

# Direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> over Pd-based catalysts: Influence of oxidation state, support and metal additives

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## Abstract

The influence of oxidation state (reduced and oxidized), support (ZrO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, SiO<sub>2</sub>, H-β, ThO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, BPO<sub>4</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>) and precious metal additives (Au, Pt, Rh and Ru) on the direct H<sub>2</sub>O<sub>2</sub> synthesis has been investigated over Pd-based catalysts. For all the supports investigated herein, the oxidized Pd catalysts showed significantly superior H<sub>2</sub>O<sub>2</sub> yields as compared to their reduced counterparts. The effect of the Pd oxidation state was found to be more important for determining the H<sub>2</sub>O<sub>2</sub> yields than the particle size and surface area properties of the catalyst system. An excellent correlation was observed between the H<sub>2</sub>O<sub>2</sub> selectivity and H<sub>2</sub>O<sub>2</sub> decomposition activity of the oxidized Pd catalysts. The oxidized Pd catalysts showed almost an order of magnitude lower H<sub>2</sub>O<sub>2</sub> decomposition activity than the reduced catalysts. The H<sub>2</sub>O<sub>2</sub> yield in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation passed through a maximum with increase in the Au concentration. Although a similar effect was also observed in case of Pt, Au was found to be a superior promoter for the direct H<sub>2</sub>O<sub>2</sub> synthesis process. Addition of Rh and Ru was found to be detrimental for the H<sub>2</sub>O<sub>2</sub> yields; these results can be explained in terms of increased H<sub>2</sub>O<sub>2</sub> decomposition activity and/or enhanced H<sub>2</sub> to H<sub>2</sub>O reaction activity in their presence. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** H<sub>2</sub>O<sub>2</sub>; Direct synthesis; Decomposition; Pd catalysts; Metal additives; Oxidation state; Supports

## 1. Introduction

H<sub>2</sub>O<sub>2</sub>, which is an environmentally benign oxidant, is expected to play an increasingly important role in the chemical industry [1]. Other applications of H<sub>2</sub>O<sub>2</sub> (such as bleach in the textile and pulp/paper industry and in treatment of waste water) are also on the rise, thus indicating the need for larger volumes of H<sub>2</sub>O<sub>2</sub>. The current commercial process for H<sub>2</sub>O<sub>2</sub> production is a circuitous process involving indirect oxidation of H<sub>2</sub> (Anthraquinone process). Since the above process is quite complex, there is a significant interest in developing a direct H<sub>2</sub> oxidation process [2]. Direct synthesis of H<sub>2</sub>O<sub>2</sub> has received considerable attention [1–14] in recent years with Pd-based systems as the catalysts of choice. In the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation over the Pd catalysts, the selective H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub> + O<sub>2</sub> → H<sub>2</sub>O<sub>2</sub>) and non-selective water (H<sub>2</sub> + 0.5O<sub>2</sub> → H<sub>2</sub>O) forming reactions occur simultaneously. Furthermore, the H<sub>2</sub>O<sub>2</sub> molecules

are unstable in presence of Pd which further facilitates its conversion to water. It is, therefore, extremely difficult to achieve high H<sub>2</sub>O<sub>2</sub> selectivity/yields. Since the side reaction involving combustion of hydrogen to water is a highly exothermic reaction, increasing the H<sub>2</sub>O<sub>2</sub> selectivity is also important for making the process non-hazardous. The challenges posed by the direct H<sub>2</sub>O<sub>2</sub> process, therefore, make it an interesting candidate for study from a scientific as well as a commercial viewpoint.

Our previous studies have suggested that oxidation state of Pd also plays a role in determining the activity/selectivity in the direct H<sub>2</sub> oxidation to H<sub>2</sub>O<sub>2</sub> process [6]. Herein, we have systematically considered this aspect by investigating the effect of Pd oxidation state on the H<sub>2</sub>O<sub>2</sub> yields over several supported Pd catalysts (Pd/ZrO<sub>2</sub>, Pd/Ga<sub>2</sub>O<sub>3</sub>, Pd/CeO<sub>2</sub>, Pd/SiO<sub>2</sub> and Pd/H-β, Pd/ThO<sub>2</sub>, Pd/CeO<sub>2</sub>-ZrO<sub>2</sub>, Pd/BPO<sub>4</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>). H<sub>2</sub>O<sub>2</sub> decomposition studies have also been undertaken on these catalysts (Pd in reduced and unreduced state) to gain further insights into the process.

