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Enhanced reaction rate for gas-phase epoxidation of propylene using H_2 and O_2 by Cs promotion of Au/TS-1

Wen-Sheng Lee [a], M. Cem Akatay [b], Eric A. Stach [b,c], Fabio H. Ribeiro [a], W. Nicholas Delgass [a,*]

[a] Forney Hall of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA
[b] School of Materials Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA
[c] Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

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ABSTRACT

Gold clusters supported on titanium silicalite-1 (hereafter denoted as Au/TS-1) with high gold loading at ~0.1–0.16 wt%, prepared by the deposition precipitation (DP) method, showed about two times enhancement in the PO rate (~ 300 versus ~ 150 $g_{PO}\ h^{-1}\ kg_{Cat}^{-1}$ at 200 °C), ~10% increase in PO selectivity (~80% versus ~70%) and ~5–10% increase in H_2 selectivity (~20% versus ~10%) when Cs_2CO_3 instead of Na_2CO_3 was used as the precipitation agent. Using Cs_2CO_3 as the precipitation agent caused a fourfold increase in Au uptake efficiency, indicating a strong interaction between Cs and Au in the Au/TS-1 system. XPS/TEM analyses for two Au/TS-1 samples with the same gold loading at ~0.16 wt% but different alkali metals (Cs versus Na) indicate that more Au was retained inside the TS-1 nanopores for the Cs sample. The presence of Cs is, therefore, proposed to help stabilize small gold clusters (<1 nm) inside the TS-1 nanoporous channels at the high gold loading (>0.1 wt%) due to the Cs/Au interaction, resulting in the promotion of PO rate per gram of catalyst. Furthermore, similar apparent activation energy at ~30 kJ $mole^{-1}$ observed for the Au/TS-1 catalysts with the presence of either Cs or Na suggests that the number, but not the nature of the active sites, is changed in the Cs-promoted samples. Finally, regardless of the type of alkali metal (Na or Cs) present in the catalysts, lower Ti content (Si/Ti molar ratio ~100) for Au/TS-1 catalysts was found to favor PO catalytic performance.

1. Introduction

The discovery that nanoscale gold particles supported on titania (Au/TiO_2) catalyze propylene to propylene oxide (PO) in the presence of hydrogen and oxygen provides a greener and sustainable PO production route as compared to the current major PO production processes (based on chlorohydrin and organic hydroperoxide intermediates) because water, instead of chlorinated organic compound wastes and/or undesired coproducts, is the only significant by-product [1,2]. Increasing the Ti dispersion on the support improved both PO rate and the stability [3–5] and has led to a focus on either mesoporous titanosilicate (Ti-MCM-41, Ti-MCM-48, Ti-TUD) [6–8] or nanoporous titanium silicalite-1 (TS-1) as preferred supports [1,5,9–11]. The PO rate was first improved to ~ 90 $g_{PO}\ h^{-1}\ kg_{Cat}^{-1}$ by using a 3D mesoporous titanosilicate, with barium as a promoter [12]. Later, Au/TS-1 showed a PO rate of ~ 100 $g_{PO}\ h^{-1}\ kg_{Cat}^{-1}$ [10], and the PO rate was further enhanced to ~ 130—140 $g_{PO}\ h^{-1}\ kg_{Cat}^{-1}$ by either introducing defect sites to TS-1 [13], pretreating the TS-1 with NH_4NO_3 before gold deposition [14], or using a solid grinding (SG) method to deposit gold clusters [1,15]. Recently, a PO rate of ~ 160 $g_{PO}\ h^{-1}\ kg_{Cat}^{-1}$, the highest PO rate at 200 °C currently reported in the literature, was achieved by refining the gold deposition precipitation (DP) conditions in the Au/TS-1 preparation [9].

