



Gold nanoparticles confined in ordered mesopores: Size effect and enhanced stability during gas-phase selective oxidation of cyclohexanol



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ABSTRACT

Gold nanoparticles (AuNPs) encapsulated in the extra-large spherical cages of ordered mesoporous silica EP-FDU-12 with controlled and narrow size distributions have been investigated for the gas-phase oxidation of cyclohexanol. The size effect of AuNPs was demonstrated that the highest TOF for oxidation of cyclohexanol was 939 h⁻¹ at 230 °C when the resulting particle size was in the range of 5–6 nm. The smaller or larger AuNPs ranging from 3.3 to 14.2 nm led to poor catalytic performances in the cyclohexanol oxidation. Importantly, AuNPs loaded in EP-FDU-12 catalyst exhibited remarkably long lifetime (>550 h) without obvious mass-specific activity decrease and poisonous coke formation, which will light the path for the large-scale industrialization of fine chemicals over noble metal catalysts.

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1. Introduction

Gold nanoparticles (AuNPs) are key heterogeneous catalysts for many industrially important processes such as low-temperature CO oxidation, hydrogenation of olefins, direct synthesis of hydrogen peroxide, cycloisomerizations and selective alcohol oxidation [1–4]. The geometrical parameters (e.g., size) of the AuNPs have been shown to determine the catalytic behavior of a nanocatalyst, especially during alcohol oxidation. Tsukuda and co-workers have prepared a series of poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized AuNPs with size ranging from 1.3 to 10 nm, and compared their catalytic performances in oxidative dehydrogenation of *p*-hydroxybenzyl alcohol in H₂O in the presence of K₂CO₃ promoters. They observed that, with decreasing the size of AuNPs from ~10 nm, the activity appeared at an Au diameter of ~5 nm and

then increased rapidly with further decreasing the size of Au clusters [5,6]. Corma et al. investigated the effect of the mean size of AuNPs loaded on TiO₂ on the catalytic performances for the oxidative dehydrogenation of cinnamyl alcohol. They found that the turnover frequency (TOF) per surface Au atom and the product selectivity were both almost independent of the Au particle size in a range of 5–25 nm, indicating that the reaction was structure insensitive [7]. However, Baiker et al. reported different size effects in the supported Au-catalysed oxidative dehydrogenation of alcohols. They prepared TiO₂ and CeO₂ supported Au catalysts with Au particle size ranging from 1.3 to 11 nm, and investigated their catalytic performances in the oxidative dehydrogenation of benzyl alcohol in different solvents. The highest activity was obtained over the catalyst with a medium mean Au size (6.9 nm) [8].

The selective oxidation of alcohols to aldehydes and ketones is one of the pivotal reactions in organic synthesis for the production of a large variety of fundamental intermediates [9–12]. Among these reactions, the transformation of cyclohexanol to cyclohexanone [13,14], is a commercially important process. The great majority selective oxidation product of cyclohexanone is consumed in the production of precursors to Nylon 6,6 and Nylon 6. Cyclohexanol and cyclohexanone are also obtained by oxida-

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tion of cyclohexane, which can be efficiently catalysed by gold nanoparticles and gold complexes [15,16]. In practice, the oxidation of alcohols with molecular oxygen can be performed in the liquid or gas phase, depending mainly on the thermal stability and volatility of the reagents and products [17]. However, a more effective route for industrial application would be gas-phase oxidation due to the convenience of catalyst separation, solvent-free conditions and higher production efficiency [18,19]. It is noted such an alternative direct gas-phase selective cyclohexanol oxidation process is also of tremendous industrial significance and is more environmentally friendly than the liquid cyclohexane oxidation and phenol hydrogenation processes that are currently employed for cyclohexanone production. Recently, several supported gold-based catalysts have been investigated for the gas-phase oxidation of primary and secondary aliphatic alcohols [20–24], while conversion of cyclohexanol remains the most difficult. It can be explained that the hydrogen connected to the α -carbon is difficult to be dehydrogenated because of the steric hindrance by cyclohexyl group. In addition, the cyclohexanol-to-cyclohexanone transformation is characteristic of low selectivity and poor activity because of reduced concentration of cyclohexanol molecule on catalyst surface and the difficulty in dissociation of β -C–H bond [25,26].

To the best of our knowledge, no correlation between the particle size and catalytic activity, in particular for the gas-phase oxidation of alcohols over well-defined metal nanoparticles, has ever been established before. The aim of this contribution was therefore to elucidate if a particle-size-derived structure-reactivity correlation is in operation for the selective cyclohexanol oxidation reaction over AuNPs confined within ordered large mesoporous space.

