Catalysis Today 149 (2010) 326–333

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic wet oxidation of phenol using membrane reactors: A comparative study with slurry-type reactors

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ARTICLE INFO

Article history:
Available online 8 October 2009

Keywords:
Catalytic membrane reactor
Catalytic wet oxidation
Phenol removal
Ce based oxides
Autoclave

ABSTRACT

The wet air oxidation of phenol over cerium mixed oxides has been carried in autoclave slurry-type reactor and also in a contactor type membrane reactor to assist about the benefits provided by the employment of the mesoporous top layer of a ceramic tubular membrane as catalyst (Ce mixed oxides) support. The effect of mixed oxide composition and use of Pt as dopant onto the phenol removal rate and selectivity towards mineralization have been studied on both types of reactor. For slurry-type reactors, two different autoclave reactors were used: one mechanically stirred highly pressurized, and the other magnetically stirred containing a porous stainless steel membrane as gas diffuser in an attempt to attain higher gas–liquid interfacial area. The performances of these reactors have been compared under similar reaction conditions (i.e. catalyst loading/liquid volume, temperature, phenol concentration) although the way in which reactants are fed to the reaction vessel (different among each other configuration) is clearly affecting the CWO phenol degradation route. From the catalytic systems studied, Pt doped Ce–Zr mixed oxides exhibit the best reaction performance in spite of the achieved phenol conversion levels are below 50%. For autoclave reactors, the gas feeding to the liquid volume by a membrane diffuser has almost no effect on phenol removal for the reaction conditions tested; whereas the catalytic membrane contactor type reactor clearly outperform autoclave reactor provided with membrane diffuser.

1. Introduction

Phenol is one of the most common organic water pollutants present in wastewater of various industries such as refineries (6–500 mg/l), coking operations (23–3900 mg/l), coal processing (9–6800 mg/l), manufacture of petrochemicals (28–1220 mg/l), and also in pharmaceutical, plastics, wood products, paint and pulp and paper industries (0.1–1600 mg/l) [1]. Phenol is a toxic compound even at low concentrations and it also contributes to off-flavours in drinking and food processing water. In recent years a tightening of official environmental regulations and a subsequent development of effective technologies for treating these wastewaters are widely observed.

There are several abatement technologies for phenol in wastewaters: separation, biochemical abatement, incineration, electrochemical oxidation, the Fenton process, photocatalysis, ozonization. However, the toxicity, concentration and loading in pollutants, energy requirements and/or economical aspects are preventing them from their use as water stream treatment technologies [2].

Wet air oxidation (WAO) [3] represents an alternative technology to treat water streams with low concentration of toxic organic compounds as phenol (too dilute to incinerate and too toxic to biotreatment). But the absence of a catalyst implies that high temperatures (150–350 °C) and oxygen pressures (0.5–20 MPa) are required [4]. Nevertheless, the use of catalysts could diminish the temperature and air pressure requirements obtaining a more efficient phenol abatement process. A considerable potential exists for this catalytic wet air oxidation (CWAO) process to ultimately destroy organic pollutants in industrial effluents [5].

CWAO processes can be divided into two groups [6]. The first one includes the use of homogeneous catalysts (mainly Cu or Fe salts) that supposes still using high temperature and pressures and the following two important problems: catalysis recollection is needed and the risk of leaching to the environment appears. The second one includes the use of heterogeneous catalysts, that avoid the need of a separation step of the catalyst (except in slurry operation) and the pollution of the water stream. Most of the active catalysts used in CWAO of phenol are solids containing either noble metals (Pt, Ru) or transition metal cations (Cu, Co, Mn, Fe) as active phases. Frequently these active compounds are supported, mainly over alumina or activated carbons and/or containing CeO_2 additives. These studies have been reviewed recently by Busca

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doi:10.1016/j.cattod.2009.05.027

et al. [1], reporting a systematic revision of recent developments in this field. Additionally, news studies focused on the optimization of several catalytic systems in CWAO of phenol or derivates are being carried out in the last months, for example: (a) platinum catalysts supported on ceria and Ce–Zr mixed oxides (Pt/CeO_2, $Pt/Ce_xZr_{1-x}O_2$) [7], (b) multi-walled carbon nanotubes (MWCNTs) [2,8], (c) sodium rectorite (Na, Ca_REC) [9], (d) Ru/TiO_2 catalysts [10], (e) carbon supported iron catalysts (Fe/AC) [11,12], (f) supported Cu(II)-polymer catalysts (Cu-PVP) [13], (g) noble metals (Pt, Pd, Ru) loaded in $Ce_{0.33}Zr_{0.63}Pr_{0.04}O_2$ catalysts [14], (h) pelletized ruthenium catalysts (Ru/CeO_2, $Ru/CeO_2–ZrO_2$) [15], and others.

