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High-performance catalytic wet air oxidation (CWAO) of organic acids and phenol in interfacial catalytic membrane contactors under optimized wetting conditions

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ABSTRACT

This paper is intended to evaluate the effect of membrane wetting on the performance of interfacial catalytic membrane contactors applied to the wet air oxidation of organic pollutants. To this aim, two wetting methods (i.e. by capillarity at ambient pressure and under dynamic vacuum) have been used prior to the oxidation tests. A series of monometallic and bi/trimetallic catalytic membranes have been prepared and tested using both wetting methods for the oxidation of formic, acetic and oxalic acids as model pollutants. In these experiments, the solution with the target pollutant was pumped along the contactor on the catalytic layer side, while air or pure oxygen was pumped along the other side. The gas/liquid interface was located within the membrane wall by means of a transmembrane pressure compensating capillary forces. In all cases, higher catalytic activites have been obtained after wetting the membranes under dynamic vacuum. On the basis of the coarse-grained nature of the membranes, wetting under vacuum might help removing air blocked in larger sized pores and cavities, allowing therefore a more accurate control of the position of the confined gas–liquid interface by the transmembrane pressure. Using optimized wetting conditions, we show promising results on the application of interfacial catalytic membrane contactors to the oxidation of phenol at room temperature and air overpressures in the range 1–4 bar.

1. Introduction

Wet air oxidation (WAO), earlier developed by Zimmerman during the 1950s [1], constitutes an attractive technology for the treatment of industrial effluents containing low to intermediate concentrations of refractory and toxic compounds for which incineration or biological remediation are inefficient and/or costly. Thermal WAO usually takes place at high temperatures (473–623 K) and pressures (2–15 MPa air, O_2 or O_3), the residence times of the liquid phase ranging from 15 to 120 min, and with typical chemical oxygen demand (COD) removal about 75–90% [2]. The high-energy demands combined with strong corrosion are detrimental for a widespread industrial application of thermal WAO.

The efficiency of WAO can be improved by the use of heterogeneous catalysts. Nevertheless, the main shortcoming of catalytic wet air oxidation (CWAO) is ascribed to the diffusion of the gaseous reactant to the catalyst surface, as well as catalyst recovery and leaching phenomena [3]. In order to improve the gas/liquid/solid contact in CWAO, the development of innovative catalytic reactors is desired. The use of catalytic membrane reactors (CMRs), coupling a catalyst and a membrane in the same unit, could be an option. Among the different types of CMRs described in the literature (i.e. extractors, distributors and contactors [4]), the application considered here corresponds to a contactor-type CMR (CMR-C). Within this family, CMR-Cs operated in interfacial mode seem the most appropriate for conducting CWAO processes applied to environmental issues. In this mode, the gas and liquid reactants are introduced separately from the opposite sides of the membrane. The gas/liquid interface is then located within the membrane wall [5]. This configuration favours three-phase contact, leading to a better accessibility of the reactants to the catalyst zone and in its turn to enhanced conversion rates at relatively mild temperature and pressure conditions [6–8]. Contrary to what is usually observed in other 3-phase reactors (e.g. slurry stirrers and trickle-beds), the gaseous reactant may not be kinetically limiting. This might be attributed not only to lower gas diffusion constraints when conveniently operated [9–12], but also to increased gas solubility in nanoconfined liquids in the vicinity of catalyst nanoparticles, as we have advanced

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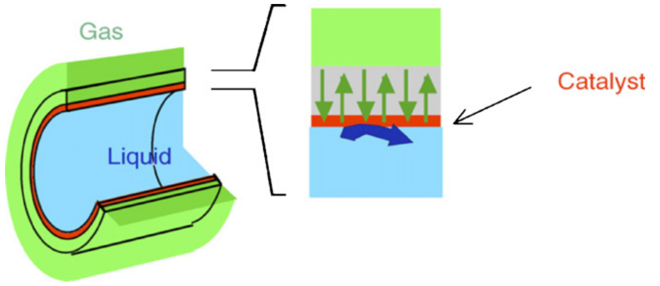

Fig. 1. Scheme of a gas–liquid interfacial membrane contactor.

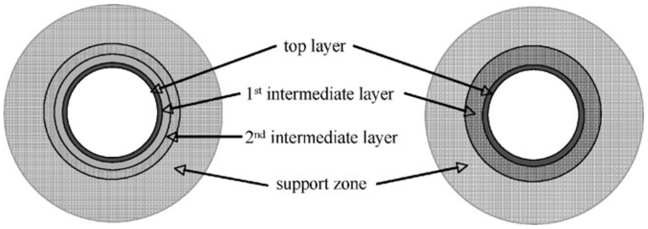

Fig. 2. Schematic cross-section of the membrane supports used in this study showing the three-layered (right) and four-layered (left) structure.

in recent studies [13,14]. Moreover the catalyst being part of the reactor, its recovery does not require any separation step from the liquid medium.

