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Role of chloride or bromide anions and protons for promoting the selective oxidation of H_2 by O_2 to H_2O_2 over supported Pd catalysts in an aqueous medium

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Abstract

The influence of protons (mineral acid) and different halide anions (F^-, Cl^-, Br^-, or I^-) in the aqueous reaction medium on H_2O_2 formation in the direct oxidation of H_2 to H_2O_2 (at 27 °C) over different supported Pd catalysts (i.e., Pd supported on carbon, alumina, gallia, silica, zirconia, or ceria) in their reduced form, and also on the activity of the catalysts for the destruction of H_2O_2 by its decomposition and/or hydrogenation reactions at the conditions close to those used in H_2 to H_2O_2 oxidation, was thoroughly investigated to gain insight into the roles of protons and halide promoters. Among the halide anions, only the chloride and bromide anions (particularly for the Pd/C and metal oxide-supported Pd, respectively), when added to acidic reaction medium, act as a catalyst promoter to drastically enhance H_2O_2 formation selectivity or H_2O_2 yield. But the presence of protons is crucial to this promoting action. The promoting action of the halides is attributed mainly to the large decrease in the H_2O_2 decomposition and hydrogenation activities of the catalyst resulting from its poisoning of the two consecutive H_2O_2 destruction reactions. It also may be due to the inhibition caused by the halide promoters for water formation directly from H_2 oxidation. The cations associated with the halide anions play only a minor role or no role in controlling the conversion or selectivity in H_2 to H_2O_2 oxidation and H_2O_2 conversion reactions. A plausible mechanism for H_2 to H_2O_2 oxidation in the presence of chloride or bromide anions in acidic aqueous medium, explaining the beneficial roles of the halide anions and protons for promoting the selective oxidation reaction, is proposed.

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1. Introduction

Direct catalytic liquid-phase oxidation of H_2 by O_2 to H_2O_2 (a versatile, environmentally clean oxidizing agent) is a process of great practical importance. It has a great potential to replace the presently practiced hydroquinone autoxidation process, which involves indirect oxidation of H_2 to H_2O_2 and has several drawbacks, including the use of a complex solvent system, loss of anthraquinone by nonselective hydrogenation, deactivation of hydrogenation catalyst, difficult product separation and waste treatment, and high capital costs. Hence, the production cost is too high to use the H_2O_2 produced by this process in wastewater treatment and production of bulk organic chemicals [1]. To meet the increasing demand for low-cost H_2O_2, particularly for use in wastewater treatment and environmentally friendly organic oxidation processes in the production of fine/specialty and bulk chemicals, much effort has been made to develop a more economical and environmentally friendly process for H_2O_2 production involving the direct catalytic H_2 oxidation in a liquid medium using different Pd catalysts.

This process is covered in a number of patents throughout the world but to date is not yet commercialized; it is considered a “dream process.” Apart from its hazardous nature, the main problem associated with the process is the low H_2O_2 selectivity (or high selectivity for water formation). This results from the undesirable highly thermodynamically favored nonselective water-forming reactions, such as the parallel H_2 to water oxidation and consecutive H_2O_2 decomposition and/or

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hydrogenation, occurring simultaneously with the desirable H_2 to H_2O_2 oxidation over the same catalyst (Pd catalyst) as follows:

$$H_2 + O_2 \rightarrow H_2O_2 + 136\ \text{kJ/mol} \quad (\Delta G^0 = -120\ \text{kJ/mol}), \tag{1}$$

$$H_2 + 0.5O_2 \rightarrow H_2O + 242\ \text{kJ/mol} \quad (\Delta G^0 = -237\ \text{kJ/mol}), \tag{2}$$

$$H_2O_2 \rightarrow H_2O + 0.5O_2 + 106\ \text{kJ/mol} \quad (\Delta G^0 = -117\ \text{kJ/mol}), \tag{3}$$

$$H_2O_2 + H_2 \rightarrow 2H_2O + 212\ \text{kJ/mol} \quad (\Delta G^0 = -354.0\ \text{kJ/mol}). \tag{4}$$

Thermodynamic data are for the reactions at 27 °C.

An improvement in the H_2O_2 selectivity/yield in the H_2 to H_2O_2 oxidation over Pd catalysts due to the addition of chloride or bromide anions in the aqueous medium has been disclosed in several patents [2–6]. Recent studies [7–10] have also shown an increase in H_2O_2 selectivity when HCl was used as the reaction medium [7–9] or when HBr was added to the reaction medium [8,10]. Very recently, we observed a drastic increase in H_2O_2 selectivity/yield due to the bromination of various supported Pd catalysts [11]. Our earlier studies [9,12] also revealed the beneficial effect of the mineral acid (protons) present in the aqueous reaction medium in making the H_2 to H_2O_2 oxidation more selective. Therefore, it is of both practical and scientific interest to know and understand the role of different halide anions and protons (mineral acid) or other cations for their promoting and/or inhibiting actions in the H_2 to H_2O_2 oxidation in an aqueous reaction medium; this would help develop a better H_2 to H_2O_2 oxidation process. The present investigation was undertaken for this purpose.

In the present investigation we studied the promoting or inhibiting action of different halides (F^-, Cl^-, Br^-, and I^-) added to the aqueous reaction medium on the H_2 to H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions over different reduced Pd catalysts (Pd supported on carbon, Al_2O_3, Ga_2O_3, SiO_2, ZrO_2, and CeO_2) in the presence or absence of protons in the reaction medium. We also evaluated the relative importance of the H_2O_2 decomposition and hydrogenation reactions in controlling H_2O_2 formation in H_2 to H_2O_2 oxidation in the presence of halide promoters.

2. Experimental

The Pd (5 wt%)/Al_2O_3 and Pd (5 wt%)/C catalysts in their reduced form were obtained from Lancaster (UK). The ZrO_2-, Ga_2O_3-, CeO_2-, and SiO_2-supported Pd (2.5 wt%) catalysts were prepared by impregnating the respective support with palladium acetate from its acetonitrile solution, drying and calcining at 500 °C in a static air for 3 h, and then reducing by ammoniacal hydrazine. All the catalysts were in fine-powder form. The presence of metallic Pd (Pd^0) phase in all of the Pd catalysts was confirmed by XRD; the Pd/Al_2O_3 and Pd/C catalysts were also characterized by XPS. Pd leaching (if any) from the Pd catalyst in the reaction medium was detected by adding an aqueous ethanolic dimethyl glyoxime (1%) solution to a 5-ml filtered reaction mixture. The resulting yellow orange precipitate indicated the presence of palladium (in trace amounts) in the reaction mixture.

The direct H_2 to H_2O_2 oxidation over the Pd catalysts was carried out in a magnetically stirred glass reactor (250 cm^3 capacity) by passing a mixture of H_2 and O_2 (4.6 mol% H_2) continuously through an aqueous acidic reaction medium with or without halide anions as described previously [9,12] at the following reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, gas flow rate = 15.5 cm^3/min, temperature = 27 °C, pressure = atmospheric, and reaction period = 3 h.

H_2O_2 decomposition (in the presence of air) over the catalyst was carried out using the same reactor containing 0.2 g of catalyst in 150 cm^3 of aqueous acidic reaction medium with or without halide anions in the presence of air by injecting 1.0 ml of 30% aqueous H_2O_2 solution into the reactor under vigorous stirring in the presence of air and measuring the gas (O_2) evolved in the H_2O_2 decomposition at 27 °C and atmospheric pressure as a function of time, using a constant pressure gas collector, for 1 h.

