Catal Lett (2008) 125:296–301
DOI 10.1007/s10562-008-9482-9

# Direct $H_2$-to-$H_2O_2$ Oxidation in Aqueous Acidic Medium Containing Br Promoter Over Pd/$Al_2O_3$ and Pd/C Catalysts Thermally Pretreated Under Different Conditions

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Received: 25 July 2007 / Accepted: 26 March 2008 / Published online: 23 July 2008

**Abstract** Influence of thermal pretreatments (under $N_2$, air or $H_2$ gas atmosphere at 500 °C or 700 °C) has been investigated for the Pd/$Al_2O_3$ and Pd/Carbon catalysts in terms of its effect on their Pd particle size and performance in the $H_2$-to-$H_2O_2$ oxidation and $H_2O_2$ destruction (by decomposition and/or hydrogenation) reactions in aqueous acidic medium containing Br promoter. The influence on the net $H_2O_2$ formation is found to depend strongly upon the catalyst support due to support–Pd cluster interactions. For both the catalysts, the thermal treatments (except in air) caused a large increase in their Pd particle size. The increase in Pd particle size caused an increase in the $H_2O_2$ formation activity of Pd/$Al_2O_3$ but a decrease in the $H_2O_2$ formation activity of Pd/C.

**Keywords** Hydrogen peroxide ·
Oxidation of $H_2$ to $H_2O_2$ · Pd/$Al_2O_3$ · Pd/C

## 1 Introduction

Direct Pd-catalyzed oxidation of $H_2$ to $H_2O_2$ by $O_2$ is of significant practical important for replacing the presently practiced hydroquinone auto-oxidation process for the production of $H_2O_2$, an environ-friendly versatile oxidizing agent. The hydroquinone auto-oxidation process involves complicated indirect oxidation of $H_2$ to $H_2O_2$ and, moreover, it is economical only for the large scale production of $H_2O_2$ [1]. The $H_2$-to-$H_2O_2$ oxidation has attracted considerable attention in recent years [2–22]. This start of a demonstration plant for this process has also been announced recently by Degussa [23]. This process, however, has not yet been commercialized because of the problems related to the $H_2O_2$ selectivity/yield and safety.

The net $H_2O_2$ formation in the $H_2$-to-$H_2O_2$ oxidation is controlled by the following parallel and consecutive reactions [13, 24].

$$H_2 + O_2 \rightarrow H_2O_2 \quad \text{(parallel } H_2O_2 \text{ forming reaction)} \tag{1}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \quad \text{(parallel direct water forming reaction)} \tag{2}$$

$$H_2O_2 \rightarrow H_2O + 0.5O_2 \quad \text{(consecutive } H_2O_2 \text{ decomposition reaction)} \tag{3}$$

$$H_2O_2 + H_2 \rightarrow 2H_2O \quad \text{(consecutive } H_2O_2 \text{ hydrogenation reaction)} \tag{4}$$

Our recent studies [13] showed that the $H_2O_2$ destruction by the consecutive water forming reactions (reactions 3 and 4) are strongly inhibited and, thereby, the net $H_2O_2$ formation (or $H_2O_2$ yield) over supported Pd catalysts is drastically increased due to the addition of $Cl^-$ or $Br^-$ anions in an aqueous acidic reaction medium. The use of chloride or bromide as the catalyst promoter in the $H_2$-to-$H_2O_2$ oxidation has also been reported in other recent studies [8, 9, 14, 19, 20]. It is also interesting to understand the influence of the particle size of Pd on the net $H_2O_2$ formation in the $H_2$-to-$H_2O_2$ oxidation process and also on the $H_2O_2$ destruction reactions under similar conditions. However, no detailed investigation on this has been reported so far.

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This investigation was under taken for studying the influence of different thermal pretreatments [under different gas (viz. inert, oxidizing or reducing) atmospheres and temperatures] on the Pd particle size and net $H_2O_2$ formation performance of the $Pd/Al_2O_3$ and Pd/C catalysts, that were used in our earlier studies [13, 20, 21].

