

The Direct Epoxidation of Propene in the Explosive Regime in a Microreactor—A Study into the Reaction Kinetics

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The usage of a microreactor system for the direct epoxidation of propene over a gold-titania-based catalyst system using a mixture of hydrogen, oxygen, and propene allows for the safe operation of the reaction in the explosive regime. A kinetic study was performed on the effect of the concentration of hydrogen, oxygen, and propene on the reaction rate as well as the catalyst deactivation and reactivation. A simple algebraic expression was developed, based on published kinetics, which provided the three reaction rate constants as a function of the feed gas concentrations. It is shown that the propene concentration does not influence the propene oxide formation rate; however, higher propene concentrations significantly reduce the catalyst deactivation rate. Hydrogen increases the rate of the epoxidation reaction, while it only has a minor influence on the rate of deactivation and reactivation. Oxygen has a beneficial effect on the epoxidation reaction: it slightly decreases the deactivation rate and is beneficial for the catalyst reactivation. It is shown that, for the gold on titania dispersed on a silica catalyst used in this study, it is advantageous to perform the direct propene epoxidation in a microreactor system at the highest possible feed concentrations for each of the reactants. This results in the highest propene oxide productivity and the lowest deactivation rate.

Introduction

Propene oxide is an important bulk chemical, produced annually in a quantity of about 7 Mtons.¹ Its primary use is as an intermediate for the production of propene glycols, polyether polyols, and polyurethanes. The traditional processes to produce propene oxide have become less attractive out of either environmental considerations (chlorohydrin process) or economic considerations (hydroperoxide processes: producing an unrelated coproduct in a more than stoichiometric quantity). In 2009 in Antwerp, a new process by DOW and BASF became operational to produce propene oxide directly and in a clean manner by first producing hydrogen peroxide out of hydrogen and oxygen and then utilizing the peroxide to epoxidize propene. The only disadvantage of this process is that it is relatively complex and utilizes three different reactors. A new process in which propene oxide can be produced directly in a single step can therefore be highly competitive.

Gold-titania catalysts have shown the capability of directly producing propene oxide using a hydro-epoxidation process using a mixture of hydrogen and oxygen. This system was already demonstrated for the first time over 10 years ago by Haruta et al.² Even though this system has been investigated extensively since then, the mechanism of these catalysts is still not well understood. The general consensus in the literature is that, over gold nanoparticles, (hydrogen)peroxide species are being produced. This hydroperoxide species is then the true oxidizing species in a second step in the reaction mechanism, epoxidizing propene over a titanium site.^{3–5} The main attractiveness of this catalyst system comes from its exceptionally high selectivity toward propene oxide (over 99% selectivity is possible) and the mild conditions at which the catalyst operates (typically lower than 473 K and atmospheric pressure). Even though this catalysts system has undergone many improvements over the past years, it still is not ready yet to be applied commercially. The main problems of the catalysts are their

stability, the relatively low activity, and the hydrogen efficiency. The hydrogen efficiency is the efficiency with which the hydrogen coreactant is utilized for the epoxidation compared to direct water formation, which is the primary competing side reaction. Typically, the best performing catalysts have a propene oxide selectivity of over 90%, a stable propene conversion level of up to 2% (10% peak), and a hydrogen efficiency of up to 30%.

The most important improvements that were made over the past years are discussed briefly. The use of high-surface-area silica–titania support materials improves both the stability of the catalyst and the activity.^{6–8} Most likely, these two aspects are linked, as these titania-silica supported catalysts allow for a higher operating temperature, while the classical gold-titania catalysts deactivate extremely fast at a higher temperature. Surface modification by silylation of the support⁹ can dramatically increase the catalyst activity, but this is at the expense of the catalyst stability. The addition of CsCl is reported to greatly improve the hydrogen efficiency.¹⁰ Further overall improvements have been made to the system by the use of promoters¹¹ and by accurately controlling the size of the gold nanoparticles^{12,13} and the nature of the titania sites in the support.^{8,14}

One factor which has been largely ignored in the investigations into this catalyst system is the reactor engineering. Typically, a simple plug flow reactor system is used, with all reactants (hydrogen, oxygen, and propene) present in a quantity of 10 vol % in an inert carrier gas. The use of higher concentrations has been avoided, to prevent operating with an explosive mixture of gases. An important exception is the work performed by the group of Oyama, who reported propene epoxidation in the explosive regime in a packed-bed catalytic membrane reactor.⁴ Feeding (part of) the hydrogen through a membrane allowed them to work safely with much higher hydrogen and oxygen concentrations (up to 40% each), which gave them a stable propene conversion of 10% at 80% propene oxide selectivity at 453 K.