This paper pursues the research activities carried out by our group in the last years in the context of the 'WaterCatox' European project, aimed at the development of catalytic membrane contactors for the WAO of toxic but diluted wastewaters [15–17]. The 'WaterCatox' process is based on multi-layered tubular porous ceramic membranes (usually made of alumina, titania, alumina coated with titania, ziconia or ceria depending on the application [9,18–20]) containing the catalyst nanoparticles in the mesoporous top layer, acting as an interfacial gas/liquid contactor (see Fig. 1). The catalyst is usually dispersed in the mesoporous layer by ionic impregnation or evaporation-crystallization using a convenient precursor (e.g. hexachloroplatinic acid in the case of Pt deposition) [21,22], or by layer-by-layer deposition methods [23], and further activated by reduction under H_2 flow at 473 K. Using these methods, Pt nanoparticles up to 1.5 nm in size can be synthesized with loadings in the contactor up to 1.5 wt.% for mean pore sizes lying in the range 5–20 nm [9].

The position of the gas–liquid interface within the membrane thickness plays a relevant role on the catalytic performance of interfacial membrane contactors, as has been reported in several studies [24–26]. Higher reaction rates can be achieved by locating this interface as close as possible to the catalytic zone by increasing the transmembrane pressure. This poses obvious problems related to the quality of the supports (need of high bubble points) and wetting taking into account their asymmetric porous structure and coarse-grained nature. The first part of this paper is therefore devoted to assess for the specific role of wetting on the CWAO performance of catalytic membranes using formic, acetic and oxalic acids as model pollutants. To this end two different kinds of wetting protocols have been considered: (1) wetting by capillarity (standard wetting) and (2) wetting "under vacuum" where the solution is forced through the porous volume by the action of primary vacuum. The second part of the paper focuses on the potentials of catalytic membranes under optimized wetting conditions for the CWAO of priority pollutants, with special insight into phenol degradation. A series of mono- and bi/trimetallic catalytic membranes have been prepared relying on noble metals and supports that have already proven their efficiency in the CWAO of carboxylic acids and aromatics [27–31].

2. Experimental

2.1. Materials

The membranes used in this study (o.d. 10 mm, i.d. 7 mm, length 25 cm) consisted of tubes made of three or four concentric layers (see Fig. 2), showing an average pore size decreasing from the outside to the internal surface of the tubes. The top layer was located on top of the inner membrane surface. Both ends of the tubes (ca. 1.5 cm on each side) were enamelled to achieve proper sealing, defining an internal active surface of ca. 50 cm^2. The membrane supports were provided by Pall-Exekia (France) and Inocermic (Germany). In the former case, the supports where made of α-Al_2O_3 covered by TiO_2 with a top layer or TiO_2 or ZrO_2 (thickness, 3–6 μm; mean pore size, 20–50 nm), while in the second case they were made of TiO_2 with a CeO_2-dopped ZrO_2 top layer (thickness, 8 μm; mean pore size, 80–100 nm). Further details on these membrane supports can be found elsewhere [19,21].

The metallic precursors used in the preparation of the catalytic membranes, all supplied by Sigma–Aldrich or Strem, were: (Pt) H_2PtCl_6 (39.8% Pt), $PtCl_2(NH_3)_2$ (65.0% Pt) and $[Pt(NH_3)_4](NO_3)_2$ (49.1% Pt); (Pd) $PdCl_2$ (59.8% Pd) and $Pd(NO_3)_2{\cdot}2H_2O$ (40.0% Pd); (Ru) $RuCl_3$ (45–55% Ru) and $Ru(NO)(NO_3)_3$ (1.5% Ru); (Cu) $Cu(NO_3)_2{\cdot}3H_2O$ (26.1% Cu); (Zn) $ZnCl_2$ (14.8% Zn) and $Zn(NO_3)_2$ (33.8% Zn); (Ni) $NiCl_2{\cdot}6H_2O$ (24.6% Ni) and $Ni(NO_3)_2{\cdot}6H_2O$ (20.1% Ni); (Fe) $Fe(NO_3)_3{\cdot}9H_2O$ (13.8% Fe); and (Co) $Co(NO_3)_2{\cdot}6H_2O$ (20.0% Co). Formic acid (98–100%, Riedel-de-Haen), acetic acid (99.7%, Sigma–Aldrich), oxalic acid (>99%, Fluka) and phenol (99%, Carlo Erba) were used as model pollutants treated during the catalytic tests. The gases (N_2, O_2 and air), purity >99.999%, were supplied by Air Liquide.

