

Factors influencing decomposition of H_2O_2 over supported Pd catalyst in aqueous medium

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Received 4 April 2006; accepted 4 July 2006

Available online 22 August 2006

Abstract

Since H_2O_2 decomposition can result in selectivity/yield loss in the direct H_2O_2 synthesis process from H_2 and O_2 over supported Pd catalysts, it is important to have an enhanced understanding about the factors affecting the H_2O_2 decomposition reaction. Herein, detailed studies have been undertaken to investigate the influence of different factors, such as (a) nature and concentration of acid in reaction medium, (b) nature and concentration of halide in presence and absence of acid in reaction medium, (c) pretreatment procedures and (d) catalyst modification by incorporation of different halides, on the H_2O_2 decomposition reaction over a 5% Pd/C catalyst in aqueous medium at 25 °C. This study has shown that the H_2O_2 decomposition activity is profoundly influenced by all the above factors. The effectiveness of the acids in suppressing the H_2O_2 decomposition activity decreased in the following order: hydroiodic acid > hydrobromic acid > hydrochloric acid \gg acetic acid > phosphoric acid > sulfuric acid > perchloric acid. The ability of the acid to decrease the H_2O_2 decomposition activity was found to very strongly depend on the nature of its associated anion. Halides, such as iodide, bromide and chloride were particularly effective in suppressing the H_2O_2 decomposition activity. Oxidation pretreatment of the catalyst was found to strongly suppress its H_2O_2 decomposition activity, while a reduction treatment was found to promote its activity. A gradual decrease in the H_2O_2 decomposition activity of the catalyst was observed with each successive usage due to *in situ* sub-surface oxidation of Pd by H_2O_2 . Halide incorporation either via the reaction medium or prior catalyst modification had a similar qualitative effect on the H_2O_2 decomposition activity.

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Keywords: H_2O_2 decomposition; H_2O_2 synthesis; Pd catalysts; Acid; Halides; Pretreatment

1. Introduction

Direct synthesis of H_2O_2 (versatile and environmentally benign oxidizing agent) from H_2 and O_2 over supported precious metal catalysts is a commercially important environment-friendly process [1]. While other precious metals have also been investigated as catalysts for this process, the main focus has been on Pd-based catalysts [2–14]. H_2O_2 , being thermodynamically less stable than water, is an intermediate product in the H_2 -to- H_2O_2 oxidation process. Its decomposition to water ($\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 0.5\text{O}_2$) is also catalyzed by Pd catalysts, which results in decreased H_2O_2 selectivity/yield in the H_2 -to- H_2O_2 oxidation process. In order to obtain high H_2O_2 selectivity in the process it is necessary to drastically reduce the H_2O_2 decompo-

sition activity of the catalyst. It is therefore essential to obtain an enhanced understanding about the factors that influence the H_2O_2 decomposition activity of Pd catalysts.

Our previous studies have suggested that factors, such as concentration of acid [15], oxidation state of Pd [7] and catalyst modification by halides [14] can have a significant influence on the H_2O_2 decomposition reaction over Pd catalysts. The current study was undertaken to obtain detailed systematic information on the various factors affecting the H_2O_2 decomposition reaction. The influence of the following factors has been investigated in this paper: (1) nature of the acid medium (acetic acid, phosphoric acid, sulfuric acid, perchloric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid); (2) concentration of the acid (0.1–1.0 M); (3) nature of halides (potassium iodide, potassium bromide, potassium chloride and potassium fluoride) in presence and absence of acidic medium; (4) concentration of halides (2.7 and 24.3 mmol dm⁻³); (5) oxidation (*ex situ* and *in situ*) and reduction treatments in presence and absence of

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acidic medium; (6) nature of halide promoters (I^- , Br^- , Cl^- , F^-) incorporated in Pd catalyst.

