

Fabrication of palladium nanoparticles immobilized on an amine-functionalized ceramic membrane support using a nanoparticulate colloidal impregnation method with enhanced catalytic properties

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Abstract—An efficient and reusable catalyst was developed by depositing palladium nanoparticles on an amine-functionalized ceramic membrane support using a nanoparticulate colloidal impregnation method. The as-prepared Pd-loaded ceramic membrane support was characterized by XRD, SEM, EDS, TEM, XPS, ICP, and its catalytic properties were investigated in the liquid-phase *p*-nitrophenol hydrogenation. A comparative study was also made with the palladium nanoparticles deposited on an amine-functionalized ceramic membrane support by an impregnation-reduction method. The palladium nanoparticles could be homogeneously immobilized on the ceramic membrane support surface, and exhibited excellent catalytic performance in the *p*-nitrophenol hydrogenation. The catalytic activity of the Pd-loaded ceramic membrane support prepared by the nanoparticulate colloidal impregnation method increased by 16.6% compared to that of impregnation-reduction method. In the nanoparticulate colloidal impregnation method, palladium nanoparticles were presynthesized, higher loading of Pd(0) could be obtained, resulting in better catalytic activity. The as-prepared Pd-loaded ceramic membrane support could be easily reused for several cycles without appreciable degradation of catalytic activity.

Keywords: Palladium Nanoparticles, Nanoparticulate Colloidal Impregnation Method, Ceramic Membranes, *p*-Nitrophenol Hydrogenation

INTRODUCTION

Metal nanoparticles have been broadly explored in the search for selective and enhanced catalytic performance, because they can provide a large number of active catalytic centers [1-3]. Due to high surface energies and large surface areas, these metal nanoparticles are considered thermodynamically unstable, and therefore tend to aggregate during reactions, leading to low catalytic stability. It is generally necessary to immobilize the metal nanoparticles on or in supports with the advantages of controlling particle nucleation and growth and reducing particle aggregation [4-6]. In contrast to free powder catalysts, membrane catalysts can be easily reused in liquid-phase reactions [5]. Ceramic membranes such as Al₂O₃, TiO₂, and ZrO₂ are attractive alternatives as catalyst supports because they can withstand high temperatures and/or pressures and high concentration of corrosive products as compared to polymer membranes [6].

The surface properties of the support are very important for the size and dispersion of metal particles, as well as the catalytic performance [7]. To effectively attach the metal nanoparticles to the support, the support surface is usually modified with suitable functional groups (e.g., NH₂ and SH groups) that strongly anchor the nanoparticles [8-10]. Apart from the surface properties, the prepara-

tion method is another key factor affecting the amounts and quality of deposited metal nanoparticles. A number of methods are available to incorporate metal nanoparticles into porous supports, with impregnation of the support by noble metal anions and subsequent reduction being the most common [11-13]. The method usually yields metal nanoparticles of non-uniform size and shape, and the degree of catalyst dispersion depends on various factors such as the type of support, the deposition pH and the concentration of precursors in the solutions. To make heterogeneous catalysts with easy control over particle size and shape, metal nanoparticles can be first synthesized in solution and then loaded on or in supports. Another effective approach is to presynthesize colloidal metal nanoparticles and directly load them onto the supports, during which the formation of nanoparticles in solution prior to their deposition permits tailoring of the nanoparticle size and surface composition [14-17].

In our previous works [18,19], we attempted to fabricate the membrane catalysts. The ceramic membrane support surface was first functionalized with amino-functional silanes such as γ -amino-propyltriethoxy silane (3-APTS) and N-(β -aminoethyl)- γ -aminopropyl trimethoxy silane (AAPTMS), and then the palladium nanoparticles were loaded on the functionalized ceramic membrane support by an impregnation-reduction method, i.e., the amine-functionalized ceramic membrane support was impregnated with the palladium precursor solution and then the palladium ions were reduced to metallic palladium nanoparticles. These as-fabricated membrane catalysts exhibited better catalytic performance in the liquid-phase

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hydrogenation of *p*-nitrophenol to *p*-aminophenol. In the present study, a nanoparticulate colloidal impregnation method was developed to fabricate Pd-loaded ceramic membrane supports, where the pre-synthesized colloidal palladium nanoparticles were immobilized on the surface of amine-functionalized ceramic membrane supports for better controlling the textural properties of palladium nanoparticles and enhancing their catalytic performance.

