



The effects of impregnation of precious metals on the catalytic activity of titanium silicate (TS-1) in epoxidation of propene using hydrogen peroxide



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ABSTRACT

Propene oxide is an important chemical intermediate and titanium silicalite (TS-1) has been widely investigated as a promising catalyst for the direct epoxidation of propene with *ex-situ* or *in-situ* produced hydrogen peroxide as an oxidant. In order to clarify the effects of the kind of precious metal and treatment process in the catalyst preparation on the propene epoxidation and the hydrogen peroxide decomposition, TS-1 was impregnated with gold and palladium via drying, calcination and reduction and the experiments to check its catalytic performance were conducted in a gas aspirating autoclave reactor in the absence of mass transfer limitations. The presence of precious metals vigorously catalyzed the side reactions and hydrogen peroxide decomposition. Some of the precious metal containing TS-1 catalysts showed high initial rates but there was no catalyst with a propene oxide yield after 5 h reaction time comparable to TS-1 alone because of the enhancement of side reactions by precious metals. The significant decline in the selectivity to propene oxide over the dried precious metal containing TS-1 catalysts was attributed to the leaching of precious metals into the reaction medium. Palladium containing TS-1 showed exceptionally high decomposition of hydrogen peroxide. Reduction and calcination increased the decomposition by forming metallic gold and palladium. Homogeneous dispersion of gold nanoparticles was achieved by a sol immobilization method which led to a decrease of propene oxide selectivity and an increase of hydrogen peroxide decomposition.

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1. Introduction

Propene oxide is an important raw material for the production of polyether polyols, propene glycols, and propene glycol ethers [1–3]. In several liquid-phase epoxidation routes to convert propene into propene oxide, much attention has been directed to heterogeneous catalytic oxidation using hydrogen peroxide as a more environmentally benign and profitable chemical process [1–15]. Titanium silicalite (TS-1) catalyst has been extensively investigated for this route because propene oxide can be produced with a high selectivity in methanol under mild conditions [4,5,10–23]. The direct

epoxidation process based on hydrogen peroxide (oxidant) and TS-1 (catalyst) was commercialized and referred to as “hydrogen peroxide-to-propene oxide” (HPPO) process. The first commercial-scale HPPO plant (production capacity: 100 kton/year) was built by Evonik and SKC in Ulsan, South Korea in 2008 [13]. Since 2009, several HPPO plants of 100–400 kton/year capacity have been launched in many places of the world, including Thailand, Belgium, China, etc [13,24]. However, from a green chemistry point of view, employing *ex-situ* produced hydrogen peroxide is less attractive due to the use of toxic chemicals and generation of a large amount of waste in the current process for hydrogen peroxide production (e.g., anthraquinone process) [25]. Moreover, hydrogen peroxide produced *via* anthraquinone process has remained relatively expensive.

It is anticipated that the direct gas-phase epoxidation of propene using O₂ or a mixture of O₂ and H₂ might take over the next generation after the HPPO process, but currently available catalysts have difficulty in attaining sufficient conversion of propene for commercial application [1,3,14,26]. Therefore, several attempts have

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been made to utilize hydrogen peroxide produced *in-situ* from a mixture of H₂ and O₂ gas for a liquid-phase epoxidation process [5,14,25,27–36]. For this purpose, the TS-1 catalyst modified by the impregnation of precious metals such as palladium, platinum and gold has been used to generate hydrogen peroxide and oxidize propene at the same time.

Hölderich and colleagues investigated the O₂–H₂ system for the liquid-phase epoxidation of propene over Pd or Pd/Pt impregnated TS-1 catalyst [5,27,28,32–34]. They emphasized the role of precious metals, because the *in-situ* generation of hydrogen peroxide on the precious metal site is the rate-determining step in the epoxidation reaction [5]. They reported that the influence of calcination carried out prior to reduction on the performance of catalyst was insignificant. The propene oxide yield and selectivity were improved by reducing the catalyst under pure N₂ and adding a suitable amount of platinum as a promoter. The propene oxide selectivity could reach as high as 71% at a propene conversion of 21% over 1% Pd and 0.01% Pt on TS-1, autoreduced by precursor ligands at 150 °C under pure N₂, in a semi-batch reactor containing a water-methanol mixture as solvent [33]. Beckman and co-workers demonstrated that a higher propene conversion and propene oxide selectivity were achieved over a (0.2% Pd + 0.02% Pt)/TS-1 catalyst using compressed CO₂ as a solvent and a side reaction inhibitor in a high pressure reactor [25].

Recently, plenty of attention has been paid to the characteristics of Au and bimetallic Au-Pd, which have been known to be highly active for the direct synthesis of hydrogen peroxide from H₂ and O₂ [37–47] when supported on TS-1 for the liquid- or gas-phase epoxidation, and the improvement of precious metals distribution on the surface of TS-1. The homogeneous distribution of Au is an important factor for epoxidation activity of Au/TS-1 catalyst: Delgass and colleagues studied the optimum conditions of deposition-precipitation (DP) to prepare Au/TS-1 catalyst on which Au is uniformly dispersed in nano-scale [42,43]. Mennemann and Claus claimed that the uptake and distribution of Au could be enhanced by adding 0.2–0.5 wt% of Co when the catalyst was prepared *via* DP method [44]. Zahn et al. published a few papers about a new preparation route for Au/TS-1 catalyst based on biomass-reduction, in which an important issue was also the distribution and stabilization of Au nanoparticles [45,46].