2. Experimental

The Pd (5%)/C catalyst in its reduced form was obtained from Lancaster (UK). The PdO and/or Pd⁰ phases were confirmed by X-ray powder diffraction, using a Holland Phillips, PW/1730 X-ray generator with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$; 40 kV, 25 Ma). Also for studying the influence of different halides incorporated in the Pd/C catalyst on its H₂O₂ decomposition activity, 5 wt% halogen (F, Cl, Br or I) was incorporated in the Pd/C catalyst by impregnating on it the respective ammonium halide from its aqueous solution using incipient wetness technique, drying and calcining in a flow of O₂-free N₂ (30 cm³ min⁻¹) at 400 °C for 1 h. Some of the catalysts were also characterized by the X-ray photoelectron spectroscopy (XPS), using a VG-scientific ESCA-3 MK II electron spectrometer to confirm the presence of adsorbed halides.

The H₂O₂ decomposition reaction over the catalysts was carried out using a magnetically stirred glass reactor (capacity: 250 cm³) containing 0.2 g catalyst in 150 cm³ aqueous reaction medium, with or without containing acid and/or halide anions, by injecting 1 ml of 30 w/v% H₂O₂ solution in the reactor under vigorous stirring and measuring the gas (O₂) evolved in the H₂O₂ decomposition at 25 °C and atmospheric pressure, as a function of time, using a constant pressure gas collector [16]. The percent H₂O₂ decomposition data was estimated as follows:

$$\text{H}_2\text{O}_2 \text{ decomposition (\%)} = \frac{V_t}{V_T} \times 100$$

where, V_t is the volume of O₂ evolved in time t and V_T is the volume of O₂ evolved in the complete decomposition of H₂O₂ in the reactor. The H₂O₂ 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 O₂ evolved in the complete H₂O₂ decomposition, V_t the volume of O₂ evolved in time t and C_A is the catalyst concentration/loading. Thermal decomposition (in absence of catalyst) was found to be insignificant for the duration of the reaction. Independent analysis of un-reacted H₂O₂ (via iodometric titration) was undertaken for selected experiments, which confirmed that the O₂ evolved provided a true measure of H₂O₂ decomposition. Some of the experiments were repeated and an excellent reproducibility (within 5%) was observed for these experiments. As the reaction involved decomposition of small amounts of diluted H₂O₂ leading to the formation of H₂O and O₂ there were no significant safety issues related to these experiments.

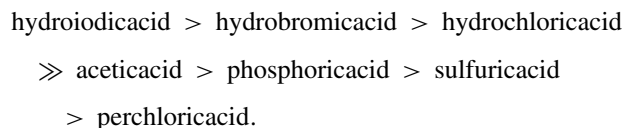
In order to study the influence of surface/sub-surface oxidation or reduction of Pd catalyst on its H₂O₂ decomposition activity, the Pd/C catalyst was pretreated by O₂ and H₂ before using the catalyst, as follows. The H₂ or O₂ gas pretreatment was carried out in the glass reactor containing the Pd/C catalyst in pure water or aqueous 0.1 M H₃PO₄, first by flushing the

reactor with O₂-free N₂ (30 cm³ min⁻¹) and then passing pure H₂ or O₂ through the reactor under vigorous stirring for 1 h at room temperature.

3. Results and discussions

3.1. Nature and concentration of acid medium

Fig. 1 shows the effect of the nature of the acid on the H₂O₂ decomposition activity. While the catalyst showed very high activity for H₂O₂ decomposition in the aqueous medium, its activity was markedly reduced in the presence of the acids. The effectiveness of the acids in decreasing the H₂O₂ decomposition activity decreased in the following order:



The acids based on their ability to suppress the H₂O₂ decomposition activity, could be broadly classified into two groups: the oxyacids (acetic acid, phosphoric acid, sulfuric acid and perchloric acid) which moderately decreased the H₂O₂ decomposition activity and the strongly suppressing halide acids (hydrochloric acid, hydrobromic acid and hydroiodic acid). Addition of the halide acids decreased the H₂O₂ decomposition activity by more than an order of magnitude (Fig. 2) as compared to a reaction medium without any acid.

