

# Direct oxidation of hydrogen to hydrogen peroxide over Pd-containing fluorinated or sulfated $\text{Al}_2\text{O}_3$ , $\text{ZrO}_2$ , $\text{CeO}_2$ , $\text{ThO}_2$ , $\text{Y}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ catalysts in stirred slurry reactor at ambient conditions

A.G. Gaikwad, S.D. Sansare, V.R. Choudhary\*

*Chemical Engineering Division, National Chemical Laboratory, Pune 411008, India*

Received 23 January 2001; received in revised form 8 June 2001; accepted 27 June 2001

## Abstract

Direct oxidation of  $\text{H}_2$  to  $\text{H}_2\text{O}_2$  over powdered PdO-containing fluorinated or sulfated  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{ThO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  catalysts with or without pre-reduction by hydrazine, using a pure water or 0.02 M  $\text{H}_2\text{SO}_4$  as reaction medium and a gaseous feed consisting of 1.7 vol.%  $\text{H}_2$  in  $\text{O}_2$ , in a magnetically stirred glass reactor at 22 °C and atmospheric pressure has been investigated. The catalysts have been characterized for their surface area and also by CO chemisorption. The performance of the catalysts in the decomposition of  $\text{H}_2\text{O}_2$  at 22 °C has also been studied. The results showed a strong influence of catalyst reduction, fluorination (or chlorination) or sulfation of the catalyst support and the acidity of reaction medium on both the conversion and  $\text{H}_2\text{O}_2$  selectivity in the direct oxidation of  $\text{H}_2$ . An acidic medium is essential for achieving both the high conversion and high selectivity in the  $\text{H}_2$  oxidation. The reduced catalysts showed much lower  $\text{H}_2\text{O}_2$  selectivity in the  $\text{H}_2$  oxidation process and much higher  $\text{H}_2\text{O}_2$  decomposition activity. The water in the  $\text{H}_2$  to  $\text{H}_2\text{O}_2$  oxidation over the above catalysts is formed in parallel and/or consecutive reactions, depending upon the catalyst used. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Oxidation of  $\text{H}_2$  to  $\text{H}_2\text{O}_2$ ; Supported palladium catalysts; Fluorinated palladium catalyst; Sulfated palladium catalyst; Decomposition of  $\text{H}_2\text{O}_2$

## 1. Introduction

Hydrogen peroxide is an environ-friendly strong oxidizing agent. Hence, its demand for domestic/industrial wastewater treatment, water disinfection, catalytic oxidation processes and other industrial applications has been increasing day-by-day. The

presently practiced anthraquinone process [1] for the production of  $\text{H}_2\text{O}_2$  has several other limitations; the cost of  $\text{H}_2\text{O}_2$  produced by this process is not low enough to use it for producing bulk chemicals and/or for wastewater treatment. It is, therefore, of great practical interest to produce  $\text{H}_2\text{O}_2$  more economically by a novel process, which is also environmentally clean, such as that based on the direct oxidation of  $\text{H}_2$ . Direct oxidation of  $\text{H}_2$  to  $\text{H}_2\text{O}_2$  over different Pd-containing catalysts has been disclosed in several patents [2,3]. But the information on this process in the published papers is scarce [2–4]. Very recently,

\* Corresponding author. Tel.: +91-20-589-3300x2163; fax: +91-20-589-3041/3355.  
E-mail addresses: vrc@che.ncl.res.in, vrc@ems.ncl.res.in (V.R. Choudhary).

we have suggested the use of a novel composite Pd-membrane catalyst for the non-hazardous direct oxidation of  $H_2$  to  $H_2O_2$  [2]. Earlier, Fu et al. [4] have carried out liquid-phase oxidation of  $H_2$  to  $H_2O_2$  in an acidic medium over Pd/fluorinated carbon catalyst at high pressures (0.5–2.3 MPa) at  $-10$  to  $25^\circ C$ ; the maximum  $H_2O_2$  selectivity reported was 8.7% (at 41%  $H_2$  conversion) even in the presence of a  $H_2O_2$  stabilizer. They have observed that the  $H_2O_2$  decomposition to water and oxygen occurs in a consecutive reaction on the same catalyst; the higher the  $H_2O_2$  decomposition activity of the catalyst, the lower is the  $H_2O_2$  selectivity in the  $H_2$  oxidation process.

