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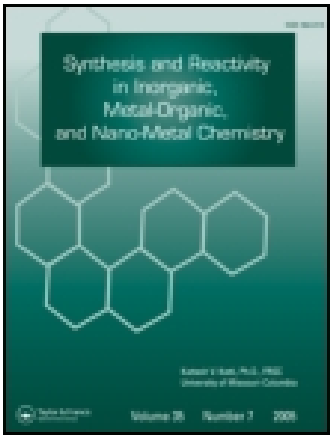

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
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Catalytic Application of Biogenic Platinum Nanoparticles for the Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol

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Accepted author version posted online: 27 Oct 2014.

To cite this article: Bingyun Zheng, Xiaolian Jing, Tareque Odoom-Wubah, Tao Kong, Huimei Chen, Daohua Sun, Jiale Huang & Qingbiao Li (2015) Catalytic Application of Biogenic Platinum Nanoparticles for the Hydrogenation of Cinnamaldehyde to Cinnamyl Alcohol, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 45:7, 967-973, DOI: 10.1080/15533174.2013.862813

To link to this article: http://dx.doi.org/10.1080/15533174.2013.862813

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry (2015) 45, 967–973

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2013.862813

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Received 16 April 2013; accepted 2 November 2013

Pt catalysts and Co doped Pt catalysts with TiO_2 as the support were prepared by the sol immobilization method based on biological synthesis process, whereby Pt nanoparticles (PtNPs) were reduced from Na_2PtCl_4 using *Cacumen Platycladi* extract (CPE). The catalytic performance of the catalysts was studied using hydrogenation of cinnamaldehyde as the model reaction. For comparison, Co doped Pt/catalysts were also prepared by traditional impregnation method, TEM observation, and XRD measurement were carried out to characterize the catalysts. The effects of different Pt loadings and Co doping amounts were investigated. The results showed that the PtNPs could be well dispersed onto the TiO_2 support with narrow size distribution between 4 and 6 nm. 1.0% was observed as the optimal Pt loading amount in our experiments showing a cinnamaldehyde conversion of 73.3% with 68.8% selectivity to cinnamyl alcohol. A proper Co doping amount was also essential to the catalytic performance of the prepared Pt/catalysts as well as a favorable for the reaction process, 1.0% doping amount showed the best activity in which a 70.4% conversion and 88.3% selectivity was achieved. Recyclability tests carried out revealed that the 1.0 Co–1.0 Pt/TiO_2 catalysts possessed possessing good durability. In this work, Co-Pt/TiO_2 catalysts prepared by the sol immobilization method based on biological reduction process, showed better selectivity than that from traditional impregnation method.

Keywords: biosynthesis, Pt, sol immobilization, cinnamaldehyde

Introduction

Pt and its alloys are mainly used as excellent catalysts for oxidation and hydrogenation processes in the petrochemical industry.[1] With the development of nanotechnology, Pt nanoparticles (PtNPs) have been demonstrated to exhibit high catalytic activity, owing to their high surface area, making synthesis of PtNPs for catalytic applications one of the highlights in related fields.[1] Consequently, well-defined PtNPs of particular shapes and sizes have been synthesized through various methods. However, conventional physical and chemical methods are not only energy intensive, because of stringent conditions, but also environmentally unfriendly, due to the use of toxic solvents or additives. Compared with conventional methods, biosynthetic methods based on microorganisms or plants have been regarded as cost-effective and environmentally benign approaches for producing highly stable metal NPs in recent years. Some efforts have been directed toward the intracellular or extracellular biosynthesis of PtNPs using microorganisms under mild conditions without auxiliary capping agents.[2–5] However, subsequent processing of NPs via intracellular biosynthesis is generally difficult, and microorganisms used for the extracellular biosynthesis of NPs must be extensively screened.[6] Living plants, plant extracts, and plant biomass are attracting more attention as simple but effective alternative candidates for the extracellular biosynthesis of PtNPs. For example, *Diospyros kaki* leaf extract,[7] *Cochlospermum gossypium* extract,[8] and honey[9] have recently been used to prepare PtNPs. Interestingly, biogenic PtNPs produced by using honey can be used as catalysts for reacting aniline with 4-aminoantipyrine in an acidic aqueous medium.[9]

