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Direct oxidation of H_2 to H_2O_2 over Pd/CeO_2 catalyst under ambient conditions: Influence of halide ions

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Abstract

Direct oxidation of H_2 by O_2 to H_2O_2 and decomposition/hydrogenation of H_2O_2 have been investigated over Pd/CeO_2 catalyst in presence of different halide ions. All reactions were carried out in an aqueous acidic (0.03 M H_3PO_4) medium at room temperature (25 °C) and atmospheric pressure. When different halide ions were added directly to the reaction medium or incorporated in the catalyst, the activity/selectivity of Pd/CeO_2 catalyst in the H_2 to H_2O_2 oxidation changed significantly, depending upon the nature of the halide ions. Different ammonium halides impregnated reduced Pd/CeO_2 catalyst calcined under inert (flowing nitrogen) and oxidizing (static/flowing air) gaseous atmospheres revealed that bulk oxidation state of Pd and the nature of the halide ions incorporated into the catalyst cooperatively control the activity/selectivity of catalyst in H_2 to H_2O_2 oxidation. Both H_2O_2 decomposition and hydrogenation were found to affect strongly depending upon the nature of the halide ions present in the reaction medium or in the catalyst. Among the different halides, bromide was found the most effective promoter for enhancing the H_2O_2 yield/selectivity in H_2 to H_2O_2 oxidation, irrespective of the Pd oxidation state in the catalyst.

Keywords: H_2 to H_2O_2 oxidation; Pd/CeO_2 catalyst; H_2O_2 decomposition; H_2O_2 hydrogenation; Br^- ions

1. Introduction

Demand for hydrogen peroxide (H_2O_2) as an environmentally friendly oxidizing agent in chemical synthesis and also for wastewater treatment is increasing continuously. The liquid-phase direct synthesis of H_2O_2 from H_2 and O_2 has been indentified as an attractive alternative to anthraquinone process, which currently, is the main commercial process accounts for >90% worldwide production of H_2O_2 [1]. Although, anthraquinone process has the advantage of avoiding direct mixing of H_2 and O_2, the process suffers from several limitations/drawbacks, such as use of costly complex solvent system to keep both reactant and product in the solution, loss of quinone due to non-selective hydrogenation, and several separation and concentration steps. The production cost of H_2O_2 is, therefore, high for this process and it is economically feasible only on a large-scale production (>20,000 tonnes per annum). The direct synthesis is expected to provide a highly cost-effective process for the production of H_2O_2 as an intermediate for chemical synthesis. The direct H_2O_2 synthesis form its elements has attracted considerable attention in recent years in academic laboratories with Pd-based catalysts [2–16]. In the Pd catalyzed H_2/O_2 reaction, both selective H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) and non-selective water ($H_2 + 0.5O_2 \rightarrow H_2O$) forming reactions occur simultaneously. Furthermore, the low stability of H_2O_2 molecules in presence of Pd facilitates it conversion to water in consecutive reaction. It is, therefore, extremely difficult to achieve high H_2O_2 selectivity/yields. Also, Pd catalyzed H_2/O_2 reaction could be explosive when operated within the flammability limits. The flammability and detonability limits for H_2 in O_2 (at 25 °C and 1 atm pressure) are 4.0% H_2 (lower) to 94% H_2 (upper) and 15% H_2 (lower) to 90% H_2 (upper), respectively. Hence, using high H_2 concentration to obtain elevated H_2O_2 yield would make the direct H_2O_2 synthesis more hazardous. Because of these two serious problems, the direct H_2 to H_2O_2 oxidation is often considered as a "dream reaction". The challenges posed by the direct H_2O_2 process, therefore, make it an interesting candidate for studying from a scientific viewpoint.

In the past several years, much interest has grown in the use of ceria (CeO_2) as a precious metal catalyst support, where ceria

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has shown great potential. Ceria supported/promoted Pd catalysts are widely use in three-way catalysis [17], catalytic wet oxidation [18], oxidation–combustion catalysts [19] etc. Ceria supported Pd catalyst [4,5,12,13] has also been employed in direct oxidation of H_2 to H_2O_2 by our group and has shown promising results.

Our previous studies [4,13] have shown that oxidation state of palladium can play an important role in determining activity/selectivity of supported Pd catalysts in direct H_2 to H_2O_2 oxidation process. Studies in several patents [20–24] have demonstrated that high selectivity for H_2O_2 formation over the Pd-based catalysts could be achieved in presence Br^- or Cl^- ions in aqueous reaction medium [20–23] or with brominated Pd catalyst [24]. We also have shown that high H_2O_2 yield/selectivity can be obtained with different Pd catalysts with incorporating Br^- ions into Pd catalysts [11] or with introducing Br^- or Cl^- ions into aqueous acidic reaction medium [12]. It has been found that in presence of hydrogen, H_2O_2 hydrogenation preferentially takes place than H_2O_2 decomposition over Pd catalyst in the presence of Cl^- or Br^- in acidic reaction medium [12] or in the Pd catalyst [14]. Recently, Strukul and co-workers [15] have investigated the performance of $SO_4{}^{2-}$. Cl^-, F^- and Br^--doped zirconia supported Pd catalysts in the direct H_2O_2 synthesis in methanol reaction medium. They noted that best catalytic results could be obtained with sulfate-doped zirconia catalyst and preferably with Pd° catalysts modified with surface oxidation. Since both Pd oxidation states in the catalyst and halide ions (present in the reaction medium or catalyst) have individual strong influence on direct H_2O_2 synthesis, it is, therefore, both scientific and practical interest to know the cooperative role of Pd oxidation states and different halide ions on the direct H_2O_2 synthesis from H_2 and O_2.

