Green-synthesized silver nanoparticles decorated on ceria nanorods for room-temperature p-nitrophenol hydrogenation

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\textbf{ABSTRACT}

In this study, silver nanoparticles (AgNPs) loaded on pre-formed CeO\textsubscript{2} nanorods (Ag-Ce) were synthesized using \textit{Jasminum subtriplinerve} Blume leaf extract as a reduc- ing agent. The mesoporous structure of CeO\textsubscript{2} was confirmed by the N\textsubscript{2} adsorption/desorption study, indicating type IV isotherms with an H3-type hysteresis loop. The high specific surface area of the Ag-Ce samples was discovered in the range of 74–80 m\textsuperscript{2}/g with an average pore diameter of 23.2–23.4 Å, and a pore volume of 0.091–0.093 cm\textsuperscript{3}/g (pure CeO\textsubscript{2} of 72 m\textsuperscript{2}/g, 23 Å, and 0.098 cm\textsuperscript{3}/g, respectively). Silver nanoparticles with spherical shapes (5–10 nm in diameter) were well dispersed on the surface of CeO\textsubscript{2} nanorods (100–200 nm in length and 20–30 nm in diameter), as shown by X-ray diffraction (XRD), Energy-dispersive X-ray (EDX) and high-resolution transmission electron microscopy (HR-TEM). Their catalytic reactivity was investigated in the hydrogenation of p-nitrophenol (p-NP) toward p-aminophenol (p-AP) using NaBH\textsubscript{4} at room temperature, exhibiting better reactivity of the Ag-Ce samples than pure CeO\textsubscript{2} nanorods. The 0.2Ag-Ce sample (0.2 wt.% Ag) showed the complete conversion of p-NP toward p-AP after 3 min using 0.2 g/L catalysts.

\textbf{INTRODUCTION}

Nowadays, the development of industrial processes has an impact on human, environmental problems, and the eco-system, especially in chemical manufacturing operations. In some cases, the quality of wastewater cannot be controlled for various reasons. Pollution by persistent organic pollutants (POPs) in wastewater is one of the most severe issues (1). Nitrophenols, the POPs in the pharmaceutical, plastic, pesticide industry, and amino compounds production, are highly toxic, hazardous substances and may harm the natural environment and eco-system (2, 3). Currently, the main techniques for handling nitrophenol compounds are (1) removing them from wastewater using chemical oxidation, photocatalytic degradation, microbial process, and physical adsorption, (2) converting them into valuable products using catalytic hydrogenation (4). The second approach seems more beneficial because it can remove these...
toxic compounds and produce economically helpful products. Typically, p-aminophenol (p-AP), as the product from catalytic hydrogenation of p-nitrophenol (p-NP) (5), is an essential intermediate in pharmaceuticals, synthetic dyes, pesticides, etc. Aminophenols have more significant economic and social benefits than nitrophenols, thus accepting numerous research interests (6).

Most catalysts for the hydrogenation of p-NPs, based on noble metal nanomaterials (such as Pt, Pd, and Au), are controlled in size and shape or deposited on suitable supports (7–9). The catalytic hydrogenation of p-NPs on precious metals usually follows four steps (4, 7): (1) adsorption of p-NP, (2) diffusion on the active sites, (3) conversion into p-AP on the catalyst surface, and (4) desorption of p-AP from the catalyst surface. Practically, noble metal-based nano-catalysts have high catalytic activity and stability, but require cumbersome preparation processes (10, 11). Moreover, the gradual exhaustion and increasingly high price of noble metals severely limit their large-scale industrial production. Therefore, alternative catalysts with equivalent (or even higher) catalytic activity should be developed on cost-effective, readily available, and eco-friendly processes.

In comparison with the mentioned metals, silver nanoparticles (AgNPs) practically showed higher chemical activity in such reactions but at a lower cost (12–15). Recently, the features of p-nitrophenol hydrogenation over Ag-based catalysts were summarized by Liao et al. (16), regarding the catalytic properties of Ag-based nanoparticles: size, shape, agglomeration/dispersion, support, pre-treatment conditions, nature of precursors, etc. Besides, effective and eco-friendly processes to prepare AgNPs have also been attractive, mainly using plant extracts as reducing and capping agents and without adding toxic chemicals (17, 18). The phytochemicals in plant extracts have been widely utilized to reduce Ag⁺ ions toward Ag⁰ (19), providing a green route applied to environmental treatment (20–22) and antibacterial (23–25). Despite developing several methods to protect humans from bacteria, nanomaterials (typically AgNPs) still play a significant role in this issue. On these approaches, AgNPs synthesized by green processes have brought a new horizon of multifunctional nanomaterials (26). Many researchers have taken the initiative in this field, using the photothermal effect (27) or light irradiation on heterostructured nanomaterials (28), inhibiting the replication of multidrug-resistant bacteria.

