Journal of Catalysis 317 (2014) 99–104

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Insights into size-dependent activity and active sites of Au nanoparticles supported on TS-1 for propene epoxidation with H_2 and O_2

Xiang Feng [a], Xuezhi Duan [a], Gang Qian [a], Xinggui Zhou [a,*], De Chen [b], Weikang Yuan [a]

[a] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China
[b] Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim 7491, Norway

ARTICLE INFO

Article history:
Received 16 March 2014
Revised 6 May 2014
Accepted 8 May 2014

Keywords:
Propene epoxidation
Uncalcined TS-1
Size-dependent activity
Au active sites
Corner sites

ABSTRACT

Propene epoxidation with H_2/O_2 is a typical structure-sensitive reaction. For a given support containing tetra-coordinated Ti species such as TS-1, the catalytic activity is greatly influenced by supported Au nanoparticle size. The identification of size-dependent activity of Au catalyst was achieved over a series of Au nanoparticles (2.6–5.1 nm) deposited on the exterior surface of TS-1 by employing uncalcined TS-1. Through this approach, we could obtain very stable Au catalysts with distinguishable and uniform-sized Au particles, which are critical for structure-sensitivity analysis. The PO formation rate ($mol_{PO}\ s^{-1}\ mol_{Au}^{-1}$) over these catalysts was found to vary with average Au diameter (d) as $d^{-2.7\pm0.3}$. Moreover, typical Au nanoparticles on uncalcined TS-1 appeared as truncated cuboctahedron with top facet of (1 1 1). Model calculations derived from the representative Au particle shape and the above size-dependent activity were then performed to show that corner sites of Au nanoparticles are dominant Au active sites for propene epoxidation.

1. Introduction

Propene oxide (PO), an important bulk chemical intermediate in petrochemical industries, is widely used to produce polyurethane and polyester resins [1]. In contrast to the traditional chlorohydrin process and several organic hydroperoxide processes for PO production, direct propene epoxidation with molecular H_2 and O_2 is more attractive because it is environmentally friendly and simple [2]. The catalysts for this reaction require both nano-sized Au particles and tetra-coordinated Ti-containing support [3–16], and the reaction follows a two-site mechanism [1,17–19]: H_2 reacting with O_2 to form hydrogen peroxide (H_2O_2) at the Au sites, and the H_2O_2 subsequently diffusing to the nearby Ti^{4+} sites to generate Ti–OOH species for propene epoxidation. The former step (i.e., the formation of H_2O_2) on the Au nanoparticles is the initiation step [1,17]. The catalytic performance of Au/Ti-containing catalysts for this reaction is typically structure-sensitive to the size and shape of Au nanoparticles [9,20–22].

To date, considerable efforts have contributed to remarkably improving the catalytic activity by tuning the size of Au nanoparticles deposited on Ti-containing supports [4,20,22–25]. This encourages us to further probe the Au size-dependent activity in order to exactly predict the maximum mass specific reactivity. To this end, two major issues for the Au catalysts need to be satisfied: (1) good stability to accurately analyze the catalytic activity and (2) nonporous and highly crystalline support to ensure that all Au nanoparticles could have access to reactants and be observed on the external surface of the support, favoring the precise determination of the Au size distribution by high-resolution transmission electron microscopy (HRTEM) [26,27]. Fortunately, we have demonstrated that by using uncalcined TS-1 with blocked micropores (TS-1-B) as support, the Au nanoparticles are prevented from entering into the micropores [3]. In addition to the improved size uniformity, Au nanoparticles are on the exterior surface of TS-1 and hence accessible to reactants and easily detected under HRTEM. Moreover, the obtained Au catalyst is stable over 30 h, long enough for a reliable evaluation of the stable catalyst activity. As a consecutive effort, further depositing different-sized Au nanoparticles on TS-1-B for the reaction and then obtaining the intrinsic size-dependent activity will be carried out in this work.