Hutchings and coworkers observed that Au-based catalysts exhibited high H<sub>2</sub>O<sub>2</sub> selectivity, but low H<sub>2</sub>O<sub>2</sub> formation rates

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at low reaction temperatures (2 °C) in a solvent mixture of methanol and water [8]. However, a considerable increase in H<sub>2</sub>O<sub>2</sub> formation rate was observed when Au was coupled with Pd in the catalyst system. It is therefore interesting to study the influence of different metal additives (and their content) on the direct H<sub>2</sub>O<sub>2</sub> synthesis. Herein, we have investigated the H<sub>2</sub>O<sub>2</sub> synthesis and decomposition at 25 °C in an acidic medium over the following precious metal added Pd-based systems:

- (a) Pd-Au/ZrO<sub>2</sub> (Au/Pd atom ratio range = 0–0.11)
- (b) Pd-Pt (Pt/Pd atom ratio range = 0–0.09)
- (c) Pd-Rh (Rh/Pd atom ratio range = 0–0.16)
- (d) Pd-Ru (Ru/Pd atom ratio range = 0–0.16)

## 2. Experimental

### 2.1. Catalyst synthesis

#### 2.1.1. Supported Pd catalysts

The Al<sub>2</sub>O<sub>3</sub> (prepared from bohemite by its calcination at 500 °C for 2 h), ZrO<sub>2</sub> (prepared from zirconyl nitrate by its hydrolysis to zirconium hydroxide by ammonium hydroxide and calcining at 500 °C for 2 h), Ga<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ThO<sub>2</sub> (prepared from thorium nitrate by its hydrolysis to thorium hydroxide by ammonium hydroxide and calcining at 500 °C for 2 h), SiO<sub>2</sub> (prepared from B-type silica gel, by calcining at 500 °C for 3 h), CeO<sub>2</sub>–ZrO<sub>2</sub> (prepared by mixing CeO<sub>2</sub> and ZrO<sub>2</sub> with Ce/Zr mole ratio of 1.0, in the presence of deionised water just sufficient to form a thick paste, drying the wet mixture in an air oven at 100 °C for 2 h and then calcining it in air at 600 °C for 3 h), H-β (Si/Al = 27 and crystal size = 1.0 μm) and BPO<sub>4</sub> (prepared from a mixture of boric acid and orthophosphoric acid with B/P mole ratio of 1.0, drying the mixture in air oven at 100 °C for 2 h and then calcining it in air at 600 °C for 3 h) supported oxidized Pd (2.5 wt%) catalysts were prepared by impregnating the respective support with palladium acetate from its acetonitrile solution by the incipient wet impregnation technique. After impregnation, the wet catalyst mass was dried at 100 °C for 2 h and then calcined under static air in a muffle furnace at 500 °C for 3 h.

The supported reduced Pd catalyst was prepared from the respective oxidized Pd catalyst by reducing it with an ammoniacal hydrazine solution at room temperature (27 °C) for 2 h followed by washing, filtration and drying at 100 °C in an air oven.

#### 2.1.2. Bimetallic catalysts

The ZrO<sub>2</sub> supported bimetallic catalysts (e.g. Au-Pd/ZrO<sub>2</sub>, Pt-Pd/ZrO<sub>2</sub>, Ru-Pd/ZrO<sub>2</sub> and Rh-Pd/ZrO<sub>2</sub>) with different noble metal (Au, Pt, Ru and Rh) loadings and constant Pd loading (2.5 wt%) were prepared by simultaneously impregnating fine particles of ZrO<sub>2</sub> with the corresponding noble metal chlorides from their aqueous acidic solution by the incipient wetness technique, drying at 100 °C for 2 h and then calcining in static air at 500 °C for 3 h.

### 2.2. Catalyst characterization

The Pd<sup>0</sup> and/or PdO phases in the supported Pd catalysts were determined by X-ray powder diffraction method using a Holland Phillips, PW/1730 X-ray generator with Cu Kα radiation (λ = 1.5406 Å; 40 kV, 25 Ma). The surface area of the catalysts was measured by the single point BET method by measuring the adsorption of nitrogen at liquid N<sub>2</sub> temperature and at the N<sub>2</sub> concentration of 30 mol% (balance helium), using a Monosorb Surface Area Analyzer (Quantachrome Corp., USA) based on dynamic adsorption/desorption technique. Before carrying out surface area measurement experiments, the catalyst (0.1–1.0 g) was pretreated in situ in the sample cell at 300 °C for 1 h in flow of (30 cm<sup>3</sup> min<sup>-1</sup>) of a mixture of helium and nitrogen to remove the traces of moisture.