In this work, we will utilize a microreactor system to perform the propene epoxidation over a gold on titania-silica catalyst.

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Microreactors have excellent potential for carrying out this reaction safely using a gas mixture which would be inside of the explosive region for a number of reasons. First, since microreactors have only a very small volume, the energy liberated from an explosion in such a channel would be less than 1 J, which would not be able to affect the integrity of the microreactor. Second, a microreactor allows for an excellent temperature control, which will dramatically diminish the risk of a runaway in the reactor. Most importantly, the fact that the characteristic length (diameter) of the reactor is smaller than the mean free path of the molecules implies that flame propagation inside the channels is not possible as the molecules transfer their energy to the wall instead of each other.¹⁵

In the microreactor system, a kinetic study is made of the epoxidation reaction, in which the rate is determined as a function of the concentration of the reactants. In this manner, we intend to determine if the gold-titania(silica) catalyst system has a greater potential to be applied, when it is used at other conditions than the traditional nonexplosive 10–10–10 vol % reactants composition.

Experimental Section

Catalyst Preparation. In this study, a catalyst consisting of 1 wt % gold on titania dispersed on silica was used, prepared in a manner similar to the method described by Nijhuis et al.¹⁶ A total of 15 g of dry silica support (Davisil 643, Aldrich, 300 m²/g, sieved diameter within 50 and 60 μ m) was dispersed in 200 g of dry isopropanol in a rotary evaporator under a nitrogen atmosphere. A total of 0.75 g of tetraethylorthotitanate was added, and the slurry was rotated for about 20 min. Thereafter, the isopropanol was slowly evaporated at 333 K at reduced pressure. The powder was dried overnight in a 353 K stove and subsequently calcined at 873 K for 4 h (10 K/min heating and cooling).

Gold was deposited on the catalyst support using a deposition precipitation method using aurochloric acid and ammonia. A total of 10 g of the support was dispersed in 100 mL of water, and using ammonia, the pH was adjusted to 9.5. A total of 575 mg of an acidic 30 wt % HAuCl₄ solution (Aldrich) was diluted in 20 mL of demineralized water and added to the support slurry over a 15 min period. During this time, the pH was kept at 9.5 using aqueous ammonia. After the addition of the gold solution, the slurry was stirred for an additional 30 min, after which it was filtered and washed 3 times using 200 mL of water. The catalyst was dried overnight at 353 K and thereafter calcined at 673 K for 4 h (10 K/min heating and cooling).

ICP analysis confirmed the gold loading to be the desired target loading of 1 wt %. The titanium content on the catalyst was 1.18 wt %. TEM analysis showed a narrow particle size distribution for the gold nanoparticles, centered at 4.5 nm.

Catalyst Testing. Catalytic tests were performed using two reactor systems. The first reactor consisted of a quartz tubular milli-reactor (6 mm inner diameter). In this reactor, 0.3 g of catalyst was loaded and tested at a gas feed of 50 N mL/min. This reactor was used for experiments at the “standard” feed concentrations of 10 vol % hydrogen, oxygen, and propene and for experiments at lower concentrations (all outside of the explosive region). The second reactor consisted of a stainless steel capillary tube (0.9 mm inner diameter), which was loaded with 20 mg of catalyst and operated at a gas feed rate of 3.3 N mL/min (i.e., identical GHSV as the first reactor). This reactor was operated at the “standard” feed concentration for all three gases and at higher concentrations within the explosive region. The oxygen was mixed with the other gases shortly before the

catalyst bed. Immediately after the catalyst bed, additional helium was added to the gas stream, diluting the gases to a composition outside of the explosive region. In this manner, the total volume of a potentially explosive gas mixture was minimized.

Both reactors had their own gas feeding section but were located in the same oven. Analyses were performed using a fast Interscience Compact GC system, equipped with a selection valve to automatically switch between the two reactors. The GC system was equipped with a Porabond Q column and a Molsieve 5A column, capable of analyzing all products and reactants in 4 min.

