Direct oxidation of H_2 to H_2O_2 and decomposition of H_2O_2 over oxidized and reduced Pd-containing zeolite catalysts in acidic medium

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Received 3 May 2002; accepted 8 August 2002

Both the conversion and H_2O_2 selectivity (or yield) in direct oxidation of H_2-to-H_2O_2 (using 1.7 mol% H_2 in O_2 as a feed) and also the H_2O_2 decomposition over zeolite (viz. H-ZSM-5, H-GaAlMFI and H-β) supported palladium catalysts (at 22 °C and atmospheric pressure) are strongly influenced by the zeolite support and its fluorination, the reaction medium (viz. pure water, 0.016 M or 1.0 M NaCl solution or 0.016 M H_2SO_4, HCl, HNO_3, H_3PO_4 and $HClO_4$), and also by the form of palladium (Pd^0 or PdO). The oxidized (PdO-containing) catalysts are active for the H_2-to-H_2O_2 conversion and show very poor activity for the H_2O_2 decomposition. However, the reduced (Pd^0-containing) catalysts show higher H_2 conversion activity but with no selectivity for H_2O_2, and also show much higher H_2O_2 decomposition activity. No direct correlation is observed between the H_2-to-H_2O_2 conversion activity (or H_2O_2 selectivity) and the Pd dispersion or surface acidity of the catalysts. Higher H_2O_2 yield and lower H_2O_2 decomposition activity are, however, obtained when the non-acidic reaction medium (water with or without NaCl) is replaced by the acidic one.

KEY WORDS: oxidation of H_2 to H_2O_2; decomposition of H_2O_2; zeolite supported Pd catalysts; Pd/H-ZSM-5; Pd/H-GaAlMFI; Pd/H-β.

1. Introduction

Liquid-phase direct oxidation of hydrogen-to-hydrogen peroxide (which is a very versatile and environ-friendly oxidizing agent [1,2]) is a process of great practical importance. This process is environmentally very clean as only water is produced as a side product. For a long time, it has been known to be catalyzed by palladium [3]. However, the decomposition of H_2O_2 in consecutive reaction ($H_2 + O_2 \rightarrow H_2O_2 \rightarrow H_2O + 0.5O_2$) poses a serious problem for the selective oxidation of H_2 to H_2O_2 [4,5]. Despite its practical importance, studies reported on this process in open literature are scarce. Fu *et al.* [4] reported 8.7% H_2O_2 selectivity (at 41% H_2 conversion) as the maximum selectivity in the reaction over Pd supported on hydrophobic fluorinated carbon as a catalyst (at 25 °C and 0.65 MPa pressure). They observed that the decisive factor in determining H_2O_2 selectivity is the hydrophobicity of the catalyst; the Pd metal particle size or area is found to be less important. Krishnan *et al.* [6] used a combination of an organic catalyst (viologen) for the activation of O_2 and Pd metal for the activation of H_2 for direct synthesis of H_2O_2, using methanol in conjunction with H_2SO_4 as the reaction medium. Generation of H_2O_2 from H_2 and O_2 over Pd-Pt/Ti-silicate [7] and hydroquinone adsorbed Pd/beta zeolite [8] catalysts was also observed earlier. Recently, we have reported non-hazardous direct H_2-to-H_2O_2 oxidation using a novel composite Pd-membrane catalyst [5]. H_2O_2 selectivity was increased markedly after the oxidation of the Pd-membrane catalyst.

Hydrogen peroxide is weakly acidic in aqueous solution [2]. Since H_2O_2 is more stable in an acidic environment, it is interesting to study the performance of palladium-containing highly acidic zeolite catalysts in the direct oxidation of H_2 to H_2O_2. The present investigation was undertaken with the objective of studying the performance of palladium (2.5 wt%)-containing highly acidic zeolite (H-ZSM-5, H-GaAlMFI, H-β and H-M) catalysts in both their oxidized and reduced forms for the liquid phase oxidation of H_2 by O_2 to H_2O_2 (using a mixed hydrogen-oxygen feed) and decomposition of H_2O_2 reactions at close to ambient conditions. The influence of fluorination of the zeolite support and the nature of the reaction medium (acidic and non-acidic aqueous medium) on both reactions has also been investigated.

