Hydrogen peroxide formation in the interaction of oxygen with boron-containing Pd catalysts prereduced by hydrazine in aqueous acidic medium containing bromide anions

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Received 22 July 2004; accepted 15 September 2004

Interaction of molecular oxygen with Pd/BPO_4 or ZrO_2 (or Al_2O_3, CeO_2, TiO_2)–B_2O_3 catalysts, prereduced by hydrazine hydrate, in an aqueous acidic (H_2SO_4 or H_3PO_4) reaction medium containing bromide ions leads to the formation of H_2O_2. However, in the absence of boron in the catalyst and also in the absence of acid and/or bromide ions in the reaction medium, almost no H_2O_2 is formed.

KEY WORDS: boron-containing Pd catalysts; hydrogen peroxide; oxygen–catalyst interactions.

1. Introduction

Hydrogen peroxide is a versatile and environmentally friendly oxidizing agent. Its demand in the textile and paper/pulp industries as a bleaching agent, water purification/disinfection, wastewater treatment and catalytic oxidation processes for the synthesis of fine/bulk chemicals has been increasing day-by-day. It is mostly produced by the anthraquinone process [1], which is based on indirect oxidation of H_2, involving multiple reactions and processing steps, and also suffers from a number of drawbacks. This process is not environ-friendly and the cost of H_2O_2 produced is high. Hence, efforts are being made to produce H_2O_2 by the direct catalytic oxidation of H_2 by O_2 using Pd catalysts [2–11]. However, because of the very broad explosion limits of O_2–H_2 gas mixture (4–96% H_2 in O_2), the direct H_2–to–H_2O_2 oxidation is highly hazardous one. It is, therefore, of great practical interest to find some non-hazardous new route for the production of H_2O_2. We report here our preliminary observations indicating the formation of H_2O_2 in the interaction of O_2 with boria containing supported palladium catalysts, prereduced by hydrazine, in aqueous acidic medium containing bromide ions. The H_2O_2 formation is non-hazardous, but it requires the presence of boron in the catalyst, the prereduction of the catalyst by hydrazine, and also the presence. of mineral acid and bromide ions in the aqueous reaction medium.

2. Experimental

The supported palladium catalysts with Pd loading of 2.5 wt% (Table 1) were prepared by impregnating $PdCl_2$ from its acetonitrile solution on boron phosphate or respective metal oxide support (with or without containing boron) by incipient wetness technique, drying the impregnated.mass in air oven at 100 °C for 2 h and then calcining it at 500 °C under static air for 3 h. The ZrO_2–B_2O_3, CeO_2–B_2O_3, TiO_2–B_2O_3 and Al_2O_3–B_2O_3 catalyst supports were prepared by mixing boric acid (H_3BO_3) with respective metal oxide [ZrO_2 (prepared from zirconyl nitrate by its hydrolysis to zirconium hydroxide, by ammonium hydroxide and calcining at 500 °C for 2 h), CeO_2 (Aldrich), TiO_2 (Loba) or Al_2O_3 (prepared from bohemite by its calcination at 500 °C for 2 h)] with the metal/boron mole ratio of 1.0 in the presence of deionised water just sufficient to form a thick paste, drying the wet mixture in air oven at 100 °C for 2 h and then calcining it in air at 600 °C for 3 h. Similarly, the boron phosphate was prepared from a mixture of boric acid and orthophosphoric acid (with B/P mole ratio of 1.0). The calcined catalyst was reduced by hydrazine by adding 3 mL hydrazine hydrate (98%) dropwise to the catalyst (3 g) while mixing thoroughly the hydrazine–catalyst mixture at a room temperature for 5 min and drying the wet catalyst mass on water bath for Ih. The catalyst–oxygen interaction was carried out in a magnetically stirred glass reactor (capacity = 250 cm^3), using 0.5 g fine particles of the prereduced catalyst in 150 cm^3 aqueous reaction medium with or without containing mineral acid and/or halide and passing O_2 (or air) through the reaction medium at a flow rate of 1.5 dm^3/h at 27 °C. The H_2O_2 formed in the reaction was analyzed by the iodometric titration. Influence of the presence of B_2O_3 in the catalyst and reduction of the catalyst by hydrogen (at 400°C) or aqueous sodium borohydride solution on the H_2O_2 formation has also been studied.

