

Direct generation of hydrogen peroxide from formic acid and O₂ using heterogeneous Pd/ γ -Al₂O₃ catalysts†

Mohammad S. Yalfani, Sandra Contreras, Francesc Medina* and Jesus Sueiras

Received (in Cambridge, UK) 25th February 2008, Accepted 13th May 2008

First published as an Advance Article on the web 27th June 2008

DOI: 10.1039/b803149e

Hydrogen peroxide formation is achieved with remarkable productivity at ambient conditions (25 °C and atmospheric pressure) in aqueous medium using a heterogeneous catalytic system; formic acid is decomposed in the presence of a continuous flow of O₂ over Pd/ γ -Al₂O₃ catalyst leading to the generation of hydrogen peroxide; the addition of a negligible amount of bromide ion improves the selectivity of the reaction.

Hydrogen peroxide has been known as a benign and efficient oxidant for various purposes such as synthesis of organic compounds, pulp and paper industry, bleaching and also oxidation of organic pollutants in industrial wastewater via the Fenton process. Hydrogen peroxide is industrially synthesized through alkyl anthraquinone as an intermediate from hydrogen and oxygen.¹ Recently, due to negative economic and environmental aspects of this process, there has been strong interest in replacing that with one in which hydrogen peroxide can be produced by direct reaction between H₂ and O₂ or as *in situ* in the reaction media.^{2–4} H₂ and O₂ are among the first choices as substrate for direct generation of hydrogen peroxide,³ what can be considered as an environmentally-friendly process. In this approach, heterogeneous catalysis is recognized as a promising technique, where Pd has shown a significant performance in formation of hydrogen peroxide.³ However, there are some drawbacks in this process, the main ones being the risk of explosivity of the O₂/H₂ mixture and the low solubility of the gases in solution, in particular hydrogen. The use of membranes to separate the reaction mixture⁵ or the use of other sources of hydrogen could overcome these difficulties. Furthermore, the use of *in situ* generated H₂O₂ in oxidation processes^{5,6} would open new possibilities, for which the *in situ* generation should be performed in operating conditions compatible with those of subsequent oxidation reactions. Bortolo *et al.*⁷ found that alcohols can act as reducing agents of palladium complexes with production of hydrogen peroxide. The main drawback of this process is use of a homogeneous catalyst which has problems concerning to separation and recycling of catalyst and products from the reaction medium. Choudhary *et al.*⁸ indicated that hydrazine

can be used as a hydrogen source for production of hydrogen peroxide leading a remarkable selectivity toward hydrogen peroxide. However, this system utilizes hydrazine which is classified as toxic and a possibly carcinogenic compound. It also requires addition of halide ions as prerequisite to proceed. Besides, presence of a mineral acid creating an extremely low pH is of importance in order to stabilize hydrogen peroxide. Recently, the same authors,⁹ proposed hydroxylamine as hydrogen source using Pd/Al₂O₃ catalyst. Although this system is sufficiently simple, hydroxylamine is known to be explosive.

Formic acid is a compound which has not been classified as either carcinogenic or explosive. It can be decomposed according to dehydration (HCOOH → CO + H₂O) or dehydrogenation (HCOOH → CO₂ + H₂).¹⁰ The process over supported-metal catalysts has also been investigated.¹¹ The studies indicated that catalytic decomposition of formic acid is predominantly inclined toward production of hydrogen and carbon dioxide when the process occurs at low temperature (<380 K) and in aqueous medium.^{10,12} Therefore, it could be utilized as a source of hydrogen in hydrogenation processes. Regarding to this fact, Hyde *et al.*¹³ carried out hydrogenation of organic compounds using hydrogen released from decomposition of formic acid. It has also been shown that formic acid can be considered as a promising substitute for H₂ in hydrodechlorination of chlorinated organic compounds.¹⁴

In this work, we perform generation of hydrogen peroxide in aqueous medium from formic acid and oxygen using Pd/ γ -Al₂O₃ catalysts at ambient conditions. This new route could be applied to produce *in situ* H₂O₂ for the subsequent oxidation purposes. Selection of supported-Pd catalyst has been based on its appreciable results in development of hydrogen peroxide formation process and decomposition of formic acid as well.^{3,12} The production rate and the selectivity of the reaction for H₂O₂ at both short and long time are of high importance in this route. The effect of halide ion on the selectivity of the reaction is also studied. According to our knowledge no result concerning to this route for generation of hydrogen peroxide has been published.

