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Enhancement of Au capture efficiency and activity of Au/TS-1 catalysts for propylene epoxidation

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Abstract

A method for enhancing the useful Au content in Au/TS-1 catalysts for vapor-phase propylene epoxidation is reported. Exposure of calcined TS-1 support to 1 M NH_4NO_3 at 80 °C, followed by vacuum drying, produced a modified TS-1 support material. Deposition precipitation of gold on these modified TS-1 supports resulted in a fourfold increase in Au capture efficiency and produced catalysts with 5–10% conversion of propylene with 75–85% selectivity for PO, at 200 °C and a space velocity of 7000 $\mathrm{ml\,h^{-1}\,g_{cat}^{-1}}$. In this system, 10% conversion and 76% selectivity amount to a rate of 134 $\mathrm{g_{PO}\,h^{-1}\,kg_{cat}^{-1}}$. An optimal Au content that is support dependent is observed for these catalysts.

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1. Introduction

The discovery by Haruta and co-workers [1] that nanoscale gold particles on titania supports provide a highly selective (∼ 99%) route to vapor-phase propylene oxide production, with the use of a mixture of propylene, oxygen, and *hydrogen* under ambient pressure, has been a significant breakthrough in heterogeneous catalysis. A direct, single-step epoxidation of propylene to propylene oxide (PO) has both practical and fundamental implications. Although the high selectivity shown for PO production in propylene/oxygen/hydrogen mixtures over Au/Ti catalysts is an important step toward a new process, further understanding of the catalytic functions is needed to guide improved catalytic formulations for partial oxidation of molecules containing allylic hydrogen.

Subsequent studies by Haruta and in other laboratories around the world have confirmed the high selectivity of these systems [2,3]. Speculation and circumstantial evidence that the role of hydrogen is to form HOOH, which is the electrophilic oxidant, has recently been supported by direct observation of HOOH formation on Au/TiO_2 systems [4]. Careful TEM studies have suggested that 2–5-nm Au particles have special properties for PO production [1]. Smaller particles have been seen to make propane in the propylene/oxygen/hydrogen reaction environment, whereas larger Au particles make CO_2. Early work in our laboratory [5] and that of others [2,6,7] have shown the activity and selectivity of Au/Ti PO catalysts to be very sensitive to the nature of the support. Au on rutile is inactive. Au on anatase or amorphous TiO_2 is active, but Au on monolayers and submonolayers of TiO_2 on silica is more active. We have concluded from this work that isolated, tetrahedrally coordinated Ti is most effective, and that led us to TS-1 as the support of choice for our studies.

The low site density is a key problem with these Au/TS-1 catalysts. The selectivity is up to commercial standards, but the activity is not. The ability to control the deposition of Au on TS-1 during deposition precipitation could allow en-

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hancement of the site density, particularly as more is learned about the nature and position of the active Ti sites. A study of the deposition precipitation (DP) parameters for Au deposition on TS-1 has shown that, at a pH of 9–10, 1–3% of the available Au in the solution was deposited on conventional TS-1 supports [8].

In this work, a newly discovered ammonium nitrate enhancement of the useful Au content in Au/titanium-silicalite-1 (TS-1) propylene epoxidation catalysts is reported. The Au capture efficiency of the support during deposition precipitation has been increased remarkably by the ammonium nitrate treatment, permitting the use of very low concentrations of the rather expensive Au precursor ($HAuCl_4 \cdot xH_2O$). The Au capture efficiency is defined as the fraction of Au from the $HAuCl_4 \cdot xH_2O$ precursor solution that is deposited on the support material during deposition precipitation. Au loadings have been enhanced while the average particle diameter of the observed gold is maintained at 5–6 nm. Furthermore, we have compared Au/TS-1 catalysts, with and without NH_4NO_3 pretreatment of the same batch of TS-1 support material and with similar Au loading, to show the enhancement in activity due to the NH_4NO_3 pretreatment.

2. Experimental

2.1. Synthesis and characterization of TS-1 supports

A method based on a non-ionic surfactant, polyoxyethylene 20-sorbitan monolaurate (Tween 20, enzyme grade; Fisher Scientific), outlined by Khomane et al. [9], was used for the preparation of the TS-1 support material. The TS-1 support materials prepared by this method were calcined in a 20% O_2/balance He mixture for 12 h at 808 K to burn out the template. The ramp rate of the calcination furnace was set at 0.7 $K\,min^{-1}$ to reach a temperature of 808 K.