## 2 Experimental

Pre-reduced Pd (5 wt.%)/$Al_2O_3$ (Alfa-Aesar) and Pd (5 wt.%)/C (Lancaster) catalysts, in their fine powdered form, were obtained from Lancaster, UK. These catalysts were thermally pretreated in a quartz tubular reactor in a flow of gas (viz. $N_2$, air or $H_2$) at 500 °C or 700 °C for 8 h. Before its use, the thermally pretreated (in air) catalyst was reduced by an ammoniacal hydrazine. The catalysts, with or without thermal treatment, were characterized by XRD [using a Holland Philips, PW/1730 X-ray generator with $CuK_\alpha$ radiation ($\lambda = 1.5406$ Å, 40 kV, 25 mA)] and by HRTEM (using a JEOL JEM-1200EX transmission electron microscope operating at 100 kV).

The $H_2$-to-$H_2O_2$ oxidation reaction over the catalysts was carried out in a magnetically stirred glass reactor (100 $cm^3$), using aqueous 0.1 M $H_3PO_4$ as the aqueous acidic reaction medium, under vigorous stirring at the following reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 $cm^3$, concentration of KBr in the reaction medium = 1.0 $mmol/dm^3$, gaseous feed = a mixture of $H_2$ and $O_2$ (1:1) at a total gas flow rate of 6.0 $cm^3$/min, pressure = atmospheric (95 kPa), temperature = 27 °C and reaction period = 1.0 h. The $H_2O_2$ formed was determined by the iodometric titration. The $H_2$ conversion, $H_2O_2$ selectivity and $H_2O_2$ yield are defined as follows:

Conversion of $H_2$ (%) = [(moles of $H_2$ converted)/(moles of $H_2$ in the feed)] × 100.

$H_2O_2$ yield (%) = [(moles of $H_2O_2$ formed)/(moles of $H_2$ in the feed)] × 100.

$H_2O_2$ selectivity (%) = [(moles of $H_2O_2$ formed)/(moles of $H_2$ converted)] × 100.

The $H_2O_2$ decomposition (in the absence of $H_2$) and hydrogenation (in the presence of $H_2$) reactions over the catalysts were carried out in the same reactor described above, in the presence of static air and static $H_2$, respectively, by injecting 1.0 $cm^3$ of aqueous 30 wt.% $H_2O_2$ through a rubber septum in the acidic reaction medium (50 $cm^3$) containing KBr (1.0 $mmol/dm^3$) under vigorous stirring and following the reactions as a function of time.

The detailed experimental procedures for carrying out the $H_2$-to-$H_2O_2$ oxidation, $H_2O_2$ decomposition and $H_2O_2$ hydrogenation reactions have been given earlier [13, 20].

## 3 Results and Discussion

Results showing the influence of thermal pretreatment to $Pd/Al_2O_3$ and Pd/C catalysts under different conditions on the Pd particle size and morphology are presented in Figs. 1 and 2. The $Pd/Al_2O_3$ and Pd/C catalysts, before and after their thermal pretreatments under different gas atmospheres ($N_2$, air or $H_2$) and/or temperatures (500 °C or 700 °C), are compared in Table 1 for their performance in the $H_2$-to-$H_2O_2$ oxidation (with $H_2/O_2$ feed ratio of 1.0) in an acidic (0.1 M $H_3PO_4$) aqueous medium containing bromide anions (1.0 $mmol/dm^3$). The Pd particle size data (obtained from HRTEM and/or XRD peak broadening) for the thermally pretreated catalysts are included in Table 1.

The $H_2O_2$ destruction [by the $H_2O_2$ decomposition (reaction 3) and hydrogenation (reaction 4)] activity of both the catalysts, before and after their thermal pretreatment, was also determined at the conditions similar or close to that employed in the $H_2$-to-$H_2O_2$ oxidation. The results of the $H_2O_2$ decomposition and hydrogenation over the $Pd/Al_2O_3$ and Pd/C catalysts, pretreated at different conditions, are presented in Figs. 3 and 4, respectively. The initial rates of the $H_2O_2$ decomposition and hydrogenation reactions over the catalysts are included in Table 1.