Nevertheless, in spite of this great effort in catalyst formulations, several problems still remain in this process [5]: (a) leaching and/or sintering of active component, (b) loss of surface of the supporting material, (c) CO poisoning of the catalyst active sites, and (d) deposition of organic or inorganic compounds on the catalyst surface (coking). Another problem is to obtain an efficient contact between gas, liquid and solid phases, in a process easily limited by the transfer of the gaseous reactant. Conventional catalytic processing (i.e. slurry reactors with bubbling of oxygen or air through a suspension of catalytic particles) often leads to poor yields due to the low oxygen concentration in contact with the catalyst or diffusion of phenol impediments [16]. Relatively few innovations have been published concerning CWAO of phenol in trickle-bed reactors (e.g. [2,10]) or other alternative solutions (e.g. modulation of gas feed composition and gas feed flow [12]), in order to improve these gas/liquid/solid contact performances. Moreover, in the reactors with a high liquid to catalyst-volumetric ratio (such as slurry and bubble column fixed bed reactors) coke deposition on the surface of catalyst particles is enhanced because oxidative coupling reactions are favoured in the bulk liquid phase [17].

One way to improve the gas/liquid/solid contact could be the use of catalytic membrane reactors (CMR) of the contactor type [18,19] as an interfacial contactor: phenol solution and air (or oxygen) being fed separately from both sides of the catalytic membrane. The gas overpressure can shift the gas–liquid interface location into the membrane wall, closer to the catalytic zone, so achieving several advantages: the oxygen concentration in contact with the catalyst layer is maximized, the desorption of pollutants into the gaseous phase is favoured, the catalyst exposure to leaching is reduced, a great flexibility for operative conditions is available and scale up issues are also facilitated. On the other hand, a proper location of the gas–liquid interphase must be ensured to take advantage of the previously quoted benefits.

Iojoiu et al. [20] using this CMR for the formic acid wet air oxidation with Pt based membranes have achieved a reaction rate more than three times higher than for a conventional slurry reactor. This gain is attributed to the shorter diffusion pathway of oxygen to the catalyst zone. In the light of these benefits an industrial up-scaling has been considered: the “watercatox” process [6,21]. The technological efficiency of this process was demonstrated by the results obtained using a pilot test unit with Pt membranes on different industrial effluents, mainly containing formic acid [6] or other compounds [21]. In spite of it, an insight into the study of optimal membrane composition and design, active phase nature and deposition, and operating conditions is still required.

On this way, this paper deals on our work with a CMR system for the CWAO of phenol using a ceramic membrane with mixed oxide catalysts based on cerium in combination with transition metals (Mn or Zr) and promoted with platinum. The use of these solids for CWAO of phenol or similar pollutants has been widely described in the literature: (a) Ce–Mn based oxides [22–30], (b) Ce–Zr based oxides [31,32], and (c) Pt promoted oxides [7,14,33,34]. Nevertheless, some problems such as the high selectivity to intermediate compounds in liquid phase and the formation of carbonaceous deposits over the catalyst surface with the subsequent losing in selectivity and stability respectively, remain still unsolved. In order to analyze the improvement in the contact method, a conventional slurry reactor and a reactor with a membrane diffuser are tested with the previously cited catalysts and at same operating conditions than for the CMR. The obtained results in terms of stability and selectivity to mineralization products are compared for the three contact modes. Furthermore, details on the membrane preparation methods and their characterization are presented.

