| Dechlorinated shellac | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 5:4, ω(Pd) 1.0 wt%) | 0.22 |
| Dechlorinated shellac | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 5:6, ω(Pd) 1.0 wt%) | 0.26 |
| Dechlorinated shellac | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 0.24 |
| Dechlorinated shellac | Pd–Ni/SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 0.38 |

Note: chlorine content listed in the table is the average result of three parallel experiments under the temperature conditions of 80 °C, time of 1.5 h, and stirring speed of 300 rpm.

2.1.4. The Optimal Conditions for the Preparation of the Catalyst and the DC Properties of the Prepared Catalyst

The research results of the influence on DC performance show that the prepared parameters plays a dominant role, such as the ultrasonic wave, amount of dispersant, mass ratio of the carrier and carrier type, and mass ratio of the active component. The optimal preparation conditions within the research scope for obtaining the Pd–Ni/γ-Al₂O₃–SiO₂ catalyst is firstly the preparation precursor under the conditions of a Pd mass fraction of 1.0 wt% and mass ratio 1:1 of Pd to Ni supporting the carrier compositied with γ-Al₂O₃ and SiO₂ with a mass ratio of 1:1, stirring speed of 500 r/min for 1 h at pH 11.5 and 30 °C and the amount of dispersant of 3 wt% after dispersal with ultrasonic sound for 5 min at 60% intensity (ultrasonic output power: 720 W). Subsequently, the obtained precursor is roasted in an air atmosphere at 500 °C for 2.5 h, and further reduced under the condition of a mixed atmosphere of hydrogen and nitrogen at 500 °C for 2 h.
The properties of the catalyst prepared under the optimal condition for chlorine removal combined in shellac are shown in Table 3, which shows that the Pd–Ni/γ-Al₂O₃–SiO₂ bimetallic catalyst has a good DC performance, and that the chlorine mass fraction in the DC product is 0.21 wt% when the catalyst is re-cycled 5 times, which is significantly less than the reported value of 0.44 wt% [18,31,32].

Table 3. Experimental result of the catalytic HDC for shellac by the prepared catalyst.

| Item                           | Catalyst Type                                      | Chlorine/wt% |
|--------------------------------|---------------------------------------------------|--------------|
| Raw material                   | -                                                 | 1.95         |
| Dechlorinated shellac          | Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 0.18         |
| Shellac dechlorinated with catalyst cycled 5 times | Pd/γ-Al₂O₃–SiO₂ (ω(Pd) 1.0 wt%) | 0.21         |

Note: chlorine content listed in the table is the average result of three parallel experiments under the temperature conditions of 80 °C, time of 1.5 h, and stirring speed of 300 rpm.

2.2. The Characterization of the Catalyst

To investigate the catalytic HDC performance of the catalysts with a Pd mass fraction of 1.0 wt% and mass ratio of Pd to Ni = 1:1, the supported carrier composited with γ-Al₂O₃ and SiO₂ with a mass ratio of 1:1 was obtained under optimal conditions, and the specific features of the catalyst, such as the mass fraction of the active constituent, physical and chemistry properties, and phase and morphology, were characterized by ICP, N₂ adsorption, STEM, XRD, and XPS.

2.2.1. ICP and N₂ Adsorption

The mass fraction of Pd and Ni determined by ICP, and the specific surface area, as well as the pore volume tested by N₂ adsorption, are shown in Table 4. It can be observed from Table 4 that the content of palladium and nickel in the catalyst is slightly different from the addition amount nominated (1.0 wt%), and the specific surface area of the Pd–Ni/γ-Al₂O₃–SiO₂ composite bimetal catalyst is mainly affected by the SiO₂ carrier. In addition, the bimetal catalyst has a pore volume of 0.46 cm³/g, which is evidently consistent with the pore volume of the carriers used. As a result, the chemical precipitation process enhanced by the ultrasonic wave can effectively load active metal palladium and nickel, and the specific surface area and pore volume of the carrier are not significantly influenced by the supported active metal Pd and Ni.

