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Research Note

Synergetic effect of two halogen promoters present in acidic reaction medium or catalyst on the H_2O_2 formation (in H_2-to-H_2O_2 oxidation) and destruction over Pd/C (or Al_2O_3) catalyst

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Abstract

A strong synergetic effect of two different halide anions (F^- and I^-, Cl^- and I^-, Cl^- and Br^-, and F^- and Br^-) at optimum concentration in the catalyst or in an acidic reaction medium was observed in the H_2-to-H_2O_2 oxidation over Pd/C, Pd/Al_2O_3, and halogenated Pd/Al_2O_3 catalysts. The synergetic effect promotes the net H_2O_2 formation by inhibiting the H_2O_2 decomposition and hydrogenation reactions. The effect is most pronounced for the combination of fluoride (or chloride) and iodide anions. The Br (1 wt%)–F (1 wt%)–Pd (5 wt%)/Al_2O_3 catalyst showed very high H_2O_2 yield (59%)/selectivity (60%) in the H_2-to-H_2O_2 oxidation.

Keywords: Synergetic effect; Hydrogen peroxide; H_2-to-H_2O_2 oxidation; H_2O_2 decomposition; H_2O_2 hydrogenation; Pd/Al_2O_3; Pd/C; Halogen promoter

1. Introduction

Hydrogen peroxide is a versatile, environmentally clean oxidizing agent; thus its use, particularly in the production of bulk and fine/specialty chemicals by a number of organic oxidation reactions, has been increasing steadily [1,2]. Oxidation of H_2 by O_2 to H_2O_2 is an environmentally clean process and involves the direct formation of H_2O_2 from H_2. It has a high potential to replace the currently practiced hydroquinone auto-oxidation process [3], which involves indirect oxidation of hydrogen to H_2O_2 and has several limitations. Therefore, direct H_2-to-H_2O_2 oxidation,

$$H_2 + O_2 \rightarrow H_2O_2, \qquad (1)$$

is of great practical importance. Unfortunately, this process also involves the thermodynamically highly favored undesirable parallel and consecutive water-forming reactions [4,5]:

$$H_2 + 0.5O_2 \rightarrow H_2O \quad \text{(parallel } H_2 \text{ combustion)}, \qquad (2)$$

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

and

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

Reactions (2)–(4) are responsible for the reduction in the net formation of H_2O_2. Although this process has been extensively patented, it has not yet been commercialized, and it is often considered a “dream process.” Apart from its hazardous nature, low H_2O_2 selectivity is the main problem associated with this process.

The use of halogen promoter anions, particularly bromide [5–8] or chloride [5,8–11] anions in acidic reaction medium [5,6,8,9,11] or in a catalyst [7,10], has been reported to improve H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation over supported Pd catalysts. Among the halides (F^-, Cl^-, Br^-, and I^-), bromide and chloride anions were found to be highly effective promoters for drastically increasing H_2O_2 formation, while largely decreasing the H_2O_2 decomposition and hydrogenation activity of supported Pd catalysts [5,7]. In contrast, fluoride anions showed no promoting effect on H_2O_2 formation, but did cause an increase in the undesirable H_2O_2 decomposition activity of the Pd catalysts with little or no effect on their H_2O_2 hydrogenation activity. Iodide anions, on the other hand, strongly inhibited all reactions, causing catalyst deactivation due to poisoning. In

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the presence of fluoride or iodide anions in the catalyst [7] or in an acidic reaction medium [5], very little or no formation of H_2O_2 occurred in the H_2-to-H_2O_2 oxidation over the supported Pd catalysts [5,7]. In this communication, we report for the first time a strong synergetic effect of two different halide anions (F^- and I^-, Cl^- and I^-, Cl^- and Br^-, and F^- and Br^-) present in the catalyst or in an acidic reaction medium at their optimum concentration on the H_2-to-H_2O_2 oxidation, largely promoting the H_2O_2 formation by inhibiting the H_2O_2 decomposition and hydrogenation reactions over Pd/C, Pd/Al_2O_3, and halogenated Pd/Al_2O_3 catalysts.