2. Experimental

The bulk catalysts (see Table 1 for composition) were synthesized by coprecipitation adding dropwise an aqueous solution of the appropriate composition containing $Ce(NO_3)_3·6H_2O$, $ZrO(NO_3)_2·xH_2O$, and $Mn(NO_3)_2·xH_2O$ (all of them Aldrich, 99.99% pure) to a NH_4OH solution (30 wt%, Panreac) [31,35]. After precipitation, the solids were filtered, washed with deionized water until no pH change, dried at 100 °C for 24 h and then calcined in air at 350 °C for 3 h. The preparation conditions used in this work has been carefully chosen considering our previous physicochemical characterization results with the same catalytic systems [36]. Moreover, the nominal composition (Ce:Zr, Ce:Mn atomic ratio) of the mixed oxides used in this work has been selected as the most active according to CWO phenol catalytic tests carried out at reference conditions in slurry-type reactors (not shown here) [37].

The incorporation of Pt over the mixed oxides was carried out by the incipient wetness impregnation technique using $H_2PtCl_6·xH_2O$ (Aldrich) as Pt precursor. An aqueous solution of 52 g Pt/l was prepared to attain Pt loadings of 1.6 wt%. The doped samples were dried overnight and Pt reduction was performed at 350 °C with pure H_2 for 2 h once the sample was exposed at 350 °C for 2 h under inert atmosphere. The as prepared solids were ground in a mortar below 75 μm of particle size to ensure a slurry-type operation under the reaction conditions (800 rpm).

The powder B.E.T. surface area has been determined by using a Pulse Chemisorb 2700 Micromeritics. Prior to adsorption experiments samples are degassed overnight at 200 °C. X-ray diffractograms have been collected with a Rigaku/Max System using CuKα radiation ($\lambda = 1.5418$ Å) from 5° to 80° with a step size of 0.010° and a step time of 2.5 s. The data were compared to reference data from the International Centre for Diffraction Data for identification purposes.

Catalytic membranes were prepared from 90 mm long, 10 mm o.d. asymmetric ceramic tubes (Inocermic) with 5 nm pores in the γ-Al_2O_3 thin layer (3 μm of thickness). The ends of the ceramic supports were sealed with a glazing compound to allow for mounting in the experimental setup for permeation and reaction experiments. The total length of the porous part available for catalyst deposition was around 50 mm. The catalytic material deposited over the membranes was obtained by the “precipitation method” already described in our previous work [36], using optimized conditions in terms of catalyst confinement inside the γ-Al_2O_3 thin layer (concentration of precursor solution,

Table 1
Bulk catalyst prepared in this work for CWO of phenol.

Composition[a]	S_{BET} (m^2/g)
$Ce_{0.75}Zr_{0.25}O_2$	89.1
$Ce_{0.5}Mn_{0.5}O_2$	87.1
$Ce_{0.75}Zr_{0.25}O_2/Pt$	86.1
$Ce_{0.5}Mn_{0.5}O_2/Pt$	62.4

[a] Nominal composition in accordance with the starting precursor concentration.

Table 2
Catalytic membranes prepared in this work for CWO of phenol.

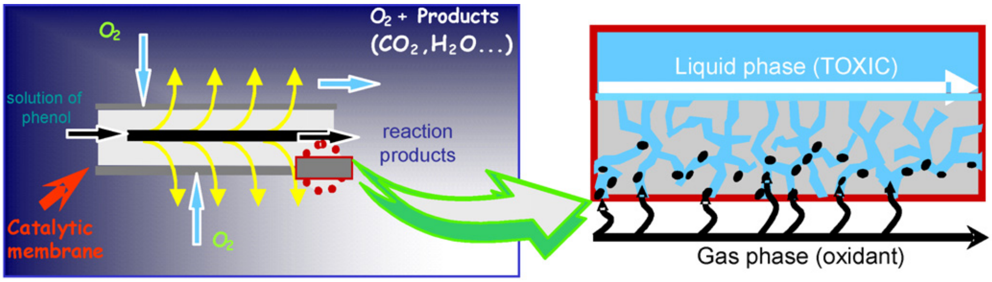
Membrane	Active phase	Mixed oxide loading[a] (mg)	Pt loading[b] (mg)	Permeation[c] (mol N_2/m^2 s Pa)	$g_{cat.}$/volume $(l)_{liq}$
A0	γ-Al_2O_3	–	–	6.0×10^{-06}	–
A4	γ-Al_2O_3/Ce–Zr[d]	56.8	–	8.3×10^{-06}	0.95
A8	γ-Al_2O_3/Ce–Mn	81.7	–	1.5×10^{-06}	1.36
A15	γ-Al_2O_3/Ce–Zr/Pt	96.5	1.0	3.8×10^{-06}	1.61
A18	γ-Al_2O_3/Ce–Mn/Pt[d]	112.7	1.2	4.4×10^{-06}	1.88
A19	γ-Al_2O_3/Pt	–	1.1	5.3×10^{-06}	0.02

[a] Calculated from weight differences.
[b] Calculated by VIS absorption.
[c] Estimated at 1 bar average pressure.
[d] Subjected to two impregnation + thermal treatment cycles.