The flammability or explosive range for the concentration of  $H_2$  in  $O_2$  is very wide (4–94%  $H_2$  in  $O_2$ ). Hence, the direct  $H_2$  oxidation process is highly hazardous one. However, it can be made non-hazardous by operating it with the  $H_2$  concentrations (in  $O_2$ ) far away from the explosion range.

This work was undertaken with the objective of studying the performance of different supported Pd or PdO catalysts (such as Pd or PdO supported on alumina, zirconia, ceria, thoria, yttria and gallia, with or without their modification by fluorination, chlorination or sulfatation) in the direct oxidation of  $H_2$  to  $H_2O_2$  using a mixed  $H_2/O_2$  feed (1.7 vol.%  $H_2$  in  $O_2$ , which is far away from the explosion range) and

also in the decomposition of  $H_2O_2$ , in a stirred slurry reactor.

## 2. Experimental

### 2.1. Catalyst preparation

The PdO-containing catalysts (Table 1) were prepared by impregnating  $PdCl_2$  from its HCl solution on  $\gamma-Al_2O_3$ ,  $ZrO_2$ ,  $CeO_2$ ,  $Y_2O_3$  or  $ThO_2$ , fluorinated  $\gamma-Al_2O_3$ ,  $ZrO_2$ ,  $Ga_2O_3$ ,  $Y_2O_3$ ,  $ThO_2$  or  $CeO_2$ , and sulfated  $ZrO_2$  or  $Ga_2O_3$  by the incipient wetness impregnation technique. After impregnation, the wet catalyst mass was dried at  $100^\circ C$  for 4 h and then calcined under static air in muffle furnace at  $500^\circ C$  for 3 h. The presence of PdO phase in the catalyst was confirmed by XRD.

Fluorination (or chlorination) or sulfatation was carried out by impregnating the respective support with ammonium fluoride (or chloride) or  $H_2SO_4$  (equivalent to 5 wt.% F, Cl or S on the support) from its aqueous solution followed by drying on hot water bath and calcining in muffle furnace at  $500^\circ C$  for 3 h.

The PdO-containing catalysts were reduced by treating them with an ammonical hydrazine solution on hot water bath for 2 h followed by washing,

Table 1  
Surface properties of the catalyst

Catalysts	Surface area ( $m^2 g^{-1}$ )	CO chemisorption (at $40^\circ C$ ) on reduced catalysts <sup>a</sup> ( $\mu mol g^{-1}$ )
PdO/ $\gamma-Al_2O_3$	174.0	4.1
PdO/fluorinated $\gamma-Al_2O_3$	203.0	18.8
PdO/chlorinated $\gamma-Al_2O_3$	171.0	5.0
PdO/ $ZrO_2$	54.5	60.1
PdO/sulfated $ZrO_2$	325.0	7.3
PdO/fluorinated $ZrO_2$	31.5	4.8
PdO/ $CeO_2$	12.4	6.1
PdO/fluorinated $CeO_2$	4.7	17.2
PdO/ $Y_2O_3$	8.1	6.1
PdO/fluorinated $Y_2O_3$	12.3	17.5
PdO/ $ThO_2$	0.7	3.7
PdO/fluorinated $ThO_2$	0.7	4.3
PdO/fluorinated $Ga_2O_3$	19.1	14.1
PdO/sulfated $Ga_2O_3$	34.9	3.8

<sup>a</sup> Reduced by a  $H_2-N_2$  mixture (10%  $H_2$ ) at  $500^\circ C$ .

filtration and drying at 100 °C in an air oven. The presence of metallic Pd phase in the reduced catalysts was confirmed by XRD.