Cinnamyl alcohol is an important α,β-unsaturated alcohol; it is a raw material and an intermediate with a wide range of applications in medicine, bactericide, fragrance, cosmetics, and pesticides.[10,11] At present, cinnamyl alcohol is industrially produced in two ways: one approach involves the saponification of storax oil and cinnamon oil, among others, using hot NaOH solution, whereas the other refers to the reduction of cinnamaldehyde by benzyl alcohol aluminum or aluminum isopropoxide. Both methods are costly and environmentally unfriendly. However, an approach to producing cinnamyl alcohol through selective

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hydrogenation of cinnamaldehyde can overcome these disadvantages.[12,13] Nevertheless, in the cinnamaldehyde molecule, the C=O and C=C bonds of the acrolein group are conjugated.[14] The former bond possesses higher bond energy compared with the latter bond, resulting in poor selectivity towards cinnamyl alcohol. Therefore, exploring efficient catalysts for selective hydrogenation is crucial. Currently, heterogeneous catalysts have received immense attention because of their favorable characteristics, including easy separability and recyclability.[10] Some Pt-based heterogeneous catalysts (e.g., Pt/MCM-48,[15] Pt/CNTs,[16] Pt/TiO_2,[17] and Pt/ZrO_2[18]) have been developed for the selective hydrogenation of cinnamaldehyde. Among them, Pt/TiO_2 has been reported to exhibit excellent catalytic activity because of the strong interaction between Pt and TiO_2 with high reducibility.[17] Moreover, its catalytic activity can be enhanced by doping a small amount of a transition metal (e.g., Co) due to the electron-deficient species of transition metals.[19] However, Pt catalysts using biosynthesized PtNPs in selective hydrogenation have not been reported hitherto.

In this work, Pt sols (or PtNPs) were biosynthesized by reducing aqueous Na_2PtCl_4 with *Cacumen Platycladi* extract (CPE) as the reducing agent. The effects of Pt loading and Co doping on the TiO_2 support and the catalytic performance of the Pt/TiO_2 and $Co–Pt/TiO_2$ catalysts prepared through sol immobilization were studied. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the Pt catalysts. To the best of our knowledge, this is the first report on the fabrication of biogenic Pt nanocatalysts for selective hydrogenation of cinnamaldehyde that highlights the potential catalytic application of PtNPs through biosynthesis.

Experimental

Materials

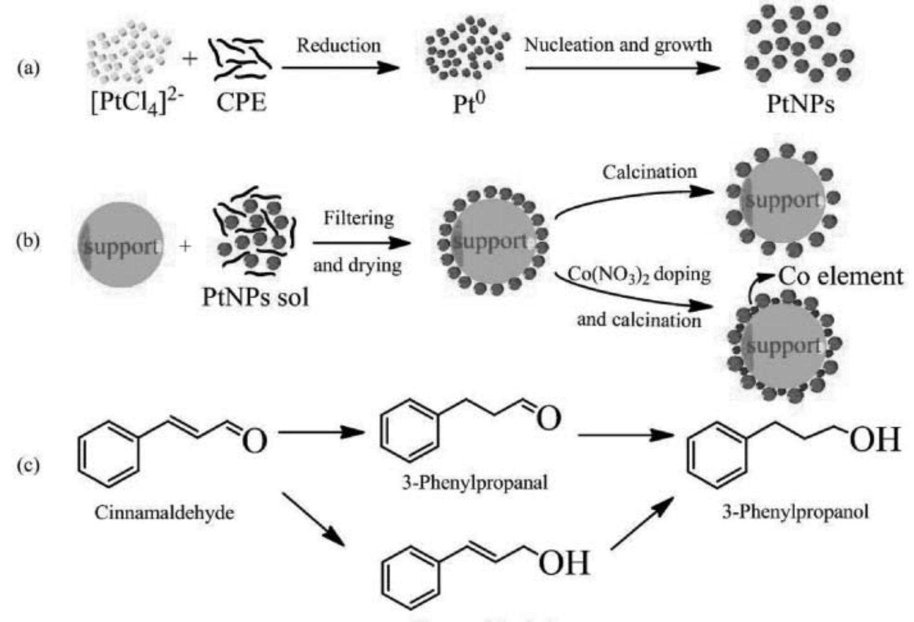
Sundried *CP* was purchased from Xiamen Jiuding Drugstore, China. Sodium tetrachloroplatinate (Na_2PtCl_4) and chloroplatinic acid (H_2PtCl_6) used as platinum precursor was supplied by Aladdin Chemistry Co. Ltd., China. TiO_2 and $Co(NO_3)_2\cdot 6H_2O$ were obtained from Sinopharm Chemical Reagent Co. Ltd., China. H_2 ($\geq$99.99%), N_2 ($\geq$99.999%) and compressed air were provided by Fuzhou Xinhang Industrial Gases Co. Ltd. (China).

