



Full Length Article

Ultrastable bimetallic catalyst with tuned surface electronic properties for highly selective oxidation of cyclohexane

Pingping Wu^a, Yunxiang Cao^a, Yue Wang^a, Wei Xing^b, Ziyi Zhong^c, Peng Bai^{a,*}, Zifeng Yan^a

^a State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, China

^b School of Science, China University of Petroleum (East China), Qingdao 266580, China

^c Institute of Chemical and Engineering Sciences, A*Star, 1 Pesek Road, 627833, Singapore



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ABSTRACT

Well-dispersed Au-Pt (2–5 nm) and Au-Pd (1–5 nm) nanoparticles (NPs) supported on mesoporous silica (meso-SiO₂) were prepared by a facile one-pot synthesis method using 3-mercaptopropyltrimethoxysilane (MPTMS) to anchor metal NPs to the support. The obtained catalysts were characterized and evaluated in cyclohexane oxidation with molecular oxygen. The bimetallic NPs catalysts prepared in this work exhibited a high stability with enhanced dispersion because of the intercalation of the metal alloy NPs in the meso-SiO₂ channels via the anchoring effect of MPTMS. The generation of surface Au^{δ-} species in Au-Pt and Au-Pd catalysts was identified due to the alloying of Au with Pt and Pd. Although the electronic modification of Au atoms weakened the capability of Au for O₂ activation and leads to lower cyclohexane conversions on bimetallic catalysts, the deep oxidation reactions were reduced and a higher selectivity of desired products, K/A oil (cyclohexanol and cyclohexanone) was achieved. This work demonstrates an effective preparation method to improve the stability and surface chemical modification of Au NP catalysts, which provides general implications for other noble metal NPs catalysts.

1. Introduction

Selective oxidation of hydrocarbons by air/molecular oxygen is of great significance in the chemical industry, which provides a greener and sustainable route for the synthesis of fine chemicals and intermediates [1,2]. Partial oxidation of cyclohexane is one of such reactions, which produces cyclohexanol and cyclohexanone (K/A oil), the important intermediates for the bulk production of polyamides and plastics. During the oxidation reaction, the deep oxidation of useful products is unavoidable to take place, which often results in the formation of useless byproducts. Therefore, it is highly desirable to develop new catalysts to improve the K/A oil selectivity for a greener chemical process.

Gold, which was revealed by Haruta and Hutchings with high catalytic activity for CO oxidation [3] and acetylene hydrochlorination [4], has shown amazing catalytic properties in these years for various catalytic reactions such as liquid phase oxidation of alkanes [5,6] and alcohols [7] when molecular oxygen (O₂) is used as the oxidant. In our previous works, we found that Au NPs with small particle sizes exhibited unique catalytic performances for selective oxidation of cyclohexane [6,8]. In the case of catalysts based on Au nanoparticles (NPs),

several parameters like particle size [9], metal-support interactions [10], chemical composition [11,12], presence of promoters, etc., are of great importance for catalysis. It has been revealed that some gold-based bimetallic catalyst systems take advantage from the presence of promoters, resulting in a higher activity [13,14].

Recently, several experimental results [15–17] and theoretical works [18] suggest that the catalytic properties of Au–Pt NPs are superior to those containing Pt or Au alone. This enhancement in catalytic activity on gold-based bimetallic systems is normally ascribed to a synergistic effect between the two metals [19]. The so called synergistic effect is generally explained by adjusting the structural and chemical state of surface metal atoms through introducing promoters [20,21]. Corma and co-workers studied the selective hydrogenation of 3-nitrostyrene on 1.5%Au@0.01%Pt/TiO₂ catalyst [22]. With a small amount of Pt introduced, the activity of hydrogenation was greatly enhanced while the chemo-selectivity to 3-vinylniline was maintained at a high level (~93%). This selectivity enhancement on the bimetallic Au–Pt catalyst is not only due to the geometric effect but also to the surface electronic variation [23]. In view of the above, forming bimetallic NPs catalyst is probably an effective route to engineer Au catalysts with enhanced activity and selectivity for partial oxidation of

* Corresponding author.