The catalytic experiments were performed in cycles. Prior to each test the catalyst was (re)activated by heating it to 573 K (10 K/min) in a 10% oxygen in helium stream for 1 h. After cooling to the desired reaction temperature, the gas feed was switched to the desired composition and a 5 h catalytic test was performed. This procedure of activating and testing was repeated for as many as 50 cycles. No changes in the performance of the catalyst were observed between subsequent cycles, indicating that this reactivation procedure was sufficient to completely remove all deactivating species and that no irreversible deactivation (e.g., sintering of the gold particles) was occurring. Experiments were performed at varying feed concentrations ranging from 2 to 80 vol % for hydrogen and oxygen and 2 to 40 vol % for propene, with the remaining part being helium. The “standard” conditions used were those commonly used in the literature, with 10 vol % for each of the three reactants. In the experiments in which the composition was varied, mostly two reactants were kept at a feed concentration of 10 vol % with only one reactant concentration being changed. Experiments were performed at different temperatures from 323 to 473 K. The kinetic study with varying feed concentrations was primarily performed at 393 K, a temperature at which the catalyst had a high selectivity (96%), a moderate catalytic activity and an excellent long-term stability. The milli-reactor had a thermocouple located inside the catalyst bed; the microreactor had a thermocouple connected to the stainless steel reactor wall at the point of the catalyst. In this manner, we recorded the actual catalyst temperature during the experiments, which is the temperature indicated in the results and discussion section.

Results

In Figure 1, the performance of the two reactors at the standard reaction conditions is compared. It can be seen that the experiments performed in the two reactors under identical reaction conditions yielded identical results, and that repeated experiments in the same reactor after a catalyst reactivation also resulted in identical results. It can be seen that, within a catalytic cycle, at first the catalytic activity increases fast, and thereafter there is a gradual decrease in the catalytic activity. This is in agreement with the typical activity pattern that is published most commonly in the literature for this type of catalyst.^{16–18} This can be explained by an initial adsorption of the propene oxide produced on the clean catalyst support, and thereafter by a deactivation of the catalyst by the build-up of inhibiting surface species.^{16,19,20}

Figure 2a–c show the propene oxide formation rate within a single catalytic cycle at different hydrogen, oxygen, and propene concentrations. It can be seen that the propene oxide production rate increases most with an increasing hydrogen concentration. In all the experiments, the selectivity is above 95%. The major side-products in our case are carbon dioxide and propane, while

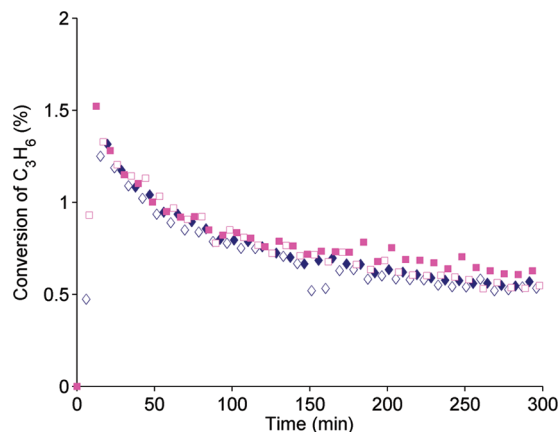


Figure 1. Performance of the capillary microreactor reactor (run 1, ◇; run 2, □) and the tubular milli reactor (run 1, ◆; run 2, ■) at standard reaction conditions (1 wt % Au on Ti-SiO₂ catalyst, gas feed 10 vol % propene, 10 vol % oxygen, 10 vol % hydrogen in helium, 393 K, 1.1 bar, GHSV 9000 mL·g_{cat}⁻¹ h⁻¹).

acetaldehyde, acetone, and propionaldehyde are the other three common byproducts.

Discussion

The identical performance of the same catalyst tested under identical conditions in both the micro- and the milli-reactor (Figure 1) was according to expectations. The experiments in this figure shows that the results are both reproducible and reactor-independent.

The reaction pattern that is observed in the catalytic cycles complicates the determination of the reaction rate dependency on the reactant feed concentrations, as it can be easily understood that both the reaction and the deactivation of the catalyst will be a function of these concentrations. Working with time averaged reaction rates might therefore produce less reliable results. Nijhuis et al.²¹ showed that it is possible to describe the catalytic pattern, in which there is first an increasing activity followed by a deactivation, by a relatively simple model. This model assumes that first the propene oxide, produced in the first part of the cycle, adsorbs on the catalyst, when the surface would reach its saturation capacity for propene oxide adsorption and the deactivation within a cycle could be modeled by a consecutive reaction of the propene oxide produced. In this previous work, however, the influence of the reactant concentrations on the reaction and deactivation rates was omitted.

The mathematical solution of the previously published model to describe our reaction curves in time was quite complex.²¹ Using this model to also determine the effect of the different reaction concentrations on the epoxidation, deactivation, and reactivation of the catalyst would involve a large number of parameters, which would make the fitted values of these parameters less reliable. For this reason, we are now using a model, in line with the mechanism that we published previously,^{16,21,22} which is only using three rates/parameters to describe the catalytic activity in time. These rates represent the following:

- The formation of propene oxide on the catalyst surface
- The reversible deactivation of the catalyst by a consecutive reaction of adsorbed propene oxide
- The reactivation of the catalyst (desorption of deactivating species (carboxylates))

Each of these rates will depend on the reactant concentrations, and in this paper, we are trying to determine this dependence.