2.2. Catalytic membrane preparation

The mono- and bi/trimetallic catalytic membranes were prepared using convenient precursors either by impregnation or by evaporation-crystallization following the experimental protocols presented in previous studies [20–22]. The metals were chosen on the basis of reported catalytic activities for the oxidation of either organic acids or phenol. The estimation of the amount of metal deposited within the membrane porosity was based both on weight uptake after deposition and on the amount of precursor solution adsorbed during the soaking step. The results obtained using both methods for monometallic membranes were found to be in good agreement, lying in the range 35–1000 $\mu g/cm^2$.

2.3. Wetting methods

Prior to the catalyst deposition, the quality of the supports was assessed by gas–liquid displacement (bubble point test) using ethanol as liquid phase and N_2 as gas. According to Laplace law, the pressure of the first bubble allows the determination of the largest passing-through pore of the support. The bubble point of the membrane will condition the maximum transmembrane pressure (i.e. gas overpressure) to be applied in the catalytic experiments. Consequently, high bubble points, approaching as much as possible to the maximum theoretical value predicted by Laplace law for the top layers (in practice >1.0 bar for pure ethanol), are necessary to avoid the formation of bubbles in the liquid side during operation. Note that, in all cases, the bubble point pressure is much lower than the pressure difference that would be expected for a 50-nm pore size top layer (about 58 bar). As a consequence, the gas/liquid interface cannot be localized in the mesoporous top layer during operation. However, our aim will be to locate the gas/liquid interface as close as possible to the top layer.

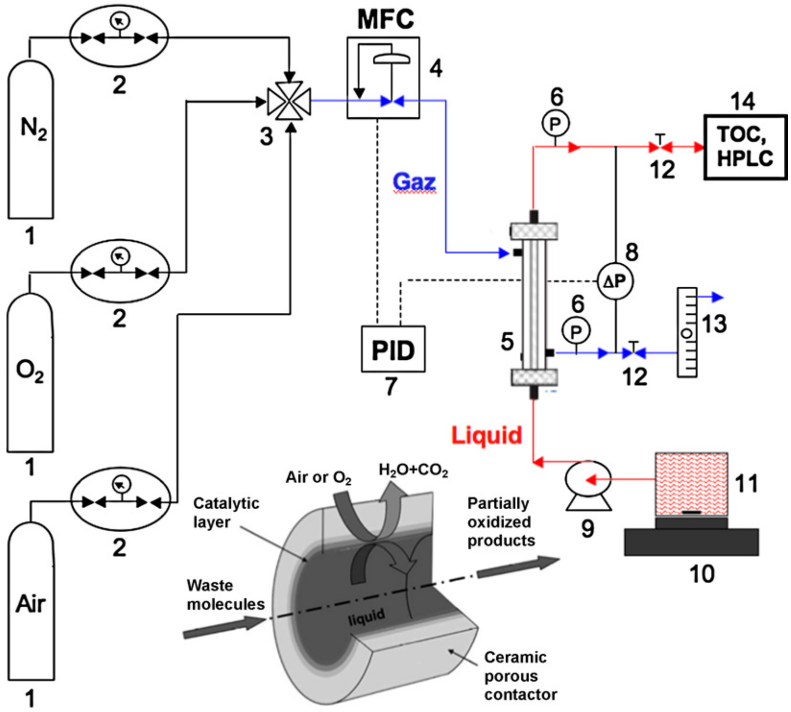

Fig. 3. Schematic drawing of a membrane reactor system. *Nomenclature*: (1) gas cylinder, (2) gas regulator, (3) multi-port valve, (4) mass-flow controller (50 mL(STP)/min), (5) membrane module, (6) pressure gauge, (7) temperature regulator (PID), (8) differential pressure gauge, (9) liquid pump, (10) magnetic stirrer and heater, (11) solution reservoir, (12) regulation valve, (13) bubble meter, (14) TOC and HPLC analyzers.

Before the gas–liquid displacement tests, the porous tubes were wetted in pure ethanol to fill the porosity with the liquid. Two different wetting methods were used: (1) normal wetting by capillarity and (2) wetting under dynamic vacuum (hereinafter referred to as vacuum wetting). The first wetting method consists of a direct ethanol impregnation of the support pores at ambient pressure by capillarity, in a similar way described by ASTM 316-86 standard procedure [32]. In the second one, the membranes were placed vertically in a two-ends module and the gas phase was evacuated by the topside up to a vacuum pressure of about 20 mbar. Ethanol was then introduced in the bottom side of the module and pumped until complete filling of the module.

