Spectroscopy and catalytic activity study of gold supported on barium titanate nanotubes for styrene epoxidation

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ABSTRACT

Gold (0.5–5 wt.%) supported on barium titanate nanotubes (Au/BaTNT) were prepared, characterized and for the first time, investigated as catalysts for selective oxidation of styrene with oxygen (O_2 or $H_2 + O_2$) and peroxides (H_2O_2 or TBHP). Conversion of styrene enhanced when H_2 was co-added to O_2 in the reactions. Au/BaTNT activated O_2 and H_2 and produced H_2O_2 *in situ* for use in oxidations. Peroxides were found better oxidants than O_2. At optimized conditions, styrene oxide selectivity of 80.1 wt.% at styrene conversion of 60.5 wt.% was achieved over Au(1 wt.%)/BaTNT using TBHP. Au particles (5.0–7.4 nm) were dispersed and decorated on the walls of BaTNT. They exhibited superior performance to the known Au catalysts in styrene oxidation. *Reactive oxygen species* formed during oxidation reactions were followed with *in situ* spectral characterizations (diffuse reflectance UV–vis and FT-Raman). Au/BaTNT was reusable in four recycles with little loss in catalytic activity.

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1. Introduction

Selective oxidation of olefins (in particular, styrene) is an important chemical reaction as the products of this reaction (epoxide and aldehyde) are building units in the manufacture of plasticizers, perfumes and pharmaceuticals [1]. Epoxides are conventionally prepared by chlorohydrin/peracid routes, which are unsafe and generate a large quantity of waste with a heavy environmental burden with respect to its disposal. Use of molecular oxygen or a more reactive form of oxygen (H_2O_2 or *tert*-butyl hydroperoxide (TBHP)) as oxidant and metal as catalyst has been exploited as a *greener* approach for this reaction. However, epoxidation of olefins by the electrophilic addition of oxygen to the carbon–carbon double bond remains one of the most significant challenges in oxidation catalysis. There have been numerous reports on the use of gold nanoparticles as catalysts for olefin oxidation [2–7]. Haruta [8] reported the direct vapour-phase oxidation of propene with molecular oxygen in presence of hydrogen over Au/TiO$_2$ catalyst obtaining epoxide selectivity higher than 90% and propene conversion of 1–2% at 30–120 °C. Reaction rate was independent on the concentration of propene. It increased with increasing oxygen and hydrogen concentrations. Hayashi et al. [9] reported that propene

adsorbed on a gold surface reacts with *oxygen species* formed at the perimeter interface between Au particles and the TiO$_2$ support through the reaction of oxygen with hydrogen. Turner et al. [4] found that Au$_{55}$ nanocrystals supported on BN are catalytically active for styrene oxidation with dioxygen achieving nearly 20% conversion with an epoxide selectivity of 14%. They found a sharp size threshold in catalytic activity. The catalytic performance of Au was described as due to altered electronic structure intrinsic to particle size. Decreasing particle size is associated with an increase in the d-electron density of the gold atoms and the onset of reactivity with dioxygen. Zhu et al. [10] described the catalytic activity of thiolate-capped gold nanoclusters (Au$_{25}$(SR)$_{18}$) in neat and SiO$_2$ supported forms for selective oxidation of styrene with molecular oxygen. Benzaldehyde formed with 70% selectivity. Deng and Friend [2] presented selective oxidation of styrene on an oxygen-covered Au(111) surface and concluded that the oxidation depends on the ability of dissociating dioxygen, which can be tuned by support and quantum size effect. Yoke-shell nanospheres confined with ultra-small Au nanoparticles catalyzed styrene oxidation with oxygen at ambient pressure affording styrene oxide yield of over 30% at 100 °C in 15 h [11]. Many oxidation reactions proceed well with the most environmentally benign oxidant – molecular oxygen. However, in many other cases, such as epoxidation reactions, molecular oxygen does not work efficiently. In such cases, a far more reactive form of oxygen species (H_2O_2 or TBHP) is necessary to produce epoxides.

