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Catalytic membrane structure influence on the pressure effects in an interfacial contactor catalytic membrane reactor applied to wet air oxidation

Eduard Emil Iojoiu [a], John C. Walmsley [b], Henrik Raeder [c],
Sylvain Miachon [a,*], Jean-Alain Dalmon [a]

[a] Institut de Recherches sur la Catalyse-CNRS, 2 Av. A. Einstein, 69626 Villeurbanne, France
[b] SINTEF, Richard Birkelands vei 2B, NO-7465 Trondheim, Norway
[c] SINTEF, P.O. Box 124 Blindern, NO-0314 Oslo, Norway

Abstract

This paper deals with the influence of catalytic membrane structure on the way the gas pressure affects the efficiency of a catalytic membrane reactor (CMR). The CMR is an interfacial contactor, used for wet air oxidation, formic acid solution and air being fed separately from both sides of the catalytic membrane. The gas overpressure can shift the gas–liquid interface into the membrane wall, closer to the catalytic zone, and therefore greatly increase the reaction rate. It has been confirmed that this was not an oxygen partial pressure effect. When compared to a conventional slurry reactor, the contactor CMR showed a reaction rate more than three times higher.

Keywords: Wet air oxidation; Catalytic membrane reactor; Interfacial contactor; Platinum; Operating conditions; Porous structure; Formic acid

1. Introduction

Freshwater resources are now regarded as an essential component for the quality of human life. Less than 1% of earth's water is usable by humans. Considering that the main part of this usable water consists of ground water that is out of direct reach, preserving fresh water supplies by adapting human activities and protecting these resources against pollution is now one of the major objectives of international environmental politics. Keeping in mind the strong connection between water quality and human health, severe regulations nowadays stipulate the quality of wastewater that can be returned into the initial freshwater supply. Therefore, any pollution from domestic, industrial or agriculture use must be eliminated using low cost technologies.

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 may not be adapted.

Non-catalytic WAO processes require high temperatures and pressures (up to 300 °C/200 bars), and are therefore considered as high energy-consuming processes. The use of large reactor volumes and acute reactor corrosion problems could affect the economy of this technology as well.

On the other hand, catalytic wet air oxidation (CWAO) seems to be a very attractive technique for the treatment of industrial effluents. The main limitation of CWAO lies in the diffusion of the gas reactant down to the solid catalyst, as well as in catalyst recovery and leaching phenomena. Therefore, the development of new innovative catalytic reactors for CWAO, in order to improve the gas/liquid/solid contact, is needed. The use of catalytic membrane reactors (CMRs) could be an option, the synergy of the catalyst and the membrane, when implemented in the same device, providing a significant advantage, as noted for hydrogenation by other authors [1–4]. However, to the best of our knowledge, there are few other works in the literature of contactor CMR use for oxidation reactions [5].

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* Corresponding author. Tel.: +33 4 72 44 53 84; fax: +33 4 72 44 53 99.
E-mail address: smiachon@catalyse.cnrs.fr (S. Miachon).

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Previous publications from our group sorted catalytic membrane reactors into three types, according to the role of the membrane: extractors, distributors and contactors [6–10]. The interfacial contactor type seems the most appropriate for the CWAO processes. In this mode, the gas and liquid reactants are separately introduced into the membrane from opposite sides. The gas–liquid interface is then located within the membrane by mean of a trans-membrane differential pressure that compensates the gas/liquid capillary pressure within the membrane pores. This configuration favours three-phase contact, leading to a better accessibility of the reactants to the catalyst that can improve the conversion rates [6,11–13]. The membrane structure and properties have to be adapted to the catalytic process, while the active phase deposition must be controlled [14,15].

The development of contactor CMRs for wet air oxidation of wastewaters is part of the European Project WATERCATOX [16]. Formic acid oxidation was used as a model reaction to study the catalytic performance of Pt impregnated membranes in interfacial contactor CMRs. Intensive research efforts have been devoted to optimise the operating reactor modes and to develop stable catalytic membranes for this process [6,7,11,17,18]. The present work presents a study of the influence of the catalyst nature and operating conditions on the catalytic performance of such a system.

