

Progress in performance and stability of a contactor-type Catalytic Membrane Reactor for wet air oxidation

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Catalytic Membrane Reactors combine a membrane that controls transfers and a catalyst that provides conversion. This paper focuses on the catalytic performance stability of interfacial contactor membranes in the wet air oxidation of formic acid. Stable catalytic membranes with high activity have been developed.

KEY WORDS: wet air oxidation; catalytic membrane reactor; contactor; catalytic performance stability; platinum; formic acid

1. Introduction

Wet air oxidation (WAO) can be applied to effluents containing low to medium concentrations of non-biodegradable and toxic compounds, as in these cases incineration is not energy effective, and biological treatments are not adapted. However, acute reactor corrosion problems as well as large reactor volumes, due to high residence time could affect the economy of this technology. An important research effort has been recently focused on the treatment of industrial effluents using catalytic wet air oxidation (CWAO) [1,2]. The main limitation of CWAO lays in the diffusion of the gas reactant down to the solid catalyst as well as to the catalyst recovery and leaching phenomena. The development of new innovative catalytic reactors for WAO is therefore needed.

The use of catalytic membrane reactors (CMRs) could be an option. Among different types of CMRs [3], the contactor CMR is known to favour the triple contact between two different reactant fluid phases and the catalyst. Contactor CMRs offer an improvement over conventional catalysts, as they provide double-mouthed pores, from the two membrane sides. This unique configuration allows very specific feed modes of the reactants to the catalyst. This can lead to higher conversion rates [4]. The membrane structure and properties have to be adapted to the catalytic process, while the active phase deposition must be controlled [5]. A contactor CMR can operate in two different modes: interfacial or flow-through mode [3]. Even if the flow-through mode offer significant advantages as the easy correlation of contact time on process requirements, improvements in activity [6] and selectivity [7] being possible, the interfacial contactor mode seems to be more adequate to the WAO process.

In the *interfacial contactor* mode, the gas and liquid reactants are separately introduced within the membrane from opposite sides. The gas–liquid interface is then located within the membrane by means of the trans-membrane differential pressure that is compensated by the capillary pressure of the liquid within the membrane pores. Detailed investigations of mass-transfer in three phase processes on membrane catalytic contactors, as well as of the effects of the gas–liquid interface location within the membrane wall on the overall process performance have been thoroughly reported [8–10].

Despite limited literature data, the CMR efficiency in water remediation has been demonstrated: the removal of nitrate [11], nitrite and pesticides from contaminated water by catalytic hydrogenation as well as the chlorinated hydrocarbon dehalogenation, using Pd supported on inorganic membranes, has been reported [12]. Contrary to conventional reactors, for which high pressures are needed to increase hydrogen concentration in the organic solvent, a contactor CMR may operate at lower gas pressures. The safety improvements due to phase separation, as well as the ability to control catalytic activity more closely, were found to be crucial advantages of this technology [12]. The development of contactor CMRs for the wet air oxidation of wastewaters is part of a European Project [13].

An environmental application of CMRs, wet air oxidation of wastewaters using interfacial contactors, was previously reported by the authors of this work [10,14–16]. Formic acid oxidation was used as a model reaction to study the catalytic performance of Pt impregnated membranes in interfacial contactor CMRs. A comparative study of the catalytic performance using CMRs and conventional reactors, under the same reaction conditions, has been reported. However, deactivation phenomena had been observed. Since then, intensive research efforts have been devoted to optimising the operating reactor modes and to developing stable catalytic membranes for this process.

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2. Experimental

2.1. Materials

The membranes used for this work have a tubular geometry with an external diameter of 10 mm, an internal diameter of ca. 7 mm and a length of 100 or 250 mm. The membranes are composed of four concentric layers (figure 1) showing an average pore size decreasing from the outside to the internal surface of the tube. The top-layer is located on the inner surface of the tubes. In order to achieve a proper sealing and smooth the surface where the o-rings seals are applied, both endings of the membranes have been covered (ca. 1.5 cm on each side) with poly(fluoroethylenepropylene), enamel or glaze. The ceramic membrane supports were provided by TAMI (France), PALL EXEKIA (France) and INOCERMIC (Germany). Several characteristics regarding the structure of these membranes are shown in table 1.