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Table 1
Formation of H_2O_2 in the interaction of O_2 with different supported Pd catalysts in the aqueous reaction medium with or without containing mineral acid and/or halide

Catalyst	Reaction medium	Halide promoter	Concn.of halide (mmol/dm^3)	Reaction period (h)	H_2O_2 formed (mmol)
Pd/ZrO$_2$–B$_2$O$_3$[a]	H_3PO_4 (0.03 M)	KBr	0.94	3	2.90
Pd/CeO$_2$–B$_2$O$_3$[a]	H_3PO_4 (0.03 M)	KBr	0.94	1	0.96
Pd/TiO$_2$–B$_2$O$_3$[a]	H_3PO_4 (0.03 M)	KBr	0.94	1	0.57
Pd/Al$_2$O$_3$–B$_2$O$_3$[a]	H_3PO_4 (0.03 M)	KBr	0.94	1	0.53
Pd/BPO$_4$[a]	H_3PO_4 (0.03 M)	KBr	0.94	3	2.89
Pd/ZrO$_2$ (or CeO$_2$, TiO$_2$, Al$_2$O$_3$)[a]	H_3PO_4 (0.03 M)	KBr	0.94	3	0.00
PdO/ZrO$_2$ (or CeO$_2$, TiO$_2$, Al$_2$O$_3$)-B$_2$O$_3$[b]	H_3PO_4 (0.03 M)	KBr	0.94	3	0.00
Pd/ZrO$_2$ (or CeO$_2$, TiO$_2$, Al$_2$O$_3$)-B$_2$O$_3$[c]	H_3PO_4 (0.03 M)	KBr	0.94	3	0.00
Pd/ZrO$_2$–B$_2$O$_3$[a]	H_2SO_4 (0.05 M)	KBr	0.94	1	1.10
Pd/ZrO$_2$–B$_2$O$_3$[a] or Pd^o/BPO$_4$[a]	Water (Without mineral acid)	KBr	0.94	3	<0.38
Pd/ZrO$_2$–B$_2$O$_3$[a] or Pd^o/BPO$_4$[a]	H_3PO_4 (0.03 M)	Without promoter	0.00	3	<0.02
Pd/ZrO$_2$–B$_2$O$_3$[a] or Pd^o/BPO$_4$[a]	H_3PO_4 (0.03 M)	KCl or KI	0.94	3	<0.01

[a] Catalyst prereduced by hydrazine.

[b] Unreduced catalyst (with its Pd in oxidized form).

[c] Catalyst prereduced by hydrogen (at 400 °C) or aqueous sodium borohydride solution.

3. Results and discussions

Results showing the formation of H_2O_2 in the interaction of O_2 with the different Pd (2.5 wt%) catalysts, with or without containing boron, in an aqueous reaction medium in the presence or absence of mineral acid (H_3PO_4 or H_2SO_4) and/or different halide ions (Cl^-, Br^- and I^-) are presented in Table 1. Influence of the concentration of acid and bromide anions present in the aqueous reaction medium and also of the reaction period on the H_2O_2 formation for the Pd/ZrO$_2$–B$_2$O$_3$ catalyst prereduced by hydrazine is shown in figures 1 and 2.

The results (Table 1) show the formation of H_2O_2 in appreciable amounts but only when

- the catalyst contains boron in the support,
- the boron containing catalyst is prereduced by hydrazine, and
- the reaction medium contains both the acid and bromide ions.

Otherwise, there is only a little or no formation of H_2O_2 (table 1). The H_2O_2 formation is markedly increased with increasing the concentration of acid (H_3PO_4) or bromide ions in the reaction medium; the increase is predominant particularly at the lower concentrations (figure 1). It is also increased with increasing the reaction period (figure 2). The formation of H_2O_2 is more pronounced when pure oxygen is used instead of air (figure 2). At the higher reaction periods, the H_2O_2 formation is leveled off, probably because of the simultaneous H_2O_2 decomposition over the Pd catalyst, nullifying the H_2O_2 formation.

It is interesting to note that, H_2O_2 formation is not observed when the boron containing Pd catalysts were prereduced by hydrogen (at 400 °C) or by aqueous sodium borohydride solution. Highly basic hydrazine chemisorbed on strongly acidic boron oxide may be playing an important role in the formation of H_2O_2 in the interaction of oxygen with the hydrazine-prereduced

