Effect of hydrogen and propylene on the hydrogen peroxide decomposition over Pt, PtO and Au catalysts

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A B S T R A C T

The decomposition of hydrogen peroxide (H 2 O 2 ) on Pt, PtO and Au catalysts has been investigated in the presence of nitrogen, propylene and hydrogen. H 2 O 2 formation on the catalyst is known to be a key intermediate step for the direct synthesis of propylene oxide (PO) from hydrogen, propylene and oxygen. Therefore, during this reaction, H 2 O 2 is in contact with the catalyst on which it is produced, propylene and hydrogen. In this work we investigate the effect of the simultaneous presence of a metal catalyst (Pt, Au) and these gases on the H 2 O 2 decomposition. The presence of hydrogen favors the decomposition of H 2 O 2 over all the studied catalysts. This is attributed to the combination of direct decomposition and hydrogenation reactions. Furthermore, hydrogen changes the catalyst from an oxidized to a more metallic state accelerating the H 2 O 2 decomposition. We also observed the positive effect of propylene on decreasing the decomposition activity of Pt and Au. The experimental results were used to estimate reaction rate constants. The obtained rate constants hinted to changes of the catalyst during the decomposition as the main reason for reaction rate changes. This was confirmed to happen for Pt but not for the Au catalyst. The decrease of H 2 O 2 decomposition on Au in the presence of propylene is due to their interaction where propylene blocks the Au active sites responsible for the H 2 O 2 decomposition.

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1. Introduction

Propylene oxide (PO), an important bulk chemical intermediate, is used for the manufacture of polyurethanes (polyether polyls), polyesters (propylene glycol) and solvents (propylene glycol ethers). PO is currently being produced with processes which are considered to be environmentally and economically not attractive [1]. Several alternatives have been investigated in the last decades. The first “green” approach for the large scale PO production was the HPPO process [2,3], Hydrogen Peroxide (HP) to Propylene Oxide (PO). Here, hydrogen peroxide (H 2 O 2 ) is reacting with propylene on a titanium silicalite-1 (TS-1) catalyst to produce PO. Water is the main by product obtained. However, this process depends on the synthesis of H 2 O 2 via the Anthraquinone-auto Oxidation (AO), which is known to be a complex and not fully green process [4]. An economic improvement of the existing technologies can be achieved with the direct synthesis of PO from hydrogen, oxygen and propylene [5]. This reaction involves two consecutive steps. First, the H 2 O 2 is in situ generated from hydrogen and oxygen on a metal catalysts (Pd, Pt, Au) [4]. Second, H 2 O 2 reacts with propylene on TS-1 catalyst to form PO. The direct PO synthesis has successfully been implemented on a lab scale level [6-19]. However several limitations such as low PO productivity, hydrogen efficiency and PO yield still hinder the large scale application of this reaction. One of the main reason for the mentioned PO limitations is the H 2 O 2 formation, rate limiting step of direct PO synthesis. The rate of H 2 O 2 production is usually not fast enough to match the PO one [20]. Therefore, an improvement of the rate limiting step is translated into an optimization of the PO production.

The direct H 2 O 2 synthesis is also an important and very challenging reaction. The complexity of this reaction is known to be related to multiple factors such as the explosive nature of the reactants, the low solubility of hydrogen, the low selectivity and the instability of H 2 O 2 [21]. The catalysts responsible for the synthesis of H 2 O 2 are also responsible for its decomposition to water lowering its selectivity to uneconomic values [21]. The H 2 O 2 decomposition reaction on metallic catalysts such as Pd, Pt and Au has been extensively investigated in literature leading to important information on how to minimise this undesired side reaction [22-28]. A possible approach to reduce the decomposition

