Gas-Phase Epoxidation of Propene with Hydrogen Peroxide Vapor

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S *Supporting Information*

ABSTRACT: A study on the gas-phase epoxidation of propene with vapor hydrogen peroxide has been carried out. The main purpose was to understand the key factors in the reaction and the relationship between epoxidation of propene and decomposition of hydrogen peroxide, which is the main side reaction. The decomposition was highly influenced by the materials used, being higher in metals than in polytetrafluoroethylene (PTFE) and glass, and it was complete when the epoxidation catalyst, TS-1, was introduced in the system. However, when propene was added, the peroxide was preferentially used for the epoxidation, even with amounts of catalyst as small as 10 mg, reaching productivities of 10.5 $kg_{PO} \cdot kg_{cat}^{-1} \cdot h^{-1}$ for a gas hourly space velocity (GHSV) of 450 000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$. The hydrogen peroxide was converted completely in all the experiments conducted, with a selectivity to PO of around 40% for all peroxide concentrations. Finally, if concentrations of propene higher than the stoichiometrically required amounts were used, the selectivity to PO increased to almost 90%.

1. INTRODUCTION

The use of aqueous hydrogen peroxide for the synthesis of propene oxide (PO) is an attractive alternative to the traditional chlorohydrin and hydroperoxide processes, in the first place, because water is the only byproduct, making it a clean technology, and, in the second place, because of the high yields that can be obtained. This reaction was first carried out by Clerici et al.,[1] who reported a conversion of hydrogen peroxide higher than 95%, with negligible decomposition and the selectivity of propene to PO of around 90%. The final step for its industrial implementation occurred in 2008, when the epoxidation of propene was coupled with the synthesis of hydrogen peroxide via the anthraquinone process and two plants were opened by Evonik and SKC and by Dow and BASF, respectively.[2,3]

Zhao et al.[4] reported the possibility of integrating the epoxidation of propene with the synthesis of hydrogen peroxide in a plasma reactor starting from a mixture of O_2 and H_2. This simplifies the overall process, since the first step does not require any solvent and the peroxide obtained has high purity. Additionally, if one considers that the H_2O_2 leaves the plasma as vapor, to perform the epoxidation in the gas phase would avoid intermediate capturing steps. This combination was first used by Su et al.,[5] who reported a yield of 0.25 $kg_{PO} \cdot kg_{cat}^{-1} \cdot h^{-1}$, selectivity of propene to PO of 95.4%, and peroxide utilization of 36.1%. A more detailed description of the gas-phase epoxidation was published by Klemm et al.,[6] who performed the reaction in a microstructured reactor coated with TS-1, both on a laboratory scale and in a pilot plant. They reached productivities higher than 1 kg of PO per kilogram of catalyst per hour and selectivities to PO based on propene higher than 90%. However, the selectivity based on peroxide that they reported was 25% in lab experiments and 60% in the pilot plant, which is still too low for being able to compete with the liquid-phase route mentioned before.

$$H_2O_2 \rightarrow 1/2 O_2 + H_2O \tag{1}$$

The main side reaction encountered when working with hydrogen peroxide vapor is its decomposition into oxygen and water (eq 1), which can occur both on the surface of the reactor and over the catalyst. The decomposition of H_2O_2 vapor over different materials, even relatively inert ones, was broadly studied in the middle of the 20th century. Satterfield et al.[7,8] and Mackenzie et al.[9] reported that, at temperatures between 15 and 450 °C, it is mainly a surface reaction, with the rate of reaction being higher over metals than over borosilicate glass or quartz. Analyzing the effect of temperature, Satterfield et al.[7] indicated that the decomposition reaches a minimum at 150 °C. The reason for higher decomposition values at lower temperatures was attributed to the adsorption of hydrogen peroxide on the walls of the glass vessel, forming a multilayer which gets thicker at lower temperatures until there is condensation. With respect to the kinetics of the decomposition of hydrogen peroxide vapor, Giguere et al.[10] and Hoare et al.[11] reported that it is a first-order reaction with respect to the concentration of hydrogen peroxide when using partial pressures of H_2O_2 higher than 0.0013 bar and that the activation energy is about 63 kJ/mol. This contrasted with the 1.5 order predicted by Satterfield et al.[7] or the bimolecular reaction published by Mackenzie et al.[9] The reasons for these discrepancies can be that the former did not use any inert gas, while both Giguere et al.[10] and Hoare et al.[11] studied the influence of various inert gases and the latter conducted his study at partial pressures of peroxide of 0.0013 bar. In a more recent study, Lin et al.[12] analyzed the decomposition of aqueous H_2O_2 in flow at high temperatures, from 100 to 280 °C, over reactor tubing of various materials. They also observed first-order reaction kinetics and their results were in agreement with the research of Hoare et al.[11] The values for the

decomposition rate constants for several materials that they reported can be seen in the third column of Table 1. The rate

