



# Selective oxidation of benzyl alcohol under solvent-free condition with gold nanoparticles encapsulated in metal-organic framework



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## ABSTRACT

A metal organic framework encapsulated gold nanoparticles noted as Au/UiO-66 were developed through double solvents method. Highly dispersed Au nanoparticles were presented within the pores of metal-organic framework (MOF) UiO-66 without deposition of the nanoparticles on the external surface or aggregation. With benzyl alcohol as substrate, Au/UiO-66 exhibited excellent catalytic performance to afford benzaldehyde as the only product. The reactions which could be carried out under solvent-free conditions offered a green process with O<sub>2</sub> of atmospheric pressure as oxidant. Water was proved to be beneficial for the reaction and the hydrophilic character of the MOF inner face facilitated its promotion effect greatly. The catalyst showed great stability and could be reused for at least eight times without obvious aggregation or leaching.

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## 1. Introduction

Chemoselective oxidation of alcohols into their corresponding aldehydes or ketones is undoubtedly one of the most important and challenging transformations in organic chemistry [1–3]. Products aldehydes or ketones are valuable both as important intermediates for organic synthesis and as high value components for fine chemicals. While stoichiometric amounts of oxidizing reagents and harsh conditions are classically required to perform the transformation, recent developments have led to the discovery of highly active heterogeneous catalytic systems, with supported metal nanoparticles being extensively studied as catalyst [4–6]. Usually, oxygen that is readily available is used as oxidant and generated water as the only by-product. Thus an environmental green oxidation process is provided.

Among various metal nanoparticles, nano-gold has attracted great attention recently due to its excellent activity and selectivity [7–10]. Many efforts have been made to this field for alcohol oxidation, including the generation of monoacids in aqueous alkaline medium [11,12] and aldehydes or ketones under mild solvent free conditions [13,14]. The support for nano-gold undoubtedly plays an important role for alcohol oxidation. For example, Abad et al. [15,16] showed a collaborative effect between gold and ceria could induce the selective oxidation of alcohols with high efficiency,

while carbon supported gold nanoparticles does not catalyze oxidation reactions in the absence of base and water. Metal-organic frameworks (MOFs), a new class of porous materials, have emerged as popular host matrices for encapsulating metal nanoparticles [17–20]. Especially, Aijaz et al. [21] reported a double solvents approach to immobilized active Pt nanoparticles into pores of MOF, which greatly avoids the aggregation of nanoparticles.

On the other hand, it is known that the moisture, i.e. water, plays an important role for CO oxidation over gold catalysts [22–24]. Also, a water-promoted mechanism of alcohol oxidation on bulk gold surface was proposed recently [25,26], leading us to try to apply the method for gold nanoparticles to study the effect of water. In spite of this, the promotion effect of water would be limited for oxidation of alcohols in organic solvents or under solvent-free conditions, since the small amount of water was difficult to contact with gold nanoparticles due to the immiscibility.

So herein, in this paper, a zirconium-based metal organic framework (UiO-66) [27–29] was synthesized and used to encapsulate gold nanoparticles. Double solvents method was employed to introduce Au into MOF pores without aggregation on the external surface of framework [21,30]. The prepared catalyst noted as Au/UiO-66, was proved to be effective catalyst for the oxidation of benzyl alcohol with O<sub>2</sub> as oxidant under atmospheric and solvent free conditions. Both high activity and excellent selectivity were exhibited without utilization of organic solvent or high pressure. Notably, the inner surface of UiO-66 with hydrophilic character derived from the metal-cluster based Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> units facilitated the promotion effect of water.

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## 2. Experimental

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The constituents were confirmed based on GC analysis. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 equipped with a 30 m × 0.32 mm × 0.5 μm HP-Innowax capillary column and a flame ionization detector. XRD data were collected with CuKα radiation on Bruker D8 ADVANCE scanning from 5° to 50°. SEM was recorded on JEOLJSM-6380LV. TEM images were taken on H-7650. Thermogravimetric analysis (TGA) was performed on TGA/SDTA851e under N<sub>2</sub> atmosphere from 50 °C to 800 °C, with a heating rate of 10 °C/min and N<sub>2</sub> flowing rate of 30 mL/min. Turnover frequency (TOF) was calculated based on gold active site determined by infrared measurements of adsorbed CO [31].

### 2.1. Catalysts preparation

#### 2.1.1. Preparation of UiO-66

UiO-66 was synthesized according to Ref. [29]. Typically, to a flask containing zirconium tetrachloride (ZrCl<sub>4</sub>, 5 mmol) and benzene-1,4-dicarboxylic acid (BDC, 5 mmol), 150 mL DMF was added. After dissolution, another 25 mL of DMF was added and the mixture was heated at 120 °C under stirring for 24 h. The white precipitate was filtered off, washed with DMF to remove the excess of the unreacted organic linker. To remove DMF, the product was immersed in dichloromethane solution for solvent exchange, after which filtration was employed again and the product was dried under vacuum overnight at room temperature.