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reaction rate is the addition of acids and halides into the reaction medium with the positive effect of poisoning the catalyst sites active for the \( \text{H}_2\text{O}_2 \) decomposition [21]. Also, the oxidation state of the metal catalyst and the concentrations of hydrogen and oxygen were also found to be crucial in the \( \text{H}_2\text{O}_2 \) decomposition reaction. The disagreement between these reported results underline the complexity of the \( \text{H}_2\text{O}_2 \) decomposition topic. During the direct PO synthesis, the intermediate \( \text{H}_2\text{O}_2 \) will be in contact not only with the metal catalysts, but also with gas reactants such as hydrogen and propylene. These will further influence the performance of the catalyst in the direct PO synthesis [20]. The main catalysts utilized for the \( \text{H}_2\text{O}_2 \) and PO synthesis are single or bi-metallic systems (Pd, Pt, Au) deposited on supports containing Ti-species [4]. In our previous study [29], we investigated the effect of Pd and PdO catalysts in the presence of propylene and hydrogen on the decomposition of \( \text{H}_2\text{O}_2 \). In the present work we focus on the effect of Pt (metal and oxide) and Au in the presence of nitrogen, hydrogen and propylene. These studies allow a complete understanding of the effect of the main metal catalysts (Pd, Pt and Au) on the decomposition of \( \text{H}_2\text{O}_2 \) in the presence of propylene and hydrogen. Moreover, the experimental data obtained in this study were utilized to derive reaction rate constants for the decomposition reaction. The study was completed with XPS analysis providing important information on the state of the several catalysts before and after the reaction.

2. Experimental method

2.1. Catalyst preparation

Au and Pt (reduced and oxidised) on SiO\(_2\) support (Davisil 643, pore size 150 Å, 200–425 mesh) were the catalysts used in the reaction of \( \text{H}_2\text{O}_2 \) decomposition. The Au catalyst on SiO\(_2\) support was synthesized using the deposition–precipitation method simplified from literature [10]. Briefly, a solution containing Au (HAuCl\(_4\), 30 wt% in HCl) was slowly added to the support dispersed in deionized water. The pH of the solution was kept constant to 9.4 with ammonia (2.5 wt%). Finally the solution was stirred for one hour, filtered and calcined at 400 °C.

The Pt catalyst on SiO\(_2\) support was synthesized with wet impregnation method. A Pt precursor, tetraamineplatinum nitrate (99.9%), was dissolved in deionized water forming a 0.5 wt% Pt-solution. The support was impregnated with the Pt-solution, dried under vacuum (6 h), in a normal oven (12 h) and then calcined at 300 °C (3 h). The calcined sample is referred in this paper as the PtO/SiO\(_2\) catalyst. The metallic Pt catalyst, referred as reduced Pt/SiO\(_2\) catalyst, was obtained after the reduction of the calcined PtO/SiO\(_2\) under a hydrogen flow at 200 °C for 2 h. The result of the reduction will lead to a mixture of metallic and oxidised Pt, however in the present work the sample was labelled as Pt/SiO\(_2\) catalyst, to distinguish it from the non metallic PtO/SiO\(_2\). The reduction of this catalyst was done just before starting the experiments with the Pt/SiO\(_2\) catalyst, to avoid its further oxidation in air.

2.2. Experimental setup

The \( \text{H}_2\text{O}_2 \) decomposition tests were carried out in a glass reactor of 100 ml. The reaction was performed at a total pressure of 6 bar and 40 °C. The initial concentration of \( \text{H}_2\text{O}_2 \) was low enough to avoid the formation of explosive mixtures. Moreover, low concentrations of \( \text{H}_2\text{O}_2 \) better reproduce the overall PO synthesis reaction where low amounts of the intermediate compound are produced. The solution was stirred continuously at 700 rpm. In Fig. 1 is shown a schematic representation of the experimental setup.

