

# INFLUENCE OF CATALYST TREATMENTS ON THE DECOMPOSITION OF HYDROGEN PEROXIDE ON SUPPORTED PALLADIUM CATALYSTS

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**Abstract**— The decomposition of hydrogen peroxide was studied on Pd catalysts between 293 K and 313 K. The apparent activation energy value was calculated for all the catalysts and it varied between 27 and 55 kJ/mol. For all the catalysts tested, treatment with hydrogen resulted in a significant increase in the reaction rate, as well as a decrease in the apparent activation energy for the reaction. All the reactions were well represented by a first order rate law with respect to H<sub>2</sub>O<sub>2</sub>. The effect of the treatment with H<sub>2</sub>O<sub>2</sub> was studied in successive reactions without catalyst exchange. A small deactivation was observed in the 5.0% Pd/AC and 0.5% Pd/AC catalysts after four H<sub>2</sub>O<sub>2</sub> decomposition reactions.

**Keywords**— Hydrogen peroxide, Palladium Catalyst, Decomposition, Kinetics.

## I. INTRODUCTION

Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, has been used in several applications, such as wastewater treatment (Pignatello, 1992; Lin *et al.*, 1998; Perathoner and Centi, 2005; Dantas *et al.*, 2006; Zazo *et al.*, 2006), as propellant for liquid propellant engines (Sisco *et al.*, 2005), in bleaching paper pulp (Lopez *et al.*, 2003; Wojciak *et al.*, 2007), and in the food and pharmaceutical industries to clean and disinfect packages (Simmons *et al.*, 1997; Verce *et al.*, 2008). In general, the efficiency of these applications depends on the decomposition of H<sub>2</sub>O<sub>2</sub> in homogeneous or heterogeneous mediums. The iron oxide catalyst has been extensively studied in wastewater treatment perhaps due to its low cost (Chou and Huang, 1999; Huang *et al.*, 2001; Hermanek *et al.*, 2007). However, other catalysts have been studied for improving the catalytic activity in those processes (Ariafard *et al.*, 2003; Petlicki *et al.*, 2005; Shivankar and Thakkar, 2005).

The production of H<sub>2</sub>O<sub>2</sub> from hydrogen and oxygen is an environmentally friendly process of great practical importance. Palladium, Pd, is the catalyst most studied for this reaction (Choudhary *et al.*, 2001; Landon *et al.*, 2003; Voloshin *et al.*, 2008; Choudhary and Jana 2008; 2009), but the decomposition of H<sub>2</sub>O<sub>2</sub> on the Pd catalyst is a parallel reaction that decreases the selectivity for H<sub>2</sub>O<sub>2</sub> and, thus, the production of H<sub>2</sub>O<sub>2</sub> becomes inefficient. The H<sub>2</sub>O<sub>2</sub> decomposition on Pd catalyst has been studied by Choudhary *et al.* (2002, 2006, 2007) under different conditions in order to identify factors that af-

fect the H<sub>2</sub>O<sub>2</sub> decomposition on Pd catalyst. They found that the decomposition of H<sub>2</sub>O<sub>2</sub> decreased with the oxidation of Pd to PdO. In addition, Choudhary *et al.* (2007) observed that the presence of halide anions (e.g. Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) in the catalyst or in the acidic medium decreased the decomposition of H<sub>2</sub>O<sub>2</sub>.

The catalytic decomposition of H<sub>2</sub>O<sub>2</sub> forms water and gaseous oxygen in an exothermic reaction. This reaction occurs on heterogeneous, homogeneous, and enzymatic catalysts but heterogeneous catalysts present advantages such as easy separation of the catalyst, and the catalyst can be used in neutral pH. The kinetics of H<sub>2</sub>O<sub>2</sub> decomposition depends on pH, the initial concentration of H<sub>2</sub>O<sub>2</sub>, the reaction temperature, and the catalyst. For example, Gurol and Lin (2002) found that the decomposition rate of H<sub>2</sub>O<sub>2</sub> was proportional to the iron oxide concentration. The H<sub>2</sub>O<sub>2</sub> decomposition decreased when this reaction was carried out in an acidic medium (Choudhary and Gaikwad, 2003). The authors suggested that the decrease in H<sub>2</sub>O<sub>2</sub> decomposition was due to the presence of H<sup>+</sup> at higher concentrations. The H<sub>2</sub>O<sub>2</sub> decomposition rate was found to be a first order reaction in relation to H<sub>2</sub>O<sub>2</sub> concentration (Oliveira *et al.*, 1998; Choudhary and Gaikwad, 2003) but another expression describing the H<sub>2</sub>O<sub>2</sub> decomposition was reported by Voloshin *et al.* (2008). The effect of pH on the decomposition of H<sub>2</sub>O<sub>2</sub> on Co(II) acetylacetonate supported on a silica-propylpiperazine matrix was observed by Oliveira *et al.* (1998).