The present work was undertaken with the objective of investigating the influence of different halide ions (viz. F^-, Cl^-, Br^- and I^-) added directly to an aqueous acidic reaction medium or incorporated in the catalyst on the performance of Pd/CeO_2 catalyst in H_2 to H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions. The Influence of Pd loading in Pd/CeO_2 catalyst and concentration of Br^- ions in acidic reaction medium on the H_2 conversion, H_2O_2 yield/selectivity in H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions have also been investigated.

2. Experimental

2.1. Preparation of oxidized and reduced Pd/CeO_2 catalysts

The CeO_2 (obtained from Aldrich) supported oxidized Pd catalyst was prepared by impregnating CeO_2 with palladium acetate from its acetonitrile solution by the incipient wetness impregnation technique. After impregnation, the wet catalyst mass was dried at 100 °C for 4 h and then calcined under static air in a muffle furnace at 500 °C for 3 h. The reduced Pd/CeO_2 catalyst was obtained from the oxidized Pd/CeO_2 catalyst by reducing it with an ammoniacal hydrazine solution at room temperature (25 °C) for 2 h followed by washing, filtration and drying at 100 °C in an air oven The color of oxidized and reduced catalysts was light brown and gray, respectively. The presence metallic Pd (Pd°) and PdO phases in the reduced and oxidized Pd/CeO_2 catalysts respectively, were confirmed by XRD.

2.2. Modification of reduced Pd/CeO_2 catalyst by its halogenation

The halogenated (viz. fluoride, chloride or bromide containing) Pd/CeO_2 catalyst was prepared by impregnating the reduced Pd/CeO_2 catalyst with the corresponding ammonium halide from its aqueous solution by the incipient wetness impregnation technique, drying at 100 °C for 2 h and then calcining under N_2 (flowing) or air (static or flowing) at 400 °C for 1 h. The ammonium halide impregnated reduced Pd/CeO_2 catalyst calcined in flowing N_2 was found to retain the metallic Pd phase in the catalyst. However, the corresponding ammonium halide impregnated reduced Pd/CeO_2 catalyst calcined in air was found to convert into the oxidized form.

2.3. Catalytic reactions

2.3.1. H_2 to H_2O_2 oxidation

The direct oxidation of H_2 by O_2 to H_2O_2 over the oxidized and reduced Pd/CeO_2 catalysts was carried out at atmospheric pressure (95 kPa) in a magnetically stirred glass reactor (capacity 250 cm^3) containing 0.5 g catalyst in a fine power form and an aqueous acidic solution (150 cm^3) as a reaction medium. A H_2/O_2 (4.6 mol% H_2) 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 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 (Kathorometer, Nucon, New Delhi) based on a thermal conductivity detector. After the reaction, the solid catalyst was separated by filtration and the filtrate was analyzed for the H_2O_2 formed in the reaction by iodometric titration. The conversion of H_2, H_2O_2 yield and selectivity were obtained as follows:

$$H_2\,\text{conversion}(\%) = \frac{\begin{array}{c}(\text{moles of } H_2 \text{ in the feed})\\ -(\text{moles of } H_2 \text{ in the effluent gases})\end{array}}{\text{moles of } H_2 \text{ in the feed}} \times 100$$

$$H_2O_2\,\text{yield}(\%) = \frac{\text{moles of } H_2O_2 \text{ formed}}{\text{moles of } H_2 \text{ in the feed}} \times 100$$

$$H_2O_2\,\text{selectivity}(\%) = \frac{\text{moles of } H_2O_2 \text{ formed}}{\text{moles of } H_2 \text{ consumed}} \times 100$$

Unless mentioned otherwise, the conversion/selectivity/yield data reported in this paper has been taken after a reaction time of 3 h. Some of the experiments were repeated and excellent reproducibility (±5% H_2O_2 yields) was observed for these experiments. The safety in the present work was ensured by using the feed H_2/O_2 closer to the lower flammability limit, so that the concentration of H_2 in the reactor exit gas was less than 4% and also care was taken to avoid spillage of catalyst on the reactor walls during the reaction.