Table 1. Influence of the Materials in the Decomposition of Hydrogen Peroxide Vapor at 140 °C and Comparison with the Results of Lin et al.[12] between 100 and 280 °C in the Liquid Phase[a]

material	decomposition (%)	rate constant from the literature[12]
quartz	30	$k = 4.0 \times 10^3 \exp\left(-\dfrac{67000}{RT}\right)$
PTFE	25	$k = 4.0 \times 10^3 \exp\left(-\dfrac{67000}{RT}\right)$
titanium	100	$k = 7.2 \times 10^5 \exp\left(-\dfrac{68200}{RT}\right)$
stainless steel	100	$k = 2.5 \times 10^5 \exp\left(-\dfrac{61900}{RT}\right)$

[a]Conditions: temperature 140 °C, 2.8 vol % H_2O_2, 14 vol % H_2O, and He flow of 100 mL/min. Rate constants for the first-order kinetics of the decomposition of peroxide in the liquid phase at temperatures from 100 to 280 °C for different materials, reported by Lin et al.[12] Rate constants, k, in inverse seconds, $R = 8.314$ J/mol·K, T in kelvin.

constants for Teflon and glass followed the same pattern, so they averaged their results and summarized them in a unique constant for both materials. On the other hand, the reaction over titanium or stainless steel was 100 times faster. They attributed the catalytic effect of the metals to a charge transfer reaction where radicals are involved.

In 2011, Klemm et al.[13] developed a microstructured falling film evaporator for hydrogen peroxide made of $AlMg_3$ due to its higher mechanical strength. The decomposition that they observed accounted for 10% of the peroxide evaporated at 130 °C. According to their observations, it occurred in the liquid phase while it was being evaporated, instead of in the vapor phase when it comes into contact with the reactor surfaces. They supported this information with the fact that they could not reduce the decomposition by diminishing the residence time, with increasing flow rate of the inert gas.

When a catalyst is added to the system, its interference with the peroxide decomposition can influence the performance of the desired reaction. In the case of TS-1, it contains titanium, which can be present as isolated tetrahedrally coordinated Ti atoms or as amorphous extra-framework titanium dioxide species. The former is assumed to be responsible for the catalytic activity of TS-1 in the oxidation of organic compounds with hydrogen peroxide. Upon contact with H_2O_2, Ti-hydroperoxy species are formed, which are intermediate species in the epoxidation of propene.[14] On the other hand, Huybrechts et al.[15] reported that the decomposition of peroxide increased when they used TS-1 with higher titanium content, even when it was in tetrahedral position. With this, they concluded that the reaction is titanium catalyzed. These observations were confirmed by the DFT calculations of Yoon et al.[16] They indicated that the Ti-hydroperoxy species, formed in the tetrahedrally coordinated Ti in TS-1, are capable of oxidizing a second equivalent of peroxide, producing radical ·OOH and $Ti(O·)(OH_2)$ species that may be involved in the decomposition of H_2O_2. Potekhin et al.,[17] studying the kinetics of the decomposition of H_2O_2 over TS-1, reported an activation energy of 72 kJ/mol, which is similar to the 68.2 kJ/mol published by Lin et al.[12] for titanium tubes. The second type of

titanium, contained in the extra-framework amorphous titania, has a stronger effect in the decomposition of hydrogen peroxide. According to Huybrechts et al.,[15] the anatase present in some of their synthesized TS-1 samples was only active for the decomposition of peroxide and not for the oxidation of organic compounds.

The aim of this work is to provide insight into the epoxidation of propene with hydrogen peroxide vapor at high temperatures, understanding the key factors in the reaction and the relationship between epoxidation and decomposition of hydrogen peroxide.

