



Polyurea-supported metal nanocatalysts: Synthesis, characterization and application in selective hydrogenation of *o*-chloronitrobenzene



Leiduan Hao, Yanfei Zhao, Bo Yu, Hongye Zhang, Huanjun Xu, Jilei Xu, Zhimin Liu*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

Polyurea (PU) spheres with size of 2–10 μm were derived through the polymerization of CO_2 with 1,4-butanediamine, and characterized by FTIR spectroscopy, scanning electron microscopy and TG analysis. It was demonstrated that the PU spheres displayed flower-like morphology with the betel thickness around 30 nm, and they had high thermal stability. The resultant PU spheres were used to immobilize metal particles, and a series of PU-supported metal nanocatalysts including Pt/PU, Au/PU, Pd/PU were prepared via just mixing the metal precursors with the PU spheres in water, followed by the reduction of metal ions by NaBH_4 . Transmission electron microscopy examination indicated that the metal nanoparticles were distributed uniformly on the surface of the PU spheres with mean particle size less than 3.0 nm, and the Pt particles existed mainly in the form of metallic state as confirmed by the X-ray photoelectron spectroscopy analysis. The performance of the Pt/PU catalyst was tested in the catalytic hydrogenation of *o*-chloronitrobenzene, and a high selectivity of 99.5% toward *o*-chloroaniline at complete conversion of *o*-chloronitrobenzene was obtained at room temperature.

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Introduction

o-Chloroaniline (*o*-CAN) is a valuable intermediate for manufacturing pharmaceuticals, agrochemicals, rubbers, dyes and pigments [1]. Catalytic hydrogenation of *o*-chloronitrobenzene (*o*-CNB) is a clean and convenient route for synthesis of *o*-CAN. However, the reduction of nitro group is complicated and the production of side products such as hydroxylamine, hydrazine and azoarane is hard to avoid [2], thus causing a low selectivity to *o*-CAN. Improving the selectivity of the hydrogenation reaction of *o*-CNB to *o*-CAN is a significant and also challenging project, and designing suitable catalysts is an efficient solution. To date, many catalysts were developed for the selective hydrogenation of *o*-CNB to *o*-CAN, among which the metal oxide-supported metal catalysts such as Pt/ γ - Fe_3O_4 [3], Pt/ Fe_2O_3 [4–6], Ni/ TiO_2 [7] have shown high performances. Moreover, it was found that the supports of the catalysts played a crucial role in the catalytic hydrogenation of *o*-CNB [8]. Though much progress has been made, it is still desirable to develop new catalysts which are easy to prepare and possess excellent performances under mild reaction conditions.

Polymer as catalyst support has attracted much attention due to their unique features [9]. In particular, polymer-supported

catalysts can combine the advantages of both homogeneous and heterogeneous catalysts, for instance, high catalytic activity and easy separation from the reaction mixture [10,11], and have been applied in many areas such as asymmetric dihydroxylation, epoxidation, and hydrogenation [12–14]. A polyethylene glycol-stabilized platinum catalyst was used for selective hydrogenation of *o*-CNB to *o*-CAN, and a selectivity higher than 98% at near complete conversion of *o*-CNB was obtained [15].

Polyurea (PU) is a kind of polymer containing urea functional group ($-\text{NH}-\text{CO}-\text{NH}-$), which shows high resistance to solvents including polar and non-polar solvents, acids or bases and far superior thermal stability than the commonly used polymers, thus widely being applied in coatings and corrosion protection areas. PU can be also used as a polymer coating in the microcapsules of the catalysts. For example, PU-encapsulated Pd and Pd–Cu bimetallic catalysts were proved to have excellent performances in the selective hydrogenation of styrene oxide and chemoselective reduction of aryl ketones [16–18]. PU is generally produced from isocyanates and amino compounds in the industrial processes. It is difficult to process PU into particles with unique structures due to its insolubility in solvents. Recently, PU was successfully synthesized via the reactions of CO_2 with diamines [19], which may provide the possibility to synthesize PU particles with specific morphology.

In the present work, PU microspheres with flower-like morphology were synthesized from the reaction of CO_2 and 1,4-

* Corresponding author. Fax: +86 10 62562821.

E-mail address: liuzm@iccas.ac.cn (Z. Liu).

butanediamine based on the reported procedure [19], and were used to immobilize noble metal nanoparticles to prepare PU-supported metal catalysts including Pt/PU, Au/PU and Pd/PU. The resultant PU spheres and the PU-supported metal catalysts were characterized by different techniques including FTIR, TG analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The performance of the Pt/PU catalyst for the selective hydrogenation of *o*-CNB to *o*-CAN was investigated, and the influence of the PU support on the reaction was discussed as well.

Experimental section

Materials

Hydrogen (99.99%) and carbon dioxide (99.99%) were provided by Beijing Analytical Instrument Company. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, HAuCl_4 , PdCl_2 , NaBH_4 and ethanol were purchased from Sinopharm Chemical Reagents Beijing Co., Ltd. 1,4-Butanediamine was purchased from TCI Chemicals. *o*-CNB and *o*-CAN were from Aladdin Reagent Company. *N*-Methyl pyrrolidone (NMP) was provided by Aldrich. The chemicals were used as received without further purification. Tetra-*n*-butylammonium tungstate was synthesized based on the reported procedure [20].