H_2PtCl_6 (39.85% Pt, Strem Chemicals) has been used as platinum precursor to prepare the catalytic membranes. Formic acid (95–98%, Riedel-de Haen) has been used to prepare the solutions tested during this work.

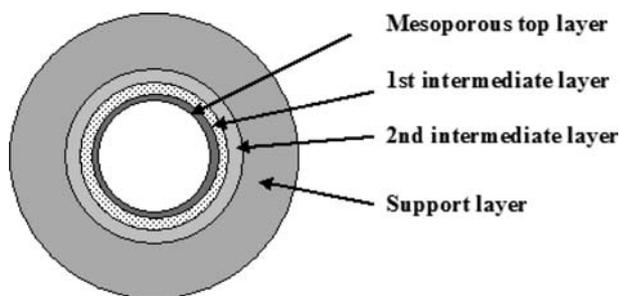


Figure 1. Schematic cross-section of the membrane showing the four-layer structure.

2.2. Catalytic membrane impregnation

The impregnation of the membrane supports has been carried out using either an anionic impregnation or an evaporation–crystallization technique. Details regarding the synthesis procedure have been already reported in our previous studies [17,18]. Let us briefly summarise here the evaporation–crystallization technique. Before impregnation, all the tubes were dried in air at 170 °C for 24 h. The samples were then soaked overnight under mechanical stirring (60 rpm), in a vertical position, within an H_2PtCl_6 precursor solution. The samples were then kept in horizontal position at room temperature under air and rotated (60 rpm) in order to allow the solvent evaporation and a uniform distribution of the precursor. Further drying has been made in nitrogen flow (60 mL min^{-1}) at 100 °C for 1 h. The impregnated membranes have been calcined overnight at 200 °C (heating rate 1 °C min^{-1}) in order to decompose the platinum precursor. The gas flux was then switched to hydrogen (60 mL min^{-1}) for 6 h, in order to reduce the Pt species to metal 60 mL min^{-1} nanoparticles. For a given metal loading, TEM characterisations showed that Pt dispersion was similar whatever the support membrane type [16,18].

2.3. Catalytic set-up

The tubular membrane was mounted in a membrane reactor using a tight seal separating the liquid and gas feeds. Two modes have been used, depending on the location of the fluids related to the membrane, the gas feed being on the inner tube side (mode 1) or on the shell side (mode 2). The liquid phase was maintained at atmospheric pressure or slightly above it. The gas overpressure was monitored and carefully controlled using a pressure-difference gauge connected to a PID regulator, acting on the gas feed through a mass-flow

Table 1
Porous structure of the 3 ceramic membrane types used in this work

Membrane structure	Membrane A (TAMI)	Membrane B1 (INOCERMIC)	Membrane B2 (PALL EXEKIA)
Top layer			
Composition	TiO_2	$\text{CeO}_2/\text{ZrO}_2$	ZrO_2
Thickness	1–2 μm	3 μm	3 μm
Pore size	5–6 nm	80 nm	20 nm
1st intermediate layer			
Composition	$\text{TiO}_2/\text{ZrO}_2$	TiO_2	$\alpha\text{-Al}_2\text{O}_3$ covered by TiO_2
Thickness	5 μm	20 μm	20 μm
Pore size	0.1 μm	0.25 μm	0.2 μm
2nd intermediate layer			
Composition	TiO_2	TiO_2	$\alpha\text{-Al}_2\text{O}_3$ covered by TiO_2
Thickness	20–30 μm	30 μm	30 μm
Pore size	0.5 μm	0.8 μm	0.8 μm
Support layer			
Composition	$\alpha\text{-Al}_2\text{O}_3/\text{ZrO}_2/\text{TiO}_2$	TiO_2	$\alpha\text{-Al}_2\text{O}_3$ covered by TiO_2
Thickness	2 mm	1.5 mm	1.5 mm
Pore size	5 μm	5 μm	12 μm

controller (figure 2). In mode 2, according to Laplace's law, a gas overpressure was used to displace the gas–liquid interface by flushing the liquid through the pores of the different layers, in order to bring it as close as possible to the active top-layer [9].