2.3.2. H_2O_2 decomposition

The H_2O_2 decomposition (in presence of air) over the catalyst was carried out in a magnetically stirred glass reactor (capacity: 250 cm^3) containing 0.2 g catalyst and 150 cm^3 of an aqueous reaction medium, with or without containing acid and/or halide ions, by injecting 1.0 ml of 30% aqueous H_2O_2 solution in the reactor under vigorous stirring and measuring the gas (O_2) liberated in the decomposition of H_2O_2 ($H_2O_2 \rightarrow H_2O + 0.5O_2$) at 25 °C and atmospheric pressure, as a function of time, using a constant pressure gas collector, for a period of 1 h. The percent H_2O_2 decomposition data was estimated as follows.

H_2O_2 decomposition (%) $= [V_t/V_T] \times 100$ (where, V_t = volume of O_2 evolved in time t and V_T = volume of O_2 evolved in the complete decomposition of H_2O_2 in the reactor). The H_2O_2 decomposition activity of the catalyst was evaluated in term of a pseudo first order rate constant (k_d) according to the first order rate expression: $\ln[V_T/(V_T - V_t)] = k_d t$ (where, V_T = volume of O_2 evolved in the complete H_2O_2 decomposition, V_t = volume of O_2 evolved in time t). From the slope of the $\ln[V_T/(V_T - V_t)]$ versus t plot, pseudo first order H_2O_2 decomposition rate constant (k_d) was evaluated.

2.3.3. H_2O_2 hydrogenation

The H_2O_2 conversion in presence of H_2 (flowing) over the reduced Pd/CeO_2 catalyst was carried out in a magnetically stirred glass reactor (capacity: 250 cm^3) containing 0.3 g catalyst and 150 cm^3 of an aqueous acidic (0.03 M H_3PO_4) solution, as follows: at first, all the air in reactor was thoroughly flushed by passing pure hydrogen and then hydrogen gas was bubbled (at a flow rate of 30 cm^3/min) through the reaction medium. After that, 3.0 ml of 30% aqueous H_2O_2 solution was injected into the reactor under vigorous stirring and the gas consumed in hydrogenation ($H_2O_2 + H_2 \rightarrow 2H_2O$) or evolved in decomposition ($H_2O_2 \rightarrow H_2O + 0.5O_2$) was measured as a function of time, using a constant pressure gas collector.

3. Results and discussion

3.1. Influence of halide ions added to reaction medium

Results showing the influence of different halide ions added to aqueous acidic (0.03 M H_3PO_4) reaction medium on the performance of oxidized and reduced Pd/CeO_2 catalysts in direct oxidation of H_2 to H_2O_2 are presented in Fig. 1. The halides were introduced in the reaction medium as potassium halides. The results in Fig. 2 show the influence of different halide ions added to the acidic (0.03 M H_3PO_4) reaction medium on H_2O_2 decomposition rate over oxidized and reduced Pd/CeO_2 catalysts. The results obtained from H_2O_2 destruction under flowing hydrogen over reduced Pd/CeO_2 catalyst in acidic (0.03 M H_3PO_4) reaction medium with or without containing different halide ions are presented in Fig. 3.

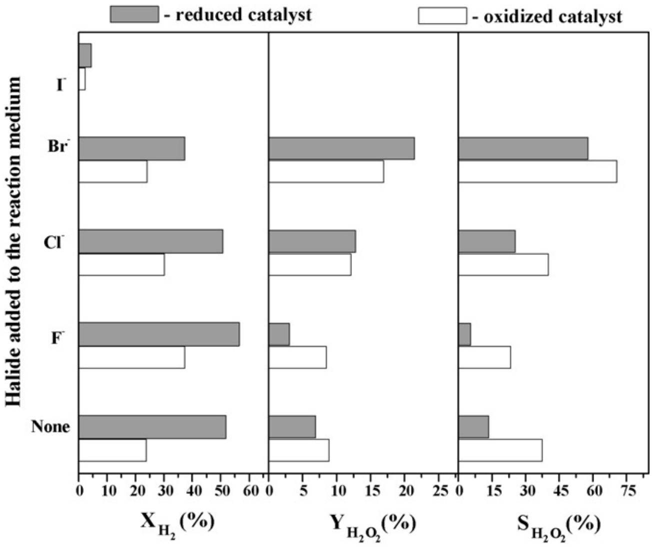

Fig. 1. Performance of oxidized and reduced Pd (2.5%)/CeO_2 catalysts in the direct H_2 to H_2O_2 oxidation in an acidic (0.03 M H_3PO_4) medium in the absence and presence of different potassium halides (concentration of halide = 0.94 mmol/dm^3) [*X*, *Y* and *S* are conversion, yield and selectivity, respectively].