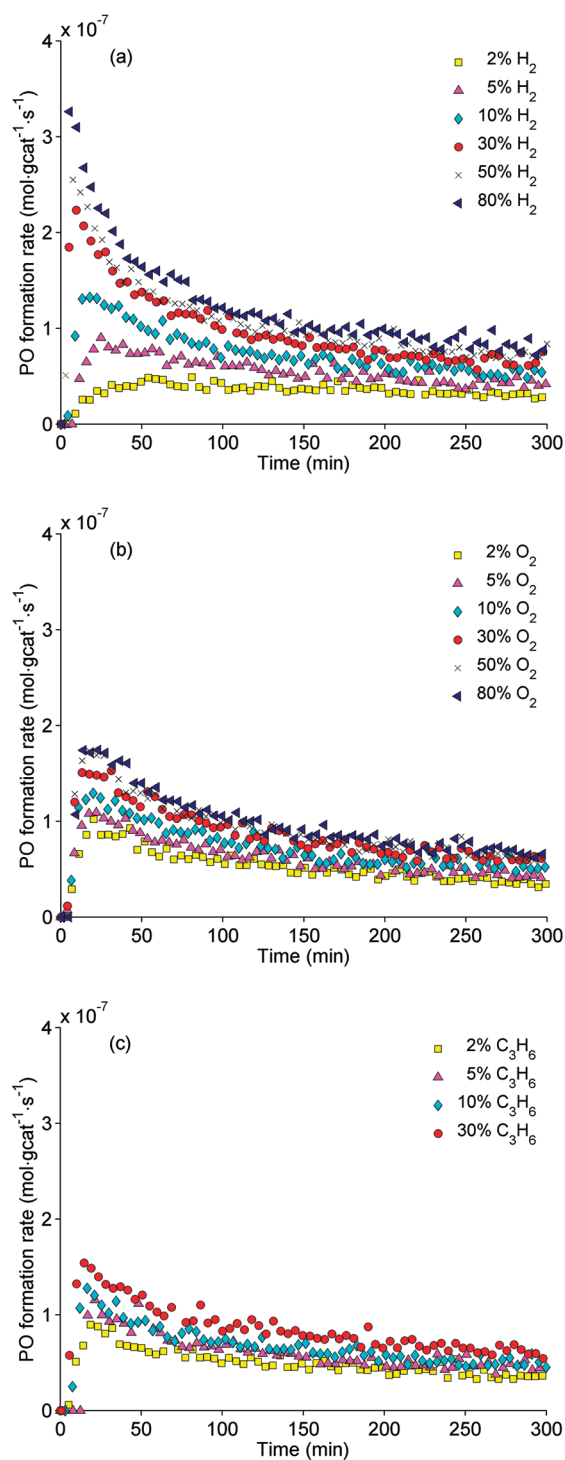


Figure 2. Propene oxide formation rate at different concentrations of (a) hydrogen, (b) oxygen, and (c) propene, respectively, while keeping the other two components constant at 10 vol % (1 wt % Au on Ti-SiO₂ catalyst, balance helium, 393 K, 1.1 bar, GHSV 9000 mL·g_{cat}⁻¹ h⁻¹).

Written in terms of reaction rates, this comes to

$$r_{\text{PO}} = r_{\text{PO},0}(1 - \theta_d) \quad (1)$$

$$\frac{\partial \theta_d}{\partial t} = k_{\text{deact}} r_{\text{PO}}(1 - \theta_d) - k_{\text{react}} \theta_d \quad (2)$$

where r_{PO} is the propene oxide formation rate (mol/g_{cat}/s), $r_{\text{PO},0}$ is the propene oxide formation rate of a catalyst without any deactivation (mol/g_{cat}/s), k_{deact} is the deactivation rate by a

