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Nanosized nickel decorated sisal fibers with tailored aggregation structures for catalysis reduction of toxic aromatic compounds

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ABSTRACT

Integration of highly-active nanoscale metal-based components into unique skeleton materials to enhance their intrinsic properties is significant for the cost-efficient application of catalyst. Here, two sisal fiber templates with different structure were chemically obtained and employed as the supporters to immobilize nickel nanoparticles by electroless deposition method in nickel bath. The coating of nickel nanoparticles (NPs) inherited preferably the micromorphology of fiber with lumen and surface micro convex structure. Compared to sisal fiber bundle (SFB), elementary sisal fibers (ESFs) afford a superior deposited substrate for Ni NPs, which exhibit highest catalytic rate constant $16.14 \times 10^{-3}\,s^{-1}$ and turnover frequency $1.82 \times 10^{-3}\,mol\,mol^{-1}\,s^{-1}$ at 20 °C and molar ratio of $NaBH_4$: *p*-NP (100) for reduction of *p*-NP with only 3.39 wt.% Ni. The outstanding performance of Ni/ESFs obtained here can be assigned to the high content of metallic nickel in nanoparticles, the flexible fiber based 3D network and the synergistic effect of Ni NPs and ESFs. Ni/ESF catalysts were also successfully applied for the catalytic hydrogenation of methyl orange (MO) and Rhodamine B (RhB). Moreover, present catalyst further exhibited excellent reusability derived from their stable physic-chemical structure and magnetically separable feature in the catalytic reaction. As a result, supported by the widely-available sisal fiber templates with tailored structures, present catalysts show the certain superiority in cost-effective hydrogenation of refractory aromatic pollutants compared to the catalysts reported in the literatures.

1. Introduction

Refractory aromatic pollutants are widespread in effluents from the pharmaceutical, dyestuff, pesticide, paper, textile industries and so on (Lyu et al., 2015; Zhao et al., 2011). Nitro-aromatic compounds and polycyclic aromatic hydrocarbon are the most common contaminants. Due to the high solubility in water, they are inevitably released into the environmental water bodies and do harm to human health (Barreto-Rodrigues et al., 2009). On the other hand, it is prone for them to be transformed to a sort of persistent pollutants due to the insufficient elimination by conventional water treatment. Additionally, in the degradation processes, more toxic byproducts may be generated easily (Hu et al., 2002; Liu et al., 2016). Thus, these issues about aromatic pollutants treatment have captured the attention of scientists to develop the effective remediation techniques for their detoxification.

Catalytic hydrogenation reactions is one important and useful chemical transformation and provide a moderate method for the efficient conversion of persistent aromatic pollutants into less toxic amino compounds under the action of atomic hydrogen (Jr. and Falconer, 1995; Kumar and Deka, 2014; Serra et al., 2016). Recently, the late transition metal based catalysts such as nickel phosphide (Liu et al., 2016), nano nickel (He et al., 2013), RANEY nickel (Wang and Rinaldi, 2012), and nano Cu (Maity et al., 2013) are the frequently employed metallic catalysts in the hydrogenation process, because they possess the feature of low cost, ready availability, comparatively low toxicity, greater sustainability, and unique reactivity profiles compared to noble metallic catalysts (Feng et al., 2015; Wang and Astruc, 2017). In the past few decades, Ni-Based nanocatalysis reduction reaction has experienced an exponential growth due to its higher stability compared to Fe or Co nanoparticles with outstanding catalysis performance (Wang

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and Astruc, 2017).

Generally, nanosized metal based catalysts can be easily synthesized by diverse rapid preparation techniques. However, in the water treatment process, the direct application of metal nanoparticles encounters great challenges against the serious agglomeration and perpetual suspension, which dramatically lowers their catalytic activity and stability (Wang et al., 2013). An effective solution is combining metal particles with the scaffold materials with unique structure as catalyst support endowing the metal nanoparticles highly dispersed with improved catalytic property and recyclability (Niu et al., 2014). For example, Pt and Ni metal catalysts have been supported on carbonaceous solids or alumina. They can increase the distance between each catalyst particles, which enables a greater exposure of substrate molecule to catalyst particles (Ombaka et al., 2013). Till now, various supports have been studied for improve the catalysis properties such as carbon nanofibers (Fakeeha et al., 2015), nanostructured thin films (Demirel et al., 2007), polymeric hollow fiber membranes (Macanas et al., 2010), anodic aluminum oxide (AAO) membranes (Dotzauer et al., 2006), polymeric nanofibrous membrane (Liu et al., 2016), alumina–silica foam (Kovalenko et al., 2009) and so on. Among these, natural materials possess hierarchical (e.g. skin collagen fiber (Guo et al., 2012)) or multilayered (e.g. natural illite clay (Akri et al., 2017)) or pore structures (e.g. woods (Ji et al., 2016)), which provide maximum possible active sites for nanoparticle growth with controlled particle size and dispersion simultaneously. More importantly, they can facilitate the fast diffusion and mass transport of reactants/products over catalyst surface and achieves high reaction rate (Kärger and Valiullin, 2013).