2.4. CMR setup and CWAO tests

The tubular membranes were mounted in a membrane reactor module using gas-tight o-rings separating the liquid and gas feeds. The gas phase was fed into the shell side, while the liquid phase was introduced into the lumen tube side at atmospheric pressure (see Fig. 3). The air overpressure (0–5 bar) was monitored and controlled using a differential pressure gauge connected to an electronic regulator, acting on the gas feed through a mass-flow controller (50 mL(STP)/min). Pure nitrogen was used to stabilize the transmembrane pressure before switching to air to start the oxidation. The membrane reactor was operated in continuous liquid flow mode at a flow rate in the range 4–5 mL/min.

The performance of the catalytic membranes was first evaluated in the CWAO of aqueous solutions of formic, acetic and oxalic acids operating at an initial concentration of 5, 6.5 and 10 g/L, respectively. Some of the membranes were also tested in the oxidation of a phenol aqueous solution at an initial concentration of 1.7 g/L. All the experiments were carried out at room temperature (20–25 °C) and in excess of oxygen. The conversion of the organic compounds was monitored using a Shimadzu TOC 5050A total organic carbon analyser and by high-performance liquid chromatography (HPLC, Varian Prostar, UV detector). The reaction rate was expressed as converted moles of reactant per unit time related to the geometric membrane area, i.e. μmol m^{-2} s^{-1}, as the membrane area is the cost-limiting factor of the process. The conversion data were accurate to ±1%.

3. Results

3.1. Effect of membrane wetting on first bubble points

Table 1 lists the main results on the first bubble points in ethanol obtained using both wetting methods (i.e. normal wetting and wetting under vacuum) for the collection of catalytic membranes prepared in this study. As can be seen, wetting plays a key role in the measured bubble points. The bubble points measured after normal wetting show an increasing trend with the wetting time, approaching after 24 h the values obtained using vacuum wetting. At shorter times, however, the difference between both wetting methods is remarkable, the bubble points measured after 1-h normal wetting showing a reduction up to 80% (sample 14) compared to the values obtained using wetting under vacuum.

The bubble points measured in ethanol using vacuum wetting for the membranes listed in Table 1 show values lying in the range 0.5–4.4 bar. These values translate into a range of maximum admissible overpressures of 1.5–14 bar during operation in aqueous solutions (the surface tensions of water and ethanol at 25 °C are 72 and 22 mN/m, respectively). These pressure limits have been taken explicitly into account for each membrane when carrying out the catalytic tests.

3.2. Effect of membrane wetting on the catalytic activity

Among the membranes listed in Table 1, two of them (i.e. membranes 3-Pt/PE and 4-Pd/IN) were chosen to assess for the influence of the wetting method on their catalytic performance. The catalytic

Table 1
Bubble point pressure (liquid, ethanol; gas, N_2) for normal wetting and wetting under dynamic vacuum and main characteristics of catalytic membranes prepared in this study ($D_{p,TL}$: mean pore size of the top layer).

Membr.	Metal/supplier (layers)	$D_{p,TL}$ (nm)	Wetting in EtOH				
			Normal				Vacuum
			1 h	6 h	12 h	24 h	1 h
1	Pt/INC (3)	100[a]	0.59	–	0.64	0.8	0.8
2	Pt/PE (4)	20[a]	–	–	1.36	1.7	1.8
3	Pt/PE (3)	50[a]	–	0.2	–	0.4	0.5
4	Pd/PE (3)	50[a]	–	0.59	1.64	1.7	1.7
5	Ru/PE (3)	50[a]	0.25	0.32	1.24	1.5	1.6
6	Cu/PE (3)	50[a]	–	0.9	1	1.1	1.1
7	Cu/INC (4)	80[c]	–	1.54	2.3	2	3.7
8	Pt–Pd/INC (4)	80[c]	–	0.53	1.4	1.7	1.9
9	Pt–Ru/PE (4)	20[a]	–	–	0.5	4.4	4.4
10	Pt–Ru/PE (3)	50[a]	0.65	–	0.99	1.2	1.3
11	Pt–Pd–Ru/PE (3)	50[a]	–	0.74	0.97	1.1	1.2
12	Pd–Ru/PE (3)	50[a]	–	0.98	1.1	1.2	1.3
13	Cu–Pd/PE (3)	50[a]	0.28	0.8	1.13	0.9	1.1
14	Cu–Pd/INC (4)	30[b]	–	0.32	1.2	2.7	1.6
15	Cu–Ni/INC (4)	80[c]	0.38	0.72	0.47	0.5	0.5
16	Zn–Ni/PE (3)	50[a]	–	0.27	1	1.1	1.1
17	Fe–Co/PE (3)	50[a]	0.4	1.34	–	1.3	1.3
18	–/INC (4)	5[b]	–	–	–	3.2	3.1

Supports: (PE) Pall Exekia; (INC) Inocermic.