Preparation of CP Extract

The biomass of *CP* for reduction was milled, and the powder was screened with a 20-mesh sieve. 3 g of the *CP* powder was then dispersed in 90 mL of deionized water in a 200 mL beaker and boiled for 5 min. Thereafter, the resulting broth was cooled down to room temperature and filtered to obtain the filtrate, which was subsequently adjusted to 100 mL by adding deionized water. The resulting CPE was refrigerated at 6°C for the biosynthesis of PtNPs within seven days after preparation.

PtNPs Sol

The Pt sol was prepared by the biosynthetic method using biomass extract of *CP*. The typical synthesis process of the PtNPs sol is shown in Scheme 1a. First, an aqueous solution with 7 mL CPE and 3 mL deionized water was heated at 90°C in an oil bath under continuous stirring for 10 min. Then 0.096 mL aqueous Na_2PtCl_4 solution (52.24 mM) was



Sch. 1. (a) Synthesis of PtNPs. (b) Preparation of Pt and Co-Pt catalysts. (c) Hydrogenation of cinnamaldehyde.

suddenly added to the flask with continuous stirring at 90°C for 24 h.

Pt Catalysts

Scheme 1b illustrates the typical preparation process for Pt/TiO_2 catalysts through sol- immobilization using the above biogenic PtNPs sol. An appropriate amount of HCl was used to adjust the pH of the PtNPs sol to 2 and 0.4 g TiO_2 was added to the Pt sols under vigorous stirring. After 1 h, the solid was collected by filtration and washed with deionized water. The obtained solid was subsequently dried at 50°C in vacuum for 4 h and then calcinated at 500°C for 4 h.

Besides, traditional impregnation method was also used to prepare Pt/TiO_2 catalysts for comparison: 0.4 g TiO_2 was suspended in a desired amount of H_2PtCl_6 solution, followed by drying at 100°C. The remaining paste was then calcinated in air at 500°C for 3 h and subsequently reduced in flowing hydrogen at 500°C for 1 h.

For the preparation of Co–Pt/TiO_2 catalysts, in addition to all the steps in the preparation of Pt/TiO_2 catalysts, 0.355 mL aqueous $Co(NO_3)_2$ (19.1 mM) was mixed with the Pt/TiO_2 composites before the calcinations procedures.

The as prepared Pt catalysts were denoted as x Pt/TiO_2 and y Co-x Pt/TiO_2, where x and y stands for the calculated weight percentage of Pt and Co in the catalyst, respectively.

Characterization

XRD

The XRD patterns of Pt catalysts were collected using an X'Pert Pro X-ray Diffractometer (PANalytical BV, the Netherlands) with Cu$K\alpha$ radiation.

TEM

Specimens for TEM were prepared by placing a drop of ethanol suspension of Pt catalysts on carbon-coated copper grids and the tests were carried out using a Tecnai F30 microscope. In addition, the size distribution and average size of the PtNPs were estimated by the same method as that in our previous work.[20]

Evaluation of Pt Catalysts

The catalytic performance of the Pt catalysts for the hydrogenation of cinnamaldehyde was tested in a stainless steel reactor (500 mL) at 60°C by dispersing 0.3 g of catalyst samples into 100 mL of alcoholic medium containing 2.5% cinnamaldehyde at 3 MPa. Reactants and hydrogenation products, such as cinnamyl alcohol, 3-phenylpropanal, and 3-phenylpropanol, among others, as illustrated in Scheme 1c,[21] were analyzed using a gas chromatographer equipped with a SE-30 capillary column and a flame ionization detector. In addition, the reactants and all products were identified based on corresponding standard samples, and a normalization calibration method was employed to quantify the consumption of cinnamaldehyde and the selectivity of the products.

