



# Stability or flexibility: Metal nanoparticles supported over cross-linked functional polymers as catalytic active sites for hydrogenation and carbonylation



Bingfeng Chen<sup>a</sup>, Fengbo Li<sup>a,\*</sup>, Zhijun Huang<sup>a</sup>, Tao Lu<sup>a,b</sup>, Guoqing Yuan<sup>a,\*</sup>

<sup>a</sup> Beijing National Laboratory of Molecular Science, Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, PR China

## ARTICLE INFO

### Article history:

Received 4 November 2013

Received in revised form 13 April 2014

Accepted 1 May 2014

Available online 9 May 2014

### Keywords:

Functional polymer

Metal nanoparticles

Hydrogenation

Carbonylation

Recoverability and recyclability

## ABSTRACT

A novel cross-linked functional polymer was prepared through copolymerization between 1, 3, 4, 6-tetraallylglycoluril and 4-vinyl pyridine. Pt and Pd nanoparticles supported over this polymeric framework (Pt/CFP and Pd/CFP) were detailedly characterized by TEM, EDS, and XPS. Pt nanoparticles were kept in the monodispersed state with the average size of 1.4 nm. Monodispersed Pd nanoparticles were about 4.5 nm. The hydrogenation of nitrobenzenes over Pt/CFP shows high activity and selectivity with the substrate to Pt ratio of 4000 under mild reactions. Pd/CFP was the catalyst for carbonylation of aryl iodides in the presence of secondary amines and acylhydrazines. Double carbonylation with secondary amines produced  $\alpha$ -ketoamides with the selectivity of 80%. Diacylhydrazine molecules were synthesized by the direct carbonylation of aryl iodide with acylhydrazine over Pd/CFP. The recyclability and recoverability of Pt/CFP were investigated through a seven-run recycling test of nitrobenzene hydrogenation. The flexibility of Pd/CFP in the carbonylation process was thoroughly explored by a 12-run recycling test. Supported Pt or Pd nanoparticles showed the macroscopic robustness in their catalytic performance in the catalytic cycle. The flexibility of metal nanoparticles and the polymeric supports guaranteed macroscopic catalytic robustness.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Most of the industrial catalysts are made of metal or metal oxide particles of a few nanometers in size and the reaction proceeds at the molecular scale. Nanocatalysis is the intrinsic property of the catalyst. Supported metal nanoparticles constitute the majority of the heterogeneous catalysts and show catalytic properties different from small atom clusters or the bulk crystal surfaces. Gold is the most famous model system [1]. The size-dependence effect is the specialty of catalysis over metal nanoparticles [2,3]. First, metal nanoparticles have irregular surfaces with abundant structural defects on the steps and kinks, which are favorable low-coordinated sites for the breaking and forming of chemical bonds [4,5]. Second, metal nanoparticles' surface offers the flexibility of structure recovering in the adsorption and desorption of the catalytic reaction. The third property, which influences catalysis, is the electronic structure of metal nanoparticles [6,7].

Metal nanoparticles are excellent catalysts for chemical synthesis [8–10]. However, active nanoparticles are not stable and show a high tendency toward agglomeration, which then leads to deactivation and precipitation. Protecting agents to stabilize metal nanoparticles include various materials, such as metal oxide [11,12], carbon materials [13], porous silica [14] and polymers [15,16]. The flexibility of metal nanoparticles is necessary for active catalytic performance. However, it results in their instability during the catalytic reaction.

Metal nanoparticles bridge the gap between homogeneous and heterogeneous catalysis. Some metal nanoparticles with stabilizing agents are soluble in the reaction medium as homogeneous catalysis. On the other hand, metal nanoparticles have an active surface as heterogeneous catalysis. However, it is a major challenge to separate the catalyst from the reaction mixture. In our previous researches [17,18], cross-linked functional polymers (CFPs) were demonstrated to be excellent supports for metal nanoparticle catalysts to be employed in the liquid phase. The swelling behavior of the polymer support facilitates the dispersion of metal nanoparticle precursors in the polymeric framework, which are further immobilized by the functional groups. Under liquid-phase conditions, the

\* Corresponding authors. Tel.: +86 10 62634920; fax: +86 10 62559373.  
E-mail addresses: [lifb@iccas.ac.cn](mailto:lifb@iccas.ac.cn) (F. Li), [yuangq@iccas.ac.cn](mailto:yuangq@iccas.ac.cn) (G. Yuan).

formation of swollen-gel phase is favorable for the involvement of all reactants in the catalytic reaction.

