A novel route for *in-situ* H_2O_2 generation from selective reduction of O_2 by hydrazine using heterogeneous Pd catalyst in an aqueous medium

Vasant R. Choudhary,* Chanchal Samanta and Prabhas Jana

Hydrogen peroxide in high yields can be generated with high efficiency at mild conditions (25 °C and atmospheric pressure) with the formation of only environment-friendly by-products (N_2 and H_2O) by a reduction of O_2 by hydrazine from its hydrate/salt with its complete conversion in a short reaction period ($\leqslant 0.5$ h) using a easily separable supported Pd catalyst (Pd/Al_2O_3, Pd/Ga_2O_3 or Pd/C) in an acidic aqueous medium in the presence of bromide anions; the presence of both acid (protons) and bromide anions is essential for the selective reduction of O_2 by hydrazine to H_2O_2 and in their absence, the reaction leads only to the formation of water.

Hydrogen peroxide is an environmentally clean oxidizing agent; the by-product of its use is only water (which is environmentally benign). Because of the increasing environmental concerns, the use of H_2O_2 in a number of organic oxidation processes (*e.g.* epoxidation of olefins, hydroxylation of aromatics/olefins, oxidation of benzylic –CH_2OH to –CHO or –COOH, *etc.*) for the synthesis of fine/speciality chemicals is widely increasing.[1–3] At present, H_2O_2 is produced commercially mainly by the autoxidation of hydroanthraquinone in a complex organic solvent, involving cyclic oxidation–hydrogenation steps.[4] This process however, is cost effective only on a large scale (>20 000 tpa). The transport, storage and handling of bulk H_2O_2 are also quite hazardous. Hence, the use of *in-situ* generated H_2O_2 for organic oxidation reactions is not only of scientific interest but also of great practical importance. A few studies have been reported on the use of *in-situ* generated H_2O_2 in liquid-phase organic oxidation reactions.[3,5–7]

The conventional method for *in-situ* H_2O_2 generation is based on the autoxidation of hydroanthraquinones by O_2 (hydroanthraquinone + $O_2 \rightarrow H_2O_2$ + anthraquinone).[3] However, the use of the autoxidation is limited because of the complex organic solvent system used to keep both the hydroquinone and quinone in their dissolved form. Moreover, the separation of the solvent, quinone and hydroquinone from the products of organic oxidation reaction is problematic. Direct oxidation of H_2 by O_2 using Pd catalyst is highly hazardous[8] and hence its use for the *in-situ* H_2O_2 generation for organic oxidation reactions is dangerous. Sheriff and coworkers[9,10] used Mn(II)/4,5-dihydroxybenzene-1,3-disulfonate as a homogeneous catalyst[9] and Mn(II)-exchanged montmorillonite clay as a heterogeneous catalyst[10] for the reduction of dioxygen by hydroxylamine to H_2O_2 with high turnover numbers (>10^4). Recently, they have reported the use of Mn(III) and Mn(IV) complexes as homogeneous catalysts for the O_2-to-H_2O_2

reduction by hydroxylamine, using acetonitrile–water mixture as the reaction medium.[11] Because of separation problem, the use of homogeneous catalyst and/or organic solvent in the reaction is problemistic. It is, therefore, of both scientific and practical interest to develop a new route for the *in-situ* H_2O_2 generation, which requires no organic solvent, produces only environment-friendly and easily separable by-product(s) and provides H_2O_2 with high yield under mild conditions, preferably using an easily separable heterogeneous catalyst. We have accomplished this difficult task. We report here our new route for the *in-situ* H_2O_2 generation from the selective reduction of O_2 by hydrazine (N_2H_4) from its hydrate/salt in an acidic aqueous medium, using Pd/C or Pd/Al_2O_3 (or Ga_2O_3) catalyst, in the presence of Br^- in the medium or in the catalyst. The presence of both the mineral acid (protons) and Br^- is a requirement for the selective oxidation of hydrazine to H_2O_2. In this method, the by-products formed are only N_2 and water, which are environmentally benign and pose no problem for their separation. Also, a complete conversion of hydrazine with high H_2O_2 yield can be accomplished in a short reaction period ($\leqslant 30$ min) at room temperature (25 °C) and atmospheric pressure.

Results (Tables 1–4) clearly show the formation of H_2O_2 with high rate in the reduction of O_2 by hydrazine from its sulfate or hydrate ($N_2H_4 + 2\,O_2 \rightarrow 2\,H_2O_2 + N_2$) over the supported Pd catalysts[12] in an aqueous acidic medium in the presence of bromide anions in the medium or in the catalyst at 25 °C and atmospheric pressure. However, since the H_2O_2 formed per mole of N_2H_4 converted is less than 2.0, the non-selective conversion of N_2H_4 to water ($N_2H_4 + O_2 \rightarrow 2\,H_2O + N_2$) also occurs simultaneously, depending upon the reaction conditions. The procedure for carrying out the oxidation reaction is given elsewhere.[13] No decomposition of N_2H_4 to N_2 and H_2 over the catalysts was observed at the reaction conditions employed for the reaction.