In our previous study (29), silver nanoparticles were synthesized using Jasminum subtriplinerve Blume (JS) leaf extract as reducing agents. The results demonstrated the presence of flavonoid, terpenoid, polyphenol, and glycosides in phytochemical compositions of the JS extract, which acts as a reducing agent for the formation of AgNPs. The optimized conditions for the synthesis of AgNPs were determined involving the light illumination, the synthesis time of 150 min, the volume ratio of AgNO₃ solution/JS extract of 18/2, the AgNO₃ concentration of 1.0 mM, and the stirring rate of 300 rpm at room temperature. The as-prepared AgNPs were formed as highly crystallized spherical particles with the nano-size range of 20–30 nm. However, the catalytic activity and stability of silver nanoparticles should be further improved. From an industrial application point of view, supported silver nanoparticles are still preferred because of their higher activation and better dispersion.

Ceria (CeO₂) has been known as an oxygen container for a long time. For many years, CeO₂ has become one of the most essential materials in catalytic processes thanks to its high oxygen ion conductivity (30–32). With the advantage of the redox property, ceria can be easily adjusted between reduced and oxidized states that cause the donation and reception of oxygen, increase the metal–support interaction, and promote the dispersion of metal species (31). Besides, CeO₂ can also absorb and desorb H₂O to give O⁻ and OH⁻, which is beneficial to p-NP hydrogenation (10). In particular, CeO₂ nanorods have been attractive thanks to the unique properties derived from low dimensionality and high surface area (33). CeO₂ nanorods are prone to expose two (110) planes and four (110) planes, more diverse than other CeO₂ shapes (34).

In this study, Ag-doped CeO₂ nanorods (Ag-Ce) with various Ag contents were synthesized by the green method, using the JS leaf extract as a reducing agent for Ag⁺ toward Ag⁰, based on ceria nanorods prepared by the hydrothermal method. The influences of Ag loading on their physicochemical properties and catalytic activity in p-NP hydrogenation toward p-AP were also investigated.

**Experimental**

**Materials**

AgNO₃ and Ce(NO₃)₃·6H₂O were purchased from Merck. NaOH and NaBH₄ were obtained from Xilong. All chemicals are used as received without purification. Jasminum subtriplinerve Blume leaf (JS) was collected from Phu Yen province of Vietnam. After washing, shredding, and drying to constant weight, 50 g of JS leaf were mixed with 1000 mL of deionized water and heated to 80°C for 2 h under stirring. Finally, the JS extract was filtered and preserved at 4°C.
Synthesis of silver nanoparticles decorated on ceria nanorods

A series of Ag/CeO$_2$ samples were prepared with three metal loadings (0.1, 0.2, and 0.3 wt.% Ag). Firstly, 2.17 g Ce(NO$_3$)$_3$·6H$_2$O and 15.4 g NaOH were dissolved in 20 and 55 mL distilled water, respectively. Then, NaOH was dropped continuously in the Ce(NO$_3$)$_3$ solution. The mixture was stirred at 600 rpm and kept going for 1 h. The mixture was then transferred to a Teflon bottle, packed in a tightly sealed autoclave, and hydrothermally treated at 130°C for 5 h. After that, the precipitate was separated and washed with distilled water until pH 7. The precipitate was centrifuged and dried at 80, 100, and 120°C for 2 h at each temperature to obtain CeO$_2$ nanorods.

The synthesis of Ag-doped CeO$_2$ nanorods using the JS extract as a reducing agent under light illumination was done according to our previous study (29). 45 mL AgNO$_3$ 1.0 mM was mixed with 5 mL JS extract, then stirred at 300 rpm. Subsequently, CeO$_2$ nanorods with particular contents were added under stirring, and the reaction time was 150 min under sunlight illumination. The catalysts of Ag-loaded CeO$_2$ nanorods are denoted as following xAg-Ce (x = wt.% Ag).