2. Experimental

The palladium-containing zeolite catalysts in their oxidized form (table 1) were prepared by impregnating $PdCl_2$ from its HCl solution on H-ZSM-5 (Si/Al = 31.1, crystal size = 4.0 μm), H-GaAlMFI (Si/Ga = 15.3, Si/Al = 49.6, crystal size = 3.7 μm), H-β (Si/Al = 27.1 and crystal size = 1.0 μm) and H-M (Si/Al = 6.6, crystal size

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<1 μm) zeolites (with or without fluorination) by the incipient wetness impregnation technique. After the impregnation, the wet catalyst mass was dried at 120 °C for 3 h and then calcined under static air at 500 °C for 4 h. Fluorination of the zeolites was carried out by impregnating the respective zeolite with ammonium fluoride (0.1 g NH_4F per gram of zeolite) from its aqueous solution by the incipient wetness impregnation technique, followed by drying on a hot water bath and then calcining in a muffle furnace at 500 °C for 2 h. The zeolites were prepared and characterized by a procedure similar to that described earlier [9–11].

The Pd/zeolite catalysts in their reduced form were obtained by reducing the corresponding oxidized catalysts with an ammoniacal hydrazine solution on a hot water bath, followed by washing, filtration and drying at 100 °C in an air oven.

The catalysts were characterized by XRD using a 1730 series Philips Refractometer with Cu K_α radiation. To determine the dispersion of Pd on the zeolite catalysts, the chemisorption of CO on the catalysts (after their reduction by H_2 pulses at 500 °C) was measured at 40 °C using a gc pulse technique [12]. The acidity of the catalysts was measured by the chemisorption of ammonia at different temperatures (150–350 °C) by the step-wise thermal desorption (from 150 to 500 °C) of the ammonia pre-chemisorbed at the lowest temperature, 150 °C [13].

Direct oxidation of H_2 to H_2O_2 over the catalysts was carried out at atmospheric pressure (95 kPa) in a magnetically stirred glass reactor (capacity = 250 cm^3) kept in a constant-temperature circulating water bath at the following reaction conditions: gaseous feed = 1.7 mol% H_2 in O_2, amount of catalyst = 0.5 g, reaction medium: pure water or aqueous solution of 0.016 M NaCl or 0.016 M H_2SO_4, HCl, HNO_3, H_3PO_4 or $HClO_4$, volume of reaction medium = 150 cm^3, temperature = 22 °C, reaction period = 3 h. The gaseous feed was continuously bubbled through the reaction medium containing the catalyst under vigorous stirring. The concentration of unreacted hydrogen present in the effluent gases, after removing water vapors from them by condensation at 0 °C, was measured by an on-line hydrogen analyzer based on a thermal conductivity detector. After the reaction the catalyst from the reaction mixture was removed by filtration and the filtrate was analyzed for the H_2O_2 formed in the reaction by iodometric titration. The conversion of hydrogen and H_2O_2 selectivity were obtained as follows: H_2 conversion (%) = {[(amount of H_2 in the feed) − (amount of H_2 in the effluent gases)] ÷ [amount of H_2 in the feed]} × 100; H_2O_2 selectivity (%) = [(amount of H_2O_2 formed) (amount of H_2 consumed)] × 100; H_2O_2 yield (%) = [(amount of H_2O_2 formed) ÷ (amount of H_2 in the feed)] × 100.

Decomposition of hydrogen peroxide over the catalysts was carried out at atmospheric pressure (95 kPa) in the magnetically stirred reactor containing 0.2 g catalyst in the liquid reaction medium (150 cm^3) at 22 °C by injecting 1.0 ml aqueous 30 wt% H_2O_2 solution in the reactor. The volume of O_2 liberated in the H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5O_2$) was measured as a function of time using a constant-pressure gas collector [14].

3. Results and discussion

The surface and bulk properties of the Pd (2.5 wt%)/zeolite catalysts are presented in table 1.

The form of the Pd present in all the oxidized (as-prepared) catalysts is found to be PdO, whereas that present in the reduced (by ammoniacal hydrazine solution) catalysts is found to be Pd^0 (*i.e.*, metallic Pd).

Table 1
Surface and bulk properties of the Pd-containing zeolite catalysts.