2. EXPERIMENTAL SECTION

2.1. Catalyst. TS-1 was synthesized following the procedure described by Shan et al.[18] to produce conventional zeolite nanocrystals. The resulting catalyst was characterized by X-ray diffraction (XRD) for crystallinity, scanning electron microscopy (SEM) for studying the particle size, ultraviolet–visible (UV–vis) for the coordination state of the titanium in the zeolite and ICP for its elemental composition.

2.2. Experimental Setup. The gas-phase epoxidation was performed in a tubular reactor with an inner diameter of 4 mm and a length of 470 mm. The material of the reactor was varied according to the experiments: quartz, polytetrafluoroethylene (PTFE), titanium, and stainless steel were used. The reactor was placed inside a tubular oven, in which the experiments were conducted at different temperatures, ranging from 120 to 160 °C. The hydrogen peroxide vapor was obtained by feeding liquid H_2O_2 (30 wt %, Sigma Aldrich, containing stabilizers) with a syringe pump (KDS 100 with a borosilicate gastight syringe SGE) through a PEEK capillary inside the reactor, where it evaporates over a bed of PFA (perfluoroalkoxy) beads at the working temperature. The syringe pump was placed inside a fridge at 7 °C to avoid decomposition of H_2O_2. The gases, helium (carrier gas) and propene, were dosed by mass flow controllers (BROOKS Instruments B.V.). The outlet gases of the reactor were analyzed online by a Compact GC (Interscience B.V.) equipped with a Rt-Q-Bond column and a Molsieve 5A column in two separate channels, both with a thermal conductivity detector (TCD). Given the limitations presented by the analysis of hydrogen peroxide vapor, which is fully decomposed at the high temperature in the injector of the GC, a capturing setup was developed. A four-way valve was installed just after the reactor, giving the possibility of diverting the flow to a capturing vessel. This vessel was immersed in a cooling bath prepared with a mixture of liquid nitrogen and ethanol (−116 °C) so that all the vapors were frozen when passing through it. The remaining gases were measured in the GC. All the oxygen measured during these runs can be directly related to the amount of hydrogen peroxide decomposed in the reactor (eq 2). To verify the validity of this method, in a number of experiments, the frozen content of the vessel was analyzed by iodometric titration to determine the peroxide concentration in the gas phase. Using this method, we could determine the hydrogen peroxide decomposition with an experimental error of less than 10%.

2.3. Decomposition Experiments. The stability of peroxide against factors like construction materials or the presence of catalyst was evaluated in the setup described above. Four different types of materials for the reactor were compared both with and without catalyst: quartz, PTFE (ERIKS, 10014664), titanium (Grade 2 titanium, DIN 17850), and stainless steel. To that end, the setup was in its capturing

position and the measured O_2 was related to the decomposed peroxide in vapor phase as explained in eq 2.

$$H_2O_2 \text{ decomposed (\%)}$$
$$= \frac{2 \times O_2 \text{ measured in GC}\left(\frac{mol}{min}\right)}{H_2O_2 \text{ pumped}\left(\frac{mol}{min}\right)} \times 100 \qquad (2)$$

Additional H_2O_2 decomposition experiments were performed in the liquid phase both at the conditions generally used in literature for the liquid-phase epoxidation and at the normal operating temperature employed during the gas-phase reaction. The former was carried out with 400 mg of catalyst, in a 100-mL stirred glass vessel at 50 °C. Methanol was used as a solvent and the concentration of peroxide was 4 wt %. The latter test was performed at 140 °C in a titanium autoclave at 12 bar, due to the high vapor pressure of methanol (10.3 bar) and the possible release of oxygen due to the higher decomposition rate of peroxide at this high temperature. In this case, a blank test was done without catalyst to evaluate the thermal decomposition before adding 100 mg of TS-1.

2.4. Epoxidation Experiments. The gas-phase epoxidation experiments were carried out in the setup described above, analyzing different parameters that can be important for the performance of the reaction.