The Au and Ti loadings were determined with a Perkin-Elmer 3110 atomic absorption (AA) spectrometer. We prepared samples for AA by digesting 0.1 g of catalyst in 2 ml of aqua regia and 1 ml of HF, in a polypropylene flask, for a period of 7 days and finally diluting the solution to 50 ml. BET surface area analysis through N_2 adsorption isotherms was done with a Micromeretics ASAP 2000 surface area analyzer after sample out-gassing under vacuum at 523 K for a period of 6 h. S_{BET} gave an indication of the total surface area of the catalyst. In addition, all catalyst supports were checked for crystallographic phase by XRD with a Siemens D500 diffractometer and Cu-K_α X-rays.

Diffuse reflectance spectroscopy (DRUV–vis) was used to observe the existence of TiO_2 phases and extraframework Ti in the TS-1 supports. DRUV–vis spectra of the powder samples were obtained with a Varian (Cary 5000) spectrophotometer with a Harrick-Scientific Praying-Mantis diffuse reflectance accessory. Samples were diluted to 10:1 with MgO (perfect reflector) and lightly ground with a mortar and pestle before they were loaded into the instrument.

The average TS-1 particle diameters $\langle D_s \rangle$ and the average Au particle diameter $\langle D_m \rangle$ were determined after analysis of a minimum of 35 particles from TEM (JOEL 2000 FX at 200 keV) micrographs and with UTHSCSA Image Tool version 3.0 image analysis software. All Au particle sizes presented are from post-reaction (steady-state kinetic analysis) TEM images, since no visible particles were present in fresh catalysts.

2.2. Post-synthesis treatments and Au deposition

The modified TS-1 support material was formed by the post-synthesis treatment of the calcined TS-1 with aqueous NH_4NO_3. In a typical treatment, 1.0 g of calcined TS-1 support material was added to 60 ml of 1 M NH_4NO_3 solution in a 100-ml beaker, and the solution mixture was stirred for 15 h at 80 °C. After the contents in the beaker were cooled to room temperature, the solid material was centrifuged out, washed in 80 ml of DI water, centrifuged again, and vacuum dried at room temperature for 12 h.

We accomplished DP of Au onto the untreated support materials by stirring 1 g of calcined TS-1 support material in 50 ml of 0.8–3.0 $mg\,ml^{-1}$ $HAuCl_4 \cdot xH_2O$ (purity 99.999% metal basis) solution at room temperature for 2–3 h. The solution pH was maintained at 9 by the addition of a few drops of 1 M Na_2CO_3. To bring about DP on the modified supports, we stirred 1 g of modified support material in 50 ml of 0.4–0.6 $mg\,ml^{-1}$ $HAuCl_4 \cdot xH_2O$ solution (pH ~ 9) at room temperature for 2–3 h. In both cases, the solid catalyst was centrifuged out, washed in 40 ml of DI water, centrifuged again, and finally vacuum dried at room temperature for 12 h. Catalysts have been identified throughout the paper as C_Au wt%_Ti wt%, and the letter N has been used to indicate catalysts that were treated with NH_4NO_3.

2.3. Catalyst activity measurements

Reaction rates, analyzed after 4–6 h of steady-state activity, were measured with a half-inch vertical stainless-steel reactor housed in a Lindberg Solar Basic furnace. Reaction gas flows were measured with bubble flow meters, and products were analyzed with a Varian 3740 gas chromatograph with an automated sampling valve. Oxygen and carbon dioxide gases were analyzed with a Chromosorb 102 packed column (Supelco; length 1.83 m, diameter 3.81 mm) and a thermal conductivity detector (TCD), while the partially oxidized products were analyzed with a fused silica Supelcowax 10 capillary column (Supelco; length 60 m, diameter 0.53 mm, film thickness 1.0 µm) with a flame ionization detector (FID). Reaction temperatures were monitored with a stainless-steel-jacketed Type K thermocouple inside of the catalyst bed. Catalytic reactions were run in a 10/10/10/70 vol% reactant mixture of hydrogen (99.9995%), oxygen (99.9995%), propylene (99.9%), and helium (99.9995%) at a

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