Applied Catalysis B: Environmental 95 (2010) 430–438

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Gold clusters supported on alkaline treated TS-1 for highly efficient propene epoxidation with O_2 and H_2

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ARTICLE INFO

Article history:
Received 11 November 2009
Received in revised form 19 January 2010
Accepted 20 January 2010
Available online 25 January 2010

Keywords:
Propene epoxidation
O_2/H_2 mixture
TS-1
Alkaline treatment
Gold cluster
H_2 efficiency

ABSTRACT

Gold could be deposited as clusters smaller than 2.0 nm in diameter on TS-1 by solid grinding (SG) of the support with dimethyl Au(III) acetylacetonate after TS-1 was pretreated in aqueous solution of alkaline metal hydroxides. While in C_3H_6 epoxidation with O_2 and H_2 mixture Au nanoparticles larger than 2.0 nm deposited on TS-1 without alkaline treatment gave a very low PO formation rate of 11 $g_{PO}\,kg_{cat.}^{-1}\,h^{-1}$, Au clusters on alkaline treated TS-1 presented a greatly enhanced rate as high as 137 $g_{PO}\,kg_{cat.}^{-1}\,h^{-1}$, which was comparable to the best data reported so far. In addition, very high H_2 efficiency reaching 47% could be obtained by gold clusters on alkaline treated TS-1.

1. Introduction

Propene epoxide (PO) is an important bulk chemical and mainly used to produce polyurethane foams and resins, and propylene glycol. Its annual worldwide production was about 7.5 million tons with a growth rate above 4.0% in 2007 [1]. PO is currently mainly produced by the chlorohydrin process and several organic peroxide processes [2]. The former is accompanied by the by-production of $CaCl_2$ together with toxic chlorinated organic compounds. The latter suffers from the mismatch of market demand between PO and co-products such as tert-butanol and styrene. Recently two new processes have been developed: a cumene hydroperoxide process in 2003 in Japan [3] and a hydrogen peroxide (H_2O_2) epoxidation process in 2008 in Belgium [4]. The cumene hydroperoxide process produces PO alone by reducing co-product, cumyl alcohol, to cumene with H_2. The H_2O_2 epoxidation process produces H_2O as the only by-product, while H_2O_2 is usually expensive and its commercial production requires two steps: anthraquinone hydrogenation and subsequent oxidation [5]. Accordingly, the common constraint of these new industrial processes is multi-staged reactions in liquid phase.

Our research group firstly reported in 1998 that gold (Au) nanoparticles (NPs, 2.0–5.0 nm) deposited on anatase TiO_2 could catalyze gas phase propene (C_3H_6) epoxidation with O_2 and H_2 mixture to produce PO with selectivity above 90% [6]. In contrast to commercial processes described above for PO synthesis, this route is simpler (one-step reaction in gas phase) and greener (with H_2O as the only by-product), and thus soon has attracted growing interests.

In the past decade anatase TiO_2, mesoporous Ti–silicate (Ti–SiO_2), and microporous titanosilicalite-1 (TS-1) have been extensively used as supports for Au catalysts for C_3H_6 epoxidation with O_2 and H_2 mixture under hourly space velocity of 4000–8000 mL $g_{cat.}^{-1}\,h^{-1}$ [6–21]. When Au NPs were supported on anatase TiO_2, they were selective to PO only at temperatures below 373 K, therefore giving C_3H_6 conversions less than 1.0% [6,13]. However, if Au NPs were loaded on the latter two supports, they were selective up to 473 K exhibiting higher catalytic performance [7,8,12,17–20]. In the presence of solid promoter $Ba(NO_3)_2$ on the catalyst and gas phase promoter trimethylamine in the reactant feed gas, 0.30 wt% Au/mesoporous Ti–SiO_2 displayed a C_3H_6 conversion of 8.5% at a PO selectivity of 91% and at a H_2 efficiency of about 35% at 423 K [8], whereas 0.05 wt% Au/TS-1(Si/Ti = 36) showed without promoters a C_3H_6 conversion of 8.8% at a PO selectivity of 81% at 473 K (H_2 efficiency has not been given),

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doi:10.1016/j.apcatb.2010.01.023

corresponding to a PO formation rate of 116 $g_{PO}\ kg_{cat.}^{-1}\ h^{-1}$ [18]. The PO formation rate over Au/TS-1 has been improved to 134 $g_{PO}\ kg_{cat.}^{-1}\ h^{-1}$ by pretreating TS-1 with NH_4NO_3 aqueous solution before Au deposition by deposition-precipitation (DP) [19] and to 132 $g_{PO}\ kg_{cat.}^{-1}\ h^{-1}$ by adding carbon pearls to the sol–gel during the synthesis of TS-1 support [20]. Recently, PO formation rate over Au/TS-1 was further improved to 200 $g_{PO}\ kg_{cat.}^{-1}\ h^{-1}$ by using a packed-bed catalytic membrane reactor, in which concentrations of O_2 and H_2 could be increased to 40% each [12].

Although DP method is very effective to prepare highly active Au/TS-1 for C_3H_6 epoxidation with O_2 and H_2 mixture [12,17–21], the capture efficiency of Au was always very low because of the hydrophobic nature of TS-1. Even though TS-1 support was pretreated with NH_4NO_3 aqueous solution before DP [19] or a certain amount of alkaline earth metal nitrates was added to the suspension of TS-1 in $HAuCl_4$ solution during DP [21], the capture efficiency of Au was still less than 20%. Recently we have reported that solid grinding (SG) of the support materials with dimethyl Au(III) acetylacetonate can deposit small Au NPs and/or clusters on organic polymers, carbons, and base metal oxides with very high Au capture efficiency (86–100%) [22,23].