In the absence of any externally added halide ions to the reaction medium, the reduced Pd/CeO_2 catalyst exhibited higher activity for both H_2 conversion and H_2O_2 decomposition, but lower selectivity for H_2O_2 formation as compared to its oxidized counterpart (Fig. 1). Thus, under the halide-free

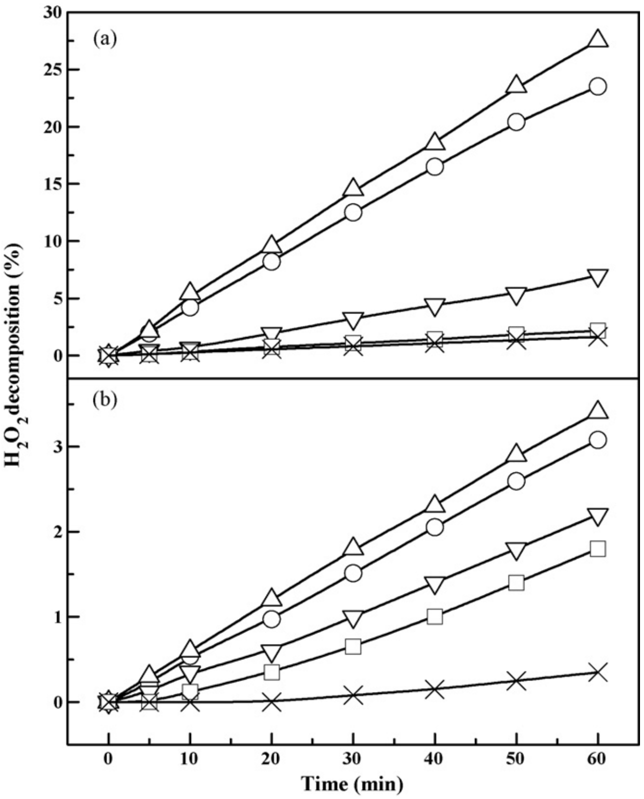

Fig. 2. Effect of different potassium halides (concentration = 0.94 mmol/dm^3) added to aqueous acidic (0.03 M H_3PO_4) medium on the H_2O_2 decomposition (at 25 °C) over (a) reduced (b) and oxidized Pd (2.5%)/CeO_2 catalysts [Potassium halide in the reaction medium: none (○), KF (△), KCl (▽), KBr (□), KI (×)].

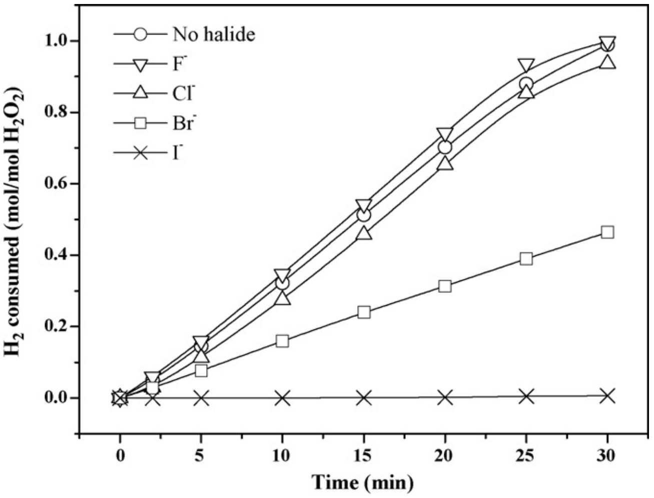

Fig. 3. Effect of different halides (concentration = 0.94 mmol/dm^3) added to aqueous acidic (0.03 M H_3PO_4) medium on the rate of H_2O_2 destruction under flowing H_2 over the reduced Pd (2.5%)/CeO_2 catalyst (at 25 °C).

condition, bulk oxidation states of Pd in the catalyst mostly control the activity/selectivity of the catalysts in the H_2 to H_2O_2 oxidation (Fig. 1) and H_2O_2 decomposition rate (Fig. 2). When halide ions were introduced in the reaction medium, a significant change in the performance of Pd/CeO_2 catalyst in the H_2 to H_2O_2 oxidation was observed. While H_2 conversion and H_2O_2 decomposition over the reduced and oxidized catalysts increased due to presence of F^- ions in the reaction medium, the presence of I^- ions caused a drastic reduction in the H_2 conversion and H_2O_2 decomposition over the catalysts. The strong poisoning effect of I^- is essentially due to its strong coordinating ability to Pd. The fluoride ion, on the other hand, is not effective (weak coordinating ligand) in suppressing the H_2O_2 decomposition. The H_2O_2 hydrogenation activity also increased due to the presence of F^- ions in the reaction medium (Fig. 3). The observed increase in the H_2 conversion and H_2O_2 hydrogenation in the presence of F^- ions in the reaction medium, is attributed to the adsorption of strong electronegative species (viz. F^- ions), which are expected to make the Pd surface more electron deficient and, thereby facilitating the adsorption of hydrogen. However, the addition of other halide ions (viz. I^-, Br^- or Cl^-) to the reaction medium decreased both the H_2 conversion and H_2O_2 decomposition/hydrogenation activities of the catalyst, indicating that the adsorption of these halide ions caused in blocking/poisoning of catalytic active sites. Here, it may be noted that with reduced Pd/CeO_2 catalyst, in absence of any halides or even in the presence of F^- ions in the reaction medium, H_2O_2 destruction under flowing H_2 proceeded via hydrogenation rather than decomposition; only gas (H_2) consumption and no gas evolution (from H_2O_2 decomposition) was observed, unlike in the case of previously studied H_2O_2 destruction over Pd/C and Pd/Al_2O_3 catalysts [12]. This observation indicates that the nature of the support employed in Pd catalyst plays an important role in determining H_2O_2 destruction pathway under H_2. The much higher H_2O_2 decomposition activity for the reduced catalyst as compared to its oxidized counterpart might be related to the higher propensity for H_2O_2 adsorption on reduced Pd sites. It may be noted that, because of lower pH of the reaction medium than isoelectric point of the catalyst support (CeO_2), only halide ions (not cations associated with halide ions) from the reaction medium are expected to be adsorbed on the catalyst. Therefore, the cations should have only a little or no influence on the H_2O_2 formation and decomposition reactions. H_2O_2, having a strong oxidizing ability in acidic medium, can oxidize halide ions (except F^- ions) present in the reaction medium. Indeed, an excess of I^- ions present in the reaction medium was found to get oxidized (by H_2O_2) to I_2 during the reaction over Pd catalysts [26]. Thus, optimum amount of halide ion should be added to reaction medium to avoid halide-promoted degradation of H_2O_2 formed in the reaction.