H_2O_2 conversion in the presence of H_2 (static) by H_2O_2 decomposition and/or hydrogenation over the catalysts was carried out in the same reactor containing 0.1 g of catalyst and 150 cm^3 of the acidic reaction medium with or without halide anions at 27 °C and atmospheric pressure as follows. First, the air in the reactor, containing the reaction medium (with or without promoters), and catalyst was completely flushed by H_2 by passing a stream pure H_2 (30 cm^3/min) through the reactor for a 1 h. Then the reactor was connected to a gas burette filled with pure H_2 over water, and 1.0 ml of 30% aqueous H_2O_2 solution was injected by a glass syringe into the reactor under vigorous stirring. The gas (H_2) consumed in the H_2O_2 hydrogenation or the gas (O_2) evolved due to the H_2O_2 decomposition was measured quantitatively at a constant (atmospheric) pressure, using the gas burette, as a function of time. In the case of a sudden gas evolution instead of gas consumption, the progress of the reaction was also followed by measuring quantitatively the unconverted H_2O_2 by iodometric titration.

H_2O_2 conversion under flowing H_2, N_2, or O_2 through the reaction medium was carried out in the same reactor containing 0.1 g of catalyst and 150 cm^3 of an aqueous acidic solution with or without halide anions, as follows. First, the air from the reactor, containing the reaction medium (with or without promoter) and catalyst was completely flushed by passing the gas under consideration; then, while passing the gas through the reaction medium at a flow rate of 30 cm^3/min, 3.0 ml of 30% aqueous H_2O_2 solution was injected into the reactor under vigorous stirring at 27 °C. The progress of the H_2O_2 conversion reaction was followed by removing the liquid reaction mixture as a function of time and analyzing the unconverted H_2O_2 by iodometric titration.

After the reaction, the catalyst was separated from the reaction mixture by filtration, washed with deionized water, and dried at 90 °C for 1 h in an air oven. It was then characterized for the adsorbed halide promoter by XPS and EDAX.

3. Results and discussion

To better understand the beneficial role played by protons and halide promoters added to the aqueous reaction medium in H_2 to H_2O_2 oxidation, the H_2 oxidation reaction was carried out using various reduced Pd catalysts (Pd/C, Pd/Al_2O_3, Pd/Ga_2O_3, Pd/SiO_2, and Pd/CeO_2) in an aqueous reaction medium in the presence or absence of mineral acid and/or different halides (KF, KCl, KBr, and KI) at 27 °C and atmospheric pressure. The H_2O_2 hydrogenation (the information on which is scarce [8,13,14]) and decomposition reactions over the catalysts at the conditions close to that used in H_2 to H_2O_2 oxidation were also been investigated.

3.1. H_2 to H_2O_2 oxidation over reduced Pd catalysts

Results showing the influence of different halides (KF, KCl, KBr, and KI) present in the acidic aqueous reaction medium (0.05 M H_2SO_4 or 0.03 M H_3PO_4) on the H_2O_2 formation in the oxidation of H_2 by O_2 over the different reduced supported Pd catalysts are presented in Tables 1 and 2. Results in Table 2 show the influence of different halides on H_2O_2 formation when no protons are present in the reaction medium. Table 3 shows the influence of the cations associated with the different chlorides or bromides present in the acidic reaction medium (0.03 M H_3PO_4) on H_2 to H_2O_2 oxidation over the Pd/C and Pd/Al_2O_3 catalysts. Fig. 1a shows the influence of the concentration of KBr in the acidic reaction medium on H_2O_2 yield in H_2 to H_2O_2 oxidation over the Pd/C and Pd/Al_2O_3 catalysts. Fig. 2a shows the influence of the concentration of acid (H_3PO_4) in the aqueous reaction medium containing bromide anions on H_2 conversion and H_2O_2 yield in H_2 to H_2O_2 oxidation over the Pd/Al_2O_3 catalyst.

The results in Table 1 reveal that in the presence of protons but the absence of halide in the reaction medium, all of the reduced Pd catalysts show little or no selectivity for H_2O_2 formation but do show high H_2 to water conversion activity. But in the presence of both protons and chloride (particularly for the Pd/C catalyst) or bromide (particularly for the metal oxide-supported Pd catalysts) anions, all of the Pd catalysts show both high activity and selectivity for H_2O_2 formation. This finding is consistent with earlier results [2–10]. Our earlier studies [9,12] showed that oxidized Pd catalysts have good selectivity for H_2O_2 formation in the presence of mineral acid, even with the absence of halide, in the medium. But this is not so for reduced Pd catalysts. This is because in the reduced Pd catalysts, which have much more H_2O_2 decomposition activity than the corresponding oxidized Pd catalysts, the H_2O_2 formed in H_2 to H_2O_2 oxidation is removed mostly through consecutive H_2O_2 decomposition.

It is also interesting to note from the results in Table 1 that the fluoride or iodide anions, even in the presence of protons, has no promoting effect on H_2 to H_2O_2 oxidation; their presence does not cause any increase in H_2O_2 yield/selectivity. The iodide anions even act as a catalyst inhibitor, almost totally deactivating the catalysts by poisoning their active sites.

Table 1
Results of the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition (in the presence of air) reactions (at 27 °C) over the different Pd catalysts in the aqueous acidic reaction medium with or without containing halide

Pd catalyst	Halide in reaction medium[a] ($mmol/dm^3$)	H_2 conversion in H_2 oxidation[b] (%)		H_2O_2 decomposition[c] (%)
		Total	To H_2O_2	
Acid in the reaction medium: H_2SO_4 (0.05 mol/dm^3)				
Pd/C	None [0.0]	54.8	0.0	57.6
	KF [2.7]	59.2	0.0	68.5
	KCl [2.7]	52.3	13.5	5.7
	KBr [2.7]	31.9	8.7	3.6
	KI [2.7]	<5.0	0.0	<1.0
Pd/Al_2O_3	None [0.0][d]	50.5	1.7	30.8
	KF [0.9][d]	56.3	0.3	50.3
	KCl [0.9][d]	50.8	4.2	4.5
	KBr [0.9][d]	45.7	23.6	2.5
	KI [0.9]	<5.0	0.0	<1.0
Acid in the reaction medium: H_3PO_4 (0.03 mol/dm^3)				
Pd/C	None [0.0]	57.2	1.5	61.4
	KF [2.7]	58.3	0.0	72.5
	KCl [2.7]	52.3	15.4	5.4
	KBr [2.7]	36.2	11.5	2.8
	KI [2.7]	<5.0	0.0	<1.0
Pd/Al_2O_3	None [0.0]	48.7	1.8	35.8
	KF [0.9]	48.9	0.0	62.4
	KCl [0.9]	45.7	5.7	10.9
	KBr [0.9]	43.8	25.8	4.9
	KBr [0.9][d,e]	54.5	27.8	1.7
	KI [0.9]	<5.0	0.0	<1.0
Pd/Ga_2O_3	None [0.0]	50.0	5.4	24.5
	KF [0.9]	50.7	2.7	36.5
	KCl [0.9]	47.8	11.3	3.9
	KBr [0.9]	39.8	22.8	2.5
	KI [0.9]	<5.0	0.0	<1.0
Pd/SiO_2	None [0.0]	52.5	0.0	59.4
	KCl [0.9]	50.6	8.5	18.9
	KBr [0.9]	40.5	22.8	4.7
	KI [0.9]	<5.0	0.0	<1.0
Pd/ZrO_2	None [0.0]	43.7	3.9	28.9
	KCl [0.9]	38.7	12.6	2.7
	KBr [0.9]	36.2	23.7	1.9
	KI [0.9]	8.9	0.0	<1.0
Pd/CeO_2	None [0.0]	51.8	6.9	23.1
	KCl [0.9]	50.7	12.8	7.6
	KBr [0.9]	37.3	21.5	2.2
	KI [0.9]	<5.0	0.0	<1.0

[a] Value given in the square brackets corresponds to the concentration of halide in the aqueous reaction medium.