In continuing our work in the area of membrane catalysts, the aim of present work was to fabricate palladium nanoparticles deposited on the amine-functionalized ceramic membrane support by a nanoparticulate colloidal impregnation method with enhanced catalytic properties. The microstructure of the Pd-loaded ceramic membrane support was characterized by XRD, SEM, EDS, TEM, XPS and ICP. The liquid-phase *p*-nitrophenol hydrogenation was taken as a model reaction to investigate the catalytic performance of the Pd-loaded ceramic membrane support. Comparative studies with the Pd-loaded ceramic membrane support prepared by an impregnation-reduction method were also performed.

EXPERIMENTAL

1. Chemicals

Tubular ceramic membrane supports with a 12-mm outer diameter, an 8-mm inner diameter, and a 6-cm length were provided by Nanjing Jiushi High-Tech Co. Ltd., Nanjing, China, which were made up of a thin α -Al₂O₃ layer (nominal pore size of 0.2 μ m) on the outer wall of an α -Al₂O₃ porous support (nominal pore size of 3 μ m). N-(β -aminoethyl)- γ -aminopropyl trimethoxy silane (AAPTS, 95%) was purchased from J&K Scientific Ltd. Palladium acetate (Pd(OAc)₂, content of Pd 47.49%) and polyvinyl pyrrolidone (PVP, K-30) were obtained from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Ethanol (C₂H₆O, AR) was purchased from Wuxi City Yasheng Chemical Co., Ltd., Wuxi, China. *p*-Nitrophenol (C₆H₅NO₃, AR) was acquired from Aladdin Industrial Corporation.

2. Preparation of PVP-stabilized Palladium Nanoparticles

Palladium nanoparticle colloid with an average diameter of about 4 nm was prepared by ethanol reduction, where PVP served as the nanoparticle stabilizer and ethanol served as the reducing agent. Typically, in a 100 mL beaker flask, 0.224 g of palladium acetate, 0.555 g of PVP and 25 mL of ethanol were first charged into the beaker flask and then the mixture was heated to 70 °C with stirring, where the mole ratio of PVP and palladium acetate was 5 : 1. After about 5 min, the mixture gradually became black and homogeneous. Subsequently, the mixture was stirred for 2 h at 70 °C and the palladium nanoparticle colloid was obtained.

3. Immobilization of Palladium Nanoparticles on Ceramic Membrane Supports

The procedure for immobilization of palladium nanoparticles on ceramic membrane supports is presented in Fig. 1. During the preparation, the tubular ceramic membrane support was sealed at both ends. First, the ceramic membrane support was immersed in 50 ml of a 0.2 g/L solution of silane in dichloromethane at room temperature for 6 h. After silanization, the ceramic membrane support was washed with ethanol to remove unreacted silane compounds and dried at room temperature for 2 h. Then, the amine-functionalized ceramic membrane support was impregnated with

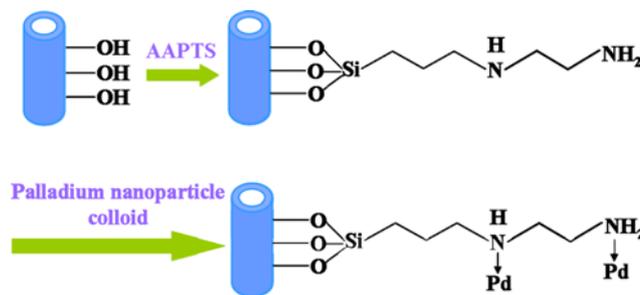


Fig. 1. Schematic representation of the steps in the preparation of palladium nanoparticles deposited on ceramic membrane support.

25 ml of a 0.04 mol/L palladium nanoparticle colloid at 40 °C for 12 h. The obtained Pd-loaded ceramic membrane support was rinsed thoroughly with distilled water and dried at room temperature for 0.5 h.