The selectivity for H_2O_2 formation would increase when H_2 combustion to water ($H_2 + 0.5O_2 \rightarrow H_2O$), and H_2O_2 decomposition and hydrogenation in consecutive reactions are completely and/or partially inhibited. The presence of Br^- or Cl^- ions in the reaction medium appreciably improved H_2O_2 yield/selectivity over both the oxidized and reduced catalysts; the increase of the H_2O_2 yield was more significant for the reduced catalyst. Thus, both the oxidation state of palladium in the catalyst and the nature of the halide ions (added to the reaction medium) cooperatively control activity/selectivity of the catalysts. Br^- was found more effective than Cl^- (on a same molar basis) in promoting H_2O_2 forming reaction. The H_2O_2 decomposition (Fig. 2) and hydrogenation (Fig. 3) activities also decreased due to the presence of Br^- (or Cl^-) ions. The non-selective H_2 to water oxidation over the catalysts is also expected to be significantly reduced due to the presence of Br^- (or Cl^-) ions; however, there is no direct evidence on it. The observed increase in H_2O_2 yield/selectivity in the presence of Br^- ions in the reaction medium may be attributed to the adsorption from reaction medium of Br^- ions on the catalyst. The adsorption of Br^- ions probably lead to blocking/poisoning of catalytic sites and electronic modification of Pd centers, resulting in inhibition for both the H_2 combustion and consecutive H_2O_2 destruction over the catalyst. In our earlier study on Pd/Al_2O_3 catalyst, we have concluded from XPS study that adsorbed Br^- ions are either close to the Pd particles in the catalyst (particularly at the metal-support interface) or mobile on the catalyst during the reaction to have their interaction with the Pd [12]. The color of the catalysts (oxidized and reduced) was found unchanged after the reaction, indicating that there was no significant change in the bulk oxidation state of palladium in the catalyst during the reaction. The reason might be of the low H_2 concentration (4.6 mol% H_2 in O_2) in the gaseous feed employed in the H_2O_2 synthesis. The solubility of H_2 in aqueous medium is quite low and therefore, it is expected that the concentration of dissolved H_2 in the reaction medium would be too low to completely reduce PdO in the catalyst. However, a change in the oxidation state of surface/sub-surface Pd in the catalyst is expected to take place during the reaction. A modification of the surface/sub-surface oxidation state of palladium in Pd/C catalyst (with different pretreatments to the catalyst) has been found to strongly influence H_2O_2 decomposition; the reductive pretreatment to the catalyst was found to increase H_2O_2 decomposition, while the oxidative pretreatment led to decrease

Table 1
Performances of the different halides impregnated reduced Pd (2.5 wt.%)/CeO_2 catalyst calcined under different gaseous atmospheres in the H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions in an aqueous acidic (0.03 M H_3PO_4) reaction medium (at 25 °C) (concentration of halide = 1.0 wt.%)

Halide incorporated in catalyst	Form of Pd (Pd° or PdO)[a]	H_2 to H_2O_2 oxidation			H_2O_2 decomposition activity
		X (H_2) (%)	Y (H_2O_2) (%)	S (H_2O_2) (%)	$k_d \times 10^4$ (min^{-1})[b]
None	Pd°	51.8	6.9	13.6	40.3
Halogenated catalyst calcined in flowing N_2 at 400 °C					
F^-	Pd°	46.4	15.4	33.2	3.5
Cl^-	Pd°	42.7	19.1	44.6	2.4
Br^-	Pd°	35.6	19.5	54.8	1.4
Halogenated catalyst calcined in static air at 400 °C					
F^-	PdO	27.3	8.9	32.7	1.6
Cl^-	PdO	31.3	10.9	34.8	1.7
Br^-	PdO	31.5	17.5	55.5	2.1
Halogenated catalyst calcined in flowing air at 400 °C					
F^-	PdO	31.5	10.9	34.6	3.2
Cl^-	PdO	27.4	11.5	41.9	2.1
Br^-	PdO	33.8	17.1	50.6	2.1

X, Y and S = conversion, yield and selectivity, respectively.