2. Experimental

2.1. Materials

The membranes used for this work are tubular, of 10 mm external diameter, 7 mm internal diameter and 250 mm length. The membranes are made of three or four concentric zones (Fig. 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 soften 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 enamel or glaze. The ceramic membrane supports were provided by PALL EXEKIA (France) and INOCERMIC (Germany). Several characteristics regarding the structure of these membranes are shown in Table 1, including the capillary pressure corresponding to the pore size of each layer, as obtained from Laplace’s law, assuming perfect wetting and mono-disperse cylindrical cross-section. Whereas these assumptions are a simplification of the real case, the values obtained give a correct order of the capillary pressure applicable to each layer.

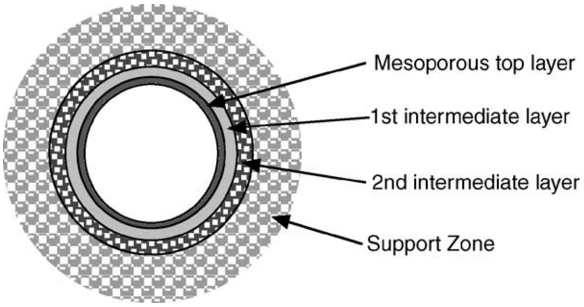

Fig. 1. Schematic cross-section of the membrane showing the layer structure. Two intermediates layers are shown, whereas one of the samples presented in this work only had one.

H_2PtCl_6 (39.85% Pt, Strem Chemicals) was used as a platinum precursor to prepare the catalytic membranes. Formic acid (95–98%, Riedel-de Haen) was used in the solutions treated during the catalytic tests.

2.2. Catalytic membrane preparation

The catalytic performance should depend strongly on the loading and the location of platinum in the membrane. Therefore, the preparation procedure had to be adapted to the catalytic process. Details concerning different possibilities for a controlled deposition in the pores of a ceramic membrane are presented elsewhere [7,14,15,19]. In this work, catalyst deposition into the membrane support pores has been carried out using evaporation–crystallization technique.

The samples were soaked with an H_2PtCl_6 precursor solution and then dried in air in order to allow the solvent to evaporate and to reach a uniform distribution of the precursor. During the evaporation step, a progressive concentration of the platinum precursor solution towards the top layer of the membrane is presumed. This allowed the platinum particles to concentrate mainly into the top layer [13]. The impregnated membranes have then been calcined at 200 °C in order to decompose the platinum precursor. The gas flux was then switched to hydrogen, in order to reduce the Pt species to metal nano-particles.

2.3. Characterization

Gas permeation measurements were performed before and after Pt deposition using a conventional set-up [14]. The estimation of the amount of platinum deposited within the wall of the membrane was based on both the mass uptake during deposition and the quantity of precursor solution absorbed within the pores during the soaking step. The results obtained through these two methods were found to be in good agreement.

The impregnated membranes were characterised by electron probe micro-analysis (EPMA) and BackScattered Electron (BSE) imaging using a JEOL JXA-8900 Superprobe. The samples for EPMA analysis were prepared by standard metallographic procedures, mounting in resin, grinding on silicon carbide paper, followed by a final polish using diamond paste. The samples were coated in a thin layer of carbon to eliminate charging. EMPA elementary maps were performed at ~2000× magnification with an

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

Membrane structure	Membrane IN INOCERMIC	Membrane PE1 PALL EXEKIA	Membrane PE2 PALL EXEKIA
Top layer			
Composition	CeO_2/ZrO_2 covered TiO_2	ZrO_2	ZrO_2
Thickness (μm)	8	2	6
Pore size (nm)	≈80	20	50
Capillary pressure (bar)	*36*	*144*	*58*
First intermediate layer			
Composition	TiO_2	TiO_2 covered α-Al_2O_3	–
Thickness (μm)	27	14	–
Pore size (μm)	0.25	0.2	–
Capillary pressure (bar)	*11.5*	*14.4*	–
Second intermediate layer			
Composition	TiO_2	TiO_2 covered α-Al_2O_3	TiO_2 covered α-Al_2O_3
Thickness (μm)	46	20	15
Pore size (μm)	0.8	0.8	0.8
Capillary pressure (bar)	*3.6*	*3.6*	*3.6*
Support zone			
Composition	TiO_2	TiO_2 covered α-Al_2O_3	TiO_2 covered α-Al_2O_3
Thickness (mm)	1.5	1.5	1.5
Pore size (μm)	5	12	12
Capillary pressure (bar)	*0.6*	*0.24*	*0.24*

For each pore size, the corresponding capillary pressure calculated from Laplace's law is provided. The layer thickness was obtained by scanning electron microscopy.

accelerating voltage of 15 kV and a step size of 0.5 μm. Normalized Pt levels were measured for each sample. The samples were also examined at higher spatial resolution in the scanning electron microscope, but these observations are not reproduced here.