Characterization of samples

The physical–chemical characteristics of the obtained samples were studied by several methods, including X-ray diffraction on Bruker D2 Phaser X-ray Diffractometer with Cu Kα radiation and recorded in 2θ = 10–80°, EDX spectrum on JEOL JST-IT 200 instrument, Raman spectra on a laser Raman spectrometer (Invia, Renishaw, UK), Fourier transform infrared spectrum on Tensor 27 Bruker instrument from 400 to 4000 cm$^{-1}$, Nitrogen adsorption–desorption isotherms on a Nova 2200e instrument, transmission electron microscopy on a JEOL JEM 1400 instrument, and Hydrogen temperature-programmed reduction (H$_2$-TPR).

The crystallite sizes of samples were calculated using the Scherrer equation (35):

$$d_{(nm)} = \frac{K\lambda}{\beta \cos \theta}$$ (1)

where $K$, the Scherrer constant, is 0.94, $\lambda$ is the wavelength of the X-ray, $\beta$ is the line width at half the maximum height of the peak in radians, and $\theta$ is the position of the peak in radians.

H$_2$-TPR was measured in a quartz microreactor using a reductant gas mixture of 10 mol% H$_2$/Ar at a flow rate of 30 mL/min with a 50 mg of sample. First, the sample was pre-treated with a high purity Ar flow for 30 min at 200°C to remove any surface impurities. Next, it was cooled down to 50°C and then heated up to 900°C with a ramping rate of 10°C/min in H$_2$/Ar flow. The consumed H$_2$ amount for the reduction of the sample was monitored by a gas chromatograph (GOW-MAC 69-350) equipped with a thermal conductivity detector (TCD).

The catalytic activity of samples

The catalytic performance of as-prepared Ag-Ce samples was investigated in the p-NP hydrogenation in the presence of NaBH$_4$ at room temperature. First, NaBH$_4$ was added to the 250 mL of an aqueous p-nitrophenol solution (20 mg/L) under magnetic stirring of 300 rpm to produce a homogeneous solution. Then as-synthesized catalyst was added to the mixture under stirring. At a given time interval, 2 mL aliquot was collected and then filtered to remove all the catalysts; the reaction solution was diluted five times and analyzed using a UV-visible spectrophotometer UV-1800 (Shimadzu) at 400 nm.

In this work, factors affecting the reaction rate were evaluated, involving Ag content, catalyst concentration, and p-NP/NaBH$_4$ molar ratio. Metal loadings (0.1, 0.2, and 0.3 wt.%) were first analyzed, then catalyst concentrations from 0.1 to 0.25 g/L were assessed; finally, p-NP/NaBH$_4$ molar ratios, including 1/150, 1/175, 1/200, and 1/225, were tested to obtain the best conditions for such a reaction.

The recyclability for the p-NP hydrogenation of the best catalyst was tested at the optimized reaction conditions for five cycles. The reaction solution was removed at the end of each batch and replaced by a fresh reaction solution to conduct the p-NP hydrogenation in succession.

Results and discussion

The XRD patterns of the CeO$_2$ nanorods (rCe) and Ag-decorated CeO$_2$ catalysts are shown in Figure 1(a). The XRD patterns of the pure CeO$_2$ sample showed the diffraction peaks at 2θ of 28.5, 33.1, 47.4, 56.3, 59.0, 69.4, 76.7, and 79.0° corresponding to the (111), (200), (220), (311), (222), (400), (331), and (420) crystal planes of the face-centered cubic structure of CeO$_2$ (JCPDS-34-0394). After Ag doping, the original cubic fluorite structure of CeO$_2$ nanorods was not altered, as proven by the unchanged diffraction peak positions. Besides, no peaks of Ag were observed in the catalysts despite reaching up to 0.3 wt.% Ag, explained by good dispersion of AgNPs on CeO$_2$ support. The highly dispersed materials have been obtained, and the small size of AgNPs is under the XRD detection limit. On the other
hand, the XRD results also showed no interaction between Ag and CeO$_2$ to form a new phase. Based on the highest peak of $2\theta = 28.5^\circ$, the average crystal sizes of CeO$_2$ were determined following the Scherrer equation (Equation (1)) (35), being 10.8, 11.7, 11.5, and 11.5 nm for rCe, 0.1Ag-Ce, 0.2Ag-Ce, and 0.3Ag-Ce, respectively.