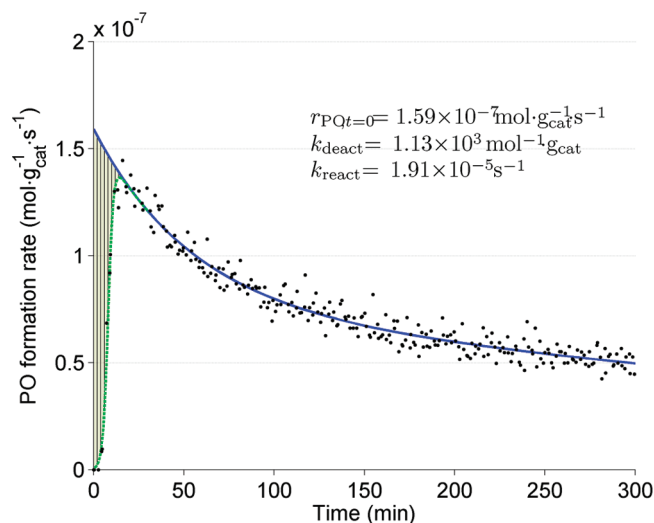


Figure 3. Extrapolation of propene oxide formation rate at standard reaction conditions (1 wt % Au on Ti-SiO₂ catalyst, gas feed 10 vol % propene, 10 vol % oxygen, 10 vp % hydrogen in helium, 393 K, 1.1 bar, GHSV 9000 mL·g_{cat}⁻¹ h⁻¹). The shadowed area denotes the amount of propene oxide adsorbed on the catalyst.

consecutive reaction of propene oxide on the catalyst (g_{cat}/mol), k_{react} is the catalyst reactivation rate (1/s), and θ_d is the number of sites lost/occupied by deactivating species carbonates/carboxylates (fraction, dimensionless). $r_{\text{PO},0}$, k_{deact} , and k_{react} are all expected to be a function of the feed gas composition.

Considering that, at the starting time ($t = 0$) of a catalytic experiment, the catalyst is considered to be clean and therefore contains no deactivated sites ($\theta_d = 0$), we can analytically solve these equations, to come up with the following expression to describe the experiments:

$$r_{\text{PO}} = r_{\text{PO},0} \left(1 - \frac{1 - \exp\left(-\left(a - \frac{1}{a}\right) k_{\text{deact}} r_{\text{PO},0} t\right)}{a - \frac{1}{a} \exp\left(-\left(a - \frac{1}{a}\right) k_{\text{deact}} r_{\text{PO},0} t\right)} \right) \quad (3)$$

$$\text{with } \frac{k_{\text{react}}}{k_{\text{deact}} \cdot r_{\text{PO},0}} = a + \frac{1}{a} - 2 \quad (4)$$

This expression is derived in Appendix A.

We will fit the three parameters ($r_{\text{PO},0}$, k_{deact} , a) to all experiments performed at different conditions. Parameter “ a ” was used to simplify eq 3 and was used using eq 4 to calculate k_{react} . This fit is performed to the catalytic data from the maximum in the catalytic activity onward (i.e., the initial part where produced propene oxide remaining adsorbed on the catalyst surface is omitted). Such a fit of these three parameters to an experiment is shown in Figure 3. It can be seen that this simple approach is able to describe the changing catalytic activity in time very well. In fitting these parameters to the reaction curves, $r_{\text{PO},0}$ primarily determines the starting point of the curve, k_{deact} determines the rate with which the activity decreases, and the ratio between k_{deact} and k_{react} determines the leveling off of the catalyst activity.

A complicating factor fitting the parameters to the reaction curves is the steepness with which the catalytic activity decreases at the beginning of the cycle, which will lead to inaccurately determined initial reaction rates. However, by using the information that the initial propene oxide produced largely remains adsorbed on the catalyst, we know that the area between the observed amount of propene oxide produced and the extrapolated curve should be equal to the amount of propene

oxide adsorbed on the catalyst. We confirmed this previously,²¹ by comparing the amount of propene oxide corresponding to this area to the gravimetrically determined amount of propene oxide that could adsorb. How this area was determined is also shown in Figure 3 (gray area). For all experiments performed at the same temperature, the amount of adsorbed propene oxide on the catalyst should be the same. Therefore, it was decided to use this information to numerically “force” the area under the curve corresponding to the amount of adsorbed propene oxide to be the same for all experiments performed at the same reaction temperature. This method greatly improved the accuracy of (scatter in) the extrapolation of the initial rate over the catalyst. This approach to decouple the propene oxide formation rate from the deactivation and reactivation rates is a key difference between this work and the other previously published kinetic studies,^{23,24} in which the “stable” propene oxide formation rate was used for the kinetic modeling.

