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# Selective decomposition of hydrogen peroxide in the epoxidation effluent of the HPPO process

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#### ABSTRACT

This work describes the selective  $H_2O_2$  decomposition in the exit stream of the epoxidation reactor employed in the Hydrogen Peroxide–Propylene Oxide (HPPO) process. Pd/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were tested. The effects of the reaction temperature and the pH of the solution on catalyst performance were investigated. It was found that the Pt catalyst is much more active than its Pd counterpart. An increase in the temperature and the pH of the solution resulted in an increase in the H<sub>2</sub>O<sub>2</sub> decomposition rate; however, a parallel increase of by-products from PO was also observed. Working with a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst under optimized reaction conditions (333 K, pH = 7), hydrogen peroxide can be completely decomposed at reaction times of 120 min with no by-products produced from propylene oxide.

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# 1. Introduction

Propylene oxide (PO) is the third-largest propylene derivative used in the chemical industry. It is commonly used for making polyurethane, unsaturated resins, surfactants, and other commercial chemicals. PO is currently produced by two different processes involving chlorohydrin and hydroperoxide [1]. Currently, due to environmental and economic concerns, there is a pressing need for new PO-synthesizing processes. An interesting alternative is the epoxidation of propene with hydrogen peroxide. This epoxidation process produces PO with very high selectivity (95% or higher) and theoretically excretes only  $H_2O$  as a by-product [1]. However, its commercialization has been hindered largely by the supply of  $H_2O_2$ .

Hydrogen peroxide is now almost exclusively produced by the anthraquinone process in large plants in which production costs are offset by the scale. The transportation cost for  $H_2O_2$  is too high to be used for the production of bulk chemicals like PO. One strategy that has been proposed thus far to address the problems of  $H_2O_2$  production involves the integration of the anthraquinone process for  $H_2O_2$  synthesis with the propene epoxidation process, a suitable solvent system has to be developed to facilitate not only the

epoxidation of propene but also the sequential hydrogenation and oxidation of alkyl-anthraquinone. Another possible solution is the direct synthesis of  $H_2O_2$  from  $H_2/O_2$  mixtures with supported palladium (or palladium alloy) catalysts in acidified solvents (water, methanol) [3–9]. The propylene oxide production based on the direct on-site synthesis of hydrogen peroxide is abbreviated as HPPO (Hydrogen Peroxide–Propylene Oxide).

The epoxidation of propylene with hydrogen peroxide on titanium catalysts is very effective [10-16], but 100% conversion of hydrogen peroxide cannot be achieved industrially in a practical reactor size. As a consequence, small amounts of hydrogen peroxide still remain at the exit of the epoxidation reactor. Hydrogen peroxide cannot be introduced in the PO purification steps because its decomposition produces oxygen, which can produce serious safety problems. A simple way to solve this drawback is to decompose the residual hydrogen peroxide at the exit of the epoxidation reactor once unreacted propylene has been separated. The oxygen gas generated by hydrogen peroxide decomposition will simply be removed by flowing an inert gas.

In the existing literature, metal oxides are often employed for hydrogen peroxide decomposition [17–22]. However, metal oxides decompose  $H_2O_2$  into hydroxyl radicals (HO•). Hydroxyl radicals are highly volatile and are capable of reacting with a wide number of organic compounds [19,21], including the organic components of the epoxidation effluent. This is detrimental for the whole process and results in a loss of the PO product. For this reason, our aim in the present work was the selection of supported noble metal catalysts



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that are active in the hydrogen peroxide decomposition with a minimal formation of hydroxyl radicals [23,24]. The metal nanoparticles deposited on the carrier substrate constitute the active phase in this reaction. In these catalysts, activity may be related to the higher adsorption of  $H_2O_2$  on reduced metal sites [23,24].

This work was undertaken with the aim to study the catalytic decomposition of hydrogen peroxide in a solution that simulates the epoxidation reactor exit stream after propylene removal in an HPPO process. This research focuses on the minimal formation of by-products derived from the organic compounds present in the stream.