## 2.2. Catalyst characterization

The surface area of the catalysts was measured by the single-point BET method, using a Monosorb Surface Area Analyser (Quantachrome, USA). Chemisorption of CO on the catalyst, after its reduction by H<sub>2</sub> at 500 °C, was measured at 40 °C using a GC pulse technique [5].

## 2.3. Catalytic reactions

The direct oxidation of hydrogen to hydrogen peroxide reaction over the catalysts was carried out in a magnetically stirred glass reactor (capacity = 250 cm<sup>3</sup>) containing 0.5 g catalyst and 150 cm<sup>3</sup> aqueous 0.02 M sulfuric acid solution as a reaction medium by bubbling continuously a hydrogen and oxygen mixture (1.7 vol.% H<sub>2</sub>) at a flow rate of 11.5 cm<sup>3</sup> min<sup>-1</sup> through the liquid reaction medium under vigorous stirring at 22 °C and atmospheric pressure (0.95 atm) for a period of 3 h. The concentration of hydrogen in the effluent gases, after removing water vapors from them by condensation at 0 °C, was measured by an online hydrogen analyzer. After the reaction, the catalyst from the reaction mixture was removed by filtration and the filtered reaction mixture was analyzed for the hydrogen peroxide formed in the reaction by iodometric titration method.

The decomposition of hydrogen peroxide over the catalysts was carried out in the magnetically stirred

reactor containing 0.2 g catalyst and 150 cm<sup>3</sup> acidic (0.02 M sulfuric acid) solution containing 0.2% (w/v) H<sub>2</sub>O<sub>2</sub>. The amount of O<sub>2</sub> liberated in the decomposition was measured as a function of time using a constant pressure gas collector [6].

## 3. Results and discussion

### 3.1. Catalysts characterization

The catalysts have been characterized for their surface area, CO chemisorption (at 40 °C) on reduced catalyst, and relative acidity (measured in terms of the amount of NaOH required to neutralize the acid sites on the catalyst). The surface properties of the catalysts are given in Table 1. The results show that the surface area, CO chemisorption and the relative acidity are strongly influenced by the fluorination, chlorination or sulfation of the supports (except ThO<sub>2</sub>) used in the catalyst. In general, the acidity is increased markedly due to the halogenation or the sulfation of the support.

### 3.2. Effect of reaction medium

Results showing the effect of acidity of the aqueous reaction medium on the performance of the different supported PdO catalysts in the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation process are presented in Table 2.

The results show strong influence of the acidity of the aqueous reaction medium on both the conversion and selectivity in the process. All the catalysts show much higher activity (H<sub>2</sub> conversion) and H<sub>2</sub>O<sub>2</sub>

Table 2  
Effect of reaction medium on conversion and selectivity in the direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> over the different catalysts (at 22 °C)

Catalyst	Reaction medium			
	0.02 M H <sub>2</sub> SO <sub>4</sub>		Pure water	
	Hydrogen conversion (%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)	Hydrogen conversion (%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)
PdO/fluorinated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	41.8	30.3	2.6	15.0
PdO/chlorinated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	43.1	28.6	4.6	8.3
PdO/fluorinated CeO <sub>2</sub>	34.4	36.4	2.6	15.0
PdO/fluorinated ZrO <sub>2</sub>	43.0	26.5	18.5	19.3
PdO/ThO <sub>2</sub>	28.2	47.3	13.9	4.1
PdO/CeO <sub>2</sub>	21.0	56.1	9.2	6.1

selectivity when acidic medium (0.02 M H<sub>2</sub>SO<sub>4</sub>) used in the process as compared to the pure water as the reaction medium. This is consistent with our earlier observation that the H<sub>2</sub>O<sub>2</sub> decomposition activity of Pd/carbon catalyst decreases markedly with increasing the concentration of H<sub>2</sub>SO<sub>4</sub> in the aqueous reaction medium [7]. In the earlier studies using Pd supported on phosphate viologen phosphonate catalyst using aqueous H<sub>2</sub>SO<sub>4</sub> as the reaction medium, there was no significant production of H<sub>2</sub>O<sub>2</sub> in the H<sub>2</sub> oxidation, even at much higher pressure [3]. The H<sub>2</sub>O<sub>2</sub> selectivity observed for the present catalysts using 0.02 M H<sub>2</sub>SO<sub>4</sub> or even water as the reaction medium is much higher than that observed earlier for Pd/fluorinated carbon catalyst using an acidic medium [4].

