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Activation of supported Pd metal catalysts for selective oxidation of hydrogen to hydrogen peroxide

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Catalytic activity of supported Pd metal catalysts (Pd metal deposited on carbon, alumina, gallia, ceria or thoria) showing almost no activity in the liquid-phase direct oxidation of H_2 to H_2O_2 (at 295 K) in acidic medium (0.02 M H_2SO_4) can be increased drastically by oxidizing them using different oxidizing agents, such as perchloric acid, H_2O_2, N_2O and air. In the case of the Pd/carbon (or alumina) catalyst, perchloric acid was found to be the most effective oxidizing agent. The order of the H_2-to-H_2O_2 conversion activity for the perchloric-acid-oxidized Pd/carbon (or alumina) and air-oxidized other metal oxide supported Pd catalysts is as follows: Pd/alumina < Pd/carbon < Pd/CeO_2 < Pd/ThO_2 < Pd/Ga_2O_3. The H_2 oxidation involves lattice oxygen from the oxidized catalysts. The catalyst activation results mostly from the oxidation of Pd metal from the catalyst producing bulk or sub-surface PdO. It also caused a drastic reduction in the H_2O_2 decomposition activity of the catalysts. There exists a close relationship between the H_2-to-H_2O_2 conversion activity and/or H_2O_2 selectivity in the oxidation process and the H_2O_2 decomposition activity of the catalysts; the higher the H_2O_2 decomposition activity, the lower the H_2-to-H_2O_2 conversion activity and/or H_2O_2 selectivity.

KEY WORDS: direct oxidation of H_2 to H_2O_2; decomposition of H_2O_2; Pd/carbon; Pd/Al_2O_3; Pd/CeO_2; Pd/ThO_2; Pd/Ga_2O_3; activation by oxidative pretreatment.

1. Introduction

Hydrogen peroxide, a strong bleaching and oxidizing agent, is very environ-friendly. Apart from its use as a bleaching agent in the textile and pulp/paper industries, its demand as an oxidizing agent for water purification (viz. wastewater treatment and water disinfection) and also for producing fine and bulk chemicals (*e.g.*, organic peroxides, epoxides from olefinic compounds, hydroxylated aromatic compounds, etc.) has been increasing day-by-day [1–4]. A number of electrochemical and chemical processes (based on isoproponal oxidation, peroxy compounds, auto-oxidation of organic compounds and cathodic reduction of oxygen, etc.) for H_2O_2 production have been developed [1,3]. However, H_2O_2 is mainly commercially produced by a process based on the auto oxidation of alkyl anthraquinone, involving indirect oxidation of H_2 to H_2O_2. This process, however, suffers from several limitations, such as the use of costly complex solvent systems, the loss of quinone due to non-selective hydrogenation, the elaborate treatments required to remove degradation products and organic matter, the deactivation of hydrogenation catalyst and also the need for effluent treatment. Hence, the H_2O_2 production cost is high for using H_2O_2 in the production of bulk organic chemicals and wastewater treatment [4]. Efforts have been made to develop more economical and environmentally clean processes for H_2O_2 production by the direct oxidation of H_2 by O_2. This process, using different Pd catalysts, is covered in a number of patents [5], but it is not yet commercialized. Studies reported on this dream reaction in open literature are scarce [6–8]. The H_2O_2 decomposition in consecutive reaction poses a serious problem for the selective oxidation of H_2 to H_2O_2. Hence, it is of great practical interest not only to drastically improve the H_2O_2 selectivity in parallel reactions ($H_2 + O_2 \rightarrow H_2O_2$ and $H_2 + 0.5O_2 \rightarrow H_2O$), but also to drastically reduce the H_2O_2 decomposition activity of the catalyst in the consecutive reactions ($H_2 + O_2 \rightarrow H_2O_2 \rightarrow H_2O + 0.5O_2$). In this paper, we have shown that the catalytic activity of supported Pd metal catalysts (viz. Pd/carbon, Pd/alumina, Pd/Ga_2O_3 and Pd/CeO_2 or Pd/ThO_2) for the liquid-phase direct oxidation of H_2 to H_2O_2 can be increased drastically, and also that for the decomposition of H_2O_2 under similar conditions can be decreased very markedly by activating the catalysts by their oxidation using different oxidizing agents.