[b] Reaction period = 3 h.

[c] Reaction period = 1 h.

[d] A significant leaching of Pd from the catalyst after the H_2-to-H_2O_2 oxidation was observed. In the other cases, there was no leaching of Pd from the catalyst.

[e] Concentration of H_3PO_4 was 0.3 mol/dm^3.

The results in Table 3 also reveal that the significant promoting effect of KCl or KBr in H_2 to H_2O_2 oxidation (see Table 1)

Table 2
Results of the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition (in the presence of air) over the Pd/C and Pd/Al_2O_3 catalysts (at 27 °C) in the aqueous medium, with or without containing halide, in the absence of any mineral acid

Pd catalyst	Halide in reaction medium[a] (mmol/dm^3)	H_2 conversion in H_2 oxidation[b] (%)		H_2O_2 decomposition[c] (%)
		Total	To H_2O_2	
Pd/C	None [0.0]	48.5	0.0	100
	KF [2.7]	–	–	100
	KCl [2.7]	43.8	0.0	68.5
	KBr [2.7]	38.5	0.0	18.0
	KI [2.7]	–	–	32.5
Pd/Al_2O_3	None [0.0]	47.2	0.0	90.5
	KCl [2.7]	45.2	0.0	62.5
	KBr [2.7]	37.7	0.0	28.7
Pd/Ga_2O_3	None [0.0]	45.0	0.0	87.5
	KBr [0.9]	31.3	0.0	45.4

[a] Value given in the square brackets corresponds to the concentration of halide in the aqueous reaction medium.

[b] Reaction period = 3 h.

[c] Reaction period = 1 h.

Table 3
Influence of the cations (associated with the halide anions) on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition (in the presence of air) reactions over the Pd/C and Pd/Al_2O_3 catalysts (at 27 °C) in aqueous acidic (0.03 M H_3PO_4) reaction medium containing chloride or bromide anions

Pd catalyst	Halide in reaction medium[a] (mmol/dm^3)	H_2 conversion in H_2 oxidation[b] (%)		H_2O_2 decomposition[c] (%)
		Total	To H_2O_2	
Pd/C	KCl (2.7)	52.3	15.0	5.4
	NaCl (2.7)	56.4	15.0	5.6
	NH_4Cl (2.7)	56.5	15.0	5.6
	HCl (2.7)	54.9	15.0	5.8
Pd/Al_2O_3	KBr (0.9)	43.8	26.0	2.6
	KBr (0.9)[d]	54.5	28.0	1.4
	NaBr (0.9)	45.4	24.0	2.5
	NH_4Br (0.9)	46.2	24.0	2.5
	HBr (0.9)	43.7	26.0	2.3

[a] Value given in the parentheses corresponds to the concentration of halide in the aqueous reaction medium.

[b] Reaction period = 3 h.

[c] Reaction period = 1 h.

[d] Concentration of H_3PO_4 was 0.3 mol/dm^3. At this concentration significant leaching of Pd from the Pd/Al_2O_3 catalyst was observed during the H_2-to-H_2O_2 oxidation.

is attributed essentially to only the chloride anions or bromide anions; the cations associated with the Cl^- or Br^- anions in the halide have little or no effect on H_2 to H_2O_2 oxidation.

The results in Table 2 clearly show that the presence of chloride or bromide anions without protons has no promoting effect for H_2 to H_2O_2 oxidation. Both halide (Cl^- or Br^-) and protonic acid in the reaction medium are essential to drastically enhance H_2O_2 selectivity/yield in H_2 to H_2O_2 oxidation.

The results in Fig. 1a indicate that the H_2O_2 yield in H_2 to H_2O_2 oxidation over the Pd/C and Pd/Al_2O_3 catalysts is passed through a maximum (at about 0.9 mmol/dm^3 for Pd/Al_2O_3 and 2.7 mmol/dm^3 for Pd/C) with increasing Br^- concentration in

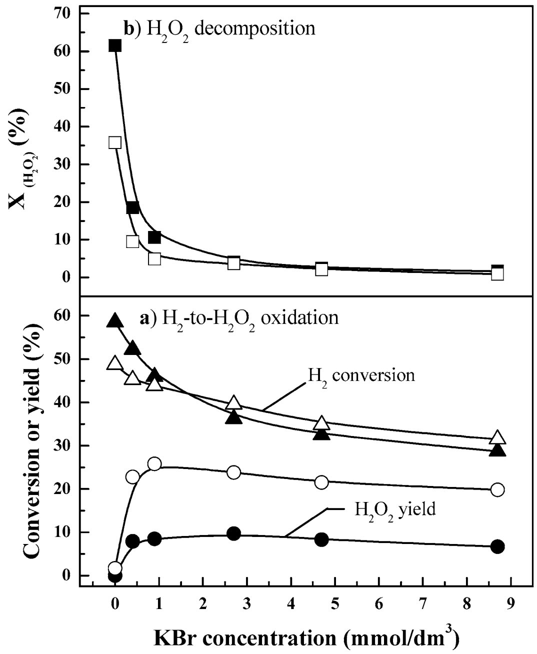

Fig. 1. Influence of the KBr concentration in the acidic reaction medium (0.03 M H_3PO_4) (a) on the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation and (b) on the conversion of H_2O_2 ($X(H_2O_2)$) in the H_2O_2 decomposition in the presence of air in the reactor over the Pd/C (solid symbols) and Pd/Al_2O_3 (hollow symbols) catalysts (at 27 °C).

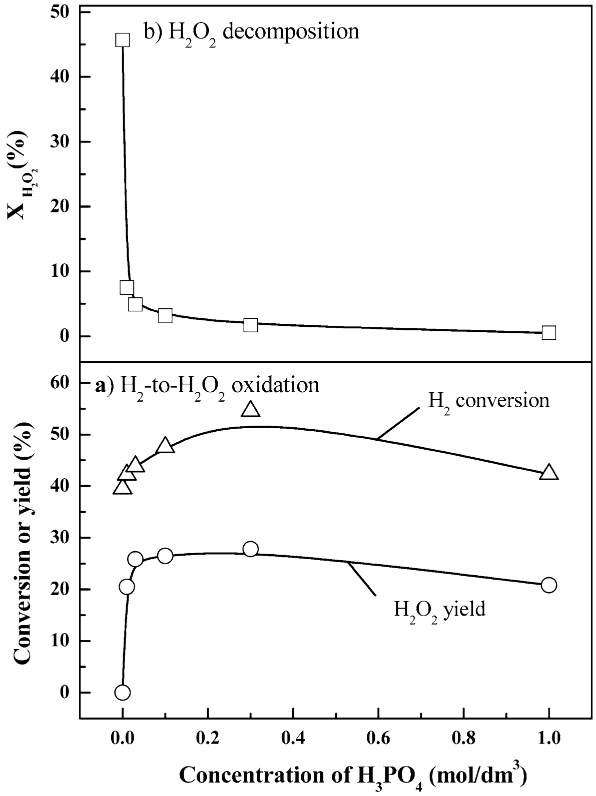

Fig. 2. Influence of acid (H_3PO_4) concentration in the aqueous reaction medium containing KBr (0.9 mmol/dm^3) (a) on the H_2 conversion and H_2O_2 yield in the H_2-to-H_2O_2 oxidation and (b) on the conversion of H_2O_2 ($X(H_2O_2)$) in the H_2O_2 decomposition in the presence of air in the reactor over the Pd/Al_2O_3 catalyst (at 27 °C).

the acidic reaction medium. The decreased H_2O_2 yield after passing through the maximum is expected because of a decrease in the catalyst activity for H_2 oxidation due to catalyst poisoning with the further increase in bromide concentration.