Here SG method was used to deposit Au on as prepared TS-1 and alkaline treated TS-1 with very high Au capture efficiency of about 100%. In C_3H_6 epoxidation with O_2 and H_2 mixture Au/TS-1 showed a very low C_3H_6 conversion of 0.6%, while Au/alkaline treated TS-1 yielded greatly improved C_3H_6 conversions. Over 0.25 wt% Au/TS-1–Na1 (see Section 2 for the preparation of TS-1–Na1) a high C_3H_6 conversion of 8.8% was achieved with PO selectivity of 82%, resulting in a high PO formation rate of 137 $g_{PO}\ kg_{cat.}^{-1}\ h^{-1}$, comparable to the best results reported by Delgass and co-workers [19,20]. In addition, a very high H_2 utilization efficiency of 47%, better than any other reported one in published publications, was achieved over Au/TS-1–Na1 with a low Au loading of 0.05 wt%. Further characterizations strongly suggest that the presence of a large number of Au clusters (1.0–2.0 nm) over the exterior surface of Au/alkaline treated TS-1 are responsible for the greatly enhanced catalytic performance.

2. Experimental

2.1. Preparation of TS-1

Tetrapropylammonium hydroxide (TPAOH, 25 wt%), 25.2 g, was dissolved in 48.0 g of H_2O. To this solution a mixture of tetraethyl orthosilicate (21.0 g) and the required amount of tetrabutyl orthotitanate was, after stirring for 0.5 h, added dropwise under vigorous stirring at room temperature. After further stirring for 12 h at room temperature, 12.0 g of poly (acrylamide-co-diallyldimethylammonium chloride) (10 wt% in water) was added. The resulting mixture was further stirred vigorously for 24 h at room temperature, transferred to a teflon-lined stainless autoclave, and then hydrothermally treated at 453 K for 120 h. Products were dried at 383 K for 24 h, and then calcined in air at 823 K for 5.0 h. The TS-1 obtained was named as TS-1(*x*), where *x* is the molar ratio of silicon (Si) to titanium (Ti).

2.2. Pretreatment of TS-1 in aqueous alkaline solution

To the suspension of 1.0 g of calcined TS-1 in 100 mL H_2O, a 1.0 M aqueous solution of NaOH, LiOH, KOH or CsOH was added dropwise under vigorous stirring at 303 K until the pH reached 12. The pH was kept at this value for the required period by dropping a small amount of aqueous alkaline metal hydroxide solution. The suspension was collected by filtration, washed 5 times with 2000 mL (total amount) of H_2O to remove residual alkaline metal hydroxide and then dried at 373 K overnight in air. The alkaline treated TS-1 was named as TS-1(*x*)–M*y*, where M (M = Li, Na, K or Cs) stands for alkaline metal hydroxide and *y* stands for *y*(h) of alkaline treatment period.

2.3. Deposition of Au by SG

Solid grinding was used to deposit Au on as prepared TS-1 and alkaline treated TS-1 [22,23]. The powder of the supports and the required amount of dimethyl Au(III) acetylacetonate [$(CH_3)_2$Au(acac)] having a vapor pressure of 1.1 Pa at 298 K were ground in an agate mortar in air for 15 min at room temperature, followed by reduction in a stream (20 mL min^{-1}) of 10 vol% H_2 in Ar at 423 K for 1.0 h. The temperature was raised from room temperature to 423 K at a heating rate of 1.0 K min^{-1}. The Au catalysts thus prepared were denoted as *z*-Au/TS-1(*x*)–M*y*, where *z* is the calculated weight percent of Au in the catalysts. Because dimethyl Au(III) acetylacetonate was sensitive to the moisture in air, during solid grinding process the relative humidity in air was required to be below 50%. If the relative humidity was high (such as 70% or above), catalysts prepared could not usually exhibit good performances.

2.4. Characterization of catalysts

Nitrogen adsorption–desorption isotherms at 77 K were recorded with a Micromeritics Tristar system. Before measurements, samples were outgassed at 473 K overnight. The BET surface area was calculated by applying the BET equation for relative pressure between 0.05 and 0.20. The pore size distribution was calculated from the adsorption branch by the Barret–Joyner–Halenda (BJH) method. HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) observations were performed to observe tiny Au clusters on a JEOL JEM-3000F transmission electron microscope equipped with digitally processed STEM imaging system. Operating voltage was 300 kV and resolution was about 0.20 nm. The catalyst sample was directly dispersed on a micro-grid supported on a copper mesh without solvent. Elemental analysis was carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

2.5. Catalytic tests

Propene epoxidation was carried out under atmospheric pressure. After the preparation of Au catalysts by solid grinding, 0.15 g of them was loaded into a vertical fixed-bed U-shaped quartz reactor with an inner diameter of 1.0 cm and then reduced by 10 vol% H_2 in Ar as described above. After the reduction Au catalysts were cooled down to room temperature in the same stream (H_2, 10 vol%), and then feed gas containing C_3H_6, O_2, H_2 and Ar with volume ratio of 10/10/10/70 was passed through at a flow rate of 20 mL min^{-1}, which corresponded to a space velocity of 8000 mL $g_{cat.}^{-1}\ h^{-1}$. Reaction temperature was raised from room temperature to 473 K with a heating rate of 1.0 K min^{-1} and then kept at 473 K. Reactants and products were analysed by on-line GCs equipped with TCD (Porapak Q column) and FID (HR-20 M column) detectors and auto-injector.

3. Results

3.1. Characterizations of supports

Fig. 1a shows the isotherms of TS-1(48) and alkaline treated TS-1(48) with NaOH aqueous solution. Over TS-1(48) the hysteresis loop, characteristic of mesopores, was absent, whereas over TS-1(48)–Na1 a small hysteresis loop can be observed, indicating the formation of small amount of mesopores. A larger