The results illustrated in Table 1 show formation of hydrogen peroxide during the reaction of formic acid with O₂ over Pd/ γ -Al₂O₃ catalysts.¹⁵ The reactions were carried out at ambient conditions (25 °C and atmospheric pressure) in aqueous medium for 1 hour using various Pd content catalysts.¹⁶ Without using the catalyst no H₂O₂ was detected through the reaction. The highest short-time production is achieved by the highest Pd content catalyst with 5% Pd. After 1 h reaction,

Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain. E-mail: francesc.medina@urv.cat; Fax: +34 977 559621; Tel: +34 977 559787

† Electronic supplementary information (ESI) available: MS profiles of the outlet gases during decomposition of formic acid in presence and in absence of oxygen over Pd5%/Al₂O₃. See DOI: 10.1039/b803149e

Table 1 H₂O₂ formation results during the reaction of formic acid with O₂ over Pd/ γ -Al₂O₃ catalysts

Catalyst	<i>D</i> ^a (%)	<i>t</i> /h	Formic acid conv./mmol	H ₂ O ₂ formation/ mmol	TOF ^b /h ⁻¹	H ₂ O ₂ selectivity (%)
Pd5/ γ -Al ₂ O ₃	5.8	0.083	0.31	0.0310	15.4	10.0
		1.0	3.60	0.0420		1.2
Pd2.5/ γ -Al ₂ O ₃	12.3	0.083	0.22	0.0135	15.4	6.2
		1.0	3.10	0.0445		1.5
Pd1/ γ -Al ₂ O ₃	19.9	0.083	0.27	0.0135	47.6	5.0
		1.0	2.52	0.0890		3.5
Pd0.5/ γ -Al ₂ O ₃	25.2	0.083	0.18	0.0075	118.2	4.2
		1.0	2.0	0.140		7.0
Pd0.1/ γ -Al ₂ O ₃	26.7	0.083	0.15	0.0037	105.6	2.5
		1.0	1.60	0.0265		1.7

^a Metal dispersion. ^b mmol H₂O₂ mmol(Pd dispersed)⁻¹ h⁻¹.

the highest amount of H₂O₂ produced is obtained by the Pd0.5%/ γ -Al₂O₃ catalyst. This catalyst also presents the highest efficiency, measured as TOF value (118 h⁻¹).

Conversion of formic acid is decreased by reducing the Pd content in the catalysts (Table 1). Selectivity of the reaction for H₂O₂ is calculated as mmol H₂O₂ formed divided by mmol HCOOH converted. According to this, selectivity of H₂O₂ (shown in Table 1) was higher at short time for the catalysts than at long time. However, for Pd0.5%/ γ -Al₂O₃ catalyst the H₂O₂ production showed highest selectivity (7%) at long time (1 h).

The phenomenon can be simply presumed to be first decomposition of formic acid over the Pd catalyst (Scheme 1A). This process is expected to lead to production of H₂ and CO₂ at these conditions as has been proved in the literature.¹² Analysis of the overhead gases of the reaction indicates only O₂ and CO₂. No CO and H₂ peaks were observed in the gas chromatogram. In addition, mass analysis profile of the outlet gases displays only masses related to CO₂ (44), O₂ (32) and 28 as a fragment of CO₂ (see Fig. 1S, ESI†). Only trace amount of MS (2) related to H₂ is observed indicating almost total consumption of released hydrogen. In order to further evidence the above results, we performed the decomposition of formic acid over the catalyst (Pd5%/ γ -Al₂O₃) in Ar atmosphere and observed only CO₂ and H₂ corresponding masses in mass analysis profile of the outlet gases (see Fig. 2S, ESI†). These results confirm that the formic acid decomposition on the catalyst at our reaction conditions rather follows dehydrogenation than dehydration. As second step, the introduced O₂ reacts with released H₂ to form hydrogen peroxide. A side-reaction of water formation is also expected to occur with a significant rate which drastically influences H₂O₂ selectivity.

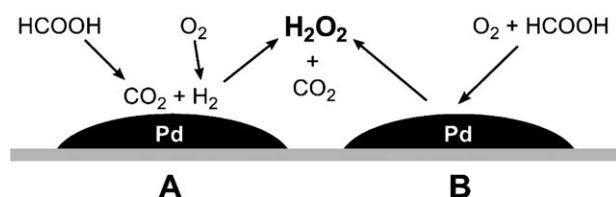
Another assumption that can be considered is the direct reaction of formic acid with O₂ (Scheme 1B) (with different stoichiometries) resulting in H₂O₂ or H₂O (HCOOH + O₂ → H₂O₂ + CO₂ or HCOOH + 1/2O₂ → H₂O + CO₂). In this

case, water formation occurs by direct reaction of HCOOH and oxygen as well as decomposition of hydrogen peroxide. Most importantly, the decomposition rate of formic acid was remarkably higher in comparison with the reaction carried out in the absence of oxygen. Thus, in the presence of oxygen, decomposition of formic acid is accelerated.