2. Experimental

The Pd/C and Pd/Al_2O_3 catalysts (with 5 wt% Pd loading) in their reduced form were obtained from Lancaster, UK, in finely powdered form. The presence of a metallic Pd phase in the Pd catalysts was confirmed by XRD. The halogenated Pd/Al_2O_3 catalysts containing single or two different halogens were prepared by impregnating using an incipient wetness technique one ammonium halide (NH_4F, NH_4Br, or NH_4I) or a mixture of two different ammonium halides from aqueous solution, drying, and calcining in a flow of N_2 at 400 °C for 2 h.

The catalytic direct H_2-to-H_2O_2 oxidation over the Pd catalysts was carried out in a magnetically stirred jacketed glass reactor (capacity, 100 cm^3) in a reaction medium of 50 cm^3 aqueous 0.1 M H_3PO_4 with 0.1 g of catalyst at a gaseous feed of 50 mol% H_2 in O_2 at a gas flow rate of 6 cm^3/min at 27 °C and 0.95 atm, for a reaction period of 1 h. For the Pd/C and Pd/Al_2O_3 catalysts, a single or a mixture of two halides was added to the reaction medium before the reaction. However, for the halogenated Pd/Al_2O_3 catalysts, no halide was added to the reaction medium and, after the reaction, no presence of halide anions in the reaction medium was detected. The H_2O_2 in the reaction mixture was determined quantitatively by iodometric titration. The H_2 conversion, H_2O_2 yield, and H_2O_2 selectivity are defined as follows: H_2 conversion (%) = {[(moles of H_2 in the feed) − (moles of H_2 in the effluent gases)] ÷ (moles of H_2 in the feed)} × 100. H_2O_2 selectivity (%) = [(moles of H_2O_2 formed) ÷ (moles of H_2 consumed)] × 100. H_2O_2 yield (%) = [(moles of H_2O_2 formed) ÷ (moles of H_2 in the feed)] × 100.

The catalytic H_2O_2 conversion (in absence or presence of H_2) over the catalyst was carried out in the same reactor containing 0.1 g of catalyst in 50 cm^3 aqueous acidic (0.1 M H_3PO_4) reaction medium with or without halide anions, by injecting through the rubber septum 1.0 cm^3 of a 30% aqueous H_2O_2 solution in the reactor under vigorous stirring. The gas evolved or consumed was measured as a function of time at 27 °C and atmospheric pressure. These experimental procedures were described previously earlier [5,7,10].

3. Results and discussion

The results given in Table 1 and Figs. 1 and 2 reveal a strong synergetic effect of two different halide anions on the formation of H_2O_2 in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 decomposition and hydrogenation reactions over the Pd/C, Pd/Al_2O_3, and halogenated Pd/Al_2O_3 catalysts in an acidic (0.1 M H_3PO_4) aqueous medium. Because of the presence of the second halide, the net rate of H_2O_2 formation increased, whereas the H_2O_2 decomposition and hydrogenation rates decreased, depending on the nature of the two different halide anions and their concentration in the reaction medium or in the catalyst, as follows.

3.1. Synergetic effect of I^- and F^- anions

In the presence of fluoride anions in either the reaction medium (4.0 mmol F^-/dm^3) or the catalyst (5.0 wt% F), the H_2 conversion in the H_2 oxidation over all the catalysts was complete (100%), but without any formation of H_2O_2. This is most probably due to the very high rates of the consecutive H_2O_2 decomposition and hydrogenation reactions (Table 1). In addition, when iodide alone was present in the medium (0.1 mmol I^-/dm^3) or in the catalyst (1.0 wt% I), both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation were very poor. However, for all catalysts, the rate of net H_2O_2 formation in the H_2-to-H_2O_2 oxidation was increased very markedly, whereas that of the H_2O_2 decomposition and hydrogenation was decreased appreciably, when both the fluoride and iodide anions were present in the medium or in the catalyst (Table 1). The H_2-to-H_2O_2 oxidation was carried out for 1 h. For the higher reaction periods, the rate of H_2O_2 formation is expected to decrease due to the increased H_2O_2 concentration, which causes an increase in the rate of H_2O_2 destruction.