Results and Discussion

XRD Characterization

The XRD patterns of the TiO_2 support and calcined Pt/TiO_2 catalysts are shown in Figure 1. Anatase crystal structure of TiO_2 remained in the XRD pattern of calcined Pt/TiO_2 catalysts. Samples with higher Pt loadings (1% and 2%) showed diffraction peaks at approximately 38.9° and 45.7° corresponding to the Pt species with a face-centered cubic structure. And no obvious Pt was detected on the catalysts with lower Pt loadings (0.5 and 1%), indicating Pt species were highly dispersed on the support. As shown in Figure 2, the XRD patterns of Co-Pt/TiO_2 catalysts showed just little difference compared with Pt/TiO_2, which means that Co doping has no significant effect on the structure of the Pt/TiO_2 catalysts.

TEM Results

TEM images of the Pt catalysts obtained based on bioreduction are shown in Figure 3. The PtNPs were well dispersed on the TiO_2 support and had a narrow size distribution of 4–6 nm. Compared with the PtNPs measuring 2.4 ± 0.8 nm freshly biosynthesized before immobilization, those of the 1.0 Pt/TiO_2 catalyst were larger (5.1 ± 2.7 nm; Figure 3b) due to aggregation under calcination. Moreover, based on the TEM images, the histogram inserts show that PtNPs over TiO_2 with particle sizes of 4.7 ± 2.5, 5.1 ± 2.7, 5.3 ± 2.7, and 5.4 ± 2.6 nm corresponds to 0.5%, 1.0%, 1.5%, and 2.0% Pt loading respectively, indicating that increasing the loading process leads to larger PtNPs. TEM images of Co -Pt/TiO2 catalysts are shown in Figure 4. After doped with different amount of Co, it was found that the higher the Co doping amount was, the smaller the mean particle size of the PtNPs became. Hence, it can be concluded that Co doping could prevent the aggregation of PtNPs under calcination.

Catalytic Activity

Effects of Pt Loading

Figure 5 shows the effects of different Pt loadings on the catalytic performance. As shown, pure TiO_2 support exhibited

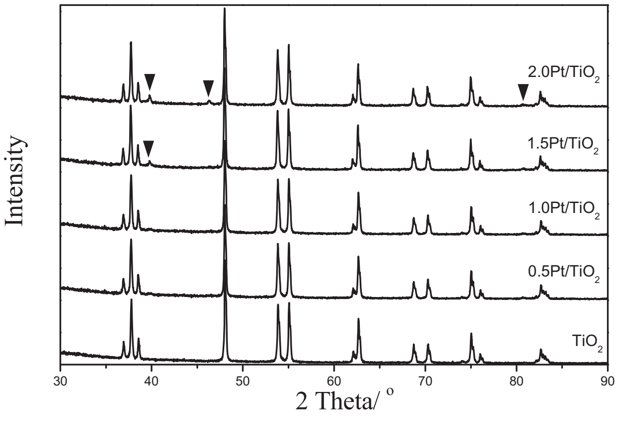


Fig. 1. XRD pattern of the TiO_2 support and the catalysts prepared by bio-method with different Pt loadings.

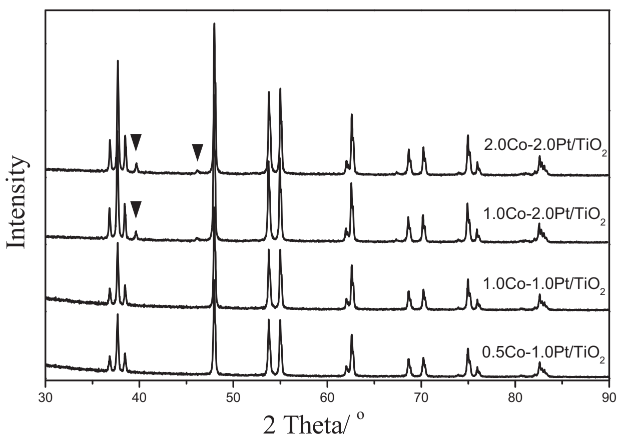


Fig. 2. XRD pattern of some catalysts with Co doping prepared by bio-method.

very low conversion rates for cinnamaldehyde (about 10%). After the biosynthesized PtNPs were immobilized onto the TiO_2 support, the selectivity to cinnamyl alcohol obviously increased significantly to above 60%. With the increasing of the Pt loadings, from 0.5% to 1.0%, a great improvement in the conversion of cinnamaldehyde was observed from 19.6% to 66.8%. As for the 1.0 Pt/TiO_2 catalysts, the rates of conversion and selectivity were calculated as 66.8% and 73.2%, respectively, indicating that the biogenic PtNPs supported over TiO_2 could be efficient catalysts for the hydrogenation of cinnamaldehyde to cinnamyl alcohol. Nevertheless, further increasing the Pt loading to 2.0% resulted in just a slight increase in the conversion of cinnamaldehyde, whereas that of the selectivity to cinnamyl alcohol slightly decreased.

