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Propylene epoxidation in a microreactor with electric heating

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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 H_2, O_2, or C_3H_6 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.

Keywords: Propylene epoxidation; Microchannel reactor; Gold catalyst

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 chlorahydrination 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 H_2O_2, 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 TiO_4 units) are highly selective toward propylene epoxidation in copresence of H_2 and O_2. However, the conversion of propylene is low, typically below 2% when nanosized gold particles are deposited on Titania, and the highest conversion obtained when TiO_2/SiO_2 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. H_2 and C_3H_6 are

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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/TiO_2 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 N_2 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 $HAuCl_4 \cdot 4H_2O$ was dissolved in 0.2 L deionized water. Under vigorous stirring, 0.5 M Na_2CO_3 solution was dropwise added to adjust the pH to 7–8. After continuous stirring for one hour, 5.0 g TiO_2 (Degussa, P25) was dispersed in the solution. The suspension was kept stirring for another two hours, and its pH maintained constant by Na_2CO_3 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 m^2/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 TiO_2, 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 $H_2/O_2/C_3H_6/N_2 = 10/10/10/70$. The outlet concentrations were measured by a GC (Agilent 4890D, Porapak Q column, FID detector, N_2 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 C_3H_6 conversion with time-on-stream at different reaction temperatures. Since no byproducts were detected at these temperatures, the C_3H_6 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, C_3H_6 conversion was increased in the first period, but decreased later because more PO had been converted to deposits which

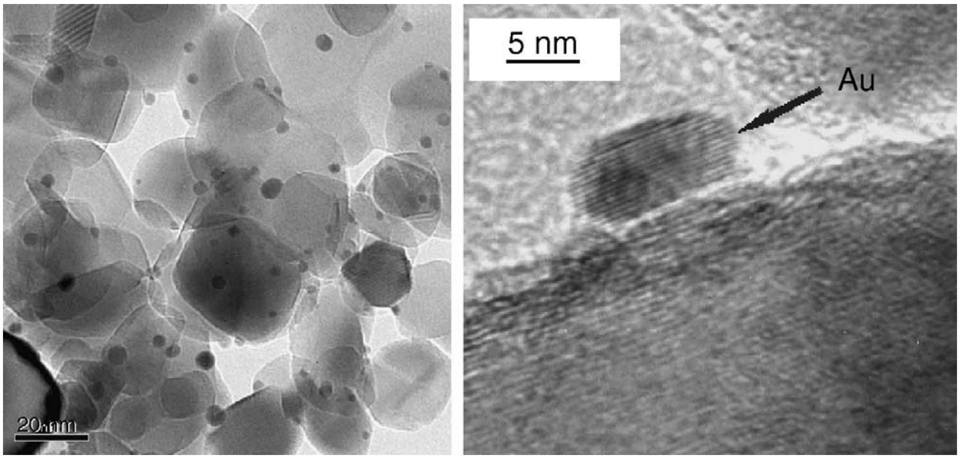

Fig. 1. TEM micrograph of the Au/TiO_2 catalyst prepared by D-P method.

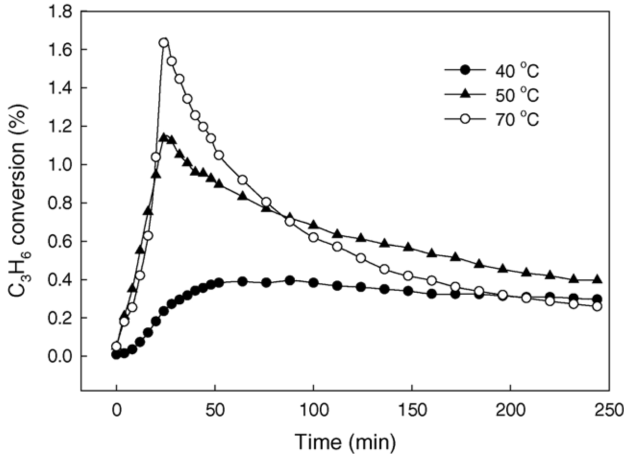

Fig. 2. Influence of temperature on propylene conversion (catalyst: 0.3 g; feed: 33 ml/min).

covered the active sites. Further increasing of the reaction temperature would not only accelerate catalyst deactivation, but also decrease significantly the epoxidation selectivity. Therefore the reaction temperature is usually below 70 °C.