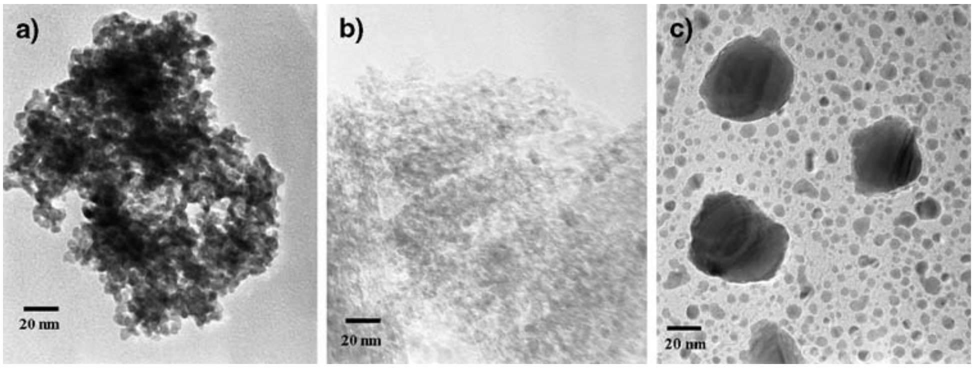

**Fig. 1** HRTEM photograph of $Pd/Al_2O_3$ with or without pretreatment [(**a**) without pretreatment, (**b**) pretreated in air at 500 °C and then reduced by ammoniacal hydrazine and (**c**) pretreated in $N_2$ at 500 °C]

**Fig. 2** HRTEM photograph of (**a**) Pd/$Al_2O_3$ pretreated in $H_2$ at 500 or 700 °C and (**b**) Pd/C with or without thermal pretreatment in $H_2$ at 700 °C