Table 1 H_2O_2 formed in the reduction of O_2 by hydrazine sulfate (at 25 °C) over Pd/Al_2O_3 in water as the reaction medium in the presence or absence of halide (reaction period = 0.5 h)

Halide in medium	Halide conc./ mmol dm^{-3}	H_2O_2 formed[c]	H_2O_2 yield (%)	Rate of H_2O_2 generation[d]
None	0.0	0.0	0.0	0.0
KF or KCl	0.94	0.0	0.0	0.0
KI	0.94	0.0	0.0	0.0
KBr	0.94	1.17	59	53.8
KBr	4.7	1.22	61	56.1
MBr[a]	4.7	1.18 ± 0.04	57–61	54.3 ± 1.8
KBr[b]	2.7	0.65	33	29.9

[a] M = H, Na or NH_4. [b] For Pd//C catalyst. [c] mol/mol of N_2H_4 converted. [d] mmol of H_2O_2 formed per gram of catalyst per hour.

Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune, 411008, India. E-mail: vrc@ems.ncl.res.in; vrc@che.ncl.res.in; Fax: + 91-20-2589.41

Table 2 H_2O_2 formed in the reduction of O_2 by hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) over halogenated Pd/Al_2O_3 (or Ga_2O_3) catalysts (halogen loading = 1.0 wt%) in water medium at 25 °C (reaction period = 0.5 h)

Halogen incorporated in catalyst	H_2O_2 formed[d]	H_2O_2 yield (%)	Rate of H_2O_2 generation[e]
Catalyst: Pd/Al_2O_3 with or without halogen			
None	0.0	0.0	0.0
F or Cl	0.0	0.0	0.0
I	0.0	0.0[f]	0.0
Br	1.23	61.5	56.7
Br[a]	0.98	25.7[g]	45.1
Br[b]	1.36	68.0	62.6
Br[c]	1.07	53.5	49.2
Catalyst: Pd/Ga_2O_3 with or without halogen			
None	0.0	0.0	0.0
F or Cl	0.0	0.0	0.0
Br	1.01	50.5	46.5

[a] Reaction period was 0.2 h. [b] 50 mmol H_3PO_4 was added to the reaction medium. [c] Hydrazine salt was $N_2H_4 \cdot 2HCl$. [d] mol/mol of N_2H_4 converted. [e] mmol of H_2O_2 formed per gram of catalyst per hour. [f] Conversion of N_2H_4 was 10%. [g] Conversion of N_2H_4 was 52%; in all the other cases it was 100%.

Table 3 H_2O_2 formed in the reduction of O_2 hydrazine monohydrate over Pd/Al_2O_3 in aqueous reaction medium in the presence or absence of mineral acid (0.1 mol dm^{-3}) and/or halide (0.94 mmol dm^{-3}) at 25 °C (reaction period = 0.5 h)

Acid in medium	Halide in reaction medium	H_2O_2 formed[a]	H_2O_2 yield (%)
None	None	0.0	0.0
H_3PO_4	None	0.0	0.0
H_2SO_4	None	0.0	0.0
None	KBr	0.0	0.0
H_3PO_4	KBr	0.85	42.5
H_2SO_4	KBr	0.80	40.0
H_3PO_4	KF or KCl	0.0	0.0
H_2SO_4	KF or KCl	0.0	0.0
H_3PO_4	KI	0.0	0.0[b]
H_2SO_4	KI	0.0	0.0[c]

[a] mol/mol of N_2H_4 converted. [b] Conversion of N_2H_4 was 10%. [c] Conversion of N_2H_4 was 12%; in all the other cases it was 100%.

Results (Table 1) reveal that in the absence of any halide or in the presence of KF or KCl in the medium, the hydrazine from the hydrazine sulfate is completely converted to water ($N_2H_4 + O_2 \rightarrow 2\,H_2O + N_2$), without formation of any H_2O_2. The addition of KI to the medium also leads to similar results except that the hydrazine conversion is drastically reduced from 100 to 10% due to poisoning of the catalyst. However, in the presence of KBr in the medium at the same (0.94 mmol dm^{-3}) or at higher concentration,

the H_2O_2 formed per mol of hydrazine was drastically increased from zero to 1.17 and 1.22, respectively, and also the hydrazine conversion was 100%. Influence of cations (H^+, Na^+, K^+ or NH_4^+) on the reaction as compared to that of the halide anions was found to be negligibly small.

The results, when the halogens (F, Cl, Br or I) are incorporated in the Pd/Al_2O_3 and Pd/Ga_2O_3 catalysts (Table 2), are quite similar to those observed for the halides in the reaction medium (Table 1). The results for the Pd/Al_2O_3 catalyst (Table 2) show that the addition of acid (H_3PO_4) in the medium causes an appreciable increase in the H_2O_2 yield (from 61.5 to 68.0%). It may be noted that the reaction medium containing the hydrazine salts is acidic (pH < 2) because of the release of associated acid molecules (H_2SO_4 or HCl) from the hydrazine salts after their dissolution in water.