Recently, Delgass et al. [28] pointed out that the active sites of Au/TS-1 catalysts for propene epoxidation with H_2/O_2 are different from those for CO oxidation. However, the actual active sites (e.g., corner, edge and surface sites) for propene epoxidation are still unknown, and thus the identification of Au active sites is highly desirable for the rational design of highly efficient Au/TS-1 catalysts. It is reported that the supported Au catalysts prepared by deposition–precipitation (DP) method usually exhibit different well-defined Au shapes, which were reported to be affected by

---

* Corresponding author. Fax: +86 21 64253528.
E-mail address: xgzhou@ecust.edu.cn (X. Zhou).

http://dx.doi.org/10.1016/j.jcat.2014.05.006
0021-9517/© 2014 Elsevier Inc. All rights reserved.

the support and preparation parameters [26,27,29–31]. To date, it is unclear what the shape of Au nanoparticles deposited on TS-1-B support is. When the Au shape is determined by HRTEM, a physical model could be employed to determine the fraction of different types of sites with the change of Au particle size [32–34]. Furthermore, model calculations derived from the above-mentioned size-dependent activity and fraction of different types of sites with particle size could also be performed to investigate the active sites (e.g., corner, edge and surface sites) of Au nanoparticles [26,27].

In this work, we first employ uncalcined TS-1 with blocked micropores and high crystallinity to support different-sized Au nanoparticles by DP method, and then test the activity of direct propene epoxidation with H_2 and O_2. The Au/TS-1-B catalyst has not only uniform and HRTEM visible Au nanoparticles enabling accurate determination of particle size, but also stable catalytic performance enabling reliable determination of Au catalytic activity. In addition, all the Au nanoparticles are exposed on the external surfaces, and thus the observed activity is free from the influence of pore diffusion. Therefore, the intrinsic size-dependent activity of the catalyst is obtained. Subsequently, we use HRTEM to characterize the shape of Au nanoparticles and thus obtain the fraction of different types of Au sites based on the Au particle shape. Furthermore, combining the size-dependent activity and the fraction of different types of Au sites, we perform calculations to predict the dominant active sites of Au nanoparticles.

2. Experimental

2.1. Synthesis of TS-1 supports

TS-1 with a Si/Ti molar ratio of 100 was synthesized according to the previous report [35]. In a typical process, 2.0 g polyoxyethylene 20-sorbitan monolaurate (Tween 20, Aldrich) was first dissolved in 28.6 mL deionized water. To this clear solution, a mixture of 22.6 g tetrapropylammonium hydroxide (TPAOH, 25 wt%) and 173 mmol tetraethylorthosilicate (TEOS, 95 wt%) was added, and then the solution was vigorously stirred at room temperature. After stirring for 0.5 h, 1.73 mmol titanium (IV) tetrabutoxide (TBOT, 99 wt%) dissolved in 20 mL isopropanol (IPA, 99.5 wt%) was added drop-wise. The solution was crystallized in a Teflon autoclave at 443 K over 18 h. The as-synthesized TS-1 was thoroughly washed with deionized water and dried overnight at room temperature. It had micropores blocked by the remaining template and hence denoted as TS-1-B. After it was further subjected to calcination at 823 K for 5.5 h, the template in the TS-1-B was removed. The obtained TS-1 had open micropores and was therefore denoted as TS-1-O.

2.2. Synthesis of Au/TS-1-B catalysts

Au/TS-1-B catalysts were prepared by the deposition–precipitation method according to the previous report [24]. 0.1 g $HAuCl_4\cdot 3H_2O$ was first dissolved in 50 mL deionized water at room temperature, followed by addition of 0.5 g TS-1-B supports. Then, the pH of the slurry was adjusted to 7.3–7.5 by 1 M sodium hydroxide solution. The slurry was further aged for different hours to tune the Au loadings, while the pH of the slurry was kept constant. Finally, the solid was centrifuged for 30 min, washed twice with 50 mL deionized water, and dried at room temperature overnight under vacuum. The as-obtained Au/TS-1-B catalysts had different Au loadings of 0.06, 0.12, 0.20, 0.24 and 0.40 wt%.

