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Drastic increase of selectivity for H_2O_2 formation in direct oxidation of H_2 to H_2O_2 over supported Pd catalysts due to their bromination

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Incorporation of bromide anions (1.0 wt%) in supported Pd catalysts (*viz.* Pd supported on Al_2O_3, ZrO_2, SiO_2, H-β or Ga_2O_3) leads to a drastic increase in their selectivity for H_2O_2 formation in the direct oxidation of H_2 to H_2O_2 by O_2 (at room temperature) in an aqueous acidic (0.03 M H_3PO_4) reaction medium; the selectivity increase is accompanied by a large decrease in the H_2O_2 decomposition activity of the catalysts.

Demand for hydrogen peroxide, as an environmentally-friendly oxidizing agent, in the paper/pulp industries, for water purification or disinfection and waste-water treatments and also for the preparation of fine and bulk chemicals has been increasing day-by-day. Efforts are therefore being made to replace the presently practised anthraquinone process for H_2O_2 production, which involves indirect oxidation of H_2 in multiple steps[1] and has several limitations/disadvantages, by a direct environmentally-friendly Pd-catalyzed H_2-to-H_2O_2 oxidation route.[2–5] However, the main problem associated with the direct H_2-to-H_2O_2 oxidation is the poor selectivity for H_2O_2 formation because of the high activity of palladium for H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\,O_2$).[2,3,6] It is, therefore, of both practical and scientific interest to kill or drastically reduce the H_2O_2 decomposition activity of Pd-catalysts by their modification so that their H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation can be drastically improved. We report here that the above difficult-to-achieve goal can very well be accomplished by incorporating bromide ions in Pd-catalysts (*viz.* Pd supported on alumina, silica, zirconia, gallia and H-β zeolite). The incorporation of other halides in the catalysts, however, either produces a little improvement in their H_2O_2 selectivity or causes adverse effects on their performance in the H_2-to-H_2O_2 oxidation.

Results showing the influence of different halide anions (F^-, Cl^-, Br^-, and I^-) incorporated in supported Pd catalysts by their halogenation on their performance 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 room temperature (27 °C) are presented in Table 1. Results in Fig. 1 show the influence of the concentration of Br^- added to the Pd/Al_2O_3 catalyst on its performance in both the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions. The Pd (5%)/Al_2O_3 was obtained from Lancaster (UK). The ZrO_2, Ga_2O_3, H-β or SiO_2 supported Pd (2.5%) catalysts were prepared by impregnating the respective support with palladium acetate from its acetonitrile solution, drying, calcining at 500 °C and then reducing by ammoniacal hydrazine. The halogenation of Pd catalyst was done by impregnating the catalyst with ammonium halide from its aqueous solution, drying and calcining in a flow of N_2 at 400 °C. The direct H_2-to-H_2O_2 oxidation was carried out in a magnetically stirred glass reactor (capacity: 250 cm^3) at the following reaction conditions: reaction medium = 150 cm^3 aqueous 0.03 M H_3PO_4, amount of catalyst = 0.5 g, gaseous feed = 4.6 mol% H_2 in O_2, gas flow rate = 15.5 $cm^3\,min^{-1}$, temperature = 27 °C, pressure = 0.95 atm, and reaction period = 3 h; by the procedure given elsewhere.[3] The H_2O_2 in the reaction mixture was determined quantitatively by an iodometric titration method. The H_2O_2 decomposition activity of the catalysts was measured in terms of the pseudo first order H_2O_2 decomposition rate constant (k_a) at 27 °C, using the same reaction medium, by the procedure given earlier.[3,6]

Table 1 Performance of supported Pd catalysts, with or without addition of different halides, in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions at 27 °C (concentration of halide in halogenated catalysts = 1.0 wt%)

Catalyst	Halide added to the catalyst	Colour of the catalyst	H_2-to-H_2O_2 oxidation			H_2O_2 decomposition
			X (H_2)[a] (%)	Y (H_2O_2)[b] (%)	S (H_2O_2)[c] (%)	activity $k_a \times 10^3$ (min^{-1})[d]
Pd^o (5 wt%)/Al_2O_3	None	Black	54.7	0.5	0.9	4.36
	Br	Gray	48.9	29.7	60.8	0.58
	F	Brownish black	62.3	0.0	0.0	398.8
	Cl	Gray	63.4	0.0	0.0	368.2
	I	Brown	9.3	3.4	33.3	0.19
Pd^o (2.5 wt%)/ZrO_2	None	Black	43.7	3.9	8.9	3.8
	Br	Faint gray	37.3	25.6	68.8	0.25
	F	Black	51.8	0.0	0.0	5.7
	Cl	Gray	50.5	3.6	7.1	2.7
Pd^o (2.5 wt%)/Ga_2O_3	None	Grayish black	50.0	5.4	10.8	4.22
	Br	Pale cream	38.5	24.8	64.5	0.38
	F	Gray	55.5	2.2	3.9	5.7
Pd^o (2.5 wt%)/H-β	None	Black	60.5	0.0	0.0	13.4
	Br	Faint gray	56.3	26.4	46.9	0.04
	F	Black	54.1	0.0	0.0	60.8
	Cl	Blackish gray	51.3	0.0	0.0	30.5
Pd^o (2.5 wt%)/SiO_2	None	Black	50.3	0.0	0.0	54.2
	Br	Faint black	38.5	23.3	60.5	0.73
	F	Black	54.7	0.0	0.0	102.3
	Cl	Black	58.4	0.0	0.0	88.7

[a] Total conversion of H_2. [b] Yield of H_2O_2. [c] Selectivity for H_2O_2. [d] k_a is pseudo first order H_2O_2 decomposition rate constant.