In Figure 4a–f, the reaction rates for the propene oxide formation, as well as the deactivation and reactivation rate constants, are shown as a function of the hydrogen, oxygen, and propene oxide concentrations. From Figure 4d–f, it can be concluded that the approach we took to “fix” the amount of adsorbing propene oxide to get more reliable $r_{\text{PO},0}$ values was effective, as there is little scatter in the data points. It can also be seen that $r_{\text{PO},0}$ is not much influenced by the propene concentration. This is in support of the view that the peroxide formation on the catalyst is the rate determining step, and not the epoxidation reaction itself. This is in agreement with the low reaction orders in propene for the epoxidation reaction that have been reported by Delgass et al.²³ and Oyama et al.⁴ The catalyst reactivation rate is not a function of the propene concentration, which is also as expected, since the desorption of strongly bound carbonate/carboxylate species does not involve propene. Surprisingly, the catalyst deactivation rate is a significant function of the propene concentration. At higher propene concentrations, the rate of deactivation is lowest. The most likely explanation for this observation is that the same species which is oxidizing propene to propene oxide, might also be responsible for the consecutive oxidation of propene oxide, causing the catalyst deactivation. Even though the formation rate of this oxidizing species is not a function of the propene concentration, the concentration of this species on the catalyst is a function of the propene concentration. A more rapid consumption of this species (shorter lifetime on the support) by propene lowers the quantity of it on the catalyst, and therefore the deactivation rate.

For the oxygen concentration, it can be seen that an increasing amount of oxygen increases the propene oxide formation, decreases the rate of deactivation, and is slightly beneficial for the catalyst reactivation. The increase in propene epoxidation rate with the oxygen concentration indicates that oxygen is involved in the rate determining step for the propene oxide formation. The observation that the consecutive oxidation of propene oxide, assumed to cause the deactivation of the catalyst, is decreasing with the increasing oxygen concentration at first would seem to be unexpected. However, in previous work, we have shown that the oxygen involved with the consecutive oxidation of adsorbed propene oxide originates from the support.^{16,22,25} The carbonate/carboxylates species, that we identified previously as the strongly adsorbed species that causes the reversible deactivation, can desorb from the catalyst aided by oxygen, as is indicated by the increase of k_{react} with an increasing oxygen concentration.