The decomposition of H<sub>2</sub>O<sub>2</sub> is an undesirable reaction in the direct H<sub>2</sub>O<sub>2</sub> synthesis process from H<sub>2</sub> and O<sub>2</sub>, while it is a desirable reaction for the generation of hydroxyl radicals in advanced oxidation processes. Thus, it is important to understand how the reaction medium conditions affect the H<sub>2</sub>O<sub>2</sub> decomposition. In other words, to improve the efficiency of the H<sub>2</sub>O<sub>2</sub> production and the advanced oxidation processes are necessary to know the kinetics of H<sub>2</sub>O<sub>2</sub> decomposition and the factors that affect its decomposition. In this work, the H<sub>2</sub>O<sub>2</sub> decomposition was studied on Pd supported on activated carbon, Pd/ZrO<sub>2</sub>, and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> between 293 K and 313 K.

## II. METHODS

### A. Catalyst Preparation

The supports used in this work were zirconia (ZrO<sub>2</sub>) supplied by Daiichi Kigenso Kagaku of Japan, alumina

( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) from Harshaw, and activated carbon (AC) manufactured by Bonechar, Brazil. The ZrO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were calcined in static air at 873 K for 10 h, while AC was washed in distilled water to remove the impurities. The washed AC was then dried at 393 K for 12 h.

The 1.0% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 1.0% Pd/ZrO<sub>2</sub>, 5.0% Pd/AC, and 0.5% Pd/AC catalysts were prepared by incipient wetness with aqueous solutions of Pd(NO<sub>3</sub>)<sub>2</sub> (Aldrich Chem. Co.). The Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O solution was prepared by dissolving Pd(NO<sub>3</sub>)<sub>2</sub> in concentrated HNO<sub>3</sub> (Merck) and distilled water. After impregnation with the aqueous solutions the solids were dried at 393 K for 24 h and calcined at 773 K for 10 h. The catalysts were reduced in flowing H<sub>2</sub> (White Martins, 99.999%) at 573 K for 3 h. The amount of Pd in the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

### B. Catalyst Characterization

The surface area of the AC, ZrO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was determined by N<sub>2</sub> adsorption at 77 K by the BET method (Brunauer *et al.*, 1938) and the percentage of exposed palladium atoms, *FA*, was calculated through the titration of preadsorbed oxygen with H<sub>2</sub>.

Titration of preadsorbed oxygen with H<sub>2</sub> was measured in a Micromeritics-ASAP 2010C. The gases used were H<sub>2</sub> (White Martins, 99.999%), O<sub>2</sub> (White Martins, 99.999%), He (White Martins, 99.9999%), and N<sub>2</sub> (White Martins, 99.999%). All gases were used as received. The amount of catalyst used in each experiment varied between 0.50 and 2.00 g. The sample was reduced in flowing H<sub>2</sub> (60 cm<sup>3</sup>min<sup>-1</sup>) at 573 K for 2 h, followed by evacuation at the same temperature for 2 h. The sample was then cooled to 373 K in vacuo and was further evacuated at this temperature for 0.5 h. Then, O<sub>2</sub> was introduced to the sample cell and an adsorption isotherm was recorded between 0.66 and 26.66 kPa. Finally, the sample was evacuated at 373 K for 0.5 h, and H<sub>2</sub> was used to titrate the chemisorbed oxygen on Pd. A second adsorption isotherm was recorded after evacuation of the sample at 373 K for 15 minutes. The gas uptake was determined as the intercept of the linear region of the isotherm.