Table 4. Physico-chemical properties of carriers and Pd–Ni/γ-Al₂O₃–SiO₂.

| Materials                  | Specific Surface Area (m²/g) | Pore Diameter (nm) | Pore Volume (cm³/g) | ω(Pd) (wt%) | ω(Ni) (wt%) |
|----------------------------|------------------------------|--------------------|---------------------|-------------|-------------|
| γ-Al₂O₃                    | 172.43                       | 12.39              | 0.45                | -           | -           |
| SiO₂                       | 155.14                       | 18.50              | 0.46                | -           | 0.96        |
| Pd–Ni/γ-Al₂O₃–SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) | 152.68                       | 19.12              | 0.46                | 0.96        | 0.98        |

In comparison to the standard classification by the International Union of Pure and Applied Chemistry (IUPAC) [33], the nitrogen isothermal adsorption–desorption equilibrium curve of the Pd–Ni bimetal catalyst-supported γ-Al₂O₃–SiO₂ composite carriers was in accordance with the stripping absorption isotherm curve of V class (Figure 3), and the hysteresis loop in the curve corresponds with type H1, indicating the existence of uniform cylindrical pores in the bimetallic catalysts [34].
The adsorption types of most mesoporous materials change under lower relative pressure, which transforms into multilayer adsorption from monolayer adsorption. When the pressure reaches a certain value, capillary condensation occurs, manifesting as a sudden increase or a sudden decrease in the adsorption–desorption isotherm. Moreover, the larger the pore diameter of the mesoporous materials, the greater the pressure capillary condensation process. However, the adsorption–desorption curve in Figure 4 shows a gentle trend without an abrupt incline or abrupt decline. The main reason for this may be that there is a large number of micropores in the bimetal catalyst in addition to the mesoporous ones, which results in the condensation of N\textsubscript{2} in the pores, resulting in slow desorption.

Figure 3. N\textsubscript{2} adsorption–desorption isotherm of the Pd–Ni/γAl\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} bimetallic catalyst.

Figure 4. XRD pattern of the Pd–Ni/γAl\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} bimetallic catalysts at different reduction times.

2.2.2. XRD and STEM

The XRD patterns of the Pd–Ni/γAl\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} catalyst obtained by reduction for 1–3 h are presented in Figure 4. The diffraction peaks at 2 theta of 40.05° and 46.70° are the characteristic diffraction peaks of palladium in a face-centered cubic structure on the crystal planes (111) and (200), respectively (PDF46-1043). No diffraction peak for Ni or NiO was found in the XRD patterns, concluding that the Pd–Ni alloy was formed [35]. According to the Scherrer formula calculation (K = 0.89) [36], the particle size of the Pd grain in the catalyst is 8.38 nm.

Combined with the construction patterns of the Pd–Ni/γAl\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} catalysts by STEM (Figure 5a), it can be determined that the Pd–Ni bimetallic particles are evenly distributed on the surface of the carrier. In Figure 5a, the white spot dispersed on the carrier material is the loaded Pd–Ni. The particle size of Pd–Ni is calculated as 2.45 nm, and the particle size range is 1–7 nm. The particle size distribution is shown in Figure 5b. The
results of the STEM statistics show that the active components of the Pd–Ni/γAl2O3–SiO2 bimetal catalysts are highly dispersed on the carrier, with a small particle size and narrow distribution range of the active components.

Figure 5. STEM (a) and particle size distribution histogram (b) of Pd-Ni/γAl2O3-SiO2 catalyst.

2.2.3. XPS

The chemical states of Pd and Ni in the Pd–Ni bimetallic catalyst supported on the carriers compositied with gamma Al2O3 and SiO2 were further investigated by XPS. The XPS spectra of the Pd 3d and Ni 2p are presented in Figures 6 and 7, respectively; all the binding energies (BEs) refer to the C1s peak at 284.8 eV of the surface adventitious carbon to compensate for the effect of surface charging.