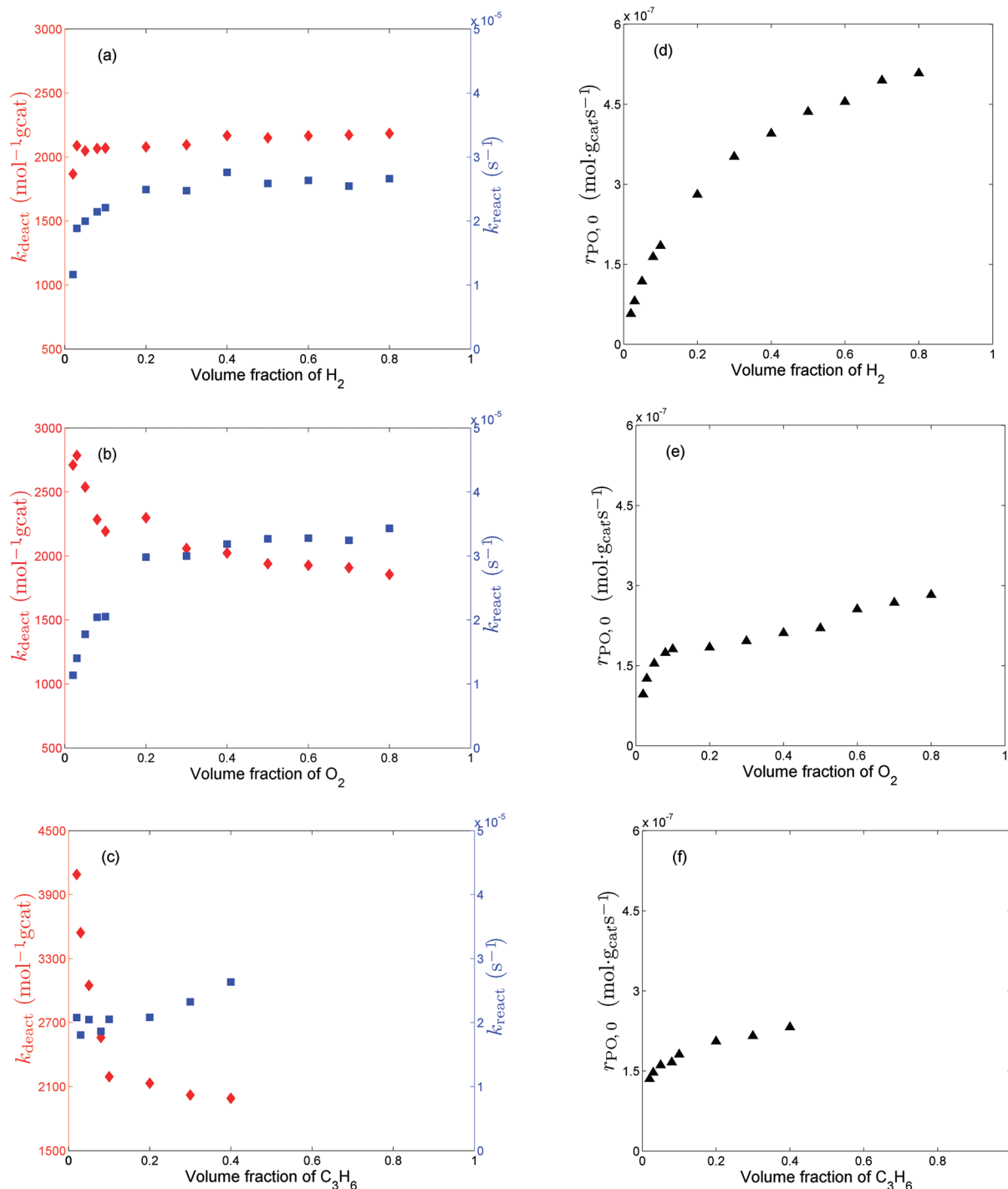


Figure 4. k_{deact} (◆), k_{react} (■), and $r_{\text{PO},0}$ at different concentrations of (a, d) hydrogen, (b, e) oxygen, and (c, f) propene, respectively, while keeping the other two components constant at 10 vol % (1 wt % Au on Ti-SiO₂ catalyst, balance helium, 393 K, 1.1 bar, GHSV 9000 mL·g_{cat}⁻¹ h⁻¹).

The propene oxide formation rate is strongly dependent on the hydrogen concentration, indicating the importance of hydrogen in the rate determining step. The deactivation is not dependent on the hydrogen concentration, and the reactivation is only weakly dependent on the hydrogen concentration. As the catalyst deactivation is caused by a consecutive oxidation of adsorbed propene oxide, it was expected that hydrogen would not play a role in this reaction. The slight influence of hydrogen on the catalyst reactivation can be explained by hydrogen being able to play a minor role in the removal of the strongly oxidized consecutive oxidation products from the catalyst surface.

It should be noted that, in the kinetic analysis made so far, the effects of the water and propene oxide that are being

produced have not been taken into account yet. Oyama et al.²⁴ showed in their kinetic analysis that propene oxide has a small positive reaction order in the water formation and the carbon dioxide formation, while no effect on the epoxidation reaction itself was reported. In our previous work, we reported that water can slow down the epoxidation reaction.²⁶ If one assumes that both water and propene oxide can affect the $r_{\text{po},0}$ values, this would mean that figures in which the $r_{\text{po},0}$ values are plotted versus the hydrogen, oxygen, and propene concentrations could exhibit a deviation as the rate changed. Since in Figure 4 these trends, however, are all approximately linear, it is assumed that neither the propene oxide nor the water produced have a large

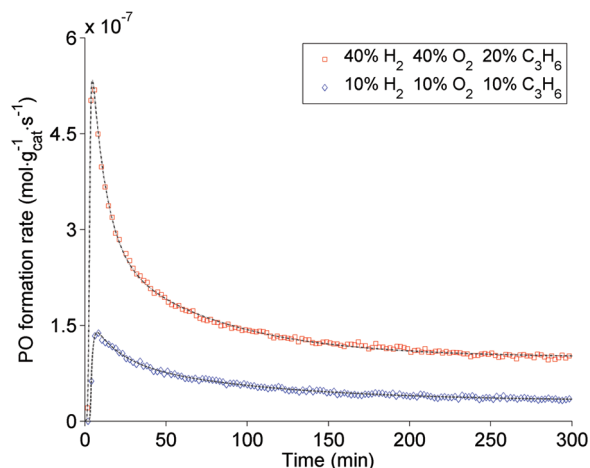


Figure 5. Propene oxide formation rate at the standard reaction conditions (\diamond : 10 vol % propene, 10 vol % oxygen, 10 vol % hydrogen in helium) and at concentrations inside the explosive region (\square : 20 vol % propene, 40 vol % oxygen, 40 vol % hydrogen) using 1 wt % Au on a Ti-SiO₂ catalyst, 393 K at 1.1 bar, GHSV 9000 mL \cdot g_{cat}⁻¹ h⁻¹.

impact on the parameters obtained. In our ongoing research, this assumption will be validated.

