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Au/TiO_2@SBA-15 nanocomposites as catalysts for direct propylene epoxidation with O_2 and H_2 mixtures

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ABSTRACT

A nanostructured Au/TiO_2@SBA-15 catalyst has been prepared and applied in propylene epoxidation with a mixture of O_2/H_2. The mesopores of SBA-15 were first deactivated by grafting of hydrophobic groups. Titanium was then selectively grafted in the micropores of SBA-15 by reaction with titanium isopropoxide followed by calcination and deposition of Au nanoparticles. The nanocomposite catalysts exhibited relatively stable propylene oxide (PO) production with small amounts of propanal and acetone byproducts. A catalyst prepared by grafting with trimethylsilyl groups, a Ti/Si ratio of 0.05 and very small Au nanoparticles (<2 nm), showed the highest catalytic activity. The improved performance appears to be related to the interaction of very small Au nanoparticles in close contact with very small sized TiO_2 domains in combination with the hydrophobicity of the fully open mesopores. The results demonstrate the possibility to improve the catalytic performance of Au–Ti catalysts through rational catalyst design.

1. Introduction

Propylene oxide (PO) is an important chemical intermediate for the production of a variety of chemicals and polymers [1]. Commercially, PO is produced via the chlorohydrin process and several hydroperoxide processes [2]. However, the chlorohydrin process results in large amounts of chlorinated compounds, and the hydroperoxide processes typically generate stoichiometric quantities of coproducts. Several companies including Dow and BASF have recently developed liquid-phase propylene epoxidation processes catalyzed by titanium silicalite-1 (TS-1) using hydrogen peroxide as the oxidant [3–6], but the processes incur the cost associated with the use of H_2O_2. Following the success of ethylene epoxidation by silver-based catalysts [7–9], direct gas-phase propylene epoxidation using molecular oxygen has also been extensively studied. The PO selectivities are very poor for silver [10–12] and copper [13,14] catalysts due to the higher reactivity of propylene as compared to ethylene. The development of gold-based catalysts supported on titania (TiO_2) or titanium-modified surfaces has been a promising research direction in recent years [15–19]. The direct propylene epoxidation by oxygen over gold-based catalysts needs hydrogen to activate oxygen under milder conditions [20], and the reactions may produce a variety of byproducts including water, carbon dioxide (the product of complete combustion), acrolein (the product of oxidation instead of epoxidation), and other hydrocarbons that result from the hydrogenation of propylene (propane), isomerization (e.g. propanal and acetone) and cracking (e.g. ethanal) of the final product [21–23]. Although Au–Ti catalysts are generally very selective (>90%), they still suffer from low propylene conversion, low hydrogen efficiency, and poor catalyst stability that need to be improved to meet the requirements (10% propylene conversion, 90% PO selectivity, and 30% hydrogen efficiency) for large-scale industrial process [16–19].

For the direct propylene epoxidation over Au–Ti catalysts, it is generally agreed that the primary role of Au is to produce peroxide species to epoxidize propylene over a Ti site [16–19,24–28] and that the size of Au particles and the nature of the titanium-containing supports are decisive to the activity of the catalysts. By using bulk TiO_2 as supports, Haruta et al. found that 2- to 5-nm Au nanoparticles are preferred for PO production. Smaller Au nanoparticles catalyze propane formation, and larger particles lead to an increase in the rate of full combustion [15]. They also found that anatase-supported catalysts give high PO selectivity but lead to fast deactivation and low PO yields, whereas rutile or amorphous TiO_2-supported catalysts result in complete combustion to CO_2 [29].

In addition, the presence of the tetrahedral-coordinated Ti sites is crucial for catalytic activity. Tetrahedral-coordinated Ti sites are involved in the adsorption of propylene [17,30]. They may serve as nucleation sites for Au nanoparticles [31] and may even probably alter the electronic structure of Au [32]. However, these sites, together with neighboring surface hydroxyl (Ti–OH or Si–OH)

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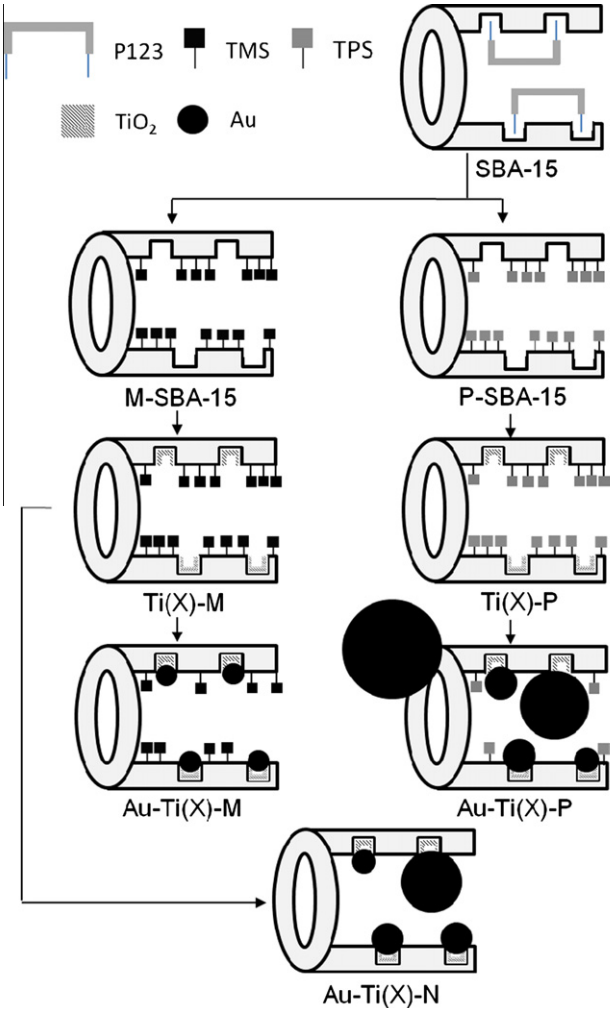
groups, may also involve in the readsorption of the PO molecules [33], which further causes catalyst deactivation by producing bidentate propoxy species, carbonates, carboxylates, and oligomers on catalyst surface [16–19,33–36]. Isolated or at least highly dispersed tetrahedral Ti sites supported on high-surface-area supports, such as mesoporous silicas [37], may therefore stabilize catalyst performance. Indeed, gold nanoparticles on Ti-modified MCM-41, MCM-48, TUD-1, and SBA-15 silicas make good catalysts with improved PO yields [21,38–44]. However, the activity loss with time on stream is still a serious issue. The hydrophobization of the Au–Ti catalysts supported on MCM-41 and MCM-48 improved propylene conversion, hydrogen efficiency, and catalyst stability [21,44], but even the silylated catalysts underwent about 35–40% activity loss after 4 h time on stream [44]. The addition of water to the feed gas was shown to suppress deactivation [45], but it also caused a decrease in the catalytic activity.