### 3.3. Effect of catalyst reduction

Results in Table 3 show the effect of reduction of the supported PdO catalysts (by hydrazine) on their performance in both the H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> oxidation and H<sub>2</sub>O<sub>2</sub> decomposition reactions at 22 °C. The kinetic data for the H<sub>2</sub>O<sub>2</sub> decomposition (at 22 °C) over the catalysts, with or without pre-reduction (by hydrazine) are presented in Fig. 1. The H<sub>2</sub>O<sub>2</sub> decomposition data could be fitted well to first-order rate law:  $\ln[1/(1-x)] = k_a t$ , where  $x$  is the fractional decomposition of H<sub>2</sub>O<sub>2</sub>,  $k_a$  the first-order rate constant and  $t$  the time.

The pre-reduced catalysts (Pd<sup>0</sup>-containing catalysts) showed much lower H<sub>2</sub>O<sub>2</sub> selectivity and also lower activity (except for Pd/CeO<sub>2</sub>) in the H<sub>2</sub>

oxidation but much higher H<sub>2</sub>O<sub>2</sub> decomposition activity. The decrease in the H<sub>2</sub>O<sub>2</sub> selectivity is because of the increased H<sub>2</sub>O<sub>2</sub> decomposition activity of the corresponding catalyst after its reduction. These comparative results clearly show that the catalysts in their oxidized form are more selective and even more active in the oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> but less active in the H<sub>2</sub>O<sub>2</sub> decomposition.

### 3.4. Comparison of supported PdO catalysts

The PdO-containing catalysts are compared in Figs. 2 and 3 for their performance both in the H<sub>2</sub> oxidation and H<sub>2</sub>O<sub>2</sub> decomposition reactions (at 22 °C), using 0.02 M H<sub>2</sub>SO<sub>4</sub> as the reaction medium. From the comparison, following important observations for the catalyst with different supports can be made.

*Al<sub>2</sub>O<sub>3</sub>-supported PdO catalysts.* Fluorination (or chlorination) has a small effect on the H<sub>2</sub> conversion activity but a very large effect on the H<sub>2</sub>O<sub>2</sub> selectivity; the later is increased drastically by the fluorination or chlorination of the  $\gamma$ -alumina. However, the H<sub>2</sub>O<sub>2</sub> decomposition (in 3 h) over these catalysts is very small when compared to the H<sub>2</sub> conversion. This shows that the formation of H<sub>2</sub>O<sub>2</sub> and water in the H<sub>2</sub> oxidation over these catalysts occurs essentially in the parallel reactions:



Table 3

Effect of the pre-reduction (by hydrazine) of catalysts on their activity/selectivity in the oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and in the decomposition of H<sub>2</sub>O<sub>2</sub> reactions

Catalyst	Oxidation of H <sub>2</sub> to H <sub>2</sub> O <sub>2</sub> (at 22 °C)		First-order apparent rate constant for H <sub>2</sub> O <sub>2</sub> decomposition (at 22 °C), $k_a \times 10^4$ (min <sup>-1</sup> )
	H <sub>2</sub> conversion (%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)	
PdO/fluorinated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	41.8	30.3	0.0
Pd <sup>0</sup> /fluorinated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	16.4	17.6	1.0
PdO/fluorinated ZrO <sub>2</sub>	43.0	26.5	1.3
Pd <sup>0</sup> /fluorinated ZrO <sub>2</sub>	18.5	16.8	9.8
PdO/CeO <sub>2</sub>	21.1	56.1	6.3
Pd <sup>0</sup> /CeO <sub>2</sub>	20.3	0.0	60.8
PdO/ThO <sub>2</sub>	28.2	47.3	5.1
Pd <sup>0</sup> /ThO <sub>2</sub>	18.5	0.0	66.4