The results in Fig. 2a shows that both H_2 conversion and H_2O_2 yield in H_2 to H_2O_2 oxidation over the Pd/Al_2O_3 catalyst are increased and then passed through a maximum with increasing acid concentration in the aqueous reaction medium, indicating the strong influence of the proton concentration in the medium on both the activity and selectivity in the reaction. At higher acid concentrations ($\geqslant 0.3\ \text{mol/dm}^3$), a significant leaching of Pd from the catalyst occurred, which may be responsible for the small decrease in H_2 conversion and H_2O_2 yield observed at these higher acid concentrations. Significant Pd leaching from the Pd/Al_2O_3 catalyst in the H_2 to H_2O_2 oxidation in the acidic medium containing 0.05 M H_2SO_4 in the absence or presence of KF, KCl, or KBr was also observed (Table 1). However, no Pd leaching was observed for the acidic medium containing H_3PO_4 at low concentration ($0.03\ \text{mol/dm}^3$) in both the absence and presence of halides. Hence, we recommend the use of H_3PO_4 (particularly at low concentration ($\leqslant 0.03\ \text{mol/dm}^3$)) over the other mineral acids, such as H_2SO_4 and HCl, as the acidic reaction medium for H_2 to H_2O_2 oxidation. Earlier studies [15] have also indicated that an aqueous hydrochloric acid, together with O_2, promotes the dissolution of Pd metal, leading to the extensive Pd leaching from the supported Pd catalyst.

3.2. H_2O_2 decomposition over reduced Pd catalysts

Results showing the influence of different halides present in the acidic or nonacidic reaction medium on the H_2O_2 decomposition activity of the different reduced Pd catalysts are given in Tables1–3. The influence of KBr concentration in the acidic reaction medium (0.03 M H_3PO_4) on the H_2O_2 decomposition activity of the Pd/C and Pd/Al_2O_3 catalysts is shown in Fig. 1b. The influence of acid concentration in the aqueous reaction medium containing bromide anions on H_2O_2 decomposition over the Pd/Al_2O_3 catalyst is shown in Fig. 2b. These results lead to the following important observations:

1. In the acidic aqueous reaction medium, the H_2O_2 decomposition activity of all the Pd catalysts is decreased drastically due to the addition of KCl, KBr, or KI in the order of KI > KBr > KCl (Table 1), but is increased due to the addition of KF.
2. In the nonacidic aqueous medium, the H_2O_2 decomposition activity of the Pd catalysts is reduced due to the addition of KCl, KBr, or KI. But compared with acidic aqueous reaction medium, the decrease in H_2O_2 decomposition activity is much smaller and has a different order for the halides (KBr > KI > KCl); see Table 2. As in the earlier case (i.e., in the presence of protons), the H_2O_2 decomposition activity of the Pd/C catalyst is not strongly influenced by the addition of KF in the nonacidic reaction medium.
3. The decreased H_2O_2 decomposition activity of the Pd/C catalyst due to the presence of different chlorides (KCl, NaCl, NH_4Cl, or HCl) in the same acidic medium is more or less the same (Table 3). This is also the case for H_2O_2 decomposition over the Pd/Al_2O_3 catalyst in the presence of various bromides (KBr, NaBr, NH_4Br, or HBr) in the same acidic medium (Table 3).
4. The H_2O_2 decomposition activity of both the Pd/C and Pd/Al_2O_3 catalysts is significantly decreased with increasing KBr concentration in the acidic medium (Fig. 1b).
5. For the same concentration of KBr ($0.9\ \text{mmol/dm}^3$) in the reaction medium, the H_2O_2 decomposition activity of the Pd/Al_2O_3 catalyst is significantly decreased with increasing acid (H_3PO_4) concentration from 0.0 to 1 mol/dm^3 (Fig. 2b).

The foregoing observations clearly show that, like H_2 to H_2O_2 oxidation, H_2O_2 decomposition (reaction (3)) over the reduced Pd catalysts is strongly influenced by the presence of Cl^-, Br^-, or I^- anions in the acidic reaction medium, but the cations in the halides have little or no influence on H_2O_2 decomposition. The halide anions act as catalyst inhibitors/poisons for H_2O_2 decomposition. Moreover, as in H_2-to-H_2O_2 oxidation, mineral acid (protons) in the reaction medium plays an important role in controlling H_2O_2 decomposition. The presence of protons is essential for drastically reducing H_2O_2 decomposition even in the presence of the halide inhibitors (Cl^-, Br^-, or I^-); higher the acid concentration, the lower the H_2O_2 decomposition. Our earlier studies [16] also showed an appreciable decrease in the rate of H_2O_2 decomposition over Pd/C catalyst with increasing acid (H_2SO_4) concentration in the reaction medium. In the absence of protons, the influence of the halide inhibitor on H_2O_2 decomposition is much lower, or it may even have an opposite effect, because of the decomposition of H_2O_2 catalyzed by the halide anions, particulary iodide anions, present in the reaction mixture at higher concentrations. In aqueous medium, increasing the iodide concentration resulted in increased H_2O_2 decomposition activity of the Pd/C catalyst, attributed mainly to the homogeneous iodide-catalyzed decomposition of H_2O_2 [17].

3.3. H_2O_2 hydrogenation/decomposition in presence of H_2 (static or flowing)

Data on the gas (H_2) consumed or the gas (O_2) evolved, as a function of time, in the reaction of H_2O_2 over the Pd/C and Pd/Al_2O_3 catalysts in the aqueous acidic medium (0.03 M H_3PO_4) containing the different halide anions at the same concentration ($2.7\ \text{mmol/dm}^3$) in the presence of H_2 (static) in the reactor are presented in Fig. 3. The negative values of the gas consumed in the presence of KF or in the absence of any halide result from the gas evolution in the reaction due to the H_2O_2 decomposition (reaction (3)).

It is interesting to note from these results that in the presence of KI, there was very little gas consumption in the hydrogenation reaction, indicating nearly complete deactivation of the catalysts due to their poisoning by the iodide. However, in the presence of KCl or KBr, the amount of H_2 consumed increased continuously and almost linearly with increasing reaction time, and the maximum amount of gas consumed in the reaction was

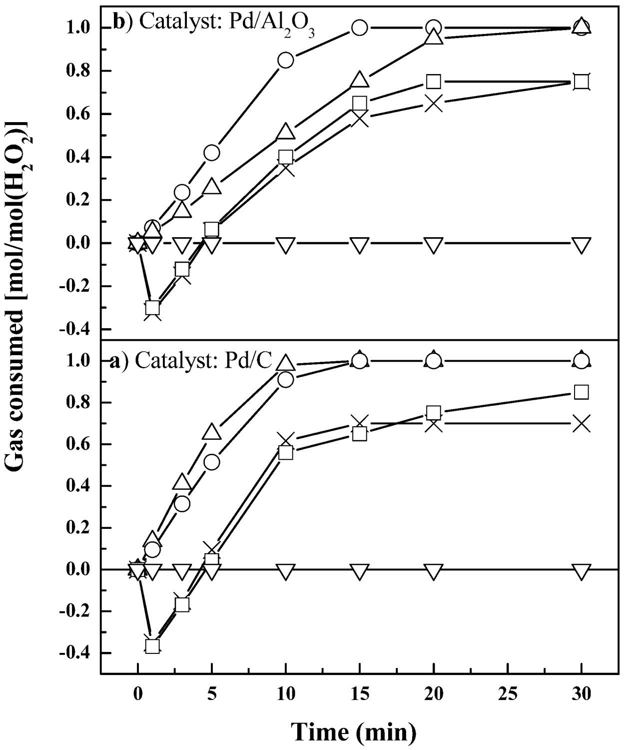

Fig. 3. Gas (H_2) consumed or gas (O_2) evolved in the reaction of H_2O_2 (at 27 °C) over the Pd/C and Pd/Al_2O_3 catalysts in aqueous acidic reaction medium (0.03 M H_3PO_4) containing different halide anions (concentration of halide = 2.7 $mmol/dm^3$) in the presence of H_2 (static) in the reactor ((□) for KF, (○) for KCl, (△) for KBr and (▽) for KI and (×) for the case when no halide present in the reaction medium).