[a] ZrO_2.

[b] TiO_2.

[c] CeO_2-doped ZrO_2.

activity of these membranes in the CWAO of formic, acetic and oxalic acids under air has been compared after both normal (2 h) and vacuum wetting methods. The results are presented in Table 2 and Figs. 4 and 5. It is noteworthy that despite the low bubble point value of membrane 3-Pt (0.5 bar), the catalytic results indicate that large defects in the membrane do not exert much influence on its catalytic performance. As a matter of fact, no bubbles were observed in the liquid side of the modules during operation for overpressures up to 3 bar. This result is consistent with the extremely low increase observed for the gas flow for pressures higher than the bubble point in the gas–liquid displacement tests (not shown).

The catalytic results show that, under Pt and Pd catalysis, the oxidation of oxalic acid is easier than that of formic and acetic acids. The activity of membrane 3-Pt in the oxidation of oxalic acid is 5 times higher than that of acetic acid and 3 times higher than the activity of formic acid. In all cases, complete mineralization was achieved.

As can be inferred from Table 2, for overpressures ≥2 bar and, whatever the acid is considered, the conversions and reaction rates achieved in the CWAO of formic, acetic and oxalic acids are remarkably higher (by 4–11 times) when subjecting the membranes to vacuum wetting prior to the catalytic tests than in the case of normal wetting (see Fig. 5 in the case of acetic acid oxidation).

Moreover, the use of pure oxygen instead of air in the CWAO of formic acid under vacuum wetting allows an increase about twice of the catalytic activity of membrane 3-Pt (see Fig. 6).

3.3. *Influence of metal loading on the catalytic membrane performance*

Fig. 7 shows the evolution of the reaction rate with the gas overpressure in the CWAO of formic acid at room temperature for three catalytic membranes (termed A–C) loaded, respectively, with 37, 50 and 620 $\mu g/cm^2$ of Pt. As can be deduced from Fig. 7, beyond a minimum value, a large increase of the metal loading does not apparently promote the membrane activity. For the sake of comparison, please note the similar reaction rates obtained for membranes B and C in formic acid oxidation at 3-bar air overpressure (169 $\mu mol\ m^{-2}\ s^{-1}$ vs. 150 $\mu mol\ m^{-2}\ s^{-1}$). For this reason, the reaction rate was calculated as a function of m^2 of area of the inner side of tube and not as function of amount of catalyst deposited.

3.4. *Phenol oxidation*

Three catalytic membranes (4-Pd, 15-Cu-Ni, 17-Fe-Co), all subjected to both normal and vacuum wetting before the catalytic tests, were tested in the room-temperature CWAO of phenol. Although a Cu-based membrane (6-Cu) has also been tested for phenol oxidation, the results reveal the absence of long-term stability due

Table 2
Summary of CWAO results of formic, acetic and oxalic acids under air for membranes 3 (Pt) and 4 (Pd) listed in Table 1 as a function of the wetting method.

Model acids	Membr.	Normal wetting/wetting under vacuum				
		Conversion, % (reaction rate, $\times 10^{-3}$ mmol $m^{-2}\ s^{-1}$)[a]				
		0.2 bar	1 bar	2 bar	3 bar	4 bar
Formic	3-Pt	1 (20)/2 (40)	4 (74)/8 (146)	6 (108)/11 (197)	7 (121)/32 (588)	–
	4-Pd	3 (60)/7 (144)	4 (78)/8 (164)	4 (71)/9 (170)	2 (40)/14 (282)	4 (85)/26 (523)
Acetic	3-Pt	1 (4)/1 (6)	2 (8)/15 (63)	2 (6)/24 (98)	2 (9)/25 (103)	–
	4-Pd	2 (40)/1 (30)	3 (70)/4 (87)	3 (90)/12 (265)	4 (108)/16 (349)	4 (114)/22 (472)
Oxalic	3-Pt	6 (236)/9 (316)	12 (461)/25 (887)	13 (473)/36 (1253)	18 (633)/38 (1336)	–
	4-Pd	2 (80)/6 (201)	4 (151)/14 (498)	10 (357)/26 (899)	15 (525)/39 (1339)	20 (678)/40 (1398)

[a] Reaction rates computed using the internal membrane surface area.