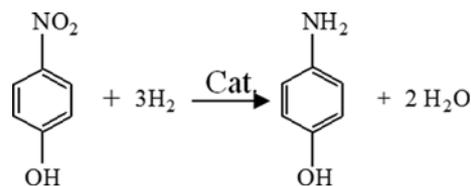
4. Catalyst Characterization

Powder X-ray diffraction (XRD) patterns of the samples were acquired on a D max/RB instrument using Ni-filtered Cu K α radiation ($\lambda=0.15418$ nm) operated at 40 kV and 40 mA with a scanning rate of 0.2°·s⁻¹. Field emission scanning electron microscope (FESEM) studies were carried out on Hitachi S-4800 FESEM. The composition was determined using energy-dispersive X-ray spectroscopy (EDS, NORAN System Six). The loading of palladium was determined by inductively coupled plasma (ICP) emission spectroscopy using an Optima 2000 DV system. For ICP analyses, the samples were digested in 10% (v/v) nitric acid solution at 60 °C for 1 h. Transmission electron microscopy (TEM) investigations were carried out on a JEOL model JEM-2100 instrument operated at 200 kV. X-ray photoelectron spectroscopic (XPS) spectra were recorded on a ULVAC PHI 5000 VersaProbe system and Al K α radiation was used as the X-ray source. The residual pressure inside the analytical chamber was about 10⁻¹⁰ mbar. The C 1s peak at 284.6 eV was used as a reference for the calibration of the binding energies.

5. Catalytic Properties Measurement

The liquid-phase hydrogenation of *p*-nitrophenol to *p*-aminophenol, depicted in Scheme 1, was used as a model reaction to evaluate the catalytic properties of the as-prepared Pd-loaded ceramic membrane support.

The *p*-nitrophenol hydrogenation was in a 300 ml stainless steel autoclave. Typically, 14 g of *p*-nitrophenol, 143 ml of ethanol and 20 ml of water were first charged into the reactor, and then the as-prepared Pd-loaded ceramic membrane support was fixed inside the autoclave. The reactor was sealed, purged with hydrogen five times to remove air, and then heated to the desired temperature of



Scheme 1. Catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol.

102 °C under slow stirring (80 rpm). After that the hydrogen pressure was raised to 1.65 MPa and the stirring rate was increased to 250 rpm, and the hydrogenation reaction started. The hydrogenation process was stopped after 1 h, and the membrane support was removed from the reactor, thoroughly washed with ethanol, and dried at room temperature for the next run. The hydrogenation products were analyzed by high-performance liquid chromatography (HPLC) (Agilent 1200 series, U.S.A.) equipped with a diode array detector (DAD) and an autosampler. Chromatographic separations were performed at 35 °C using a ZORBAX Eclipse XDB-C18, 5 μm , and 4.6 mm \times 250 mm column. A mobile phase composed of 80% methanol and 20% water at a flow rate of 1 ml/min was used. In the study, the catalytic activity of the as-prepared Pd-loaded ceramic membrane support was expressed by the hydrogenation rate, which was calculated as the amount of hydrogen consumed per hour per surface area of the membrane support.

RESULTS AND DISCUSSION

1. Characterization of Pd-loaded Ceramic Membrane Supports

The textural properties of palladium nanoparticles deposited on the ceramic membrane support were characterized in detail by many techniques including XRD, SEM, EDS, ICP, TEM and XPS.

Fig. 2 gives the XRD patterns of Pd-loaded ceramic membrane support and bare ceramic membrane support. Compared to the ceramic membrane support, two new peaks are observed, which can be indexed to the (111) and (200) reflections from fcc palladium (JCPD #00-005-0681). The results indicate that the palladium nanoparticles are successfully bound to the surface of amino-functionalized ceramic membrane support. The broadening of the Bragg reflections from palladium clearly suggests that the formed palladium particles are small, and the calculated average crystallite size is 3.7 nm according to the Scherrer equation [20].