2. Experimental

Pd/carbon and Pd/alumina catalysts (Pd loading = 5 wt%) were obtained from Lancaster (UK). Pd/Ga_2O_3, Pd/CeO_2 and Pd/ThO_2 catalysts (Pd loading = 2.5 wt%) were prepared by impregnating Ga_2O_3, CeO_2 and ThO_2, respectively, with palladium acetate or chloride,

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calcining in air at 773 K for 1 h and reducing by hydrazine. The catalysts were activated by pretreating them with different oxidizing agents: 0.1 M $HClO_4$ (treating 5 g catalyst with 10 cm^3 of 1.0 M $HClO_4$ at 368 K on a water bath for 2 h and then calcining in an air oven at 573 K for 3 h), H_2O_2 (treating 2 g catalyst with 80 cm^3 of 30 wt% H_2O_2 for 2 h at 303 K, then filtering, washing and drying at 373 K), air [in an air oven at 523 K (for Pd/carbon) or 773 K (for other catalysts) for 2 h] or N_2O [under flowing N_2O at 423 K (for Pd/carbon) or (523 K for Pd/alumina) for 2 h].

The catalysts were characterized by powder XRD (using a Holland Philips PW/1710 X-ray generator with Cu K_α radiation and scintillation counter) for determining their bulk metallic Pd and PdO phases and also by XPS (using a VG Scientific ESCA-3 MK II electron spectrometer). The Pd/Al_2O_3 catalyst before and after the oxidizing treatments was also characterized by passing a number of H_2 pulses (5–10 pulses, each of size 0.14 cm^3), one after another over the catalyst in a quartz micro-reactor (i.d. 4.2 mm), connected to a gas chromatograph at 500 °C using helium as a carrier gas. The water formed in the catalyst reduction ($PdO + H_2 \rightarrow Pd^0 + H_2O$) during the passage of each H_2 pulse was measured quantitatively using a Poropak-Q column.

The catalytic oxidation of H_2 to H_2O_2 was carried out in a magnetically stirred glass reactor (capacity: 250 cm^3), containing 0.5 g catalyst in a fine powder form and 150 cm^3 aqueous 0.02 M H_2SO_4 as a reaction medium. A gas mixture containing 2.8 vol% H_2 in O_2 (flow rate: 11.5 cm^3 min^{-1}) was bubbled continuously through the reaction medium under vigorous stirring at 295 K and atmospheric pressure (96 kPa) for a period of 3 h. The concentration of H_2 in the reactor effluent gases was measured by an on-line H_2 analyzer. For studying the involvement of lattice oxygen from the catalyst, the reaction of H_2 with the catalyst was carried out in the absence of O_2 gas for 1 h, using pure H_2 (47 cm^3 min^{-1}) as a feed. The H_2O_2 produced in the H_2 oxidation was determined by the iodometric titration method.

The decomposition of H_2O_2 over the catalysts was carried out in the above reactor containing 0.2 g catalyst and 150 cm^3 of 0.02 M H_2SO_4, by injecting 6 cm^3 of 5.0 wt/v% H_2O_2 solution in the reactor and measuring the O_2 evolved in the H_2O_2 decomposition at 295 K as a function of time, using a constant-pressure gas collector [9].

Both the H_2 oxidation and H_2O_2 decomposition reactions over the catalysts were carried out in the absence of liquid–solid and/or gas–liquid mass-transfer control. This was confirmed by increasing the stirring speed by increasing the voltage applied to the magnetic stirrer from 180 to 260 V and observing no significant change in the conversion in both cases (the H_2-to-H_2O_2 oxidation over $HClO_4$-treated Pd/carbon and the H_2O_2 decomposition over the Pd/carbon without any pretreatment).

3. Results and discussion

Results in table 1 show the influence of oxidative pretreatment to the Pd/carbon and Pd/alumina catalysts (by different oxidizing agents) on their catalytic activity (at 295 K) in the H_2-to-H_2O_2 oxidation and also in the H_2O_2 decomposition (at 295 K). Figure 1 shows the relationship between the H_2O_2 selectivity in the oxidation of H_2 to H_2O_2 and the H_2O_2 decomposition activity of the Pd/carbon and Pd/alumina catalysts with or without their activation by the different oxidizing agents. The H_2O_2 decomposition activity is expressed in terms of the first-order apparent rate constant (k_a) for the H_2O_2 decomposition (the time required for half the reaction is also provided).