Effects of Co Doping

Figure 6 illustrates the effect of Co doping on the conversion of cinnamaldehyde and selectivity to cinnamyl alcohol. In order to invegate the effect of Co doping on Pt/ TiO_2 catalysts, the Pt loading was fixed at 1% with the Co doping increased from 0.5% to 2% and the same reaction conditions as those described in the legend to Figure 5, were used to evaluate the activity of the Co doping catalysts. As shown in Figure 6, although the selectivity to cinnamyl alcohol increased from 38.5% to 63.6% compared with pure TiO_2 support, the 1.0 Co/TiO_2 catalyst without Pt loading exhibited a very low conversion (<20%). As for the Co-Pt/ TiO_2 catalysts, increasing the Co doping amount, resulted in a minimal increase in the selectivity toward cinnamyl alcohol that is from 67.2% to 76.7%. When the Co doping was 0.5%, the conversion of cinnamaldehyde was even lower than that without Co in Figure 5. On the contrary, increasing the Co doping to 1.0%, the conversion was greatly improved reaching a maximum of 88.3%. The conversion increased slightly when the Co doping was upped to1.5% in comparison with the 1.0% Co

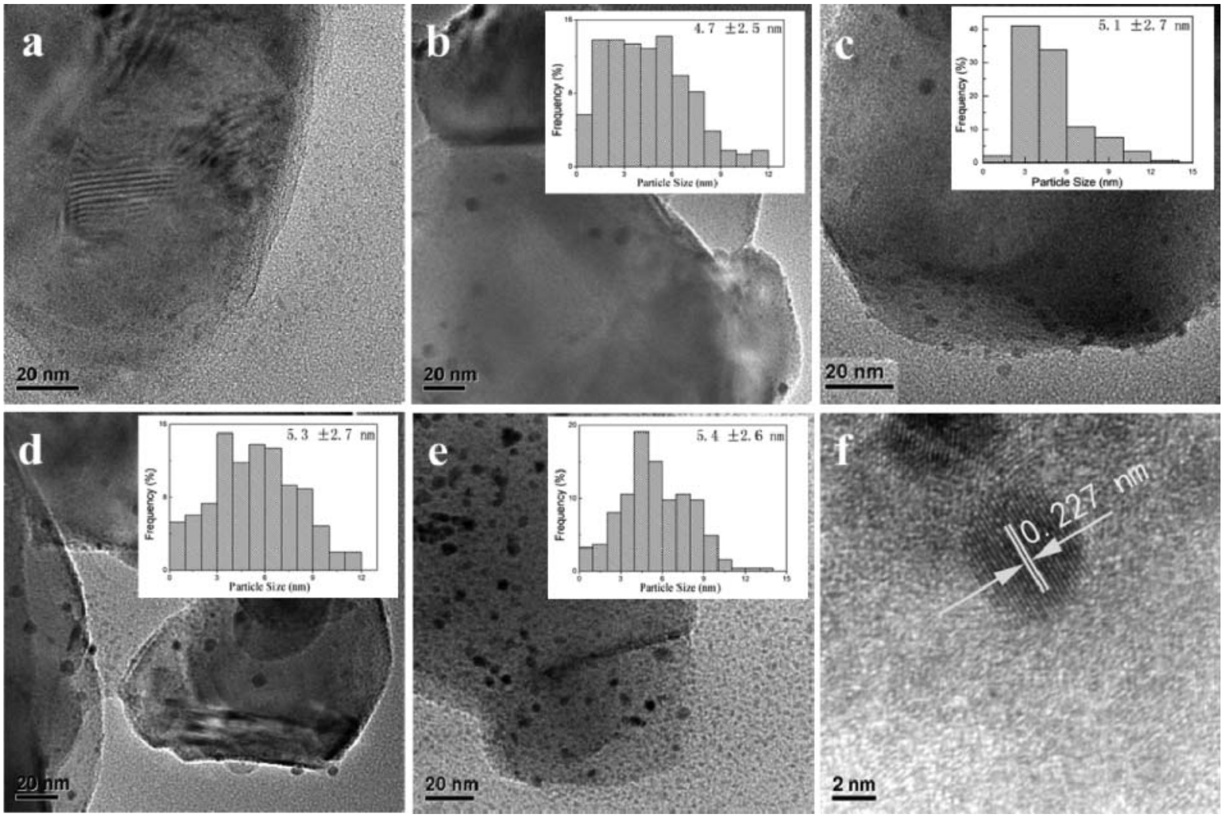


Fig. 3. TEM images of the biosynthesized catalysts: (a) TiO_2, (b) 0.5 Pt/TiO_2, (c) 1.0 Pt/TiO_2, (d) 1.5 Pt/TiO_2, (e) 2.0 Pt/TiO_2, and (f) HR-TEM of PtNPs on the catalysts.