The effect of the acid concentration on the H₂O₂ decomposition activity is shown in Fig. 3. In both the cases (sulfuric acid and phosphoric acid) there was a clear suppression of the H₂O₂ decomposition activity with increasing acid concentration (0.01–1.0 M). This indicates that the H₂O₂ decomposition

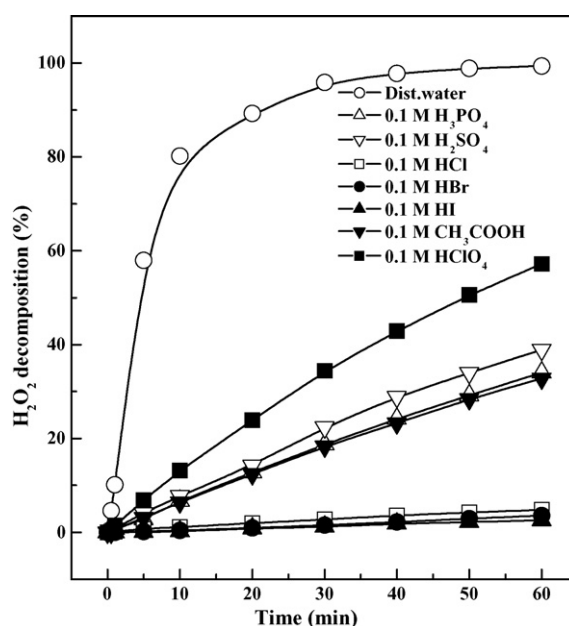


Fig. 1. Effect of different reaction mediums on the decomposition of H₂O₂ (at 25 °C) over the reduced Pd/C catalyst.

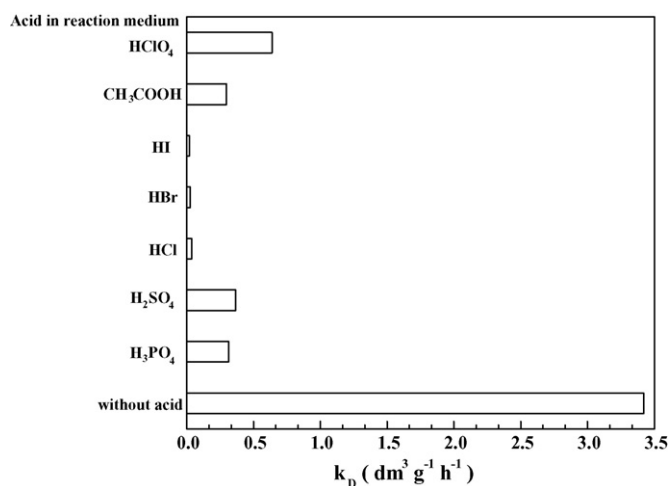
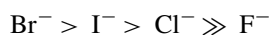


Fig. 2. H₂O₂ decomposition activity (k_D) of reduced Pd/C catalyst in different reaction mediums.

activity decreases with increasing proton concentration in the reaction medium. This may be attributed to the increased stability of H₂O₂ in presence of protons probably due to decreased interaction of the protonated H₂O₂ molecules with the catalyst surface. However, if the ability of the acid to donate protons to the reaction medium was the only criterion for determining the effectiveness of the acid, perchloric acid (which is a much stronger acid than acetic acid) would be expected to have a much larger effect on the H₂O₂ decomposition activity. Since this was not observed, it is apparent that the associated anions of the acid present in the reaction medium play an important role in determining the H₂O₂ decomposition activity.

3.2. Nature and concentration of halides in presence and absence of acidic reaction medium

Since the halide acids were particularly efficient in decreasing the H₂O₂ decomposition activity, the effect of the halide ions was investigated in presence and absence of an acidic reaction medium. Results showing the influence of different halides (potassium salts) and their concentrations in the aqueous medium on the H₂O₂ decomposition over the reduced Pd/C catalyst are presented in Fig. 4. The H₂O₂ decomposition activity of the catalyst was strongly suppressed in the presence of chloride, iodide and bromide anions in the reaction medium. In contrast the presence of fluoride ions had a negligible effect. The nature of the anion was thus found to be critical in determining the H₂O₂ decomposition activity. At a halide concentration of 2.7 mmol dm⁻³, the effect of the anions in reducing the H₂O₂ decomposition activity decreased in the following order:



Halide anions are known to adsorb on the catalyst surface [17]. Depending on their properties, it appears that the adsorbed anions block/modify the active catalytic sites and thereby influence the H₂O₂ decomposition activity.