In a typical \( \text{H}_2\text{O}_2 \) (Sigma Aldrich, 30 wt%, containing stabilizers) decomposition experiment, a solution of methanol (used as solvent), \( \text{H}_2\text{O}_2 \) (0.11–0.09 wt% in methanol) and 20 mg of catalyst were charged in the autoclave. The reactor was pressurized with nitrogen, hydrogen and propylene according to the experiment. The concentration of \( \text{H}_2\text{O}_2 \) in time was measured with ceric sulfate (Sigma Aldrich, 0.05 N) titration method. The detailed titration method has been reported elsewhere [30].

The commercial \( \text{H}_2\text{O}_2 \) contains stabilizers to avoid decomposition during transportation and handling of the material. However, in the presence of metallic nano particles (Pt, PtO and Au) the decomposition reaction cannot be suppressed and further stabilizers are required in the reaction condition. In literature, it has been reported that the addition of stabilizers (acids and halides) is crucial for the direct \( \text{H}_2\text{O}_2 \) synthesis and reactions without acids and halides lead only to water formation [31,32]. The presence of stabilizers will have a crucial effect in the direct propylene oxide reaction synthesis as already shown elsewhere [33].

3. Results and discussion

3.1. Catalyst characterization

To detect the morphology and the particle size of the synthesized catalysts, transmission electron microscope (TEM, FEI Tecnai G2 Sphera) images were recorded. In Figs. 2, 3 and 4 are shown the main characteristic images of the different catalysts with the
Fig. 2. TEM image and particle size distribution of Pt/SiO$_2$ catalyst.

Fig. 3. TEM image and particle size distribution of PtO/SiO$_2$ catalyst.

Fig. 4. TEM image and particle size distribution of Au/SiO$_2$ catalyst.
particle size distribution evaluated over 30 TEM images for the same catalyst. The metal loadings were quantified by ICP elemental analysis. The main information on the utilized catalysts is summarized in Table 1.

3.2. Effect of the gases on the decomposition

In our previous work [29], we reported the experiments for the decomposition of H₂O₂ on the SiO₂ material, used as a support for the metallic particles (Pt, PtO and Au). We showed that the SiO₂ support does not affect the decomposition of H₂O₂. In the present work, Pt/SiO₂, PtO/SiO₂ and Au/SiO₂ catalysts were tested in the decomposition of H₂O₂ in the presence of nitrogen, hydrogen and propylene. Their combination might influence the decomposition of H₂O₂ in situ generated during the PO synthesis. The first experiment conducted was the decomposition of H₂O₂ on metal catalysts in the presence of nitrogen. This allows to isolate and study only the effect of the metals on the decomposition being nitrogen an inert gas. These results were then utilized as a reference for the decomposition of H₂O₂ in the presence of propylene and hydrogen. In Figs. 5, 6 and 7 are shown the decomposition trends for the different catalysts in the presence of the nitrogen, propylene and hydrogen.

From a qualitative comparison of H₂O₂ conversion curves in time for the metallic catalysts and different gases, an evident difference between all the cases analysed is observed. This indicates that the operating conditions have an influence on the decomposition reaction. The first statement that can be deduced from our experimental data is that hydrogen increases the decomposition rate of all the investigated metals. This trend was also observed in our previous work on the decomposition of hydrogen peroxide on Pd catalyst [29].