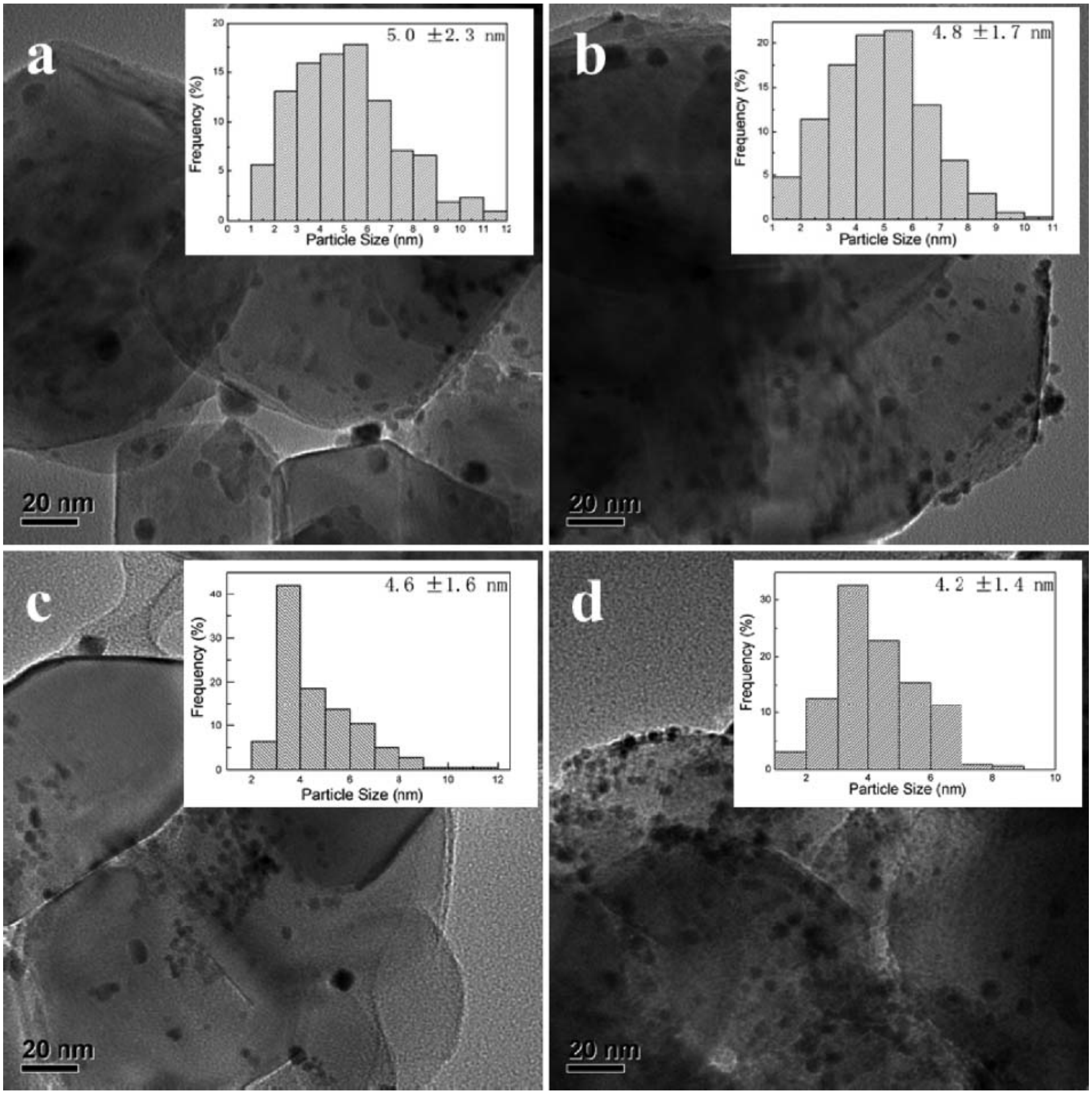


Fig. 4. TEM images of the biosynthesized catalysts: (a) 0.5 Co-1.0 Pt/TiO_2, (b) 1.0 Co-1.0 Pt/TiO_2, (c) 1.5 Co-1.0 Pt/TiO_2, and (d) 2.0 Co-1.0 Pt/TiO_2, respectively.

catalysts. However, when the Co doping amount was increased to 2.0% a dramatic decrease in the conversion was observed. Englisch et al.[22] suggested that a stronger interaction exists between Co and Pt because of micropolarization due to the electronic effects of Co. Therefore, the stronger interaction could polarize $C = O$ more easily, making the hydrogenation of $C = O$ easier and thereby enhancing the selectivity to cinnamyl alcohol. However, for the phenomenon of diminished conversion of cinnamaldehyde with higher Co doping, we speculated that the excess cobalt (n_{Co}:$n_{Pt} = 3.3$) might have covered the PtNPs loaded on the TiO_2, thus slowing down the reaction rate, leading to the conversion of cinnamaldehyde simultaneously showing a downward trend.

Durability of the Pt Catalysts