The bulk structure of the samples was determined by the powder X-ray diffraction, XRD, using a Philips model X'Pert diffractometer, with Cu K $\alpha$  radiation, operated at 40 kV and 40 mA.

### C. Kinetic Measurements

The rate of H<sub>2</sub>O<sub>2</sub> decomposition was measured using a volumetric method by measuring the volume of O<sub>2</sub> evolving from the reaction. All reactions were carried out at atmospheric pressure and over the range of 293 K-323 K. Between 50 and 200 mg of catalyst were dispersed in 250 mL of deionized water, and the reaction system was maintained at the desired temperature in a water bath. The mixture was stirred mechanically with Teflon blades. Then, the H<sub>2</sub>O<sub>2</sub> decomposition was started by injecting between 1 mL and 10 mL of H<sub>2</sub>O<sub>2</sub> into the reaction system. The O<sub>2</sub> that evolved during the

reaction was measured in different time intervals for at least 1 h.

In order to study the influence of the treatment applied to the Pd catalysts in its H<sub>2</sub>O<sub>2</sub> decomposition activity, the Pd catalyst was treated by H<sub>2</sub> and deionized water before the reaction. In addition, successive reactions of H<sub>2</sub>O<sub>2</sub> decomposition were carried out on the same catalyst. For the catalysts treated with H<sub>2</sub>, the system was purged in flowing pure N<sub>2</sub> for at least 1 h and the catalyst was reduced in flowing H<sub>2</sub> (2.0 cm<sup>3</sup> s<sup>-1</sup>) at 298 K for 1 h. Then, the H<sub>2</sub> was switched to pure N<sub>2</sub> and the H<sub>2</sub>O<sub>2</sub> decomposition was started after the system had reached the desired temperature. The catalyst treatment using deionized water was carried out by adding between 50 and 200 mg of catalyst in 500 mL of water maintained under vigorous stirring for 1 h at 298 K. Some catalysts were used for successive reactions. The procedure used in this case was the same procedure applied to the catalysts used in single reactions.

The intra-particle mass transfer effect on the H<sub>2</sub>O<sub>2</sub> decomposition was studied by carrying out the reaction at 313 K using a size of catalyst in the range of 38-208  $\mu$ m, while the external mass transfer effect was computed using different stirrer speeds.

The reaction temperature for the decomposition of H<sub>2</sub>O<sub>2</sub> on Pd catalysts was varied between 293 and 323 K, and the initial concentration of H<sub>2</sub>O<sub>2</sub> was fixed at 0.062 mol/L for the calculation of the apparent activation energy. To determine the reaction order with respect to H<sub>2</sub>O<sub>2</sub>, the initial concentration of H<sub>2</sub>O<sub>2</sub> was varied between 0.050 and 0.300 mol/L.

## III. RESULTS AND DISCUSSION

The specific surface areas of the AC, ZrO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were about 550, 20, and 160 m<sup>2</sup>g<sup>-1</sup>, respectively. The amount of Pd determined by ICP-AES was 0.98%, 0.95%, 5.1%, and 0.49% for the 1.0% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 1.0% Pd/ZrO<sub>2</sub>, 5.0% Pd/AC, and 0.5% Pd/AC catalysts, respectively. These results showed a good agreement between the Pd added to the catalyst and that measured by ICP-AES, indicating that the catalyst preparation was conducted well. The *FA* values as measured by titration of preadsorbed oxygen with H<sub>2</sub> were 53.0%, 34.0%, 11.0%, and 58.0% for 1.0% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 1.0% Pd/ZrO<sub>2</sub>, 5.0% Pd/AC, and 0.5% Pd/AC catalysts, respectively.