### 2.3. Reaction procedure

#### 2.3.1. H<sub>2</sub>O<sub>2</sub> synthesis

The direct oxidation of H<sub>2</sub> by O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> over the supported Pd catalysts was carried out at atmospheric pressure (95 kPa) in a magnetically stirred glass reactor (capacity 250 cm<sup>3</sup>) containing 0.5 g catalyst in a fine power form and an aqueous acidic solution (150 cm<sup>3</sup>) as a reaction medium. A H<sub>2</sub>/O<sub>2</sub> (4.6 mol% H<sub>2</sub>) gas mixture was bubbled (using a fine glass tip) continuously through the reaction medium containing the catalyst under vigorous stirring at a constant temperature. The temperature of the reaction was controlled by continuously passing water through the reactor jacket from thermostatic bath. The concentration of unreacted hydrogen present in the effluent gases, after removing the water vapors from them by condensation at 0 °C, was measured by an online hydrogen analyzer (Kathometer, Nucon, New Delhi) based on a thermal conductivity detector. After the reaction, the solid catalyst from the reaction mixture was separated by filtration and the filtrate was analyzed for the H<sub>2</sub>O<sub>2</sub> formed in the reaction by iodometric titration. The conversion of H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> yield and selectivity were obtained as follows:

H<sub>2</sub> conversion (%)

$$= \frac{(\text{moles of H}_2 \text{ in the feed}) - (\text{moles of H}_2 \text{ in the effluent gases})}{\text{moles of H}_2 \text{ in the feed}} \times 100$$

$$\text{H}_2\text{O}_2 \text{ yield (\%)} = \frac{\text{moles of H}_2\text{O}_2 \text{ formed}}{\text{moles of H}_2 \text{ in the feed}} \times 100$$

$$\text{H}_2\text{O}_2 \text{ selectivity (\%)} = \frac{\text{moles of H}_2\text{O}_2 \text{ formed}}{\text{moles of H}_2 \text{ consumed}} \times 100$$

Some of the experiments were repeated and an excellent reproducibility (±5% for H<sub>2</sub>O<sub>2</sub> yields) was observed for these experiments. The repeatability of the iodometric titration experiments in terms of determining H<sub>2</sub>O<sub>2</sub> concentration was within 3%. Constant calibrations were undertaken to ensure the accuracy of the analysis. The flammability and detonability limits for H<sub>2</sub> in O<sub>2</sub> (at 25 °C and 1 atm pressure) are 4.0% H<sub>2</sub> (lower) to 94% H<sub>2</sub> (upper) and 15% H<sub>2</sub> (lower) to 90% H<sub>2</sub>

(upper), respectively. The process could be hazardous when operated within the flammability limits, particularly when the flammable reaction mixture is ignited or subjected to a dry Pd catalyst. The safety in the present work was ensured by using the feed  $H_2/O_2$  mixture close to the lower flammability limit, so that the concentration of  $H_2$  in the reactor exit gas was less than 4.0% and also care was taken to avoid spillage of catalyst on the reactor walls during the reaction. The  $H_2$  gas flow rate was very small (0.7 ml/min); however, a flame arrester for  $H_2$  (a 100 cm long and 3.0 mm o.d. ss tube packed with glass beads) was used between the  $H_2$  cylinder and reactor to avoid flame propagation back to the  $H_2$  cylinder, as a precautionary measure.

### 2.3.2. $H_2O_2$ decomposition

The  $H_2O_2$  decomposition reaction over the catalysts was carried out using a magnetically stirred glass reactor (capacity: 250  $cm^3$ ) containing 0.2 g catalyst in 150  $cm^3$  aqueous reaction medium, with or without containing acid and/or halide anions, by injecting 1 ml of 30% (w/v)  $H_2O_2$  solution in the reactor under vigorous stirring and measuring the gas ( $O_2$ ) evolved in the  $H_2O_2$  decomposition at 25 °C and atmospheric pressure, as a function of time, using a constant pressure gas collector [15]. The percent  $H_2O_2$  decomposition data was estimated as follows:

$$H_2O_2 \text{ decomposition (\%)} = \frac{V_t}{V_T} \times 100$$

where  $V_t$  is the volume of  $O_2$  evolved in time  $t$  and  $V_T$  is the volume of  $O_2$  evolved in the complete decomposition of  $H_2O_2$  in the reactor. The  $H_2O_2$  decomposition activity of the supported Pd catalysts was evaluated in term of a first order rate constant ( $k$ ) according to the first order rate expression:  $\ln [V_T / (V_T - V_t)] = kC_A t$  (where  $V_T$  is the volume of  $O_2$  evolved in the complete  $H_2O_2$  decomposition,  $V_t$  the volume of  $O_2$  evolved in time  $t$  and  $C_A$  is the catalyst concentration/loading).