The EDS spectra of pure CeO$_2$ nanorods showed the characteristic peaks of Ce and O with the mass ratio of 83.28:17.72, being equivalent to the theoretical mass ratio (81.4:18.6). Meanwhile, the EDS spectra of the Ag-doping samples indicated the characteristic peaks of Ce, O, and Ag with the corresponding mass ratios, as shown in Figure 1(b). EDS mapping images depicting the distribution of elements on the surface of the catalysts (Figure 2) showed that the Ag active phase has a uniform distribution on the surface of the support. From the EDS and XRD results, it can be concluded that with a low loading contents (0.1–0.3 wt%), AgNPs were formed and uniformly dispersed on the surface of CeO$_2$ nanorods.

For illustrating structural features and the crystalline quality of Ag-Ce samples, the Raman spectra of CeO$_2$ and Ag-Ce samples were investigated as shown in Figure 1(c). The strongest signal appeared at 461 cm$^{-1}$, attributed to the F$_{2g}$ vibration mode of the fluorite structure of CeO$_2$. This peak was also found in three Ag-doping samples with lower intensity with increasing Ag composition. On the other hand, there was a small peak at 594 cm$^{-1}$ in the CeO$_2$ graph, which was shifted to lower frequencies at 590, 586, and 560 cm$^{-1}$ of 0.1, 0.2, and 0.3 wt.% Ag, indicating the formation of oxygen vacancies in CeO$_2$ nanorods. There were some visible characteristic peaks due to the Ag-Ce interaction at 613, 773, 1185, 1360, 1560, and 1595 cm$^{-1}$ (36), and this trend has increased with a higher Ag concentration.

The surface modification of Ag-Ce samples has been achieved through FT-IR spectra (Figure 1(d)), with the coupled peaks in 420–415 and 1270–1250 cm$^{-1}$ related to the characteristic vibration of CeO$_2$, the 550 cm$^{-1}$ peak attributed to the stretching vibration of Ce–O. According to Negi et al. (37), the Ag–O stretching vibration at 550 cm$^{-1}$ may be overlapped by the CeO$_2$’s vibration, assigned to the interaction between Ag and O during the redox reaction between Ag$^+$ and Ce$^{3+}$. The FT-IR spectra of catalysts also exhibited fluctuations on the higher band at 3300 cm$^{-1}$ of the surface OH group and at 1630 cm$^{-1}$ of the H–OH group; the peaks at
2930 and 2852 cm\(^{-1}\) correspond to C–H stretching. The absorption peaks were not significantly different after metal doping, confirming that AgNPs were inserted into the CeO\(_2\) lattice and highly dispersed on the CeO\(_2\) supports.

The adsorption–desorption isotherms of Ag-doped and undoped CeO\(_2\) nanorods (in Figure 3(a)) show that all samples obey type IV isotherms with the H3 class of the IUPAC classification at a relative pressure of 0.42–0.90 (38, 39). Type IV isotherms represent a mesoporous structure, favoring adsorption and transport reactants and intermediates during the reaction. There is almost no difference in hysteresis loop slope for the catalysts, indicating that the CeO\(_2\) nanorod structure is still maintained after silver doping. The isotherms of samples indicated no capillary condensation at lower relative pressures (0.1–0.3), confirming no porous capillary in the CeO\(_2\) structure. Figure 3(b) depicts the BJH pore size distributions of Ag-Ce catalysts: all the samples have the pore size distribution in 10–60 nm and their maxima at more than 20 nm, designating the presence of mesopores. The pore size distributions were unaffected by Ag-doping in all samples. The main textural and structural characteristics of samples are shown in Table 1. The pure ceria exhibited a BET value of 72 m\(^2\)/g, an average pore diameter of 23 Å, and a pore volume of 0.098 cm\(^3\)/g. The addition of Ag (0.1–0.3 wt.%) led to a slight increase in the surface area (74–80 m\(^2\)/g), the average pore diameter (23.2–23.4 Å). Meanwhile, the pore volume slightly decreased (0.091–0.093 cm\(^3\)/g).