# 2. Experimental methods

### 2.1. Catalysts

Alumina-supported palladium and platinum catalysts were employed in this work.  $Pd/Al_2O_3$  and  $Pt/Al_2O_3$  (0.5 wt%) shaped as cylindrical pellets (3.2 mm × 3.2 mm) were purchased from Johnson Matthey. The effectiveness factor is comparable in both catalysts since this only depends on the intrinsic kinetic constant of each catalyst and both exhibit a similar shape and size, being the operating temperature the same in both cases. These catalysts are commercially distributed in the reduced (metallic) state. For comparative purposes, cylindrical pellets (3.2 mm × 3.2 mm) of bare  $\gamma$ -alumina were employed.

# 2.2. Catalysts characterization

Textural properties were determined from the adsorptiondesorption isotherms of nitrogen recorded at 77 K with a Micromeritics TriStar 3000. The specific area was calculated by applying the BET method to the range of relative pressures ( $P/P^0$ ) of the isotherms between 0.03 and 0.3 and taking a value of 0.162 nm<sup>2</sup> for the cross-section of adsorbed nitrogen molecule at 77 K.

Powder X-ray diffraction (XRD) patterns were recorded in the 0.5–10°  $2\theta$  range using step mode (0.05, 5 s) with a Seifert 3000 XRD diffractometer equipped with a PW goniometer with Bragg–Brentano  $\theta/2\theta$  geometry, an automatic slit, and a bent graphite monochromator.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a Mg K $\alpha$  ( $h\nu$  = 1253.6 eV) non-monochromatic X-ray source. The samples were degassed in the pretreatment chamber at room temperature for 1 h prior to being transferred into the instrument's ultra-high vacuum analysis chamber. The silicon, oxygen, sulfur and carbon signals were scanned several times at a pass energy of 20 eV in order to obtain good signal-to-noise ratios. The binding energies (BE) were referenced to the BE of the C 1s corelevel spectrum at 284.9 eV. The invariance of the peak shapes and widths at the beginning and end of the analyses indicated constant charge throughout the measurements. Peaks were fitted by a non-linear least square fitting routine using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction [25].

## 2.3. Hydrogen peroxide decomposition

Catalysts were tested in the decomposition of hydrogen peroxide. The catalytic tests were performed in a high pressure stirred reactor (Autoclave Engineers) equipped with a falling basket. In a typical run, the catalyst ( $H_2O_2$ /metal = 1200/1 molar) was put inside an autoclave with 325 g of liquid mixture. The reactor was purged with N<sub>2</sub> and pressured to 0.5 MPa. When the pressure reached a constant value, the mixture was heated up to the reaction temperature by maintaining continuous stirring (1000 rpm).

#### Table 1

Textura	l properties of	the cata	lysts	employed	
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Catalyst	BET surface area $(m^2/g)$	Pore Volume (ml/g)	Pore diameter (nm)
$Pd/Al_2O_3$	99.1	0.24	10
$Pt/Al_2O_2$	97 7		10

To start the reaction, the basket was lowered, putting the catalysts in contact with the reaction mixture. Hydrogen peroxide and water concentrations were measured by iodometric and Karl–Fischer standard titrations, respectively. The concentration of the organic compounds was determined by GC-FID using an Agilent 6850 instrument fitted with a DB-WAX capillary column. The reaction mixture was prepared to simulate the effluent of the epoxidation reactor in an HPPO process after the elimination of propylene. This mixture consists of the following: 506 ppm acetaldehyde, 12.74 wt% OP, 73.2 wt% MeOH, 0.49 wt% 1-methoxy-2-propanol, 0.78 wt% 2-methoxy-1-propanol, 0.59 wt% 1,2-propanediol and 2 wt%  $H_2O_2$  [6].

# 3. Results and discussion

#### 3.1. Structural characteristics of the catalysts

Palladium and platinum catalysts were tested in the selective  $H_2O_2$  decomposition at 333 K. Both catalysts were active (Fig. 1). However, the  $Pt/Al_2O_3$  catalyst was more active than its Pd counterpart, reaching total conversion in 120 min. No changes in the concentration of propylene oxide were detected, but small changes in PO concentration can be masked by analytical errors. For this reason, it may be more accurate to monitor the time dependence of the concentration of by-products derived from PO.