Fig. 3 contains the FESEM images of ceramic membrane supports before and after immobilization with palladium nanoparticle colloid. Obvious differences can be observed in both FESEM images. The membrane support surface becomes rougher as the

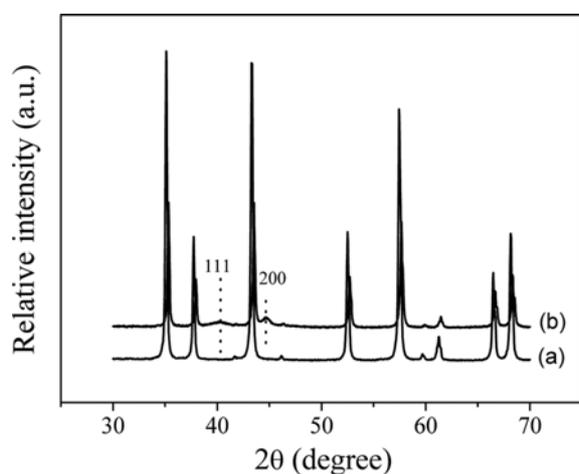


Fig. 2. XRD patterns of (a) ceramic membrane support and (b) Pd-loaded ceramic membrane support.

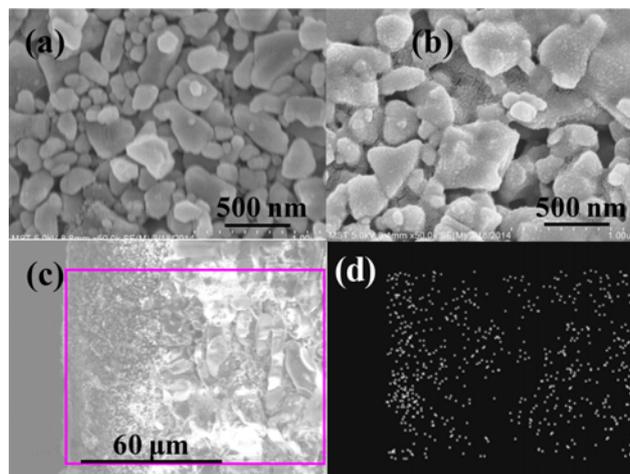


Fig. 3. (a) Surface FESEM image of ceramic membrane support, (b) surface FESEM image of Pd-loaded ceramic membrane support, (c) EDS analysis of cross section of Pd-loaded ceramic membrane support.

palladium nanoparticles are loaded on the amino-functionalized ceramic membrane support. Fig. 3(b) clearly shows that the pre-synthesized palladium nanoparticles can be uniformly dispersed on the membrane support surface, similar with our previous work [21]. However, compared to the Pd-loaded ceramic membrane support prepared by an impregnation-reduction method, the deposited palladium nanoparticles are not legible, which should be caused by the PVP added in the synthesis of palladium nanoparticle colloid as presented in section 2.2. It is seen from Fig. 3(c) that the palladium nanoparticles are predominantly located in the membrane surface layer, owing to the higher area of the surface layer compared to that of the large pore support layer [21].

TEM images of palladium nanoparticles in the colloid and on the membrane support are shown in Fig. 4. From the TEM images of palladium nanoparticle colloid, the palladium nanoparticles are well separated without apparent aggregation, and the particle size is about 4 nm, which is consistent with the result of XRD in Fig. 2.

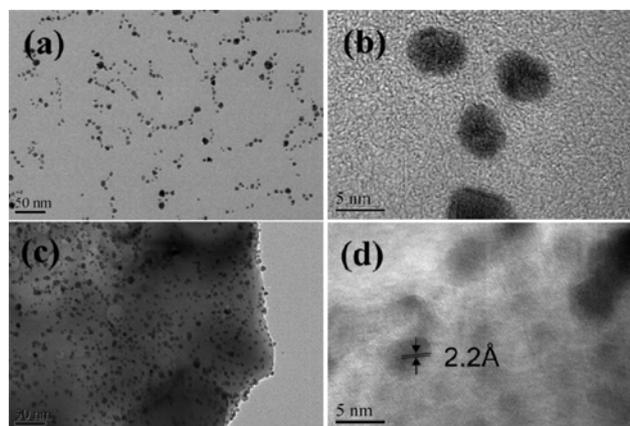


Fig. 4. TEM images of (a), (b) palladium nanoparticle colloid and (c), (d) the powder taken from the top membrane layer of Pd-loaded ceramic membrane support.