On increasing the concentration of the halide from 2.7 to 24.3 mmol dm⁻³ the H₂O₂ decomposition activity further decreased in case of the Cl⁻ and Br⁻ ions, while there was no corresponding effect in case of F⁻ ions. Interestingly, in case of the I⁻ ions the H₂O₂ decomposition activity actually increased on increasing its concentration in the aqueous medium. This may be attributed to the homogeneous iodide (present in large excess) catalyzed decomposition of H₂O₂.

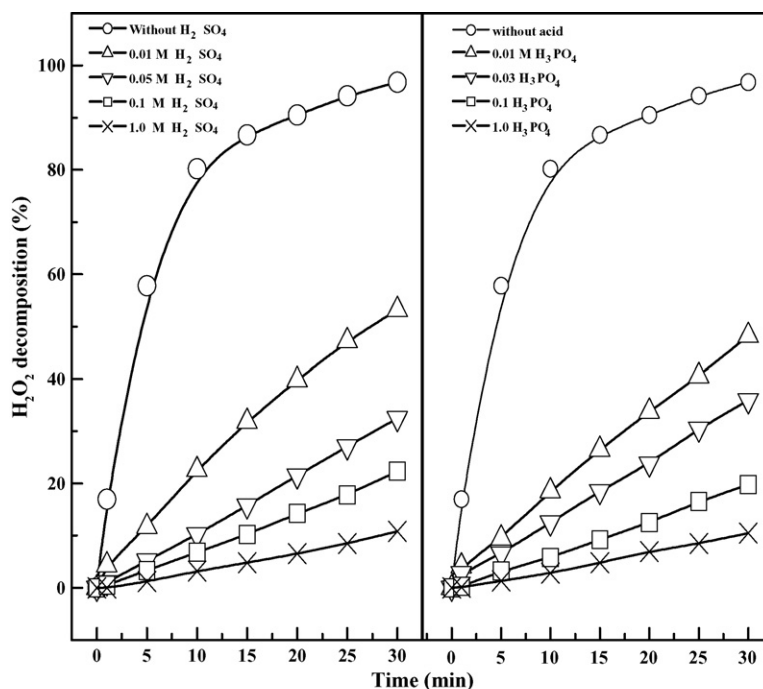


Fig. 3. Effect of H₂SO₄ and H₃PO₄ acid concentrations in aqueous medium on the rate of H₂O₂ decomposition over the reduced Pd/C catalyst.

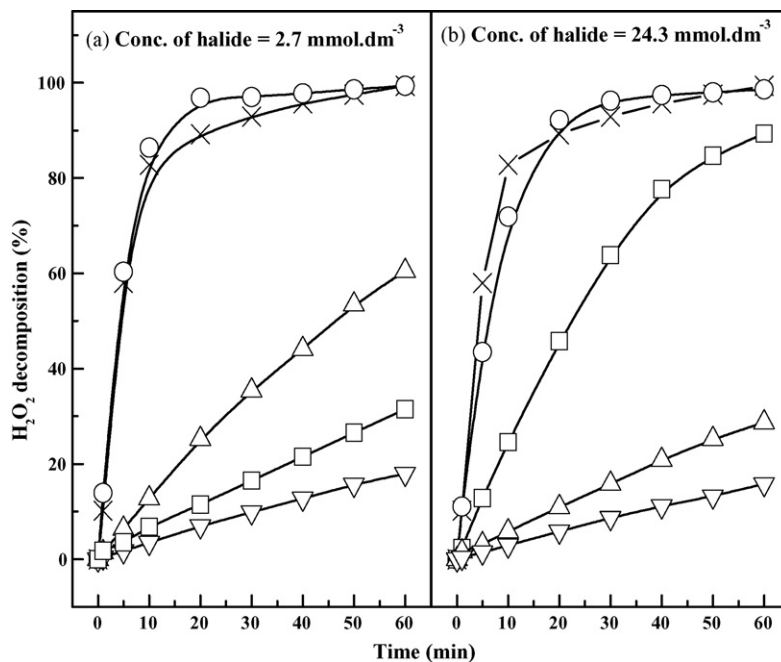


Fig. 4. (a and b) Effect of different halides and their concentrations in aqueous (pure water) reaction medium on the decomposition of H_2O_2 (at 25°C) over the reduced Pd/C catalyst (halides in the reaction medium: without halide (\times), KF (\circ), KCl (\triangle), KBr (∇) and KI (\square)).