The concentration of these compounds remained almost constant for the two metal catalysts  $(Pd/Al_2O_3 \text{ and } Pt/Al_2O_3)$  (Fig. 1). A blank experiment was performed using metal-free  $\gamma$ -alumina  $(Al_2O_3)$  pellets. The  $\gamma$ -alumina alone is active in the hydrogen peroxide decomposition reaction (Fig. 1), but the hydrogen peroxide conversion is clearly smaller than that observed with the metal catalysts. This reaction was previously observed [24], suggesting that the decomposition occurs on the surface with the formation of HO• or HO<sub>2</sub>• radicals. The formation of radicals affects the formation of by-products (Fig. 1). For this system, the formation of 2-methoxy-1propanol, 1-methoxy-2-propanol and 1,2-propanediol is evident.

These results indicate that  $Pt/Al_2O_3$  is the most active catalyst (Fig. 1). The characterization results showed no differences in the textural properties of both samples (Table 1). XRD analysis (not shown here) showed the diffraction peaks of  $\gamma$ -alumina without any diffraction line originating from the metal species. This confirms the high dispersion of platinum, most probably as very small clusters with a size of less than 3 nm supported on the alumina substrate.

The chemical state of the platinum or palladium was derived from the X-ray photoelectron spectra. The Pd 3d and Pt 4d corelevels showed the characteristic spin–orbit splitting of Pd 3d and Pt 4d levels. The most intense (Pd  $3d_{5/2}$  or Pt  $4f_{7/2}$ ) component of the doublet is located at lower binding energies, and the least intense (Pd  $3d_{3/2}$  or Pt  $4f_{5/2}$ ) component is located at higher binding energies. Chemical information can be extracted from each of these components, but attention will only be paid to the more intense one (Pd  $3d_{5/2}$  or Pt  $4f_{7/2}$ ). Fresh samples showed the presence of one component (Table 2) corresponding to a well-dispersed metallic species on alumina (Pd  $3d_{5/2}$  336.0 eV, Pt  $4f_{7/2}$  314.0 eV). In addition, the XPS of the used samples showed the presence of two components (Table 2): one due to the metallic species similar to that found in the fresh samples and another located at a higher binding energy (Pd  $3d_{5/2}$  337.8 eV or Pt  $4f_{7/2}$  316.9 eV) due



Fig. 1. Hydrogen peroxide (a) and by-products (b) derived from PO concentration profiles during the H<sub>2</sub>O<sub>2</sub> decomposition at 333 K using Pd and Pt catalysts and alumina support.

to the presence of an oxidized species ( $Pd^{2+}$  or  $Pt^{2+}$ ). The presence of these oxidized species points to a mechanism of  $H_2O_2$  decomposition that involves redox processes where oxidized and reduced metal species participate.

Quantitative XPS data (Table 2) revealed that the surface Pd(Pt)/Al ratio is higher for Pd than for Pt in both the fresh and used catalysts. These results indicate that metal exposure is higher in the Pd catalyst than in its Pt counterpart, meaning it has higher dispersion. However, the Pt catalyst is clearly more active in hydrogen peroxide decomposition than its Pd counterpart. Thus, Pt has higher intrinsic activity than palladium for this reaction.

# 3.2. Catalytic activity

The catalysts were tested for the decomposition of hydrogen peroxide present in a liquid mixture that simulates the exit stream of an industrial HPPO reactor. The effects of reaction temperature and the pH of the solution on catalyst performance were analyzed in some detail.

#### 3.2.1. Influence of temperature

The influence of reaction temperature was studied by checking the performance of the  $Pt/Al_2O_3$  catalyst at temperatures in the range of 313–353 K. It was observed that an increase in reaction temperature is paralleled by an increase in the decomposition rate of hydrogen peroxide (Fig. 2). The  $H_2O_2$  concentration drops very quickly, with a conversion of greater than 90% after a 15 min

Table	2
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XPS analysis data for fresh and used catalysts.

Catalyst	Binding Energy (eV) of Pd 3d <sub>5/2</sub> and Pt 4d <sub>5/2</sub> Levels	Surface Atomic Ratio (Pt or Pd)/Al	
Pd/Al <sub>2</sub> O <sub>3</sub> fresh	336.0	0.0083	
Pd/Al <sub>2</sub> O <sub>3</sub> used	337.9 (34)	0.0120	
	336.0 (66)	0.0120	
Pt/Al <sub>2</sub> O <sub>3</sub> fresh	314.0	0.0041	
Pt/Al <sub>2</sub> O <sub>3</sub> used at	316.8 (42)	0.0042	
333 K	314.2 (58)	0.0042	
Pt/Al <sub>2</sub> O <sub>3</sub> used at	316.9 (53)	0.0042	
353 K	314.2 (47)	0.0042	
Pt/Al <sub>2</sub> O <sub>3</sub> used at	316.9 (42)	0.0040	
353 K and pH = 10	314.2 (58)	0.0040	