In the previous works of generation of H₂O₂, the requirement of halide ion and mineral acid has been stressed in order to achieve the process with high selectivity.^{3,8} As shown in Table 2, addition of different dosages of bromide ion to the reaction medium displays interesting changes in the H₂O₂ production process. First, decomposition of formic acid especially at long time is appreciably diminished. Considering that decomposition of formic acid occurs prior to hydrogen peroxide formation, it could be described that halide ions block the active sites of the catalyst to adsorb formic acid and hamper this trend. In other words, halide ion behaves as a poison for formic acid decomposition reaction. In order to confirm the above hypothesis, we fulfilled the catalytic decomposition of formic acid in Ar atmosphere at 50 °C (to observe clearly the phenomenon) using Pd5%/ γ -Al₂O₃ with and without Br⁻ ion (10⁻⁴ mol). In the presence of Br⁻ the decomposition rate of formic acid was clearly lower than in the absence of Br⁻. A similar trend was observed for the decomposition of H₂O₂, mainly at low Br⁻ content. Consequently, bromide can control decomposition of H₂O₂ and improve its selectivity. As shown in Table 2, by decreasing the concentration of bromide to 10⁻⁵ mol in the reaction medium, H₂O₂ selectivity using Pd5%/ γ -Al₂O₃ reaches a respectable value of 21% at long time. Further decreasing of bromide to 10⁻⁶ mol results again in increasing of formic acid decomposition and thereupon decreasing of H₂O₂ selectivity. H₂O₂ selectivity for the catalysts with lower Pd content (as shown in Table 2) was influenced by bromide but not to the same extent as for Pd5%/ γ -Al₂O₃.

Productivity of the catalysts with lower Pd amount can also be described regarding to their ability to decompose hydrogen peroxide. As shown in Fig. 1, the decomposition rate of hydrogen peroxide is abated by decreasing the Pd amount in catalysts. In other words, hydrogen peroxide molecules demonstrate more resistance when they are exposed to the low Pd catalysts.

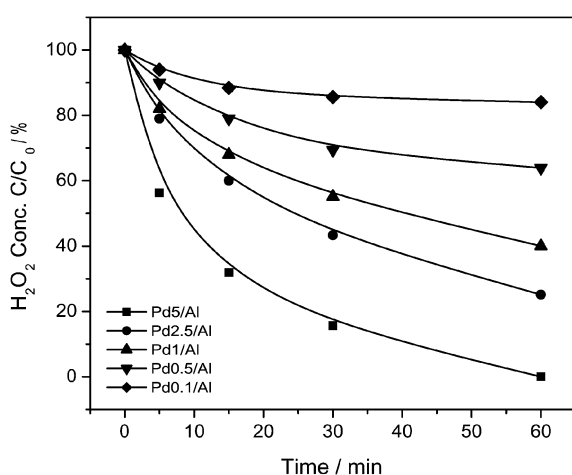
Our catalytic system shows a marked stability property because no Pd leaching was detected in aqueous medium after the end of each run. Hence, the catalyst can be easily recovered at the end of the reaction.



Scheme 1 Suggested approaches toward generation of H₂O₂ from formic acid and O₂ over Pd/ γ -Al₂O₃; A: two steps, B: one step.

Table 2 H₂O₂ formation results during the reaction of formic acid with O₂ over Pd/ γ -Al₂O₃ catalysts in presence of KBr

Catalyst	KBr/mol	t/h	Formic acid conv./mmol	H ₂ O ₂ formed/mmol	H ₂ O ₂ selectivity (%)
Pd5/ γ -Al ₂ O ₃	10 ⁻⁴	0.083	0.22	0.0074	3.4
		1.0	0.36	0.0099	2.8
Pd5/ γ -Al ₂ O ₃	10 ⁻⁵	0.083	0.19	0.0197	10.4
		1.0	0.70	0.1430	20.5
Pd5/ γ -Al ₂ O ₃	10 ⁻⁶	0.083	0.38	0.0445	11.7
		1.0	3.55	0.0670	1.9
Pd1/ γ -Al ₂ O ₃	10 ⁻⁵	0.083	0.28	0.0074	2.7
		1.0	0.43	0.0345	8.0
Pd0.5/ γ -Al ₂ O ₃	10 ⁻⁴	0.083	0.44	0.0025	<1
		1.0	0.54	0.0148	2.8
Pd0.5/ γ -Al ₂ O ₃	10 ⁻⁵	0.083	0.23	0.0123	5.4
		1.0	0.68	0.0271	4.0
Pd0.1/ γ -Al ₂ O ₃	10 ⁻⁵	0.083	0.21	0.0099	4.7
		1.0	0.36	0.0123	3.4

**Fig. 1** H₂O₂ decomposition profile over Pd/ γ -Al₂O₃ catalysts.

As conclusion, we attained a new route to produce hydrogen peroxide with several advantageous properties including simplicity, cleanness and most importantly is environment-friendly. It performs at ambient conditions and in aqueous medium. The productivity and selectivity of the system are noteworthy. In the presence of a negligible amount of bromide ion the selectivity of H₂O₂ increases remarkably. Nevertheless, both productivity and selectivity of the system have still a significant potential for improvement. The decomposition of formic acid to H₂ and CO₂ at ambient conditions,^{10,12} introduces formic acid as eligible replacement for pure hydrogen in the hydrogen peroxide formation process. This hydrogen peroxide generation approach could be proposed to be used for oxidation of organic compounds.