As we show in our previous work for Pd catalyst [29] and as reported in literature, the main decomposition of H₂O₂ on the metal species is believed to happen through the dissociative adsorption of H₂O₂ on the catalyst. This leads to the formation of two OH radicals. The presence of hydrogen, which also dissociatively adsorbs on the catalyst, favors the further hydrogenation of these active radicals to water [34,22,24]. The comparison of H₂O₂ conversion curves (Figs. 5, 6 and 7) also show that the decomposition of H₂O₂ on the PtO is much faster in the presence of hydrogen in comparison to the nitrogen. The presence of hydrogen affects the oxidation state of the catalyst reducing it to a more metallic material, therefore more active in the decomposition [34,36]. An opposite trend is observed for the decomposition in the presence of propylene. In fact, the H₂O₂ decomposition becomes much slower for the Pt and Au catalyst and remains similar to the case in the presence of nitrogen for the PtO catalyst. This suggests that the propylene is not influencing the decomposition reaction on the PtO catalyst showing a limited interaction between this gas and PtO catalyst. The neutral effect of propylene was also observed in our previous work on the PdO catalyst [29] showing that the oxidized metals are much stable materials in the decomposition of
of H$_2$O$_2$ and have a reduced interaction with propylene. Something different happens for the metallic surfaces (Pt and Au). A drastic decrease of the H$_2$O$_2$ decomposition is observed in the presence of propylene. This suggests a strong interaction between the propylene and the metal surfaces which blocks the active sites of the decomposition. The presence of propylene in the direct PO synthesis has the advantage of decreasing the decomposition of H$_2$O$_2$ on the metal catalysts. However, its effect on these metals is still not fully understood.

3.3. Estimation of the reaction rate constants (k)

The experimental study of the evolution of H$_2$O$_2$ concentration in time (see Figs. 5, 6 and 7) allows to estimate kinetic parameters such as the constant reaction rate (k) of the decomposition. Quantifying the reaction constants allows to better compare the decomposition rates of our different systems. The experimental data were fitted with a first order kinetic expression. Due to the low initial concentrations of H$_2$O$_2$, a first order kinetic equation becomes a good approximation for the decomposition reaction [37]. In fact, for low initial concentrations the surface coverage of H$_2$O$_2$ becomes very small and proportional to the concentration. Therefore, the Langmuir–Hinshelwood rate mechanism becomes a first order rate equation.

$$\frac{dC_A}{dt} = -k \cdot C_A$$ (1)

The rate constants for the different cases are estimated with non linear regression of the data using Athena Visual Studio. The rate constant values are reported in the tables below. The quality of the fit is assessed based on the value of $R^2$ which represents the discrepancy between the experimental and the predicted values. The values of $R^2$ are reported for the different decomposition rate constants. Moreover, the goodness of the fit is also ensured by the calculated confidence intervals being always smaller than the value of the parameter itself.

Fig. 8 shows the experimental values of the H$_2$O$_2$ decomposition on Pt catalyst and in the presence of propylene, nitrogen and hydrogen together with the predicted ones. The estimated values of the constant reaction rates (k) are reported in Table 2. As observed above (see Figs. 5, 6 and 7), the estimated values of k confirm that the decomposition of H$_2$O$_2$ is much faster in the presence of hydrogen. The first order rate equations well predict the reaction rate constants for the hydrogen and nitrogen. However, the fitting of the H$_2$O$_2$ decomposition in the presence of propylene is quite poor ($R^2 = 0.76$). The H$_2$O$_2$ decomposition on Pt catalyst in the presence of propylene is not well described with a first order rate equation.

Fig. 9 shows the experimental values of the H$_2$O$_2$ decomposition on Pt catalyst and in the presence of propylene, nitrogen and hydrogen together with the predicted values. The estimated values of the constant reaction rates (k) are reported in Table 3. As observed from the experimental results, (see Fig. 5, 6 and 7) the estimated values of k confirm that the decomposition of H$_2$O$_2$ is much faster in the presence of hydrogen (Table 4).

Fig. 10 shows the experimental values of the H$_2$O$_2$ decomposition on Au catalyst and in the presence of propylene, nitrogen and hydrogen together with the predicted ones. The estimated values of the constant reaction rates (k) are reported in Table 2. Also for the Au catalyst, the decomposition of H$_2$O$_2$ in the presence of hydrogen becomes faster in comparison to the rest of the gases (propylene and nitrogen). Similarly to the Pt catalysts, the fitting of the H$_2$O$_2$ decomposition in the presence of propylene is quite poor. This condition is not well described with a first order rate equation.