Both the carbon- and alumina-supported Pd metal catalysts show no activity for the conversion of H_2 to H_2O_2, but high activity for the oxidation of H_2 to water and also very high H_2O_2 decomposition activity (table 1). However, both catalysts become active for

Table 1

Effect of the activation by oxidation with different oxidizing agents of the Pd/carbon and Pd/alumina catalysts on their performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions (at 295 K).

Catalyst	Oxidizing agent	H_2-to-H_2O_2 oxidation		H_2O_2 decomposition	
		H_2O_2 yield (%)	H_2 conversion (%)	Time for half the reaction (min)	Rate constant k_a (min^{-1}) × 10^3
Pd/carbon	Nil	0.0	37.8	4.1	84.2
	$HClO_4$	7.9	53.4	32	9.4
	H_2O_2	4.6	70.9	48	2.1
	N_2O	2.4	63.6	6.5	47.6
	Air	1.9	63.5	6.0	52.8
Pd/alumina	Nil	0.0	30.2	12	44.5
	$HClO_4$	6.3	39.4	160	1.8
	H_2O_2	3.2	41.8	100	3.0
	N_2O	3.0	43.1	19	16.1

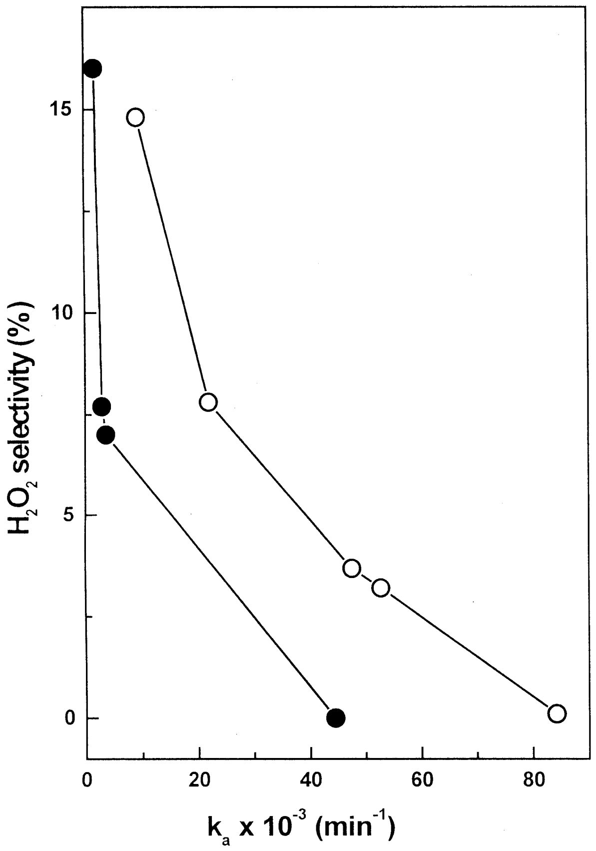

Figure 1. Relationship between the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation (at 295 K) and the H_2O_2 decomposition activity (k_a) at 295 K of the Pd/carbon (○) and Pd/alumina (●) catalysts (k_a = first-order apparent rate constant for H_2O_2 decomposition reaction).

the H_2-to-H_2O_2 oxidation and, at the same time, their H_2O_2 decomposition activity is decreased drastically. It may be noted that the H_2O_2 yield observed for the perchloric-acid-treated Pd/carbon (or alumina) is much higher than the highest H_2O_2 yield (3.6%) observed earlier for the Pd/fluorinated carbon catalyst [6], even at a much higher pressure (μ6 atm). The pressure at which the H_2-to-H_2O_2 oxidation is carried out in the present studies is much lower than that (>20 atm) generally used in the patent literature on this process [5]. It may be noted that, because of a decrease in the volume, higher pressure favors the H_2O_2 formation in the process.

The results in figure 1 reveal that the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation shows a strong dependence upon the H_2O_2 decomposition activity of the catalyst. This indicates a close relationship between the two; the lower the H_2O_2 decomposition activity the higher the H_2O_2 selectivity in the H_2 oxidation. Apart from the decomposition, the H_2O_2 loss may also be due to the hydrogenation of H_2O_2 on the catalyst. Nevertheless, the observed close relationship between the H_2O_2 selectivity and H_2O_2 decomposition activity is very interesting; it provides an important criteria for developing a better catalyst.