By increasing catalyst loading, the C_3H_6 conversion was increased, as seen in Fig. 3a. However, Fig. 3b shows that the averaged reaction rate decreased when the catalyst loading was increased. Since the gas concentration changed only a little along the reactor because of low C_3H_6 conversion, decrease of averaged reaction rate with increased catalyst loading was most probably because the PO formed in the upstream was adsorbed by the catalyst in the downstream. For the same catalyst loading, increasing feeding rate led to a decreased propylene conversion as a result of shorter contacting time, as seen in Fig. 4. Fig. 5 shows that the propylene conversion increased with the linear velocity while the contact time was kept unchanged by increasing the catalyst loading. Obviously the reaction was affected by film diffusion.

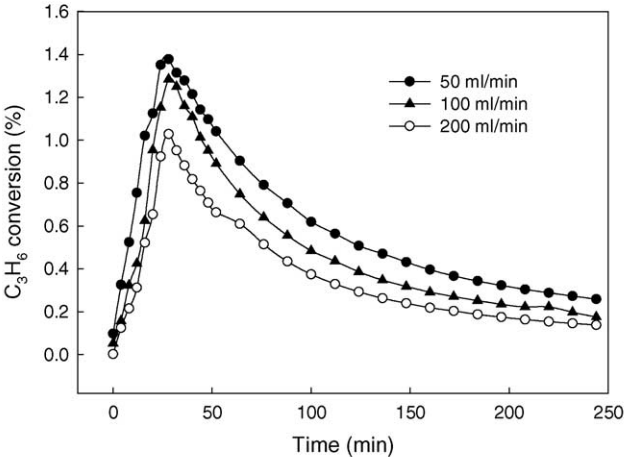

Fig. 4. Influence of feed rate on propylene conversion (temperature: 50 °C; catalyst: 0.3 g).

Comparing Fig. 2 with Figs. 3a and 4, one can find that deactivation is more sensitive to temperature than to PO concentration, since during the later period, the PO formation rate was lower even when the temperature was higher, which emphasizes the importance of temperature control.

Alternatively, one can increase the concentrations of the reactant to increase the reaction rate. The most frequently used gas mixture for propylene epoxidation experiments, $H_2/O_2/N_2/C_3H_6$ = 10/10/10/70, is within flammability limits [3,8,9]. Increasing C_3H_6, H_2 and O_2 concentrations will enter the explosion limits. To suppress possible explosions, all spaces in the tubing and reactor were filled with chopped stainless fibers (0.65 μm diameter) for experiments with gas mixture in the explosion limit. With this safety measure, experiments were carried out under elevated reactant concentrations, which revealed that the reaction rate was increased considerably, as shown in Fig. 6. It is interesting to find that H_2 and O_2 have the same influence on the reaction rate, from which one can assume formation of an

