Journal of Catalysis 267 (2009) 202–206

Contents lists available at ScienceDirect

Journal of Catalysis

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

Research Note

Enhanced reactivity of direct propylene epoxidation with H_2 and O_2 over Ge-modified Au/TS-1 catalysts

Tong Liu [a], Pelin Hacarlioglu [b], S. Ted Oyama [b,*], Meng-Fei Luo [a], Xiao-Rong Pan [a], Ji-Qing Lu [a,*]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China
[b] Environmental Catalysis and Nanomaterials Laboratory, Department of Chemical Engineering (0211), Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

ARTICLE INFO

Article history:
Received 13 July 2009
Revised 3 August 2009
Accepted 3 August 2009
Available online 10 September 2009

Keywords:
Propylene epoxidation
Au catalyst
TS-1
Germanium
Modification

ABSTRACT

The epoxidation of propylene with H_2–O_2 mixtures was studied over a gold catalyst supported on a Ge-modified TS-1 catalyst at 170 °C. Shifts of X-ray diffraction lines to lower angle showed that the Ge was incorporated into the structure of the TS-1. The presence of Ge more than doubled the conversion from 1.6% to 4% while increasing selectivity from 87% to 91%. Density functional theory calculations indicated that the origin of the enhanced activity was a ligand effect of Ge on Ti, which lowered the activation energy for the critical epoxidation step.

1. Introduction

The direct propylene epoxidation to propylene oxide (PO) with H_2 and O_2 over gold catalysts supported on Ti-containing materials has attracted much attention [1] since it was first reported by the group of Haruta in 1998 [2]. Catalysts that have been investigated include gold supported on titania [2,3] and on various titanosilicates, including Ti–MCM-41, Ti–MCM-48, TS-2, and Ti-β [4–9]. However, these catalysts usually give propylene conversion less than 2% and suffer serious deactivation, because of the deposition of products on the catalyst surface. The group of Delgass found that Au supported on a microporous titanium silicalite-1 (TS-1) gave active, stable catalysts [10–13], as did our group for Au on Ti–TUD [14–16].

In order to enhance the reactivity, much attention has been paid on the modification of the support. Sinha et al. [17] prepared a gold catalyst deposited on a silylated three-dimensional mesoporous titanosilicate and found that it gave very high propylene conversion, although it experienced deactivation. Chowdhury et al. [18] found that adding trimethylamine in the reaction stream improved catalyst stability and H_2 efficiency, which they ascribed to the elimination of surface acidic sites. For the TS-1 support, Cumaranatunge and Delgass [11] reported that treating TS-1 with NH_4NO_3 improved the reactivity, probably due to increases in gold content. The same group [19] found further improvements in rate by introducing mesoporous scale defects through the addition of carbon pearls during the TS-1 synthesis. Lu et al. [20] found that a Mg-promoted catalyst gave a 50% enhancement of activity, due to increased Au capture efficiency and dispersion.

Theoretical calculations suggest that defects in TS-1 play an important role in the reactivity of propylene epoxidation. Wells et al. [21] carried out a density functional theory (DFT) study of hydroperoxy (OOH) intermediates and found that Ti sites located adjacent to Si vacancies in the TS-1 lattice are more reactive than fully coordinated Ti sites, which were inactive.

All the above-mentioned findings suggest that improvements of the Au catalyst for propylene epoxidation may lie in the modification of the support. The current work was inspired by the findings of Oldroyd et al. who modified MCM-41 materials with Ge(IV) species prior to the grafting of tetracoordinated Ti(IV) and found that the resulting catalyst was more active for cyclohexene epoxidation with H_2O_2 compared to unmodified Ti–MCM-41 [22]. In this work, we demonstrate that modification of TS-1 by Ge(IV) species, gives enhanced reactivity for propylene epoxidation with H_2 and O_2. A possible role of Ge is discussed, based on the theoretical calculation results.

2. Experimental

2.1. Synthesis of TS-1 and Ge-modified TS-1

For a typical synthesis of TS-1, 173 mmol of tetraethylorthosilicate (TEOS, 98%) was added to an aqueous solution of HCl

---

* Corresponding authors. Fax: +1 540 231 5022 (S.T. Oyama), +86 579 82282595 (J.-Q. Lu).
E-mail addresses: oyama@vt.edu (S.T. Oyama), jiqinglu@zjnu.cn (J.-Q. Lu).

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.08.002

(0.05 M), then a solution of 1.7 mmol of titanium (IV) tetrabutoxide (TBOT, 99%) dissolved in 20 cm^3 of isopropanol (99.5%) was added dropwise. After stirring for 15 min, 8 g of tetrapropylammonium hydroxide (TPAOH, 20% solution) was added dropwise to form a transparent gel, which was aged for 2 h at room temperature (RT), dried at 100 °C overnight, and finely ground. A quantity of TPAOH two times the weight of the solid was added and the mixture was crystallized in a Teflon autoclave at 448 K for 24 h. The solid was collected via centrifugation, washed thoroughly with deionized water, dried in vacuum at RT, and calcined at 773 K for 5 h (ramp of 3 $°C\ min^{-1}$).

The Ge-modified TS-1 was synthesized in a similar manner, except that the addition of TBOT in the TS-1 synthesis was replaced by the addition of a mixture of TBOT and tetra-*n*-butylgermanium. For the nomenclature a sample designated as 0.02Ge–TS-1(100) indicates a molar ratio of Ge/Ti of 0.02 and of Si/Ti of 100.