Fig. 4(c) highlights that the palladium nanoparticles are homogeneously immobilized on the ceramic membrane support, in good agreement with the result of FESEM. Furthermore, the particle size of palladium nanoparticles deposited on the ceramic membrane support is also about 4 nm, the same as that of palladium nanoparticle colloid, indicating that the impregnation process has no obvious influence on the particle size of palladium nanoparticles. A similar particle size was obtained for the palladium nanoparticles deposited on the ceramic membrane support synthesized by an impregnation-reduction method [21]. As given in Fig. 4(d), the characteristic lattice fringes of 2.2 Å spacing confirms the (111) planes of the face-centered cubic Pd (0) structure [22].

The palladium loaded on the membrane support as estimated by ICP analysis is 0.39 mg/cm² of membrane support area (corresponding to 8.8 mg of palladium mounted in the reactor for the catalytic reactions), similar to the value of 0.43 mg/cm² membrane support area (corresponding to 9.7 mg of palladium mounted in the reactor for the catalytic reactions) for the Pd-loaded ceramic membrane support synthesized by an impregnation-reduction method [21]. The results suggest that the preparation methods used in our work do not obviously affect the loading amount of palladium nanoparticles deposited on the ceramic membrane support. This may be explained by the following facts. For both preparation methods, the ceramic membrane support was modified by the same silane coupling agent AAPTS, and the modification conditions were almost the same. Therefore, the microstructure and amounts of amino group would be similar. In addition, the palladium nanoparticles were loaded on the ceramic membrane support through the bridge of silane coupling agent. As a result, the palladium loading can be comparable with respect to both preparation methods.

X-ray photoelectron spectroscopy was used to test the element valence state on the membrane support. XPS survey spectrum of the powder taken from the top membrane layer of Pd-loaded ceramic membrane support is shown in Fig. 5. The main peaks observed in the survey spectrum are Al 2p, C 1s, Pd 3d, N 1s and O 1s. The elements Al and O should come from the ceramic membrane support [19], while the elements N and Pd mainly come from the silane coupling agent AAPTS and palladium nanoparticles, respectively.

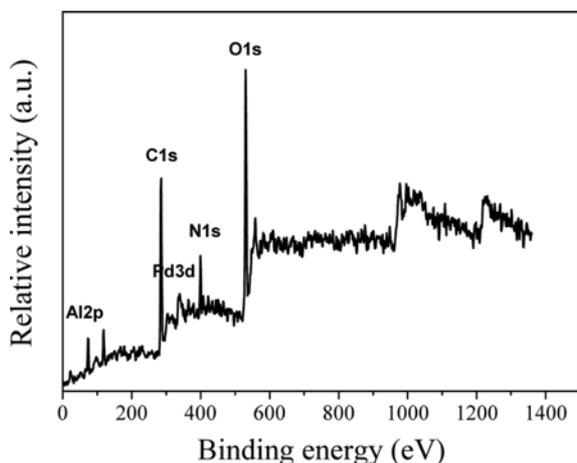


Fig. 5. XPS survey spectrum of the powder taken from the top membrane layer of Pd-loaded ceramic membrane support.

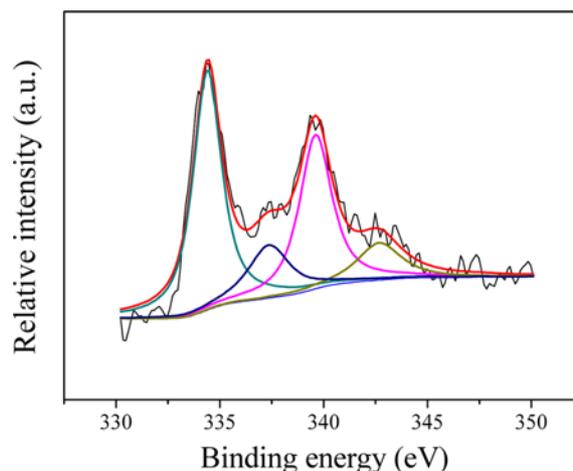


Fig. 6. Pd 3d XPS spectrum of the powder taken from the top membrane layer of Pd-loaded ceramic membrane support.