Using the knowledge of this simple analysis on the epoxidation, deactivation, and reactivation provided, we performed an experiment at a gas composition of 40% hydrogen, 40% oxygen, and 20% propene. This experiment is shown in Figure 5, compared to an experiment performed at the “classical” gas composition. It can be seen that performing this reaction under these conditions in a microreactor system greatly improves the propene oxide reaction rate by over a factor of 4, improving the maximum yield from 1.3 to 2.4%. It should be noted that the propene oxide yield can be improved even more, by increasing the reaction temperature. The highest propene oxide yield that we obtained with our Ti-SiO₂ supported catalysts at the standard 10–10–10% reaction conditions is 2.8% at 443 K. Currently, we are expanding the study in the microreactor over a wider temperature and pressure range and also including the water production, as well as the effect of water and propene oxide in the gas phase, so that we can come to a complete mechanistic understanding on all the relevant processes occurring at the catalyst surface and also determine the optimal reaction conditions for this process, taking into account both the activity and the stability of the catalyst.

Conclusions

The usage of a microreactor system for the direct epoxidation of propene over a gold-titania-based catalyst system using a mixture of hydrogen, oxygen, and propene allows for the safe operation of the reaction in the explosive regime. The propene concentration does not influence the propene oxide formation rate; however, higher propene concentrations significantly reduce the catalyst deactivation rate. Hydrogen increases the rate of the epoxidation reaction, while it only has a minor influence on the rate of deactivation and reactivation. Oxygen has a beneficial effect on the epoxidation reaction, slightly decreases the deactivation rate, and is beneficial for the catalyst reactivation. It can be concluded that it is highly beneficial to perform the direct propene epoxidation in a microreactor system at the highest possible feed concentrations for each of the reactants, as this results in the highest propene oxide productivity and the lowest deactivation rate.

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Appendix A

The propene epoxidation rate is given by

$$r_{\text{PO}} = r_{\text{PO},0}(1 - \theta_d) \quad (\text{A.1})$$

where θ_d represents the sites that are deactivated and $r_{\text{PO},0}$ is the initial reaction rate without deactivation.

This equation explains that the propene epoxidation rate is equal to an initial rate, times the number of sites that are still available for the reaction ($1 - \theta_d$).

The deactivation is caused by the consecutive reaction of the propene oxide produced. This rate is therefore dependent on a rate constant, the propene oxide formation rate, and the fraction of sites that are still active ($1 - \theta_d$). In addition, the deactivating species desorb slowly from the sites (regeneration reaction).

The balance for the deactivated sites is therefore

$$\begin{aligned} \frac{d\theta_d}{dt} &= \left(\frac{d\theta_d}{dt}\right)_{\text{deactivating}} - \left(\frac{d\theta_d}{dt}\right)_{\text{regenerating}} \\ \frac{d\theta_d}{dt} &= k_{\text{deact}} r_{\text{PO}}(1 - \theta_d) - k_{\text{react}} \theta_d \\ \frac{d\theta_d}{dt} &= k_{\text{deact}} r_{\text{PO},0}(1 - \theta_d)^2 - k_{\text{react}} \theta_d \end{aligned} \quad (\text{A.2})$$

Rewriting eq A.2 results in

$$\frac{1}{k_{\text{deact}} r_{\text{PO},0}} \frac{d\theta_d}{dt} = \theta_d^2 - \left(2 + \frac{k_{\text{react}}}{k_{\text{deact}} r_{\text{PO},0}}\right) \theta_d + 1 \quad (\text{A.3})$$

Equation A.3 can be rewritten as

$$\frac{d\theta_d}{\theta_d^2 - \left(2 + \frac{k_{\text{react}}}{k_{\text{deact}} r_{\text{PO},0}}\right) \theta_d + 1} = k_{\text{deact}} r_{\text{PO},0} dt \quad (\text{A.4})$$

We denote a ($a > 1$) as the root of $\theta_d^2 - [2 + k_{\text{react}}/(k_{\text{deact}} r_{\text{PO},0})]\theta_d + 1 = 0$; then we have

$$a + \frac{1}{a} = 2 + \frac{k_{\text{react}}}{k_{\text{deact}} r_{\text{PO},0}} \quad (\text{A.5})$$

Analytically solving eq A.4, results in

$$\theta_d = \frac{1 - \exp\left(-\left(a - \frac{1}{a}\right)k_{\text{deact}} r_{\text{PO},0} t\right)}{a - \frac{1}{a} \exp\left(-\left(a - \frac{1}{a}\right)k_{\text{deact}} r_{\text{PO},0} t\right)} \quad (\text{A.6})$$

Combining eqs A.1 and A.6 finally results in

$$r_{\text{PO}} = r_{\text{PO},0} \left(1 - \frac{1 - \exp\left(-\left(a - \frac{1}{a}\right)k_{\text{deact}} r_{\text{PO},0} t\right)}{a - \frac{1}{a} \exp\left(-\left(a - \frac{1}{a}\right)k_{\text{deact}} r_{\text{PO},0} t\right)}\right) \quad (\text{A.7})$$

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