Catalyst	Form of catalyst (oxidized or reduced)	Crystalline phases	Dispersion of Pd on zeolite (%)	Ammonia chemisorption ($mmol\,g^{-1}$)		
				150 °C	250 °C	350 °C
Pd/H-ZSM-5	Oxidized	PdO, ZSM-5	2.2	0.56	0.26	0.10
Pd/F/H-ZSM-5	Oxidized	PdO, ZSM-5	5.7	0.50	0.21	0.05
Pd/H-GaAlMFI	Oxidized	PdO, ZSM-5	12.4	0.35	0.22	0.11
Pd/F/H-GaAlMFI	Oxidized	PdO, ZSM-5	7.8	0.26	0.16	0.08
Pd/H-β	Oxidized	PdO, β-zeolite	11.9	0.47	0.23	0.11
Pd/F/H-β	Oxidized	PdO, β-zeolite	6.0	0.27	0.10	0.03
Pd/HM	Oxidized	PdO, M-zeolite	19.0	0.53	0.16	0.09
Pd/F/HM	Oxidized	PdO, M-zeolite	11.1	0.22	0.08	0.05
Pd/H-ZSM-5	Reduced [a]	Pd^0, ZSM-5	2.5	0.60	0.31	0.17
Pd/H-GaAlMFI	Reduced [a]	Pd^0, ZSM-5	13.0	0.41	0.24	0.18
Pd/H-β	Reduced [a]	Pd^0, β-zeolite	12.1	0.64	0.45	0.19

[a] Catalyst reduced by ammoniacal hydrazine solution.

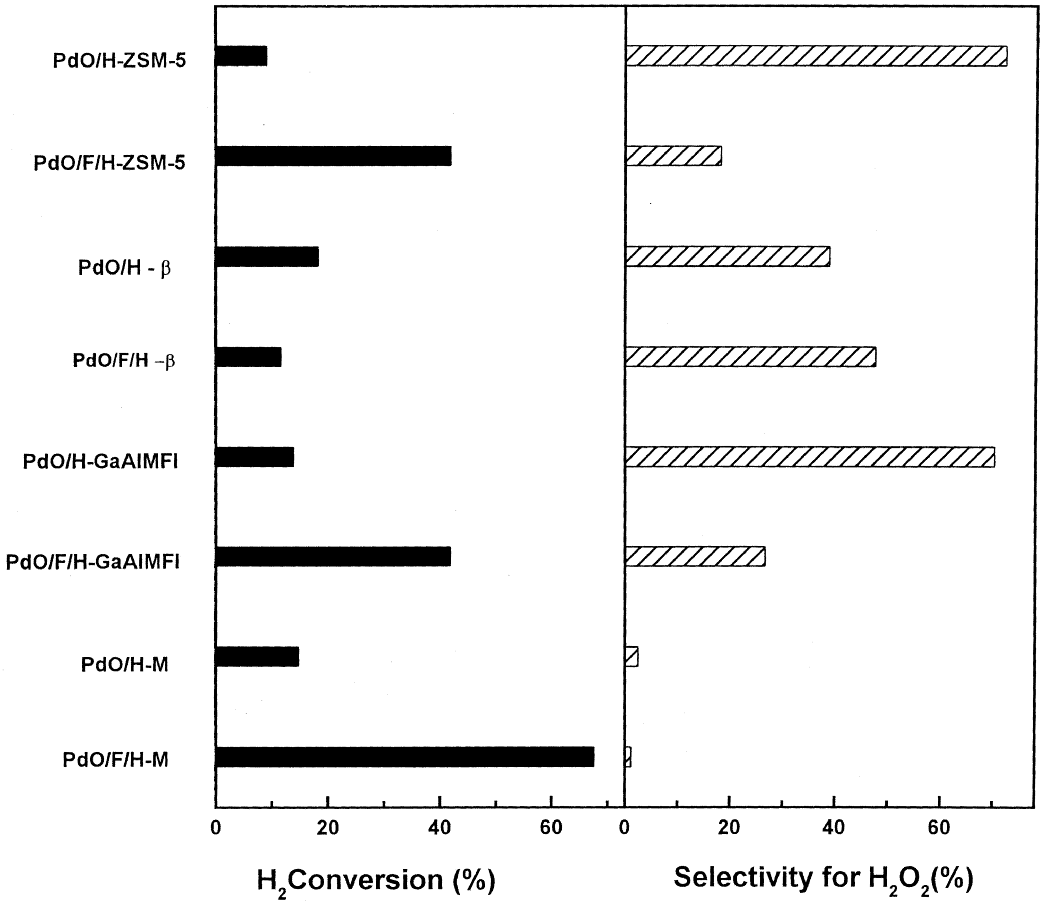

Figure 1. Results on the oxidation of H_2 to H_2O_2 over the oxidized palladium-containing zeolite catalysts (reaction medium: 0.016 M H_2SO_4).