## 3. Results and discussions

### 3.1. Effect of mass transfer on the reaction between $H_2$ and $O_2$

The rate of the reaction between the  $H_2$  and  $O_2$  in liquid medium is known to depend on the mass transfer of the reactants to the catalyst sites [8]. It is, therefore, important that experiments to investigate the formation of  $H_2O_2$  in the reaction between  $H_2$  and  $O_2$  should be carried out under conditions at which the mass transfer has minimal influence on the reaction rate. Fig. 1 shows the conversion of  $H_2$  for different agitation rates with all other variables remaining constant. The stirring speed was adjusted by altering the applied voltage (V) to the magnetic stirrer. At the lower stirring speeds, the conversion of  $H_2$  was found to depend

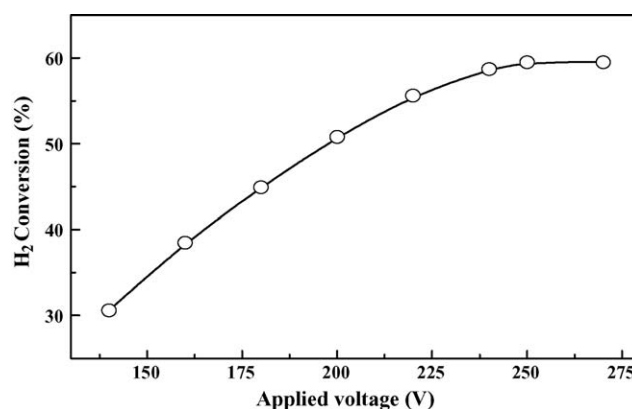


Fig. 1. Effect of the stirring speed on the conversion of  $H_2$  in the reaction between  $H_2$  and  $O_2$  over the reduced Pd/C catalyst in aqueous acidic (0.03 M  $H_3PO_4$ ) reaction medium [reaction conditions: volume of the reaction medium = 150  $cm^3$ , amount of catalyst = 0.5 g,  $H_2$  concentration in  $O_2$  = 4.6 mol%, reaction temperature = 25 °C and reaction period = 3 h].

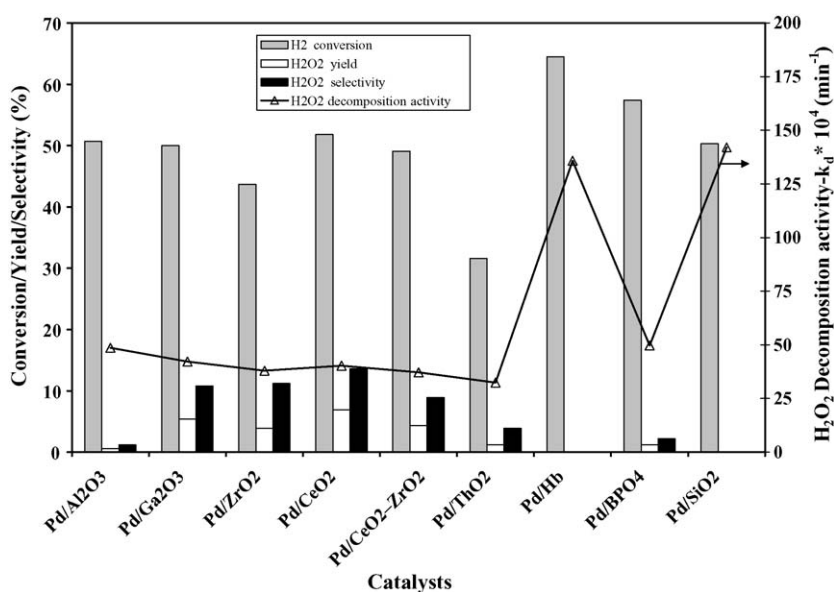


Fig. 2. Results of the direct oxidation of  $H_2$  to  $H_2O_2$  over different reduced Pd catalysts (Pd loading = 2.5 wt%) [reaction conditions: reaction medium = 0.03 M  $H_3PO_4$ , volume of reaction medium = 150  $cm^3$ , amount of catalyst = 0.5 g, reaction temperature = 25 °C,  $H_2$  concentration in  $O_2$  = 4.6 mol% and reaction period = 3 h].