Durability is a very important criterion for catalysts to be considered for practical application. Recyclability tests were conducted to assess the durability of the 1.0 Co–1.0 Pt/TiO_2 catalysts. The catalysts after reaction were recovered by centrifugation, washed with ethanol several times to remove the binding substances on the catalysts, dried without further calcination, and then reused under the same reaction conditions. As shown in Figure 7, the conversion of cinnamaldehyde was kept at above 80% after three cycles with a steady selectivity to cinnamyl alcohol almost unchanged. The conversion of cinnamaldehyde and selectivity toward cinnamyl alcohol after the fifth cycle, were 79.2% and 67.3%, respectively, indicating that

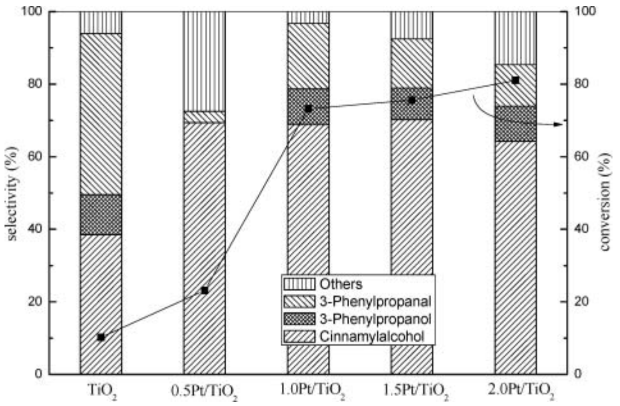


Fig. 5. Catalytic performance of the Pt catalysts. Reaction conditions: cinnamaldehyde, 2.5 mL; ethanol, 97.5 mL; catalyst, 0.3 g; reaction temperature, 60°C; reaction pressure, 3 MPa; reaction time, 3 h.

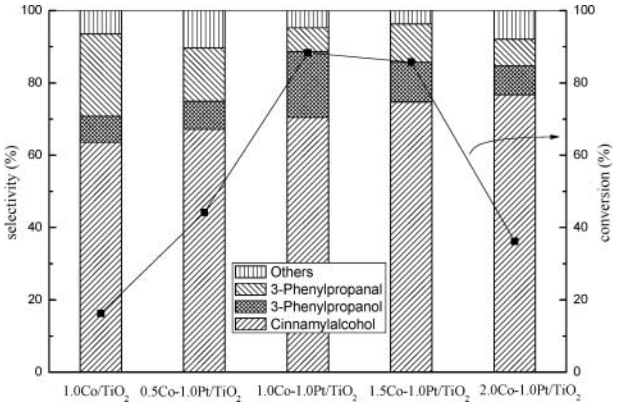


Fig. 6. Catalytic performance of the Co–Pt/TiO_2 catalysts.