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Choudhary and co-workers [12–14] reported that Au supported on a range of oxides (MgO, CaO, SrO, BaO, Al_2O_3, Ga_2O_3, In_2O_3, Tl_2O_3, TiO_2, Cr_2O_3, MnO_2, Fe_2O_3, CoO_x, NiO, CuO, ZnO, Y_2O_3, ZrO_2, La_2O_3, Ce_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Tb_2O_3, Er_2O_3, Yb_2O_3 and U_3O_8) is active for oxidation of styrene yielding styrene oxide (SO) with anhydrous TBHP (in benzene) as oxidant. Supports play a crucial role in catalytic reactions providing anchoring sites to metal nanoparticles and influencing the reaction rates. Yin et al. [15] studied the epoxidation of styrene over Au/mesoporous Al_2O_3. Zhang et al. [16] elucidated the crystal face selective deposition of Au and the higher activity of Au nanoparticles of 2–3 nm deposited at lateral faces {10$\bar{1}$0} of a layered double hydroxide compound (LDH) in the oxidation of styrene by TBHP. Au_{25} clusters immobilized on hydroxyapatite (HAP) showed best catalytic performance for epoxidation of styrene in toluene medium [17]. Gold supported S- and ionic liquid fragments-containing periodic mesoporous organic silicas showed good oxidation activity with H_2O_2 as oxidant [18,19]. Development of easily scalable, efficient, epoxide selective and stable solid catalyst for styrene epoxidation is still a challenge. Further, the mechanism of oxidant activation and *reactive oxygen species* formed over Au during reactions are not fully understood.

Titanate nanotubes (TNT) are particularly attractive hosts for catalytically active metal nanoparticles because of their well-defined mesoporous one-dimensional structure, high specific surface area and ion-exchange capability [20–23]. Their semiconducting properties lead to strong support-metal interaction which could influence the catalytic performance of metal nanoparticles. We report here, for the first time, the catalytic activity of Au supported on barium titanate nanotubes (Au/BaTNT) in epoxidation of styrene with different oxidants such as O_2, $H_2 + O_2$, aqueous H_2O_2, aqueous TBHP and 5.5 M TBHP in decane. The influence of reaction parameters such as oxidant, solvent, Au loading (on BaTNT), catalyst amount, substrate/oxidant mole ratio, temperature and reaction time on the yield of styrene oxide is probed. The scope of Au(1 wt.%)/BaTNT for oxidation of a range of substituted styrenes is reported. Reusability of the catalyst is also probed. In situ UV–vis and FT-Raman spectroscopies are used to investigate the *reactive oxygen species* formed during the oxidation reaction. Earlier, we reported the use of gold supported on TNT for alcohol oxidation with molecular oxygen [24,25].

2. Experimental

Titanium dioxide (98%, anatase TiO_2), sodium hydroxide (NaOH) and barium nitrate were obtained from Thomas Baker Chemicals Ltd., Chloroauric acid ($HAuCl_4 \cdot 3H_2O$) was procured from HiMedia Chemicals Ltd. All reagents were used as received.

2.1. Catalyst preparation

BaTNT was prepared by ion-exchanging preformed sodium titanate nanotubes (NaTNT) with Ba^{2+} ions. In a typical preparation, 2.5 g of NaTNT (dried at 100 °C for 2 h) was added to 120 ml of aqueous $Ba(NO_3)_2$ solution (0.5 M) taken a beaker. The suspension was heated to 80 °C and stirred for 8 h. The solid was separated and the same procedure was repeated two more times. Then, the isolated solid was washed with deionized water and dried at 110 °C overnight to obtain BaTNT. The sodium form of titanate nanotubes (NaTNT) were prepared by alkali treatment of anatase titania [24–26].

In a typical preparation of Au/BaTNT, an appropriate amount of 2 mM aqueous solution of $HAuCl_4 \cdot 3H_2O$ was added drop-wise to 1 g of BaTNT suspended in 100 ml of deionized water followed by vigorous stirring at 80 °C for 12 h while keeping in dark. The solid formed was filtered, washed with deionized water and dried

at 110 °C for 20 h to obtain the final material. The materials were then reduced in flowing hydrogen at 250 °C for 2 h to yield the final catalysts with input Au loading of 0.5–5 wt.%.