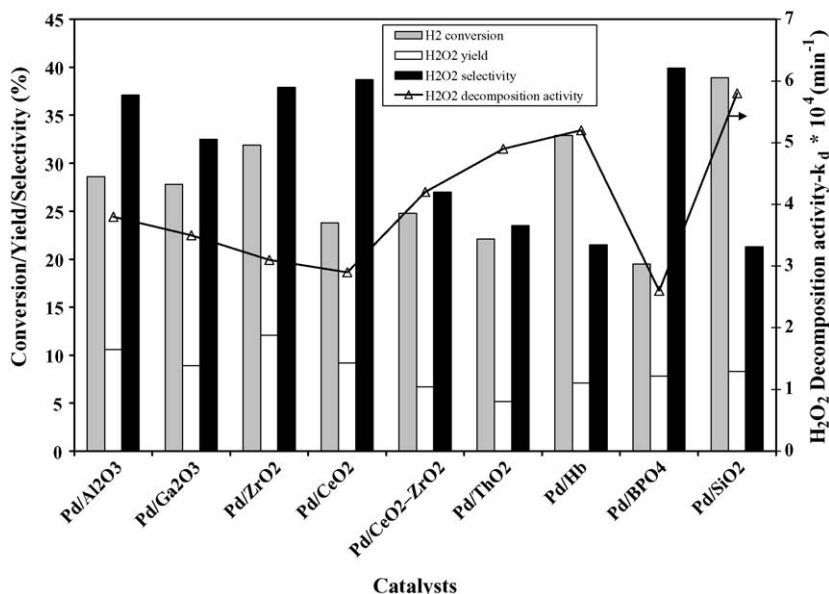


Fig. 3. Results of the direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> over different oxidized Pd catalysts (Pd loading = 2.5 wt%) [reaction conditions: reaction medium = 0.03 M H<sub>3</sub>PO<sub>4</sub>, volume of reaction medium = 150 cm<sup>3</sup>, amount of catalyst = 0.5 g, reaction temperature = 25 °C, H<sub>2</sub> concentration in O<sub>2</sub> = 4.6 mol% and reaction period = 3 h].

on the stirring speed. However, above 230 V there was no significant change in the H<sub>2</sub> conversion, indicating the absence of gas–liquid mass transfer effect on the reaction. For the subsequent experiments, the stirrer speed was fixed at 260 V.

### 3.2. Influence of the Pd oxidation state on the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> reaction over different supported Pd catalysts

Figs. 2 and 3 reveal the performance of the different supported Pd catalysts in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation with Pd in the reduced (Pd<sup>0</sup>) and oxidized state (PdO), respectively. The H<sub>2</sub>O<sub>2</sub> decomposition activity for the different catalysts is also

shown. The H<sub>2</sub> conversion activity of the reduced catalysts was higher than that for the oxidized forms. However, the oxidized Pd catalysts had a considerably higher selectivity for the H<sub>2</sub>O<sub>2</sub> formation. Also, the H<sub>2</sub>O<sub>2</sub> decomposition activity was an order of magnitude higher for the reduced Pd catalysts. The higher H<sub>2</sub>O<sub>2</sub> decomposition activity for the reduced Pd catalysts may be related to the higher propensity for H<sub>2</sub>O<sub>2</sub> adsorption on reduced Pd sites.

In case of the direct H<sub>2</sub> oxidation process, the selectivity for H<sub>2</sub>O<sub>2</sub> may decrease either due to combustion side reaction (H<sub>2</sub> + 0.5O<sub>2</sub> → H<sub>2</sub>O) or secondary reactions of H<sub>2</sub>O<sub>2</sub> leading to further water formation. Therefore, a lowering of the H<sub>2</sub>O<sub>2</sub>

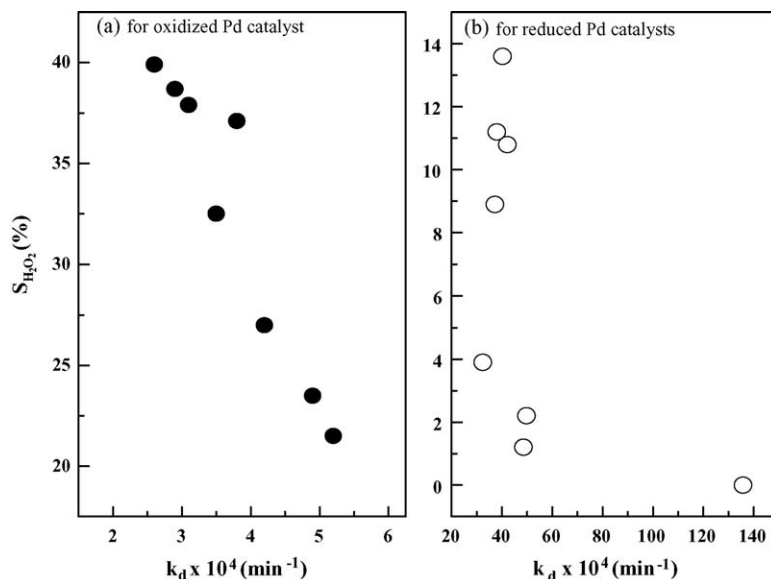


Fig. 4. Variation of H<sub>2</sub>O<sub>2</sub> selectivity ( $S_{\text{H}_2\text{O}_2}$ ) in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation with the H<sub>2</sub>O<sub>2</sub> decomposition activity for the different supported oxidized (a) and reduced (b) Pd catalysts ( $k_d$  = pseudo-first order H<sub>2</sub>O<sub>2</sub> decomposition rate constant).