2.4. CMR catalytic set-up and experiments

The tubular membrane was mounted in a membrane reactor using a tight seal separating the liquid and gas feeds. The gas phase was fed on the shell side. The liquid phase was introduced on the inner tube side and was maintained close to atmospheric pressure. The gas overpressure was monitored and carefully controlled using a pressure-difference gauge connected to an electronic regulator, acting on the gas feed through a mass-flow controller (50 ml_N/min). The membrane reactor operated in continuous liquid flow mode (close to 7 ml/min). The gas overpressure steady state was reached using nitrogen, before switching to air to start the oxidation. The initial concentration of formic acid was 5g/l. All experiments were carried out at room temperature (20 °C).

The conversion of formic acid was monitored using a Shimadzu TOC 5050A total organic carbon analyser. The reaction rate presented in CMR experiments is related to the membrane area, as the membrane area is the cost-limiting factor of such a process. For the purpose of comparison with the conventional reactor, it can also be related to the mass of active phase. Taking into account Laplace's law on capillary pressure, the gas–liquid interface can be displaced from the support zone towards the top layer, where the catalyst is located, by increasing the gas overpressure. For optimal control, the sealing and porous structure of the membrane and the reactor design were adapted to withstand gas overpressures up to a few atmospheres. Catalytic experiments were carried out at gas overpressures up to 5 bars.

2.5. Conventional reactor operation

The wet air oxidation of formic acid was also carried out in a conventional, ideally stirred (1200 rpm), batch reactor under conditions similar than in the CMR. An initial solution of formic acid 5 g/l was oxidised using air under 3.6 bar air overpressure at 20 °C. Particular attention was given to the catalyst preparation. In order to avoid any bias, material was removed from a CMR membrane by scraping the tube top layer. This made sure that the very same catalytic material was used in both CMR and conventional reactor configurations. An IN membrane was loaded with a lower amount of platinum than the sample described in Table 1 (1 mg Pt), to ensure that the whole platinum was concentrated into the top layer. The $Pt/CeO_2/ZrO_2/TiO_2$ obtained by scraping was used in the batch reactor.

3. Results

3.1. Catalytic membrane characterisation

The structures of the ceramic membranes do not seem to be modified after platinum deposition, as only negligible changes in the nitrogen permeance values were detected.

The deposited platinum level was found to be similar in the three membranes: 27 mg Pt in the case of the IN membrane and 35 mg Pt for the PE samples.

Fig. 2 shows BSE images and EPMA Pt and Zr maps of the three membranes after Pt deposition. It should be pointed out that the backscattered images were recorded using a small probe size to show accurate detail of the microstrucure. For mapping, a much larger beam diameter and higher probe current were used, to generate a strong analytical signal. As a result, the apparent top-layer thickness is greater in the maps than in the backscattered images, due to a corresponding loss of spatial resolution.

As mentioned earlier (see Table 1), the layer thicknesses of the three membranes are different, as the intermediate and top layers were seen to be thicker on the IN membrane. The PE2 membrane offers, from this point of view, the shorter distance of only 15 μm between the support zone and the top layer. As for the elemental distribution across the membrane wall, one can note two major differences.

In the case of the ceria doped zirconia IN membrane, Zr is seen to infiltrate the first intermediate layer to a significant degree. On PE membranes, on the other hand, the zirconia distribution appears more restricted to the actual top layer. One can also note the deeper extension of Pt in the IN than in PE membranes, extending into the first intermediate layer. On the contrary, PE membranes show Pt more localised in the rather thin top layer. Of course, the display of the EPMA maps is qualitative but these observations were confirmed by EPMA profiles [15]. In any case, the low concentration Pt that may be spread over the rest of the membrane wall would not provide a large catalytic activity: SEM observations, not reproduced here, show that where Pt lies outside the top layer, it is present in coarse intergranular clusters which will present a much lower catalytic surface area relative to the separate nano-particles in the top layer.