In our previous studies, we have demonstrated that the unique three-dimensional porous structure of EP-FDU-12 silica support (cage size > 25 nm) allows two or more AuNPs to be encapsulated in every extra-large cage at high particle concentrations (10–35 wt%), which is extremely difficult to be achieved by conventional synthetic methods [27,28]. Therefore, it is possible for us to investigate the effect of Au particle size on the aerobic gas-phase oxidation of cyclohexanol to cyclohexanone. Notably, by selecting different meso-structure of ordered mesoporous EP-FDU-12 as well as tuning calcination temperature, it is feasible to vary the AuNPs size from 3.3 to 14.2 nm. The gold catalysts showed promising activity at relatively low reaction temperature (180–250 °C), and they are all highly selective for cyclohexanol-to-cyclohexanone transformations (selectivity > 99.5%). Importantly, on one hand, the optimal size for gold nano-catalyst loaded on large-pore mesoporous silica is in the range of 5–6 nm, smaller or larger will both lead to worse catalytic activity; on the other hand, soluble sub-nanoparticles of gold or homogeneous mononuclear catalysts have been demonstrated to possess a very high catalytic activity [29–32]. In addition, AuNPs within the extra-large pores exhibited unexpected long lifetimes without evident activity decrease during more than 550 h reaction.

2. Experimental

2.1. Catalyst preparation

A mesoporous silica with large pore and window size, EP-FDU-12 was employed as support of Au NPs. Certain physical structure of EP-FDU-12 was well controlled by synthetic parameters such as the addition of salts and hydrothermal temperature. In a typical synthesis, 0.50 g of Pluronic F127 (EO₉₆PO₇₀EO₉₆, MW = 12 000 g/mol), 0.60 g of trimethylbenzene (TMB) and 1.25 g of KCl were dissolved in 50 mL of 1 M HCl at 14 ± 0.1 °C. After stirring for 1 h, 2.08 g of tetraethyl orthosilicate (TEOS) was added to this solution, followed

by stirring at same temperature for 24 h. The molar ratio of F127: KCl: TEOS: TMB: HCl: H₂O was 0.00147: 0.62: 0.37: 0.185: 1.85: 100. Then the mixture was transferred into an autoclave and heated at 140 °C for 24 h. The resulting solid product was collected by filtration, washed with water. The organic templates were removed by microwave digestion.

For the synthesis of AuNPs, 100 mg of AuPPh₃Cl was mixed with 400 μ L of dodecanethiol in 20 mL of benzene, to which 84 mg of NaBH₄ was added in one portion. The mixture was stirred at 55 °C for 7 h before cooled to room temperature. The precipitate was separated by centrifuge, washed with ethanol, and collected after drying.

AuNPs was loaded into EP-FDU-12 support by a colloid deposition process from non-aqueous solution. The Au loading amounts were fixed at 5 wt%, which were evidenced by ICP-OES results. A series of Au/EP-FDU-12 catalysts with different Au NPs size were obtained by calcination treatments at temperature range from 350 to 750 °C. The samples were registered by the gold nanoparticles TEM size, for instance AuNPs/EP-FDU-12-5.2.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using Cu K α radiation (40 kV and 40 mA). Nitrogen adsorption isotherms were measured at –196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, calcined samples were degassed under vacuum at 200 °C in the port of the adsorption analyzer. Inductively coupled plasma mass spectrometry (ICP-MS) were analyzed by Thermo Electron XSENIES. Transmission electron microscopy (TEM) images were carried out on a JEOL JEM-1230 operated at 100 kV. The sample was embedded in epoxy resin, and then microtomed into sub-100 nm ultra thin film at room temperature. These thin film samples floated on water or other solvents were collected by copper mesh with polymer micro grid for TEM imaging.

2.3. Catalytic reaction

The oxidation of cyclohexanol was carried out in a fixed-bed vertical glass reactor ($h = 250$ mm, $d = 12$ mm), fitted with a glass frit carrying the 100 mg catalyst mixed with quartz sand. The oxygen stream (8 mL/min) was controlled by a mass flow instrument and the liquid reagent (0.9 mL/h) was supplied through a syringe pump. However, in order to avoid explosion problems, a flow reactor may be better [33]. Liquid vaporisation occurred on the reactor wall prior to the catalytic bed. Typical reaction temperature range was 200–250 °C. The gaseous products such as CH₄, CO and CO₂ were not detected on online gas chromatograph (GC) with thermal conductivity detector (TCD) detector. The liquid products and unreacted cyclohexanol were collected by using a cold trap and analyzed by a GC with flame ionization detector (FID) detector. The selectivity was calculated as mol of produced cyclohexanone per mol of reacted cyclohexanol and >99% of carbon mass balance in the case of selectivity ~99%. GC–MS (QP2010) was employed to confirm the by-products produced during the catalytic process, and minor cyclohexene and cyclohexanone were detected.

3. Results and discussion

3.1. Control of the particle size of AuNPs

The AuNPs and SiO₂ support were separately prepared. AuNPs with a narrow size distribution have been synthesized via a facile one-phase method in which NaBH₄ is employed as reducing agents [34]. By analyzing of TEM images, the obtained AuNPs have uniform size of 3.3 ± 0.5 nm, as shown in Fig. 1a. Ordered mesoporous SiO₂

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