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Ionic liquid-enhanced immobilization of biosynthesized Au nanoparticles on TS-1 toward efficient catalysts for propylene epoxidation

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ABSTRACT

The direct vapor-phase epoxidation of propylene in the presence of hydrogen and oxygen was studied at a space velocity of 7000 mL h^{-1} g$_{cat.}^{-1}$ over gold catalysts with varying gold and titanium contents prepared by ionic liquid-enhanced immobilization (ILEI) method in which biosynthesized gold nanoparticles (GNPs) were immobilized onto the titanium silicalite-1 (TS-1) supports through the assistance of a small amount of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]). The results showed that [BMIM]$^+$ specially adsorbed onto the support to increase its isoelectric point, leading to the enhanced immobilization. The propylene conversion of 14.6% and PO formation rate of 164.4 g$_{po}$ K g$_{cat.}^{-1}$ h^{-1} were higher than those in any other reports, probably attributing to enhanced interaction between the GNPs and TS-1. Furthermore, the excellent activity and high selectivity of the Au/TS-1 catalysts at a relatively high reaction temperature might be attributed to the existence of residual biomolecules on the catalysts.

1. Introduction

Propylene epoxide (PO) is an important bulk chemical widely used for the production of polyether polyols, polyurethane foams, propene glycol, and propene glycol ethers [1]. PO is industrially produced using chlorohydrin and Halcon (hydroperoxide) processes [1,2]. The former process produces environmentally unfriendly chlorinated by-products, while the later process produces large quantities of coproducts such as tert-butyl alcohol and styrene, which pose economic problems when their demand is lower than that of PO. Therefore, a great deal of effort has been put into catalytic epoxidation of propylene since the late 1990s. Clerici et al. utilized titanium silicalite (TS-1) catalyst for the epoxidation of propylene in the liquid phase using hydrogen peroxide [3,4]. However, the cost of H_2O_2 is very high and also there are handling problems when operating with H_2O_2 [5].

In 1998, a significant demonstration of gas-phase propylene epoxidation was reported by Hayashi et al. [6], who discovered that Au/TiO_2 catalysts with very fine and highly dispersed gold nanoparticles (GNPs) (2.0–5.0 nm) through deposition–precipitation (DP) exhibited a high selectivity (>90%) toward PO at low propylene conversion (~1%) using mixture of propylene, oxygen, and hydrogen under ambient pressure. To date, it has been reported that the gas-phase epoxidation of propylene has been performed over GNPs supported on a number of Ti-containing materials like TiO_2, TiO_2/SiO_2, TS-1, Ti-MCM-41, Ti-MCM-48, three-dimensional Ti–Si mesoporous materials (3D-Ti–Si), Ti-HMS, and so on [7–18]. The density functional theory (DFT) of hydroperoxy (OOH) intermediates on various model titanosilicalite Ti centers explained how microstructural aspects of Ti sites affect propylene epoxidation reactivity. It also demonstrated that a well-defined tetrahedral titanium center is essential for epoxidation [19]. These works have suggested that the isolation of Ti in tetrahedral sites is a requirement for a stable and active catalyst, motivating people to focus on TS-1 as the catalyst support. Taylor et al. found that addition of carbon pearls during the preparation of TS-1 would enhance the activity and stability of the responding Au/TS-1 catalysts prepared by DP in propylene epoxidation [16]. Though the DP method to prepare Au/TS-1 catalysts for propylene epoxidation with O_2 and H_2 mixture is very effective [10,13–18], the Au capture efficiency was always very low. A study on the DP method for Au/TS-1 catalysts has shown that only 1–3 wt.% of the gold available in solution was deposited on conventional TS-1 supports at pH of 9–10 [17]. Even though deposition of gold could be significantly boosted by pretreating TS-1

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supports with NH_4NO_3 aqueous solution prior to DP [15], the capture efficiency of Au was still less than 20 wt.%. The sol-immobilization (SI) technique is also an effective method for the preparation of gold catalysts [20–23]. Compared with the DP method, the SI method has advantages because 100 wt.% of the gold in solution can be immobilized on support materials. This method has been used to prepare gold catalysts for benzyl alcohol oxidation [20,22], low-temperature CO oxidation [21,23], and propylene epoxidation [24].

In recent years, room-temperature ionic liquids (ILs) have also attracted much attention due to their special properties, such as negligible vapor pressure, wide liquid temperature range, excellent chemical stability, high thermal stability, and the strong solvent power for a wide variety of organic, inorganic, and polymeric molecules. Many reactions have been carried out in ILs [25,26]. ILs are also a good media to stabilize metal NPs [27,28] and have been used to immobilize metal NPs onto solid supports to prepare supported catalysts. For example, Han and coworkers demonstrated that Pd and Ru NPs in IL 1,1,3,3-tetramethylguanidinium lactate (TMGL) immobilized onto supports, which were obtained through reducing metal precursors by H_2, resulted in highly active heterogeneous catalysts [29–31] due to the excellent synergistic effects of IL, support, and metal nanoparticles.