For the Pd/C catalyst, with increasing concentration of fluoride in the presence of iodide (0.1 $mmol/dm^3$) or of increasing concentration of iodide in the presence of 1.0 $mmol/dm^3$ fluoride, both the H_2O_2 yield and selectivity increased while the H_2 conversion decreased (Figs. 1a_1 and 1b_1). In the case of the Pd/Al_2O_3 catalyst, the H_2O_2 yield and selectivity both first increased and then passed through a maximum with increasing fluoride concentration in the presence of iodide (0.1 $mmol/dm^3$) (Fig. 1a_2) or of increasing iodide concentration in the presence of 4.0 $mmol/dm^3$ fluoride (Fig. 1c_1) in the medium. This indicates that an optimum concentration of halides is needed to achieve the best results (i.e., highest H_2O_2 yield and/or selectivity).

3.2. Synergetic effect of I^- and Cl^- anions

In the presence of 1.0 $mmol/dm^3$ chloride in the reaction medium, the H_2 conversion in the H_2-to-H_2O_2 oxidation was high ($\geqslant$98%) but both the H_2O_2 yield and selectivity were poor for the Pd/C and Pd/Al_2O_3 catalysts (Table 1). However, when 0.1 $mmol/dm^3$ iodide was added to the medium, the H_2O_2 yield and selectivity both increased markedly and the rates of the H_2O_2 decomposition and hydrogenation reactions decreased appreciably.

With increasing concentration of iodide (in the presence of chloride), H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation over the Pd/C and Pd/Al_2O_3 catalysts first increased and

Table 1
Results of the H_2-to-H_2O_2 oxidation and H_2O_2 conversion in the presence and absence of H_2 over the Pd/C and Pd/Al_2O_3 catalyst in the acidic medium containing single halide or two different halides

Halide in medium/catalyst (mmol/dm^3)[a] [wt%][b]		Conversion of H_2 (%)	Yield of H_2O_2 (%)	Selectivity for H_2O_2 (%)	Net rate of H_2O_2 formation (mmol/(g_{cat} h))	Time for half H_2O_2 conversion (min)	
I	II					In air	In H_2
Catalyst: Pd/C (with or without halide(s) in the reaction medium)							
KF (1.0/4.0)	Nil	100	0.0	0.0	0.0	11	<1.0
KI (0.1)	Nil	91	3.0	3.3	2.1	23	<1.0
KF (1.0)	KI (0.1)	86	4.9	5.7	3.4	25	≈1.0
KF (4.0)	KI (0.1)	82	5.5	6.7	3.8	26	≈1.0
KCl (1.0)	Nil	98	6.5	6.7	4.5	30	3.0
KCl (1.0)	KI (0.1)	79	22	28	15	Large {38}[c]	18
KBr (0.1)	Nil	92	22	30	15	56	<1.0
KBr (0.1)	KCl (1.0)	87	37	42	25	Large {32}[c]	12
Catalyst: Pd/Al_2O_3 (with or without halide(s) in the reaction medium)							
KF (4.0)	Nil	100	0.0	0.0	0.0	Large {38}[c]	<1.0
KI (0.1)	Nil	94	4.2	4.5	2.9	Large {17}[c]	25
KF (4.0)	KI (0.1)	69	17	25	12	Large {18}[c]	37
KCl (1.0)	Nil	100	9.5	9.5	6.5	Large {22}[c]	11
KCl (1.0)	KI (0.1)	81	25	30	17	Large {12}[c]	26
Catalyst: Halogenated Pd/Al_2O_3 (containing one or two different halogens)							
F [5.0 wt%]	0.0	100	0.0	0.0	0.0	1.0	<1.0
I [1.0 wt%]	0.0	28	5.7	20	3.9	V. large {1}[c]	V. large[d]
F [5.0 wt%]	I [1.0 wt%][b]	41	13	32	9.0	V. large {1}[c]	V. large[e]
Br [1.0 wt%]	Nil	93	51	55	35	V. large {3}[c]	12
Br [1.0 wt%]	F [1.0 wt%]	98	59	60	41	V. large {3}[c]	13
Br [1.0 wt%]	F [5.0 wt%]	99	57	57	39	V. large {2}[c]	14