From the catalyst characterization data in table 2, the following important observations can be made:

1. The Pd/carbon and Pd/alumina catalysts without any oxidizing treatment contain only metallic Pd as a bulk phase. However, a PdO phase appeared along with the metallic Pd in both catalysts after their oxidizing treatment by either of the oxidizing agents.
2. The formation of bulk PdO or sub-surface PdO in the case of the oxidized Pd/alumina catalysts is further confirmed by observing a substantial amount of water in their H_2 reduction (at 500 °C). No formation of water was detected for the case of Pd/alumina without any oxidizing treatment.
3. X-ray photoelectron spectra of Pd($3d_{5/2}$) and Pd($3d_{3/2}$) electrons with observed binding energy of 337.2 and 342.7 eV, respectively, of the catalysts with or without the activation correspond to the Pd^{2+} oxidation state. This indicates that, even for the catalyst without oxidizing pretreatment, the surface Pd-species are PdO (which is formed by strongly chemisorbed oxygen from air).

Table 2

Properties of the Pd/carbon and Pd/Al_2O_3 catalysts activated by their oxidation with different oxidizing agents.

Catalyst	Oxidizing agent	XRD phase(s) (Pd^0 or PdO)	Water formed in reduction by H_2 (mmol g^{-1})[a]	Binding energy (eV)					Surface Cl/Al (or C) ratio
				O(2s)	Pd($3d_{5/2}$)	Pd($3d_{3/2}$)	Al($2p_2$)	Cl($2p_{3/2}$)	
Pd/carbon	Nil	Pd^0	–	533.3	337.5	342.7	–	199.0	<0.001
	$HClO_4$	Pd^0, PdO	–	532.6	337.4	342.5	–	199.6	0.015
	H_2O_2	Pd^0, PdO	–	532.5	337.3	343.0	–	200.4	<0.001
	N_2O	Pd^0, PdO	–	532.4	337.1	342.6	–	200.2	<0.001
	Air	Pd^0, PdO	–	533.1	337.2	342.5	–	199.7	<0.001
Pd/Al_2O_3	Nil	Pd^0	0.0	532.8	337.2	342.5	75.6	193.8	0.010
	$HClO_4$	Pd^0, PdO	0.30	531.8	337.1	342.5	74.8	199.7	0.012
	H_2O_2	Pd^0, PdO	0.05	531.6	336.8	342.0	74.7	192.1	0.008
	N_2O	Pd^0, PdO	0.01	532.0	337.2	342.6	74.9	199.3	0.005

[a] Water formed in the catalyst reduction by H_2 in the first five pulses of H_2 at 500 °C.

Table 3
Properties and performance (in the H_2-to-H_2O_2 and H_2O_2 decomposition reactions at 295 K) of the reduced and air-oxidized (at 773 K) supported Pd (2.5%) catalysts.

Catalyst	XRD phase(s) (Pd^0 or PdO)	H_2-to-H_2O_2 oxidation		H_2 decomposition	
		H_2O_2 yield (%)	H_2 conversion (%)	Time for half of the reaction (min)	Rate constant k_a $(min^{-1}) \times 10^3$
Reduced Pd/CeO_2	Pd^0	0.0	20.3	50	6.1
Oxidized Pd/CeO_2	PdO	11.8	21.1	Very large (20% in 4 h)[a]	0.6
Reduced Pd/ThO_2	Pd^0	0.0	18.5	47	6.6
Oxidized Pd/ThO_2	PdO	13.3	28.2	Very large (18% in 4 h)[a]	0.5
Reduced Pd/Ga_2O_3	Pd^0	0.0	34.9	52	6.0
Oxidized Pd/Ga_2O_3	PdO	17.95	21.03	Very large (10% in 4 h)[a]	0.34

[a] H_2O_2 conversion after a certain reaction period.