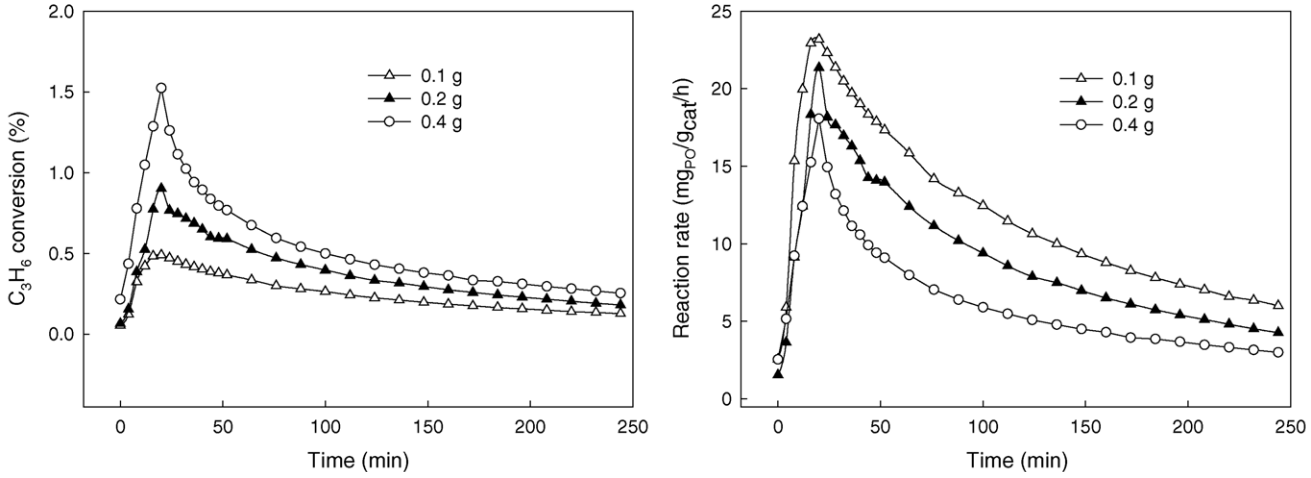

Fig. 3. Influence of catalyst loading on propylene conversion (a) and reaction rate (b) (temperature: 50 °C; feed: 33 ml/min).

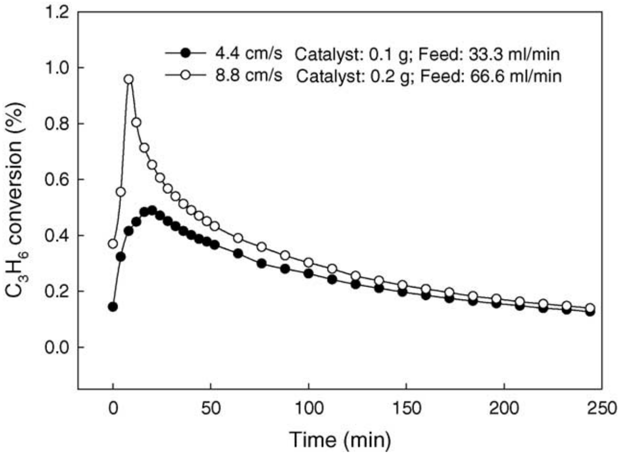

Fig. 5. Influence of linear velocity on propylene conversion (temperature: 50 °C).

intermediate from equimolar H_2 and O_2, which then reacts with propylene to form propylene oxide.

To determine the best condition for catalyst regeneration, fresh and deactivated catalysts were characterized by thermal analysis. TG-DTG curves shown in Fig. 7, which were obtained under flowing air with a temperature increasing rate of 5 °C/min, reveals that the deactivated catalysts might be regenerated at temperature higher than 280 °C. Experiments showed that the catalyst activity could be recovered after regeneration in flowing air (50 ml/min) at 300 °C for 30 min, as seen in Fig. 8. The BET surface area and pore volume, 53.1 m^2/g and 0.366 cm^3/g for the deactivated catalyst, came back to 62.1 m^2/g and 0.364 cm^3/g after the first cycle regeneration, very close to those of the fresh catalyst. After the tenth cycle regeneration, the BET surface area was still as high as 60.6 m^2/g. Fig. 8 shows the recovery of catalyst activity after the first and tenth cycle of regeneration.

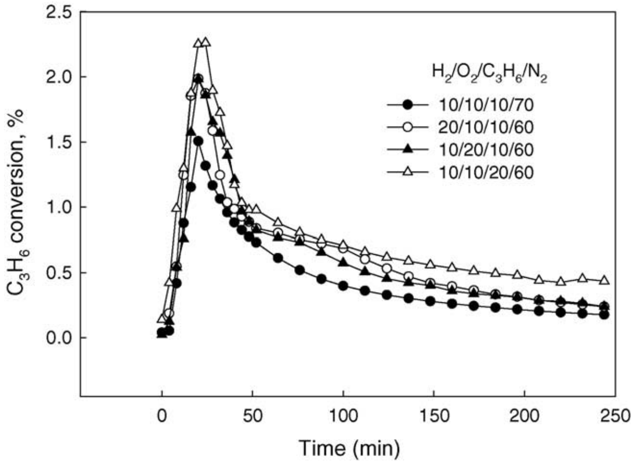

Fig. 6. Influence of feed composition on propylene conversion. (temperature: 50 °C; catalyst: 0.3 g; feed: 33 ml/min).