Table 1  
Surface and bulk properties of the different reduced Pd catalysts

Catalyst	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Average Pd particle size (nm)
Pd (2.5%)/Al <sub>2</sub> O <sub>3</sub>	176.0	24.0 <sup>a</sup>
Pd (2.5%)/Ga <sub>2</sub> O <sub>3</sub>	36.0	22.0 <sup>a</sup>
Pd (2.5%)/CeO <sub>2</sub>	18.0	45.0 <sup>b</sup>
Pd (2.5%)/ZrO <sub>2</sub>	59.0	54.0 <sup>b</sup>
Pd (2.5%)/ThO <sub>2</sub>	1.0	–
Pd (2.5%)/SiO <sub>2</sub>	231.0	12.0 <sup>a</sup>
Pd (2.5%)/CeO <sub>2</sub> -ZrO <sub>2</sub>	8.0	–
Pd (2.5%)/BPO <sub>4</sub>	25.0	–
Pd (2.5%)/H-β	165.0	18.0 <sup>a</sup>

<sup>a</sup> Determined by using Scherrer's formula.

<sup>b</sup> Obtained from TEM.

conversion activity of the catalyst should increase the H<sub>2</sub>O<sub>2</sub> selectivity in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation. In line with this, a good correlation was observed between the selectivity for H<sub>2</sub>O<sub>2</sub> in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation process and the H<sub>2</sub>O<sub>2</sub> decomposition activity for the oxidized catalysts (Fig. 4a). Metal particle size and surface area data for the different reduced Pd catalysts are shown in Table 1. The properties of the reduced Pd catalysts were found to be less important in determining the H<sub>2</sub>O<sub>2</sub> yield/selectivity in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation. The reduced Pd catalysts in general, gave more or less similar results (little or no H<sub>2</sub>O<sub>2</sub> selectivity) in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation because of their extremely high H<sub>2</sub>O<sub>2</sub> decomposition activity (Fig. 2).

### 3.3. Effect of metal additives

Results showing the influence of gold (Au) concentration in the oxidized Pd-Au/ZrO<sub>2</sub> catalyst on its performance in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation reaction at 25 °C in an aqueous acidic (0.03 M

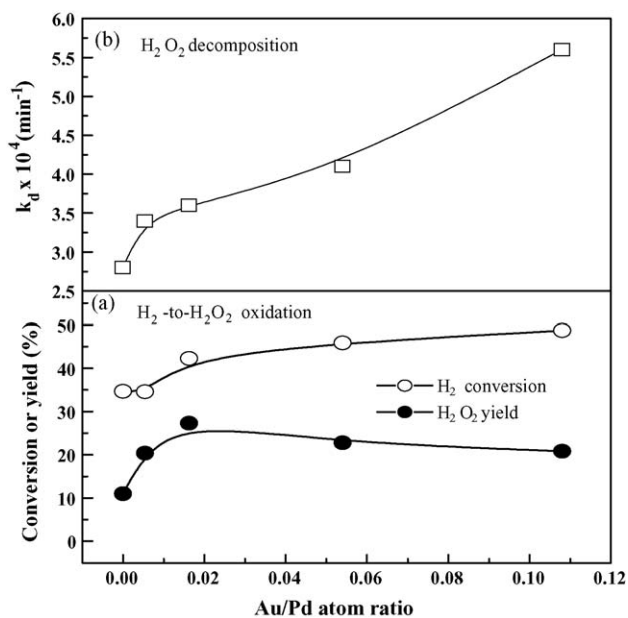


Fig. 5. Influence of the concentration of gold loading in the oxidized Pd/ZrO<sub>2</sub> catalyst on the: (a) H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation and (b) H<sub>2</sub>O<sub>2</sub> decomposition rate constant ( $k_d$ ) in aqueous acidic (0.03 M H<sub>3</sub>PO<sub>4</sub>) reaction medium (at 25 °C).