The conversion and selectivity to PO of hydrogen peroxide ($X_{H_2O_2}$, $S_{H_2O_2 \text{toPO}}$) and propene ($X_{C_3H_6}$, $S_{C_3H_6 \text{toPO}}$) were calculated following eqs 3−6:

$$X_{H_2O_2} = \frac{P_{H_2O_2}^{IN} - P_{H_2O_2}^{OUT}}{P_{H_2O_2}^{IN}} \times 100 \qquad (3)$$

$$S_{H_2O_2 \text{toPO}} = \frac{P_{PO}}{P_{H_2O_2}^{IN} - P_{H_2O_2}^{OUT}} \times 100 \qquad (4)$$

$$X_{C_3H_6} = \frac{P_{C_3H_6}^{IN} - P_{C_3H_6}^{OUT}}{P_{C_3H_6}^{IN}} \times 100 \qquad (5)$$

$$S_{C_3H_6 \text{toPO}} = \left\{ P_{PO} \middle/ \left[P_{PO} + P_{propanal} + P_{acetone} + \frac{2P_{acetaldehyde}}{3} \right.\right.$$
$$\left.\left. + \frac{P_{CO_2}}{3} + \frac{P_{CO}}{3} \right] \right\} \times 100 \qquad (6)$$

The effect of the concentration of hydrogen peroxide and propene was evaluated by maintaining one of them at a constant concentration in excess and varying the concentration of the other. Helium was used as inert gas, with flows of 50 and 100 mL/min. In all these experiments, the temperature was maintained at 140 °C

The influence of the catalyst loading was also tested. To that end, different amounts of the synthesized TS-1, ranging from 10 to 100 mg, were packed in the reactor. The epoxidation was carried out at a total flow rate of 64 mL/min, 3.7 vol % H_2O_2, and 13 vol % C_3H_6 at a temperature of 140 °C.

The behavior of the system at different temperatures was evaluated by varying the temperature of the oven between 120 and 160 °C. The concentrations of peroxide and propene were 2.4 and 0.8 vol %, respectively, maintaining a total flow rate of 116 mL/min.

3. RESULTS AND DISCUSSION

3.1. Hydrogen Peroxide Decomposition. Four different types of reactor materials were tested for their interaction with vapor hydrogen peroxide. The levels of decomposition varied to a high extent, as shown in Table 1.

It was observed that, as reported by Satterfield et al.[7] and Lin et al.,[12] the decomposition over quartz and PTFE is considerably smaller than the decomposition over metals, being all the H_2O_2 vapor added in the latter case decomposed immediately. The values for the decomposition over Teflon were, however, the lowest. This result is not in agreement with what Satterfield et al.[7] published, where the decomposition rate over the polymer at 120 °C was twice as high as over borosilicate glass. The reason for this discrepancy could be the fact that quartz can participate in a cation exchange mechanism, attracting cations like Na^+, K^+, or Ca^+ that can act as active centers for the H_2O_2 decomposition.[7] While, on the other hand, the surface of PTFE is more inert to ion exchange. Another contribution to this explanation can be the hydrophobicity of the polymer, which prevents water and peroxide to accumulate over its surfaces at lower temperatures, reducing the surface decomposition.

It was chosen to perform the gas-phase epoxidation experiments in a quartz reactor due to its higher thermal resistance and its lower permeability to helium, which is the carrier gas used.

During the tests performed in the liquid phase, the addition of the catalyst was found to have little effect under the mild conditions employed normally for the liquid phase epoxidation (50 °C). According to the experiments, only 0.5% of the initial peroxide added was decomposed in contact with 400 mg of TS-1 after 3 h. It is worth noting that the catalyst employed in this study contains certain amounts of extra-framework titanium (see Supporting Information). However, the low peroxide decomposition observed in our liquid-phase experiments indicates that the amount of extra-framework Ti is low and does not significantly affect the catalyst performance. When the temperature was increased to 140 °C, the decomposition increased dramatically both with and without catalyst (Figure 1). The trend observed without the catalyst can be seen as similar to the results obtained in the gas phase in the empty flow reactor. The decomposition at higher temperatures occurs
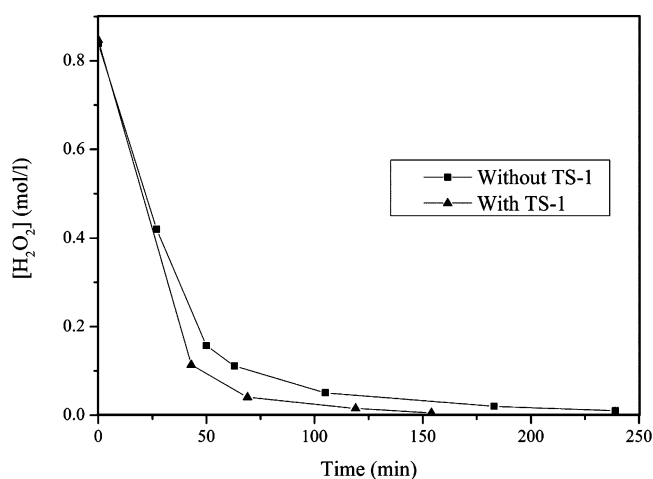