Results showing the influence of different halide anions and their concentrations in the aqueous acidic reaction medium ($0.1\text{ M H}_3\text{PO}_4$) on the decomposition of H_2O_2 over the reduced Pd/C catalyst are presented in Fig. 5. The rate of H_2O_2 decomposition over the catalyst was drastically reduced in the presence of chloride, bromide or iodide anions in the acidic reaction medium. The H_2O_2 decomposition rate was further reduced with increasing halide (*viz.* Cl, Br^- or I^-) concentration in the acidic reaction medium. The observed decrease in the H_2O_2 decomposition activity may be attributed to combined presence

of protons and halide anions (site poisoning) in the reaction medium. Interestingly, the H_2O_2 decomposition activity of the catalyst was increased in the presence of fluoride anions in the reaction medium. The catalytic activity for H_2O_2 decomposition was further increased with increasing the fluoride concentration in the reaction medium. Further studies need to be undertaken to understand this complex effect exhibited by F^- ions in the acidic reaction medium.

Based on these studies described in the previous two sections, it is apparent that the effectiveness of the acid for suppressing

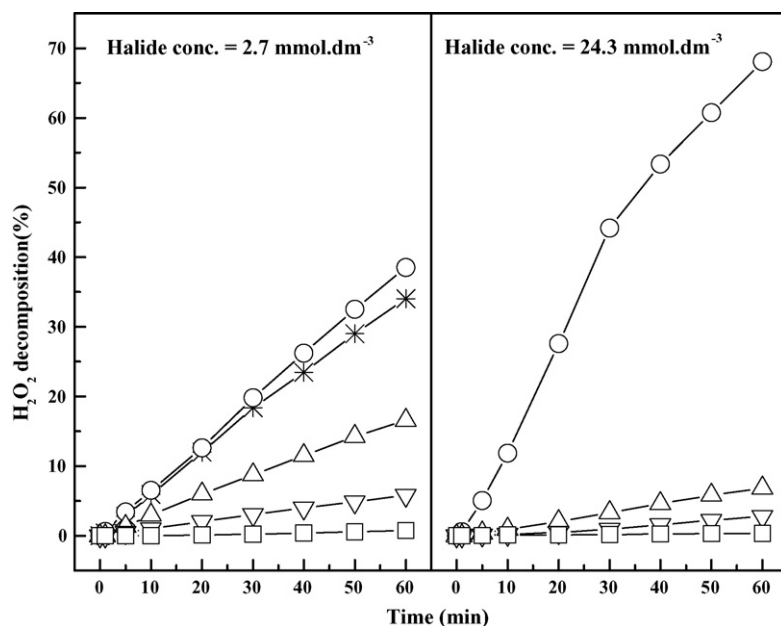


Fig. 5. Effect of different halides and their concentrations in aqueous acidic ($0.1\text{ M H}_3\text{PO}_4$) reaction medium on the H_2O_2 decomposition (at 25°C) over the reduced Pd/C catalyst (halides in the reaction medium: without halide ($*$), KF (\circ), KCl (\triangle), KBr (∇) and KI (\square)).