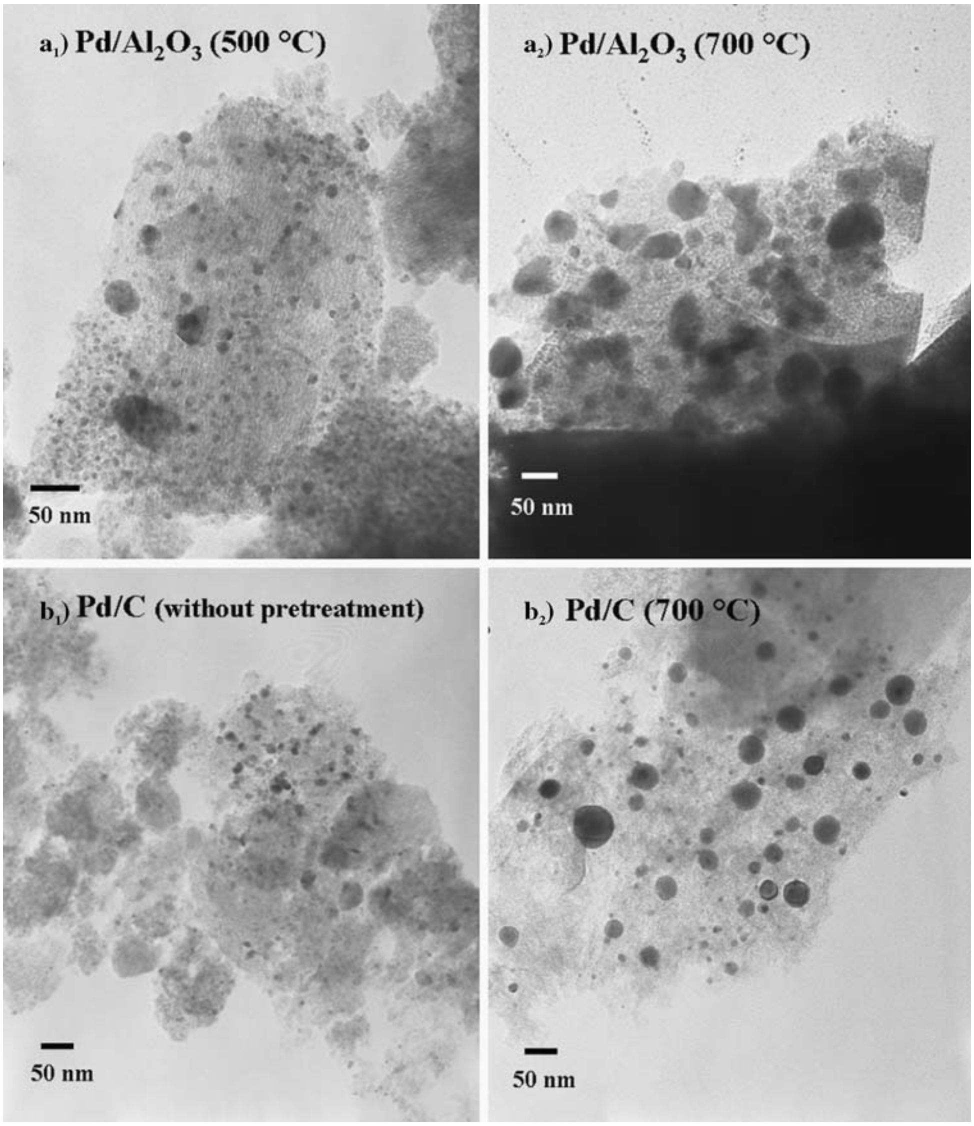

**Table 1** Results of the direct oxidation of $H_2$ to $H_2O_2$ and $H_2O_2$ destruction, in presence of air or $H_2$, over the thermally pretreated Pd/$Al_2O_3$ and Pd/C catalysts

| Thermal pretreatment to catalyst | | Particle size of Pd (nm) | | $H_2$-to-$H_2O_2$ oxidation | | | Initial rate of $H_2O_2$ destruction ($h^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| Gas atm. | Temp. (°C) | HRTEM | XRD | $X_{H_2}$[a] (%) | $Y_{H_2O_2}$[b] (%) | $S_{H_2O_2}$[c] (%) | In air[d] | In $H_2$[e] |
| *Catalyst: Pd/$Al_2O_3$* | | | | | | | | |
| Without pretreatment | | 8 | – | 89.8 | 44.0 | 49.0 | 0.10 | 1.4 |
| $N_2$ | 500 | 8 & 25 | – | 82.7 | 45.5 | 55.0 | 0.04 | 1.5 |
| Air | 500[f] | 7 | 10 | 78.3 | 27.8 | 35.5 | 0.05 | 2.1 |
| $H_2$ | 500 | 9 & 17 | – | 97.4 | 51.6 | 53.0 | 0.03 | 1.9 |
| $H_2$ | 700 | 20 & 30 | 28 | 95.5 | 53.5 | 56.0 | 0.02 | 1.6 |
| *Catalyst: Pd/C* | | | | | | | | |
| Without pretreatment | | 7 | 8 | 100 | 36.8 | 36.8 | 0.24 | 2.7 |
| $H_2$ | 700 | 20 & 40 | 29 | 81.6 | 29.8 | 36.5 | 0.20 | 2.1 |

[a] $X_{H_2}$ is conversion of $H_2$; [b] $Y_{H_2O_2}$ is yield of $H_2O_2$; [c] $S_{H_2O_2}$ is selectivity of $H_2O_2$; [d, e] $H_2O_2$ destruction by its decomposition and hydrogenation, respectively; [f] After the thermal treatment, the catalyst was reduced by ammoniacal hydrazine

## 3.1 Influence of Thermal Pretreatment to $Pd/Al_2O_3$

The XRD of $Pd/Al_2O_3$ catalyst without pretreatment indicated that the catalyst contains very small size Pd particles (i.e. highly dispersed) on boehmite; the XRD peak for Pd (at $2\theta = 40°$) was very small. XRD of the catalyst, calcined in air at 500 °C and subsequently reduced in presence of hydrazine, showed a broad peak for Pd (at $2\theta = 40°$) and transformation of boehmite to $\gamma$-alumina. The thermally treated $Pd/Al_2O_3$ at 500 °C or 700 °C showed narrow XRD peak for Pd on $\gamma$-alumina.