The catalysts differ in their Pd dispersion (measured by the CO chemisorption) and also in their acidity, measured in terms of the ammonia chemisorbed at 150, 250 and 350 °C. The fluorination of the zeolite support has resulted in a decrease in the Pd dispersion, except for the H-ZSM-5-based catalyst. It has also caused a decrease in the acidity of all the Pd/zeolite catalysts. However, after the reduction (by the ammoniacal hydrazine solution), the acidity of the Pd/zeolite catalyst is increased appreciably.

Results showing the influence of zeolite (used for supporting the palladium catalyst), fluorination of the zeolite, reaction medium and catalyst reduction (by ammoniacal hydrazine solution) on both the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions over the Pd/zeolite catalysts at 22 °C are presented in figures 1–5 and table 3.

3.1. *Effect of zeolite support and its fluorination*

The results in figures 1 and 2 indicate that the zeolite support used in the catalysts and also the fluorination of zeolite have a strong influence on their performance in both reactions. The influence of fluorination is consistent with that observed earlier for Pd catalysts with fluorinated supports [4,15].

For the H_2-to-H_2O_2 oxidation, the Pd/H-ZSM-5 showed highest selectivity (72%) for the H_2O_2 but lowest H_2 conversion (9.2%) activity, whereas the Pd/F/H-M showed highest H_2 conversion (68%) activity but lowest H_2O_2 selectivity (1.1%). For their H_2-to-H_2O_2 conversion activity (*i.e.*, H_2O_2 yield), the catalysts show the following order: Pd/F/H-GaAlMFI (11.3%) > Pd/H-GaAlMFI (9.8%) > Pd/F/H-ZSM-5 (7.7%) > Pd/H-β (7.2%) > Pd/H-ZSM-5 (6.6%) > Pd/F/H-β (5.6%) ≫ Pd/F/H-M (0.7%) > Pd/H-M (0.4%) (the value in parentheses corresponds to the H_2O_2 yield obtained in the H_2-to-H_2O_2 oxidation). Except for the H-β-zeolite-based catalysts, in all cases the fluorination of zeolite in the catalysts has resulted in a significant increase in the H_2O_2 yield. However, a comparison of the H_2 conversion, H_2O_2 selectivity or H_2O_2 yield data (figure 1) for the catalysts with their surface properties, Pd dispersion and surface acidity (table 1) shows that there is no direct correlation between the two. Fu *et al.* [4] also observed that the Pd metal particle size is not important for deciding the H_2O_2 selectivity.

The results in figure 2 reveal that the oxidized Pd/zeolite catalysts have very poor H_2O_2 decomposition activity (in 3 h the H_2O_2 decomposition over all the catalysts was less than 4% even when the amount of catalyst used was smaller, 0.2 g). Because of the

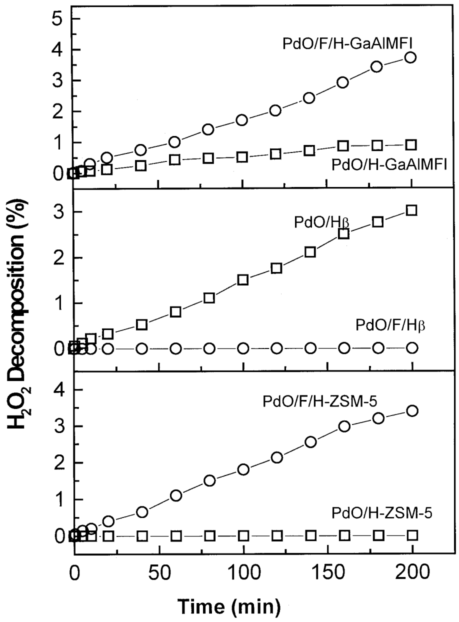

Figure 2. Results on the H_2O_2 decomposition over the oxidized palladium-containing zeolite catalysts (reaction medium: 0.016 M H_2SO_4).