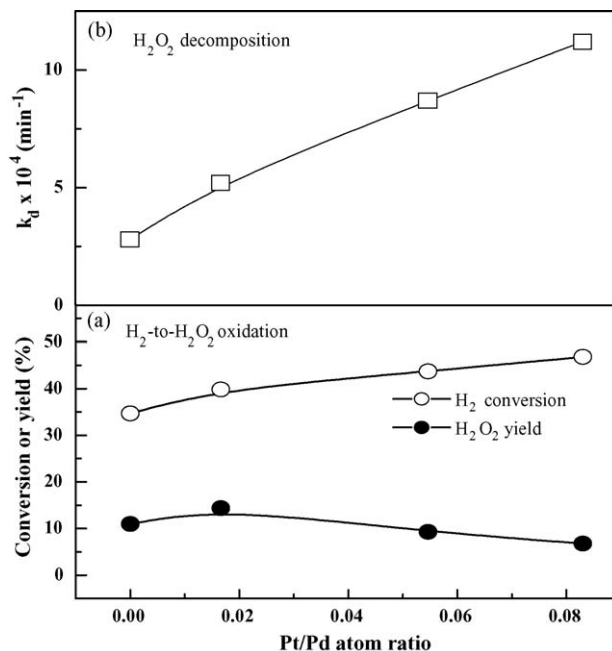


Fig. 6. Influence of the concentration of Pt in the oxidized Pd (2.5%)/ZrO<sub>2</sub> catalyst on the: (a) H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation and (b) H<sub>2</sub>O<sub>2</sub> decomposition rate constant ( $k_d$ ) in aqueous acidic (0.03 M H<sub>3</sub>PO<sub>4</sub>) reaction medium (at 25 °C).

H<sub>3</sub>PO<sub>4</sub>) medium are presented in Fig. 5a. The H<sub>2</sub> conversion over the catalyst was found to increase with the increasing gold loading in the catalyst. However, the H<sub>2</sub>O<sub>2</sub> yield in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation initially increased (more than doubled) and then decreased slightly with increase in the Au concentration. Thus, an optimum Au concentration is required for achieving high H<sub>2</sub>O<sub>2</sub> yields in the reaction under the investigated experimental

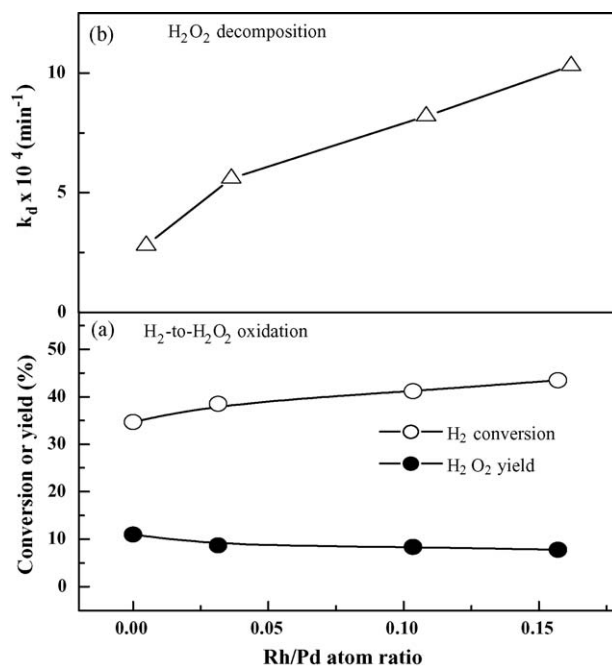


Fig. 7. Influence of the concentration of Ru in the oxidized Pd (2.5%)/ZrO<sub>2</sub> catalyst on the: (a) H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation and (b) H<sub>2</sub>O<sub>2</sub> decomposition rate constant ( $k_d$ ) in aqueous acidic (0.03 M H<sub>3</sub>PO<sub>4</sub>) reaction medium (at 25 °C).

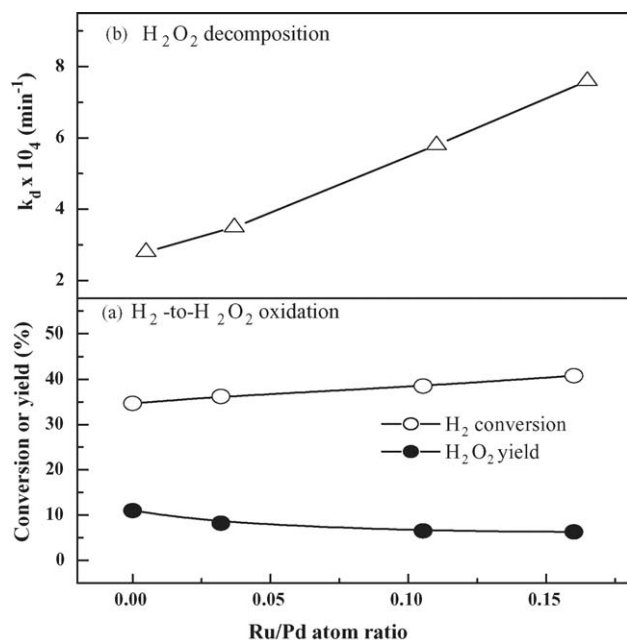


Fig. 8. Influence of the concentration of Rh in the oxidized Pd (2.5%)/ZrO<sub>2</sub> catalyst on the: (a) H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation and (b) H<sub>2</sub>O<sub>2</sub> decomposition rate constant ( $k_d$ ) in aqueous acidic (0.03 M H<sub>3</sub>PO<sub>4</sub>) reaction medium (at 25 °C).