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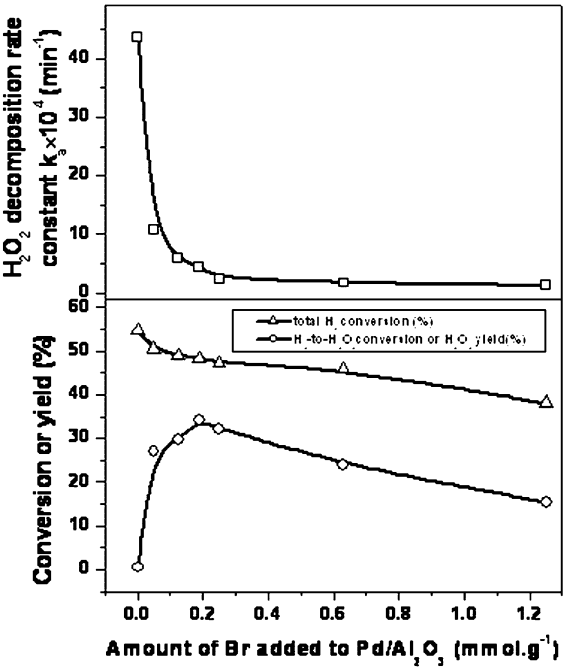

Fig. 1 Influence of the amount of Br added to Pd (5 wt%)/Al_2O_3 on its catalytic activity in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions (at 27 °C).

The results in Table 1 can be summarized as follows:

1) All the supported Pd catalysts, before their bromination, show little or no selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation but high activity for the H_2O_2 decomposition.

2) After bromination of the Pd catalysts, their H_2O_2 yield and/or selectivity is drastically increased, whereas their activity for the H_2O_2 decomposition is drastically reduced. The total H_2 conversion is also decreased but to a smaller extent. The H_2O_2 concentration achieved for the brominated Pd catalysts was 8.6 ± 1.0 mmol dm^{-3}. The catalysts could be reused without a significant loss in their activity in the reaction. Also no leaching of Pd from the catalysts during the reaction is observed, indicating long catalyst life.

3) The incorporation of iodide in the Pd/Al_2O_3 catalyst results in a marked decrease both in its H_2 conversion (in the H_2-to-H_2O_2 oxidation) and H_2O_2 decomposition activities.

4) The incorporation of fluoride or chloride anions in the Pd catalysts caused an increase in the H_2 conversion (except for the Pd/H-β) but no improvement in the H_2O_2 yield and/or selectivity. Because of fluorination or chlorination, the H_2O_2 decomposition activity of the Pd catalysts is increased markedly.

The results in Fig. 1 reveal that there is an optimum concentration of Br in the brominated Pd/Al_2O_3 ($\cong$0.2 mmol g^{-1}) for achieving highest H_2O_2 yield (*i.e.* H_2-to-H_2O_2 conversion) in the H_2-to-H_2O_2 oxidation. With the increase in the amount of Br added to the Pd/Al_2O_3 catalyst, the H_2O_2 yield is passed through a maximum and the H_2 conversion is decreased to a small extent but the H_2O_2 decomposition activity of the catalyst is decreased sharply.

The XRD analysis of the catalysts (Table 1) indicated that the palladium present in all the catalysts was in metallic (Pd^0) form.

The highly improved performance of the supported Pd catalysts after their bromination is attributed to the inhibition caused by the bromide ions (present in the catalysts) to the H_2O_2 decomposition reaction, which is a consecutive reaction, responsible for the indirect oxidation of H_2 to water. The inhibition is expected because of the interaction of bromide anions with palladium, changing its electronic properties, depending upon the concentration of bromide anions. The direct oxidation of H_2 to water ($H_2 + 0.5\ O_2 \rightarrow H_2O$) over the supported Pd catalysts may also be inhibited to some extent due to the presence of bromide anions in the catalyst. It may be noted that the use of halide promoters added into the acidic reaction medium for the H_2-to-H_2O_2 oxidation[7] is undesirable because of their highly corrosive nature. This serious problem is avoided in the present case by incorporating the halide directly in the solid catalyst. Further detailed studies are necessary to understand the role played by the different halide anions incorporated in the Pd-catalysts for the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions.

In summary, the incorporation of bromide ions, particularly at optimum concentration, in the supported Pd catalysts by their bromination causes a drastic improvement in their performance (both the H_2O_2 selectivity and yield) in the direct oxidation of H_2 to H_2O_2.

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