[a] Confirmed by XRD.

[b] Pseudo first order H_2O_2 decomposition rate constant (at 25 °C).

in H_2O_2 decomposition activity [25]. Palladium leaching from the catalyst in reaction medium was not observed in the absence or presence of different halide ions under the mild acidic (0.03 M H_3PO_4) reaction medium employed in this study. The problem of palladium leaching in the aqueous acidic medium could be avoided with using a less corrosive acidic solution and preferentially at lower acid concentration. Our earlier study [11] has shown that phosphoric acid (H_3PO_4) is one of the best oxoacids could be used as a reaction medium for miniming palladium leaching from the catalyst even in the presence of Cl^- or Br^- anions.

3.2. Influence of halide ions incorporated in the catalyst

Since reduced Pd/CeO_2 catalyst exhibited much higher H_2 conversion than its oxidized counterpart, further studies have been made with the reduced catalyst. The performance of different halides incorporated Pd (2.5%)/CeO_2 catalyst in the H_2 to H_2O_2 oxidation and H_2O_2 decomposition are shown in Table 1.

The strong cooperative influence of halide ions and Pd oxidation state in the catalyst on the H_2 to H_2O_2 oxidation and H_2O_2 decomposition was supported by the following observations:

- The F^- or Cl^- or Br^- impregnated catalyst pretreated (calcined) under flowing N_2 showed much higher H_2 conversion activity as compared to the corresponding catalyst pretreated under air (flowing or static).
- The increase in H_2O_2 yield/selectivity was more for F^- or Cl^- or Br^- incorporated catalyst when calcined under flowing N_2 as compared to the corresponding catalysts calcined under air (staic or flowing).
- The selectivity for H_2O_2 formation was significantly improved due to Br^--modification of the catalyst, irrespective of the pretreatment conditions. The H_2 conversion and H_2O_2 decomposition activities of the catalyst were reduced due to the Br^--modification of the catalyst; the decrease in the latter was more significant.
- The halides incorporated catalysts calcined under static air showed very similar catalytic performance in the H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions as compared to the corresponding catalysts calcined under flowing air.

The H_2O_2 yield/selectivity was increased after F^- or Cl^- or Br^- -modification of the catalyst under flowing N_2. However, in comparison to the PdO/CeO_2 catalyst (Fig. 1), NH_4F or NH_4Cl impregnated Pd°/CeO_2 (reduced) catalyst calcined in static or flowing air did not produce better H_2O_2 yield/selectivity. Our previous study [11] has shown that fluorinated or chlorinated Pd/Al_2O_3, Pd/ZrO_2, Pd/SiO_2 catalysts (in their reduced state) calcined under flowing N_2 were highly active for water formation in the H_2/O_2 reaction. However, with the fluorinated or chlorinated reduced Pd/CeO_2 catalyst (pretreated in flowing N_2), an appreciable H_2O_2 yield/selectivity was obtained in the direct H_2O_2 synthesis. This indicates that support plays an important role in Pd–halide interaction in the catalyst. Interestingly, Br^--containing Pd/CeO_2 catalyst calcined under either nitrogen or air (static or flowing) showed high selectivity for H_2O_2 formation and low H_2O_2 decomposition activity. Thus, Br^- has greater contribution in controlling activity/selectivity of Br^- Pdo/PdO couple system than oxidation state of Pd. The presence of Br^- ions either in the reaction medium (Fig. 1) or catalyst (Table 1) was found to promote the selectively for H_2O_2 formation to a similar magnitude, which indicates that Br^- ions added to the reaction medium were eventually adsorbed on the catalyst. The essential role of Br^- is to inhibit the formation of OH radicals from H_2O_2, which is the primary reaction responsible for H_2O_2 destruction because of the lower energy required for the cleavage of HO–OH bond (213 kJ/mol), as compared to that (369 kJ/mol) required for the cleavage of H–O_2H bond and also to inhibit the direct H_2 to water oxidation over the catalyst. It may be noted that during thermal pretreatment (at 400 °C) of the different ammonium halides (NH_4F, NH_4Cl and NH_4Br) impregnated Pd/CeO_2 catalyst under gaseous atmosphere, ammonium halides were decomposes into ammonia and corresponding hydrogen halides ($NH_4\ X \rightarrow NH_3 + HX$, where X = F, Cl or Br). Thus, the improvement in H_2O_2 selectivity was essentially due to the halide ions. However, influence of the counter cations on the H_2 to H_2O_2 oxidation has been observed for Pd/Al_2O_3 catalyst when different bromide precursors (viz. KBr, NaBr, HBr) employed in the Br^--modification of the catalyst [26].

