



Au/TS-1 catalyst prepared by deposition–precipitation method for propene epoxidation with H₂/O₂: Insights into the effects of slurry aging time and Si/Ti molar ratio



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ARTICLE INFO

Article history:

Received 18 November 2014

Revised 9 February 2015

Accepted 10 February 2015

Available online 29 March 2015

Keywords:

Propene epoxidation

Aging time

Si/Ti molar ratio

Au location

Catalytic performance

ABSTRACT

Au/TS-1 catalyst prepared by deposition–precipitation method is efficient for propene epoxidation with H₂/O₂, and its performance is significantly affected by the preparation parameters and the properties of support. In this work, effects of the slurry aging time and Si/Ti ratio of support on the location of Au nanoparticles inside or outside the micropores of TS-1 supports are examined by multi-techniques such as in situ characterization and molecular dynamics simulation, and the as-obtained catalysts are tested for propene epoxidation. It is found that longer slurry aging time facilitates the evolution of Au complex into smaller sized species which is easier to locate inside the micropores. Accordingly, the as-reduced catalyst has more tiny Au nanoparticles that are extremely active inside micropores and shows higher initial PO formation rate (g_{PO} h⁻¹ g_{Au}⁻¹). In addition, high Si/Ti ratio of TS-1 also favors the deposition of Au nanoparticles inside micropores, resulting in higher initial activity but lower stable activity.

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1. Introduction

Propylene oxide (PO) is an important bulk chemical intermediate for producing a variety of derivatives such as polyurethane foams, resins, and propylene glycol. Compared with traditional chlorohydrin and several organic hydroperoxide processes, direct propene epoxidation with molecular H₂ and O₂ to PO provides a greener, simpler, and more sustainable route [1,2]. For this reaction, the synergy between Au nanoparticles and isolated Ti⁴⁺-containing supports is indispensable because the synthesized H₂O₂ by H₂ and O₂ on Au nanoparticles should transfer to nearby isolated Ti⁴⁺ sites to form Ti-OOH, which is responsible for the oxidation of propene to PO [3–6]. Therefore, Au/Ti-containing catalysts (e.g., Au/TS-1) that are prepared by deposition–precipitation (DP) method show excellent catalytic performance [5–22], because the Au nanoparticles could be selectively deposited close to the active titanium sites rather than the inactive silicon sites when the pH of solution is higher than the isoelectric point of silicon sites [6].

To date, considerable and successful efforts have been devoted to improve the performance of the Au/TS-1 catalysts by optimizing the DP process [7,21–25]. For example, Delgass et al. reported that, compared with cesium hydroxide and ammonium hydroxide,

Na₂CO₃ was a better neutralizing agent for Au catalyst preparation [26]. Lu et al. showed that the pH of the solution would affect the Au-loading efficiency, and a pH of 7 is better for the catalyst toward PO synthesis [24]. Lee and Zanella et al. reported that the aging time of Au and support slurry in DP process is critical to the catalytic performance of Au catalysts [27,28]. Recently, Delgass et al. showed that by prolonging the slurry aging time from 1 to 10 h, the initial PO formation rate of Au/TS-1 catalyst increased from ca. 80 to 160 g_{PO} h⁻¹ kg_{Cat}⁻¹ at 200 °C, which was possibly because the contact time between the support and Au complexes affects the active sites for PO formation [22]. This catalyst was shown to have the highest activity without adding any promoters. However, mechanistic insights into the effect of slurry aging time on the structural properties and performance of Au catalysts are desired to the rational design of more effective Au/Ti-containing catalysts for direct propene epoxidation.

The Si/Ti molar ratio is also reported to have significant influence on the DP process and catalytic performance of Au catalysts [13,22,24,25]. For example, Oyama et al. reported that different Si/Ti molar ratios could affect Au capture efficiency in the DP process [24]. Delgass et al. showed that the optimum Si/Ti molar ratio was 100 [7,21,22]. However, this result is not consistent with the previous understanding of Haruta et al. [13,25,29] that a low Si/Ti molar ratio (e.g., 36) of Au/titanosilicate catalyst will result in a higher activity because the in situ generated hydroperoxy

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complexes can be more efficiently utilized. To date, this debate still remains unresolved [22] and in-depth understanding on the effect of Si/Ti molar ratio on structural properties of Au catalysts is still lacking.

It is well known that in the DP process, chloroauric acid, which is a widely used Au precursor, evolves into different forms that have different sizes and affinities to the support [27,30]. When the slurry aging time and the Si/Ti molar ratio of the support are varied, the composition of Au complexes and their interactions with supports may be different. It is expected that completely different structural properties such as size and location of Au nanoparticles on the internal or external surfaces of support will be obtained, and the catalytic performance will also be different. Therefore, understanding the effects of these variables will undoubtedly be beneficial to improve the performance of the Au/TS-1 catalyst for PO synthesis.

The present work aims to understand the effect of Au slurry aging time and the Si/Ti molar ratio of TS-1 support on Au location and the performance of Au/TS-1 catalyst for propene epoxidation. We first use in situ UV–vis and molecular dynamics simulations to study the composition and size of Au complexes at different lengths of aging time and then use HRTEM, XPS, and N₂ physisorption to determine the size and the location of the Au nanoparticles on the support. It is revealed that longer aging time of Au slurry and higher Si/Ti molar ratio of support enable small-sized Au complexes with smaller mass transfer resistance to easily enter into the micropores of support. As a result, the reduced catalyst has more highly active Au nanoparticles inside the micropores and thus exhibits higher initial PO formation rate but faster deactivation due to micropore blocking. The insights reported here not only unravel the effect of slurry aging time and Si/Ti molar ratio of support on Au location both experimentally and theoretically, but also resolve the reported controversial issue of optimum Si/Ti molar ratio of Ti-containing supports.