2.2. Characterization techniques

Elemental composition ($Au^{0/+}$, Ba^{2+} and Na^+) of the catalysts was analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; Spectro Arcos). Powder X-ray diffraction (XRD) of the catalyst samples was done on a Philips X'Pert Pro diffractometer using Cu-Kα_1 radiation ($\lambda = 0.15406$ nm) and a proportional counter detector. Measurements were done in the scan range (2θ) of 5–80° at a scan speed of 4°/min. Textural properties of the catalysts [specific surface area (S_{BET}), pore volume (V_p) and average pore diameter (d_p)] were determined from N_2 physisorption studies conducted at −196 °C using a Quantachrome USA (Autosorb-1C) equipment. Prior to N_2 adsorption, the samples were evacuated at 200 °C for 2 h. It was calibrated using a reference alumina sample (supplied by Quantachrome, USA). The samples for transmission electron microscopy (TEM) analysis were prepared by drop casting the catalyst material (which is already dispersed in isopropanol) on a holey-carbon film supported by a 300 mesh copper TEM grid. The analysis was performed using a FEI Tecnai F20 instrument with a 200 kV field emission gun. The mean particle size of Au was determined by inspection of several micrographs taken from various positions. The mean particle diameter (d_{av}) was calculated using the formula: $d_{av} = 6\sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of particles having a diameter of d_i. One hundred particles were chosen to determine the mean diameter of gold particles. A Shimadzu UV-2700 spectrophotometer equipped with an integrating sphere attachment (ISR 2200) was used to acquire diffuse reflectance UV–vis (DRUV-vis) spectra of the powder samples. $BaSO_4$ was used as a reference standard. The DRUV-vis spectra were recorded for bare BaTNT and Au/BaTNT and for the samples contacted with a known quantity of solvent (H_2O, acetonitrile—ACN), oxidant (H_2O_2, TBHP) and/or styrene. FT-Raman spectra of the catalysts were recorded in the range 200–1500 cm^{-1} using a Horiba JY LabRaman HR 800 Micro Raman spectrometer with 630 nm exiting energy generated by a He-Ne laser operating at 20 mV. The strength and density of basic sites in the catalysts were determined by temperature-programmed desorption (TPD) studies on a Micromeritics Auto Chem 2910 instrument using CO_2 as probe molecule. In a typical experiment, 0.1 g of the catalyst was taken in a U-shaped quartz sample tube. The catalyst was pre-treated in He (30 ml/min) at 250 °C for 1 h, then it was cooled to 25 °C and a mixture of CO_2 in He (10 vol%) was fed to the sample (30 ml/min) for 1 h. Further, the sample was flushed with He (30 ml/min) for 1 h at 100 °C. Baseline was checked for stability before acquiring the data points in the temperature range of 100–500 °C. The area of the desorption peaks gave the amount of basic sites present in the catalysts. Acidity of the samples was estimated in a similar manner using NH_3 instead of CO_2 as probe molecule. X-ray photoelectron spectra (XPS) was recorded on a VG Microtech Multilab ESCA 3000 spectrometer with Al-Kα radiation ($h\nu = 1486.6$ eV). The binding energy scale was referenced to the C 1s line at 284.6 eV.

2.3. Reaction procedure

Epoxidation of styrene over Au/BaTNT catalysts was carried out at atmospheric pressure taking 0.05 g of catalyst, 10 mmol of styrene, 10 mmol of anhydrous TBHP (5.5 M in decane) or 70% aqueous TBHP or 30% aqueous H_2O_2 in a glass reactor (25 ml) placed in an oil bath at 80 °C and fitted with a water-cooled reflux condenser and magnetic stirrer. The reaction was conducted for 15 h. After the completion of the reaction, the reactor was cooled to room temperature and then the catalyst was separated by cen-