3.3. *Effect of Pd loading*

Results showing the influence of Pd loading in the reduced Pd/CeO_2 catalyst on its performance in H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions in acidic (0.03 M H_3PO_4) medium in absence of any halide and in presence of Br^- ions are presented in Figs. 4 and 5, respectively. Under the halide-free condition, H_2 conversion and H_2O_2 decomposition activities of the catalyst increased with increasing Pd loading in the catalyst, but H_2O_2 selectivity passed through a maximum (Fig. 4). The increase of Pd loading in the catalyst also caused an increase in H_2O_2 decomposition activity of the catalyst and consequently, H_2O_2 yield was decreased.

With bromide-containing reaction medium (Fig. 5), the H_2O_2 yield increased with increasing Pd loading from 0.5 to 1.0 wt%, but remained almost constant when Pd loading was increased from 1 to 2.5 wt%. In this case also, H_2 conversion and H_2O_2 decomposition activities of the catalyst increased with increasing Pd loading in the catalyst. However, the H_2O_2 selectivity increased and then passed through a maximum with increasing Pd loading in the catalyst. Park and co-workers [27] have also shown that amount of H_2O_2 produced was increased sensitively with increasing Pd loading up to optimum value and subsequently decreased slightly when Pd loading was further increased. The observed influence of Pd loading on the H_2O_2 formation and H_2O_2 decomposition may be attributed to the increase in Pd surface and/or particle size. Further detailed investigation is necessary for understanding the Pd loading effect.

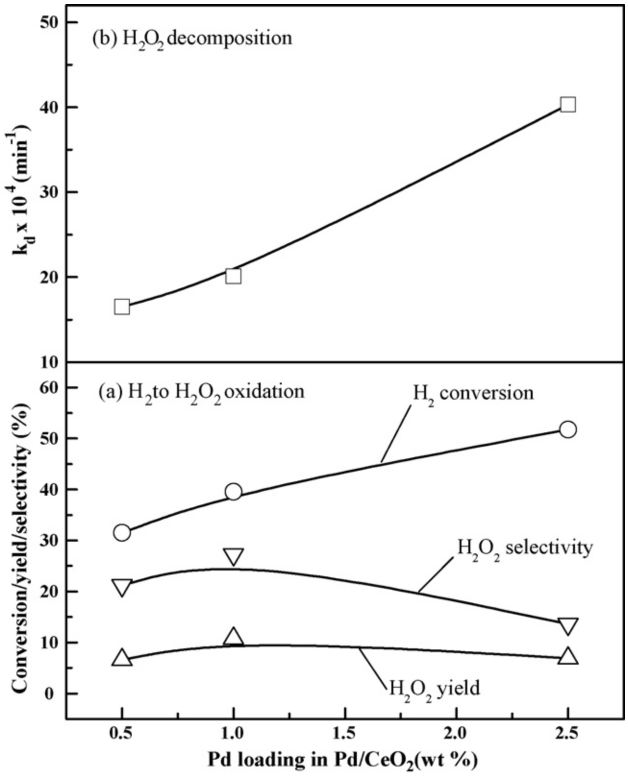

Fig. 4. Effect of Pd loading in the reduced Pd/CeO_2 catalyst on its performance in the (a) H_2 to H_2O_2 oxidation and (b) H_2O_2 decomposition in aqueous acidic (0.03 M H_3PO_4) medium (at 25 °C).

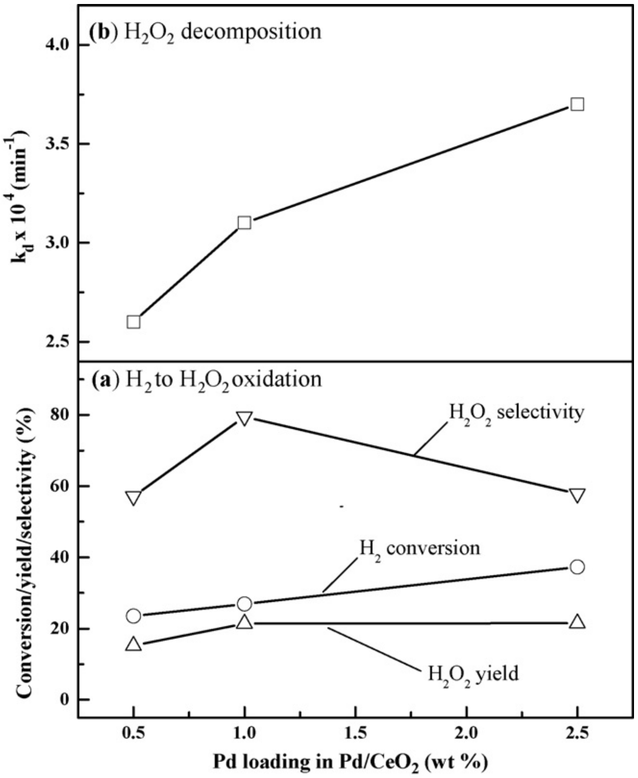

Fig. 5. Effect of Pd loading in the reduced Pd/CeO_2 catalyst on its performance in the (a) H_2 to H_2O_2 oxidation (b) and H_2O_2 decomposition in aqueous acidic (0.03 M H_3PO_4) medium containing Br^- ions (0.94 mmol/dm^3) (at 25 °C).