These results confirm the successful grafting of AAPTS and palladium nanoparticles onto the ceramic membrane support. The oxidation state of Pd on the ceramic membrane support was established by the Pd 3d XPS narrow spectra. As shown in Fig. 6, spin-orbital coupling effect results in the splitting of the 3d emission from palladium into two discrete peaks centered at 336 eV and 341.4 eV, which correspond to 3d_{5/2} and 3d_{3/2} core levels of metallic palladium. At the same time, characteristic peaks of Pd(II) at 337 and 342 eV also can be found in the spectra, which indicates palladium acetate was not reduced completely in the preparation of palladium nanoparticle colloid. The content of Pd(II) accounts for 24% of the total amount of palladium on the membrane support. Combined with the result of ICP, we can conclude that the loading of Pd(0) is 0.296 mg/cm² of membrane support area, a primary requirement for the Pd-catalyzed hydrogenation reactions, which is higher than that for the impregnation-reduction method (0.254 mg/cm² of membrane support area). Fig. 7 is the N 1s XPS spectrum that consists of a single peak at 399.1 eV with a full width. Two peaks at 400.05 and 403.55 eV were found in the N 1s XPS spectrum for the Pd-

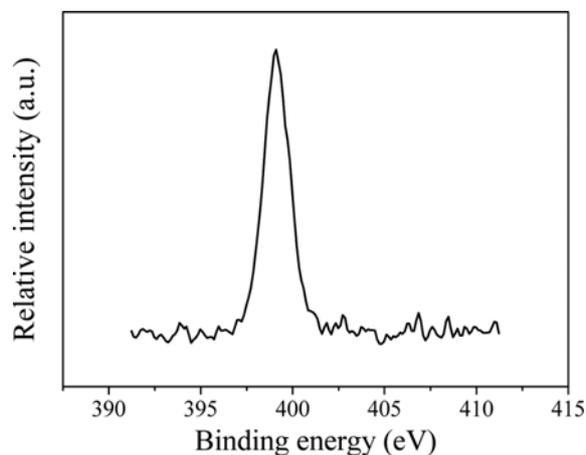


Fig. 7. N 1s XPS spectrum of the powder taken from the top membrane layer of Pd-loaded ceramic membrane support.

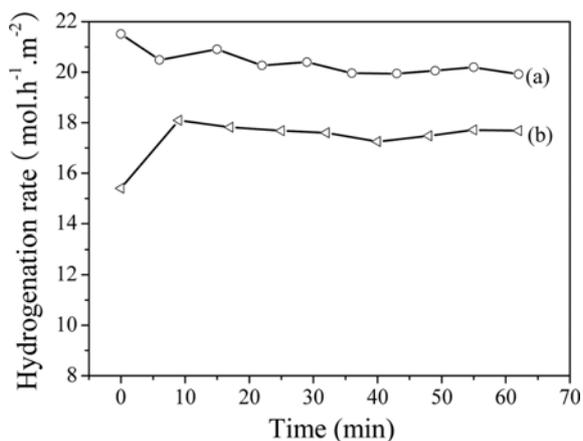


Fig. 8. Hydrogenation rate of Pd-loaded ceramic membrane support prepared by (a) nanoparticulate colloidal impregnation method and (b) impregnation-reduction method.

loaded ceramic membrane support synthesized by an impregnation-reduction method [21]. The difference between both samples may be caused by abundant nitrogen in PVP capping the palladium nanoparticles.