As to the gold active sites for the PO reaction, gold particles with size 2–5 nm were cited for both Au/TiO_2 and other Au/Ti-based oxides by Haruta et al. [16,17]. On the other hand, density functional theory (DFT) calculations and experimental results suggest that nano-gold clusters (<2 nm) can be energetically favorable for the H_2O_2 formation from O_2 and H_2 [18–20]. Since the Au sites in the Au–Ti catalysts for the PO reaction are generally accepted to be responsible for H_2O_2 generation (while the Ti sites catalyze epoxidation) [21,22], small gold clusters inside the TS-1 nanopores can be active sites for the PO reaction if they are in close proximity to Ti. The latter statement was also supported by our DFT calculation results [9–11,23]. Gold clusters with size ~1.4 nm on the external surface of the TS-1 have been proposed to be the dominant gold active sites for the PO reaction in Au/TS-1 [1]. On the other hand, our recent work in which a specially designed silicalite-1 (S-1)-coated TS-1 material was used as the support confirms the activity of the small gold clusters inside the TS-1 nanopores [24]. Therefore, the nature of the gold active sites in Au–Ti catalysts for the PO reaction is still under debate. Herein, we report that the

* Corresponding author. Fax: +1 765 494 0805.
E-mail address: delgass@purdue.edu (W. Nicholas Delgass).

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PO rate (per gram of catalyst) of Au/TS-1(121)Cs catalysts (the number in the parenthesis represents Si/Ti molar ratio and Cs indicates that Cs_2CO_3 was used as a precipitation agent during the deposition precipitation (DP) process) can be further enhanced to around two times higher than that of the highest reported PO rate at 200 °C [9]. A specific interaction between the Au and Cs in the Au/TS-1(121)Cs catalysts, which is induced within the nanopores in the TS-1, has also been identified for the first time. It is proposed that the presence of Cs can help stabilize the small gold clusters (<1 nm) inside the TS-1 nanoporous channels at relatively high gold loading (>0.1 wt%), which increases the number of the gold active sites, leading to the significantly higher PO rate per gram of catalyst found. We also show that lower Ti content (Si/Ti molar ratio ~100) in Au/TS-1 catalysts (with either Na_2CO_3 or Cs_2CO_3 as a precipitation agent) favors PO catalytic performance.

2. Experimental methods

2.1. Synthesis of titanium silicalite-1

Titanium silicalite-1 (TS-1) with different Si/Ti molar ratios was synthesized following the same micellar media method reported previously [9,25]. To avoid the variations caused by using different batches of TS-1, multiple batches of TS-1 were synthesized and then mixed to create the TS-1 supply. Therefore, the TS-1 used in this work shares the same physical/chemical properties.

2.2. Synthesis of Au/TS-1

Gold was deposited onto TS-1 by the DP method, and the preparation conditions were similar to those reported in [9]. For a typical Au/TS-1 preparation, 2–4 g TS-1 was added to an aqueous solution (40 mL) of $HAuCl_4{\cdot}3H_2O$ (Alfa Aesar, 99.99%) with concentration ca. 1.75–7.5 g L^{-1}, and the slurry was stirred for 10–30 min at 900 rpm at RT. An appropriate amount of 1 N (1 Normal) aqueous solution of Na_2CO_3 (J.T. Barker Chemical Co.) or 1 M (1 Molar concentration, which is equal to 2 N) aqueous solution of Cs_2CO_3 (Sigma, 99.99%) or K_2CO_3 (Aqua Solutions, ACS) or Rb_2CO_3 (Alfa Aesar, 99%) was then added immediately by pipette to give an alkali/Au molar ratio ~4–5, targeting the final pH of the slurry at the end of the pH adjustment to be ~6–8. The slurry was stirred for 5–6 h at RT to allow the pH to reach the target value, after which the solid was separated by centrifugation and then washed by suspending the catalyst in 50 mL D.I. water and stirring for 1–2 min. Some samples with higher gold loading (>0.1 wt%) were achieved by using longer mixing time (9.5–16 h) at RT. Finally, the catalyst was separated by centrifugation and dried in a vacuum oven at RT overnight. Catalysts were named by gold loading, Si/Ti molar ratio and type of precipitation agent, such that a catalyst with gold loading 0.1 wt%, Si/Ti molar ratio = 121, and prepared by using Cs_2CO_3 as a precipitation agent is 0.1Au/TS-1(121)Cs.

