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Palladium–pyridyl catalytic films: A highly active and recyclable catalyst for hydrogenation of styrene under mild conditions

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ABSTRACT

Palladium–pyridyl catalytic films, $(PdCl_2/bpy)_n$, were created by alternating immersions of a substrate in $PdCl_2$ and bpy (bpy = 4, 4′-bipyridyl) solutions. The as-prepared $(PdCl_2/bpy)_{10}$ catalyst demonstrated a remarkable catalytic activity toward hydrogenation of styrene under mild conditions and the turnover frequency (TOF) is as high as 6944 h^{-1}. Pd(II) ions of $(PdCl_2/bpy)_n$ films are *in situ* reduced to Pd nanoparticles (NPs) during the hydrogenation of styrene process, which results in the catalytic activity of the films. The results of X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) further demonstrate that Pd(II) ions of $(PdCl_2/bpy)_n$ films were gradually converted to Pd(0) states. The catalytic activity is related to bilayer numbers and the activity increases with the number of bilayers below 10 bilayers. The solid substrates coated with $(PdCl_2/bpy)_n$ multilayer catalysts were easily removed from the reaction mixture without separation filtration. Moreover, $(PdCl_2/bpy)_n$ catalysts were reused for 10 consecutive reactions without loss of activity. The present $(PdCl_2/bpy)_n$ heterogeneous catalysts have the advantages of easy separation and good recyclability.

1. Introduction

In recent years, the synthesis of supported metal nanoparticles (NPs) for heterogeneous catalysis has received considerable attention, owing to the great advantage of heterogeneous catalysts such as good recyclability [1–6]. Moreover, palladium is the most effective and versatile for a variety of organic catalytic reactions [7–9]. Pd NPs included in porous metal–organic frameworks (MOFs) have attracted increasing interest. For example, Pd NPs supported on MIL (MIL for Materials from Institut Lavoisier) series were prepared by our group and exhibited good recyclability for carbon–carbon coupling reaction [5,6]. On the other hand, the technology of catalytic film is a promising area among current heterogeneous catalytic technology, because the technology can simultaneously complete two tasks of catalytic reaction and product separation. Films-based catalysts share common features with traditional heterogeneous Pd NPs immobilized on insoluble supports, including catalyst separation and recovery. Moreover, films-based catalysts are easily removed from the reaction mixture without separation filtration.

The layer-by-layer (LbL) technology, which simply involves alternating adsorption of polycations and polyanions, has become a popular technique for thin film preparation [10–12]. LbL technology offers a versatile platform for controlling catalyst properties. To date, polyelectrolyte multilayers (PEMs) prepared by LbL method have been explored as matrices for synthesis of zero-charge Pd NPs in order to generate large surface area heterogeneous catalyst [13–17]. For example, Wang reported PAA/PEI-Pd(0) LbL films supported on magnetic nanoparticles in order to make the separation more simple [16]. Ren et al. reported as-prepared Pd–PVP (PVP = poly(4-vinylpyridine)) LbL multilayers modified substrate used as heterogeneous catalyst for selectively catalytic hydrogenation of aromatic conjugated alkenes at room temperature [17]. However, the above-mentioned building blocks are PEMs and the heterogeneous catalytic hydrogenation of LbL films using small organic molecules as building blocks such as pyridyl ligands have been rarely explored. LbL self-assembly based on metal ion-ligand interaction can yield multifunctional films. Each metal ion is separated and connected by small organic ligands. To date, functional palladium–pyridyl complexes were loaded within LbL multilayers by alternate adsorption of palladium ion and pyridyl ligand layers onto solid slides [18–22]. However, how to fully develop their properties of palladium–pyridyl multilayers with orderly structure remains challenging. Recently, our group has also reported palladium-pyridyl multilayer films as highly active catalysts for the Suzuki and Heck reaction [23,24]. Palladium–pyridyl complexes are released from loaded slides and

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used as catalyst reservoir during the catalytic process. Catalyst loading is easily controlled to quite a low degree.

In our present study, we will utilize palladium–pyridyl complexes loaded slides for catalytic hydrogenation reactions, because hydrogenation of C=C double bonds is of significant importance due to great demands in chemical, petro-chemical, pharmaceutical, and food industries [25]. Hydrogenation of styrene was applied as a test reaction to study the catalytic activity of $(PdCl_2/bpy)_n$ films (Scheme 1). Palladium–pyridyl catalytic films exhibited a remarkable catalytic activity toward hydrogenation of styrene. The catalytic films are not desorbed from slides and have good recyclability. The process of the palladium ions reduced to Pd NPs was discussed through X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

2. Materials and methods

2.1. Materials

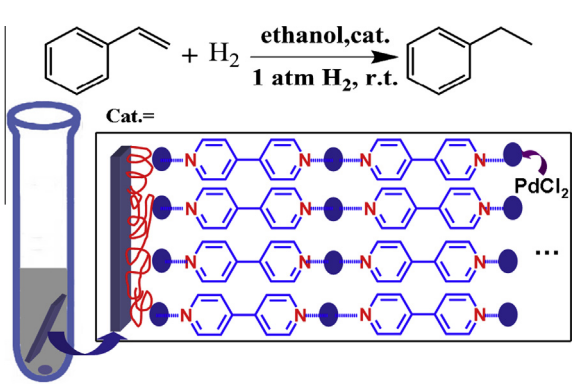
Poly(ethylenimine) (PEI, MW = 60,000, 50 wt% aqueous solution) and 4, 4′-bipyridyl (bpy) were purchased from Aldrich. Palladium chloride was from Shanghai Jiuling Chemical Co., Ltd. Styrene and ethanol were from Sinopharm Chemical Reagent Co., Ltd. Millipore filtered water was used in all experiments (Milli-Q, 18.2 MΩ cm).