The membrane reactor operated either in continuous mode, the liquid being passed continuously through the reactor, or in recycling mode, the liquid phase being recycled into the reactor for a total volume of 300 mL. The initial concentration of formic acid was 5 g/L. The gas overpressure stationary state was reached using nitrogen, before switching to air to start the oxidation.

The conversion of formic acid was monitored using a Total Organic Carbon analyser Shimadzu TOC 5050A. In order to continuously follow the conversion of formic acid, when the reactor was operated in recycling mode, a high precision pH-meter (Hanna Instruments pH 301) was used as well.

3. Results and discussion

Beside the experimental conditions, the performance of the interfacial catalytic contactor will be function of a series of parameters, like the respective positions of the catalyst zone and the gas–liquid interface, the transfer resistance of reactants and products, deactivation phenomena, etc. Optimal conditions have been sought depending on the different membrane material studied.

3.1. Membrane A

As a first mode, the interfacial contactor has been used with the gas reactant flowing in the lumen, the liquid being introduced in the shell side (mode 1). Due to the capillary forces, the liquid penetrates up to the internal surface of the tube, where the catalyst is located. In this way, the gas–liquid interface is close to the active

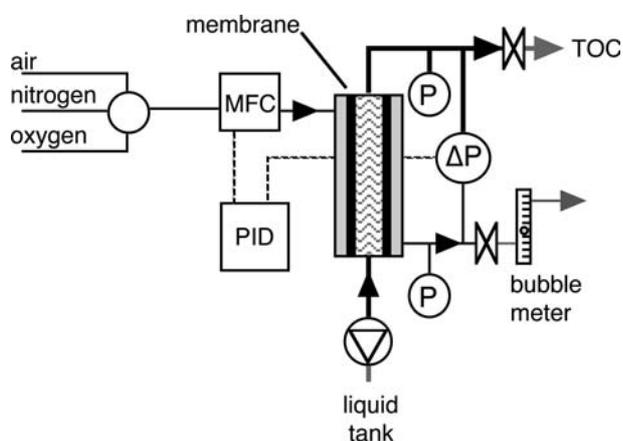


Figure 2. Schematic diagram of the set up (MFC: Mass Flow Controller, PID: regulator, P: pressure sensor, ΔP : differential pressure sensor, TOC: Total Organic Carbon analysis). Mode 2 (liquid in contact with the top-layer), continuous operation.

phase, which should facilitate the access of the gas reactant to the catalyst. Moreover, this situation should be stable, as high gas overpressures would be needed to push the liquid out of the active top layer when defect-free. As a matter of fact, according to Laplace's law, these pressures could be as high as 40 MPa for 5-nm pores.

For this contactor mode, at room temperature and with a gas overpressure of 120 kPa, the initial reaction rates were in the range 0.6–0.9 $\text{mmol s}^{-1} \text{g}_{\text{Pt}}^{-1}$ [15]. This performance has to be compared to the rate of 0.2 $\text{mmol s}^{-1} \text{g}_{\text{Pt}}^{-1}$ achieved in a conventional slurry reactor using the same catalytic material in a powder state under the same reaction conditions (temperatures, pressures, concentrations, catalyst loading, etc.). It has been also checked up that the slurry reactor operated in chemical regime (ideally stirred reactor) [15]. This suggests the CMR may lead to a significant improvement of the overall catalytic process. As stressed in the introduction, the advantage of the interfacial contactor was attributed to the facilitated access of the gaseous reactant. Another hypothesis explaining the better performance of the contactor, would be an effect of gas solubility increase, due to the presence of the gas–liquid interface in the active mesopores [15].