2.3. Characterization

The crystal phases of TS-1-B and TS-1-O supports were characterized by XRD (Rigaku D/Max2550VB/PC, Cu Kα radiation). The surface areas and pore volumes of the supports and Au catalysts were measured in a volumetric adsorption unit (Micromeritics ASAP 2020). The Au loadings were determined by AAS (ZEEnit 600). 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) images were obtained on a Tecnai G2 F20 S-Twin equipped with a digitally processed STEM imaging system.

2.4. Catalytic testing

Au/TS-1-B catalysts with different average Au particle sizes were tested in a quartz tubular reactor (i.d., 8 mm) loading 0.15 g catalyst of 60–80 mesh particle size. The reactor was heated from room temperature to 200 °C at a rate of 0.5 °C min^{-1}. Testing of the catalytic performance for gas-phase propene epoxidation was then conducted at 200 °C under atmosphere pressure, with a feed concentration of 10/10/10/70 vol.% of C_3H_6, H_2, O_2 and N_2, and at a space velocity of 14,000 mL h^{-1} g_{cat}^{-1}. The feed and product concentrations were measured online by two gas chromatographs (Agilent 6890). One chromatograph equipped with thermal conductivity detectors (TCD) was used to detect hydrocarbons, H_2, O_2, N_2, CO_x and H_2O with a 5A column (3 mm × 3 m) and a Porapak Q column (3 mm × 3 m). The other equipped with a flame ionization detector (FID) was used to detect oxygenates (e.g., propene, propane, acetaldehyde, PO, acetone and propanal) with a Porapak T column (3 mm × 3 m).

3. Results and discussion

3.1. Size-dependent activity of Au/TS-1-B catalyst

Fig. 1a shows the XRD spectra of the TS-1-B and TS-1-O supports. Similar to traditional crystalline TS-1-O support, the TS-1-B support is also highly crystalline with standard MFI structure. The presence of the orthorhombic symmetry is evidenced by the lack of splitting peaks at ca. 24.5° [35]. Fig. 1b shows the N_2 adsorption–desorption isotherms of both TS-1-B and TS-1-O supports. The TS-1-B support is almost nonporous, as indicated by the very small uptake in the isotherm at $P/P_0 < 0.02$ and the negligible micropore volume (i.e., 0.01 $cm^3\ g^{-1}$) compared with that of traditional TS-1-O support (i.e., 0.23 $cm^3\ g^{-1}$). As explained in Ref. [36], the nonporous characteristic of the TS-1-B support is because the micropores are blocked by TPA template, with its nitrogen atom at the center of channel intersection and the propyl groups extending along the channels.

The highly crystalline structure of the TS-1-B support provides a sharp contrast between Au nanoparticles and support. Moreover, the blocked micropores guarantee that all nanoparticles are on the exterior surface and thus no tiny Au nanoparticles could be hidden from view inside the micropores [26]. Therefore, counting the Au nanoparticles observed under HRTEM will give a reliable particle size. Fig. 2(a–e) presents the typical HRTEM images of Au/TS-1-B catalysts with different Au loadings. For each catalyst, the entire Au nanoparticles observed by HRTEM were counted for averaged particle size to reduce statistical error. The average Au particle size ranged from 2.6 to 5.1 nm with increasing Au loading from 0.06 to 0.40 wt%.

Because of the high detection limit of the HRTEM [23], the Au nanoparticles smaller than 0.8 nm which are also active toward PO production are difficult to be identified and counted. To estimate the statistical error, we have used high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) with resolution of 0.20 nm to determine the fraction of the tiny Au particles. Figs. 2f and S1 show the images of the Au/TS-1-B