Table 2
Comparison of the catalysts for the formation of H_2O_2 from H_2 and O_2 under identical conditions.

Catalyst	TOR (mmol g^{-1} h^{-1})[a]	TON (h^{-1})[b]	Ref.
PdO/HZSM-5	87	17.1	Present work
PdO/F/H-ZSM-5	100	7.5	Present work
PdO/H-β	93	3.3	Present work
PdO/F/H-β	73	5.2	Present work
PdO/H-GaAlMFI	126	4.3	Present work
PdO/F/H-ZSM-5	147	8.0	Present work
PdO/F/Al_2O_3	133	7.1	16
PdO/Cl/Al_2O_3	160	32.0	16
PdO/F/CeO_2	53	3.1	16
PdO/F/ZrO_2	120	25.0	16
PdO/ThO_2	173	46.8	16
PdO/CeO_2	153	25.1	16
Pd/Al_2O_3[c]	5.5	0.03	5
Pd/Al_2O_3[c] oxidized by H_2O_2	39.6	0.20	5

[a] Turnover rate (*i.e.*, rate of H_2O_2 formed (mmol) per gram catalyst per hour).

[b] Turnover number (moles of H_2O_2 formed per mole of surface Pd or PdO per hour).

[c] Pd(5%)/Al_2O_3 obtained from Lancaster Chemicals (UK).

fluorination of zeolite, the H_2O_2 decomposition activity is, however, increased for the H-ZSM-5 and H-GaAlMFI zeolite-containing catalysts, but it is decreased for H-β zeolite-containing catalysts.

Since the H_2O_2 decomposition of the oxidized catalysts is found to be very small, the formation of water in the H_2-to-H_2O_2 oxidation is expected mostly in the parallel reactions (reactions (1) and (2)):

$$H_2 + O_2 \rightarrow H_2O_2 \tag{1}$$

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{2}$$

rather than in the consecutive reaction (reaction (3)):

$$H_2 + O_2 \rightarrow H_2O_2 \rightarrow H_2O + 0.5O_2. \tag{3}$$

It may be noted that the H_2O_2 yield or selectivity in the H_2 oxidation using an aqueous H_2SO_4 reaction medium for the oxidized Pd zeolite (*viz.* H-ZSM-5, H-GaAlMFI and H-β, with or without fluorination) is much higher than that reported earlier for the Pd/fluorinated carbon [4] and Pd-phosphate–viologen-phosphate [6] catalysts.

The palladium-containing zeolite catalysts are compared with other earlier reported catalysts for their TOR (turnover rates, amount of H_2O_2 formed per unit mass of catalyst per unit time) and TON (turnover number, moles of H_2O_2 formed per mole of surface Pd or PdO per hour) in table 2.

3.2. *Effect of reaction medium*

In order to study the effect of the liquid reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition, both reactions were carried out on oxidized Pd/H-β and Pd/F/H-β catalysts at 22 °C, using pure water or an aqueous solution containing different acids (0.016 M) or NaCl (0.016 M or 1.0 M) as the reaction medium. The results (figures 3 and 4) show a strong effect of the reaction medium on the performance of the catalyst in both reactions. When the reaction medium is changed from pure water to an aqueous acid solution (0.016 M), both the H_2O_2 selectivity and H_2O_2 yield are increased very markedly, depending upon the acid used in the reaction medium. For the H_2O_2 yield (in H_2-to-H_2O_2 oxidation), the different acidic reaction media show the following order: HCl (13.3%) > HNO_3 (8.2%) > H_3PO_4 (7.7%) > H_2SO_4 or $HClO_4$ (7.2%) ≫ distilled water (2.5%) (the value in parentheses corresponds to the H_2O_2 yield obtained in the H_2-to-H_2O_2 oxidation). It is interesting to note that when sodium chloride is present in the reaction medium at high concentration (1.0 M), the H_2O_2 selectivity is reduced almost to zero. Also for the Pd/F/H-β, both the conversion and H_2O_2 selectivity are increased when the reaction medium is changed from pure water to 0.01 M H_2SO_4 (figure 3).

The observed higher H_2O_2 yield for the HCl reaction medium is most probably attributed to the presence of halide anions (Cl^-) in the reaction medium. Earlier patent literature [17] showed a strong halide effect for the efficient hydrogen peroxide production by direct H_2 oxidation using supported metal catalysts.

