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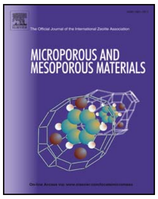

Pd NPs supported on N-doped carbon layer coated ZrSBA-15 for efficient heterogeneous catalysis reactions

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ABSTRACT

Through hydrothermal synthesis and impregnation-reduction processes, a series of Pd-based nanocomposites using N-doped carbon layers coated ZrSBA-15 as the supports have been manufactured, aiming to upgrade the catalytic activity and stability of the catalysts. Pentaethylenehexamine (PEHA) was served as a nitrogen source to generate N-doped carbon (CN) layers that were pre-deposited into the acidic platelet framework ZrSBA-15, and then followed by introducing Pd^0 nanoparticles (NPs) onto it, finally leading to the formation of target composite Pd/CN-ZrSBA-15. The samples were characterized by XRD, TEM, SEM, N_2 adsorption-desorption isotherm, FTIR, XPS etc. The catalytic performance of as-prepared catalysts was evaluated by the aerobic oxidation of benzyl alcohol and the reduction of 4-NP, respectively. Duo to the platelet-like morphology with shortened channels and the modification of N-doped carbon layers, which could effectively decrease pore blocking in the process of preparation and reactions as well as enhance the metal-support interaction, the derived catalysts could afford 85% conversion of benzyl alcohol and 100% selectivity of benzaldehyde, and the conversion of 4-NP was also up to 96%. More remarkably, the catalysts could be reused at least ten times without significantly loss in catalytic activity.

1. Instruction

Nowadays, the employ of supported noble metal heterogeneous catalysts, owning to its excellent selectivity and reusability in organic synthesis of desirable fine chemicals, is prevalent in industrial applications and academic research [1–3]. The catalyst performance for specific applications is fundamentally determined by the constituent and structure of the metal component and the interaction with the support. In particular, Palladium (Pd) nanoparticles dispersed on various supports as catalysts have been extensively studied not only in the oxidation reactions but also in the hydrogenation reduction reactions of fine chemicals [4,5]. It is well known that Pd-base catalysts have long life, high catalytic activity, selectivity, which can be improved through the change of preparation methods, it also can be regenerated and activated repeatedly.

Besides, in the advancement of the supported catalysts, the supports or carriers play an increasingly vital role in immobilizing the active constituent, improving the structure and thermal stability, enhancing the availability of active components, and increasing the reaction selectivity, etc [6–9]. As support materials, ordered mesoporous silica materials with uniform pore size distribution and a large surface area have aroused widespread research interest. Amongst them, SBA-15 has been one of the most thoroughly and widely studied mesoporous silica materials, due to its excellent properties when found in the last two decades [10–12]. And, SBA-15 has large specific surface area, highly uniform 2D hexagonal array of pores structure, good thermal and mechanical stability [13].

Up to now, many reported works have been concerned about the synthesis of hybrid nanocomposite materials via forming different metal or metal oxide nanoparticles on SBA-15 support for a variety of applications in different fields such as catalysis [14,15], adsorption and separation [16,17], drug delivery [18], biomedicine [19], etc. Furthermore, in order to disperse and anchor the active components more efficiently, the morphology of SBA-15 was modified into different shapes such as rod-like [20], fiber-like [21], and platelet-like. By comparison, it is not difficult to find that the platelet-like SBA-15 material is superior to the other morphology in the aspects of mass transportation and less pore blocking of catalysts [22]. Hence, to obtain the platelet-like SBA-15, Zr-containing SBA-15 was manufactured to form the quite shortened channels, which is easy for molecular

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diffusion, thus improving reaction efficiency [23–25]. It is worth mentioning that the incorporation of Zr atoms can improve the hydrothermal stability of the pore walls and also greatly increase the amount of lattice defects in the framework, thus increasing acidic sites to intensify the metal-support interactions between ZrSBA-15 and Pd NPs, as compared to purely SBA-15 [26].

Recently, it is reported that the catalytic activity of the supported Pd-based catalysts has be greatly improved by various strategies like chemical doping with heteroatoms onto the defective sites of carbon and hybridizing together with other catalysts [27], especially the chemical doping such as nitrogen [28,29], sulfur [30], and phosphorous [31]. Among them, nitrogen-rich nanostructures with abundant sites are favorable to anchor the metal particles on its surface, and N-doped porous carbons have been used as support to load Pd NPs for alcohol oxidation [32]. Nevertheless, considering that the morphology of porous carbons and pore length go against the polyphase catalysis process occurring at liquid-solid interfaces [33], ZrSBA-15 was fabricated to get the morphology of thicker pore walls, short pore channels, high framework stability and platelet shape, which has been successfully employed as support in alcohol oxidation [34]; yet, ZrSBA-15 modified by N-doped carbon species has been mentioned rarely, even it might contribute fascinating message toward the catalytic applications in fine chemical synthesis.

Herein, this work aims to employ the nitrogen-rich carbon materials as accelerator to improve the recycling performance of Pd-based catalysts. That is, a coating of N-doped carbon species was immobilized onto the interior framework of ZrSBA-15 utilizing a simple carbonization method, by which is to enhance the metal-support interaction of the catalytic composites. Subsequently, Pd NPs about 2.0–4.0 nm were encapsulated into CN-ZrSBA-15 by impregnation-reduction method.