Figure 6. XPS spectra of the Pd 3d peaks of PN-1:1.

The Pd 3d XPS spectrum could be decomposed into four components at BE = 333.2, 335.0, 338.5, and 340.3 eV (Figure 6). The ones at BE = 335.0 and 340.3 eV correspond to the 3d5/2 and 3d3/2 levels of the zero-valent palladium (Pd0) species, which is in good agreement with the determination of the BE of the zero-valent palladium [37,38], whereas the ones at BE = 333.2 and 338.5 eV correspond to the Pd2+ species; however, this value is quite different from previous reports on Pd2+ [39,40], probably due to the strong interaction between Pd and double supports.

Similar to the results obtained for Pd 3d5/2 BE, the XPS response for the Ni 2p3/2 core-level spectrum consists of 2 peaks at 854.3 and 862.0 eV, respectively (Figure 7). The former is inconsistent with the BE of the zero-valent nickel (855.0 eV) due to the existence of Ni2+ species [41,42]. The latter at a higher BE is related to the Ni2+ species, which may originate from the combination of the Ni constituent and the Pd component to form Pd–Ni bimetallic nanoparticles [43].
The chemical states of Pd and Ni in the Pd–Ni bimetallic catalyst supported on the single carrier (Pd–Ni/γ-Al₂O₃–SiO₂, m(Pd): m(Ni) = 1:1, ω(Pd) 1.0 wt%), and the Pd–Ni bimetallic catalyst supported on the single carrier (Pd–Ni/γ-Al₂O₃, m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%) and Pd–Ni/SiO₂ (m(Pd):m(Ni) = 1:1, ω(Pd) 1.0 wt%), mainly due to the following two reasons. First of all, Pd is the main active component of the catalyst for the hydrogenation reaction. The bimetal catalyst with a Pd base formed by adding the second component metal Ni can enhance the catalytic activity of Pd [14,15]. Secondly, STEM (Figure 5a) and STEM (Figure 5b) analysis and characterization indicate that the average particle size of the active catalyst Pd–Ni prepared in this study is 2.45 nm, and its distribution range is 1–7 nm. The smaller and narrower the particle size of the active ingredients, the greater the catalytic activity [44,45].

3. Materials and Methods

3.1. Materials

γ-Al₂O₃ (99.99 wt%) with an average particle size of 20 nm and specific surface area of 172.43 m²/g, as well as SiO₂ (99.8 wt%) with a mean particle size of 30 ± 5 nm and specific surface area of 155.14 m²/g purchased from Xuan Cheng Jing Rui New Material Co., Ltd. (Xuancheng, China) were used in the experiments of the present work. PdCl₂ with a Pd
content higher than 59.5 wt% was purchased from Shanxi Kaida Chemical Engineering Co., Ltd. (Baoji, China). Ni(NO$_3$)$_2$·6H$_2$O, HCl, NaOH, and polyethylene glycol (PEG-6000), all in analytical reagents, were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Additionally, double-distilled water was used in the experiment.