The catalyst activation which led to the observed drastic changes in the catalytic properties of the Pd/carbon and Pd/alumina catalysts seems to be attributed mostly to their Pd oxidation, forming bulk or at least sub-surface PdO. The observed large differences in the activated catalysts by the different oxidizing treatments may, however, be due to chlorination (in the case of $HClO_4$-pretreated catalysts) or different extent of Pd oxidation (in case of the H_2O_2 and N_2O pretreated catalysts). The higher H_2O_2 yield for $HClO_4$-pretreated catalysts may also be due to the catalyst chlorination; the surface Cl/C or Al ratio is increased after the treatment (table 2). However, the surface Cl/Al ratio for the H_2O_2 and N_2O pretreated Pd/alumina catalyst is lower, but their H_2-to-H_2O_2 conversion activity is much more than that of the parent catalyst (Pd/alumina) (tables 1 and 2). This supports the hypothesis that the catalyst activation results mainly from the formation of bulk or sub-surface PdO.

In order to obtain a further support to the above hypothesis, results for the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the reduced and oxidized Pd/CeO_2, Pd/ThO_2 and Pd/Ga_2O_3 catalysts are presented in table 3. These results are complimentary to the previous ones (table 1). All the reduced catalysts (which contain only metallic Pd as Pd species) show no activity for the H_2-to-H_2O_2 conversion, but the oxidized catalysts (which contain PdO as Pd species) show high activity for the H_2O_2 formation in the H_2 oxidation. The H_2O_2 decomposition activity of the oxidized catalysts is much lower than that of the reduced ones.

Among all the oxidized Pd catalysts with different supports, the oxidized Pd/Ga_2O_3 shows highest H_2-to-H_2O_2 conversion (H_2O_2 yield); the promising catalysts with different supports can be ordered for their H_2-to-H_2O_2 conversion activity as follows: $HClO_4$-treated Pd/alumina < $HClO_4$-treated Pd/carbon < oxidized Pd/CeO_2 < oxidized Pd/ThO_2 < oxidized Pd/Ga_2O_3 (tables 1–3). Also, the order for H_2O_2 decomposition activity of these catalysts is exactly opposite to their H_2O_2 selectivity in the H_2 oxidation (tables 1–3). This also supports the existence of a close relationship between the H_2O_2 decomposition activity and the H_2O_2 selectivity of the catalysts.

The involvement of lattice oxygen from the activated catalyst in the H_2-to-H_2O_2 oxidation was confirmed by observing the formation of H_2O_2 in an appreciable amount in the reaction over the activated catalysts at 295 K in the absence of free-O_2. This also supports the presence of bulk or sub-surface PdO in the activated catalysts. Results showing the amount of H_2O_2 formed over the Pd/carbon and Pd/Al_2O_3 catalysts with or without the $HClO_4$ pretreatment and also over the reduced and oxidized Pd/CeO_2 and Pd/ThO_2 catalysts are presented in table 4. The lattice oxygen used up in this non-catalytic H_2-solid reaction could be replenished by treating the catalyst with O_2. In the case of the untreated Pd/carbon or alumina and reduced Pd/CeO_2 or ThO_2 catalysts, no formation of H_2O_2 was detected. Also, when the H_2 concentration in the H_2 and O_2 feed-gas mixture was increased from 2.8 to 63.3%, the H_2O_2 yield and selectivity in the H_2 oxidation over $HClO_4$-treated Pd/carbon were found to decrease from 7.9 to 2.9% and from 14.9 to 3.2%, respectively. This indicates that an excess of oxygen is essential for obtaining high selectivity and/or yield for H_2O_2.

The above results indicate that the presence of bulk or sub-surface PdO makes the supported Pd catalysts selective or more active in the H_2-to-H_2O_2 oxidation.

Table 4
Oxidation of H_2 to H_2O_2 over the activated Pd catalyst[a] in the absence of O_2 gas (295 K).

Catalyst	H_2O_2 formed ($\mu mol\,g^{-1}$ catalyst)
$HClO_4$-treated Pd/carbon	15.1
$HClO_4$-treated Pd/alumina	16.8
Oxidized Pd/CeO_2	18.0
Oxidized Pd/ThO_2	60.0

[a] For the catalysts without activation, there was no formation of H_2O_2.

Also, the activation of H_2O_2 for its decomposition on the catalyst containing bulk or sub-surface PdO seems to be less favored. Further studies are required for a better understanding of these aspects and reaction mechanism for the selective oxidation of H_2 to H_2O_2 over the activated supported Pd catalysts.

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