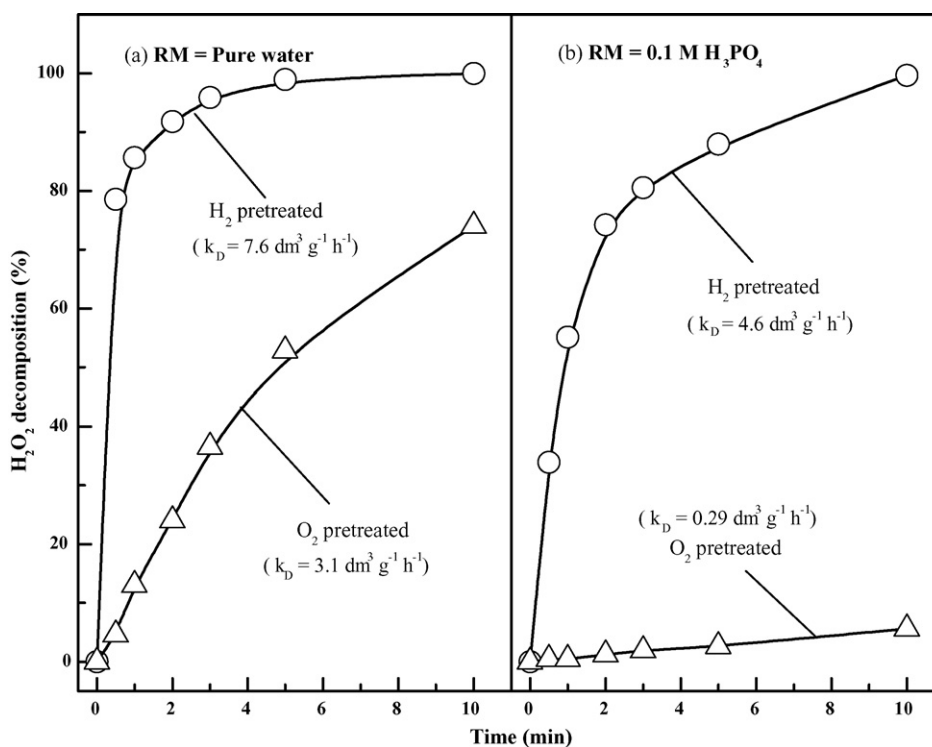


Fig. 6. (a and b) Influence of H₂ and O₂ pretreatments to the Pd/C catalyst on its H₂O₂ decomposition activity (at 25 °C) in aqueous (pure water) and aqueous acidic (0.1 M H₃PO₄) reaction medium.

the H₂O₂ decomposition activity depends on the nature of its associated anions and its ability to donate protons to the reaction medium.

3.3. Catalyst pretreatment

Results illustrating the influence of H₂ and O₂ pretreatments to the Pd/C catalyst on its H₂O₂ decomposition activity in non-acidic aqueous and acidic aqueous (0.1 M H₃PO₄) reaction mediums are presented in Fig. 6. While the H₂ pretreated catalyst showed a very high H₂O₂ decomposition activity, the O₂ pretreated catalyst showed much lower H₂O₂ decomposition activity. The observed much higher H₂O₂ decomposition activity of the H₂ pretreated catalyst may be attributed to the surface/sub-surface reduction of Pd in the catalyst. Whereas, the lower H₂O₂ decomposition activity of the O₂ pretreated catalyst may be related to the surface/sub-surface oxidation of Pd to PdO in the catalyst. The ability of Pd⁰ to form stable intermediate Pd–H species is expected to assist the H₂O₂ decomposition reaction. In line with the study described in the previous section, the H₂O₂ decomposition activity of the pretreated catalysts in the presence of acid was found to be considerably lower than that in the absence of the acid.

Results showing the successive *in situ* pretreatment of the catalyst during the decomposition of H₂O₂ over the catalyst in aqueous medium on its H₂O₂ decomposition activity are presented in Fig. 7. The H₂O₂ decomposition activity of the catalyst decreased after its use in the H₂O₂ decomposition. The observed gradual decrease in the H₂O₂ decomposition activity (Fig. 7) of

the catalyst with each successive use may be attributed to the sub-surface oxidation of Pd by H₂O₂, which is a strong oxidizing agent. These results suggest that in the H₂-to-H₂O₂ oxidation over reduced Pd catalyst, the activity and selectivity of the catalyst is expected to vary with the reaction time and usage pattern.

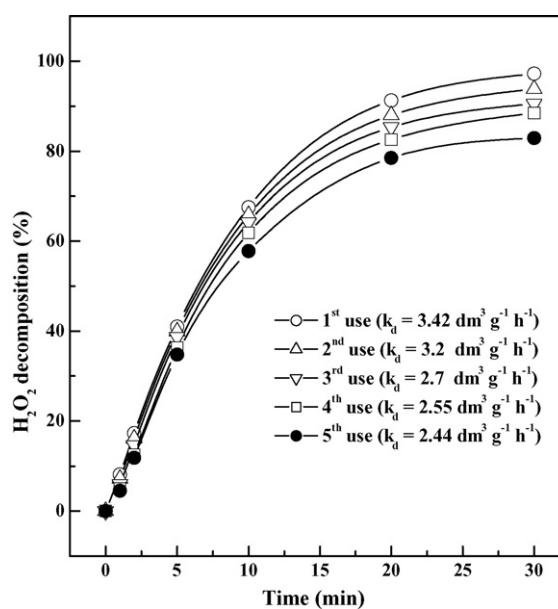


Fig. 7. Effect of the catalyst oxidation by the successive pretreatment by H₂O₂ (in the reaction medium) on the decomposition of H₂O₂ (at 25 °C) over the Pd/C catalyst.