Figure 1. Decomposition of H_2O_2 at 140 °C in the liquid phase with and without catalyst, using methanol as a solvent.

on the surface of the titanium reactor, as this reaction is catalyzed and speeded up by the surface of the metal. The incorporation of the catalyst to the system resulted in a faster consumption of the hydrogen peroxide, being partly decomposed and partly used for oxidizing the methanol to form formaldehyde. However, the half-life time of H_2O_2 under these conditions was about 30 min, which is much longer than the typical residence time of 3−7 s in the gas phase flow reactor.

When the catalyst was tested in the packed bed flow reactor at 140 °C by feeding peroxide vapor and water, 100% of the peroxide added was decomposed, even when only 10 mg of TS-1 were loaded in the reactor. The difference between this behavior and the one observed in the liquid phase at the same temperature can be due to, first, the higher availability of the catalyst in a flow system and the stabilizing effect of the liquid and, second, the higher affinity of TS-1 for methanol than for water.[19] In the liquid-phase experiments, part of the Ti sites responsible for the decomposition of peroxide were coordinated with methanol, thus being less available for the decomposition of peroxide over TS-1.

The introduction of a flow of propene together with the hydrogen peroxide vapor changes the product distribution obtained. Figure 2 shows the selectivity of hydrogen peroxide
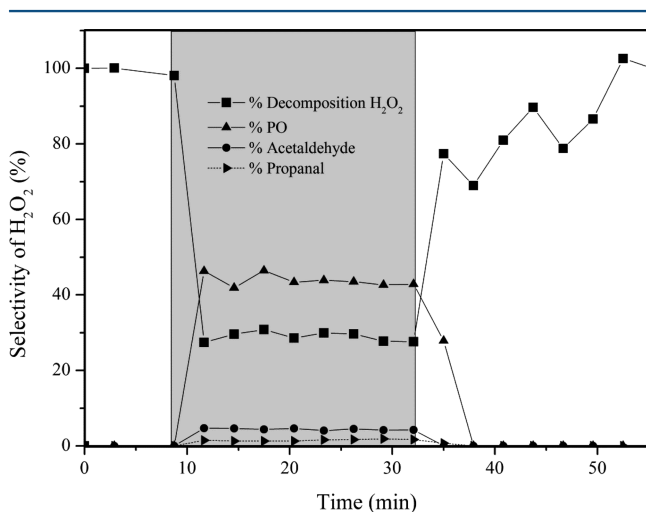

Figure 2. Selectivity of hydrogen peroxide to its decomposition into O_2 and H_2O, PO, acetaldehyde, and propanal when C_3H_6 is added (greyed area) versus time on stream. Temperature 140 °C, He flow 150 mL/min, 1.67 vol % H_2O_2, and 13 vol % C_3H_6.

to the decomposition and to the production PO and byproducts. It can be seen that hydrogen peroxide is still converted completely, but it is primarily used for the epoxidation of propene. This implies that the epoxidation rate is faster than the decomposition rate. The same as in the liquid phase epoxidation, where the selectivity of hydrogen peroxide to PO is around 95%, with the decomposition being very small.[1] This fact was also observed by Huybrechts et al. in 1992[15] when they reported that, despite the fact that the decomposition over TS-1 was titanium catalyzed, the efficiency of H_2O_2 for catalytic oxidations was generally high (60−90%). Looking at the activation energies of both reactions over TS-1 in methanol in the range from 25 to 50 °C, they are 28.5 kJ/mol for the epoxidation[20] and 72 kJ/mol for the decomposition.[17] In the case of the gas-phase reaction, considering the Arrhenius equation, an increase of the temperature from 50 to 140 °C results in an increase of the decomposition rate

constant of about 230 times, which is much larger than the almost 9 times increment of the epoxidation constant. Therefore, this easily explains why our experimentally observed epoxidation/decomposition ratio at 140 °C is much lower than those reported by others in the liquid phase at 50 °C. For example, Shin and Chadwick,[20] working at 40 °C in the liquid phase, reported that the utilization of H_2O_2 was 88% with only 0.3% of the peroxide being decomposed after 5 h and a selectivity to PO of 95%. Their ratio epoxidation/decomposition (PO formed/H_2O_2 decomposed) is higher than 250, while in our study, this ratio was within a range between 1.5 and 0.005, depending on the reaction conditions used.

