

Propylene epoxidation in a microreactor with electric heating

Yu-Hang Yuan^a, Xing-Gui Zhou^{a,*}, Wei Wu^a, Yi-Ran Zhang^a,
Wei-Kang Yuan^a, Lingai Luo^b

^a State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Campus Box 369,
130 Meilong Road, Shanghai 200237, China

^b LOCIE, ESIGEC-Université de Savoie, Campus Scientifique, Savoie Technolac, 73376 Le Bourget-Du-Lac cedex, France

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Abstract

Gas phase propylene epoxidation on gold catalysts has attracted wide attention from industry and academia due to its high selectivity. However, it suffers from low propylene conversion and rapid catalyst deactivation. Experiments showed that propylene conversion could be increased by raising H₂, O₂, or C₃H₆ concentration in the feed, but the feed compositions were within the explosion limit. It was also shown that the activity of the used catalyst could be fully recovered, but the regeneration temperature was 280 °C, much higher than that for reaction. Therefore a microchannel reactor was devised to suppress explosion and was constructed with FeCrAlloy, to raise the temperature rapidly for catalyst regeneration by electric heating. In two minutes the temperature of the reactor could be raised from 50 to 300 °C. Catalysts were coated on the alloy belt by dip coating, and the performance of the reactor was evaluated under different operating conditions. Results showed that in the microreactor the overall reaction rate was controlled mainly by the intrinsic reaction rate, and also influenced by film diffusion to a certain extent. The deactivated catalyst was regenerated in the microchannel reactor and the activity was fully recovered.

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1. Introduction

Propylene oxide (PO) is mainly used for the production of polyester polyols and propylene glycol, which are the starting materials of polyurethane and unsaturated polyesters. Industrially, PO is produced either by chlorohydrination process or by co-oxidation (Halcon) process [1]. The former consumes a large amount of chlorine and lime which are finally converted to useless and environmentally unfriendly wastes, while the latter produces equimolar amounts of co-products and requires heavy capital investment. Since the discovery of the titanium silicate TS-1 by Taramasso [2], a new pathway for the epoxidation of propylene has been opened, which uses hydrogen peroxide as the oxidant. This process is indeed very selective to propylene oxide, but it involves the use of expensive H₂O₂, which is unstable and difficult to handle. This is the main reason why it is being used as the model reaction for the

world's first pilot-scale microreactor for heterogeneously catalyzed gas-phase syntheses run by Degussa, Uhde and several universities. Allured by the success of direct oxidation of ethylene, great efforts have been made to find efficient catalysts for propylene epoxidation in vapor phase with molecular oxygen as the oxidant. However, most of the catalysts suffer from low epoxidation selectivity.

Recently, Hayashi et al. [3] found that gold particles of nanometer sizes dispersed on Ti containing substrates (where Ti is in the form of isolated tetrahedrally coordinated TiO₄ units) are highly selective toward propylene epoxidation in copresence of H₂ and O₂. However, the conversion of propylene is low, typically below 2% when nanosized gold particles are deposited on Titania, and the highest conversion obtained when TiO₂/SiO₂ or titanosilicates are used as the support not exceeding 6% [4,5]. As a result, considerable work has been devoted to the reaction and deactivation mechanism [6,7], aiming at developing more efficient catalysts.

There are two other problems associated with the direct gas phase epoxidation on gold catalysts. H₂ and C₃H₆ are

* Corresponding author. Tel.: +86 21 6425 3509; fax: +86 21 6425 3528.
E-mail address: xgzhou@ecust.edu.cn (X.-G. Zhou).

highly flammable. For safety reasons, the lab experiments were usually carried out at conditions away from the explosion limits. However, evidences show that, to increase the reaction rate, high H_2 , O_2 and C_3H_6 concentrations that are within the explosion limit are favorable. The second problem comes from the fast deactivation of the catalyst. The catalyst has to be regenerated after being run for a period of a few hours.

In this article, a microreactor is devised to circumvent these two problems, with small flow channel to prevent from possible explosion, and interior electric heating for rapid temperature response. Au/TiO₂ catalyst is prepared by D-P method, and is characterized for performance evaluation and to determine the conditions for catalyst regeneration. After a brief description of the principle and fabrication of the microreactor, the procedure for catalyst coating is described, followed by performance evaluation of the reactor.