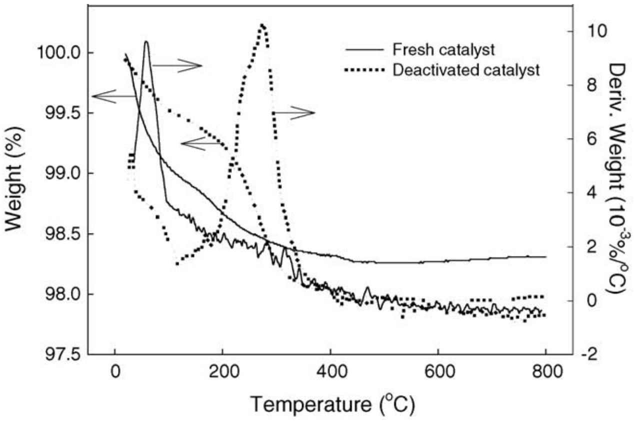

Fig. 7. TGA profiles of fresh and deactivated Au/TiO2 catalysts.

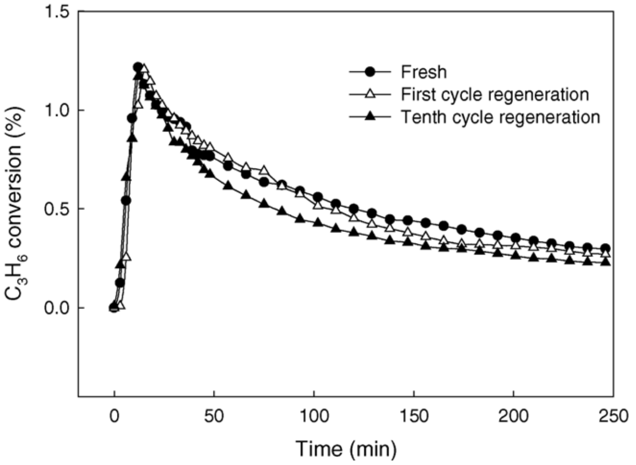

Fig. 8. Recovery of the reaction activity after 1st and 10th cycle of regeneration.

4. Microchannel reactor: principle and fabrication

Catalyst evaluation in the previous section showed the following three facts:

(a) The catalyst losses its activity rapidly and should be regenerated. However, there is a large gap between the temperature for reaction (below 70 °C) and the temperature for regeneration (as high as 280 °C).
(b) Deactivation, and side reaction as well, is sensitive to temperature.
(c) Increase reactant concentrations will increase the reaction rate but will enter the explosion limit.

Before any possible commercialization considerations, these problems have to be resolved. Better temperature control is not difficult. However, increasing the reactor temperature rapidly for catalyst regeneration is a big challenge for traditional reactors. Heating from the wall of the reactor will result a large temperature gradient along the heat flow direction, while using high temperature influent (which may contain over heated steam) will result in a large temperature gradient along the mass flow direction. Moreover, because of the low heat conductivity of the catalyst layer and the low heat capacity of the gas mixture, it will take a long time to raise the temperature from below 70 °C to higher than 280 °C. In addition, in traditional reactors for large-scale production, operation within the explosion limits is strictly prohibited, rending increasing reaction rate by increasing reactant concentrations impossible.

To break down these barriers, a microchannel reactor constructed with electrically conductive material has been devised. By taking advantage of the Joule effect, the reactor can be heated from the internal and the temperature can be increased rapidly. By controlling the characteristic size of the flow channel, explosions can be effectively suppressed. Among all flammable gases, hydrogen has the smallest quenching distance of 0.3 mm. Therefore, if the flowing channel is smaller than 0.3 mm, any gas mixture can be safely used. Finally, because the microchannel reactor provides a large specific surface, the reaction temperature can be easily adjusted and controlled.