3.2. The Catalyst Preparation Procedure

A total of 89.3 mg PdCl$_2$ was weighed and dissolved in 100 mL 0.5 mol/L HCl solution. Then, a certain amount of Ni(NO$_3$)$_2$·6H$_2$O and carrier were added into the solution. The addition amount of Ni(NO$_3$)$_2$·6H$_2$O was determined according to the mass ratio of Pd to Ni. The carrier was made of a single compound of γ-Al$_2$O$_3$ or SiO$_2$, or a composite consisting of γ-Al$_2$O$_3$ and SiO$_2$, with a total mass of 5.0 g. While composed by γ-Al$_2$O$_3$ and SiO$_2$, the addition ratio was determined according to the experimental conditions. While the pH value of the slurry obtained was adjusted by 11.5 with an NaOH solution of 0.2 mol/L, a 0.15 g (amount of 3 wt% to mass of carrier) dispersant (polyethylene glycol) was added and then dispersed with an ultrasonic cell crushing apparatus (UH-1200E, Tianjin Autosience Instrument Co., Ltd., Tianjin, China) for a specified time, and then precipitated for 1 h under a stirring speed of 500 rpm at 40°C with a cantilevered electric mixer (GZ, Jiangyin Boli scientific instrument Co., Ltd. Jiangyin, China) in a digital water bath kettle (HH-S1, Changzhou Nuoji instrument Co., Ltd. Changzhou, China). Subsequently, the sludge as-received was filtrated under vacuum conditions with a circulating water vacuum pump (SHZ-D III, Gongyi instrument Co., Ltd., Gongyi, China), the filter cake obtained was washed with distilled water until no Cl$^-$ could be tested in the filtrate, and was dried at 60°C in a digital display drying oven (MGE GZX-9030, Shanghai Boxun industrial Co., Ltd. Shanghai, China) for 12 h to obtain the precursor of the catalyst. Finally, the monometallic Pd and/or bimetallic catalysts with different Pd–Ni ratios supported over different carriers were prepared after the precursors were roasted in a tubular atmospheric furnace (KSYO-6.3-16C, Shanghai Yifeng electric Co., Ltd. Shanghai, China) at air atmosphere at 500°C for 2.5 h and then reduced in mixing gases with nitrogen and hydrogen (the hydrogen and nitrogen flow were 0.15 L/min and 0.3 L/min, respectively, at ambient temperature and atmospheric pressure) at 500°C for 2 h.

3.3. The Experimental Procedure on the DC Performance and Activities of the Catalyst

To investigate the DC properties of the prepared catalysts, DC experiments of chlorine combined in bleached shellac were carried out by using Pd–Ni bimetallic catalysts supported over different carriers, γ-Al$_2$O$_3$, SiO$_2$, and/or composites of γ-Al$_2$O$_3$ and SiO$_2$, and the catalyst of Pd supported on the composite carrier of γ-Al$_2$O$_3$ and SiO$_2$. The bleached shellac used in the study was purchased from a company in Yunnan province, and the experiment of the catalytic HDC in liquid phase was conducted to eliminate the chlorine combined in shellac referring to the DC reaction conditions reported [18]. Take 100 g of bleached shellac dissolved in 700 mL 95% ethanol (in volume), then 2.1 g of prepared catalyst was added to react under the conditions of a hydrogen flow rate of 0.1 L/min at 80°C for 1.5 h. Consequently, the product of the reaction was filtered to separate the catalyst used under vacuum while cooling to room temperature, then the obtained filtration was distilled for the separation of ethanol under vacuum. Finally, dechlorinated bleached shellac was obtained after the remains from the distillation were washed with the double distilled water and dried in the oven at vacuum.

The catalytic performance of the prepared catalysts was evaluated by DC efficiency that was calculated as the following Equation (1). The catalytic activity of the catalyst was evaluated by the DC efficiency of the catalyst after continuous use for five times. This was performed as the catalyst, isolated by filtration under vacuum conditions in the first DC experiment, continues to be used circularly in the subsequent DC experiment with bleached shellac.

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$ (1)
where $\eta$ is the DC efficiency, in wt%; $C_0$ is the initial content of the chlorine in the raw material, in wt%; $C_t$ is the chlorine content in the product that is dechlorinated with the catalyst, in wt%.

3.4. The Analyzing Procedure and Method of Characterization

The mass fraction of the Pd and Ni contained in the prepared catalyst was determined by the inductively coupled plasma atomic emission spectrometer (ICP-AES, ThermoScientific iCAP 6500 radial, Waltham, MA, USA), and the content of chlorine in the bleached shellac, before and after the DC was determined according to the method of GB/T 8143-2008 [46].