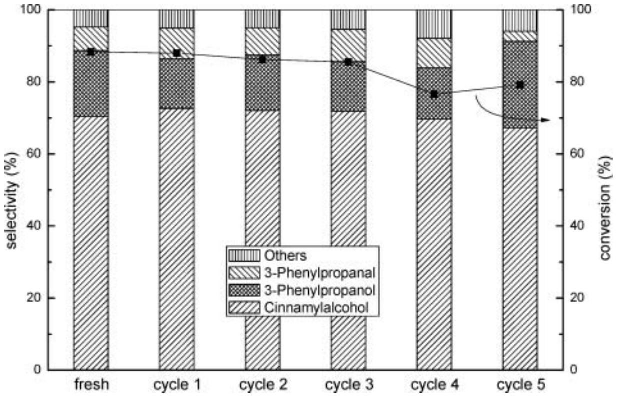


Fig. 7. Catalytic performance of recyclable bioreduction catalysts under the following conditions: cinnamaldehyde/catalyst ratio, 2.5 mL:0.3 g; reaction temperature, 60°C; reaction pressure, 3 MPa; reaction time, 3 h.

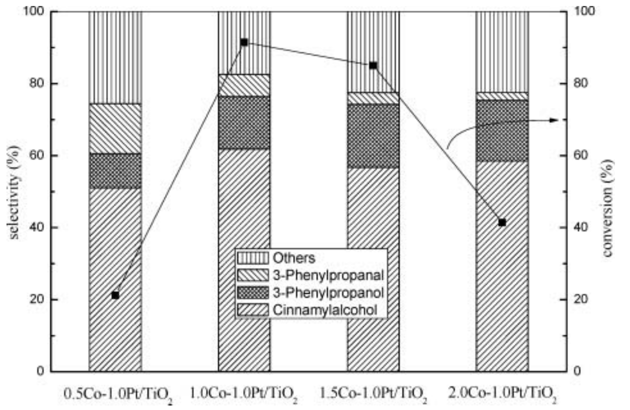


Fig. 8. Catalytic performance of the Co–Pt catalysts prepared by impregnation method.

the 1.0 Co–1.0 Pt/TiO_2 catalysts possessed high durability. These results have characterized promising catalysts for the selective hydrogenation of cinnamaldehyde based on biosynthesized PtNPs.

Comparison of the Biosynthesis-Assisted Catalysts with Traditional Catalysts Prepared by Impregnation

Figure 8 shows the catalytic performance of the catalyst prepared by traditional impregnation method. The different amount of Co had just little influence on the selectivity, but had a significant impact on the conversion to the desired product, which is similar to the bio-synthesized sample. It is worth noting that with the same amount of Co doping and Pt loading, the catalysts with Co doping of 0.5% prepared by traditional impregnation method showed much lower conversion than that by the bio-method. The selectivity to cinnamyl alcohol of Co-Pt/TiO_2 prepared by traditional impregnation method was obviously lower than that by the bio-method.

Conclusions

A sol immobilization method based on the biosynthesis of Pt sols with CPE was used to prepare Pt/TiO_2 and Co-Pt/TiO_2 catalysts for the selective hydrogenation of cinnamaldehyde. Co-Pt/TiO_2 catalysts were also prepared by traditional impregnation method for comparison with the biosynthesized sample. This study investigated the catalytic application of Pt catalysts for the hydrogenation of cinnamaldehyde to cinnamyl alcohol based on the biosynthesis of Pt sols with CPE. The biogenic PtNPs supported on TiO_2 could be efficient catalysts for the hydrogenation of cinnamaldehyde to cinnamyl alcohol. The 1.0 Co–1.0 Pt/TiO_2 catalysts, showed significant conversion rates of cinnamaldehyde and selectivity towards cinnamyl alcohol 88.3% and 70.4%, respectively. Proper amounts of Co doping enhanced the catalytic performance, with the catalysts prepared by biomediated method showing higher selectivity to cinnamyl alcohol than the catalysts prepared by impregnation method. In summary, the results of this study have demonstrated the efficiency of biosynthetic PtNPs as competitive catalysts for selective hydrogenation of cinnamaldehyde.

Funding

This work was supported by the Research Fund for the Doctoral Program of Higher Education of China (20110121120018) and the Start-up Foundation for Scientific Research Team Innovation of Putian University.

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