2. Catalyst characterization

Gold loadings were determined using a Shimadzu AA670 atomic absorption spectrometer after gold was digested from the catalyst with an aqua regia solution. Total surface areas (S_{BET}) were obtained from BET analysis of N₂ adsorption isotherms using a Micromeritics ASAP 2010 surface area analyzer after catalyst outgassing under vacuum at 393 K. The analysis of absorbed components on the catalyst was carried out using TGA (TA SDTQ thermal analyzer). Gold particle size and morphology were determined using TEM (FEI Tecnai 20 S-TWIN, accelerating voltage: 200 kV). The micrograph of catalyst coatings was determined using SEM (JEOL JSM-6360LV).

3. Catalyst preparation and evaluation

The catalyst was prepared by D-P method. At 70 °C, 0.25 g HAuCl₄·4H₂O was dissolved in 0.2 L deionized

water. Under vigorous stirring, 0.5 M Na₂CO₃ solution was dropwise added to adjust the pH to 7–8. After continuous stirring for one hour, 5.0 g TiO₂ (Degussa, P25) was dispersed in the solution. The suspension was kept stirring for another two hours, and its pH maintained constant by Na₂CO₃ solution. The precipitation was filtered, washed several times to remove chloride, dried under vacuum for 12 h, and calcined in a muffle furnace. The furnace temperature was increased from room temperature to 400 °C at a rate of 5 °C/min, and was then kept constant for 4 h. The catalyst (80–120 mesh) had a gold loading of 2.4 wt.% and a BET surface area of 61.1 m²/g. The average size of the Au particle was about 3.5 nm and the shape of the Au particle was almost semispherical, with a large perimeter between Au and TiO₂, as revealed by the TEM micrograph (Fig. 1).

The activity of the catalyst was evaluated in a stainless steel tube with 4 mm i.d. Glass fiber was first packed to avoid blowing out of the catalyst. In order to achieve an equal distribution of the gas, quartz sands were packed at both ends of the catalyst bed. Inlet gas compositions and flow rates were adjusted by mass flow controllers. Unless otherwise specified, the feed composition was H₂/O₂/C₃H₆/N₂ = 10/10/10/70. The outlet concentrations were measured by a GC (Agilent 4890D, Porapak Q column, FID detector, N₂ carrier gas). A thermal couple was installed at the outlet of the catalyst bed to determine the reaction temperature.

Fig. 2 shows the changes of C₃H₆ conversion with time-on-stream at different reaction temperatures. Since no byproducts were detected at these temperatures, the C₃H₆ conversion was regarded almost the same as the PO yield. The measurements clearly revealed that the catalyst lost its activity rapidly. Active site losses due to irreversible chemical adsorption of PO and possible further PO transformation (ring opening on the catalyst) to deposits were considered to be responsible for catalyst deactivation [6]. Under an elevated reaction temperature, C₃H₆ conversion was increased in the first period, but decreased later because more PO had been converted to deposits which

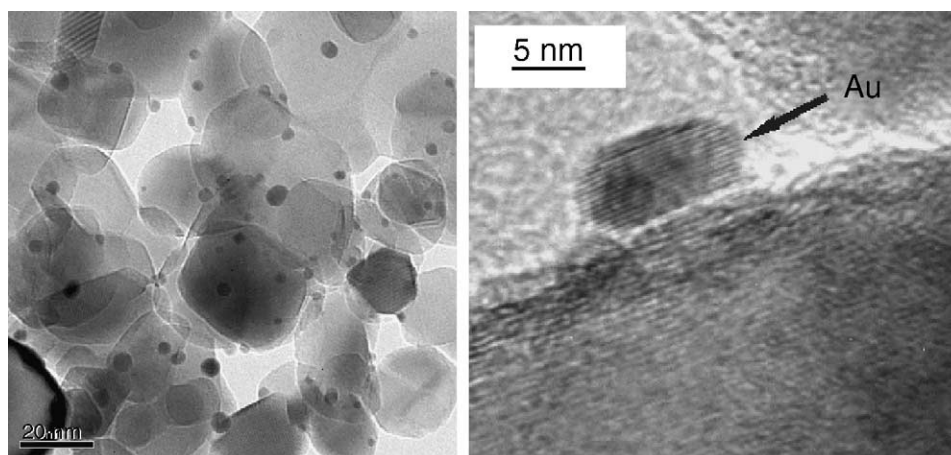


Fig. 1. TEM micrograph of the Au/TiO₂ catalyst prepared by D-P method.

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