1.0 mol (H_2)/mol (H_2O_2). Also, at the time of maximum gas consumption, the H_2O_2 from the reaction mixture was completely converted, indicating the conversion of H_2O_2 only by its hydrogenation (reaction (4)).

In contrast, in the presence of KF or in the absence of halide, there was a sudden gas evolution in the initial short reaction period of about 1.0 min due to very fast H_2O_2 decomposition (reaction (3)), followed by continuous consumption of the gas in the hydrogenation of H_2O_2 (reaction 4) and/or O_2 (reaction (2)), as shown in Fig. 3. (The O_2 was produced in the initial fast H_2O_2 decomposition.) In this case, the H_2O_2 from the reaction mixture was completely converted within the reaction period of about 3.0 min (Fig. 4). However, the gas consumption continued for a longer period because of the oxidation of H_2 by O_2 to water. Thus, H_2O_2 conversion over the Pd catalysts in the presence of H_2 is very complex, and the reactions (reactions (2)–(4)) involved in H_2O_2 conversion are strongly dependent on the nature of the halide anions present in the acidic reaction medium.

Results showing the influence of the presence of different halides on the rate of H_2O_2 destruction by the decomposition (reaction (3)) and/or hydrogenation (reaction (4)) in the presence of H_2 for the Pd/C and Pd/Al_2O_3 catalysts are presented in Fig. 4. Data on the extent of H_2O_2 conversion by the individual H_2O_2 decomposition and hydrogenation reactions in the presence of the various halides after the reaction period of 0.5 h (i.e., for 100% H_2O_2 conversion) are given in Table 4. In the case of the H_2O_2 conversion under H_2 in the presence of fluoride anions or the absence of halide, the conversion of H_2O_2 by its decomposition alone was estimated from the maximum amount of gas (O_2) evolved (Fig. 3), using the H_2O_2 decomposition (reaction (3)) stoichiometry. Because H_2O_2 hydrogenation (which consumes H_2 according to reaction (4)) may or may not occur

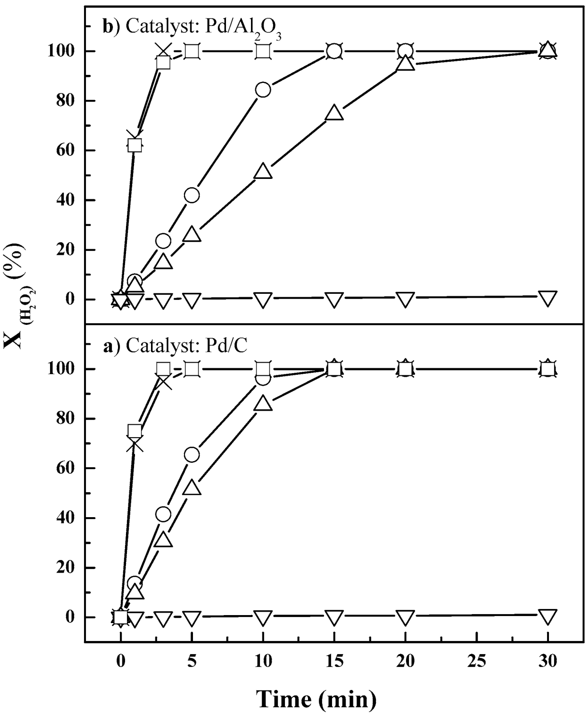

Fig. 4. Influence of the presence of different halides (2.7 $mmol/dm^3$) in the acidic reaction medium (0.03 M H_3PO_4) on the H_2O_2 conversion ($X(H_2O_2)$) in the reaction of H_2O_2 over the Pd/Al_2O_3 and Pd/C catalysts (at 27 °C) in the presence of H_2 (static) in the reactor ((×) in the absence of any halide, (□) for KF, (○) for KCl, (△) for KBr).

Table 4
Influence of the presence of different halides (2.7 $mmol/dm^3$) on the conversion of H_2O_2 by its decomposition and/or hydrogenation in the reaction of H_2O_2 over the Pd/C and Pd/Al_2O_3 catalysts in aqueous H_3PO_4 (0.03 M) medium in the presence of H_2 (static) in the reactor (reaction period = 0.5 h)

Halide in the reaction medium	H_2O_2 conversion[a] (%)		
	By decomposition	By hydrogenation	Total
Catalyst: Pd/C			
None	$\geqslant 70.0$	$\leqslant 30.0$	100
KF	$\geqslant 74.0$	$\leqslant 26.0$	100
KCl	0.0	100.0	100
KBr	0.0	100.0	100
Catalyst: Pd/Al_2O_3			
None	$\geqslant 65.0$	$\leqslant 35.0$	100
KF	$\geqslant 60.0$	$\leqslant 40.0$	100
KCl	0.0	100	100
KBr	0.0	100	100

[a] The H_2O_2 conversion by the individual H_2O_2 decomposition and hydrogenation reactions were evaluated from the amount of gas consumed (in the H_2O_2 hydrogenation) or evolved (in the H_2O_2 decomposition), measured volumetrically, in the complete conversion of H_2O_2 to water and taking into consideration the stoichiometry of the H_2O_2 decomposition and hydrogenation reactions, using the data from Fig. 3.

simultaneously with H_2O_2 decomposition, and because H_2O_2 decomposition may continue for a further period after the maximum amount of gas evolved, the observed value of the maximum amount of gas evolved may be equal to or less than that actually evolved due to H_2O_2 decomposition. Hence, the actual value for the conversion of H_2O_2 by its decomposition is equal to or larger than the reported value (Table 4).

In the presence of H_2, H_2O_2 is destroyed over the Pd catalysts by decomposition and/or hydrogenation. The influence of the various halides on H_2O_2 conversion is in the following order: KF $\ll$ KCl < KBr $\ll$ KI. In the presence of KI, the conversion of H_2O_2 was negligible (<1.0% at 0.5 h); however, in the presence of other halides or in their absence, H_2O_2 conversion was complete between 3 and 30 min, depending on the halide (Fig. 4).

The results in Fig. 4 and Table 4 reveal that in the absence of any halide anions or in the presence of F^- anions, H_2O_2 destruction in the presence of H_2 is due mainly to H_2O_2 decomposition, and that the H_2O_2 decomposition rate is much higher than that observed in the absence of H_2 (Table 1). But in the presence of the Cl^- or Br^- anions, only the H_2O_2 hydrogenation reaction is responsible for H_2O_2 destruction, thus revealing its greater importance than H_2O_2 decomposition in the presence of H_2 for these halide promoters.