However, as shown in figure 3, the high initial reaction rate was followed by a rapid decrease of the catalyst activity. Two distinct deactivation mechanisms were identified. The first was rapid (a few hours) and reversible, as the catalyst could be regenerated by a thermal treatment under hydrogen. In parallel to this first mechanism, a second deactivation process occurred, that was shown to be much slower and irreversible. Due to this second mechanism, the activity following a regeneration decreased when compared to that observed after the previous regeneration. Progressively, the activity after regeneration fell to zero, as shown in table 2.

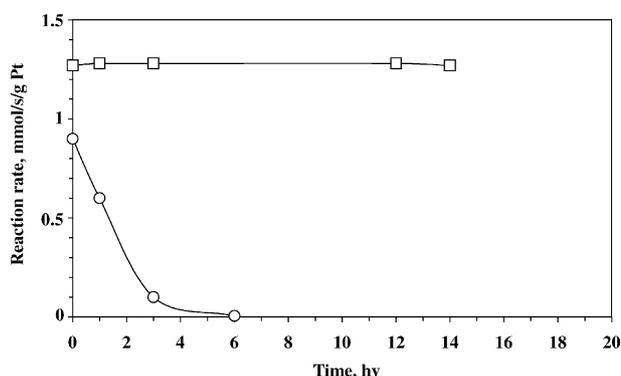


Figure 3. Reaction rate ($\text{mmol s}^{-1} \text{g}_{\text{Pt}}^{-1}$) as a function of time during the oxidation of formic acid in an interfacial contactor Catalytic Membrane Reactor at 20 °C, using Pt-impregnated membranes: membrane A (o); membrane B1 (■).

The first mechanism was attributed to an excess of oxygen on the active surface, as suggested by Dijkgraaf *et al.* [19] and was likely linked to the above-mentioned high oxygen concentration and easy gas transfer. In this mode, the membrane reactor seems to be adversely affected by its own conception.

The second deactivation mechanism was attributed to fouling of the active layer, as a parallel drastic decrease of the membrane permeance was observed (from about $30 \mu\text{mol s}^{-1} \text{m}^{-2} \text{Pa}^{-1}$ to 0). Due to the somewhat limited chemical resistance of the $\alpha\text{-Al}_2\text{O}_3$ in acidic media, there was likely formation of aluminium formiate species that were decomposed during oxidation within the active layer, leading to its fouling and a progressive activity decrease. As shown in figure 4, the presence, after reaction, of high aluminium contents in the top-layer (initially exempt of Al) was confirmed by EDS analyses [14].

To avoid the short-term deactivation, i.e. reducing the local oxygen concentration within the catalytic pores, it was suggested to use the other contactor feeding mode, liquid inside the tube, gas outside (mode 2). In this mode, a gas overpressure will control the position of the gas–liquid interface with respect to the active top-layer. An

increase of the gas pressure will move the interface inside the macroporous layers towards the catalytic mesoporous top-layer. In this way, the gas pressure will regulate the diffusion path of oxygen and then its transfer and concentration in the active layer. However, due to some technical problems with the seals and the membrane structure, the application of a sufficient gas overpressure resulted in gas leakages in the liquid phase. Therefore, mode 2 was not possible with membranes of type A.

3.2. Membranes B

These materials do not contain alumina, or do not present alumina in contact with the reactants (see table 1). If the long-term deactivation is originated by alumina, they present a clear advantage when compared to the membranes of type A.

Moreover, as we suspected that high oxygen concentrations may also contribute to the deactivation, it has been decided to use these membranes using the mode liquid inside, gas outside (mode 2). Furthermore, when compared with the other mode (mode 1, gas inside, liquid outside) the position of the gas–liquid interface inside the macroporous layers may give additional benefits from the shorter diffusion path of reactants and products in the liquid phase [8, 9] and by the limited amount of membrane material in contact with the acidic medium. Finally, as industrial effluents may contain particulates, this feeding mode will limit membrane fouling.