3.4. *Influence of bromide concentration*

Since Br^- was found the most effective catalyst promoter for the selective oxidation of H_2 to H_2O_2, the effect of Br^- concentration in the reaction medium on H_2O_2 yield/selectivity was studied further. The H_2O_2 yield in H_2 to H_2O_2 oxidation sharply increased (particularly at the lower Br^- concentrations) and then passed through a maximum with increasing Br^- concentration in the reaction medium (Fig. 6). However, H_2 conversion and H_2O_2 decomposition over the catalyst decreased continuously with increasing Br^- concentration in the reaction medium. Thus, an optimum concentration of Br^- in the reaction medium is essential for achieving the maximum H_2O_2 yield in the reaction under the investigated experimental conditions. The observed lower H_2 conversion and H_2O_2 decomposition rate over the catalyst at

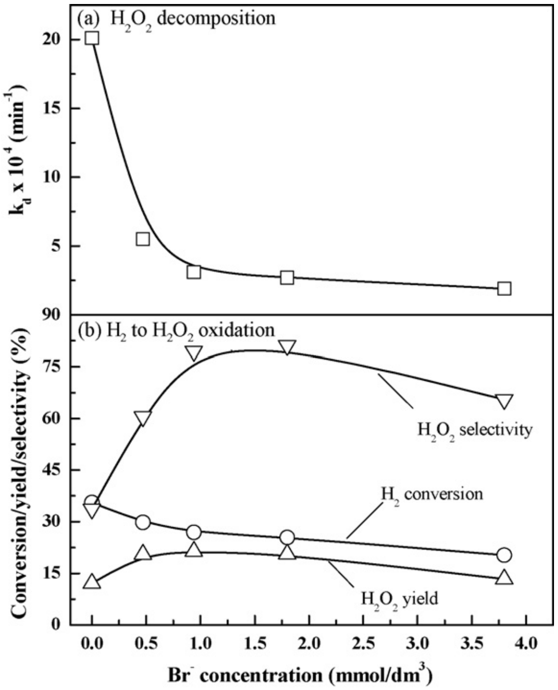

Fig. 6. Effect of Br^- concentration in an aqueous acidic (0.03 M H_3PO_4) medium on the H_2 conversion, H_2O_2 yield, H_2O_2 selectivity in the H_2 to H_2O_2 oxidation (a) and H_2O_2 decomposition (b) over the reduced Pd (1%)/CeO_2 catalyst (at 25 °C).

higher Br^- concentration is probably due to poisoning/blockage of more catalytic active sites.

4. Concluding remarks

1. Under halide-free condition, the bulk oxidation states of Pd in the catalysts mostly control the activity/selectivity of catalyst in H_2 to H_2O_2 oxidation and the rate of H_2O_2 decomposition while with halide-containing system, both the oxidation state of Pd in the catalyst and the nature of the halide ions (added to the reaction medium or incorporated into the catalyst) cooperatively control the activity/selectivity of the catalyst.
2. In the absence of any externally added halide ions to the reaction medium, reduced catalyst exhibited much higher activity for both H_2 conversion and H_2O_2 decomposition but much lower selectivity for H_2O_2 formation as compared to its oxidized counterpart.
3. In the presence of F^- ions in the reaction medium, the reduced Pd/CeO_2 catalyst led to low H_2O_2 formation due to its increased H_2O_2 decomposition activity. However, the corresponding PdO-containing catalyst had higher H_2O_2 formation selectivity.
4. The H_2O_2 yield was increased significantly for both the oxidized and reduced Pd/CeO_2 catalysts due to the presence of Br^- ions in acidic reaction medium; the increase was particularly significant for reduced catalyst. Cl^- also promoted H_2O_2 formation selectivity but it was found less effective (on a molar basis) than Br^-. Br^- was found unique in promoting the H_2O_2 selectivity, irrespective of Pd oxidation state in catalyst. An optimum concentration of Br^- ions in the acidic reaction medium or in the catalyst was important for obtaining maximum H_2O_2 yield in H_2 to H_2O_2 oxidation.
5. Both H_2O_2 decomposition and hydrogenation activities of reduced catalyst were inhibited due to presence of Cl^-, Br and I^- ions, but F^- ions promoted the activity for H_2O_2 decomposition/hydrogenation. At the same halide concentration, poisoning/blocking effect of I^- was found highest among the halides. The effectivity of different halides on the H_2O_2 decomposition/hydrogenation was in the following the order (highest to least): I > Br > Cl > F.
6. H_2 conversion and H_2O_2 decomposition activities of the catalyst increased with increasing Pd loading in the catalyst under both the halide-free and bromide-containing reaction mediums. The H_2O_2 selectivity in H_2 to H_2O_2 oxidation, however, passed through a maximum with increasing Pd loading in the catalyst.

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