Fecralloy (Fe/Cr/Al = 70/25/5) was used as the constructing material of the microchannel reactor, because of its relative large resistivity. It was shaped to a belt 0.1 mm thick and 20 mm wide. For the belt to generate enough Joule heat with a specified current (rated by the power source), the ohmic resistance of the alloy belt had to be large enough. The belt we used had a total resistance of 2.13 Ω and was 3 m in length which was considerably long. To make the reactor compact, it was folded 11 times, forming 12 channels. The height of the flow channel was controlled by pressing uniformly distributed dimples on the belt.

For the reactor to function properly, at the contacting points between the dimples and the belt beneath, good electrical insulation was required. This was fulfilled by coating a thin layer of titanic gel, which was then calcined to form electrical insulting titania. For this purpose, 34 ml titanium butoxide was mixed with 134.5 ml anhydrous alcohol and 9.6 ml diethanolamine. Under vigorous stirring and nitrogen protection, 21.8 ml alcohol solution (H_2O/C_2H_5OH = 9/100) was added dropwise to form a light yellow sol. The titanic sol was coated on the Fecralloy belt by dip coating which was dried at 100 °C for 5 min to form titanic gel. The dip coating process was repeated and finally the belt was calcinated at 100 °C for 30 min, followed by a temperature increase (6 °C/min) to 520 °C and kept at 520 °C for 1 h.

To prepare catalyst coating on the belt, electrical insulation was first examined. Au/TiO_2 suspension was prepared by D-P method according to the procedure described above, which was then filtered, washed and redispersed in distilled water by ultrasonic wave. The suspension was then coated on the belt by dip coating and dried with infrared light. Coating and drying were repeated several times to control the thickness of the coating. Finally, the belt was calcinated according to the same temperature program described above. Fig. 9 shows the SEM micrograph of the washcoating and catalyst on the Fecralloy.

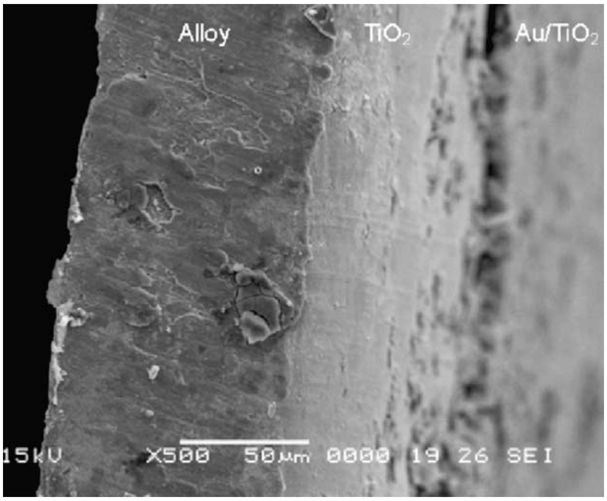

Fig. 9. SEM image of the catalyst coating.

After washcoating preparation and catalyst coating, the belt was installed in a stainless housing. A thermocouple was positioned at the exit of the belt packing. Fig. 10 summarizes the fabrication procedure and the assembly of the reactor.