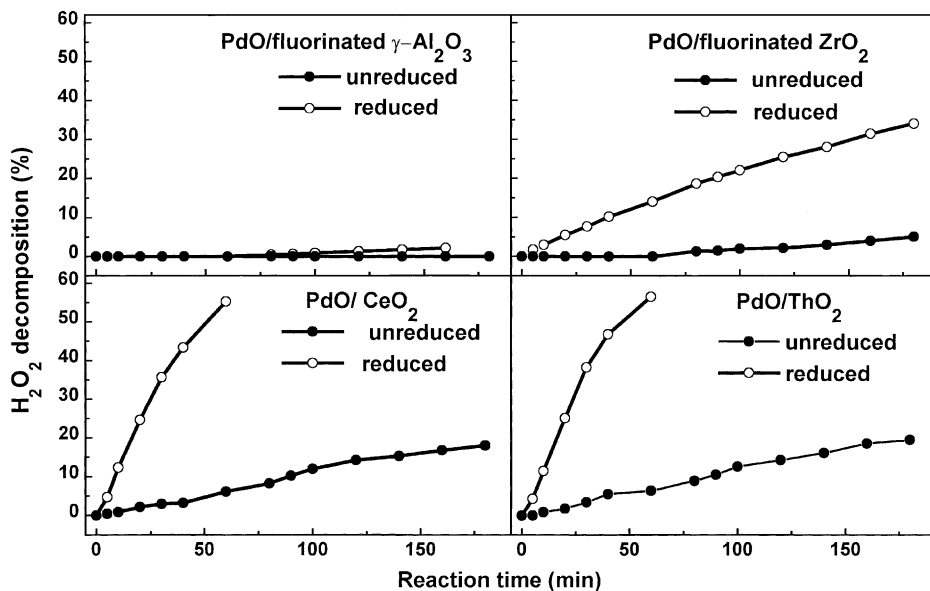


Fig. 1. Kinetic data for the decomposition of  $H_2O_2$  (at  $22^\circ C$ ) over the different catalysts.