2.2. Layer-by-layer assembly $(PdCl_2/bpy)_n$ multilayer films

Multilayer films of $(PdCl_2/bpy)_n$ were prepared according to our previous work [24]. Unlike bpy concentration of 2 mM in the reference [24], the concentration of bpy was 5 mM. The specific methods are as follows: The quartz slides (size 25 m m × 12 m m × 1 mm) (or single-crystal silicon slides) were cleaned with a "piranha solution" at 80 °C for 40 min, and thoroughly rinsed with water. Further purification was carried out by immersion in an $H_2O/H_2O_2/NH_3OH$ (5:1:1) (V/V/V) bath for 30 min at 70 °C. The clean slides were first immersed in PEI solution for 20 min. The slides pre-coated with PEI were alternately immersed in $PdCl_2$ aqueous solution (5 mM, 10 mL) and bpy (5 mM, 10 mL) ethanol solution for 30 min. The substrates were washed with water and dried with nitrogen stream after each immersion. By repeating the above procedure, $(PdCl_2/bpy)_n$ multilayer films were prepared.

2.3. Analysis of Pd in $(PdCl_2/bpy)_n$ films

The quartz slide coated with $(PdCl_2/bpy)_n$ was dissolved by aqua regia (10 mL). The Pd content was determined by inductively coupled plasma OES spectrometer (ICP-OES).



Scheme 1. Schematic diagram of the hydrogenation of styrene catalyzed by the solid substrate coated with $(PdCl_2/bpy)_n$ films.

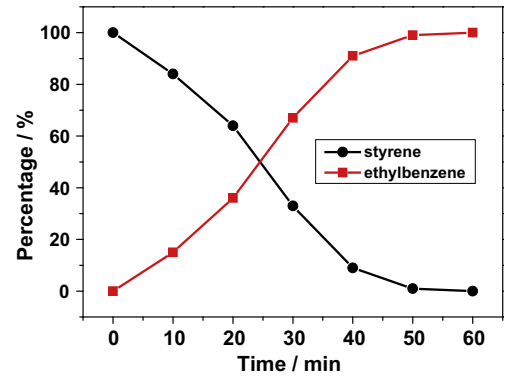


Fig. 1. Kinetics of styrene hydrogenation catalyzed by $(PdCl_2/bpy)_{10}$ film.

2.4. Typical procedures for the hydrogenation of styrene

Hydrogenation reactions were carried out in a hydrogen atmosphere (1 atm) at 35 °C. Typically, styrene (0.5 mmol), absolute ethanol (10 mL) and the quartz slide coated with $(PdCl_2/bpy)_{10}$ film were added to the tubes. The tube was sealed with a Teflon cap and evacuated and backfilled with H_2 three times. The mixture was stirred at a constant stirring speed in the tube under a hydrogen atmosphere. The conversion and selectivity were determined by GC analysis (430 GC).

2.5. Instrument

High-resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 45° using PHI Quantum 2000 scanning ESCA microprobe (Physical Electronics, USA) with an Alα X-ray line (1486.6 eV). Transmission electron microscopy (TEM) was generated on a JEM-2010 operated at 120 kV. Small pieces of a multilayer film were scraped off the quartz substrate in ethanol and transferred to a copper grid. Gas chromatography (GC) was performed on 430 GC (Varian, USA). Analysis of Pd content was measured by inductively coupled plasma OES spectrometer (ICP-OES) (Ultima2, France).

3. Results and discussion

3.1. Catalytic performance of $(PdCl_2/bpy)_n$ for the hydrogenation of styrene

The multilayer films of $(PdCl_2/bpy)_n$ were prepared by alternately immersing quartz slide pre-coated with PEI layer in $PdCl_2$

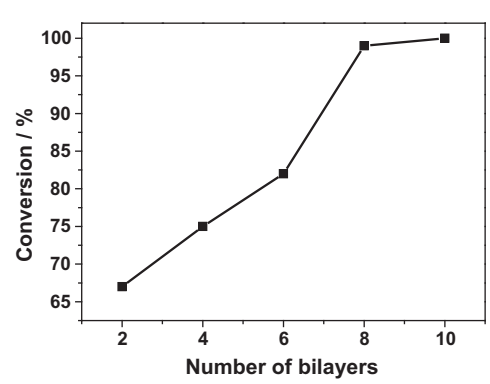


Fig. 2. Relationship between styrene conversion and the number of $(PdCl_2/bpy)_n$ bilayers during the same time (60 min).