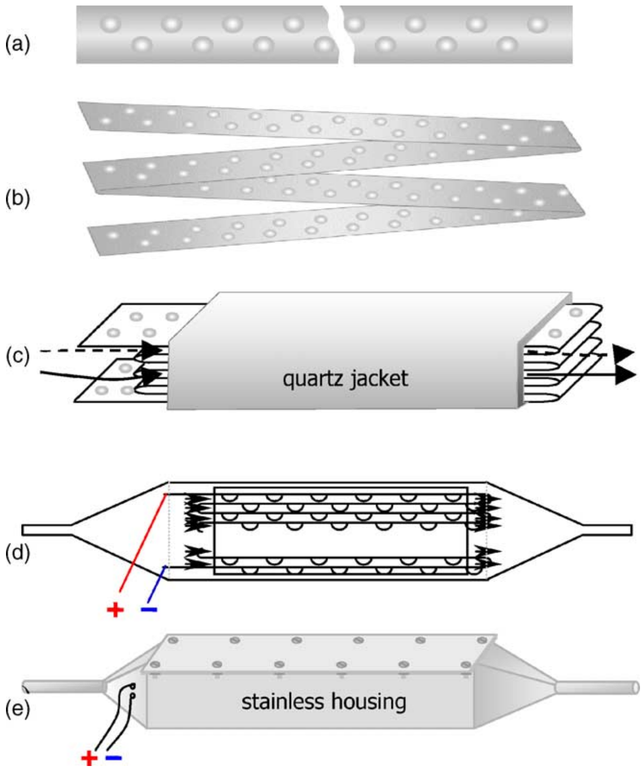

Fig. 10. Microchannel reactor assembly. (a) Metal alloy belt with dimples; (b) bending of the belt; (c) quartz jacket and flowing modes; (d) interior details, and (e) exterior appearance.

5. Temperature response

Because heat insulation of the reactor in the present form is very difficult, temperature response of the adiabatic reactor with electric heating is illustrated by estimation. With assumption of adiabatic condition and infinite heat transfer between the wall (belt) and the fluid, the energy balance is

$$\frac{dT}{dt} = \frac{J - (T - T_{in})F_{in}\bar{C}_p}{M_w C_{pw}}$$

where T_{in} and T are the inlet and outlet temperatures of the fluid, M_w and C_{pw} the mass and heat capacity of the belt, and F_{in} and $\bar{C}_p$ the gas fluid rate and averaged heat capacity. J is the Joule heat released by ohmic heating.

Simple calculation reveals that the temperature of the reactor can be raised rapidly to the temperature for regeneration in two minutes with a heating current of 5 A. If the reactor is cooled down by purging air of 25 °C, it takes less than ten minutes to bring the temperature back to below 50 °C with an apparent gas velocity of 1.4 m/s in a flowing channel 270 μm high.

6. Reactor evaluation

In the microreactor, any gas mixture could be used as the feed. However, the reactor in the present form had a space at the inlet for connecting the belt to a power source, which could not be filled with stainless fibers because of possible short circuiting. Therefore experiments were carried out with feed composition of $H_2/O_2/C_3H_6/N_2 = 10/10/10/70$. The height of the channel for gas flowing was 270 μm.

Preparation of catalyst coating for the microreactor was time-consuming. Therefore, the catalyst was regenerated for repeated use. After the catalyst had lost its activity, the feed was switched to air at a flow rate of 50 ml/min and the reactor was heated to 280 °C by increasing the electric current and maintained at 280 °C for 20 min. It was then cooled down by purging air at a large flow rate. Because of the large heat capacity of the reactor housing, heating the reactor took much longer time than was needed under adiabatic conditions. Fig. 11 compares the catalyst performance after regeneration, showing that the catalyst activity was even a little higher than that of the fresh catalyst.

Fig. 12 shows the changes of propylene conversion as the feeding rate was increased. In the tubular reactor, it was found increasing feeding rate (higher than 50 ml/min) decreased the C_3H_6 conversion; whereas in the micro-channel reactor, increasing feeding rate (from 22 to 44 ml/min) resulted in a higher C_3H_6 conversion, indicating film diffusion control in the microreactor. At higher feeding rate, the influence of film diffusion can be neglected, and the conversion will decrease with increasing feeding rate, as in the tubular reactor.

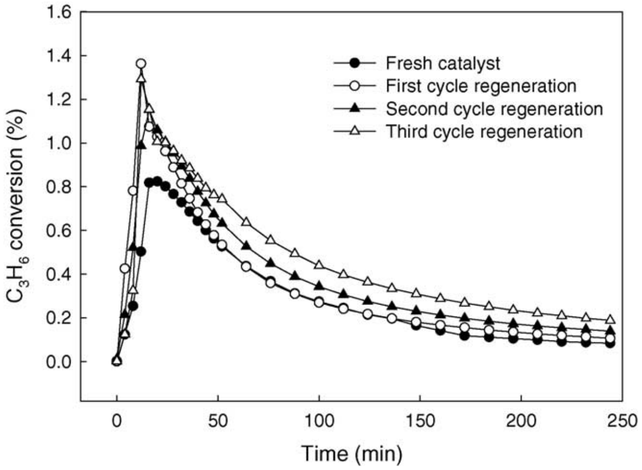

Fig. 11. Influence of regeneration times on catalyst performance in the microreactor.