When hydrazine hydrate was used instead of the hydrazine salts, in the absence of acid in the medium no H_2O_2 formation in the hydrazine oxidation is observed even though in the presence of bromide anions. In the absence of either bromide anions or mineral acid or both, the oxidation of hydrazine hydrate leads only to the formation of N_2 and water (Tables 3 and 4). With increasing the acid/hydrazine mole ratio, the H_2O_2 yield (or H_2O_2 formed per mol of hydrazine consumed) is increased appreciably. Among the mineral acids, the most preferable for the selective reduction of O_2 to H_2O_2 is sulfuric acid.

Table 4 H_2O_2 formed in the reduction of O_2 by hydrazine monohydrate over halogenated Pd/Al_2O_3 (halogen loading = 1.0 wt%) in aqueous reaction medium in the presence or absence of mineral acid (at 25 °C) (reaction period = 0.5 h)

Halogen in catalyst	Acid in medium	Conc. of acid/mol dm^{-3}	Acid/N_2H_4 mole ratio	Conv. of N_2H_4 (%)	H_2O_2 formed[b]
None	H_3PO_4	0.1	2.27	100[a]	0.0
F or Cl	H_3PO_4	0.1	2.27	100[a]	0.0
I	H_3PO_4	0.1	2.27	9.5[a]	0.0
Br	None	0.0	0.0	100[a]	0.0
Br	H_3PO_4	0.02	0.45	100	0.30
Br	H_3PO_4	0.2	4.5	60.2	0.88
Br	H_2SO_4	0.04	0.91	100	1.16
Br	H_2SO_4	0.02	0.45	87.3	0.84
Br	HCl	0.09	2.05	100	1.11
Br	HBr	0.09	2.05	39.5	0.7

[a] Reaction period = 1.0 h. [b] mol/mol of N_2H_4 converted.

From the above results, it can be concluded that the reduction of O_2 by hydrazine (from hydrazine salt or hydrate) leads to H_2O_2 formation with high yields only in the presence of Br^- anions and protons (mineral acid). In their absence or in the presence of other halides and acid, only water (without even traces of H_2O_2) is formed in the reaction.

The hydrazine oxidation is not economically feasible for the large-scale production of H_2O_2 as a commodity chemical. However, although hydrazine is toxic and carcinogenic, since the reaction is fast and completed in a short period (<30 min), even at room temperature and atmospheric pressure, leaving no traces of unconverted hydrazine, it has high potential for providing an efficient route for the *in-situ* generation of H_2O_2. It is environment-friendly, involving no objectionable by-products or organic solvent, unlike the hydroanthraquinone-to-H_2O_2 oxidation.

Notes and references

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12 The Pd (5%)/Al_2O_3 and Pd (5%)/C catalysts in their reduced form were obtained from Lancaster (UK). The Ga_2O_3 (Aldrich) supported Pd (2.5%) catalyst was prepared by impregnating the support with palladium acetate from its acetonitrile solution, drying and calcining at 500 °C for 3 h and then reducing by ammoniacal hydrazine. The halogenation of the Pd catalysts was done by impregnating the catalyst with ammonium halide from its aqueous solution, drying and calcining in a flow of oxygen-free N_2 at 400 °C for 1 h.
13 The catalytic reduction of O_2 by hydrazine to H_2O_2 over the Pd catalysts was carried out in a magnetically stirred jacketed glass reactor (capacity: 100 cm^3) by passing continuously pure O_2 (99.5%) through an aqueous reaction medium in the presence or absence of different halide anions and/or mineral acids at the following reaction conditions: volume of reaction medium = 50 cm^3, amount of catalyst = 0.1 g, hydrazine salt or hydrazine hydrate = 2.3 mmol, O_2 flow rate = 10 cm^3 min^{-1}, temperature = 25 °C and pressure = atmospheric (0.95 atm). The initial concentration of hydrazine or its salt and catalyst was 46 mmol dm^{-3} and 2.0 g dm^{-3}, respectively. The temperature of the reaction was controlled by passing continuously thermostated water maintained at desired temperature through the reactor jacket. The H_2O_2 from the reaction mixture (after separating the catalyst from the reaction mixture by filtration) was determined by iodometric titration and also by decomposing the H_2O_2 by MnO_2 and measuring the O_2 evolved quantitatively, according to the H_2O_2 decomposition reaction ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$); both the methods gave the same results. The unconverted hydrazine (if any) was determined by its titration against potassium iodate in a mixture of aqueous acidic (HCl) and $CHCl_3$ medium. The reactor effluent gas was analysed by gas chromatography. Only N_2 and O_2 are found in the gaseous products, indicating the formation of N_2 as the only other main product in both the selective and non-selective oxidation of hydrazine.