Results showing the influence of KBr concentration in the acidic reaction medium on the H_2O_2 hydrogenation activity of the Pd/C and Pd/Al_2O_3 catalysts are presented in Fig. 5. It is interesting to note from this figure that the time required for half of the H_2O_2 destruction in the presence of H_2 over the Pd catalysts is sharply increased and then levels off with increasing Br^- concentration in the reaction medium. This reveals that the H_2O_2 hydrogenation rate is sharply decreased with increasing Br^- concentration in the low concentration region (0–3.0 mmol/dm^3).

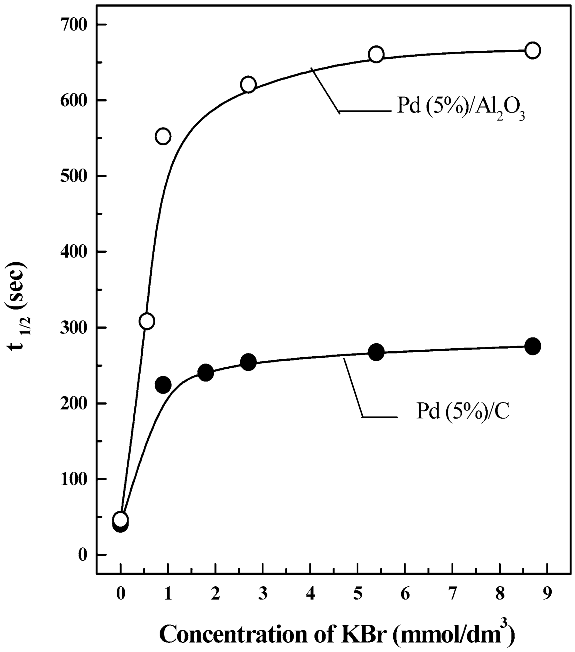

Fig. 5. Influence of the concentration of KBr in the acidic reaction medium (0.03 M H_3PO_4) on the time required for half the H_2O_2 conversion reaction ($t_{1/2}$) over the Pd/C (●) and Pd/Al_2O_3 (○) catalysts (at 27 °C) in the presence of H_2 (static) in the reactor.

Comparing the results in Table 1 with those in Figs. 4 and 5 reveals that H_2O_2 conversion in the presence of H_2 over the Pd/C and Pd/Al_2O_3 catalysts, even at lower concentrations, is much faster than H_2O_2 decomposition over the same catalysts under similar conditions (except the gas atmosphere). The much higher destruction activity of the Pd catalysts observed in the presence of H_2 is attributed to the hydrogenation of H_2O_2 and also to the increased H_2O_2 decomposition activity of the catalyst, resulting from the reduction by H_2 of the surface and subsurface PdO from the catalyst. Our earlier studies [9,12,13,18] showed that the bulk and/or surface oxidation of reduced Pd catalysts caused a significant decrease in their H_2O_2 decomposition activity. This is also the case when the H_2O_2 conversion reaction over the Pd/Al_2O_3 catalyst was carried out in the presence of flowing N_2, O_2, or H_2 gas (Fig. 6); the rate of H_2O_2 decomposition under flowing N_2 or O_2 was found to be much slower than that under flowing H_2 in the presence of bromide anions.

The results in Fig. 6 also indicate very fast conversion of H_2O_2 by its hydrogenation and/or decomposition in the absence of halide in the acidic reaction medium. In this case, there was a small explosion after a spark occurred on the reactor walls, mostly due to an uncontrolled fast H_2 combustion (by the O_2 produced in the initial rapid H_2O_2 decomposition) over the catalyst thrown from the reaction mixture on the reactor walls. The wet catalyst thrown on the reactor wall after drying is very

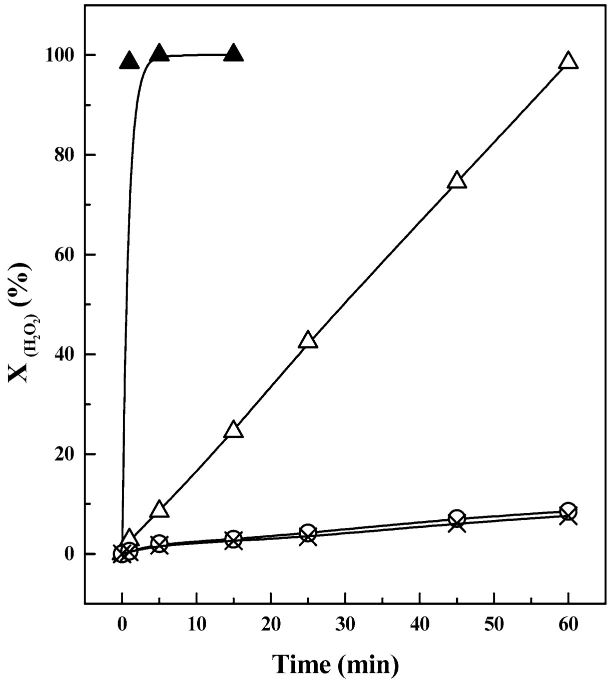

Fig. 6. Influence of the gas (N_2, O_2 or H_2) flowing through the acidic reaction medium (0.03 M H_3PO_4) with or without containing KBr (0.9 mmol/dm^3) on the conversion of H_2O_2 ($X(H_2O_2)$) over the Pd/Al_2O_3 at 27 °C ((○) under flowing N_2, (×) under flowing O_2, (△) under flowing H_2 and (▲) under flowing H_2 but in the absence of any halide). In the absence of any halide, the H_2O_2 conversion under the flowing H_2 led to an explosion.

dangerous because it catalyzes the H_2 combustion, leading to explosion if the gas mixture is within its explosion limits. The observed linear or close to linear increase in the conversion of H_2O_2 by its hydrogenation in the presence of chloride or bromide anions (Figs. 4 and 6) indicates that the hydrogenation reaction is zero order (with respect to H_2O_2), independent of the H_2O_2 concentration.

3.4. *Correlation between the H_2O_2 formation in H_2 oxidation and the H_2O_2 decomposition and hydrogenation*

Comparing the results for H_2 to H_2O_2 oxidation (Table 1, Figs. 1a and 2a) with those for H_2O_2 decomposition (Table 1, Figs. 1b and 2b) and also for H_2O_2 conversion in the presence of H_2 (Figs. 3–6) suggests a close relationship between the two. The higher the H_2O_2 formation activity of the Pd catalyst, the lower the H_2O_2 decomposition and/or hydrogenation activity of the catalyst under similar reaction conditions. But the reverse is not true; in the presence of KI, H_2O_2 decomposition/hydrogenation over the Pd catalyst is highly inhibited, but H_2O_2 formation in H_2 to H_2O_2 oxidation over the same catalyst is not enhanced.

The comparison of results thus leads to a conclusion that the observed drastic increase in H_2O_2 formation activity of the Pd catalysts due to the presence of halide anion promoters (viz. chloride or bromide anions) in the acidic medium can be attributed mostly to the inhibition of H_2O_2 decomposition and/or hydrogenation caused by the selective poisoning or modification by adsorbed halide anion promoter of catalytic sites responsible for the consecutive H_2O_2 decomposition and hydrogenation reactions (reactions (3) and (4)). The halide anions may also cause an inhibition of the parallel H_2 to water oxidation reaction, thereby promoting H_2 to H_2O_2 conversion, by selectively poisoning or modifying the catalytic sites for the dissociative adsorption of O_2 [8,10,19]. It should be noted that although the same reaction conditions (except the gas atmosphere) were used in all the foregoing reactions, differing oxidizing and reducing gas atmospheres (i.e., a mixture of H_2 and O_2 for H_2 to H_2O_2 oxidation, air for H_2O_2 decomposition, and H_2 for H_2O_2 hydrogenation) may cause changes in the oxidation state of surface Pd in the catalyst. Nevertheless, the influence of halide promoters on the reaction is so great that the foregoing conclusions can be safely drawn from the results. The highly complex nature of these reactions makes it almost impossible to study all of the reactions under totally identical conditions for the purpose of comparison.