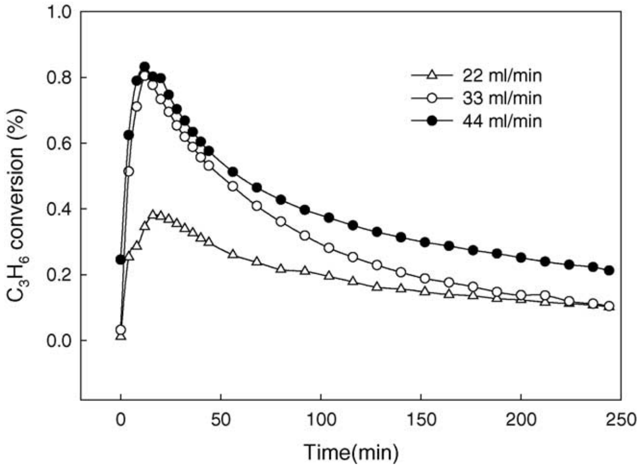

Fig. 12. Influence of feed rate on propylene conversion in the microreactor (temperature: 50 °C; catalyst: 0.7 g).

Fig. 13 shows the influences of reaction temperature on the C_3H_6 conversion. Similarly, the C_3H_6 conversion increased in the first period but decreased in the later as a result of more inactive deposits formed on the active sites as the reaction temperature was increased. Also shown in this figure is the conversion obtained in the tubular reactor (10 mm i.d.) under the same feeding composition, feeding rate, catalyst loading and reaction temperature, which was much higher than that obtained in the microreactor. In the tubular reactor the apparent velocity was 7.1 mm/s, close to the linear velocity 8.6 mm/s in the channel of the microreactor. However, since the catalysts were mainly titania powder of 20 nm and the aggregates were about 250 nm according to the product description of P25 (Degussa), the linear velocity in the channels of catalyst bed would be much higher. Therefore, the reaction in the microchannel reactor was affected by film diffusion more strongly than in the tubular reactor.

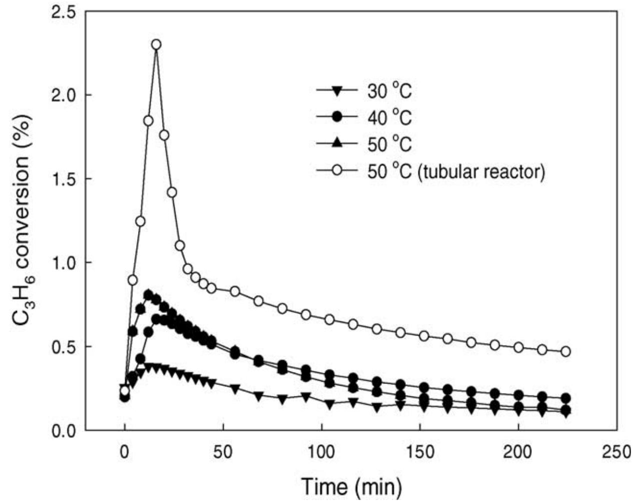

Fig. 13. Propylene conversion changing with reaction temperature and compared with that in tubular reactor (temperature: 50 °C; catalyst 0.7 g, feed: 33.3 ml/min).