Although the use of such GNPs has a high potential for propylene epoxidation, CO oxidation reactions, and so on, novel, cost-effective, and “greener” approaches for the preparation of gold catalysts should be developed, because GNP production remains expensive and/or involves hazardous chemicals. Biosynthesis of GNPs as an emerging highlight of the intersection of nanotechnology and biotechnology has received increasing attention due to a growing need to develop environmentally benign technologies in material in the last decade [32–37]. As an alternative to chemical methods, biosynthesis methods can be used to synthesize NPs with a narrow size distribution and a desired diameter without any auxiliary surfactant or capping agent, owing to the presence of plant biomass that plays dual roles as both reductant and stabilizer [37–42]. However, the application of the biosynthesized GNPs to catalytic system has been little reported. Vilchis-Nestor et al. prepared Au(AgAu)/SiO_2–Al_2O_3 catalysts for the oxidation and hydrogenation of CO [43], and our group has attempted to prepare Au/TS-1 catalysts for propylene epoxidation by bio-reduction synthesis method [44,45]. As mentioned above, the combination of biosynthesis and ILs may provide a new way to prepare highly efficient Au catalysts. In the present work, we report an ionic liquid-enhanced immobilization (ILEI) method to prepare the Au/TS-1 catalysts for the epoxidation of propylene. In this method, biosynthesized GNPs were immobilized onto TS-1 by IL 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) from their solution. The Au/TS-1 catalysts showed an excellent performance for the vapor-phase propylene epoxidation in the presence of hydrogen and oxygen. Therefore, the ILEI method was effective for preparation of the Au/TS-1 catalysts. The method was totally different from the IL immobilization method previously reported [29–31]. In this work, the role of [BMIM][BF_4] in the ILEI method for the Au/TS-1 catalysts was investigated in detail. To the best of our knowledge, this is the first report on enhanced immobilization of biosynthesized GNPs onto solid support using IL, which will be a breakthrough for the fabrication of supported Au catalysts.

2. Experimental

2.1. Materials

C. platycladi, purchased from Xiamen Jiuding Drugstore, China, was first milled and screened by a 20-mesh sieve for further experiments. The IL, [BMIM][BF_4] (99%), was purchased from Shanghai Cheng Jie Chemical, Co. Ltd. Other chemical reagents mentioned were purchased from Sinopharm Chemical Reagent Co. Ltd., China, and were used as received.

2.2. Synthesis of TS-1 supports

TS-1 supports were synthesized using the method developed by Khomane et al. [46]. In a typical synthesis, 12.7 mL of a 40 wt.% tetrapropylammonium hydroxide (TPAOH) solution and 2 g of polyoxyethylene 20-sorbitan monolaurate (Tween 20) were dissolved in 35 mL deionized (DI) water. This solution was added dropwise to 24.6 mL of tetraethylorthosilicate (TEOS) in a polypropylene Erlenmeyer flask with vigorous stirring for 1 h. Then, 1.1 mL of titanium(IV) butoxide (TBOT) was dissolved in 6.2 mL of isopropanol under stirring. The solution was then added to the TEOS mixture dropwise during vigorous stirring. Finally, another 4.6 mL of TPAOH solution was added dropwise to the mixture under vigorous stirring, leading to a molar composition of 1.000 Si:0.029 Ti:0.300 TPAOH for the resulting synthesis solution. Afterward, the mixture was stirred for 1 h and then the mixture was transferred to a sealed Teflon-lined pressure vessel and heated at 170 °C for 24 h to facilitate the crystallization process. Next, the solid was collected via centrifugation which after being washed thoroughly with DI water, was dried in vacuum at 320 K for 24 h, and finally calcined at 550 °C for 5 h. The TS-1 support with a Si/Ti ratio of 35 was labeled as TS-1(35). Other TS-1(x) supports with different Si/Ti ratios were synthesized in the same manner.

2.3. Preparation of Au/TS-1 catalysts

The gold sol was prepared by the biosynthetic method employing plant biomass extract. In order to obtain *C. platycladi* extract, the carefully weighted biomass, 4.0 g, was added to 400 mL DI water in a conical flask of 500 mL capacity. The mixture was thereafter shaken at a rotation rate of 150 rpm for 2 h at 30 °C and filtrated to get filtrate for further experiments. In a typical synthesis of GNPs, an appropriate amount of aqueous $HAuCl_4$ solution (48.56 mM) was added to 25 mL extract in a conical flask to have a final concentration of Au(III) 0.5 mM, and the mixture was then vigorously stirred for 1 h at room temperature. It should be noted that the solution turned reddish-pink in a few seconds after $HAuCl_4$ was added into the extract, indicating fast reduction of Au^{3+} ions [37]. Afterward, 0.5 g TS-1 and 0.1 mL [BMIM][BF_4] were added to the gold sols under vigorous stirring. After 1 h, the suspension was filtered through a cellulose filter membrane with the size of pores 0.45-mm, and the retained solid was washed three times with DI water. Finally, the obtained solid, after being dried at 50 °C in vacuum for 24 h, was calcinated at 375 °C for 6 h. Thus, the obtained Au catalysts were denoted as zAu/TS-1(x)-IL, where z was the calculated weight percent of Au in the catalysts. The reference catalyst 0.5Au/TS-1(35) was synthesized in the same manner without [BMIM][BF_4], and the catalyst 0.5Au/TS-1(35)-pH was prepared through acidifying the colloid solution at pH 2 by sulfuric acid.

2.4. Characterization of the catalysts

Surface area of the TS-1 supports was measured in a Micromeritics Tristar system (Tristar 3000). Before measurements, samples were outgassed at 300 °C for 3 h. X-ray diffraction (XRD) measurement was taken on an X'Pert Pro X-ray Diffractometer (PANalytical BV, The Netherlands) operated at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. The diffuse reflectance ultraviolet–visible (DRUV–vis) spectra of the support were taken on a Varian Cary-5000 spectrometer equipped with a diffuse-reflectance accessory, using dehydrated $BaSO_4$ as a reference in the range of 200–800 nm. UV–vis spectroscopy analyses of the liquid samples