The authors would like to acknowledge URV for the PhD fellowship given to M. S. Y. and funding AIRE 2006/02, and also AEI, ref. A/5188/06. Spanish Ministry of Science and Education is appreciated for the funding given to Dr Sandra Contreras in Ramon y Cajal program.

Notes and references

- W. T. Hess, *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. J. K. Kroschwitz and M. Howe-Grant, Wiley, New York, 4th edn, 1995, vol. 13, pp. 961–995.

- J. M. Campos-Martin, G. Blanco-Brieva and J. L. G. Fierro, *Angew. Chem., Int. Ed.*, 2006, **45**, 6962.
- J. H. Lunsford, *J. Catal.*, 2003, **216**, 455.
- M. G. Clerici and P. Ingallina, *Catal. Today*, 1998, **41**, 351.
- S. Niwa, M. Eswaremoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba and F. Mizukami, *Science*, 2002, **295**, 105.
- Y.-G. Zhang, L.-L. Ma, J.-L. Li and Y. Yu, *Environ. Sci. Technol.*, 2007, **41**, 6264.
- R. Bortolo, D. Bianchi, R. D'Aloisio, C. Querci and M. Ricci, *J. Mol. Catal. A: Chem.*, 2000, **153**, 25.
- V. R. Choudhary, C. Samanta and P. Jana, *Chem. Commun.*, 2005, 5399.
- V. R. Choudhary and P. Jana, *Catal. Commun.*, 2007, **8**, 1578.
- N. Akiya and P. E. Savage, *AIChE J.*, 1998, **44**, 405.
- T. van Herwijnen, R. T. Guzalaki and W. A. de Jong, *J. Catal.*, 1980, **63**, 94.
- E. M. Cordi and J. L. Falconer, *J. Catal.*, 1996, **162**, 104.
- J. R. Hyde and M. Poliakoff, *Chem. Commun.*, 2004, 1482.
- F.-D. Kopinke, K. Mackenzie, R. Koehler and A. Georgi, *Appl. Catal., A*, 2004, **271**, 119.
- The Pd/ γ -Al₂O₃ catalysts were synthesized by conventional incipient wetness impregnation. An aqueous solution of PdCl₂ acidified by hydrochloric acid was added to an aqueous slurry of γ -Al₂O₃ (prepared by sol-gel method) stirring vigorously. The mixture was aged stirring for 1 h, heated under vacuum at 60 °C and eventually dried at 110 °C for 12 h. The precipitate was calcined in static air at 400 °C for 3 h and reduced under a flow of pure hydrogen (20 ml min⁻¹) at 200 °C for 2 h. H₂ chemisorption was performed using a Micromeritics ASAP 2010 apparatus.
- The hydrogen peroxide formation reactions were implemented at ambient conditions ($T = 25$ °C and atmospheric pressure) in a magnetically stirred three-necked glass reactor with a capacity of 100 ml. The volume of the reaction was always 50 ml containing 25 mmol formic acid in H₂O. The amount of catalyst was 0.1 g in all the reactions. Oxygen was passed bubbling into the reaction medium with a flow rate of 20 ml min⁻¹. The temperature of the reaction was controlled using a water-bath. H₂O₂ formation and formic acid decomposition were monitored by sampling at regular time intervals and analysing by iodometric titration and high performance liquid chromatography HPLC (Shimadzu LC-2010 equipped with a Acclaim OA column and SPD-M10A detector and using 100 mM Na₂SO₄ at pH 2.65 adjusted by methanesulfonic acid as mobile phase), respectively. The overhead exhausted gases of the reaction were analyzed online using a gas chromatography (Shimadzu GC-14B with a TEKNOKROMA Propapack R column, TCD detector and He as carrier gas) and a mass analyser (PFEIFFER VACUUM, GSD 301 O₂, Omnistar™). The reaction solution at the end of each run after filtration was analysed by atomic absorption spectroscopy to detect leached Pd. H₂O₂ decomposition reactions were performed at ambient conditions using a 50 ml aqueous solution containing 100 ppm H₂O₂ and 0.1 g catalyst. H₂O₂ degradation was monitored by iodometric titration.