### *3.1.1 Influence on Pd Particle Size*

A comparison of the HRTEM results for the thermally pretreated $Pd/Al_2O_3$ at 500 °C under different gas atmospheres (Figs. 1 and 2) shows that (a) the treatment under air causes redispersion of the Pd with a small decrease in the Pd particle size (Fig. 1b), and (b) after the treatment under $N_2$ or $H_2$, some of the Pd particle grow into much larger Pd particles, leading to a biomodal dispersion of the Pd particles (Figs. 1c and 2a). The increase in the treatment temperature from 500 to 700 °C under $H_2$ results in a further growth of both the small and large Pd particles (Fig. 2a). The HRTEM photographs (Figs. 1 and 2) show that the Pd particles for all the thermally treated catalysts have irregular shape. The Pd particle size determined from the XRD peak broadening for Pd (at $2\theta = 40°$) for the different thermally treated $Pd/Al_2O_3$ catalysts is consistent with that observed from HRTEM of the catalysts (Table 1).

### *3.1.2 Influence on Catalytic Performance*

From the results in Table 1, the following important observations can be made. The influence of thermal treatment to $Pd/Al_2O_3$ at the same temperature (500 °C) on the net $H_2O_2$ formation (in the $H_2$-to-$H_2O_2$ oxidation) and $H_2O_2$ destruction activities of the catalyst depends strongly on the gas atmosphere ($N_2$, air or $H_2$) employed in the treatment, as follows.

- The treatment under $N_2$ caused a decrease in the $H_2$ conversion activity but an increase in the $H_2O_2$ selectivity/yield. It caused a large decrease in the $H_2O_2$ decomposition activity but a little or no change in the $H_2O_2$ hydrogenation activity.
- The treatment under air (followed by reduction with hydrazine) caused an appreciable decrease in both the $H_2$ conversion activity and $H_2O_2$ selectivity. It also caused a large decrease in the $H_2O_2$ decomposition activity but an appreciable increase in the $H_2O_2$ hydrogenation activity. Earlier studies on Au/Zeolite, and Au–$Pd/Al_2O_3$ (or $TiO_2$) catalysts [11, 15, 16] also showed that after calcinations at 400 °C (in air), the catalysts show less activity for the $H_2O_2$ formation.
- The treatment under $H_2$ caused an appreciable increase in both the $H_2$ conversion activity and $H_2O_2$ selectivity/yield. However, it resulted in a large decrease in the $H_2O_2$ decomposition activity but an increase in the $H_2O_2$ hydrogenation activity.
- Among the different gas atmosphere employed during the thermal pretreatment, the best catalyst performance for the $H_2$-to-$H_2O_2$ oxidation is observed when $Pd/Al_2O_3$ was thermally pretreated in $H_2$ atmosphere. The thermal treatment in air resulted into the catalyst having poor activity and selectivity in the $H_2$-to-$H_2O_2$ oxidation.

A comparison of the results for the $Pd/Al_2O_3$ catalysts pretreated in $H_2$ at 500 and 700 °C (Table 1) reveals the following important information. With increasing the pretreatment temperature from 500 to 700 °C,

(1) the Pd particle size of the catalyst increases markedly,
(2) both the $H_2O_2$ selectivity and yield increase, but
(3) the $H_2O_2$ decomposition and hydrogenation activities of the catalyst decrease.

It is interesting to note that the observed large growth of Pd particles (or the catalyst sintering) has caused only a very small decrease in the $H_2$ conversion activity, while significantly increasing the $H_2O_2$ selectivity and yield. The observed increase in the $H_2O_2$ formation activity is consistent with the appreciable decrease in both the $H_2O_2$ decomposition and hydrogenation activities of the catalyst.