From the fitting of the experimental data with a first order rate equation (see Fig. 8, 9 and 10), it was evident that this equation was
not accurately describing all the investigated decomposition reactions. Some cases show a discrepancy between the experiments and the predicted values. This suggests that the decrease of the decomposition rate is not simply attributed to the decrease of the reactant concentration. Moreover, the rate in these cases showed a clear transition between two different trends. Both, the first and the last part of the reaction rate (concentration) in time follow a first order behaviour. Such a behaviour can be explained with the deactivation or the change of the oxidation state of the catalyst. Therefore we decided to fit the experimental data that presented a discrepancy from the predicted values with a modified first order power law equation. In this equation, we assume that the reaction rate of H₂O₂ is changing during the decomposition. The equation also includes the transition time between the two reaction rates. Therefore, two different k values (k₁, k₂) and a transition time (tᵣ) are the parameters estimated with Eq. (2) (Table 5) (Fig. 12).

\[
\frac{dC_A}{dt} = \left( k_1 \times \frac{(t_f - t)}{t_f} + k_2 \times \frac{t}{t_f} \right) \times C_A
\]  

(2)

The modified first order equation perfectly fits the H₂O₂ decomposition on Pt in the presence of nitrogen and propylene, and on Au in the presence of the propylene. These were the experimental data that could not be described with a normal first order equation. A slow down of the reaction is observed for the Pt and Au catalysts in the presence of propylene noticeable from the decrease in time of the constant rate value from k₁ to k₂. This decrease of the decomposition reaction on Pt and Au in time suggests changes to the catalysts which become more stable during the reaction. Therefore, we conducted XPS analysis of the fresh and used Au and Pt catalysts in the presence of propylene. In both cases, the propylene decreases the decomposition of H₂O₂. The results are shown in (Figs. 13 and 14) (Table 6).

Fig. 13 shows the XPS results of the fresh and the used Pt/SiO₂ catalyst in the presence of propylene. The used sample presents an increase of the PtO/Pt peak area ratio compared to the fresh sample.

This indicates that the amount of the oxide metal present in the sample has increased during the decomposition reaction (blue and purple line).

Fig. 14 shows the XPS results of the fresh and used Au/SiO₂ catalyst in the presence of propylene. The ratio between the oxidized and the metal Au catalyst has not changed after the reaction showing that Au is very stable in the reaction conditions. For the Pt/SiO₂ catalyst, the XPS analyses show that an increase of the PtO/Pt ratio is observed after the reaction in the presence of propylene. The decrease of the decomposition reaction rate on Pt catalyst is associated to a change in the oxidation state of the metal. This result is in agreement with the literature [34]. In fact, it has been reported that the oxidized state of a metal is more stable in the H₂O₂ decomposition. H₂O₂ is a strong oxidizer that can itself change the state of the catalyst [23]. However, if the changing of the oxidation state of Pt/SiO₂ due to H₂O₂ would be the only cause of the changing of the decomposition reaction rate, the decomposition rate in the presence of propylene and nitrogen would be similar. However, as shown in Fig. 14, the decomposition rate in the presence of only nitrogen was faster in comparison to the propylene one. Therefore, the presence of propylene, which competes with H₂O₂ to adsorb on the catalyst active sites [29], in combination with the transition of Pt from a metallic to a more oxidized state leads to a more stable catalyst towards the decomposition. Similar effect to the Pt is
observed for the Au catalyst in the presence of propylene. However, from the XPS analysis it is evident that the ratio between metal and oxidized state of Au does not change during the reaction. Therefore, the change in the oxidation state is not responsible for the decrease of the decomposition rate. This is attributed to the interaction between the Au and propylene, as observed in the reaction of hydrogen oxidation [38]. This suggests that the propylene adsorbs on the Au particles blocking and decreasing the number of active sites available for the decomposition reaction. Therefore, the same effect of propylene with Pt and Au on decreasing the H2O2 decomposition rate is deriving from different interactions of this gas with the metal catalysts. In the first case (Pt), the effect of the propylene presence is combined with the change of the oxidation state making the catalyst more stable towards the decomposition reaction. In the second case, the oxidation state of Au is not affected by H2O2, however propylene adsorbs on the metal catalyst blocking the sites active for the H2O2 decomposition. These results show that the interaction of propylene and Au is much stronger compared to the one with Pt leading to a stronger decrease of the decomposition activity of the metal.