Sisal fiber (*Agave sisalana*) is the most widely used plant fiber in the world and is very easily cultivated due to its short renewal times (Oliveira et al., 2015). It is normally extracted from sisal leaf with renewable, abundant and low-cost tubular features. To effectively utilize this kind of industrial crop, diverse novel application like catalyst support should be developed. Sisal fiber has huge lumen, large aspect ratio and insoluble cellulosic structure (Liu et al., 2012; Ramesh et al., 2013), which render it good candidate as the supporter of active nanoparticles. It is valuable to investigate the enhancement effect of sisal fiber on the catalytic performance of active nanoparticles (i.e. nickel based NPs) immobilized in/on the fiber template. Furthermore, it is well known that leaf fibers are usually applied in form of fiber bundle coated by wrinkles of cuticle (Liu et al., 2014). In fiber bundle, numbers of single fibers are embodied with spiral arranged fibril on their surface and this type of hierarchical structure can be hold and even highlighted after single fibers are separated from each other by suitable chemical treatment (Pommet et al., 2008; Sorieul et al., 2016). Compared to fiber bundle, the separated fibers are more liable to offer more sites for nanoparticles' immobilization and the interaction between reactants/products and catalyst due to their higher specific surface area (Kärger and Valiullin, 2013). However, sisal fiber just has been employed as fiber bundle (Oliveira et al., 2015; Hemachandran et al., 2017) or as mineralized carbon fiber (He and Li, 2007) for particle supporting hitherto. Therefore, it is extremely valuable to enhance rather than compromise the properties of nanoscale nickel catalyst through supporting them by separated sisal fiber with multilevel structure.

In this contribution, sisal fibers were treated chemically to obtain two bio-templates: separated elementary fibers and fiber bundle. The templates were employed as the supporters to immobilize nickel nanoparticles on their surface by electroless deposition method in nickel bath. Furthermore, the feasibility of as-prepared nanocomposite was demonstrated in the catalytic reduction of *p*-nitrophenol (*p*-NP), methyl orange (MO) and Rhodamine B (RhB). The recycle tests were also performed to assess the comprehensive catalytic property.

2. Material and methods

2.1. Materials

Sisal fibers were kindly provided by Dong-Fang Sisal Company (Guangdong, China). The composition and crystallinity of fibers are shown in Table S1 determined by the method reported in literatures (Liu et al., 2013; Mariano et al., 2016). Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), sodium tartrate ($C_4H_4Na_2O_6$), hydrazine monohydrate ($N_2H_4{\cdot}H_2O$), sodium hydroxide (NaOH), concentrated hydrochloric acid, concentrated sulphuric acid were from Sinopharm Chemical Reagent Co., Ltd. Stannous chloride hydrate ($SnCl_2{\cdot}2H_2O$), palladium Chloride ($PbCl_2$), γ-aminopropyltrimethoxysilane (APTMS), sodium chlorite ($NaClO_2$), Sodium borohydride ($NaBH_4$,96%), 4-nitrophenol were all obtained from Aladdin Industrial Corporation. All chemicals used in the experiments were all analytical reagent grade and without further purification.

2.2. Template preparation of sisal fiber

Sisal fibers were treated by mercerization method reported previously (Eronen et al., 2009; Zhu et al., 2012). The raw fibers were cut into about 5 cm lengths by hand before the chemical treatment. Then the fibers were immersed into 5 wt% NaOH solution for 3 h at 50 °C with the bath ratio (weight ratio of fiber to solution) 3 g: 100 ml. After the mercerizing process, the fibers were washed with deionized water twice. Then the fibers were performed using sodium chlorite in 10% acetic acid aqueous solution (pH = 4.0) (bath ratio: 1 g: 50 ml). After reaction for 2 h at 70 °C, the fibers were rinsed carefully with deionized water. Then 17.5% sodium hydroxide solution was applied for 20–40 min at 20 °C to remove most of the hemicellulose in fibers (bath ratio: 1 g: 50 ml). As a result, elemental sisal fiber (ESF) was successfully prepared. Alternatively, sisal fiber bundles (SFBs) were obtained just by the treatment of 17.5% sodium hydroxide solution. Finally, previous treated fibers were washed with water and 70% ethyl alcohol twice and dried at 80 °C for further treatment.

2.3. Preparation of nickel nanoparticles decorated sisal fibers

As shown in Scheme 1, the dried elementary sisal fibers and sisal fiber bundles with 3 g weight were immersed in ethanol solution (200 ml) of 0.1% 3-aminopropyltrimethoxysilane (APTMS) for 12 h, and then cleaned with ethanol and deionized water, respectively. Finally, the grafted fibers were heated at 80 °C to remove solvent. 3 mg of sisal fibers were treated with a mixture aqueous solution (100 ml) of 10 g/L $SnCl_2$ and 30 ml/L HCl by slight agitation at 25 °C for 3 min for surface sensitization. After being rinsed with deionized water, the fibers were activated by the immersion in 100 ml solution of 0.25 g/L $PdCl_2$ and 20 ml/L HCl at 25 °C for 2 min. The activated sisal fiber were successfully obtained after cleaned by deionized water, which were then immersed into nickel eletroless plating solution (200 ml) containing $NiCl_2$ (5 g/L), sodium tartrate (7 g/L), hydrazine monohydrate (30 g/L) at 70 °C for several minutes with pH of 10.0 by using 2 mol/L sodium hydroxide solution. After the electroless plating, Ni/elementary sisal fibers (Ni/ESFs) and Ni/sisal fiber bundle (Ni/SFB) with different nickel loading content were rinsed with deionized water and freeze dried at −80 °C.

2.4. Characterization

The scanning electron microscopy image, energy dispersive X-ray spectroscopic analysis (EDS) and emission scanning electron microscope elemental distribution mapping of samples were from a JEOL JSM-6510L scanning electron microscope with energy dispersion X-ray fluorescence analyzer installed. All samples were sputtering-coated with gold before examination.