## 3.2 Influence of Thermal Pretreatment to Pd/C

The XRD of Pd/C (without pretreatment) showed that the XRD peak for Pd was very small and broad, indicating the presence of very small particles of Pd in the catalyst. After the thermal treatment at 700 °C in $H_2$, much larger and sharper XRD peaks for Pd (at $2\theta = 40°$ and $47°$) due to the growth of Pd particles during the thermal treatment were observed.

The HRTEM photographs of Pd/C catalyst with and without the thermal treatment (Fig. 2b) also show a large increase in the Pd particle size of the catalyst after its thermal treatment at 700 °C (in $H_2$). The Pd particles have irregular shape. These observations are similar to that observed for the $Pd/Al_2O_3$ thermally treated in $H_2$ at 500 or 700 °C (Figs. 1a and 2a).

The thermal treatment to Pd/C, however, caused a large decrease in the $H_2$ conversion activity of the catalyst without significantly affecting the $H_2O_2$ selectivity in the $H_2$-to-$H_2O_2$ oxidation; after the thermal treatment, the $H_2O_2$ yield decreased appreciably (Table 1). The thermal treatment also resulted in a decrease in both the $H_2O_2$ decomposition and hydrogenation activities of the catalyst. These observations are different from that for the $Pd/Al_2O_3$ catalyst thermally pretreated under the similar conditions. For the $Pd/Al_2O_3$ catalyst, after its thermal treatment (at 700 °C in $H_2$), both the $H_2$ conversion and $H_2O_2$ selectivity (and consequently the $H_2O_2$ yield) increased appreciably and also both the $H_2O_2$ decomposition and hydrogenation activities of the catalyst decreased (Table 1). This indicates that the influence of thermal treatment to the Pd catalysts in terms of its catalytic performance depends upon the catalyst support. The presence of catalyst promoter (adsorbed $Br^-$ anions [13]) the support–Pd cluster interactions of the catalyst (i.e. metal–support interaction) play an important role in determining the net $H_2O_2$ formation activity. It seems that the smaller particles are active because they interact more strongly with the support.

The rate of $H_2O_2$ decomposition over the $Pd/Al_2O_3$ and Pd/C catalysts shows dependence upon the $H_2O_2$ concentration (Figs. 3a and 4a). In our earlier studies, the $H_2O_2$ decomposition over the Pd/C [25, 26] and $Pd/Al_2O_3$ [13, 26] catalysts was found to be first order with respect to $H_2O_2$. However, $H_2O_2$ conversion vs. reaction time plots for the $H_2O_2$ hydrogenation over the catalysts are linear (Figs. 3b and 4b) indicating that the hydrogenation reaction is zero order with respect to the $H_2O_2$ concentration.

A comparison of the $H_2O_2$ decomposition and hydrogenation rates (Table 1, Figs. 3 and 4) shows that the $H_2O_2$ hydrogenation activity of all the $Pd/Al_2O_3$ and Pd/C catalysts is considerably higher than their $H_2O_2$ decomposition activity. The destruction of $H_2O_2$ (by reactions 3 and 4) after its formation in the $H_2$-to-$H_2O_2$ oxidation in the acidic medium containing Br promoter is, therefore, controlled mostly by the $H_2O_2$ hydrogenation.