It is also interesting to note that the presence of chloride or bromide anions not only causes an increase in both H_2O_2 yield and selectivity in H_2 to H_2O_2 oxidation, but also makes the process less hazardous by drastically reducing the rate of highly exothermic H_2O_2 decomposition and hydrogenation reactions (reactions (3) and (4)) and also by arresting the hazardous H_2 combustion (reaction (2)).

The observed negative effects of the fluoride in inhibiting the H_2O_2 decomposition and hydrogenation activities of the Pd catalysts may be attributed to the higher electronegativity and much larger positive standard electrode potential of fluorine and, consequently, to the lower reducing strength (electron-donating ability) of fluoride anions compared with the other halide anions. The electron-donating ability of chloride and bromide anions is intermediate between that of the fluoride and iodide anions, and hence the halide anions are more effective in inhibiting the H_2O_2 decomposition and hydrogenation reactions, promoting H_2O_2 formation in the H_2 to H_2O_2 oxidation without drastically affecting the H_2 oxidation activity of the Pd catalysts. The strong poisoning effect of the iodide anions may be attributed to their strong affinity to Pd, whereas F^- is relatively a noncoordinating ligand to Pd.

It may be noted that the Pd catalysts, after their use in the H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions in the acidic medium containing chloride or bromide anions, followed by their filtration and drying (at 90 °C), also show good H_2O_2 formation activity and very poor H_2O_2 decomposition activity in the respective reactions in the acidic medium, even when no chloride or bromide promoter is added to the reaction medium. This can be expected because of the adsorption of halide anions on the catalysts during their use in the reactions in the presence of the halide promoters. The halide-prepoisoned Pd catalysts, such as brominated Pd/Al_2O_3, also showed similar results in earlier work [11]. The adsorption of halide anions during the reactions was further confirmed by the XPS (Fig. 7) and EDAX analysis of the used catalysts.

3.5. *Role of protons and halide anion promoters in the H_2-to-H_2O_2 oxidation*

In the presence of mineral acid (protons), because the pH of the reaction medium is lower than the isoelectric point of the catalyst supports, only the halide anions (not the cations associated with the halide anions) from the reaction medium are adsorbed on the supported Pd catalysts. Thus, the cations show only little or no influence on the H_2 to H_2O_2 oxidation and H_2O_2 decomposition reactions (Table 3). The modification of the catalysts through a change in the electronic environment on their surface due to the halide anions adsorbed on or close to Pd^0 is mostly responsible for the observed effects on the H_2 to H_2O_2 oxidation and H_2O_2 decomposition and hydrogenation reactions. XPS analysis of the fresh and used (in H_2 to H_2O_2 oxidation in the acidic (0.03 M H_3PO_4) medium containing KBr (2.7 mmol/dm^3)) catalysts shows that after the reaction, the relative surface Pd to O (for the Pd/Al_2O_3) and Pd to C (for the Pd/C) ratios increased from 0.025 to 0.028 and from 0.022 to 0.027, respectively, indicating that the bromide anions are directly adsorbed not on the Pd surface, but rather on the catalyst support. The difference in binding energy for the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ electrons is decreased from 5.21 to 5.08 eV for Pd/Al_2O_3 and from 5.46 to 4.84 eV for Pd/C after the catalysts are used in H_2 to H_2O_2 oxidation, indicating a modification of the electronic environment/properties of Pd in the catalysts. For the fresh and used (with KBr promoter) Pd/C catalysts, the Pd $3d_{5/2}$ binding energy was 335.3 and 335.2 eV, respectively, and the Pd $3d_{3/2}$ binding energy was 340.7 and 340.1 eV, respectively. For the fresh and used (with KBr promoter) Pd/Al_2O_3 catalyst, the Pd $3d_{5/2}$ binding energy was 334.9 and 335.1 eV,

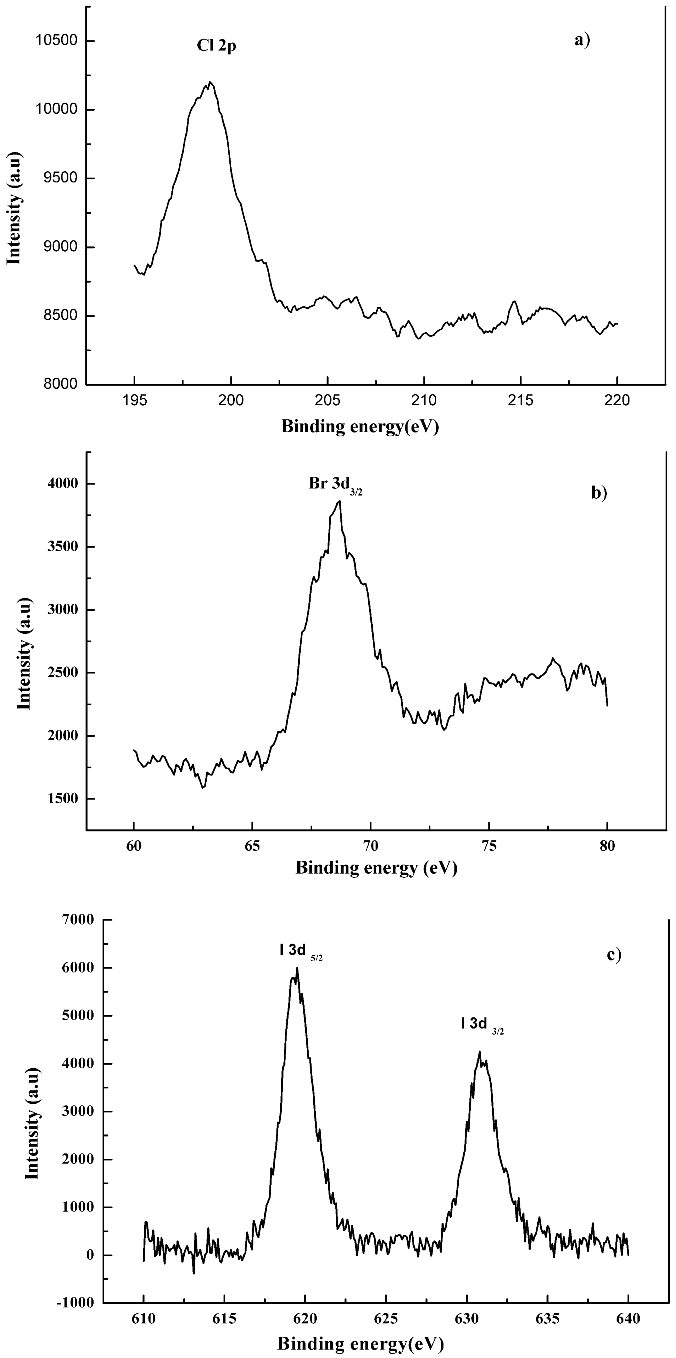

Fig. 7. X-Ray photoelectron spectra for the Pd/C catalyst after its use in the H_2-to-H_2O_2 oxidation in acidic (0.03 M H_3PO_4) medium containing different halides (a) KCl, (b) KBr and (c) KI (concentration of halide = 2.7 $mmol/dm^3$).

respectively, and the Pd $3d_{3/2}$ binding energy was 340.1 and 340.2 eV, respectively. This finding also indicates that the adsorbed bromide anions are either close to the Pd particles in the catalysts (particularly at the metal–support interface) or mobile on the catalyst surface during the reaction to have their interactions with the Pd.