The results of the H_2O_2 decomposition (figure 4) indicate that the H_2O_2 decomposition activity of the oxidized Pd/H-β catalyst is decreased in the presence of an acid or NaCl in the aqueous reaction medium.

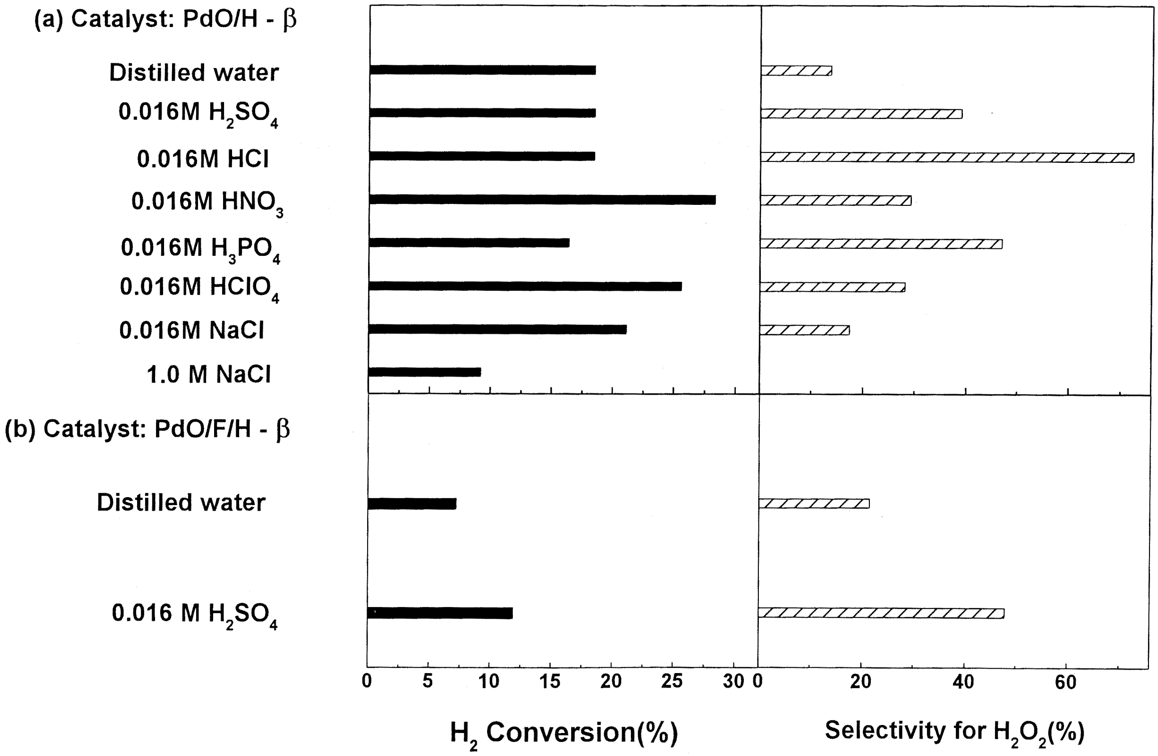

Figure 3. Results on the oxidation of H_2 to H_2O_2 over the oxidized PdO/H-β and PdO/F/H-β catalysts using different reaction media.

At the acid concentration (0.016 M) used in the present study, the structure of the zeolites was not affected during the reactions. Representative XRD spectra for the Pd/H-β and Pd/H-GaAlMFI catalysts before and after the H_2-to-H_2O_2 oxidation using 0.016 M H_2SO_4 as the reaction medium are presented in figure 6. Comparison of the spectra shows no significant change in the structure of the respective zeolite after the reaction.

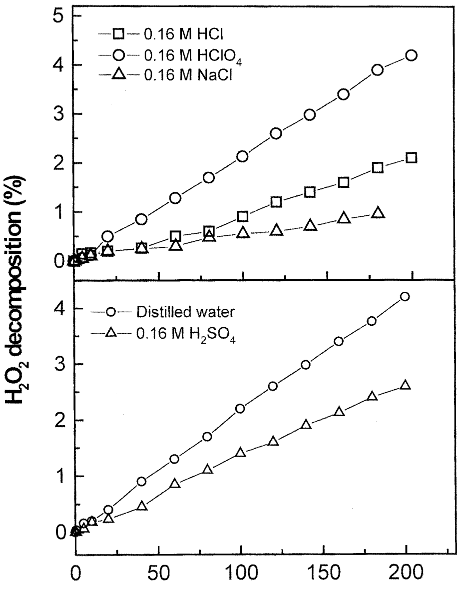

Figure 4. Results on the H_2O_2 decomposition over the oxidized PdO/H-β catalyst using different reaction media.