2. Experimental

2.1. Synthesis of TS-1 supports and Au/TS-1 catalysts

Titanium silicalite-1 (TS-1) supports with different Si/Ti molar ratios were synthesized according to the previously published procedure [22,31]. A typical process began with the addition of 3.5 g polyoxyethylene 20-sorbitan monolaurate (Tween 20, Aldrich) to 45 mL deionized water, which was followed by dropwise addition of a mixture of 44.8 g tetrapropylammonium hydroxide (TPAOH, 25 wt%) and 66.4 g tetraethylorthosilicate (TEOS, 95 wt%). The solution was vigorously stirred at room temperature for more than 0.5 h. Titanium (IV) tetrabutoxide (TBOT, 99 wt%) dissolved in 20 mL isopropanol (WAKO, 99.5 wt%) was then added dropwise. The final solution was further stirred for over 1 h and crystallized in a Teflon autoclave at 423 K for over 18 h. The as-synthesized solid was thoroughly washed with deionized water and dried overnight at room temperature, followed by calcination at 823 K for 5.5 h to remove the TPA template. The obtained TS-1 supports are designated according to the Si/Ti molar ratio. For example, a TS-1 sample with a Si/Ti molar ratio of 100 is designated TS-1(100). Au/TS-1 catalysts were prepared by the deposition–precipitation (DP) method outlined in our previous reports [4–6]. Besides, 0.5 g TS-1 was mixed with 0.1 g HAuCl₄·3H₂O and 50 mL H₂O for 30 min. Subsequently, the pH of Au and TS-1 slurry was adjusted to 7.3–7.5 by 1 M NaOH and maintained for different hours to tune the Au loading. The solid was then centrifuged for 30 min, washed twice with deionized water, and dried at 28 °C under vacuum. The slurry aging time mentioned in this work represents the time maintained at the pH of 7.3–7.5.

2.2. Catalyst characterization and quench molecular dynamics simulations

The crystal phases of the TS-1 supports were characterized by X-ray diffraction (XRD, Rigaku D/Max2550VB/PC, Cu K α radiation). The types of Au complexes were determined by in situ ultraviolet–visible spectroscopy which was recorded on a spectrometer (AvaSpec-2048) equipped with a transmission dip probe. The pore diameters and pore volumes of the Au/TS-1 catalysts were measured by nitrogen at 77 K with Micromeritics ASAP2020 instrument. Each sample was degassed at 523 K for 4 h, and then analyzed for 3 days to obtain the complete adsorption–desorption isotherm. The Au loadings were determined by atomic absorption spectroscopy (AAS, ZEEnit 600). The high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JSM-2010. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was taken on a Tecnai G2 F20 S-Twin equipped with a digitally processed STEM imaging system. The metal particle sizes and distributions were determined by measuring more than 150 randomly selected particles. The chloride ion concentration was examined by ion chromatography (Dionex 600). The surface Au/Si molar ratios were determined by X-ray photoelectron spectroscopy (XPS) on a Kratos XSAM-800 instrument using Al K α X-ray with 1486.6 eV as the excitation source.

Quench molecular dynamics simulation was conducted to obtain the stable structures of Au complexes. Materials Studio package and the Universal Force Field were used for this purpose, and the simulation was conducted at 298 K in the microcanonical ensemble (NVE). A time step of 1 fs was adopted, and the total simulation time was 100 ps. Geometry optimization calculations were performed every 5 ps. By comparing the energies of the quenched structures, the lowest energy conformation of Au complexes was identified.

2.3. Catalytic testing

The performance of the catalyst for gas-phase propene epoxidation was carried out at normal pressure in a quartz tubular reactor (i.d. 8 mm) using 0.15 g catalyst of 60–80 mesh particle size. The feed concentration was fixed at 10/10/10/70 vol.% of C₃H₆, H₂, O₂, and N₂ (at a space velocity of 14,000 mL h⁻¹ g_{cat}⁻¹). The reactor was heated from room temperature to 200 °C for reaction. The concentration of reactants and products was measured online by two gas chromatographs (Agilent 6890) equipped with TCD (Porapak Q and 5A columns) and FID (Porapak T column) detectors.

3. Results and discussion

3.1. Effect of slurry aging time

UV–vis spectroscopy is a powerful tool to characterize the evolution of Au complexes at different lengths of aging time. Fig. 1a shows the UV–vis spectra of Au complexes at different pH levels. At pH of 2.2, there are two intense adsorption bands assigned to the ligand to metal charge transfer transitions from chlorine *p* to gold *d* orbitals. The two bands at ca. 240 and 313 nm are associated with $p_{\sigma} \rightarrow d_{x^2-y^2}$ and $p_{\pi} \rightarrow d_{x^2-y^2}$ transitions, respectively [32,33]. At a higher pH level, the Au complexes hydrolyze with the exchange of chloride for hydroxyl ions. This leads to the blueshift and the decreased intensity of the bands, which are in accordance with the results of Baatz et al. [34]. Table 1 shows the composition of Au complexes (e.g., [AuCl₄]⁻, [AuCl₃(OH)]⁻, [AuCl₂(OH)₂]⁻, and [AuCl(OH)₃]⁻) at different pH levels [35,36]. From the spectra (Fig. 1a) and compositions of Au complexes (Table 1) at different

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