The HR-TEM analysis was performed to investigate the microstructural characteristics of a 0.2Ag-Ce nanocomposite. SAED images (Figure 4(a)) showed three crystallite planes of CeO\(_2\) along with AgNPs. The HR-TEM images proved the stability of CeO\(_2\) nanorods after Ag
doping (Figure 4(b)). The CeO2 nanorods were 100–200 nm in length and 20–30 nm in diameter. Three planes of structured fluorite CeO2 nanorods involved in the (111), (200), and (220) with the d-spacings of 0.32, 0.29 and 0.20 nm, respectively. Besides, the formation of spherical AgNPs exposed to CeO2 nanorods was also observed. The estimated d-spacing of 0.15 nm was assigned to the (111) crystal plane of the Ag phase. The size of AgNPs was estimated in the range of 5–10 nm. Compared with pure Ce nanorods and Ag nanoparticles (shown in Figure 4(c,d)), the particle sizes of Ag nanoparticles and Ce nanorods in the catalyst samples are smaller, proving a positive interaction in the incorporation of AgNPs into CeO2, in which CeO2 improved the dispersion of AgNPs.

The H2-TPR profiles of pure CeO2 nanorods and Ag-containing sample by hydrogen consumption are shown in Figure 5. The intensity signal displays a low temperature of 100–200°C, medium temperature of 200–550°C and above 550°C. In the first range, pure ceria has no peak but a couple of peaks observed in 0.2Ag-Ce signal may be attributed to Ag2O reduction or the interaction between silver and ceria (40). In the middle range, rCe shows a high peak at 450°C, while this peak has shifted to 350°C in the presence of Ag, assigning to the reduction of oxidized Ag and CeO2 surface (41). This determines the homogeneity of small Ag nanoparticles on ceria surface, according to XRD and HR-TEM results (10). In the highest temperature range, the signal demonstrates the interfacial interaction between Ag species and bulk CeO2. Instead of a peak at 816°C in CeO2 signal, there are two peaks at 680 and 820°C in the 0.2Ag-Ce sample. In general, the companionship of Ag plays a key role in increasing the reduction capacity of the sample. The results evidenced that the well-dispersed Ag across the Ag-Ce nanocomposites boosted the synergistic effect between Ag and CeO2, facilitating the redox cycle of catalyst, thus improving the catalytic activity of green synthesized silver nanoparticles decorated on ceria nanorods.

The catalytic activity of the as-prepared Ag-Ce samples was estimated via p-NP hydrogenation at room temperature in the presence of NaBH4. In alkaline conditions (generated by the hydrolysis of NaBH4), the formation of p-nitrophenolate ions (O$_2$NC$_6$H$_4$O$^-$) resulted in a red-shift of the maximum absorption wavelength from 317 nm to 400 nm (4). The catalytic hydrogenation of p-NP into p-AP in the presence of NaBH4 can be described as follows (4):

\[
\begin{align*}
O_2NC_6H_4OH + OH^- & \rightarrow O_2NC_6H_4O^- + H_2O \\
BH_4^- + OH^- & \rightarrow B(OH)_4^- + e^- + H_2 \\
e^- + H_2 & \rightarrow H^- \\
O_2NC_6H_4O^- + H^- & \rightarrow O_2NC_6H_4OH
\end{align*}
\]

Figure 6(a) shows the absorbance curves of the p-NP solutions using Ag-Ce samples with different silver contents. For the pure CeO2 sample, the absorption peak at 400 nm of the p-nitrophenolate ion decreased, while the typical absorption peak of p-AP at 297 nm started appearing after 10 min. For Ag-Ce samples, the absorption peak of p-nitrophenolate ion decreased sharply, and the formation of p-AP could be observed after

| Samples | BET surface area, m$^2$/g | Pore diameter, Å | Pore Volume, cm$^3$/g | Crystallite size, nm |
|---------|--------------------------|-----------------|---------------------|---------------------|
| rCe     | 72                       | 23.0            | 0.098               | 10.8                |
| 0.1Ag-Ce| 74                       | 23.2            | 0.091               | 11.7                |
| 0.2Ag-Ce| 80                       | 23.4            | 0.093               | 11.5                |
| 0.3Ag-Ce| 79                       | 23.3            | 0.092               | 11.5                |

**Table 1.** Textural properties of CeO2 nanorods and the catalysts.
only 3 min. Apparently, the addition of Ag in the ceria lattice enormously enhanced the catalytic efficiency compared to pure ceria nanorods. Although CeO$_2$ has lower reactivity compared to Ag-Ce catalysts, its high catalytic capacity is related to its unique ability to store and release oxygen. Figure 6(b,c) shows the dependence of C/C$_0$ and ln(C/C$_0$) on the reaction time of three catalyst samples. The higher Ag content the catalyst loaded, the more efficient the catalyst. However, 0.3Ag-Ce showed a lower activity than 0.2Ag-Ce. This may be due to the agglomeration of Ag when increasing the active component, leading to larger AgNPs and declining a specific surface area. Besides, the reaction was evidenced to obey the pseudo-first kinetic model, with the highest reaction rate constant of 1.23 min$^{-1}$ on a 0.2Ag-Ce sample.