reaction time and complete conversion after 30 min. In addition, the increase in the temperature from 313 K to 353 K is accompanied by a parallel increase in the formation of byproducts from PO, yielding 1-methoxy-2-propanol, 2-methoxy-1-propanol, and 1,2-propanediol (Fig. 2). The side reactions participating in the formation of such products are a serious drawback for an industrial application because the decomposition of unreacted hydrogen peroxide yields a loss of the desired PO product. Therefore, separation/purification units are imperative and could result in an increase in the operation process costs in order to reduce the loss of PO selectivity.

Surface analysis of spent catalysts via XPS analysis demonstrated the presence of two platinum species,  $Pt^0$  and  $Pt^{2+}$  (Table 2). The proportion of oxidized species increased with the reaction temperature. This effect can be attributed to the higher oxidation capability of hydrogen peroxide at increased temperatures. Quantitative XPS data, i.e., Pt(Pd)/Al surface atomic ratios, reveal valuable information (Table 2). The Pt/Al surface atomic ratio of the Pt catalyst does not change after use in the reaction at different temperatures and is very close to the value determined on the fresh catalyst. These results indicate that the Pt catalyst is a robust system and is particularly well suited for the target reaction under the reaction conditions selected in this work.

#### 3.2.2. Effect of pH

Hydrogen peroxide decomposes in aqueous solutions at basic pH. We have tested the effect of the solution pH on the catalyzed decomposition of hydrogen peroxide present in a propylene-free mixture that simulates the exit stream of an industrial HPPO reactor. The hydrogen peroxide decomposition slightly increases in the basic solution (Fig. 3), but no significant changes are observed in the formation of PO by-products. As a consequence, the increased formation of PO by-products is clearly more affected by an increase in the reaction temperature than an increase in the pH of the solution over this short reaction time. Nonetheless, working with a basic solution is not recommended for an industrial process because corrosion-resistant equipment is required, and a neutralization unit should be incorporated. Thus, the use of a basic solution does not result in enough of an increase in the reaction rate to justify the



Fig. 2. Hydrogen peroxide and by-products derived from PO concentration profiles during the H<sub>2</sub>O<sub>2</sub> decomposition at 333 K and 353 K using a Pt catalyst.



Fig. 3. Hydrogen peroxide and by-products derived from PO concentration profiles during the H<sub>2</sub>O<sub>2</sub> decomposition at 353 K and varying pH using Pt.

complication in the industrial process needed for its implementation.

# 4. Conclusions

The selective decomposition of hydrogen peroxide present in the exit stream of the epoxidation reactor in an HPPO process can be performed with an alumina-supported platinum (or palladium) catalyst without significant formation of by-products derived from propylene oxide. A Pt/Al<sub>2</sub>O<sub>3</sub> catalyst working at the optimum temperature (333 K) completely decomposes the hydrogen peroxide present in the exit stream at reaction times no longer than 120 min.

Quantitative XPS data revealed that the Pd catalyst has a higher number of exposed atoms on the surface than its Pt counterpart, even though the Pt catalyst is much more active. This indicates that Pt atoms display a higher intrinsic activity in the reaction of hydrogen peroxide decomposition than their Pd counterpart.

Accurate measurement of the binding energies of core-electrons in the used catalysts revealed the presence of two Pt species, suggesting that the decomposition reaction occurs via a redox mechanism where oxidized and reduced metal species are involved. Platinum dispersion does not seem to be modified after use in the reaction under several reaction conditions, and Pt catalyst remains similar to that of the fresh catalyst. These findings indicate that Pt/Al<sub>2</sub>O<sub>3</sub> is a robust and stable catalyst for the target reaction.

Increases in the reaction temperature and/or pH resulted in a higher  $H_2O_2$  decomposition rate, but they also increased the formation of by-products from PO. The loss of PO selectivity and by-product formation are not desirable from an industrial point of view because separation/purification units have to be added to the plant hardware, resulting in an increase in operation process costs and process economy.

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