2. Hydrogenation of *p*-Nitrophenol on the Pd-loaded Ceramic Membrane Supports

Pd nanoparticles can exhibit excellent catalytic performance in hydrogenation reactions under suitable reaction conditions [23,24]. Owing to higher efficiency and being environmentally benign, catalytic hydrogenation of *p*-nitrophenol is a promising route to synthesize *p*-aminophenol that is of great commercial importance as an intermediate for the preparation of analgesic and antipyretic drugs [25,26]. Therefore, the hydrogenation of *p*-nitrophenol to *p*-aminophenol is selected as a model reaction for testing the catalytic properties of as-prepared Pd-loaded ceramic membrane support.

Fig. 8 shows the catalytic activity of the as-prepared Pd-loaded ceramic membrane support; for comparison, the result of the Pd-loaded ceramic membrane support prepared by an impregnation-reduction method in our previous work [21] is also presented. It is interesting to find that the catalytic activity of Pd-loaded ceramic membrane support synthesized by a nanoparticulate colloidal impregnation method is obviously higher compared to the impregnation-reduction method. For example, at about 60 min, for the former, the hydrogenation rate is about 20.4 mol/(h·m²), while the hydrogenation rate is about 17.5 mol/(h·m²) for the latter. The results highlight that the preparation method is of great importance for fabricating the palladium nanoparticles on the ceramic membrane support, and the nanoparticulate colloidal impregnation method is beneficial to enhancing the catalytic performance of Pd-loaded ceramic membrane support. We can see from the previous characterization results that the preparation methods adopted in our work have no obvious effect on the particle size, morphology and dispersion of palladium nanoparticles deposited on the amino-functionalized ceramic membrane support. However, the composition of palladium nanoparticles can be significantly affected by the preparation method as shown by the XPS characterization. Compared to the impregnation-reduction method, the nanoparticulate colloidal

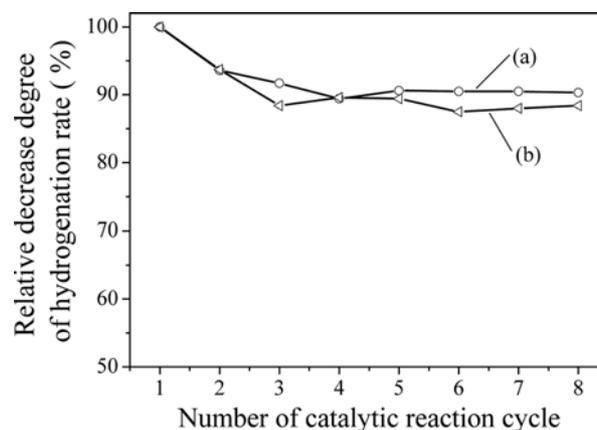


Fig. 9. Catalytic stability investigation of Pd-immobilized ceramic membrane support prepared by (a) nanoparticulate colloidal impregnation method and (b) impregnation-reduction method.

idal impregnation method can make more proportion of Pd(0), resulting in more active catalytic centers and higher catalytic activity. In addition, the hydrogenation rate increases about 16.6%, obviously proportional to the increased degree of Pd(0) content (16.5%). These results suggest that higher Pd(0) content is the key factor for enhanced catalytic activity of Pd-loaded ceramic membrane support synthesized by the nanoparticulate colloidal impregnation method.

A number of catalytic hydrogenation cycles were carried out to investigate the recycle performance of the as-prepared Pd-loaded ceramic membrane support. In the present work, the catalytic stability is expressed by the ratio of the hydrogenation rate after a certain number of reaction cycles to that during the first reaction cycle. Fig. 9 plots the relative decrease degree of hydrogenation rate against the number of catalytic reaction cycle, and at the same time the catalytic stability result of Pd-loaded ceramic membrane support prepared by the impregnation-reduction method [21] is also given for direct comparison. For the Pd-loaded ceramic membrane support prepared by the nanoparticulate colloidal impregnation method, the catalytic activity first decreases and then almost keeps stable, and the decreased degree of catalytic activity after eight continuous hydrogenation cycles is about 9.5%. Similar results are observed for the Pd-loaded ceramic membrane support prepared by the impregnation-reduction method. The results indicate that the preparation methods adopted in our work have no obvious influence on the catalytic stability of Pd-loaded ceramic membrane support. It can be assumed that the palladium nanoparticles were all immobilized on the ceramic membrane support through the bridge of silane coupling agent AAPTS for both preparation methods, leading to similar catalytic stability. To understand the deactivation reasons, the recovered Pd-loaded ceramic membrane support after eight continuous hydrogenation cycles was characterized by ICP and TEM. The ICP result shows the palladium content is 0.35 mg/cm² of membrane support area, namely, the leaching degree of palladium is about 10.3% after eight continuous hydrogenation cycles, matching the decreased degree of catalytic activity. In addition, the TEM images of Pd-loaded ceramic membrane support after eight continuous hydrogenation cycles in Fig. 10 show that the palladium