The parameters, such as the specific surface area and pore volume of the bimetallic catalysts prepared, were tested using a nitrogen adsorption analyzer (Quadrasorb-evo, Quantachrome Instruments, Boynton Beach, FL, USA) under the conditions of an operating temperature of 150 °C. Before testing, the sample was degassed under vacuum for 3 h. The phase composition of the catalyst, and crystallinity and grain size of the active component were detected by X-ray diffraction analysis (XRD) using a PANalytical X’Pert Pro diffractometer (PANalytical, Almelo, The Netherlands), equipped with an X’Celerator detector (analytical conditions: CuKα at 30 kV and 20 mA, $\lambda = 0.15045$ nm, 2theta range 10–80°). The morphology, particle size, and distribution of the bimetal catalyst samples were observed by using a Tecnai G2 TF30 (Dutch FEI Company, Eindhoven, The Netherlands) scanning transmission electron microscope (STEM/TEM). Approximately 200 individual metal particles were counted for the prepared catalyst and the mean metal particle size was calculated as the surface-area-weighted average size ($\bar{d}_i$) according to Equation (2).

$$\bar{d}_i = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where $n_i$ is the number of particles of diameter $d_i$. These data were reported at a 95% confidence interval. Moreover, the metal dispersion (D) and the mean metal particle size ($\bar{d}_i$) of the prepared catalysts were also determined from the CO chemisorption at room temperature in a Micromeritics Chemisorb 2750 automated system equipped with ChemiSoft TPx software.

An X-ray photoelectron spectroscopy spectrometer (XPS) (Japanese ulvac-phi, PHI5000 Versaprobe II) with an Al Kα radiation source operating at 15 kV and 50 W was used to characterize the binding forms of Pd and Ni in the catalyst, and high resolution scans of the elemental lines were recorded at a 46.95 eV pass energy of the analyzer to identify the chemical state of each element. In order to discharge the pollution, the energy spectrum line was corrected with C 1s photoelectron binding energy (284.8 eV).

4. Conclusions

(1) The nano bimetal catalyst Pd–Ni supported by the composite carrier of $\gamma$Al$_2$O$_3$ and SiO$_2$ can be effectively prepared by the method of chemical precipitation enhanced by the use of ultrasonic sound. An ultrasonic wave, the additional amount of dispersant, the property and mass ratio of the carrier, and the proportion of active ingredients all have effects on the DC performance of the prepared catalyst.

(2) The optimal conditions to prepare the precursor for the catalyst is stirring precipitation for 1 h at 40 °C and pH 11.5 under the speed of 500 r/min, after a 5 min dispersal with ultrasonic sound at an intensity of 60% (ultrasonic output power: 720 W), while the carrier mass ratio is 1:1 and the amount of polyethylene glycol added is 3 wt%. Additionally, the catalyst Pd–Ni/$\gamma$Al$_2$O$_3$–SiO$_2$ (m (Pd): m (Ni) = 1:1, $\omega$ (Pd) 1.0 wt%) prepared with the precursor obtained as a result of the conditions has a perfect DC performance.

(3) In comparison to the carrier before the adsorption of the active metal, the specific surface area and the pore volume of the catalyst does not significantly change. Additionally, the dispersion degree of the active ingredient in the catalyst is high, and the average particle size of Pd–Ni is 2.45 nm with a distribution range of 1–7 nm.
(4) The catalytic hydrogenated DC performance of the catalyst has good stability. The chlorine mass fraction of the product after being dechlorinated with the catalyst is 0.18 wt%, and it is 0.21 wt% when the catalyst is re-cycled 5 times, which is still lower than that reported in the literature.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12040370/s1, Table S1: The data of Figure 1a, Table S2: The data of Figure 1b, Table S3: The data of Figure 2.

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Data Availability Statement: The data will be sent with the present study as supplemented file.

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