In this study, we tried to clarify and compare the influences of the kind of precious metal and preparation method on the activity of TS-1 in the liquid-phase epoxidation of propene with *ex-situ* hydrogen peroxide. In particular, we tried to reveal the effects of drying and calcination on the epoxidation activity of the precious-metal-loaded TS-1 catalysts. It is generally known that the use of precious metals are disadvantageous in HPPO reactions, where *ex-situ* H₂O₂ was used as an oxidant: Hölderich and colleagues explained some detrimental effects of Pd loading on the HPPO activity of TS-1 catalysts, such as the blocking of Ti sites of TS-1 by the counter anion of metal precursor, or the decomposition of hydrogen peroxide on the Pd site [5]. However, in spite of such recognition, it has not been fully elucidated yet how the activities of Pd, Au, Pd-Au-loaded TS-1 catalysts change along with their preparation procedures (*i.e.*, drying-calcination-reduction). It is supposed that it might be difficult to handle this issue in the previous literatures, because propene oxide yield and selectivity were too low when the catalysts were calcined (or reduced) at high temperature [27].

Another important aim of this work is to apply a sol immobilization method to achieve more homogenous dispersion of Au nanoparticles on TS-1 support. The sol-immobilized Au/TS-1 was compared with conventional impregnated catalysts in terms of metal distribution and epoxidation activity. Even in the H₂–O₂ reaction systems, where H₂O₂ is generated and consumed *in-situ*, the precious metal-loaded TS-1 catalysts were inactive if they were not prepared in a proper way. It was usually due to agglomeration of precious metals on the outer surface of TS-1, which caused a

detrimental impact on the hydrogen peroxide production in the H₂–O₂ system [33]. Thus, we tried to induce a homogeneous distribution of Au over TS-1 by applying sol-immobilization method.

Lastly, it should be addressed that the activities were measured under *ex-situ* hydrogen peroxide reaction system, because in the H₂–O₂ systems (*i.e.* *in-situ* hydrogen peroxide systems), the supply of hydrogen peroxide is limited due to the occurrence of side reactions to produce water. It was considered that by using *ex-situ* hydrogen peroxide directly as oxidant, we could separate the effects of the formation of hydrogen peroxide and make the effects more recognizable.

2. Experimental

2.1. Catalyst preparation

TS-1 catalyst was synthesized according to the method described in the literature [16,48]. A solution of 1.5 g of tetraethyl orthotitanate (TEOT, Fluka) was gradually added to 45 g of tetraethyl orthosilicate (TEOS, Fluka) with magnetic stirring for 30 min. An aliquot of 100 g of 20 wt% tetrapropylammonium hydroxide solution (TPAOH, Fluka) was then gradually added to the mixed solution under stirring. After keeping the mixture at 60 °C for 3 h, 56 g of deionized water was added to the solution. The molar reagent ratios of the final solution were SiO₂/TiO₂ = 32.7, TPAOH/SiO₂ = 0.46, and H₂O/SiO₂ = 35. The resulting solution was transferred to an autoclave in an oven and crystallized at 175 °C for 48 h without stirring. After cooling the solution to room temperature, the crystalline product was separated by centrifugation, washed with deionized water, dried at 100 °C for 2 h, heated at a rate of 5 °C/min and then finally calcined at 550 °C for 5 h in an air-atmosphere furnace. The resulting catalyst was ground into a fine powder with a pestle and mortar.

The precious metal containing TS-1 catalysts were prepared by impregnation using HAuCl₄·3H₂O (Sigma-Aldrich) and PdCl₂ (Sigma-Aldrich). TS-1 produced in the same batch – therefore, the molar ratio of Si/Ti remained the same – was used and precalculated quantity of precious metal solutions was added with an intention to achieve 1% content of each precious metal in the resulting catalyst. As a result, the precious metal contents are 1% and 2% in the monometallic and bimetallic TS-1 catalysts, respectively. 8.2 g of 1 wt% HAuCl₄·3H₂O aqueous solution was added to 4 g of TS-1 for 1 wt% Au/TS-1. 6.8 g of 1 wt% PdCl₂ aqueous solution was added to 4 g of TS-1 for 1 wt% Pd/TS-1. For 1 wt% Au–1 wt% Pd/TS-1, 8.4 g of 1 wt% HAuCl₄·3H₂O aqueous solution and 7 g of 1 wt% PdCl₂ aqueous solution were simultaneously added to 4 g of TS-1. After mixing for 30 min, all samples were dried at 90 °C for 15 h. Some of each dried catalyst was heated at a rate of 5 °C/min and calcined in static air at 400 °C for 3 h. Some of each dried catalyst was reduced with 10% H₂ in Ar at a flow rate of 100 mL/min and a heating rate of 2 °C/min from room temperature to 200 °C at which the catalyst was kept for 3 h. In this paper, these catalysts would be named as dried, calcined or reduced catalyst according to its treatment process of supporting precious metals on TS-1.

The Au/TS-1 catalyst was also synthesized by a sol immobilization method using a stabilizing agent to control the size and dispersion of gold nanoparticles. A gold sol prepared using Tetrakis(hydroxymethyl)phosphonium chloride (THPC, Sigma-Aldrich)/NaOH was used as a stabilizing system as described in the literature [49]. For the preparation of 1 wt% Au on TS-1 catalyst, 230 mL of deionized water, 10 mL of 0.2 M NaOH solution and 4 mL of THPC solution (1 mL of 80 wt% THPC in 100 mL deionized water) were mixed under stirring. After a few minutes a solution of 0.139 mL of HAuCl₄ (30 wt%, Sigma-Aldrich) in 5 mL of deionized water was added. There was an immediate change of colour of

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