### Table 6

<table>
<thead>
<tr>
<th>C8H16</th>
<th>k1</th>
<th>8.72 x 10⁻³ ± 9.7 x 10⁻⁴</th>
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<tbody>
<tr>
<td></td>
<td>k2</td>
<td>1.45 x 10⁻⁴ ± 3.8 x 10⁻⁴</td>
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<tr>
<td></td>
<td>tr</td>
<td>129 ± 85</td>
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<tr>
<td>R²</td>
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<td>0.98</td>
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Fig. 13. XPS analysis of Pt/SiO2 catalyst before (left) and after (right) the reaction in the presence of propylene.

Fig. 14. XPS analysis of Au/SiO2 catalyst before (left) and after (right) the reaction in the presence of propylene.

### 4. Summary

The decomposition of H2O2 on metal catalysts (Pt, PtO and Au) is affected by the presence of hydrogen and propylene gases. This was shown to be true also for the Pd and PdO catalyst, as observed in our previous work [29]. Hydrogen and propylene are the reactants needed for the direct synthesis of propylene oxide (PO). We show that the presence of hydrogen increases the decomposition of H2O2 due to the combined effect of the decomposition and the hydrogenation reactions. These results clearly indicate that an improvement of the direct PO synthesis can be achieved by controlling and lowering the concentration of hydrogen in the system. Moreover, the first order dependence of the decomposition rate on the concentration of H2O2 suggests to avoid the formation of high H2O2 concentrations during the direct PO synthesis reaction. The immediate consumption of the H2O2 in situ generated with propylene to form PO in combination with low values of hydrogen ensure low H2O2 concentrations in the system. The presence of propylene decreases the decomposition activity of all the metal catalysts analysed in this study (as also observed for Pd and PdO catalysts [29]). Thus, higher propylene concentrations are recommended to be used in the direct PO synthesis. Since the interaction between propylene and Au reduces the decomposition rate more than for the other metals, traces of Au are recommended to be used in the final catalyst for the direct PO synthesis. Moreover, other metal catalysts show to be very sensitive to the reaction conditions (XPS results). The presence of higher O2 in the system, in combination with lower hydrogen and propylene can be implemented to favour the metal transition to a more oxidized state as it was shown to be more stable towards the decomposition reaction. Also, the neutral effect of the nitrogen in the system, allows lowering the...
concentration of H2 and operating the system with a mixture of nitrogen and oxygen. The presence of nitrogen would favour the safe operating conditions without any relevant effect on the decomposition of H2O2. Therefore, the final catalyst-reactor design for the direct synthesis of PO should ensure lower hydrogen content in combination with high propylene and oxygen. The neutral presence of nitrogen is important for safety reasons. The catalyst to be utilized is a metal catalyst (Pd or Pt preferably in an oxidized state) in combination with small amounts of Au.

5. Conclusions

The effect of hydrogen and propylene on the H2O2 decomposition on Pt, PdO and Au catalysts was investigated. We showed that the presence of hydrogen contributes to a fast decrease of the H2O2 concentration due to the combination of decomposition and hydrogenation reactions. Propylene decreases the H2O2 decomposition interacting with the metal catalysts. The theoretical results show that some of the investigated cases have a change in time of the decomposition reaction rate. This was proved to be due to the change of the oxidation state for the Pt and propylene system and to the strong interaction between the metal and propylene for the Au system. The propylene causes a decrease of the H2O2 decomposition interacting in different ways with Pt and Au.

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