The hydrogen peroxide decomposed in the small amounts of extra-framework titanium contained in the synthesized TS-1 will not be affected by the addition of the flow of propene, since these sites are not active for the epoxidation. Therefore, a catalyst in which most of the Ti is outside the framework of the zeolite, will mostly decompose the H_2O_2 vapor and produce very small amounts of PO. In the absence of amorphous Ti, it can be expected that the epoxidation/decomposition ratio will be even higher.

3.2. Gas-Phase Epoxidation. The main side reaction during the gas-phase epoxidation of propene was the decomposition of hydrogen peroxide into oxygen and water. Nevertheless, some carbon-containing byproducts were also observed: acetaldehyde, CO, and CO_2 from the subsequent oxidation of propene oxide at high temperatures and propanal and small amounts of acetone from the isomerization due to the opening of the C(3)−O and the C(2)−O bonds, respectively. Additionally, small amounts of propionic acid, acetic acid, and propene glycol were detected. TGA analysis of the spent catalyst showed the deposition of organic compounds, which were burned at 220 °C and represented 1% of the amount of PO produced. These compounds can be associated with the olygomerization or polymerization of propylene oxide in the presence of water (Scheme 1).

Scheme 1
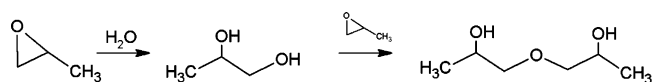
The use of hydrogen peroxide in excess with respect to propene was not possible, since all the peroxide added reacted with full conversion in all the experiments, partially to give PO and byproducts and partially being decomposed. This contrasts with the findings of Klemm et al.,[6] who reported that only after a modified residence time of 0.12 $g_{cat}\cdot s/mL$ STP they obtained full conversion of hydrogen peroxide. By maintaining an excess of propene and varying the concentration of peroxide below stoichiometric amounts, the selectivity to PO remains constant around 40%, only increasing slightly with the peroxide concentration. This value is higher than the 25% reported by Klemm et al.[6] for the experiments in their laboratory setup. In Figure 3, it can be seen that there is an almost constant ratio between the partial pressure of H_2O_2 and the PO formed, which indicates that the two competing reactions (epoxidation and decomposition) are both probably of the same order with respect to peroxide, evolving in the same manner as the concentration of the reactant is increased. In this case, the ratio epoxidation/decomposition (PO formed/H_2O_2 decomposed) was 1.5.
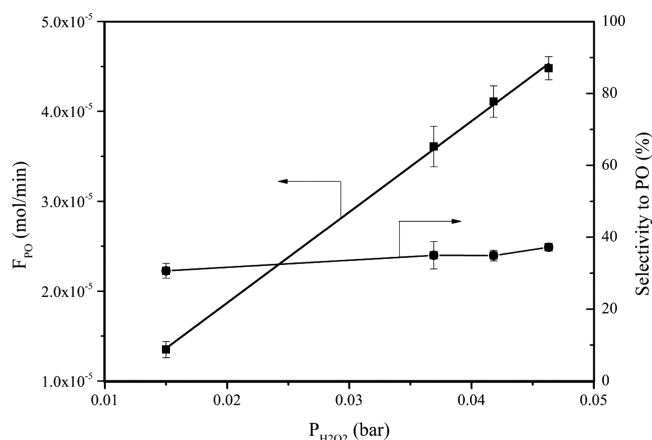
Figure 3. Dependence of the PO production and selectivity of hydrogen peroxide to PO on the concentration of H_2O_2. Excess of C_3H_6 (0.07 bar), 50 mg TS-1, total flow 50 mL/min.
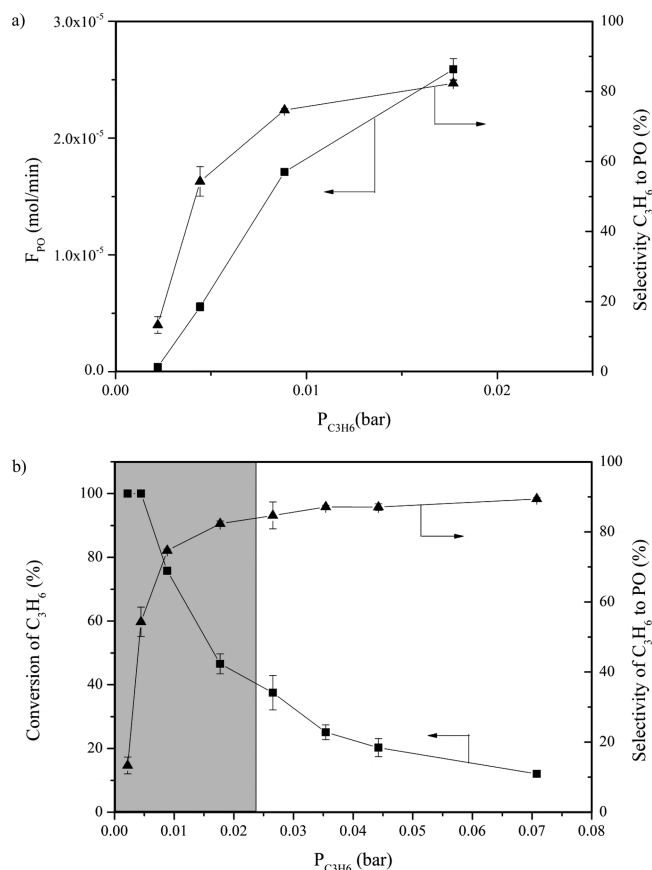