CFPs supported metal nanoclusters had been applied in commercial production of MIBK from acetone and hydrogen in 1965 [19]. EnCat catalyst by Reaxa was another commercial catalyst based on polyurea supported palladium [20]. Typical CFPs consist of three components: chemical structure, cross-linked, and functional groups. Chemical structures are the main polymer chain such as poly-DMA, polyacrylate, poly-MMA, and PS. The most employed cross-linkers are DVB and MBAA. Functional groups are used to anchor metal nanoparticles' precursors. There are two types of attachment strategies: ion-pair interaction ( $-\text{SO}_3^-$ ,  $\text{COO}^-$  and  $-\text{NR}_3^+$ ) and chelating interaction (Lewis base groups: amino, pyridyl, benzimidazolyl, thiol, methylsulfide, and nitrile) [21–24]. Supported metal species are mostly noble metals, such as Pt, Pd, Ru, Rh, and Au [25,26]. There are three methods to prepare CFPs supported metal nanoparticles: (1) introduction of a suitable metal precursor into CFPs and generation of metal nanoparticles through reduction or decomposition of the precursor (RIMP), (2) incorporation of metal precursors into CFPs during the polymerization and generation of metal nanoparticles through reduction or decomposition of the precursor (IMPR), (3) direct introduction of prepared metal nanoparticles into CFPs (IPMN) [27]. Kobayashi et al. [28–30] have reported “polymer-microencapsulated catalysts” and “polymer-incarcerated catalysts”, which provide new insights into the preparation and catalytic application of polymer-supported metal nanoparticles. Recently, Yamada et al. [31] have found a novel CFPs-supported metal nanocluster catalyst: self-assembled poly (imidazole–palladium) exhibits high catalytic activity and excellent reusability in several C–C formation reactions. The aim of these proposed strategies is to achieve high catalytic activity with good recoverability and recyclability.

In this work, a new cross-linker based on glycoluril [32,33] was synthesized and then copolymerized with 4-vinyl pyridine to produce cross-linked functional polymeric support for metal nanoparticles. Pt and Pd nanoparticles over this CFP were prepared and their catalytic properties in hydrogenation and carbonylation were further investigated. The catalytic behavior and transform of supported metal nanoparticles during the reaction were explored to interpret the structure–property relation.

## 2. Experimental

### 2.1. Preparation of 1, 3, 4, 6-tetraallylglycoluril

A three-neck 100 ml flask was flushed with argon. Anhydrous DMSO (40 ml) was added and glycoluril (1.42 g, 10 mmol) was dissolved. Then potassium tert-butoxide (5.62 g, 50 mmol) was gradually added and the mixture was further stirred for 1.0 h.

Allyl bromide (7.0 ml, 80 mmol) was injected into the reaction mixture and the reaction was performed at 25 °C for 20 h. 500 ml aqueous solution of HCl (0.1 M) was added into the reaction mixture. 100 ml ethyl acetate was used to extract the mixture and the organic phase was washed by saturated NaCl aqueous solution (100 ml) for three times. After being dried by  $\text{MgSO}_4$ , the solvent was removed. 1.53 g target product was obtained after purification over silica column with the eluent of ethyl acetate/petroleum ether (60–90 °C) (v/v, 3:2). All procedures were performed in argon atmosphere.