[a] The values in parentheses are the concentrations of respective halide in the medium.
[b] Values in the brackets are the concentrations of the respective halogen in the halogenated Pd/Al_2O_3 catalyst.
[c] Values in the curly brackets are the H_2O_2 conversions in 1 h.
[d] 10% H_2O_2 conversion, respectively, in 1 h.
[e] 20% H_2O_2 conversion, respectively, in 1 h.

then passed through a maximum. However, H_2 conversion decreased continuously and very markedly (Figs. 1b$_2$ and 1c$_2$). A similar trend was observed when the chloride concentration in the medium was increased in the presence of 0.1 mmol/dm^3 iodide (Fig. 2); however, the decrease in the H_2 conversion was much smaller. These observations also point to an optimum concentration of the halides for achieving the best results in the H_2-to-H_2O_2 oxidation. The decreases in H_2 conversion indicate that the iodide and chloride anions poison the catalytically active sites and that iodide is the most effective catalyst poison.

3.3. Synergetic effect of Cl^- or F^- and Br^- anions

The present results (Table 1) and earlier studies [5,7] showed that bromide is the best halide promoter for the H_2-to-H_2O_2 oxidation over the Pd catalysts. The presence of bromide also drastically reduces the rates of H_2O_2 decomposition and hydrogenation reactions over the Pd catalysts [5,7]. However, the addition of chloride (1.0 mmol/dm^3) to the reaction medium containing 0.1 mmol/dm^3 bromide caused an appreciable increase in both the H_2O_2 yield and selectivity, while largely decreasing the rates of the H_2O_2 decomposition and hydrogenation reactions over the Pd/C catalyst (Table 1). Similarly, the incorporation of 1 wt% fluorine in the brominated Pd/Al_2O_3 (1.0 wt% Br) also resulted in an appreciable increase in both the H_2O_2 yield (from 51 to 59%) and selectivity (from 55 to 60%) in H_2-to-H_2O_2 oxidation, while decreasing the rates of the H_2O_2 decomposition and hydrogenation reactions (Table 1). These increases and decreases were relatively small, however. The higher fluoride concentration (5 wt%) also caused an increase in H_2O_2 selectivity and yield of the brominated catalyst, with a relatively smaller increase. This also points to the need for an optimum concentration of F in the brominated Pd/Al_2O_3 catalyst to achieve the best catalyst performance. These results clearly show a synergetic effect of the two halogens in the catalyst on the H_2O_2 formation and destruction reactions, thereby improving H_2O_2 yield and selectivity in the process. Further work on the optimization of Br and F concentration in the catalyst may lead to a better catalyst for the oxidation process.

The synergetic effect is expected to arise from the modification of the electronic properties of the Pd catalyst through the interactions of the two halogen anions (which differ appreciably in electronegativity and electron affinity) with the Pd clusters in the catalyst; the electronegativity and electron affinity of halogens occur in the order F > Cl > Br > I and Cl > F > Br > I, respectively. The combined effect of the two halides on the electronic properties of the Pd clusters seems to retard the rate of O–O bond cleavage of O_2 ($O_2 + 2Pd \rightarrow 2Pd{\cdot}O$) and H_2O_2 ($2Pd + H_2O_2 \rightarrow 2Pd{\cdot}OH$), thereby reducing the rates of the H_2 combustion [5,6,11,12] and H_2O_2 decomposition and hy-