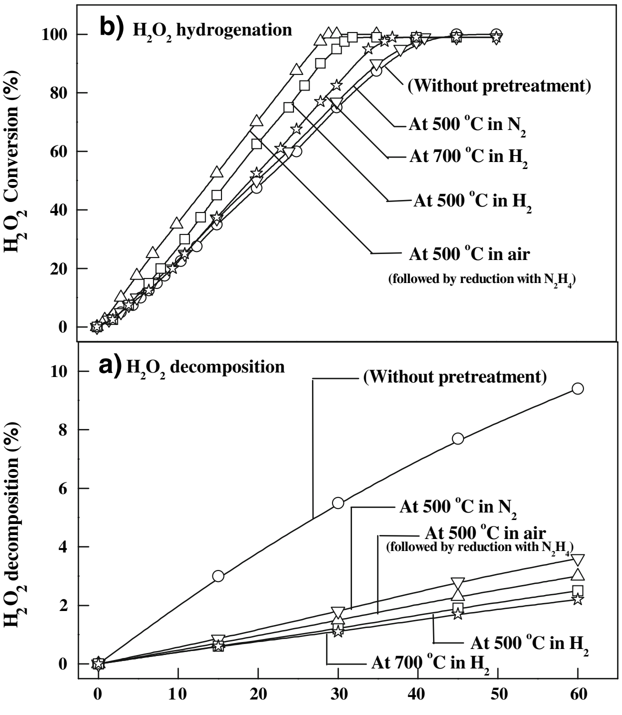

**Fig. 3** Effect of the different thermal pretreatments to $Pd/Al_2O_3$ catalyst on its $H_2O_2$ decomposition (in air) and hydrogenation (in $H_2$) activities

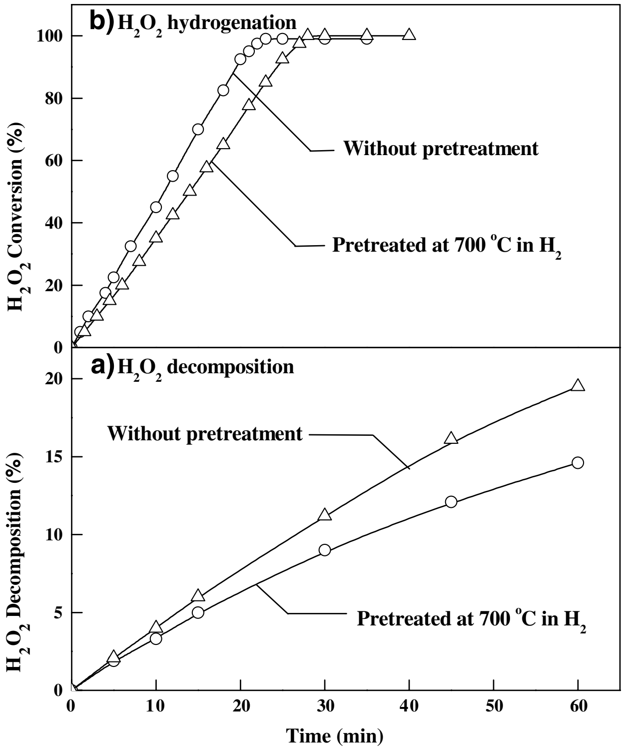

**Fig. 4** Effect of the different thermal pretreatments to Pd/C catalyst on its $H_2O_2$ decomposition (in air) and hydrogenation (in $H_2$) activities

## 4 Conclusions

The pretreatment (at 500 or 700 °C) under inert ($N_2$) or reducing ($H_2$) atmosphere caused a large increase in the Pd particle size of $Pd/Al_2O_3$ and Pd/C catalysts. However, the influence of thermal pretreatment to the supported Pd catalysts on their catalytic performance in the $H_2$-to-$H_2O_2$ oxidation and $H_2O_2$ decomposition/hydrogenation reactions cannot be generalized; it depends upon the catalyst support. The Pd particle growth is beneficial for increasing the net $H_2O_2$ formation over $Pd/Al_2O_3$ but it is detrimental for the net $H_2O_2$ formation over Pd/C in the presence of Br promoter in the acidic medium. The support–Pd cluster interactions in the presence of catalyst promoter (adsorbed $Br^-$ anions) seem to play important role in deciding the net $H_2O_2$ formation activity of the supported Pd catalysts.

**Acknowledgments** VRC and PJ are grateful to CSIR (New Delhi) for the award of Emeritus Scientist Scheme and UGC (New Delhi) for the award of a Senior Research Fellowship, respectively.

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