3.3. *Effect of catalyst reduction*

A comparison of the results for the reduced catalysts with those for the oxidized (as-prepared) ones (table 3 and figures 4 and 5) shows a very strong influence of the catalyst reduction on both reactions. After the reduction, the hydrogen conversion activity of the catalysts (in the H_2 oxidation) is increased drastically, but the catalysts become totally non-selective for the H_2O_2 formation and moreover their H_2O_2 decomposition activity is also increased drastically (table 3). This clearly shows that for the catalysts to be selective in the H_2-to-H_2O_2 oxidation process under the present reaction conditions, the palladium in the catalyst should be in its oxidized (PdO) form.

It is also interesting to note that, as compared to the reduced catalysts, the oxidized catalysts show very poor activity for the H_2O_2 decomposition. The observed very high H_2O_2 decomposition activity with no H_2O_2 selectivity for the reduced catalysts suggests that, in the H_2 oxidation over the reduced catalysts, H_2O_2 may be an intermediate product formed according to the consecutive reaction (reaction (3)), but as soon as it is formed it is decomposed to water. The reduced catalysts show no activity for the H_2O_2 formation from

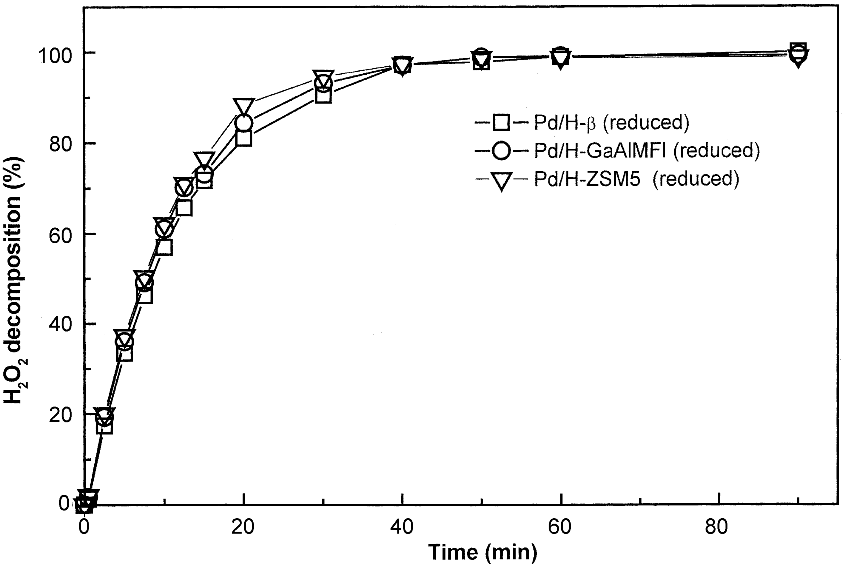

Figure 5. Results on the H_2O_2 decomposition over the reduced catalysts (Pd/H-β, Pd/H-GaAlMFI and Pd/H-ZSM-5) (reaction medium: 0.016 M H_2SO_4).