Clearly, there is considerable scope for further improvement in gold catalysts for PO production. Here, we report a new type of Au/TiO_2@SBA-15 catalysts that make use of the bimodal pore arrangement of SBA-15 silica [46,47]. Our approach is exemplified in Scheme 1. The mesopores of SBA-15 were first grafted with hydrophobic trimethylsilyl (TMS) or triphenylsilyl (TPS) groups [48,49]. The micropores were subsequently vacated and functionalized by grafting with $Ti(iOPr)_4$ at different loadings. Finally, gold was introduced by a standard method. The intermediate and final Au/TiO_2@SBA-15 materials were thoroughly characterized by nuclear magnetic resonance (NMR) spectroscopy, inductively coupled plasma-mass spectroscopy (ICP-MS), N_2 physisorption, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM). When tested for the direct propylene epoxidation with O_2/H_2, most of the Au/TiO_2@SBA-15 catalysts showed marginally better but more stable activities as compared to the reported Au/Ti-SBA-15 [41,42] and some other mesoporous silica-based Au–Ti catalysts [21,40]. More interestingly, all the Au/TiO_2@SBA-15 catalysts only produced water and small amounts of isomerization byproducts (i.e. propanal and acetone) in addition to the main product PO. Furthermore, we found that the most active catalyst had the smallest Au nanoparticles among all the Au/TiO_2@SBA-15 catalysts, and its high catalytic activity is most likely due to the very small size of Au in it. The relation of the structural properties of the nanocomposites to the catalytic performance will be discussed.



Scheme 1. Schematic representation of the preparation of functionalized SBA-15 and Au/TiO_2@SBA-15 nanocomposites.

2. Experimental

2.1. Catalyst preparation

Mesoporous SBA-15 silica was synthesized by adding tetraethoxysilane (TEOS) to a HCl solution of Pluronic P-123 (EO20PO70EO20), resulting in a mixture with a molar composition of 1 TEOS:0.017 P-123:0.54 HCl:100 H_2O. The mixture was stirred at 35 °C for 24 h and further aged at 60 °C for 24 h. The product was filtered and dried at 90 °C. The mesopores of SBA-15 were selectively vacated by stirring the as-synthesized SBA-15 in 45 wt.% H_2SO_4 solution at 95 °C for 24 h [50,51]. The open mesopores in the acid-treated SBA-15 were grafted with TMS or TPS groups. For the grafting with TMS groups [48,49], the dried acid-treated SBA-15 was poured into a toluene solution of trimethylchlorosilane (TMCS) and stirred at room temperature for 0.5 h. Alternatively, the dried silica sample was refluxed in a pyridine solution of triphenylchlorosilane (TPCS) at 120 °C for 24 h to be grafted with TPS groups. Subsequently, the micropores of the materials were vacated by a thermal treatment at 250 °C in air, resulting in samples referred to as M-SBA-15 (grafted with TMS groups) and P-SBA-15 (grafted with TPS groups) (cf. Scheme 1).

For the incorporation of Ti with different titanium-to-silicon (Ti/Si) molar ratios, the functionalized SBA-15 samples were evacuated and heated at 200 °C for 6 h and then impregnated with calculated amounts of titanium isopropoxide in dry isopropanol. The impregnated samples were dried under flowing nitrogen at room temperature for 48 h and then heated to 350 °C in air for 0.5 h. The TiO_2-incorporated samples are referred to as Ti(x)-Y, where x denotes the target Ti/Si ratio ($x = 0.01$, 0.05, and 0.10) and Y denotes the type of grafted hydrophobic groups (with Y being M or P for TMS- or TPS-grafted samples, respectively). For the purpose of comparison, a portion of the Ti(x)-M samples was further heated at 450 °C in air for 3 h to completely decompose the hydrophobic groups. These samples are designated as Ti(x)-N.

Gold particles were deposited on the TiO_2-incorporated samples by a deposition–precipitation method using an aqueous solution of $HAuCl_4$ and NaOH as the precipitant. In a typical preparation, an aqueous solution of $HAuCl_4$ (0.17 g $HAuCl_4 \cdot 4H_2O$ in 50 mL water) was first prepared at room temperature followed by adjustment of the solution pH to 7.0 using aqueous NaOH [52]. The TiO_2-incorporated support (0.5 g) was immersed in a small amount of acetone followed by suspension in water (50 mL) and adjustment of the solution pH to 7.0. The $HAuCl_4$ solution was then added to the stirred suspension at 35 °C. The solution pH was again adjusted and kept at 7.0, and the mixture was stirred for 2 h before the product was filtered, washed, dried in air at 90 °C overnight, and