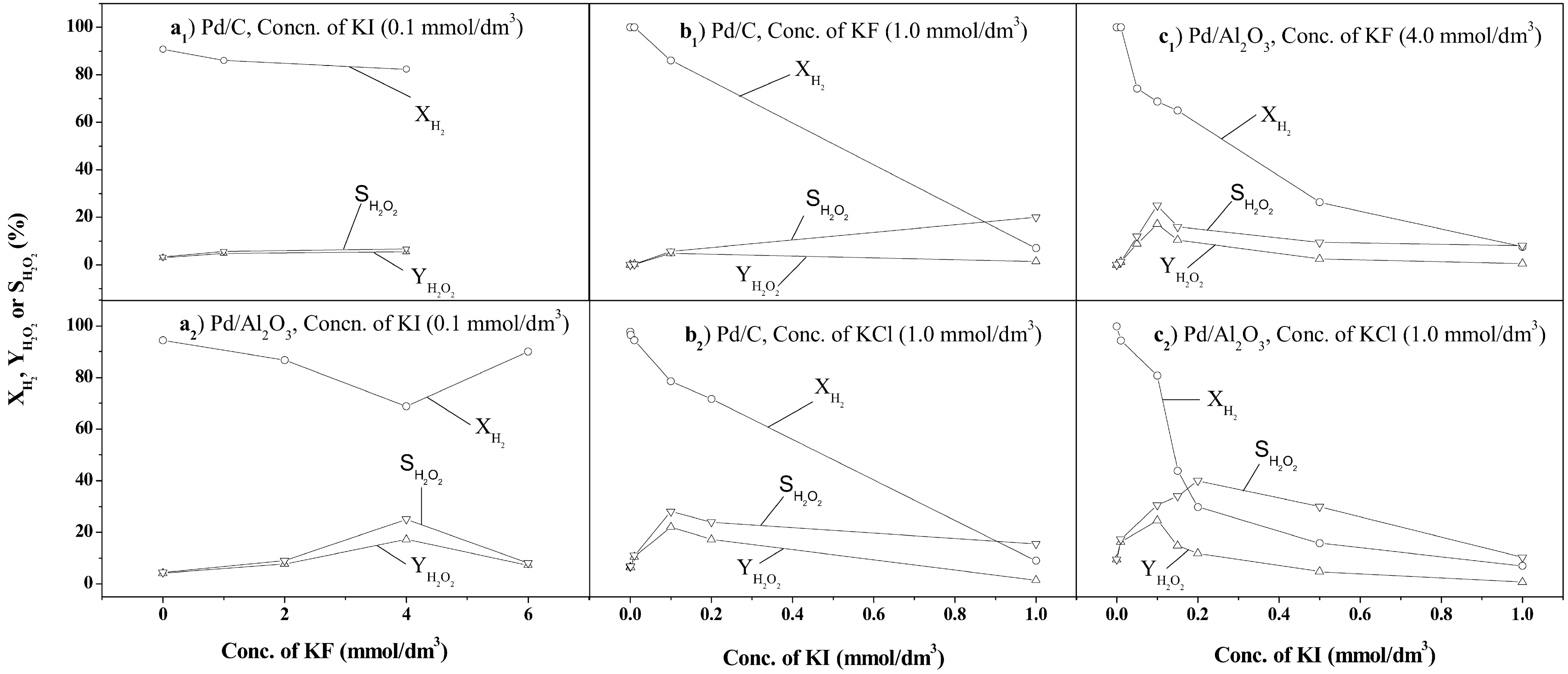

Fig. 1. Effect of (a) concentration of KF added to the acidic medium containing 0.1 mmol/dm^3 KI in case of the Pd/C and Pd/Al_2O_3 catalysts, (b) concentration of KI added to the acidic medium containing 1.0 mmol/dm^3 KF or KCl in case of the Pd/C catalyst, and (c) concentration of KI added to the acidic medium containing 4.0 mmol/dm^3 KF or 1.0 mmol/dm^3 KCl in case of the Pd/Al_2O_3 catalyst, on the H_2 conversion in the H_2-to-H_2O_2 oxidation.