The XRD analysis for 0.5% Pd/AC, 1.0% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and 1.0% Pd/ZrO<sub>2</sub> indicated no presence of metallic Pd, suggesting that the size of the Pd particles are so small (< 5 nm) or amorphous that they cannot be analyzed by x-ray diffraction. In fact, the *FA* value for 1.0% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> suggests a Pd particle size of 2.11 nm, while Pd particle sizes of 3.29 nm and 1.93 nm were calculated for 1.0% Pd/ZrO<sub>2</sub> and 0.5% Pd/AC, respectively. For the 5.0% Pd/AC catalyst, a *FA* value of 11.0% was obtained, which corresponds to a particle size of 10.18 nm. The particle size determined by XRD was 12.0 nm for the 5.0% Pd/AC catalyst, indicating a good agreement between the particle sizes measured by chemisorption and XRD. Thus, the *FA* values obtained

by titration of preadsorbed oxygen with  $H_2$  were in good agreement with the results observed in XRD analysis. Metallic Pd was observed by XRD for 5.0% Pd/AC treated with  $H_2$ , indicating that PdO was reduced to metallic Pd by  $H_2$ .

In order to verify the external mass transfer limitations, the  $H_2O_2$  decomposition was carried out at 313 K using different stirrer speeds. We observed that the reaction rate was not affected by the stirrer speeds, indicating that the  $H_2O_2$  decomposition was not limited by external mass transfer. The intra-particle mass transfer limitation was observed in this work for a particle size larger than 125  $\mu m$ . Thus, the experiments were carried out with a particle size between 38 and 125  $\mu m$  to avoid mass transfer effects on the reaction rate.

Figure 1 shows the variation of  $H_2O_2$  concentration as a function of reaction time for an initial  $H_2O_2$  concentration of 0.062 mol/L.  $(H_2O_2)_0$  denotes the initial  $H_2O_2$  concentration and  $(H_2O_2)$  is the  $H_2O_2$  concentration at time  $t$ . The  $H_2O_2$  concentration decreased with the increasing reaction time. The  $H_2O_2$  concentration decreased from 0.062 to 0.018 in 180 minutes for the 5.0% Pd/AC catalyst, while a decrease of 0.062 to 0.005 in 80 minutes was observed for the 0.5% Pd/AC catalyst. For 1.0% Pd/ $\gamma$ - $Al_2O_3$  and 1.0% Pd/ $ZrO_2$  catalysts, the decrease in  $H_2O_2$  concentration as a function of time was very similar. We observed a decrease in the  $H_2O_2$  concentration of 86% and 79% in 90 minutes of reaction for the 1.0% Pd/ $\gamma$ - $Al_2O_3$  and 1.0% Pd/ $ZrO_2$  catalysts, respectively. The decrease in the  $H_2O_2$  concentration over time was higher for catalysts with higher  $FA$  values, indicating that the  $H_2O_2$  decomposition depended on the surface area of Pd. Experiments with initial  $H_2O_2$  concentration in the range of 0.048-0.300 mol/L showed similar behavior that one using initial  $H_2O_2$  concentration of 0.062 mol/L. A plot of  $\ln[(H_2O_2)_0/(H_2O_2)]$  as a function of time was made for all catalysts using initial  $H_2O_2$  concentration of 0.062 mol/L (Fig. 2). The results showed a straight line for all catalysts, indicating a first-order kinetic law in relation to  $H_2O_2$  concentration. Thus, the reaction rate increased linearly when the initial  $H_2O_2$  concentration was increased.

In order to verify the influence of the catalyst treatment using deionized water on  $H_2O_2$  decomposition, the 5.0% Pd/AC catalyst was used in this reaction at 293 K and 303 K. The initial concentration of  $H_2O_2$  decreased as the reaction time increased in both temperatures, as shown in Fig. 3. However, the decrease in the initial concentration of  $H_2O_2$  was faster for the catalysts treated with deionized water, indicating that this treatment can remove adsorbed species on the surface of the catalyst, thus increasing the reaction rate. Similar behavior was observed for the Pd catalysts treated with  $H_2$  (Fig. 4) and we observed that the decrease in the concentration of  $H_2O_2$  was much greater for the catalysts treated with  $H_2$  than for the untreated catalysts. The treatment of oxidized Pd catalysts with  $H_2$  leads to the formation of metallic Pd, as observed by XRD. In fact, PdO reduction by  $H_2$  has been studied by several

