Palladium nanoparticles supported on a two-dimensional layered zeolitic imidazolate framework-L as an efficient size-selective catalyst

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ABSTRACT

A new Pd@ZIF-L hybrid catalyst having a unique crosshair-star shape with a size of about 20 μm was synthesized, in which a two-dimensional layered zeolitic imidazolate framework-L (ZIF-L) was used as a support to immobilize palladium nanoparticles via an assembly method. The hybrid catalyst with unique cushion-shaped cavities between layers with a size of 6.64 Å can be used for the diffusion of specific reactants not achievable by other ZIF systems such as ZIF-8. The crystal structure and morphology of Pd@ZIF-L are strongly dependent on the synthesis conditions. Palladium nanoparticles with an average size of 3 nm are homogeneously encapsulated in the ZIF-L crystals. The as-synthesized Pd@ZIF-L catalyst favors the conversion of alkenes with larger molecular sizes, and exhibits excellent molecule-size-selectivity and anti-leaching performance.

1. Introduction

Metal nanoparticles (MNPs) have been widely investigated for their potential applications in catalysis [1—3]. Due to the small grain size, a significant volume of the microstructure is composed of interfaces/grain boundaries and hence a large fraction of the atoms resides in grain boundaries, leading to more catalytic sites and enhanced catalytic performance [4]. Furthermore, recent advances in controlling the particle size and shape have opened up the possibility to optimize the particle geometry, providing the optimum size and surface properties for specific reactions [5]. Due to high surface energies and large surface areas, these MNPs are thermodynamically unstable, and therefore tend to aggregate during reactions, resulting in a significant decrease in the catalytic activity [6—8]. In this regard, solid materials with confined void spaces such as zeolites, metal organic frameworks (MOFs) and polymers are used as supports for MNPs immobilization. By utilizing the interaction or space limitations between the metal and the support, the agglomeration of MNPs can be prevented [9,10].

Zeolitic imidazolate frameworks (ZIFs), a sub-family of metal-organic frameworks (MOFs) [11,12], are highly ordered porous solids that consist of inorganic metal ions bridged by imidazolate ligands. Compared to other types of MOFs, ZIFs exhibit better thermal, hydrothermal and chemical stability [13]. Owing to their high porosity, large surface area and better stability, ZIFs provide great potential as hosts for various MNPs. Loading MNPs into the pores of ZIFs could limit the growth of MNPs within the confined cavities and also the migration and aggregation of MNPs during the reaction [14—16], thus increasing their catalytic activity and stability. There are two main strategies to obtain ZIF-immobilized MNPs — (1) the loading of ZIFs with molecular precursors followed by their subsequent decomposition inside the pores of ZIFs [17—19]. (2) The encapsulation of pre-synthesized MNPs inside the growing host frameworks [20]. The latter is more desirable as it avoids the formation of MNPs on the external surface and damaging the ZIF frameworks during the after-treatment processes which may occur in the former strategy.

Selection of ZIFs as supports for MNPs immobilization is one of the most important steps because the physical—chemical properties of ZIFs such as the pore structure can significantly affect the corresponding catalytic performance of MNPs@ZIFs. Each ZIF has a definite window size, such as ZIF-8 has small-pore apertures of 3.4 Å, which allow reactants having smaller molecule sizes than the

window size to easily diffuse into the pores to reach the active site or MNPs, thus showing outstanding molecular-size selectivity. For example, Pd@ZIF-8 showed high activity for ethylene hydrogenation, but no detectable activity was observed for cyclooctene hydrogenation [21]. These results were clearly due to the molecule-size-selective property of the ZIF-8, because the ethylene molecules (2.5 Å) are small enough to diffuse through the pore apertures of the ZIF-8 (3.4 Å), but not the cyclooctene molecules with a size of 5.5 Å. Recently, we have successfully synthesized a new two-dimensional zeolitic imidazolate framework (ZIF-L) in zinc salt and 2-methylimidazole aqueous solution at room temperature [22]. ZIF-L, comprised of identical building blocks of ZIF-8, has two-dimensional crystal lattices stacked layer-by-layer forming cushion-shaped cavities between layers. The two neighboring two-dimensional *sod* layers in ZIF-L are bridged by hydrogen bonds. They are parallel to each other and 3.97 Å apart, and the cushion-shaped cavities are 6.64 Å [23]. The special pore structure makes ZIF-L a good candidate for MNPs immobilization.

In this work, Pd@ZIF-L was synthesized via an assembly method that involves the successive adsorption of palladium nanoparticles onto the continuously forming surfaces of the growing ZIF-L crystals. The obtained Pd@ZIF-L was characterized by X-ray diffraction spectroscopy (XRD), inductively coupled plasma emission spectroscopy (ICP-AES), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and nitrogen sorption studies. Liquid-phase hydrogenation of alkenes with different molecular sizes namely 1-hexene (1.7 Å), cyclohexene (4.2 Å), cyclooctene (5.5 Å) and tetraphenylethylene (6.7 Å) were used to evaluate the molecular-size-selectivity of the as-prepared Pd@ZIF-L.