Preparation of PU spheres

The copolymerization of 1,4-butanediamine with CO_2 was performed in a Teflon-lined stainless steel reactor of 22 mL coupled with a magnetic stirrer. In a typical experiment, 1,4-butanediamine (5 mmol), tetra-*n*-butylammonium tungstate (0.25 mmol) as the catalyst, and NMP (1 mL) as the solvent, were loaded in the reactor. Then the reactor was sealed and CO_2 was charged into the reactor up to 3 MPa. The reactor was transferred to an oven and heated at 160 °C for 12 h. After the reaction, the reactor was cooled down in an ice-water bath and the gas inside was slowly vented. The obtained solid was washed with deionized water and ethanol for several times. The white solid was thoroughly dried in vacuum and the PU powders were obtained finally.

Preparation of PU-supported metal nanocatalysts

The PU-supported metal nanocatalysts including Pt/PU, Au/PU and Pd/PU were prepared using the same procedure. In a typical experiment to prepare Pt/PU with the weight mass of Pt at 2 wt%, the PU powder (400 mg) was first dispersed in deionized water (750 mL) with the assistance of sonication in an ultrasonic water bath, and an accurate amount of H_2PtCl_6 aqueous solution (5.45 mL with the Pt concentration of 1.498 g/L) was then added with a pipettor under vigorous stirring. After being stirred for 12 h, an aqueous solution of NaBH_4 (20 mL, 1 mg/mL) was added dropwise into this suspension. The resultant solid was centrifuged and washed with deionized water and ethanol, followed by being dried in vacuum at 60 °C overnight, denoted as Pt/PU for characterization and further use.

Similarly, Au/PU and Pd/PU with the metal mass of 2 wt% were prepared using the corresponding metal precursors, respectively.

General procedure for the hydrogenation of *o*-CNB

Hydrogenation reaction of *o*-CNB was performed in a stainless steel reactor of 22 mL coupled with a magnetic stirrer. In a typical experiment, the Pt/PU catalyst (2 wt%, 40 mg) dispersed in 3 mL of ethanol was loaded in the reactor, followed by the addition of 5 mmol of *o*-CNB. The air in the reactor was removed via

evacuation, and then H_2 gas was charged into the reactor up to the desired pressure to start the reaction. During the reaction process, the H_2 pressure maintained unchanged by supplying H_2 continually. After the desired reaction time, the reactor was cooled down in ice-water and vented carefully. The catalyst was separated via centrifugation and washed with ethanol three times for next run. The liquid mixture was analyzed by a gas chromatography (Agilent 4890D) equipped with an Innovax capillary column and a Varian FID-GC flame ionization detector. *N,N*-Dimethylformamide (DMF) was used as the internal standard for GC measurement.

Characterization

The morphology and microstructure of the PU support and the PU-supported metal nanocatalysts were examined by SEM on a field emission microscope (JEOL JSM-6700F) and by TEM on a transmission electron microscope (JEM-2010, JEOL, Japan) operated at 200 kV. FTIR spectrum was collected on a TENSOR 27 FTIR at a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al- $K\alpha$ radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. TG analysis of the polymer sample was performed on a PE Pyris TGA instrument with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under the atmosphere of N_2 .

Results and discussion

Characterization of the PU support

In this work, PU was synthesized via the copolymerization of 1,4-butanediamine with CO_2 as illustrated in equation (1). As expected, the polymer could not be dissolved in all the common solvents except for concentrated sulfuric acid, suggesting good tolerance to common solvents. Fig. 1 shows the FT-IR spectrum of the resultant PU, which displayed the bands at 1575 cm^{-1} , 1620 cm^{-1} , 3327 cm^{-1} assigning to CO–NH amide II bond, C=O amide I bond and the N–H bond, respectively, thus indicating not only the formation of the urea functional group but also the formation of the intermolecular hydrogen bonds [21].

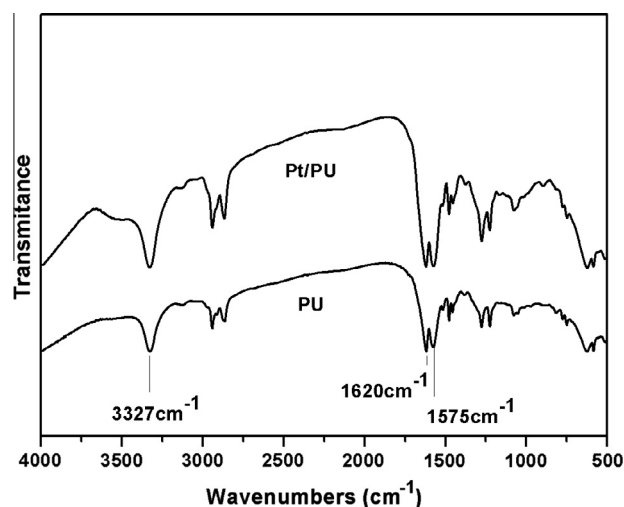


Fig. 1. FTIR spectra of PU and Pt/PU.

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