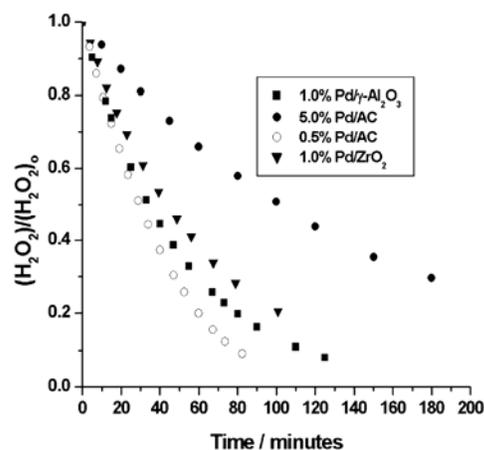


Figure 1. Decomposition of  $H_2O_2$  on supported Pd catalysts at 303 K.

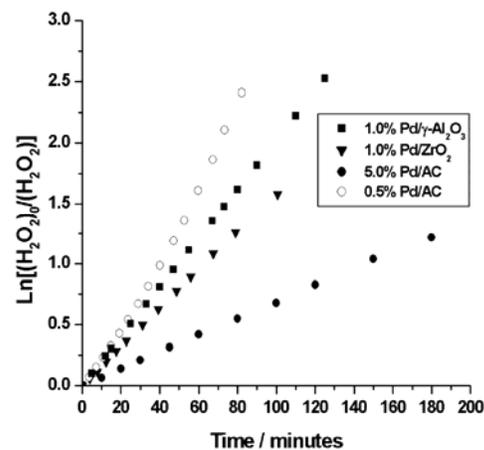


Figure 2. Decomposition kinetics of  $H_2O_2$  on supported Pd catalysts at 303 K.

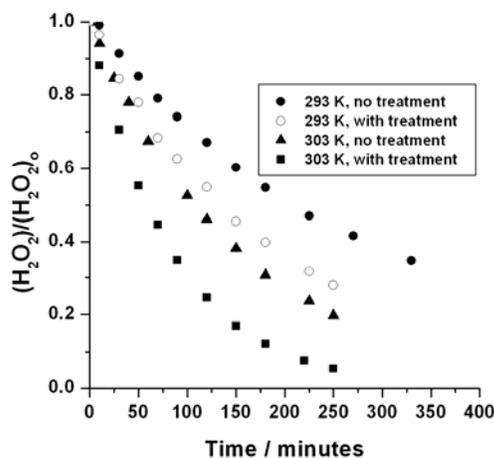


Figure 3. Effect of the catalyst treatment with distilled water on the decomposition of  $H_2O_2$  on 5.0% Pd/AC.

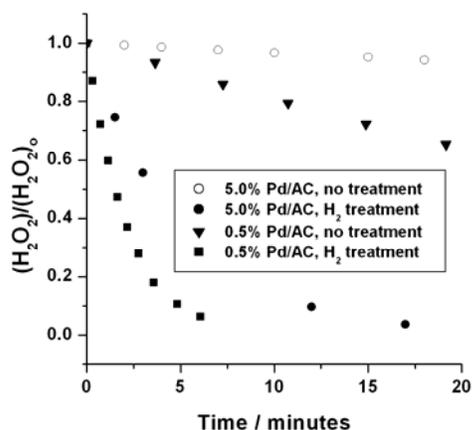


Figure 4. Effect of  $H_2$  treatment on the activity of Pd/AC catalysts for the decomposition of  $H_2O_2$  at 293 K.