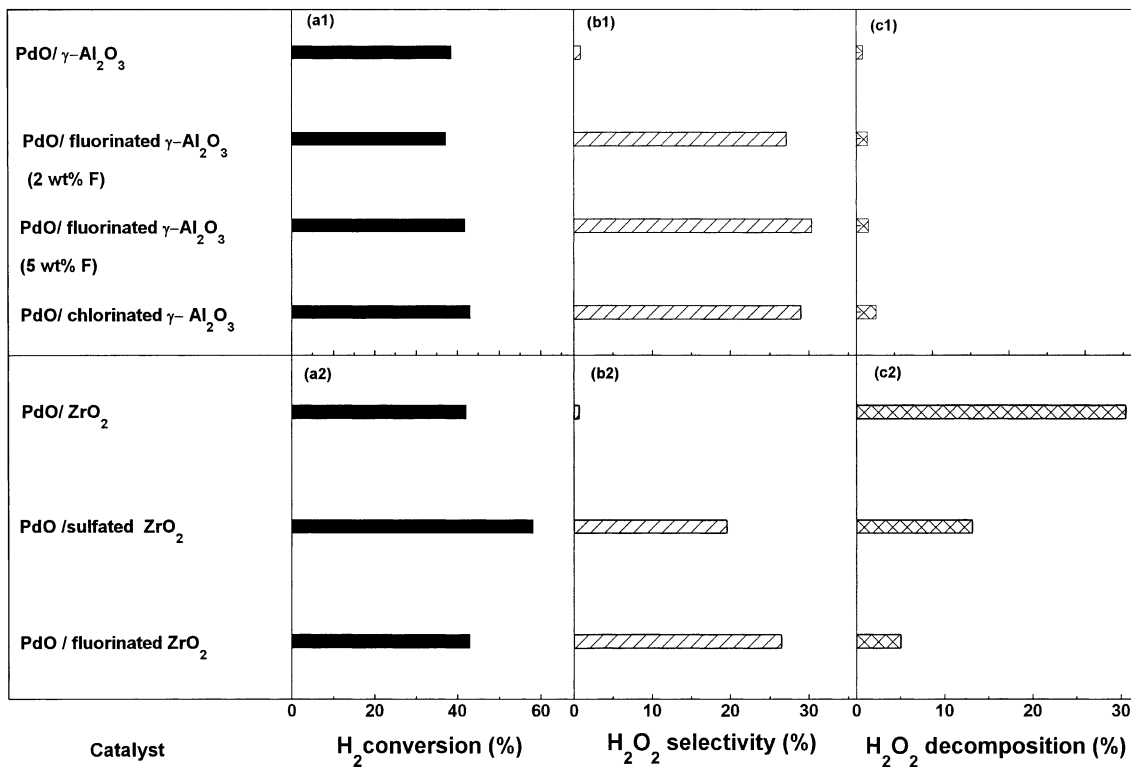


Fig. 2. Performance of the alumina- and zirconia-supported (with or without modification) PdO catalysts in the direct oxidation of  $H_2$  to  $H_2O_2$  (at  $22^\circ C$ ) and also in the decomposition of  $H_2O_2$  (at  $22^\circ C$ ).