Figure 4. (a) Dependence of the PO production rate and the selectivity of propene to PO on the partial pressure of C_3H_6. (b) Conversion and selectivity of C_3H_6 as a function of the partial pressure of propene. Greyed area: Excess of hydrogen peroxide. White area: Excess of propene. Constant $P_{H_2O_2}$ = 0.024 bar. Total flow rate: 100 mL/min. Temperature: 140 °C. 10 mg of TS-1.

The influence of the catalyst loading was evaluated by varying the amount of catalyst in the range from 100 to 10 mg. The use of even lower quantities did not give accurate results due to bypassing of the flow past the catalyst. It was observed that even with loadings of TS-1 of 10 mg, the conversion of hydrogen peroxide was always complete, obtaining in all cases, for the same given reaction conditions, the same amount of propene oxide and the same amount of oxygen from the decomposition. With 10 mg of catalyst, the productivity of PO goes up to 10.5 $kg_{PO}/kg_{cat}\cdot h$ at a gas hourly space velocity (GHSV) of 450 000 $mL/g_{cat}\cdot h$, which is higher than the minimum required 1 $kg_{PO}/kg_{cat}\cdot h$ for industrial implementation.[6] The reason for this behavior is that the full conversion of hydrogen peroxide occurs already in the first section of the catalyst bed, because both reactions happen very fast. Therefore, the remainder of the catalyst has no effect in the reaction. This can be seen with the bare eye, since after the reaction, the initial part of the catalyst bed has a yellowish coloration, associated with a peroxo moiety which is a result of the interaction of the Ti atoms in the framework of the zeolite with H_2O_2/H_2O.[21] The rest of the catalyst remains white, which implies that when the reactant stream reaches it, H_2O_2 has been already fully converted.

When working below stoichiometric concentrations of propene, a progressive increment in PO formation was observed as the $P_{C_3H_6}$ increased (squares in Figure 4a). On the other hand, the low selectivity of propene to PO at very low concentrations of the reactant should be noticed. In this case, the main products were CO, CO_2, and acetaldehyde, suggesting that the big excess of peroxide can be responsible for the further degradation of propene oxide. As the amount of propene increases, the peroxide present is not enough for the subsequent oxidation of the formed PO, resulting in the growth of the selectivity. When concentrations higher than stoichiometrically needed were used, the selectivity approached 90% (Figure 4 b). Contrary to the selectivity, the conversion of propene decreased as the partial pressure of propene increased, even when concentrations of propene below stoichiometry were used. As explained before, according to our observations, the decomposition and the epoxidation are of the same order in hydrogen peroxide; however, the epoxidation rate also depends on the concentration of propene. According to Shin et al.,[20] in the liquid phase this order is 0.63. Therefore, if the

concentration of propene is not high enough, the epoxidation rate will decrease, while the decomposition rate remains the same. This results in a situation where the decomposition rate is faster than the epoxidation rate. In this case, most of the peroxide is consumed before it can react with all the propene available, resulting in a lower conversion of the latter.