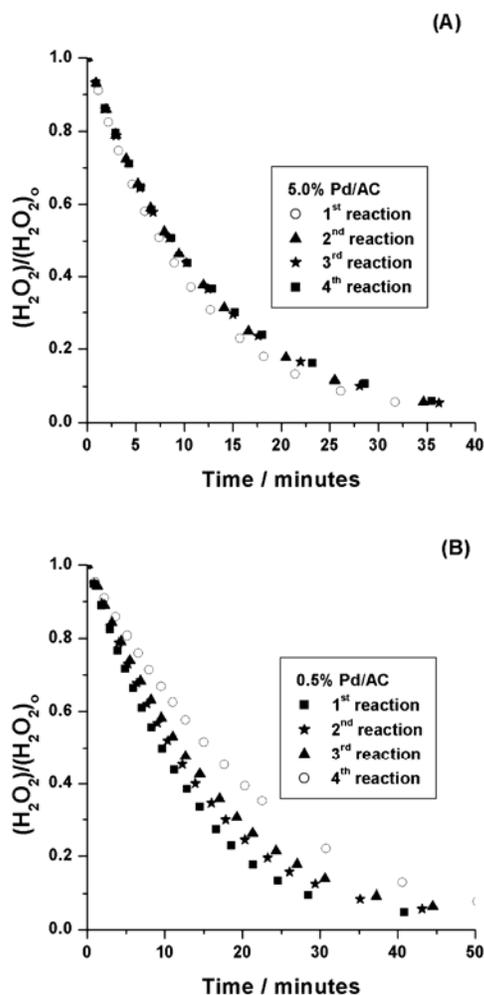


Figure 5. Effect of successive reactions on the decomposition of  $H_2O_2$  at 303 K on (A) 5.0% Pd/AC and (B) 0.5% Pd/AC.

authors (Crozier *et al.*, 1998; Okumura and Niwa, 2000; Yang *et al.*, 2002; Takeguchi *et al.*, 2003), who observed that the PdO can be reduced to metallic Pd at

room temperature. Thus, the high  $H_2O_2$  decomposition rate on Pd catalyst treated with  $H_2$  can be attributed to the presence of metallic Pd, which is more active in  $H_2O_2$  decomposition. Similar results were found by other authors (Choudhary *et al.*, 2001; 2002; 2006) in the  $H_2O_2$  decomposition on supported Pd catalysts.

Successive reactions of  $H_2O_2$  decomposition on 5.0% Pd/AC and 0.5% Pd/AC catalysts were carried out without catalyst exchange at 298 K, and the results are shown in Fig. 5. We can observe that the  $H_2O_2$  decomposition activity remained practically constant during four successive reactions of  $H_2O_2$  decomposition on 5.0% Pd/AC catalyst (Fig. 5A), indicating that the  $H_2O_2$  decomposition itself causes a small deactivation process in the 5.0% Pd/AC catalyst. For the 0.5% Pd/AC catalyst, the  $H_2O_2$  decomposition activity decreased slowly after its use in each successive reaction, suggesting a deactivation of the catalyst (Fig. 5B). The deactivation of the 0.5% Pd/AC and 5.0% Pd/AC catalysts can be attributed to the oxidation of Pd by  $H_2O_2$ . This deactivation can suggest a different oxidation rate of Pd by  $H_2O_2$ , and this oxidation appears to depend on the particle size of the catalyst. Other works (Lieske and Volter, 1985; Tobias *et al.*, 2006) have shown that the oxidation of Pd by  $O_2$  depends on the particle size of Pd, and small particles are easily oxidized. Thus, the deactivation of the catalyst in the successive  $H_2O_2$  decompositions appear to depend on the particle size of the catalyst, and small particles tend to have a high deactivation process, as observed in Fig. 5. A similar behavior was found in both the 1.0% Pd/ $Al_2O_3$  and 1.0% Pd/ $ZrO_2$  catalysts.