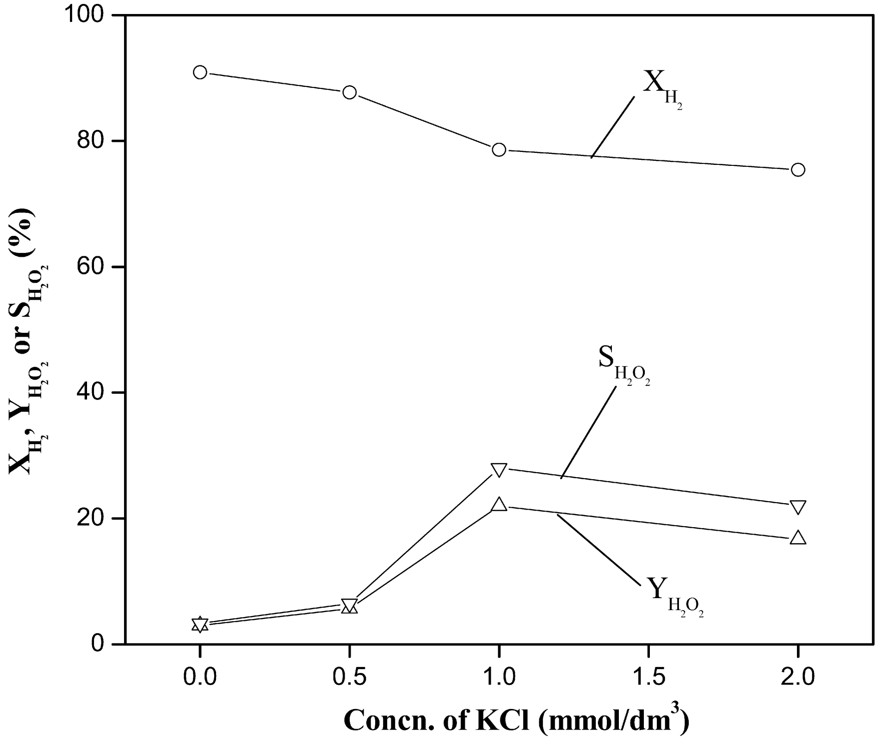

Fig. 2. Effect of the concentration of KCl added to the acidic medium containing 0.1 mmol/dm^3 KI in the H_2-to-H_2O_2 oxidation over the Pd/C catalyst.

drogenation [5,11] reactions. However, the decrease in H_2O_2 selectivity at the higher halide concentration (Figs. 1 and 2) indicates that the favorable modification of the electronic properties of catalyst occurs only in a particular range of halide concentrations, probably depending on the relative concentration and nature of the halides anions. Further thorough studies are needed to gain more insight into the very complex issues of the synergetic effects and the decreased H_2O_2 selectivity at the higher halide concentrations.

Fluorine and chlorine are highly electronegative halogens, and thus fluorination or chlorination of the Pd catalysts also may cause modification of the support properties, particularly the acidity of the support (alumina or carbon) of the Pd catalysts. For example, alumina contains only Lewis acid sites, but protonic acid sites are created after fluorination [13]. It should be noted that, apart from the halide promoter, the presence of protons is also required for the selective formation of H_2O_2 [5]. The increase in the H_2O_2 yield and selectivity after the addition of fluorine in the brominated Pd/Al_2O_3 catalyst may be at least partly attributed to the creation of protonic acidity due to fluorination of the alumina support.

The synergetic effect depends on the concentration of the two halides (Figs. 1 and 2); it is more pronounced when the two halogen promoters differ greatly in electronegativity and/or electron affinity. The presence of more than two halides is also expected to produce a synergetic effect on the H_2O_2 formation in the H_2-to-H_2O_2 oxidation. Thus, there is a large scope for greatly improving the H_2O_2 formation in H_2-to-H_2O_2 oxidation by optimizing the concentrations of two or more halides in the medium or in the Pd catalyst.

4. Conclusion

H_2O_2 formation with a much higher selectivity/yield in the direct oxidation of H_2 by O_2 to H_2O_2 over supported Pd catalysts in an acidic medium can be accomplished using two halogens (F^- and I^-, Cl^- and I^-, Cl^- and Br^-, and F^- and Br^-) as catalyst promoters at their optimum concentrations in the medium or in the catalyst, instead of using either of the two halogens alone. The two halogen promoters have a synergetic effect. They promote H_2O_2 formation by inhibiting the H_2O_2 decomposition and hydrogenation reactions. The synergetic effect is most pronounced for the combination of fluoride (or chloride) and iodide anions. Fluorinated and brominated Pd/Al_2O_3 is a highly promising catalyst for the selective H_2-to-H_2O_2 oxidation with high yields.

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