3.2. Catalytic results in CMR

3.2.1. IN membranes

The rate of formic acid oxidation by air is presented on Fig. 3, as a function of air overpressure, in the case of the IN (Inocermic) membrane. This graph also shows the theoretical boundaries of capillary pressures between the layers, as defined in Table 1. The reaction rate increases with air

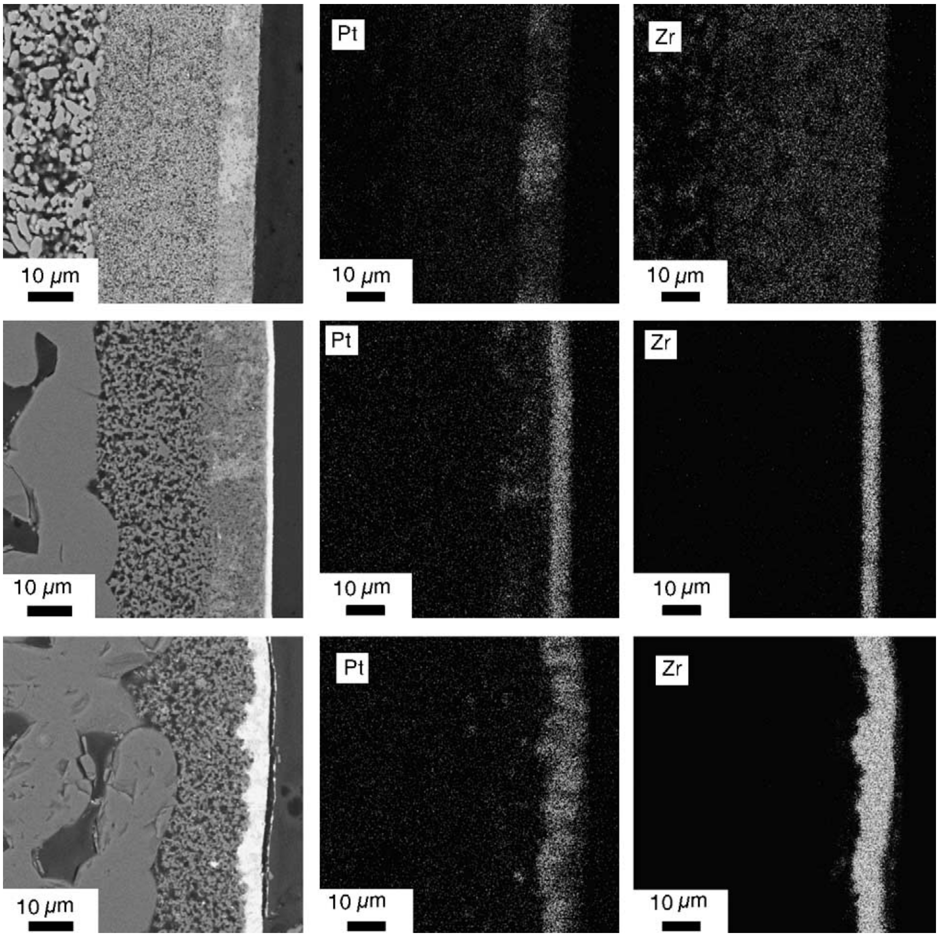

Fig. 2. BSE cross-section (left) and electron probe micro-analysis (EPMA) mapping showing the location of platinum (middle) and zirconium (right) for Pt impregnated IN (top), PE1 (middle), and PE2 (bottom) membranes. Due to the way the data are acquired, there is a slight difference in magnification and field of view between the backscattered images and the composition maps.

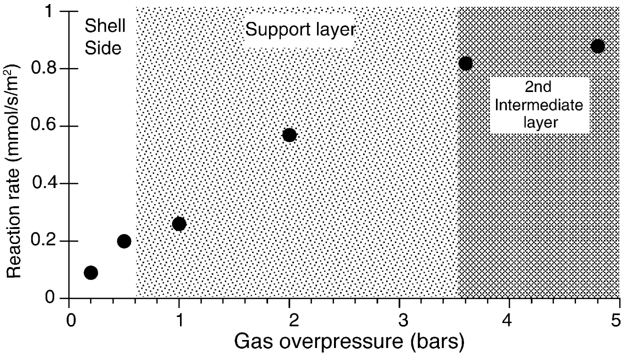

Fig. 3. Reaction rate (mmol/(s m^2)) as a function of gas overpressure (air) during the oxidation of formic acid in an inter facial CMR at 20 °C, using Pt-impregnated IN (four layer, 27 mg Pt) membrane. The white, light grey and dark grey pressure zones show the location of the gas–liquid interface as a function of gas overpressure, as assumed from Laplace's law.

pressure, up to 0.9 mmol/(s m^2). The curve increases approximately linearly up to 3.6 bar pressure and flattens above this value.