The influence of the temperature on the epoxidation is shown in Figure 5. At the conditions employed in these experiments, the conversion of hydrogen peroxide is 100% and the conversion of propene is around 75%, at all temperatures. However, with increasing temperature, the selectivity of propene to PO raises from 70.2% at 120 °C to 75.8% at 150 °C. There are several factors that can explain this effect. First, at temperatures below the boiling point of hydrogen peroxide (140 °C) there can be a small amount of condensation of the reactant on the walls of the reactor or on the catalyst, that, as Satterfield et al.[7] explained, forms a multilayer and favors slightly the decomposition of hydrogen peroxide with respect to the epoxidation. Because both reactions occur so fast, it can also be that the rate limiting step is the diffusion of propene to the active Ti sites where the hydrogen peroxide is adsorbed. With increasing temperature, the propene will reach faster the hydroperoxy species, and the epoxidation will occur preferentially. The activation energies can also play a role in the effect of the temperature in the competitive reactions of this system: epoxidation and decomposition. Both the reaction rate constant
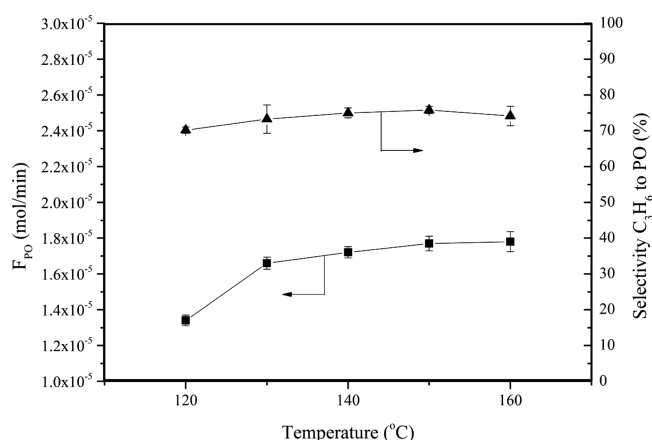
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Figure 5. Influence of the temperature in the PO production and in the selectivity of propene to PO: 2.4 vol % H_2O_2, 0.8 vol % C_3H_6, total flow rate: 116 mL/min, 14 mg TS-1.

of the decomposition and of the epoxidation increase with the temperature according to the Arrhenius equation. The fact that there is a point where the increase in temperature is not translated into an increase in the PO productivity (150 and 160 °C give approximately the same results) can be associated to the stronger increase of the decomposition constant compared to the epoxidation one, since the activation energy of the former is higher than the latter.

4. CONCLUSIONS

When working with H_2O_2 vapor, the main side reaction is its decomposition into oxygen and water. This is a surface reaction at temperatures below 450 °C and it is highly dependent on the materials that will be in contact with the chemical. Therefore, special attention should be paid to the selection of the working materials for the reactor and the piping. The decomposition at 140 °C over PTFE and quartz was 25 and 30%, respectively, while all the peroxide added was immediately decomposed when the reactor was made of a metal like titanium or stainless steel. The addition of the catalyst, TS-1, resulted in the full decomposition of the peroxide vapor. However, when a flow of propene was introduced, even though the conversion remained 100%, the peroxide was more selectively used for the epoxidation of propene, indicating that, at these conditions, the epoxidation rate is faster than the decomposition rate.

The gas-phase epoxidation of propene was achieved successfully, obtaining PO productivities of 10.5 $kg_{PO}/kg_{cat}\cdot h$ using only 10 mg of catalyst and a GHSV of 450 000 mL/$g_{cat}\cdot h$. This implies that, at the temperatures of this study, the reaction is very fast. The conversion of hydrogen peroxide vapor was 100% in all the experiments and at all the conditions tested and its selectivity to propene oxide was around 40% at different concentrations of peroxide used. In this case, an almost constant ratio between the partial pressure of peroxide and PO formed was obtained, implying that both the epoxidation and the decomposition are of the same order in peroxide. The analysis of the influence of the amount of propene added leads one to conclude that, as long as the concentration of propene is higher that the stoichiometrically required, its selectivity to PO will be close to 90%. Finally, an increase in the temperature up to 160 °C was translated in an increase in the amount of PO produced probably due to the higher decomposition of vapor peroxide at temperatures below its boiling point.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The preparation method for the synthesis of zeolite TS-1, as well as its characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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