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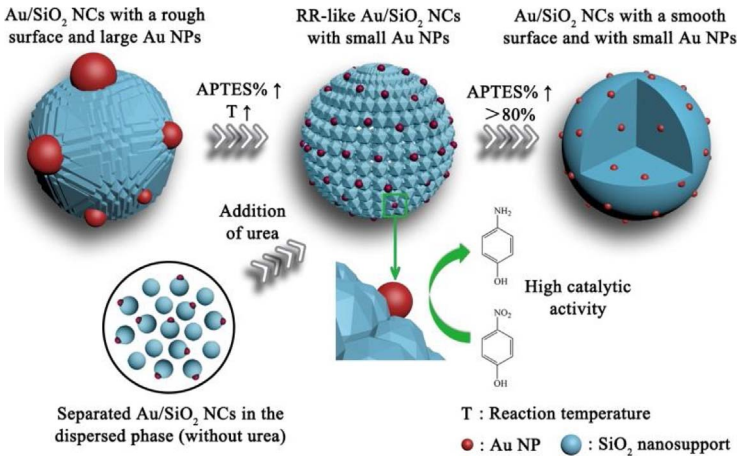
Influence of synthesis parameters on particle properties and catalytic activity of rice roll-like Au/SiO_2 nanocatalysts prepared in inverse miniemulsions

Yi Shang[a], Zhihai Cao[a,*], Hangnan Chen[a], Yangyi Sun[a], Jia Yao[a], Lin Yang[a], Dongming Qi[a], Ulrich Ziener[b]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology and Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, 310018, China
[b] Institute of Organic Chemistry III—Macromolecular Chemistry and Organic Materials, University of Ulm, Albert-Einstein-Allee 11, Ulm, 89081, Germany

GRAPHICAL ABSTRACT



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ABSTRACT

In our previous paper, we reported the synthesis of easily recyclable and highly active rice roll-like (RR-like) Au/SiO_2 nanocatalysts (NCs) in inverse miniemulsions [Colloids Surf. A 517, 2017, 52–62]. In the present contribution, the influences of three key synthesis parameters, including the 3-aminopropyltriethoxysilane (APTES) content, reaction temperature, and urea amount, on the particle properties of the Au/SiO_2 NCs were systematically investigated. The role of these synthesis parameters in the formation of SiO_2 nanosupports and Au nanoparticles (NPs) was discovered. The RR-like SiO_2 nanosupports could only be formed in the systems within the range of 20–80 mol% of APTES content, at reaction temperatures above 60 °C, and with more than 0.72 mg of urea. The $AuCl_4^-$ ions could be immobilized onto the aminopropyl-functionalized SiO_2 nanosupports through a coordination interaction. The immobilized ions were reduced by the aminopropyl groups at elevated temperatures. The APTES content and reaction temperature play an important role in controlling the particle size and its distribution of Au NPs. The catalytic activity of Au/SiO_2 NCs depends significantly on the APTES content.

* Corresponding author.
E-mail address: zhcao@zstu.edu.cn (Z. Cao).

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The RR-like Au/SiO_2 NCs with smaller immobilized Au NPs and higher specific surface area display higher catalytic activity towards hydrogenation of *p*-nitrophenol.

1. Introduction

Au nanoparticles (NPs) have become a kind of commonly-used nanocatalysts (NCs), as they may display an excellent catalytic activity towards many organic reactions, such as *p*-nitrophenol (*p*-NPh) reduction [1], alkyne hydrochlorination [2], alkene epoxidation [3], and alcohol oxidation [4]. However, in the application of Au NPs, they easily undergo agglomeration due to the high surface energy. Therefore, much effort has been spent to suppress the agglomeration of Au NPs. One effective strategy is to immobilize Au NPs onto various porous supports, such as SiO_2 [5,6], TiO_2 [7–9], C [10], and metal–organic frameworks [11–14]. SiO_2, which could be easily synthesized through the (modified) Stöber method [15], has been often used as support for Au NPs taking advantage of its high specific surface area, tunable pore properties, good chemical and thermal stabilities, good mechanical strength, and good biocompatibility [16–18]. Versatile techniques have been devised to prepare Au/SiO_2 NCs, such as impregnation, colloidal deposition, and deposition-precipitation [19–22]. However, these synthetic techniques often suffer from the low immobilization efficiency of Au NPs to the SiO_2 nanosupports.