#### 2.1.2. Preparation of Au<sup>3+</sup>/UiO-66

Encapsulation of Au<sup>3+</sup> precursors was carried out using double solvents method [30]. Typically, 0.2 g of UiO-66 was suspended in 40 mL of dry *n*-hexane as hydrophobic solvent and the mixture was sonicated for 20 min until it became pseudo-homogeneous. After stirring for a while, 0.16 mL of aqueous solution containing 0.068 mmol HAuCl<sub>4</sub> · 4H<sub>2</sub>O was added dropwise over a period of 20 min with constant vigorous stirring. The resulting solution was continuously stirred for 3 h. After stirring, the product which settled down to the bottom of the sample vial was isolated from the supernatant by decanting and drying in air at room temperature. The synthesized sample was further dried under vacuum overnight at room temperature.

#### 2.1.3. Preparation of Au/UiO-66

The reduction of the catalysts was carried out using an overwhelming reduction (OWR) approach [30]. Typically, after drying of Au<sup>3+</sup>/UiO-66, 40 mL dry *n*-hexane was added again and the mixture was sonicated for 20 min until it became pseudo-homogeneous. Then NaBH<sub>4</sub> solution (5 mL, 0.6 mol/L) was added under vigorous stirring to generate the catalyst as dark purple suspension. Au/UiO-66 was isolated through centrifugation and washed with water before drying under vacuum overnight at room temperature.

### 2.2. Solvent free oxidation of benzyl alcohol

A 25 mL round-bottomed flask containing 15 mL benzyl alcohol, 0.05 g Au/UiO-66, 0.2 g K<sub>2</sub>CO<sub>3</sub>, was kept under a constant temperature of 80 °C. Oxygen was inputted into the bottom of the suspension with a flowing rate of 0.004 m<sup>3</sup>/h. The reaction was allowed to proceed under vigorous stirring and samples were withdrawn periodically. Before analysed by GC, catalyst in the samples was separated through centrifugation. When the oxidation process was finished, Au/UiO-66 was recovered through centrifugation,

washed with water and hexane and dried under vacuum before reuse.

## 3. Results and discussion

### 3.1. Preparation and characterization of the catalyst

Recent work by Juan-Alcañiz et al. [32] reported a post-functionalization method with oxamate as chelating agent to immobilize and stabilize active metal sites of small metal nanoparticles such as Cu, Pd, and Au. Different from the post-functionalization method, the double solvents and overwhelming reduction process used in this work would be simpler. UiO-66 is a zirconium-based metal organic framework built from hexamers of eight-coordinated ZrO<sub>6</sub>(OH)<sub>2</sub> and 1,4-benzenedicarboxylate (BDC) linkers, with pore volume of 0.471 cm<sup>3</sup>/g and surface area of 891 m<sup>2</sup>/g [28]. The inner surface of UiO-66 showed hydrophilic character and thus offered possibility for encapsulation of Au<sup>3+</sup> precursors with double solvents method. When UiO-66 was suspended in a large amount of hydrophobic solvent dry *n*-hexane, a small amount of aqueous precursor solution, with a volume slightly less than the pore volume was added slowly. The small amount of aqueous precursor solution would go inside the hydrophilic pore, and the deposition of gold precursors on the outer surface could be minimized. The hydrated UiO-66 was deposited in the bottom of *n*-hexane and could be separated easily through decantation.

The pore windows of UiO-66 with diameters of 6–11 Å are big enough for the precursor compounds HAuCl<sub>4</sub> to diffuse into the pores [27]. At the same time, the cavities of UiO-66 are relatively smaller than most reported MOF encapsulated metal catalyst, which will be helpful in preventing Au aggregation. In this way, each cavity containing Au nano-particles similarly served as a micro-reactor in which oxidation process was conducted. Recently, water was reported to be an important factor in some Au catalyzed oxidation reactions. Chang and co-authors found that molecular oxygen can be activated via a hydroperoxyl (OOH) intermediate produced by abstracting a hydrogen atom from co-adsorbed methanol or water [25]. In their study of methanol oxidation, extra water molecules significantly promoted the hydrogen-transfer reactions between CH<sub>3</sub>OH...O<sub>2</sub> and H<sub>2</sub>O...O<sub>2</sub> co-adsorbates, which greatly lowered the activation barrier of OOH formation. Kumar et al. [11] also reported the important role of water in oxidation of alcohols into the corresponding carbonyl acids. In our case, the inner surface of UiO-66 showed hydrophilic character, so promotion effect of water was facilitated due to the easy contact and the effect of water will be discussed in detail in the following part.

After the encapsulation of Au precursors in the pores of UiO-66, a high-concentration NaBH<sub>4</sub> solution (0.6 M) was used for overwhelming reduction process according to Ref. [30]. Highly dispersed Au nanoparticles with average size of about 5 nm were formed within the pores of UiO-66 without deposition of the nanoparticles on the external surface or aggregation. This was confirmed by the TEM pictures as shown in Fig. 1(a). The specific octahedral and tetrahedral shapes of the crystals are not clearly visible in the SEM images in Supplementary Information as reported in Ref. [28], which can be the result of the applied synthesis conditions, and is also reflected in the relatively small surface area. SEM images of Au/UiO-66 suggested that the morphology was maintained during the encapsulation of gold nanoparticles.

Fig. 2 shows XRD patterns of UiO-66 and Au/UiO-66, respectively. UiO-66 generated through the coordination of ZrCl<sub>4</sub> and BDC exhibited great crystal structure and the XRD pattern matched well with the reported references [27–29]. The diffraction peaks at low angles could still be observed in the curve of Au/UiO-66, which indicated the maintenance of framework structure during

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