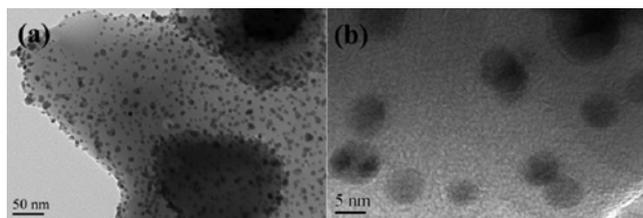


Fig. 10. TEM images of the powder taken from the top membrane layer of Pd-loaded ceramic membrane support after eight catalytic reaction cycles.

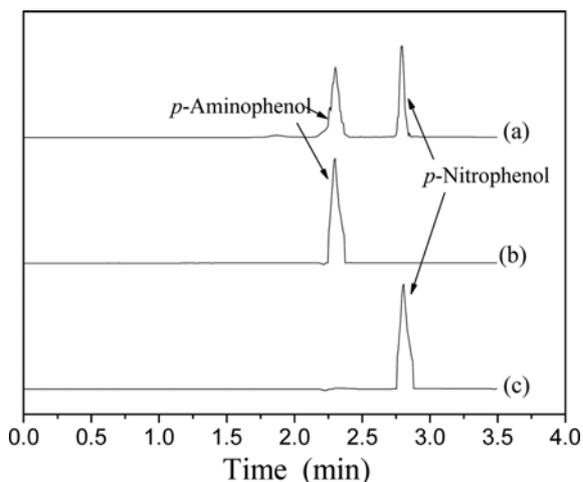


Fig. 11. HPLC analyses of (a) the reaction products catalyzed by the Pd-immobilized loaded ceramic membrane support, (b) analytical grade *p*-aminophenol and (c) analytical grade *p*-nitrophenol.

dispersion and particle size do not change obviously as compared to the fresh ones as presented in Fig. 4. In conclusion, palladium leaching during the continuous hydrogenation cycles is the main reason for the decrease of catalytic activity of the as-prepared Pd-loaded ceramic membrane support. Similar results have been found by other researchers [27,28]. Metal leaching in the reaction medium was considered as one of the main causes of catalyst deactivation in liquid-phase reactions [27].

To evaluate the catalytic selectivity of the as-prepared Pd-loaded ceramic membrane support, the products were analyzed by HPLC and the results are given in Fig. 11. Beside the reactant *p*-nitrophenol, only target product *p*-aminophenol is found, indicating the high catalytic selectivity of the as-prepared Pd-loaded ceramic membrane support in the *p*-nitrophenol hydrogenation, in agreement with our previous work [18,19,21].

CONCLUSIONS

Palladium nanoparticles were deposited on an amine-functionalized ceramic membrane support to prepare a Pd-loaded ceramic membrane support with the nanoparticulate colloidal impregnation method where a higher loading of Pd(0) was obtained. Compared to the impregnation-reduction method, the Pd-immobilized ceramic membrane support prepared by the nanoparticulate col-

loidal impregnation method had higher catalytic activity and comparative stability in the *p*-nitrophenol hydrogenation to *p*-aminophenol. The results of this explorative study are encouraging, and further research is in progress to improve the performance of the as-fabricated Pd-loaded ceramic membrane support by optimizing the preparation conditions of palladium nanoparticle colloid.

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