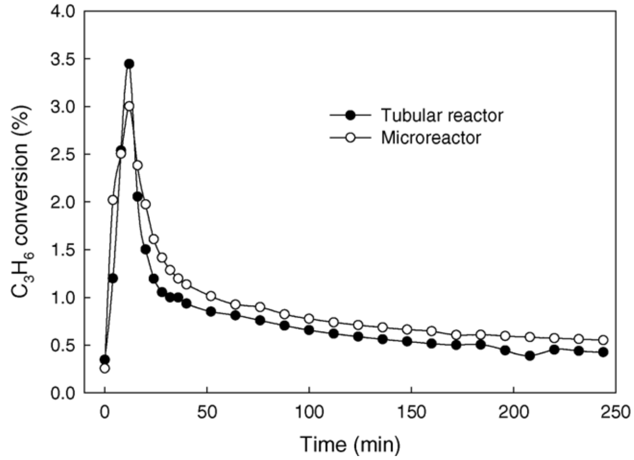

Fig. 14. Propylene epoxidation in microreactor and tubular reactor (temperature: 50 °C; catalyst: 1.4 g; feed: 33.3 ml/min).

To the same dimension of the belt assembly, the catalyst loading was increased to 1.4 g. The conversion was found to increase very significantly and became comparable to the conversion obtained from the tubular reactor (10 mm i.d.) packed with 1.4 g catalyst, as shown in Fig. 14. Though the linear velocity was slightly increased to 9.6 mm/s in this case, it could not account for so significant an increase in the conversion. Therefore the dominant factor for the low C_3H_6 conversion was considered to be the low intrinsic reaction rate of the Au/TiO_2 catalyst.

7. Conclusion and discussion

Au/TiO_2 catalyst was prepared and its performance evaluated in a tubular reactor. The reaction rate was low but was increased considerably by increasing feed H_2, O_2, or C_3H_6 concentration, which was in the explosive limit. The catalyst lost its activity rapidly and was sensitive to the reaction temperature. Based on TG analysis, and verified by experiments, regeneration at temperature higher than 280 °C was needed to recover the catalyst activity. A microchannel reactor with interior electric heating was devised to suppress possible explosions and to rapidly raise the temperature for catalyst regeneration. The reactor was evaluated under different operating conditions, showing that the conversion was controlled mainly by the intrinsic reaction rate, but simultaneously influenced by film diffusion. Catalyst regeneration was successful by heating the reactor with electricity to 280 °C in flowing air.

The hydrogen efficiency was 26% under normal operating condition (catalyst, 0.4 g; temperature, 50 °C; Feed, 33.3 ml/min; composition, $C_3H_6/H_2/O_2/N_2 = 10/10/10/70$) in a tubular reactor. As a result the adiabatic temperature rise is over 30 °C for a propylene conversion of 1.2%. Apparently, heat removal should be taken into account for the reactor to be commercialized, by using an integrated heat-exchanger for example.

The performance of the microchannel reactor was not fully exploited in this article. For a better understanding of this reactor, detailed modeling of the reaction kinetics and mass and heat transfer is needed, based on which the performance of the reactor can be exploited by optimization. This work is currently undertaken.

Acknowledgement

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References

[1] S.J. Ainsworth, C&EN (1992) 9.
[2] M. Taramasso, G. Perego, B. Notari, US Patent 4,410,501 (1983).
[3] M. Haruta, B.C. Uphade, S. Tsubota, A. Miyamoto, Res. Chem. Intermed. 24 (1998) 329.
[4] B.S. Uphade, Y. Yamada, T. Akita, T. Nakamura, M. Haruta, Appl. Catal. A 215 (2001) 137.
[5] A.K. Sinha, S. Seelan, T. Akita, S. Tsubota, M. Haruta, Appl. Catal. A 240 (2003) 243.
[6] T.A. Nijhuis, B.J. Huizinga, M. Haruta, J.A. Moulijn, Ind. Eng. Chem. Res. 38 (1999) 884.
[7] G. Mul, A. Zwijnenburg, B. Linden, M. Makkee, J.A. Moulijn, J. Catal. 201 (2001) 128.
[8] Y.A. Kalvachev, T. Hayashi, K. Tanaka, M. Haruta, Stud. Surf. Sci. Catal. 110 (1997) 965.
[9] E.E. Stangland, K.B. Stavens, R.P. Andres, W.N. Delgass, J. Catal. 191 (2000) 332.