E-mail address: baipeng@upc.edu.cn (P. Bai).

cyclohexane.

However, quite in the opposite, an anti-synergistic effect was observed on Au-Pd/CeZrO₄ catalysts for water gas shift reaction, CO oxidation and formic acid decomposition by Hutchings and co-workers [24]. The introduction of small amount of Pd (5%) resulted in a large decrease (reduction of TOF by 80%) of catalytic activity for both CO oxidation and water-gas shift reactions. This significant activity decrease shows a close dependence on NP size, and the mean particle size increased from 4.45 nm to 6.15 nm after introducing 5% of Pd to Au. In their latest work [25], it was also found that the deactivation of Au/CeZrO₂ catalyst was due to the agglomeration of Au clusters and small NPs to larger ones. In contrast, well dispersed small-sized Au NPs led to high catalytic activity. Various traditional preparation methods, such as adsorption method [21], deposition-precipitation method [24,26], and sol immobilisation method [20,27] have led to the good dispersion of noble metal NPs in the fresh catalysts. However, the thermal stability and recyclability of these catalysts are generally poor [28]. Thus, it is desirable to develop new methods to prepare bimetallic NP catalysts with high stability.

On the other hand, the introduction of Pd to Au was found to modify the surface chemical state of Au NPs, resulting in the decrease of active Au⁰ (or Au^{δ+}) sites [29]. These Au⁰ (or Au^{δ+}) sites are favorable to activate O₂ to form active species during oxidation reaction [26], and a higher concentration of activated O₂ species may lead to the increase of deep oxidation reactions, resulting in a lower selectivity of useful products. Therefore, it inspired us to think that it may be possible to achieve a high K/A oil selectivity through modifying the chemical state of Au NPs with the introduction of a second metal. As a consequence, a balance of catalytic activity and useful products selectivity may be achieved in cyclohexane oxidation through simultaneously controlling noble metal NP size and the concentration of active Au⁰ (or Au^{δ+}) sites. In our previous work, a thiol-containing organosilane (MPTMS) was found to effectively cap the Au NPs (~2.5 nm) and linked the NPs to the pore wall of mesoporous silica in a one-pot synthesis, resulting in a highly dispersed Au NPs catalyst [6]. Therefore, in this work, we attempted to prepare a series of mesoporous silica supported Au-Pt and Au-Pd alloy NPs catalysts through a one-pot method employing MPTMS as an anchoring agent. The obtained catalysts were characterized and evaluated in the cyclohexane oxidation with molecular O₂.

2. Experimental

2.1. Chemicals

HAuCl₄·xH₂O (Sinopharm Chemical), H₂PtCl₆·6H₂O (Sinopharm Chemical), PdCl₂ (Sinopharm Chemical), tetraethyl orthosilicate (TEOS, 98%, Sinopharm Chemical), triblock co-polymer PEO₂₀PPO₇₀PEO₂₀ (P123, Aldrich), mercaptopropyltrimethoxysilane (MPTMS, 97%, Aldrich), hydrochloric acid (37%, Sinopharm Chemical), cyclohexane (99.99%, Sinopharm Chemical) and absolute ethanol (99.98%, Sinopharm Chemical) were used as received without further purification.

2.2. Preparation of catalysts

In a typical synthesis of 1 wt.%Au-1 wt.%Pt/SiO₂ catalyst, 4 g of P123 was dissolved in 30 mL of deionized water at room temperature followed by adding 120 mL of 0.74 M HCl solution into this clear solution. A mixture of 8.4 g TEOS and 0.784 g MPTMS with a molar ratio of 10:1 was slowly added. Finally, 6.4 mL of 0.02 M HAuCl₄·xH₂O solution (for an Au loading of 1 wt.%) and/or 6.5 mL of 0.02 M H₂PtCl₆·6H₂O solution (for a Pt loading of 1 wt.%) was added. After stirring at 40 °C for 24 h, the mixture was transferred to a Teflon-lined stainless steel autoclave to undergo a static hydrothermal treatment at 100 °C for 24 h. The solids were filtered off, washed with deionized water till no Cl⁻ was detected using a AgNO₃ solution, vacuum dried at