2.2. Preparation of supported Au catalysts

Supported Au catalysts were prepared using the deposition–precipitation method. A 100 cm^3 solution of $HAuCl_4 \cdot 4H_2O$ (2 $mg\ cm^{-3}$) was heated to 343 K under vigorous stirring. After adjusting the pH of the solution to 7 using a 0.1 M NaOH solution, 1 g of support (TS-1 or Ge–TS-1) was added, and the suspension was aged at 343 K for 1 h. After cooling to RT, the solids were collected via centrifugation, washed with 50 cm^3 of deionized water, centrifuged again, and vacuum dried at RT overnight. The resulting solid was not calcined further. Actual Au, Ti, and Ge contents in the catalysts were determined by inductively coupled plasma (ICP) measurements. In the description of the catalysts, a catalyst designated as 0.22Au/0.02Ge–TS-1(100) indicates that the Au loading in the catalyst was 0.22 wt% and that the support was TS-1 with a Si/Ti ratio of 170 and a Ge/Ti ratio of 0.02.

2.3. Characterization and theoretical calculations

BET areas were obtained on a Quantachrome Autosorb-1 apparatus. X-ray diffraction (XRD) measurements were carried out with a PANalytical X'Pert PRO powder diffractometer using Cu Kα radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images were obtained on a JEM2010 microscope (200 kV). The geometries of the compounds were obtained by energy minimization of the structures using a DFT method in Gaussian 98. The optimizations were conducted using the Becke3lyp hybrid functional with a 6-311G (2d, *p*)-polarized basis set.

2.4. Catalytic testing

Epoxidation of propylene was carried out in a quartz tubular microreactor of 8 mm diameter and 180 mm length equipped with an axial quartz-sheathed thermocouple, using 0.3 g catalyst of 100–140 mesh size without dilution. The catalyst was heated in a reaction gas mixture ($C_3H_6/H_2/O_2/N_2 = 1/1/1/7$ with flow rates of 3.5/3.5/3.5/24.5 $cm^3\ min^{-1}$, controlled by mass flow meters) from RT to reaction temperature in 6 h. The products were analyzed online using a gas chromatograph (Shimazu GC-2014) equipped with a flame ionization detector and a thermal conductivity detector, attached, respectively, to a FFAP capillary column (0.32 mm × 60 m) and a Porapak Q compact column (3 mm × 3 m). The FFAP and Porapak Q were used to detect oxygenates (acetaldehyde, PO, acetone, propionaldehyde, acrolein, acetic acid, and isopropanol) and H_2O and CO_2, respectively. The following definitions were used.

Propylene conversion = moles of (oxygenates + $CO_2/3$)/moles of propylene in feed.

PO selectivity = moles of PO/moles of (oxygenates + $CO_2/3$).

3. Results and discussion

The XRD patterns show the structure of the TS-1 support [23], which is almost unperturbed with Ge substitution or gold loading (Fig. 1a). Close examination shows that there is a small trend for decreasing angle with Ge content (Fig. 1b). This corresponds to an increase of unit cell size, which is consistent with the larger size of Ge over Si and indicates incorporation of Ge in the TS-1 structure. The TEM characterization shows that the Au particles are similar in size and distribution in all samples (Fig. 2). The sizes range from 2 to 4 nm, a range expected to give good selectivity to PO [15].

The PO activity of the various Au catalysts was obtained at steady state, after 5 h reaction (Table 1). The 0.13Au/TS-1(100) catalyst gives a propylene conversion of 1.6% and a PO selectivity of 87%, which are comparable to the results in the literature [20]. The Ge-modified TS-1 supports give higher conversions. The most reactive catalyst, 0.14Au/0.04Ge–TS-1(100), gave a propylene conversion of 4.0% and a PO selectivity of 91%, corresponding to a PO formation rate of 66 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$. This is a greater than 2-fold enhancement compared to the unmodified 0.13Au/TS-1(100) catalyst (25 $g_{PO}\ h^{-1}\ g_{cat}^{-1}$). The turnover frequency (TOF) based on Ti was $0.76 \times 10^{-3}\ s^{-1}$ for the 0.13Au/TS-1(100) catalyst which is slightly lower than $1.17 \times 10^{-3}\ s^{-1}$ for a 0.52Au/TS-1 catalyst_48-162 reported by Yap et al. [10] at similar reaction conditions, but higher

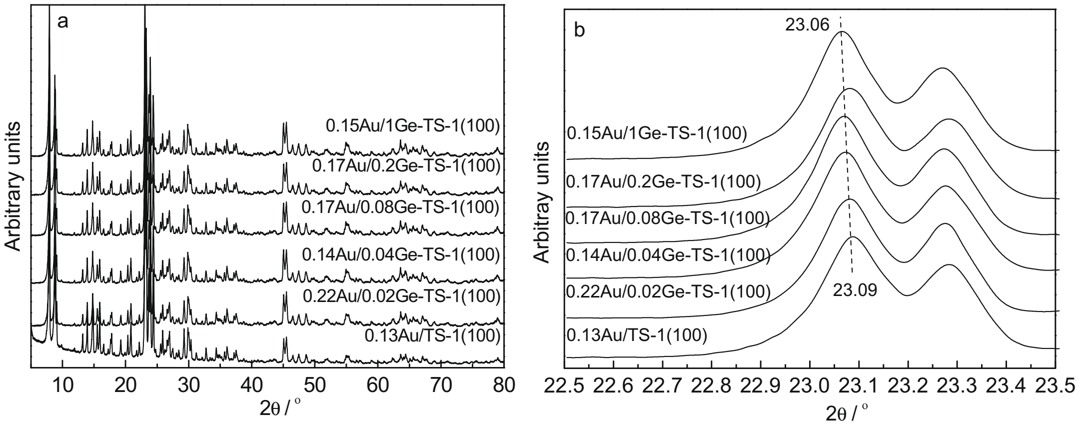

Fig. 1. XRD patterns of various Au/TS-1(100) catalysts.