The sealing and the porous structure of membranes B are adapted to withstand gas overpressures up to few atmospheres. According to Laplace's law, at gas overpressures above 150 kPa, the liquid phase should be displaced from the support into the second intermediate layer. At 360 kPa, the gas–liquid interface should be located at the boundary between the first and the second intermediate layers. It can be moved to the edge of the mesoporous catalytic top layer at gas overpressures close to 1400 kPa.

Experiments using gas overpressures up to 400 kPa were carried out at room temperature, the gas–liquid interface being controlled efficiently (no gas bubble in the liquid exit of the contactor). For these conditions, both membranes of type B showed a similar behaviour. As indicated in figure 3, catalytic membranes B demonstrated a stable activity, in contrast to membranes A, which, due to their rapid (reversible) deactivation were inactive after a few hours time-on-stream. According to our hypothesis, this stability is due to the regulated oxygen transfer occurring when using mode 2, which prevented the poisoning effect of an oxygen excess. Other experiments, carried out at 80 °C (similar gas overpressure) confirmed the stability of the membranes B for such reaction times.

Membranes B were also stable for long times on stream. Table 2 shows, that after 100 h reaction, they

Table 2
Catalytic activity ($\text{mmol s}^{-1} \text{g}_{\text{Pt}}^{-1}$) as a function of time on stream

Time on stream, (h)	Initial	100	240
Membrane A ^a	0.9	0.5	<0.1
Membrane B1	1.3	1.3	–

^a Catalytic activity measured after a regeneration step.

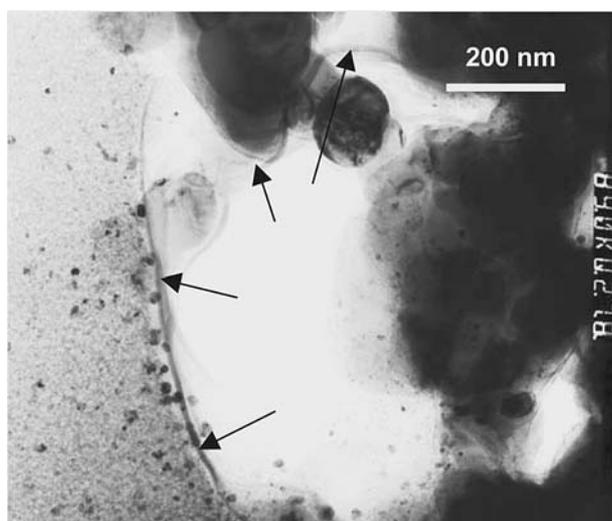


Figure 4. TEM-micrograph showing the interface between the top mesoporous layer and the second intermediate layer for a Pt-impregnated membrane A. The arrows indicate the presence of an amorphous film deposit [14].

kept their initial activity, when membranes A lost more than 40% and are almost totally inactive after ca. 200 h of reaction. This long-term stability of membranes B is likely due to the fact that their compositions are adapted to withstand such acidic media.

4. Conclusion

It has been shown that the performance of an interfacial catalytic membrane contactor in a WAO model reaction depends on various parameters. The membrane should be made of materials presenting a pore size distribution that allows the application of a controlled reactant pressure without direct gas–liquid mixing. This is necessary to rule and adapt the position of the gas–liquid interface with respect to the catalytic layer, which allows the optimization of reactants and products transfers. In this study, it has been shown that the combination of an adapted feeding mode and of materials that withstand the reaction medium resulted in a stable catalytic activity.

When compared to a conventional slurry reactor, the contactor CMR showed a promising performance. This suggests that reaction conditions, in terms of pressure and temperature, might be significantly improved over the existing wastewater treatment technology. Significant recent advances in performance prompt us to consider industrial up-scaling [13,20]. Moreover, its continuous operating mode is another advantage when industrial application is considered.

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