80 °C oven overnight, and finally calcined in air at 500 °C for 6 h. Au-Pd/SiO₂ samples were prepared following the similar procedure to that of Au-Pt/SiO₂ with 0.01 M PdCl₂ solution as Pd precursor.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a X'Pert PRO MPD system with a Cu Kα radiation of wavelength λ = 0.15418 nm. N₂ adsorption-desorption isotherms were measured at -196 °C on an automatic volumetric sorption analyzer (Micromeritics, ASAP2020) after degassing at 200 °C for 4 h under vacuum. The microstructures of the catalysts were characterized on a high-resolution transmission electron microscope (HRTEM, JEM 2100 from JEOL) operated at 200 kV. Scanning transmission electron microscopy (STEM) high angle annular dark field (HAADF) images and X-ray energy dispersive spectra (XEDS) of the metallic particles were obtained using a JEOL JEM-2100F with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an AXIS HIS 165 spectrometer (Kratos Analytical) with a monochromatized Al Kα X-ray source. C 1s electron binding energy corresponding to graphitic carbon at 284.5 eV was applied as a binding energy (BE) reference for calibration. The solid ultraviolet-visible (UV-vis) spectra analysis was performed on a UV-vis-NIR scanning spectrophotometer (Shimadzu, UV-3101 PC) by using BaSO₄ as an internal reference. The Au loading in the catalysts was measured using an VISTA-MPX (Varian) inductively-coupled plasma optical emission spectrometer (ICP-OES) by dissolving the solid catalysts in a 2:1 mixture of aqua regia/HF aqueous solution. Prior to the analysis, a certain amount of dissolved solution was diluted to 50 mL. The reducibility of catalysts was measured by hydrogen temperature programmed reduction (H₂-TPR) using a TPD/TPR analyzer (Autochem II, USA).

2.4. Selective oxidation of cyclohexane

The selective oxidation of cyclohexane was carried out in a 100 mL high pressure batch reactor (Model: SLM100, Beijing Easychem Science and Technology Development Company, China). Typically, 20 mL of cyclohexane and 50 mg of a solid catalyst were added into the reactor. After purging with O₂ for three times, the reactor was heated to 140 °C and the O₂ pressure was adjusted to 0.8 MPa under stirring. After 1 h of reaction, the reactor was cooled down to room temperature and the mixture was dissolved by ethanol. An excessive amount of triphenylphosphine (Ph₃P) was added to the reaction mixture to completely reduce the cyclohexyl hydroperoxide (CHHP), an intermediate in the cyclohexane oxidation to cyclohexanol. The reaction products were collected and analyzed using an offline gas chromatogram (GC, Agilent 6820 series) equipped with a flame ionization detector (FID) and a Restek Stabilwax-DA capillary column packed with cross-bond PEG treated with nitroterephthalic acid (30 * 0.32 * 0.25). The turnover frequency (TOF) was calculated based on moles of K/A oil produced on per mole of surface Au per hour.

The regeneration and recycle of the catalyst was conducted as follows. The catalyst was retrieved from the reaction mixture by centrifugation after 1 h of reaction and washed thoroughly with ethanol, followed by drying at 80 °C overnight. Finally, the dried catalyst was reduced under H₂ atmosphere at 500 °C for 1 h and then subjected to the next cycle.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1(a) shows XRD patterns of 1 wt.%Au/SiO₂, 1 wt.%Au-1 wt.%Pt/SiO₂ and 1 wt.%Pt/SiO₂. Three weak diffractions at 38.18, 44.43 and 64.55° observed for 1 wt.%Au/SiO₂ reflect the presence of cubic Au NPs (JCPDS card no.: 65-8601), while for 1 wt. Pt/SiO₂, three

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