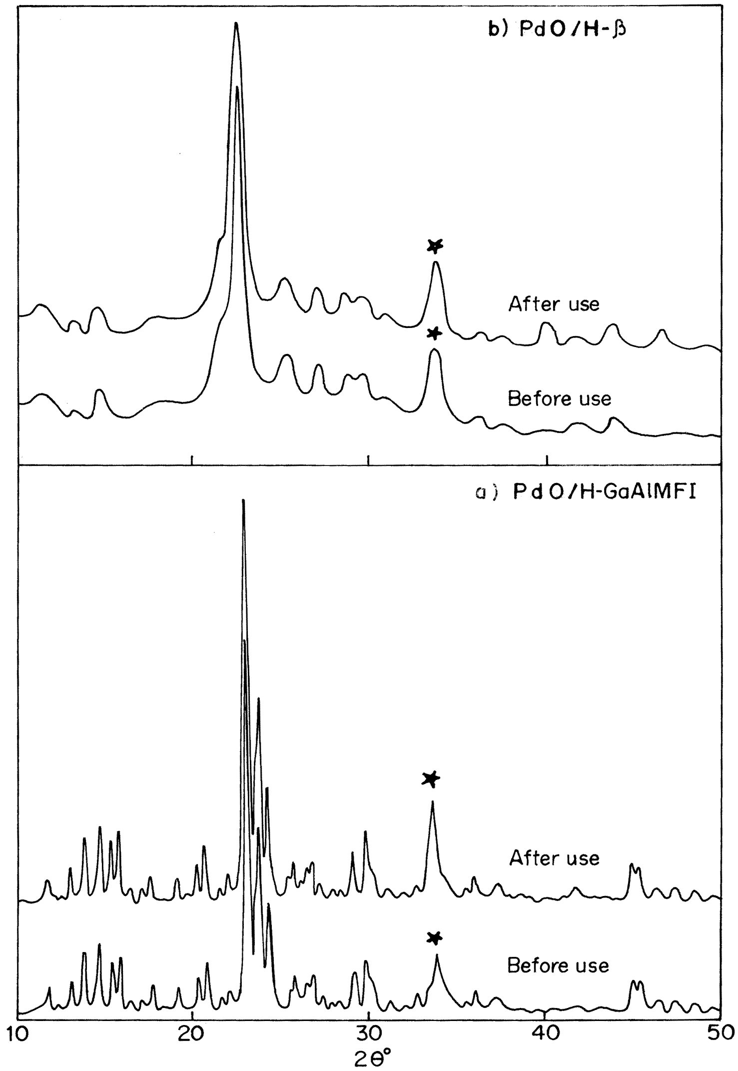

Figure 6. XRD spectra of the oxidized palladium-containing H-β and GaAlMFI zeolite catalysts before and after their use in the H_2-to-H_2O_2 oxidation (reaction medium: 0.016 M H_2SO_4) (★ PdO phase).

Table 3
Effect of catalyst reduction on performance of the Pd-containing zeolite catalysts in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions at 22 °C (reaction medium: 0.016 M H_2SO_4).

Catalyst	Form of catalyst (oxidized [a] or reduced [b])	H_2-to-H_2O_2 oxidation		H_2O_2 decomposition rate constant, $k_d \times 10^3$ (min^{-1})
		Hydrogen conversion (%)	H_2O_2 selectivity (%)	
Pd/H-ZSM-5	Oxidized	9.2	72.2	<0.001
	Reduced	59.0	0.0	88
Pd/H-GaAlMFI	Oxidized	13.9	70.4	0.001
	Reduced	58.3	0.0	86
Pd/H-β	Oxidized	18.5	38.9	0.001
	Reduced	61.5	0.0	76

[a] As prepared (containing palladium as PdO).
[b] Reduced (containing palladium as Pd^0) by the ammoniacal hydrazine solution.

H_2 and O_2 mostly because of their very high H_2O_2 decomposition activity. A further detailed investigation is necessary for understanding the role of Pd^0 and PdO in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reactions.

4. Conclusions

The zeolite support and its fluorination, liquid reaction medium and form of palladium (PdO or Pd^0) present in the Pd-containing zeolite (viz. HZSM-5, H-GaAlMFI, H-β and H-M) catalysts have a strong influence on both the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition reaction over the catalysts. Among the catalysts, the best performance for the H_2-to-H_2O_2 oxidation is shown by the oxidized Pd/F/H-GaAlMFI catalyst and the order for the performance (H_2O_2 yield) of the oxidized (*i.e.*, PdO-containing) zeolite catalysts is as follows: Pd/F/H-GaAlMFI > Pd/H-GaAlMFI > Pd/F/H-ZSM-5 > Pd/H-β; Pd/H-ZSM-5 > Pd/F/H-β ≫ Pd/F/H-M > Pd/H-M. The catalyst reduction (*i.e.*, reduction of PdO to Pd^0) results in a large increase in the H_2 conversion activity of the catalyst with a total loss of its H_2O_2 selectivity in the H_2 oxidation, mostly due to a drastic increase in its H_2O_2 decomposition activity. The presence of an acid in the aqueous reaction medium is essential for obtaining high H_2O_2 selectivity or yield in the H_2-to-H_2O_2 oxidation.

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