conditions. The observed lower H<sub>2</sub>O<sub>2</sub> yield at the higher Au concentration in the catalyst may be attributed to the higher H<sub>2</sub>O<sub>2</sub> decomposition activity of the catalyst, as shown in Fig. 5b. The initial increase in H<sub>2</sub>O<sub>2</sub> yield may be related to the decrease in the H<sub>2</sub> to H<sub>2</sub>O side reaction (due to presence of Au). Previous studies have shown that Au catalysts show a high selectivity for H<sub>2</sub>O<sub>2</sub> formation in the direct H<sub>2</sub>O<sub>2</sub> synthesis process [8]. This may be related to the ability of the Au to form stable hydroperoxy species which are considered to be the precursors for H<sub>2</sub>O<sub>2</sub> [16]. The increase in the secondary decomposition reaction of H<sub>2</sub>O<sub>2</sub> (Fig. 5b) however probably dominates at higher Au concentration leading to a maximum in H<sub>2</sub>O<sub>2</sub> yield with Au content.

Results showing the influence of Pt concentration in the oxidized Pd-Pt/ZrO<sub>2</sub> catalyst on its performance in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation in an aqueous acidic (0.03 M H<sub>3</sub>PO<sub>4</sub>) reaction medium are presented in Fig. 6a. The H<sub>2</sub> conversion activity of the catalyst increased with the increase in the Pt concentration in the catalyst. Similar to the Au case, the H<sub>2</sub>O<sub>2</sub> yield also passed through a maximum as a function of Pt content. However, in case of Pt addition, the initial increase in H<sub>2</sub>O<sub>2</sub> yield was lower than that observed on Au addition; H<sub>2</sub>O<sub>2</sub> yield increased only by a factor of ~1.5 in the Pt case. Interestingly the H<sub>2</sub>O<sub>2</sub> yield at higher Pt concentrations quickly dropped below that of monometallic Pd-based catalyst; this was in contrast to the Au case (Fig. 5a). The observed decrease in the H<sub>2</sub>O<sub>2</sub> yield/selectivity in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation with the increase in the Pt concentration in the catalyst may be attributed to the increased H<sub>2</sub>O<sub>2</sub> decomposition activity of the catalyst (Fig. 6b) and decreasing stability of the hydroperoxy species (precursor for H<sub>2</sub>O<sub>2</sub> formation [10,16]) eventually leading to water formation. The decreased stability of the hydroperoxy species at higher Pt content is probably related to the superior ability of Pt to catalyze the scission of the O–O bond [10].

Presence of Ru and Rh in the catalyst was found to be detrimental to the H<sub>2</sub>O<sub>2</sub> yields (Figs. 7 and 8). It is apparent that in case of Ru and Rh, the increase in H<sub>2</sub> conversion was not sufficient to compensate for the loss in H<sub>2</sub>O<sub>2</sub> selectivity due to increase in the secondary H<sub>2</sub>O<sub>2</sub> decomposition (Figs. 7b and 8b) and enhancement of the direct non-selective parallel H<sub>2</sub> to water oxidation side reaction.

#### 4. Concluding remarks

1. The H<sub>2</sub> conversion activity of the reduced Pd catalysts was higher than that for the oxidized forms. However, the oxidized Pd catalysts had a significantly higher selectivity for the H<sub>2</sub>O<sub>2</sub> formation.
2. The H<sub>2</sub>O<sub>2</sub> decomposition activity was an order of magnitude higher for the reduced Pd catalysts. Correspondingly the oxidized catalysts showed significantly superior H<sub>2</sub>O<sub>2</sub> yields.
3. Catalyst properties such as particle size and surface area were found to be less important than the oxidation state in determining the H<sub>2</sub>O<sub>2</sub> selectivity.
4. The H<sub>2</sub>O<sub>2</sub> yield in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation passed through a maximum with increase in the Au concentration. A similar effect was also observed in case of Pt. However, Au was found to be a superior promoter for the direct H<sub>2</sub>O<sub>2</sub> synthesis process.
5. Presence of Rh and Ru was found to be detrimental for the direct H<sub>2</sub>O<sub>2</sub> synthesis process.

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