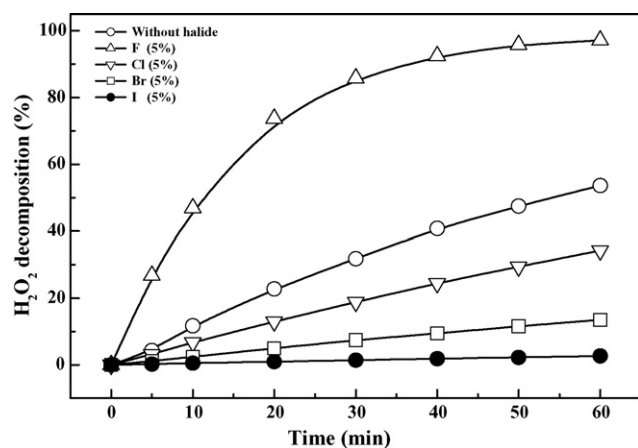
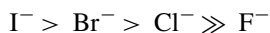


Fig. 8. Influence of the different halogens incorporated in the Pd/C catalyst on its activity for H_2O_2 decomposition (at 25°C) in aqueous acidic ($0.05\text{ M H}_2\text{SO}_4$) reaction medium.

3.4. Halide-modified catalyst

Results depicting the influence of different halide-modified Pd/C catalysts on its H_2O_2 decomposition activity in an aqueous acidic ($0.05\text{ M H}_2\text{SO}_4$) reaction medium are presented in Fig. 8. XRD analysis of the halide-modified catalyst showed that metallic Pd phase remained intact in the catalyst even after the halide incorporation procedure. The H_2O_2 decomposition activity of the catalyst increased markedly after its fluorination. However, incorporation of the chloride, bromide or iodide in the catalyst caused a reduction in the H_2O_2 decomposition activity of the catalyst. The influence of the incorporated halides in reducing the H_2O decomposition decreased in the following order:



It is noteworthy that presence of halide ions in form of potassium salts in the acidic reaction medium exhibited a similar influence on the H_2O_2 decomposition activity (Fig. 5). This may be related to the fact that even when the halides are introduced in the reaction medium, they are eventually adsorbed on the catalyst surface.

4. Concluding remarks

1. The effectiveness of the acids in decreasing the H_2O_2 decomposition activity decreased in the following order: hydroiodic acid > hydrobromic acid > hydrochloric acid \gg acetic acid > phosphoric acid > sulfuric acid > perchloric acid. Presence of acid (proton donor) in the reaction medium decreased the

decomposition activity by decreasing H_2O_2 adsorption on decomposition sites.

2. The H_2O_2 decomposition activity of the Pd/C catalyst was strongly suppressed in the presence of chloride, iodide and bromide anions in the reaction medium. In contrast the presence of fluoride ions had a promotional effect on the decomposition. The nature of the anion was thus found to be critical in determining the H_2O_2 decomposition activity.
3. While the H_2 pretreated catalyst showed a very high H_2O_2 decomposition activity, the O_2 pretreated catalyst showed much lower H_2O_2 decomposition activity. The observed much higher H_2O_2 decomposition activity of the H_2 pretreated catalyst may be attributed to the surface/sub-surface reduction of Pd in the catalyst. Whereas, the lower H_2O_2 decomposition activity of the O_2 pretreated catalyst may be related to the surface/sub-surface oxidation of Pd to PdO in the catalyst.
4. Halides whether present in the reaction medium or incorporated in the catalyst (*via* catalyst modification) had a similar qualitative effect on the H_2O_2 decomposition activity.

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