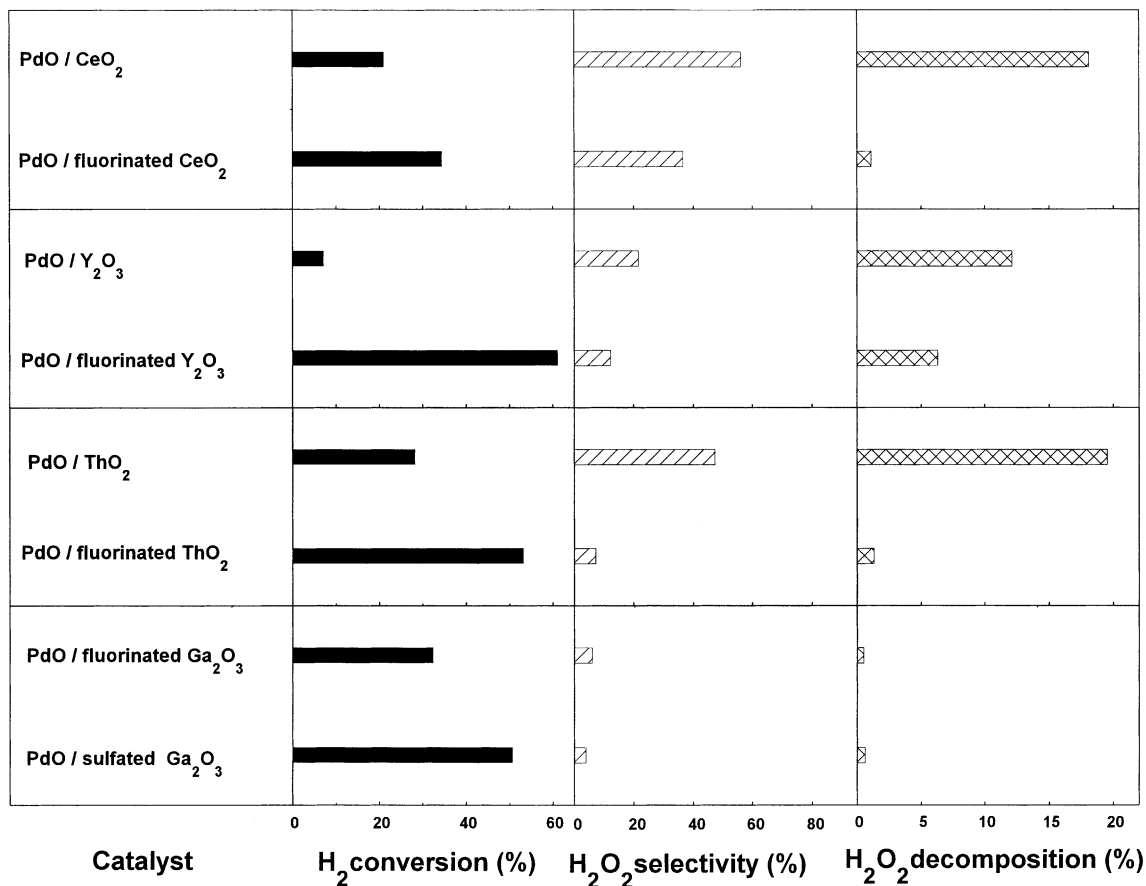


Fig. 3. Performance of the ceria-, yttria-, thoria- and gallia-supported (with or without modification) PdO catalysts in the direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> (at 22 °C) and also in the decomposition of H<sub>2</sub>O<sub>2</sub> (at 22 °C).

Because of the very poor activity of the catalysts for H<sub>2</sub>O<sub>2</sub> decomposition, the possibility of water formation in the H<sub>2</sub> oxidation in the consecutive reaction



is small.

The higher H<sub>2</sub>O<sub>2</sub> selectivity and the lower H<sub>2</sub>O<sub>2</sub> decomposition activity of the fluorinated or chlorinated Al<sub>2</sub>O<sub>3</sub>-containing catalyst may be due to its increased acidity (protonic acidity) resulting from the halogenation of Al<sub>2</sub>O<sub>3</sub> [8].

*ZrO<sub>2</sub>-supported PdO catalysts.* In this case also, the H<sub>2</sub>O<sub>2</sub> selectivity is increased drastically after the fluorination or sulfation of the support. However, unlike the alumina-supported PdO catalysts, the

ZrO<sub>2</sub>-supported PdO catalysts also have high H<sub>2</sub>O<sub>2</sub> decomposition activity, which is decreased after fluorination or sulfation due to the increased acidity. Hence, the formation of H<sub>2</sub>O<sub>2</sub> and water in the H<sub>2</sub> oxidation over these catalysts is expected also by the consecutive reaction (reaction 2).

*CeO<sub>2</sub>-, Y<sub>2</sub>O<sub>3</sub>- and ThO<sub>2</sub>-supported PdO catalysts.*

In these cases, the fluorination of support results in an increase in the H<sub>2</sub> conversion but a decrease in both the H<sub>2</sub>O<sub>2</sub> selectivity and the H<sub>2</sub>O<sub>2</sub> decomposition activity of the catalyst (Fig. 3). The H<sub>2</sub>O<sub>2</sub> decomposition activity of PdO/fluorinated CeO<sub>2</sub> (or ThO<sub>2</sub>) catalyst is very low and hence the formation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O over the catalyst is expected mainly by the parallel reactions (reaction 1). However, the H<sub>2</sub>O<sub>2</sub> decomposition

activity of the PdO/ThO<sub>2</sub>, PdO/CeO<sub>2</sub> and PdO/Y<sub>2</sub>O<sub>3</sub> is quite high. Hence, over these catalysts, the formation of water in the H<sub>2</sub> oxidation is expected mainly by the consecutive reaction (reaction 2).

*PdO/fluorinated (or sulfated) Ga<sub>2</sub>O<sub>3</sub> catalysts.* These catalysts showed high H<sub>2</sub> conversion activity but very poor selectivity for H<sub>2</sub>O<sub>2</sub> and also poor H<sub>2</sub>O<sub>2</sub> decomposition activity, indicating formation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O in the H<sub>2</sub> oxidation mainly by the parallel reactions (reaction 1).

When compared for the H<sub>2</sub>O<sub>2</sub> yield [conversion (%) × selectivity (%) / 100] obtained in the H<sub>2</sub> oxidation process, the catalysts showed the following order (Figs. 2 and 3): PdO/ThO<sub>2</sub> > PdO/fluorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > PdO/fluorinated CeO<sub>2</sub> > PdO/chlorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > PdO/CeO<sub>2</sub> > PdO/fluorinated ZrO<sub>2</sub> ≥ PdO/sulfated ZrO<sub>2</sub> > PdO/fluorinated Y<sub>2</sub>O<sub>3</sub> > PdO/fluorinated ThO<sub>2</sub> > PdO/fluorinated Ga<sub>2</sub>O<sub>3</sub> ≥ PdO/sulfated Ga<sub>2</sub>O<sub>3</sub> > PdO/Y<sub>2</sub>O<sub>3</sub> > PdO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ≥ PdO/ZrO<sub>2</sub>.