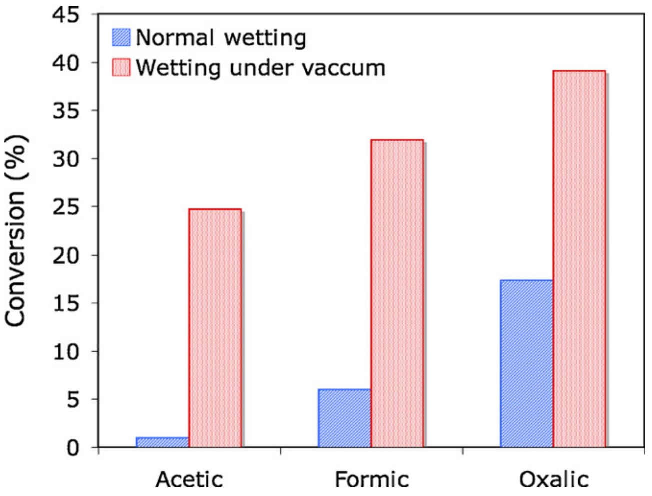

Fig. 4. Influence of support wetting on the room-temperature CWAO performance of formic, acetic and oxalic acids under air for membrane 3-Pt.

to Cu leaching in the presence of phenol solutions. In the former three membranes, the catalytic activity of the membranes is promoted when using vacuum wetting. The effect of wetting is more remarkable at higher overpressures, the reaction rate at 4-bar air overpressure showing an increase up to 50%.

Among the three membranes tested, membranes 4-Pd and 17-Fe–Co provide the highest activities in phenol oxidation, the phenol conversion and reaction rate reaching values up to 30% and 200 μmol m^{-2} s^{-1}. However, membrane 15-Cu–Ni provides the highest TOC reduction, being practically coincident with the phenol conversion measured by HPLC. Fig. 8 shows the TOC reduction performance of membrane 15-Cu–Ni subjected to both normal and vacuum wetting protocols in the room-temperature CWAO of phenol. In this case, using vacuum wetting and extremely mild oxidation conditions (room temperature and 4-bar air overpressure), the TOC reduction for this membrane reaches a value ca. 10%. The intermediates formed (not analyzed in detail) are enriched in a variety of small-chain organic acids.

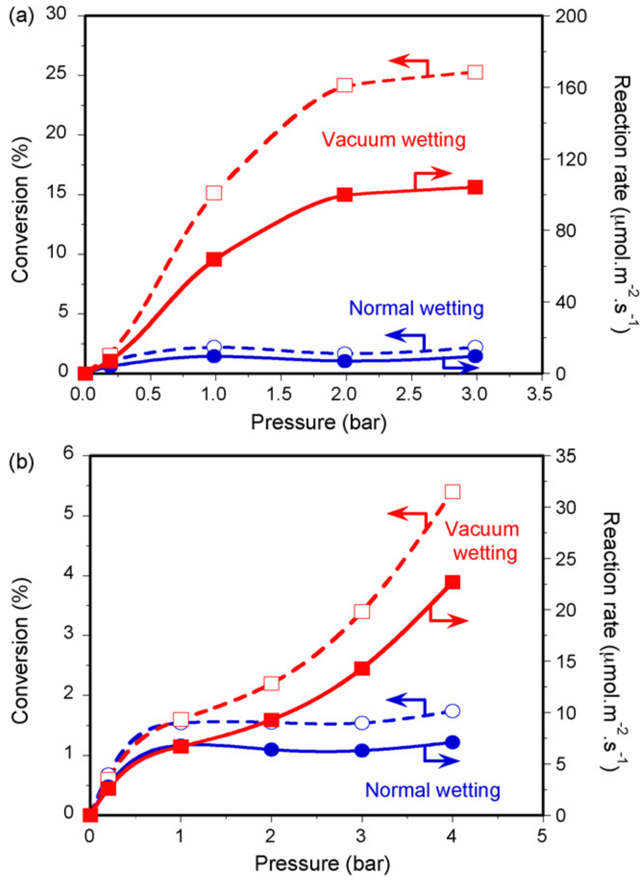

Fig. 5. Evolution of the conversion and reaction rate as a function of gas overpressure in the room-temperature CWAO of acetic acid under air subjected to normal (2 h) and vacuum wetting. On top, membrane 3-Pt; on bottom, membrane 6-Cu.