In recent years, inverse miniemulsion technique has been proven to be an effective method to prepare various hydrophilic nanoparticles or nanocomposite particles [23,24]. In a typical inverse miniemulsion system, polar nanodroplets are homogenously dispersed in a hydrophobic continuous phase. Each polar nanodroplet can be regarded as a separated nanoreactor [23]. Landfester et al. prepared hydrophilic SiO_2 and TiO_2 NPs through a sol–gel process of hydrophilic inorganic precursors [25,26]. We prepared SiO_2 nanocapsules through a sol–gel process of commercially available hydrophobic silica precursors in inverse miniemulsions [27]. Recently, we further prepared various noble metal/inorganic support NCs, such as Ag/TiO_2, Au/TiO_2, Au/SiO_2, and Pd/SiO_2 NCs, through a two-step process in inverse miniemulsions [28–31]. In detail, we first prepare inorganic nanosupports through a sol–gel process of inorganic precursors, and subsequently, noble metal NPs are formed through reduction of noble metal salts by post-addition of a strong reducing agent [28–31]. This technique holds many advantages including versatile combinations of the noble metal and inorganic supports and the high immobilization efficiency of noble metal NPs. However, the noble metal NPs synthesized by the two-step process display a relatively large particle size and broad particle size distribution. Very recently, we reported a one-step inverse miniemulsion-based technique for preparation of rice roll-like (RR-like) Au/SiO_2 NCs through introduction of 3-aminopropyltriethoxysilane (APTES) to the reaction system [32]. In addition to participation in the formation of SiO_2 nanosupports, APTES could reduce gold salts to Au NPs, simultaneously. Finally, RR-like Au/SiO_2 NCs containing narrowly size-distributed sub–10 nm Au NPs were prepared through this technique. The RR-like Au/SiO_2 NCs displayed excellent catalytic activity, recycling catalytic performance, and reversible pH-dependent colloidal stability.

As a successive work of the preparation of RR-like Au/SiO_2 NCs through one-step process in inverse miniemulsions, the influences of critical parameters on the particle properties of SiO_2 nanosupports and Au NPs were systematically investigated to understand their role in the formation of Au/SiO_2 NCs and finally to controllably synthesize Au/SiO_2 NCs with a RR-like SiO_2 nanosupports and narrowly size-distributed small Au NPs. The APTES content and reaction temperature display a significant influence on the particle morphology of the SiO_2 nanosupports and the particle size and particle size distribution of Au NPs. Urea plays an important role in the formation of the RR-like morphology of SiO_2 nanosupports. The catalytic activity significantly depends on the particle properties of the Au/SiO_2 NCs.

2. Experimental section

2.1. Materials

Tetrachloroauricacid ($HAuCl_4$, 48%–50%), tetramethoxysilane (TMOS, 98%), APTES (99%), dimethyl sulfoxide (DMSO, 99%), urea (99%), *p*-nitrophenol (*p*-NPh, 99%), and sodium borohydride ($NaBH_4$, 98%) were purchased from Aladdin Chemistry Co. Ltd. and used as received. *n*-Hexadecane (HD, 98%) was purchased from Macklin. Poly (ethylene-*co*-butylene)-*b*-poly(ethylene oxide) (P(E/B)–PEO) with number average molecular weight of 7100 g mol^{-1} was synthesized according to the literature [33]. The molecular weights of the hydrophobic (E/B) and hydrophilic (EO) blocks are 4000 and 3100 g mol^{-1}, respectively. These weights resulted in a P(E/B)–PEO hydrophilic − lipophilic balance of 8.7. Cyclohexane (99.5%) and ethanol (99.7%) were purchased from Hangzhou Gaojing Fine Chemical Co. Ltd. Demineralized water was used in all experiments.

2.2. Preparation of Au/SiO_2 NCs

0.3 g aqueous solution of urea with various concentrations (0–0.14 mol L^{-1}) was mixed with 1.0 g of DMSO, and then 0.043 g of $HAuCl_4$ was added to the mixed polar solution, which was used as the dispersed phase. 4 wt% of P(E/B)–PEO relative to the dispersed phase was dissolved in 12.5 g of HD to form a hydrophobic solution, which was used as the continuous phase. These two solutions were mixed with an agitation of 700 rpm at 40 °C for 15 min to form a crude emulsion. The crude emulsion was sonicated by using a pulse mode (work 12 s, break 6 s) at 42% maximum power of the Scientz JY92-IIDN sonifier for 9 min to form an inverse miniemulsion.

Two grams of the prepared inverse miniemulsion was added to a glass vessel, and then the mixtures of TMOS and APTES with various molar contents of APTES (0–100 mol%) were dropwise added to the inverse miniemulsion, respectively. The sol–gel process of two silica precursors ran for 24 h with an agitation of 400 rpm at various temperatures (40–90 °C) to obtain dispersions of the Au/SiO_2 NCs. The recipes of the prepared Au/SiO_2 NCs are listed in Table 1.

The obtained Au/SiO_2 NCs were purified through two centrifugation–redispersing cycles in cyclohexane and three centrifugation–redispersing cycles in ethanol to obtain purified Au/SiO_2 NC powders. The Au/SiO_2 NCs were dried in a vacuum oven at 50 °C overnight. The dried powders for catalytic tests were further calcined at 500 °C for 1 h in a muffle furnace to remove organic components.

2.3. Evaluation of the complexation of $AuCl_4^-$ with APTES

The interaction between the $AuCl_4^-$ ions and APTES was evaluated by ultraviolet–visible (UV–vis) spectroscopic measurements. In detail, 0.04 g of $HAuCl_4$ was dissolved into 10 g of ethanol, and then various amounts of APTES (0–0.07 g) were added to the solution of $HAuCl_4$. After mixing by magnetic agitation of 700 rpm for 1 min, the UV–vis spectra of the mixed solutions were recorded on a Shimadzu UV-2600 UV–vis spectrometer.

2.4. Evaluation of the catalytic activity of the Au/SiO_2 NCs

Catalytic activity of the Au/SiO_2 NCs was evaluated by hydrogenation of *p*-NPh with $NaBH_4$. Five milligrams of the Au/SiO_2 NCs was