3.2.2. PE membranes

PE membranes of both types (three and four layers) show a catalytic behaviour similar at low pressures, but quite different at higher pressure, as presented in Fig. 4. At 4.8 bars, the three-layer catalytic membrane exhibits a large increase in catalytic activity when compared to the previous values obtained at 3.6 and 4.5 bars, whereas its four-layer counterpart activity remains stable over this pressure range. Moreover, in both cases steps are clearly visible in the reaction rate curve.

3.3. Conventional reactor result

Batch operation in the conventional reactor leads to a catalytic activity of 0.3 mmol/(s g_{pt}) under 3.6 bar air overpressure. This value can be compared to the results obtained on the very same material in membrane form (IN low loading membrane) in similar conditions. Relating activity to the mass of metal, the CMR showed an activity of 1.1 mmol/(s g_{pt}).

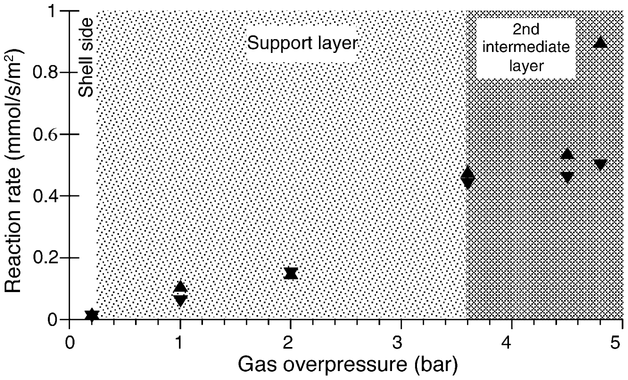

Fig. 4. Reaction rate (mmol/(s m)) as a function of gas overpressure (air) during the oxidation of formic acid in an inter facial CMR at 20 °C, using Pt-impregnated (▼) PE1 (four layer, 35 mg Pt) and (▲) PE2 (three layer, 35 mg Pt) membranes. The white, light grey and dark grey pressure zones show the location of the gas–liquid interface as a function of gas overpressure, as derived from Laplace's law.

4. Discussion

Before making any comment on the form of the pressure effect curves presented, we must stress the fact that using pure oxygen instead of air did not increase the kinetics of the CMR by more than 10–20%, in the same conditions of temperature and total pressures. Therefore, the gas overpressure influence on the reaction kinetics shown in Figs. 3 and 4 can be reasonably attributed to a shift of the gas–liquid interface within the membrane wall, as suggested by previous studies [11,17,20].

4.1. IN membranes

To illustrate the concept of gas–liquid interface shift, Fig. 3 shows three pressure zones. On the left hand side, below 0.6 bar, the air overpressure is still below the Laplace capillary pressure for 5 μm pores. Therefore, one can, on average, assume that the interface is kept at the external surface of the tube. At this point, the diffusion path length of oxygen to the catalytic zone is a maximum, and therefore, the kinetics of the CMR quite slow. As one increases the pressure, the interface is shifted deeper within the large pores of the support wall, as precisely studied by Vospernic et al. [17], thus decreasing the diffusion path for oxygen and therefore increasing the reaction rate. At some point, corresponding to the average pore size of the next layer (0.8 μm pore size, close to 3.6 bar capillary pressure), the interface would reach that layer.

Depending on the pore size radial distribution of the layer, the interface is kept somewhere within that layer, or, if all the pores are flushed out, at the limit of the first intermediate layer. As it is very difficult to precisely estimate this radial distribution, the real position of the interface at pressures between 3.6 and 5 bars (the dark grey zone of Fig. 3) is not certain. Laplace's law is valid for perfect capillaries, while membranes layers present interconnected pores with a certain size distribution. This pressure range might mean any location from the upper to the lower limit of the second intermediate layer. Indeed, moving the interface deeper into the first intermediate layer would mean applying a gas overpressure corresponding to its capillary pressure, i.e. close to 11 bars.

Nevertheless, as the pore size is abruptly reduced from 5 down to 0.8 μm, it can be expected that the linear influence of gas overpressure over the gas–liquid interface location is lower than that in the support zone. This would explain the change of shape of the reaction rate curve in the high-pressure zone.