### 2.2. Preparation of cross-linked functional polymer (CFP)

The copolymerization was performed in a 100-ml two-neck flask under argon flow. 1, 3, 4, 6-tetraallylglycoluril (1.51 g,

5 mmol) and 4-vinyl pyridine (1.07 ml, 10 mmol) were dissolved in 20 ml anhydrous toluene. Azobisisobutyronitrile (164 mg, 0.05 mol/L) was used as the radical initiator and the polymerization proceeded at 60 °C for 21 h. The resulting solid materials were filtered and extracted by petroleum ether for three times. After being dried under vacuum, yellow solid (0.89 g) was obtained.

### 2.3. Preparation of Pt/CFP and Pd/CFP

CFP (250 mg) was fully swollen in 30 ml anhydrous ethanol. And then  $\text{K}_2\text{PtCl}_4$  (28 mg, 0.0674 mmol) was added. The mixture was further stirred at room temperature for 20 h.  $\text{NaBH}_4$  (25.5 mg, 0.674 mmol) in 6.0 ml water was injected and the reduction proceeded for 3.0 h. Finally, a 100 ml mixture of petroleum ether and diethyl ether was added into the mixture and the resulting precipitate was collected. After being dried under vacuum, brown solid (Pt/CFP, 216 mg) was obtained. Pt/CFP (50 mg) was calcined in air at 600 °C for 3 h. The final ash was dissolved in mixture  $\text{HNO}_3$  and HCl aqueous solution (4.0 ml). The solution was diluted to 100 ml with deionized water. The Pt concentration was determined by ICP-AES. The calculated Pt load of Pt/CFP was 2.02 wt%.

CFP (400 mg) was fully swollen in 50 ml anhydrous ethanol. And then  $\text{PdCl}_2[\text{CH}_3\text{CN}]_2$  (70 mg, 0.27 mmol) was added. The mixture was further stirred at room temperature for 20 h.  $\text{NaBH}_4$  (70 mg, 1.85 mmol) in 16 ml water was injected and the reduction proceeded for 3.0 h. Finally, a 150 ml mixture of petroleum ether and diethyl ether was added into the mixture and the resulting precipitate was collected. After being dried under vacuum, deep gray solid (Pd/CFP, 392 mg) was obtained. Pd/CFP (50 mg) was calcined in air at 600 °C for 3 h. The final ash was dissolved in mixture  $\text{HNO}_3$  and HCl aqueous solution (4.0 ml). The solution was diluted to 100 ml with deionized water. The Pd concentration was determined by ICP-AES. The calculated Pd load of Pd/CFP was 1.10 wt%.

### 2.4. Hydrogenation of nitrobenzenes over Pt/CFP

To a 10-ml Schlenk tube, were added nitrobenzene (1.0 mmol), THF (2.0 ml) and the catalyst (S/Pt: 4000). The Schlenk tube was flushed by hydrogen flow and then directly connected to a hydrogen balloon (1.0 atm). After the given reaction time, the catalyst was separated by simple filtration. The reaction results were determined by GC. In the seven-run recycling test, the catalyst was separated by filtration and washed by ethyl acetate and diethyl ether after each testing run. The catalyst was dried vacuum and then recycled into the next batch.

### 2.5. Carbonylation of aryl iodide in the presence of secondary amines over Pd/CFP

To a 100-ml autoclave, were added aryl iodide (1.0 mmol), secondary amine (5.0 mmol), the catalyst (Pd: 0.78 mol%),  $\text{Cs}_2\text{CO}_3$  (1.14 g, 3.5 mmol), LiI (9.0 mg, 0.0479 mmol) and toluene (5.0 ml). The autoclave was flushed by CO flow and pressurized to 4.0 MPa. The reaction was performed at 120 °C for the given time. The reaction mixture was extracted with ethyl acetate. Double carbonylation and mono carbonylation products were obtained by purification over silica column with the eluent of ethyl acetate/petroleum ether (60–90 °C) (v/v, 1:4). In the 12-run recycling test, the catalyst was separated by filtration and washed sequentially by water, ethyl acetate and diethyl ether after each testing run. The catalyst was dried vacuum and then recycled into the next batch.

Download English Version:

<https://daneshyari.com/en/article/39876>

Download Persian Version:

<https://daneshyari.com/article/39876>

[Daneshyari.com](https://daneshyari.com)