As is known, the selective catalytic oxidation of alcohols to corresponding aldehydes is one of the most predominant organic reactions in industrial applications and laboratory research, particularly the production of benzaldehydes, which has been widely used in medicine, spices and foods [35–37]. In addition, 4-nitrophenyl (4-NP) is one of the most common organic contaminants in industrial waste water because of its high solubility and stability. Furthermore, its reduction resultant 4-aminophenol (4-AP) is a pretty important organic fine chemical intermediate of indicator, synthetic dyes and other materials. And Pd based catalysts for catalytic reduction of 4-NP to 4-AP have been applied in the recent progress [38,39]. As a consequence, to demonstrate the significant enhancement of catalytic performance, both probing reactions of catalytic aerobic oxidation of benzyl alcohol to benzaldehydes and the reduction of 4-NP, which are well-known model reactions in laboratory-scale reactions, were selected as to evaluate the performance of as-fabricated catalysts. Namely, various reaction factors and recycling capability was conducted out to establish the relationship between preparative conditions and applied aspects. And also, some contrast experiments have been carried out in optimum conditions using different catalysts.

2. Experimental section

2.1. Materials and chemicals

Pentaethylenehexamine (PEHA) and triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) were purchased from Sigma-Aldrich and used as supplied. Potassium tetrachloropalladate (II) (K_2PdCl_4), tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl, 37%), zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$), benzyl alcohol, and benzaldehyde were bought from the China National Medicines Co. Ltd. and used as received. Other chemicals like 4-nitrophenol (4-NP) and $NaBH_4$ were obtained from Aladdin Chemistry Co. Ltd., China. Nitrobenzene was used as internal standard for the gas chromatography (GC) assays. All chemicals were analytical grade and used without further purification.

2.2. Catalyst preparation

2.2.1. Synthesis of ZrSBA-15

ZrSBA-15, with shortened pore channels, was synthesized directly by a hydrothermal route according to the reported literature using tetraethylorthosilicate (TEOS) as the silica source, P123 as the template and HCl as the pH controlling agent [40]. Briefly, Pluronic P123 (5.0 g) was fully dissolved in de-ionized water, and concentrated hydrochloric acid (HCl, 37%, 30 mL) was added under continuous stirring at ambient temperature for 30 min. Then, zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, 0.8 g) was added in the mixture for stirring 30 min at 40 °C. Subsequently, TEOS (11 mL) was added dropwise. This solution obtained should be kept in 40 °C under vigorously stirring for 24 h. After that, the solution was transferred into a Teflon-lined autoclave and placed statically in the oven at 100 °C for another 24 h. In the end, the acquired crystallized precipitate was filtered, washed with de-ionized water, dried at 80 °C, and then further calcined at 550 °C for 5 h to remove the template agent.

2.2.2. Synthesis of CN-ZrSBA-15

Preparation of PEHA/ZrSBA-15: Typically, PEHA/ZrSBA-15 (1:2) was synthesized through deposition as follows. To dissolve 2.0 g of as-prepared ZrSBA-15 in ethanol (100 mL), mixing and dissolving. To prepare the solution of pentaethylenehexamine (1.0 mL) and ethanol (2–3 mL), and add it into the mixture solution dropwise. Then, the resulted mixture was vigorously stirred for 6 h at 60 °C in the water bath. The obtained mixture was separated with centrifuge, and dried in oven overnight. Furthermore, the thickness of N-doped carbon layer was controlled by changing the ratio of PEHA to ZrSBA-15. Ultimately, the optimal mixing ratio of PEHA to ZrSBA-15 was confirmed as 1:2 via the catalytic efficiency of the reaction mentioned in this article. And if no clear specifications, the ratio of PEHA to ZrSBA-15 was represented as 1:2.

Preparation of CN-ZrSBA-15: ZrSBA-15 coated with N-doped carbon layer (CN-ZrSBA-15) was fabricated by the carbonization of as-achieved PEHA/ZrSBA-15, which was carried out in a programmable tube furnace under N_2 atmosphere. Traditionally, the as-prepared PEHA/ZrSBA-15 placed in a crucible was thermally heated at the desired temperature for 4 h with a heating rate of 5 °C min^{-1}. Finally the samples were cooled to room temperature. The final product after calcination was marked as CN-ZrSBA-15. In order to confirm the optimum calcination temperature, the samples were calcined in N_2 atmosphere at 400, 500, 600, 700 and 800 °C for 4 h, respectively. And if no clear indications, the calcination temperature of CN-ZrSBA-15 was denoted as 600 °C.

2.2.3. Synthesis of Pd/CN-ZrSBA-15 nanocomposite

Pd/CN-ZrSBA-15 nanocatalyst was manufactured by the following procedures. CN-ZrSBA-15 (0.5 g) was ultrasonically dispersed in de-ionized water (100 mL) to a homogeneous turbid liquid. Subsequently, a certain amount aqueous solution of K_2PdCl_4 was added into the above solution. After being stirred for 4 h at room temperature, excess amount of $NaBH_4$ solution prepared freshly was added dropwise, and continuously stirred for another 20 h. Then the Pd nanoparticles were obtained from the reduction of divalent Pd and anchored on the PEHA functionalized ZrSBA-15. Finally, the heterogeneous catalysts were achieved by centrifugation, washed repeatedly with de-ionized water and ethanol to have no chloride ion detected, and dried overnight in a vacuum at 60 °C. The final obtained catalyst was denoted as Pd/CN-ZrSBA-15. As comparison intention, the catalyst ZrSBA-15 supported Pd NPs directly was prepared with the same method aforementioned consistently, named as Pd/ZrSBA-15. Moreover, the diverse loading amounts of Pd nanoparticles of the catalysts have be studied, which are 2.0, 2.5, 3.0, 3.5, 4.0 wt%, respectively, named x-M-S (e.g. 3.0-Pd/CN-ZrSBA-15). It should be noted that all of the catalysts supported Pd NPs were prepared by using an impregnation-reduction process. Besides, the