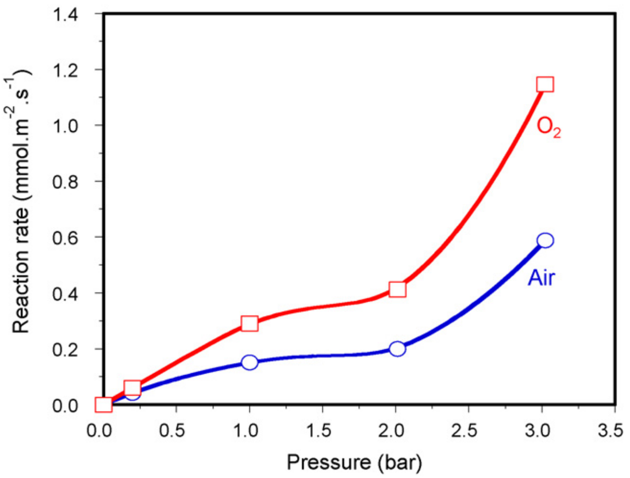

Fig. 6. Reaction rate as a function of gas overpressure in the room-temperature CWAO of formic acid under air and pure oxygen for membrane 3-Pt subjected to vacuum wetting.

4. Discussion

4.1. *Gas/liquid/catalyst triple contact in catalytic membranes as a function of membrane wetting*

As has been stated above, the position of the confined gas/liquid interface near the catalytic zone in the membrane wall plays a crucial role on the final performance of interfacial CMR-Cs. Due to the multi-layered structure of the membranes, the position of the gas/liquid interface is expected to depend strongly on the

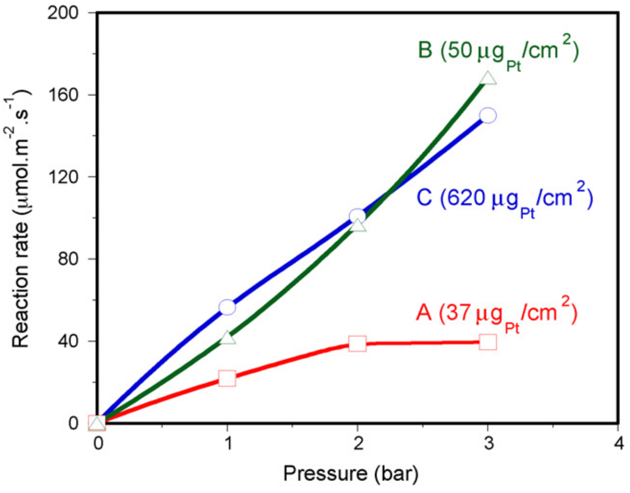

Fig. 7. Evolution of the reaction rate as a function of gas overpressure in the room-temperature CWAO of formic acid under air using three different Pt-impregnated catalytic membranes (three-layered supports, top layer 50-nm ZrO$_2$) subjected to vacuum wetting: (A) 37 $\mu g_{Pt}/cm^3$, (B) 50 $\mu g_{Pt}/cm^3$ and (C) 620 $\mu g_{Pt}/cm^3$.

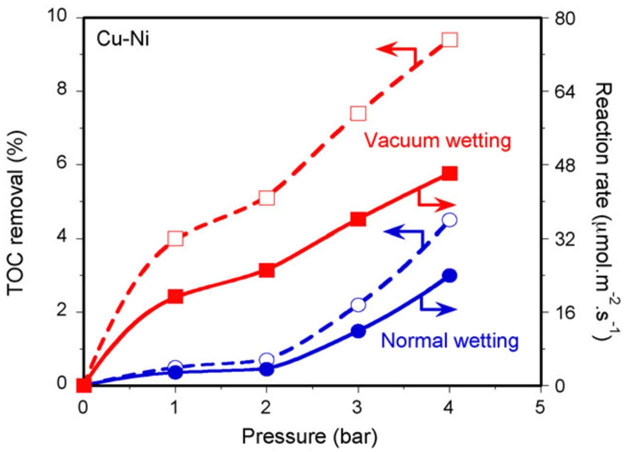

Fig. 8. Evolution of the TOC removal and reaction rate (TOC basis) as a function of gas overpressure in the room-temperature CWAO of phenol under air subjected to normal (2 h) and vacuum wetting for membrane 15-Cu–Ni.

wetting protocol. As a matter of fact, wetting a membrane at ambient pressure relying on capillary forces (normal wetting) is only expected to provide effective liquid impregnation in the case of large pores (>0.1 μm), as in the case of MF membranes. In contrast, in the case of membranes showing smaller sized pores (<0.1 μm), as in the case of the membranes used in this study, this 'normal' wetting protocol seems unsuitable. This explains why, in addition to the high pressures involved, gas–liquid displacement is not recommended for the determination of pore size distributions in UF and NF membranes (pore size of top layer <50 nm), and only used as a primary integrity test. In this case, Hg porosimetry is preferred on the basis of the better wetting capacity of Hg [33].