In the absence of protons, H_2O_2 decomposition over the Pd catalysts in the presence of chloride, bromide, or iodide anions, even at higher concentrations, is much higher than that observed in the presence of protons (Tables 1 and 2). This is expected because of the presence of free/unadsorbed halide anions at higher concentrations in the absence of protons. It may also be noted that H_2O_2 is more stable in the acidic medium and that its decomposition over the reduced Pd catalysts in the presence of bromide promoter is drastically inhibited due to the presence of protons (Fig. 2b).

The halides (Cl^- and Br^- anions) are effective in promoting H_2 to H_2O_2 oxidation and inhibiting H_2O_2 destruction reactions only in the presence of protons. To explain the roles of the protons and halide anions in promoting H_2O_2 formation; we propose the following plausible mechanism involving elementary ionic and free radical reactions for H_2 to H_2O_2 oxidation:

$$S + X^- \rightarrow S.X^-, \tag{5}$$

$$2S + H_2 \rightarrow 2S.H, \tag{6}$$

$$S + O_2 \rightarrow S.O_2, \tag{7}$$

$$2S + O_2 \rightarrow 2S.O, \tag{8}$$

$$S.O_2 + S.X^- \rightarrow S.O_2^- + S.X, \tag{9}$$

$$S.O_2^- + S.H \rightarrow S.HO_2^- + S, \tag{10}$$

$$S.HO_2^- + H^+ \rightarrow S.H_2O_2, \tag{11}$$

$$S.H_2O_2 + S \leftrightarrows 2S.OH, \tag{12}$$

$$S.H_2O_2 + S.H \rightarrow S.OH + H_2O + S, \tag{13}$$

$$S.OH + S.H \rightarrow H_2O + 2S, \tag{14}$$

$$2S.OH \rightarrow S.O + H_2O + S, \tag{15}$$

$$S.O + 2S.H \rightarrow H_2O + 3S, \tag{16}$$

$$S.O_2^- + H^+ \rightarrow S.HO_2, \tag{17}$$

$$S.HO_2 + S.H \rightarrow S.H_2O_2, \tag{18}$$

$$S.H_2O_2 \rightarrow S + H_2O_2, \tag{19}$$

and

$$S.X + S.H \rightarrow S.X^- + H^+ + S, \tag{20}$$

where S is the active site on the Pd catalyst and X is Cl or Br. In the presence of both protons and halide promoter, the halide anions are adsorbed on the catalyst while poisoning and/or modifying its active sites, resulting in the following:

- The dissociative adsorption of O_2 (reaction (8)) and, consequently, reaction (16), leading to direct H_2 to water oxidation, is reduced.
- The dissociation of H_2O_2 (reaction (12)), leading to the formation of water by reaction (15), is reduced.
- Reactions (13) and (14), leading to H_2O_2 hydrogenation, are inhibited.

The protons and adsorbed halide anions participate in H_2 to H_2O_2 oxidation according to reactions (9), (11), and (17) and are regenerated by reaction (20). At a greater-than-optimal concentration of halide anion promoter, more catalytic sites are blocked and/or modified by the adsorbed halide anions, ultimately decreasing the catalytic activity and, consequently, the H_2O_2 yield in the oxidation process.

4. Conclusion

From this investigation into the H_2O_2 decomposition and hydrogenation reactions and H_2 to H_2O_2 oxidation over various Pd catalysts in aqueous acidic or nonacidic reaction medium with or without different halide anions (F^-, Cl^-, Br^-, and I^-), following important conclusions can be drawn:

1. In the absence of halide in the acidic reaction medium, the Pd catalysts show little or no formation of H_2O_2 in H_2 to H_2O_2 oxidation, but the catalysts show high activity for both the H_2O_2 decomposition and hydrogenation reactions.
2. Adding fluoride anions to the acidic reaction medium causes an appreciable increase in the activity of the Pd catalysts for both the H_2O_2 decomposition and hydrogenation reactions. It also causes a small increase in H_2 conversion in H_2 to H_2O_2 oxidation but with little or no formation of H_2O_2.
3. In the presence of iodide anions in the acidic reaction medium, the Pd catalysts are almost completely deactivated due to poisoning for all of the reactions. The poisoning action of iodide is attributed mainly to its strong coordinating ability to Pd.
4. The addition of chloride or bromide anions to the acidic reaction medium causes a drastic decrease in both the H_2O_2 decomposition and hydrogenation activities of the Pd catalysts. It also causes a significant increase in H_2O_2 formation (i.e., H_2O_2 yield) in H_2 to H_2O_2 oxidation. However, the cations associated with the halide anions have little or no influence on the H_2O_2 decomposition and H_2 to H_2O_2 oxidation reactions. In addition, there is an optimum concentration of the halide anions for achieving the highest H_2O_2 yield in H_2 to H_2O_2 oxidation.
5. The presence of acid (protons) in the reaction medium is essential to achieving the beneficial/promoting effect of the chloride or bromide anions on H_2O_2 formation in H_2 to H_2O_2 oxidation. In the absence of protons, the inhibition of H_2O_2 decomposition activity of the Pd catalysts caused by halide anion promoters is much smaller than that in the presence of protons, leading to little or no net H_2O_2 formation in H_2 to H_2O_2 oxidation.
6. In the presence of H_2, H_2O_2 conversion over the Pd catalysts in the acidic medium occurs by the simultaneous H_2O_2 decomposition and hydrogenation reactions, depending on the halide anions in the medium. In the absence of halide or the presence of fluoride anions, it is due mainly to H_2O_2 decomposition, whereas in the presence of chloride or bromide anions, it is due mainly to H_2O_2 hydrogenation.
7. In general, the rate of H_2O_2 destruction in the absence of H_2 is much less than that in the presence of H_2 under similar reaction conditions.
8. Significant leaching of Pd from the catalysts was observed when the acid used in the medium was 0.05 M H_2SO_4 or $\geqslant$0.3 M H_3PO_4, but no leaching was observed when using $\leqslant$0.03 M H_3PO_4. An aqueous H_3PO_4 at the lower concentration is recommended as the acidic medium for H_2 to H_2O_2 oxidation.
9. A close relationship exits between the H_2O_2 formation in H_2 to H_2O_2 oxidation over the Pd catalysts and the destruction of H_2O_2 by its decomposition and/or hydrogenation over the catalyst under similar reaction conditions; the higher the H_2O_2 formation activity of the catalyst, the lower its activity for the H_2O_2 decomposition and hydrogenation reactions.
10. The protons and chloride or bromide anions play their roles in combination with each other for promoting/enhancing H_2O_2 formation in H_2 to H_2O_2 oxidation. In the absence of either or both of these, little or no formation of H_2O_2 occurs in the reaction over the reduced Pd catalysts. A plausible mechanism for H_2 to H_2O_2 oxidation, explaining the roles of both the protons and the halide anion promoter, is proposed.

In summary, the H_2 to H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions over reduced Pd catalyst in an aqueous reaction medium are strongly influenced by the type of halide anions (F^-, Cl^-, Br^- or I^-) and their concentration in the reaction medium and also by the presence of protons in the medium. Bromide or chloride anions, at optimum concentrations, promote H_2 to H_2O_2 oxidation, causing a drastic increase in H_2O_2 formation but only in the presence of protons. In the halide-promoted H_2 to H_2O_2 oxidation reaction, H_2O_2 hydrogenation rather than H_2O_2 decomposition plays a dominant role in controlling H_2O_2 formation; under similar conditions, H_2O_2 hydrogenation is much faster than H_2O_2 decomposition.

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