4.2. PE membranes

What is described above can be applied qualitatively with no major objection to membrane PE1. However, the behaviour of the PE2 membrane might contribute to a better understanding of the interface location at pressures of 3.6 bars and above. As mentioned for the IN membrane, the influence of pressure on the actual interface location within the PE1 second intermediate layer would be moderate. Moreover, the interface shift would be blocked once it reached the first intermediate layer.

On the other hand, in membrane PE2, a thinner second intermediate layer, and especially the absence of an additional intermediate layer before the catalytic zone, makes the situation quite different. It can be suggested, in this case, that the sudden increase in reaction rate above 4.6 bars would correspond to the actual flushing of all or part of the 0.8 μm layer. In the PE1 membrane, this would still maintain the gas–liquid interface at a respectable distance from the catalytic layer of at least 14 μm (the thickness of the next layer plus some current layer). On the other hand, in the PE2 membrane, the interface would then be shifted into contact with the catalytic top layer, reducing the oxygen diffusion path towards zero, hence the observed reaction rate increase.

4.3. Comparisons

As can be seen in Figs. 3 and 4, the IN catalytic membranes offer higher conversion rates at lower pressure range. Even if it is quite difficult to compare such different materials, several arguments can be put forward to explain this.

First, the catalytic phase is different. The contribution of the catalyst support to catalytic activity may be important in some cases. As described in previous work on WAO [21], ceria doped zirconia gives a higher catalytic activity than pure zirconia to the supported metal. A second argument can take into account the larger depth of Pt distribution. A wider catalytic zone may help to shorten the diffusion path of oxygen. Third, the pore size radial distributions of the IN and PE layers may be different. This could smooth the gas–liquid interface shift. Finally, the larger top layer pore size may also have a significant influence. As described in a previous article from this project [20], the reaction rate is limited by the diffusion of oxygen into the liquid phase, down to a critical distance between the gas–liquid interface and the membrane catalytic zone. When the interface reaches this depth, the reaction rate may then be limited by the diffusion of formic acid in the liquid phase into the porous network of the catalytic zone. Therefore, one can expect that a larger pore size in this zone may accelerate formic acid diffusion from the liquid side of the membrane, favouring the reaction.

4.4. Comparison with conventional catalyst

Comparing catalytic results between conventional batch reactors and CMRs may be problematic. First of all, the catalytic activity of the membranes are reported with respect to their surface area, as it is the main investment costs, whereas powder catalyst activity is usually reported with respect to the mass of precious metal. In the case of high loading membranes (such as the ones presented above), part of the platinum is spread over the whole thickness of the membrane wall, which is not the case in low loading membranes. As was mentioned earlier, by using a low loading membrane, one can be sure that the amount of platinum is the same in the membrane and the powder obtained by scraping the top layer. These arguments give reason for the comparison in favour of the CMR, being more than three times more active than the conventional batch reactor in similar conditions. The CMR seems to allow a better oxygen transport to the active sites, by shortening its diffusion path. This is made possible by the specific configuration of the membrane catalyst, presenting two inlets, each for a different phase taking part in the reaction, which is not possible in the powder catalyst pores.

One can also note that the value obtained on the CMR in this work (1.1 mmol/(s g_{pt})) is slightly higher than those reported in previous papers from our group [6] in the same conditions, but now without any deactivation.

5. Conclusion

In the configuration used in the work, the interfacial contactor CMR showed a strong sensitivity to the gas overpressure. By shifting the gas–liquid interface closer to the membrane zone, where platinum catalyst is concentrated, one can significantly increase the efficiency of the reactor. This air pressure effect was not related to a conventional oxygen partial pressure influence on the reaction kinetics, as switching to pure oxygen did not give a large increase in reaction rate.

The influence of the catalytic membrane structure and catalyst location on the gas–liquid interface shift has been shown, through the catalytic behaviour of the reactor. A new structure including a single intermediate layer has been developed, according to the above mechanism, and has shown impressive improvements in catalytic efficiency at higher gas overpressures. The interfacial contactor CMR showed a reaction rate more than three times higher than that obtained using a conventional slurry reactor using exactly the same catalytic materials and conditions. The gain in catalytic activity has been attributed to a shorter diffusion path of oxygen to the catalyst zone.

These results suggest that existing wastewater treatment technology can be improved using contactor CMRs running at milder reaction conditions than conventional reactors. In the light of these benefits in terms of catalytic performance, an industrial up-scaling has been considered [16]. These recent advances are now being applied to the wet air oxidation of industrial effluents, in order to optimise the process to complex wastewater treatment.

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