Vacuum wetting allows overcoming the inherent shortcomings ascribed to normal wetting by removing the air stored in the membrane pores. This forces the liquid to penetrate to the membrane porosity, favouring the 3-phase gas/liquid/catalyst contact in the catalytic experiments. Using vacuum wetting, the catalytic activity is enhanced by a factor of 3–16 in the air-assisted CWAO of aqueous solutions of formic, acetic and oxalic acids at room temperature (see Figs. 4 and 5). In the case of using oxygen instead of air, under vacuum wetting, the catalytic activity can be promoted by a factor of 2 (see Fig. 6).

It is also noteworthy that the use of vacuum wetting instead of wetting by capillary has also potential benefits in the synthesis of supported zeolite (MFI) and MCM-type membranes, as we have put forward in two recent studies [34,35]. In both cases, the use of static or dynamic vacuum wetting helps improving the penetration of the precursor solution into the porous network, allowing the synthesis of nanocomposite crystallites rather than thin films on top of a support.

4.2. *Catalyst dispersion in membrane porosity*

The experiments performed in the catalytic oxidation of aqueous solutions of formic acid depicted in Fig. 7 reflect that only a small part of the deposited metal (Pt in this case) is active in the reaction. This observation is consistent with the conclusions addressed by Vospernik et al. [12] from their experimental and simulation studies on Pt-catalyzed acetic acid oxidation in interfacial membrane contactors. The fact that only a part of the catalyst is active is justified by the catalytic membrane protocols used in the preparation of these membranes (impregnation and evaporation-crystallization), leading to partial metal concentration in the membrane top layer [21].

Unlike these classical techniques for catalyst deposition, higher accuracy in the localization of the catalyst in the mesoporous top layer can be achieved through the use of layer-by-layer deposition methods from a suspension of catalyst nanoparticles. The proof-of-concept of this technique has been recently demonstrated by Bruening and co-workers [23], the membranes showing promising results in the CWAO oxidation of aqueous solutions of formic acid and phenol at mild temperature and pressure conditions. In addition to the benefits of the layer-by-layer technique in terms of catalyst economy, it is worth mentioning that this technique allows the definition of the reaction rate related to the mass of active metal, i.e. μmol/(g_{cat} s), as the catalyst is well-localized. This allows in its turn a more direct comparison with other reactor configurations.

4.3. *Prospects in aromatics oxidation*

The results plotted in Fig. 8 indicate that, although the application of interfacial membrane contactors to phenol oxidation is still in an early stage, the results obtained here on Cu–Ni membranes are promising for a prospective application of interfacial CMR-Cs to the CWAO of aromatic compounds under mild temperatures and pressures. As in the case of oxidation of carboxylic acids, the use of proper membrane wetting seems imperative to optimize the capacity of these reactors in the oxidation of aromatics. Moreover, the fact that, using appropriate catalysts, these reactors also show good oxidation performance for acetic and oxalic acids (see Figs. 4 and 5), usually found as end-of-chain intermediates in the degradation pathway of aromatics, is also oustanding. Our results are especially promising for acetic acid oxidation, usually refractory to CWAO due to catalyst deactivation by the formation of carbonates (see for instance Ref. [36]). The results presented in this study open up interesting perspectives in the conception of multimetallic membrane systems (preferentially bimetallic, based on Pt/Pd and Ru, see for instance Refs. [37–40]) under optimized catalytst deposition conditions and liquid wetting, for the simultaneous concerted oxidation of aromatics and (intermediate) acids in the same membrane unit.

5. Final remarks

We have shown in this paper that membrane wetting plays a crucial role on the performance of catalytic membrane contactors. Liquid impregnation in the membrane porosity not only affects the maximum admissible gas overpressures in the contactor to limit bubble formation in the liquid phase, but also conditions the gas/liquid/catalyst contact in the membrane wall and how this contact is governed by gas overpressure. On the basis of the coarse-grained nature of the membranes, vacuum wetting might help removing air blocked in smaller sized pores and cavities, allowing therefore a more accurate control of the position of the confined gas–liquid interface by means of the transmembrane pressure. In all cases, as a consequence, normal wetting lacks of reproducibility. Using optimized metal deposition protocols and wetting conditions, interfacial membrane contactors appear as promising candidates for the oxidation of aromatics at mild temperature and pressure conditions.

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