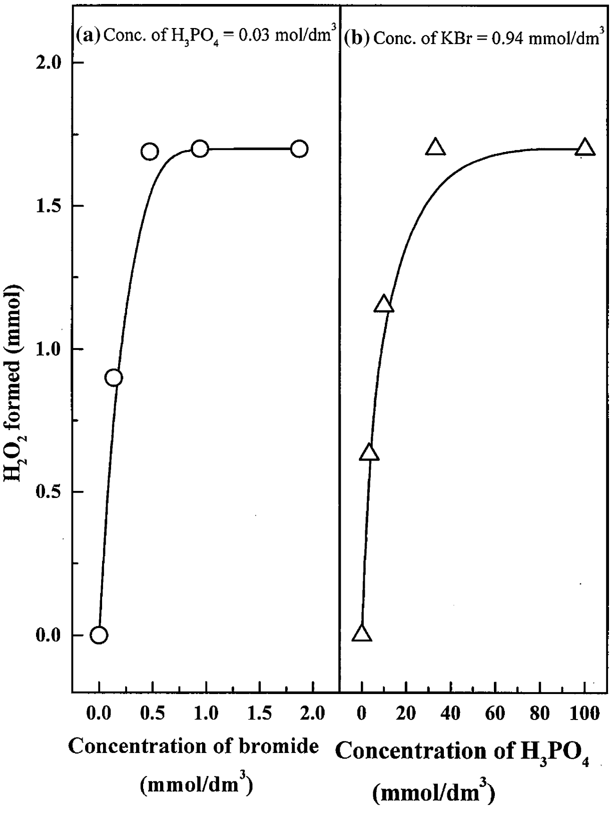

Figure 1. Effect of the concentration of bromide anions (a) and phosphoric acid (b) in the reaction medium on the H_2O_2 formation for the hydrazine reduced Pd/ZrO$_2$–B$_2$O$_3$ catalyst (reaction medium = 1 h).

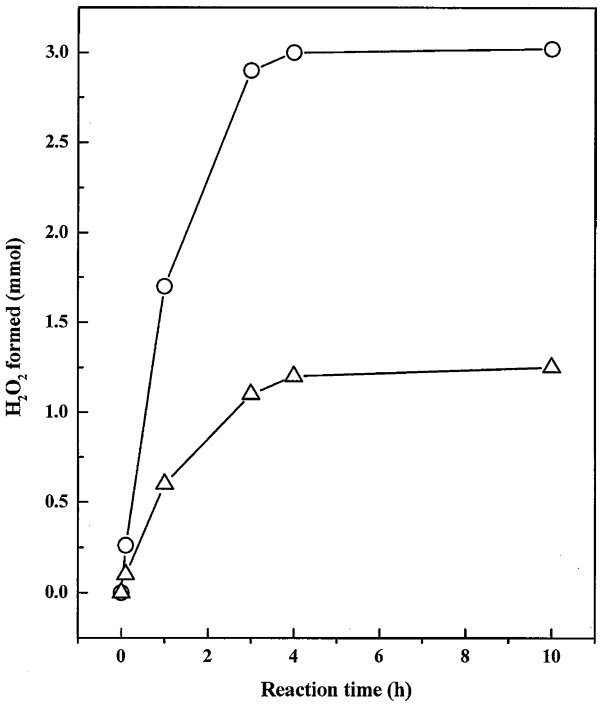

Figure 2. Effect of the reaction time on the H_2O_2 formation by interaction of pure O_2 (O) and air (Δ) with the hydrazine reduced $Pd/ZrO_2–B_2O_3$ catalyst in aqueous reaction medium containing H_3PO_4 (0.03 M) and KBr (0.94 mmol/dm^3).

catalysts. The source of hydrogen for the H_2O_2 formation is very likely to be the chemisorbed hydrazine. However, the dissolved hydrogen in the palladium and/or the H^+ form in the acidic medium may be involved in the H_2O_2 formation. Further detailed investigation is necessary for understanding the H_2O_2 formation and the role of the essential factors (viz. the presence of boron in the support, the catalyst prereduction by hydrazine, and the presence of mineral acid and bromide anions in the reaction medium), having very strong influence on the formation of H_2O_2 in the interaction/reaction of O_2 with the supported Pd catalysts in an aqueous reaction medium.

It may be noted that the formation of H_2O_2 in the present case in non-hazardous; unlike in the direct oxidation of H_2, there is no formation of explosive gas mixture.

4. Conclusions

An appreciable amount of H_2O_2 is formed in the interaction of O_2 with hydrazine-prereduced supported Pd catalysts containing boron in an aqueous reaction medium containing mineral acid and bromide anions. The presence of boron in the catalyst, the prereduction of the catalyst by hydrazine and also the presence of mineral acid and bromide anions in the reaction medium, are very critical factors; in the absence of either of them, there is a little or no formation of H_2O_2.

Acknowledgment

Authors are grateful to Council of Scientific and Industrial Research (CSIR, New Delhi) for Senior Research Fellowship (for CS) and Emeritus Scientist Scheme (for VRC).

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