2.3. Synthesis of Ti-Cabosil EH-5

Approximately 15 g of as-received Cabosil EH-5 was added into ~150 mL deionized water (hereafter denoted as D.I. water) to make a thick paste, and the paste was directly dried at 145 °C in a static oven overnight. After drying, ~12 g of dried Cabosil EH-5 was suspended into ~100 mL isopropyl alcohol (IPA, Alfa Aesar, HPLC Grade, 99.7+%) and the slurry was stirred for a few min. An appropriate amount of titanium (IV) butoxide (TBOT, Alfa Aesar, <99%) was then added to give the Ti content ~0.36 wt% of the finished catalyst, which corresponds to ~1.7% of a monolayer of Ti over SiO_2, assuming the Si site density to be 1×10^{15} atoms cm^{-2} and using the measured BET surface area = 265 m^2 g^{-1} (after water treatment). The final solution was stirred at RT for 1 h and then stirred at 85 °C for another 1–2 h (until all the IPA evaporated). The white solid was then calcined at 550 °C for 6 h with a ramping rate 2 °C min^{-1} in a flow of air ~150–200 mL min^{-1} to remove both residual IPA and the organic ligands.

2.4. Synthesis of Cs-TS-1(121), K-TS-1(121) and Cs-TS-1(121)-DP

For Cs-TS-1(121), approximately 8 g of TS-1(121) was mixed with 28 mL D.I. water. After a few minutes of stirring, ~4.4 g $CsNO_3$ (Sigma, 99.99%) was added to the slurry, and the slurry was stirred at 900 rpm at RT overnight. This Cs ion-exchanged TS-1(121) was separated via centrifugation and washed by ~100 mL D.I. water once. The solid was then dried under vacuum at RT overnight. For K-TS-1(121), the preparation procedure was similar to that for Cs-TS-1(121), except ~2.5 g KNO_3 (Aqua Solutions, ACS grade) was added in place of the $CsNO_3$. For Cs-TS-1(121)-DP, the preparation procedure was to mimic the Au deposition process except HCl (Mallinckrodt Baker) instead of $HAuCl_4{\cdot}3H_2O$ (Alfa Aesar, 99.99%) and was used to adjust the pH of the slurry solution. 2 g of TS-1(121) was suspended to an aqueous solution (40 mL) with 9.6×10^{-5} mole of HCl and then an appropriate amount of 1 M aqueous solution of Cs_2CO_3 (Sigma, 99.99%) that gives Cs/Cl molar ratio ~4.2 was then added to the slurry. The slurry was stirred for 5 h at RT, and a few drops of 0.03 M HCl were added to reach the final pH of the slurry ~6.25. The solid was then separated by centrifugation and then washed by suspending the sample in 50 mL D.I. water and stirring for 1–2 min. Finally, the sample was separated by centrifugation and dried in a vacuum oven at RT overnight.

2.5. Post-treatment of fresh Au/TS-1(121)Na by Cs

In order to further understand the effect of Cs promotion, a series of fresh Au/TS-1(121)Na samples with three different gold loadings (0.007, 0.06, and 0.14 wt%) were prepared according to the procedure described above. Once the Au/TS-1(121)Na samples were dried, different concentrations of $CsNO_3$ (Sigma, 99.99%) solution (low, medium and over dosage, approximately ~2 mL) were added to each gold loading of the Au/TS-1(121)Na samples (approximately 1 g) by impregnation and then the Cs dosed samples were dried in a vacuum oven at RT overnight to remove excess water. Those samples were then directly tested under reaction conditions without any pretreatment. The actual Cs/Au molar ratio obtained for the Cs dosed sample was determined by atomic absorption spectroscopy.

2.6. Characterization

The MFI structure of the TS-1 supports was confirmed by the XRD pattern (XRD, Scintag X2 diffractometer, Cu Kα radiation with scanning rate 1.2° min^{-1}). The Ti coordination in TS-1 was evaluated by UV–vis spectroscopy (DRUV–vis, Varian Cary 5000 outfitted with Harrick Praying Mantis optics and using $BaSO_4$ as the reference). Gold particle sizes were determined by high-resolution transmission electron microscopy (HRTEM, FEI Titan, 300 keV) and metal contents retained in the samples (Au, Ti, and alkali metals) were determined using atomic absorption spectroscopy (AAS, Perkin–Elmer AAnalyst 300). BET surface area as well as the pore volume were measured using N_2 adsorption isotherms (Micromeritics ASAP 2000 with samples degassed at 250 °C for at least 8 h before N_2 adsorption). Surface composition was obtained by X-ray photoelectron spectroscopy (XPS) measured with a Kratos Axis Ultra DLD spectrometer using Al Kα monochromatic X-ray radiation at 1486.6 eV and referenced to the Si 2p line at 103.4 eV [26].