The H<sub>2</sub>O<sub>2</sub> yields obtained over the PdO supported on ThO<sub>2</sub> (13.3%), fluorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (12.7%) or CeO<sub>2</sub> (12.5%), chlorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (12.3%), CeO<sub>2</sub> (11.8%), fluorinated or sulfated ZrO<sub>2</sub> (11.4%), and fluorinated Y<sub>2</sub>O<sub>3</sub> (7.4%) catalysts are much higher than that (3.6%) reported earlier over the Pd/fluorinated carbon catalyst.

#### 4. Conclusions

From the above studies on the direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> decomposition reactions over the different fluorinated or sulfated Al<sub>2</sub>O<sub>3</sub>-, ZrO<sub>2</sub>-, CeO<sub>2</sub>-, Y<sub>2</sub>O<sub>3</sub>-, ThO<sub>2</sub>- and Ga<sub>2</sub>O<sub>3</sub>-supported PdO or Pd catalysts, the following important conclusions have been drawn.

1. The modification by fluorination or sulfation of Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> support causes a drastic increase in the H<sub>2</sub>O<sub>2</sub> selectivity of the catalyst but that of CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and ThO<sub>2</sub> results in a

decrease in the selectivity and an increase in the H<sub>2</sub> conversion activity of the catalyst in the H<sub>2</sub> oxidation. The PdO/ThO<sub>2</sub>, PdO/fluorinated/chlorinated or sulfated Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>, and PdO/CeO<sub>2</sub> are promising catalysts for the direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>.

2. The water in the H<sub>2</sub> oxidation over the supported PdO catalysts is formed in the parallel and/or consecutive reaction, depending upon the support used in the catalyst. It is formed mostly by the parallel reaction over the fluorinated (or chlorinated) Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub> and sulfated Ga<sub>2</sub>O<sub>3</sub>-supported PdO catalysts but by the consecutive reaction over the ZrO<sub>2</sub>-, CeO<sub>2</sub>-, Y<sub>2</sub>O<sub>3</sub>- and ThO<sub>2</sub>-supported PdO catalysts.
3. The catalysts after the reduction of their PdO to Pd<sup>0</sup> (by hydrazine) showed much lower selectivity in the oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and much higher H<sub>2</sub>O<sub>2</sub> decomposition activity.
4. Both the activity and H<sub>2</sub>O<sub>2</sub> selectivity (in the H<sub>2</sub> oxidation) of the catalysts depend strongly on the acidity of the aqueous reaction medium; the selectivity is much higher when the reaction medium is acidic.

#### References

- [1] G. Goor, W. Kunkel, O. Weiberg, in: B. Elver, S. Howkins, R. Ravenscrafty, G. Schulz (Eds.), Ullman's Encyclopedia of Industrial Chemistry, Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, pp. 443–466.
- [2] V.R. Choudhary, A.G. Gaikwad, S.D. Sansare, *Angew. Chem. Int. Ed.* 40 (2001) 1776.
- [3] V.V. Krishnan, A.G. Dokoutchaev, M.E. Thompson, *J. Catal.* 196 (2000) 366.
- [4] L. Fu, K.T. Chung, R. Fiedorow, *Stud. Surf. Sci. Catal.* 72 (1992) 33.
- [5] V.R. Choudhary, L.K. Doraiswamy, *Ind. Eng. Chem. Prod. Res. Dev.* 10 (1978) 218.
- [6] V.R. Choudhary, M.G. Parande, P.H. Brahame, *Ind. Eng. Chem. Fundam.* 21 (1982) 472.
- [7] V.R. Choudhary, A.G. Gaikwad, unpublished work.
- [8] V.R. Choudhary, *Ind. Eng. Chem. Prod. Res. Dev.* 16 (1977) 12.