The effect of catalyst concentration on the catalytic activity of the best sample (0.2Ag-Ce) is shown in Figure 6(d). When the catalyst concentration increased from 0.1 to 0.15 g/L, the conversion of p-NP increased significantly and reached the complete conversion with the 0.2 g/L catalyst. The higher the catalyst content the larger the contact surface, resulting in higher conversion efficiency.

The effect of p-NP/NaBH$_4$ molar ratio is illustrated in Figure 6(e). All samples were analyzed at 3 min, with the complete conversion of p-NP toward p-AP. Starting from 1/150, when increasing the concentration of NaBH$_4$, the formation of p-AP also increased and the maximum absorption peak at 297 nm was obtained in the case of 1/175. However, a slight decrease in absorption band at 297 nm was found if increasing the molar ratio up to 1/200 or 1/225. It can be seen that the greatly high NaBH$_4$ concentration decreased the apparent rate of reaction, possibly due to the adsorption of active H$_2$ species, which occupied active sites for p-NP hydrogenation. Furthermore, the H$_2$ formation generated bubble air, interfering p-NP to spread on catalyst surface (42, 43).
The effect of reaction duration on the p-NP hydrogenation is presented in Figure 6(f). After only 3 min of reaction, the complete conversion of p-NP took place for 0.2Ag-Ce catalyst. Moreover, the absence of the absorption bands at 222, 245, 278, and 312 nm indicated that no other byproducts were formed during the catalytic hydrogenation.

The recyclability for p-NP hydrogenation using 0.2Ag-Ce catalyst in the operational parameters (the catalyst dosage of 0.1 g/L and the p-NP/NaBH₄ molar ratio of 1/175) was measured for 10 min at continuous cycles (Figure 7). A gradual decline in p-NP conversion was observed after each run. The efficiency of p-NP hydrogenation decreased by 34% after six cycles, namely 100% in the first cycle and 66% in the fifth cycle. This decrease can be rationally attributed to the active sites on the surface being covered by the sediments of the previous reaction.
batch and the loss of the catalyst during the recovery of the catalyst.

Table 2 compares the activity of different catalysts in p-NP hydrogenation. In our study, 0.2Ag-Ce sample had much shorter time to complete p-NP conversion. Therefore, silver nanoparticles decorated on CeO2 nanorods prepared by a green and simple process could be a promising approach for the efficiency of p-NP hydrogenation.

**Conclusions**

This study has emphasized the efficiency of Ag-Ce systems in catalytic hydrogenation of p-NP toward p-AP. By a simple and eco-friendly process, Ag-Ce catalysts were successfully obtained with smaller particle size and higher surface area than the pure CeO2 nanorods, due to well-dispersed AgNPs, thus improving available oxygen lattice species on the CeO2 surface. Therefore, the catalytic performance was enhanced in the p-NP hydrogenation. Using 0.2Ag-Ce sample with 0.2 g/L catalyst concentration, the complete p-NP conversion toward p-AP was obtained after 3 min. Taking into account the convenience of catalyst preparation and their predominant properties, this catalytic system is promising to extend the p-NP hydrogenation in large-scale industries.

**Acknowledgements**

We acknowledge the support of time and facilities from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

**Data availability statement**

The data used to support the findings of this study are included within the article.

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**Table 2.** Various catalysts in the hydrogenation of p-NP at room temperature.

| Catalysts (Ref.) | Time for complete conversion, min | mmol p-NP/ (g catalyst·h) |
|-----------------|-------------------------------|--------------------------|
| This study      | 3                             | 14.4                     |
| Ag/CeO2 (10)   | 11                            | 6.8                      |
| Ag@BCN (44)*   | 6**                           | 69.7                     |
| Ag/PAN (44)**  | 70                            | 0.57                     |
| Ag@CeO2 (45)   | 7                             | 0.51                     |
| Pd/C (8)       | 6                             | 33.7                     |
| Pd/Fe2O3 (8)   | 5                             | 12.8                     |

*BCN: Boron carbon nitride; **The reaction was taken place at 35°C; ***PAN: Polyacrylonitrile.
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