2. Experimental

2.1. Chemicals

Zn(NO$_3$)$_2$·6H$_2$O (99%) and 2-methylimidazole (2-MeIM) (99%) were purchased from Sigma–Aldrich. Pd(OAc)$_2$ was acquired from Sin-platinum Metals Co., Ltd., China. *p*-Nitrophenol (99.5%) was supplied by Aladdin. Hydrazine hydrate (N$_2$H$_4$·H$_2$O) was obtained from Lingfeng Chemical Reagent Co., Ltd., China. KBH$_4$ and polyvinylpyrrolidone (PVP) were supplied by Sinopharm Chemical Reagent Co., Ltd., China. NaOH was provided by Xilong Chemical Co., Ltd., Guangxi, China. Ethanol was supplied by Yasheng Chemical Co., Ltd., Wuxi, China. Deionized water (electrical conductivity <12 μs cm^{-1}) was produced in-house. All materials were used as received without further purification.

2.2. Preparation of Pd@ZIF-L

The procedure for immobilization of palladium nanoparticles in ZIF-L is presented in Scheme 1.

Firstly, Pd NPs colloid was prepared by a reduction method of Pd(OAc)$_2$. Typically, 0.5 mM of Pd(OAc)$_2$ and 2.83 mM of PVP were dissolved in 40 ml of methylene dichloride to yield the precursor solution. 11 ml of a reduction solution composed of hydrazine hydrate, potassium borohydride and sodium hydroxide with the molar ratio of 3:20:1 was added into the precursor solution under vigorous stirring, and the reaction was stirred at room temperature for 3 h. The obtained miscible liquid was washed with methylene dichloride for several times to remove the excess PVP in the solution, and then dispersed in 100 ml of deionized water to produce the Pd NPs colloid. Secondly, Pd@ZIF-L was prepared by an assembly method according to the literature [20]. The pre-
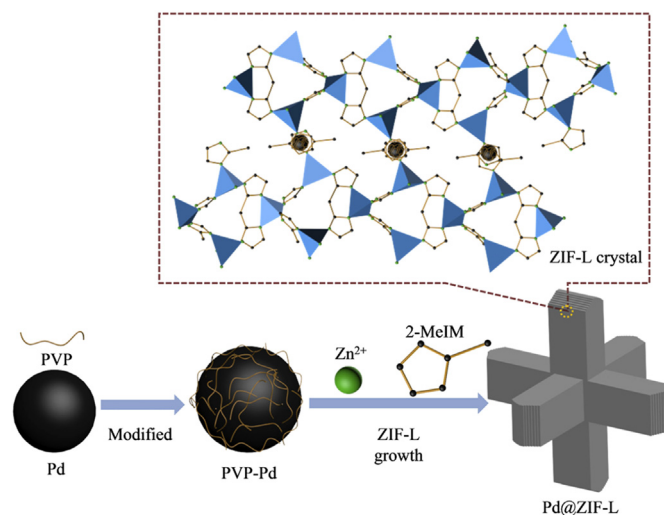
Scheme 1. Schematic of the preparation of Pd@ZIF-L catalyst.

synthesized Pd NPs colloid (10 ml) was mixed with a solution of 2-MeIM in deionized water (100 ml, 50 mM) at room temperature. Afterward a solution of zinc nitrate hexahydrate in deionized water (100 ml, 2.5 mM) was added quickly, and the mixture was stirred briefly at room temperature for 20 s and left for 48 h without stirring. The resulting black powder was collected by centrifugation, washed by deionized water for several times, and dried at 80 °C for 12 h to produce the ZIF-L immobilized palladium catalyst, denoted as Pd@ZIF-L-I. ZIF-L was prepared under the same conditions as the Pd@ZIF-L-I except for the addition of Pd NPs colloid. For comparison, the hybrid catalyst was synthesized under other conditions by changing the amount of Pd NPs colloid, the reaction time and the stirring time. Pd@ZIF-L-II was achieved with a reaction time of 24 h. The catalyst obtained by adding 15 ml of Pd NPs colloid is marked as dia(Zn)-I, while the one obtained by stirring the reaction solution for 48 h is denoted as dia(Zn)-II.

2.3. Characterization of Pd@ZIF-L

X-ray diffraction (XRD) patterns were obtained in the 2θ range of 5–50° on a Rigaku MiniFlex 600 diffractometer using Cu Kα radiation performed at 40 kV and 15 mA with a 2θ step of 0.02°. The microscopic morphology of the catalysts was examined using a field emission scanning electron microscope (FESEM, Hitachi S-4800II) and high resolution transmission electron microscopy (HRTEM, Jeol JEM-200CX). The HRTEM samples were prepared by sonication in ethanol for 10 min and then deposited onto carbon-coated copper grids. The content of palladium was determined by inductively coupled plasma emission spectroscopy (ICP-AES, Optima 2000DV). The measurements were performed at the Pd standard (340.458 nm). For ICP analyses, the samples were digested in 10% (v/v) nitric acid solution at 60 °C for 1 h. Thermal gravimetric analysis (TGA) measurements were performed on a NETZSCH STA 449 F3 Thermoanalyzer, and about 15 mg of each sample was used for the TGA analysis. Fourier-transform infrared (FT-IR) spectra were obtained using a Nicolet 8700 spectrometer with KBr pellets. Nitrogen physisorption isotherms were measured at 77 K on an automatic volumetric adsorption apparatus (Micromertics ASAP 2020). The samples were filled into glass ampoules and outgassed in high vacuum at 120 °C for 12 h before the start of the sorption measurements. For sorption analyses, the samples were immersed in methanol at 60 °C for 2 h. X-ray photoelectron spectrometry (XPS) was performed on Thermo ESCALAB 250 equipped with a