In all the experiments performed in this work, we observed that the reaction rate of  $H_2O_2$  decomposition on supported Pd catalysts can be described by a first-order kinetic law in relation to  $H_2O_2$  concentration (Fig. 2). Table 1 shows the reaction rate measured at 293 K using an initial concentration of  $H_2O_2$  of 0.062 mol/L and the apparent activation energy calculated for  $H_2O_2$  decomposition on supported Pd catalysts. The reaction rate for the catalysts treated with  $H_2$  varied between  $67 \times 10^{-3}$  and  $90 \times 10^{-3}$  mol  $g^{-1} min^{-1}$ , while for the Pd catalysts that were not treated, the reaction rate varied between  $1.10 \times 10^{-3}$  and  $2.60 \times 10^{-3}$  mol  $g^{-1} min^{-1}$ . The Pd catalysts treated with  $H_2$  showed a reaction rate 35-50 fold higher than the Pd catalysts not treated with  $H_2$  (Table 1). This fact can be attributed to the presence of metallic Pd due to the reduction of PdO to Pd by  $H_2$ . Other authors (Choudhary *et al.*, 2001; 2002; 2006) have observed similar results. The apparent activation energy varied between 30 and 50  $kJ mol^{-1}$  for Pd catalysts. These values are high when compared to the 17.65  $kJ mol^{-1}$  obtained by Choudhary and Gaikwad (2003). However, Voloshin *et al.* (2008) found a value of 70.9  $kJ mol^{-1}$  for the apparent activation energy for the decomposition of  $H_2O_2$  on Pd/ $SiO_2$ . Ariafard *et al.* (2003) obtained apparent activation energy values between 32 and 41  $kJ mol^{-1}$  for  $H_2O_2$  decomposition on  $La_{0.9}Sr_{0.1}Ni_{1-x}Cr_xO_3$  perovskites. Apparent activation

Table 1. Reaction rate and apparent activation energy for the decomposition of H<sub>2</sub>O<sub>2</sub> on supported Pd catalysts.

Catalyst	Initial reaction rate at 293 K (10 <sup>-3</sup> mol g <sup>-1</sup> min <sup>-1</sup> )	Apparent activation energy (kJ mol <sup>-1</sup> )
5.0% Pd/AC	1.13	50.8
5.0% Pd/AC treated with H <sub>2</sub>	67.20	30.0
5.0% Pd/AC treated with distilled water	1.77	45.1
0.5% Pd/AC	2.53	46.7
0.5% Pd/AC treated with H <sub>2</sub>	88.92	27.7
1.0% Pd/γ-Al <sub>2</sub> O <sub>3</sub>	2.16	44.1
1.0% Pd/γ-Al <sub>2</sub> O <sub>3</sub> treated with H <sub>2</sub>	82.23	39.6
1.0% Pd/ZrO <sub>2</sub>	1.54	50.0
1.0% Pd/ZrO <sub>2</sub> treated with H <sub>2</sub>	76.63	33.7

energy values between 30 and 60 kJ/mol have also been found in other works (Lin and Gurol, 1998; Oliveira *et al.*, 1998). Thus, the apparent activation energy values found in this work are in good agreement with the values found in other works. All Pd catalysts showed high catalytic activity for the H<sub>2</sub>O<sub>2</sub> decomposition. However, the H<sub>2</sub>O<sub>2</sub> decomposition activity was higher for the 0.5% Pd/AC treated with H<sub>2</sub>. Thus, the activity of the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> depends on the treatment applied to the catalyst.

#### IV. CONCLUSIONS

In this work, the influence of process parameters on H<sub>2</sub>O<sub>2</sub> decomposition were studied for the supported Pd catalysts. The H<sub>2</sub>O<sub>2</sub> decomposition depends on the treatment applied to the catalysts. The catalysts treated with H<sub>2</sub> resulted in a larger rate of H<sub>2</sub>O<sub>2</sub> decomposition, indicating a reduction of PdO to metallic Pd by H<sub>2</sub>. This reduction was confirmed by XRD. The treatment with distilled water had a small effect on the rate of H<sub>2</sub>O<sub>2</sub> decomposition, suggesting a removal of impurities on the catalyst surface. After four successive decompositions of H<sub>2</sub>O<sub>2</sub>, we observed a small deactivation for the Pd/AC catalysts. This fact was attributed to oxidation of metallic Pd to PdO by H<sub>2</sub>O<sub>2</sub>.

All reactions were well represented by a first-order rate law with respect to H<sub>2</sub>O<sub>2</sub>. The apparent activation energy varied between 27 and 40 kJ/mol for the supported Pd catalysts treated with H<sub>2</sub>, while for the supported Pd catalysts not treated with H<sub>2</sub>, the apparent activation energy values were close to 50 kJ/mol. The H<sub>2</sub>O<sub>2</sub> decomposition activity was higher for the 0.5% Pd/AC treated with H<sub>2</sub>, indicating that the metallic Pd is more active than the PdO for the H<sub>2</sub>O<sub>2</sub> decomposition.

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