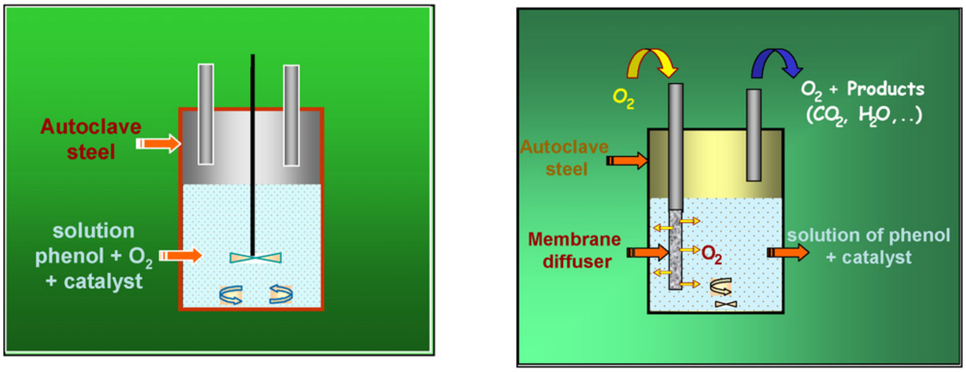
intermediate drying period, washing step and reagent-contact configuration). It basically consisted on the support impregnation with the precursor solution fed to the internal side during 3 min, a subsequent washing with deionized water followed by an intermediate drying at room temperature and a final NH_4OH impregnation from the inner surface. After drying at 25 °C for 24 h, the membranes were calcined under similar conditions to those used for powder catalysts. The estimated mixed oxide loading by weight difference ranged from 16 (A4 membrane) to 100 (A19 membrane) g mixed oxide/m^2 of contactor. Pt doped catalytic membranes were prepared by soaking the membrane in the acid hexacloroplatinic acid solution (0.3 g/l) for 60 min [34]. The estimated Pt loadings by UV–vis were around 1 g Pt/m^2 of contactor. Table 2 compiles the main properties of the catalytic membranes tested for catalytic wet oxidation of phenol including the percentage of Knudsen contribution to total N_2 permeation flux evaluated at 1 bar as average pressure.

The as prepared catalytic membranes were also characterized by SEM-EDX analysis and XPS analysis (not shown here) to ascertain about the location and composition of the catalytic phases formed.

The catalytic tests using phenol as a model pollutant from aqueous solution (1000–3000 ppm) have been carried out at 140 °C. In each experiment, the progress of the reaction and the catalytic activity were monitored by measurement of the liquid composition as a function of time at appropriate intervals by TOC (TOC-5500 Shimadzu) and GC analysis (CE Instruments HRGC MEGA 2 Series) equipped with a FID detector and a BP21 capillary column (30 m length and 0.53 mm in diameter) capable to resolve phenol from organic intermediates (acetic and formic acid). For membrane reactor and autoclave with membrane diffuser experiments, the gas phase was continuously monitored with a CP-4900 Micro-GC to evaluate the selectivity towards mineralization products (i.e. CO_2). To check carbon balance at the final reaction time, TPO analysis coupled to mass spectrometry, TGA and C, H, N elemental analysis were carried out for spent catalytic membranes and residual bulk catalysts respectively. These analyses allowed to quantify the selectivity towards carbonaceous deposits. However, for conventional autoclave reactor, the carbon mass balances were not closed and the mineralization selectivity was estimated by difference.



(a) Concept of the catalytic membrane reactor type contactor.



(b) Conventional autoclave type "slurry" reactor. (c) Autoclave reactor with membrane diffuser.

Fig. 1. Reactor configurations used in this work for CWO of phenol. (a) Concept of the catalytic membrane reactor type contactor. (b) Conventional autoclave type "slurry" reactor. (c) Autoclave reactor with membrane diffuser.

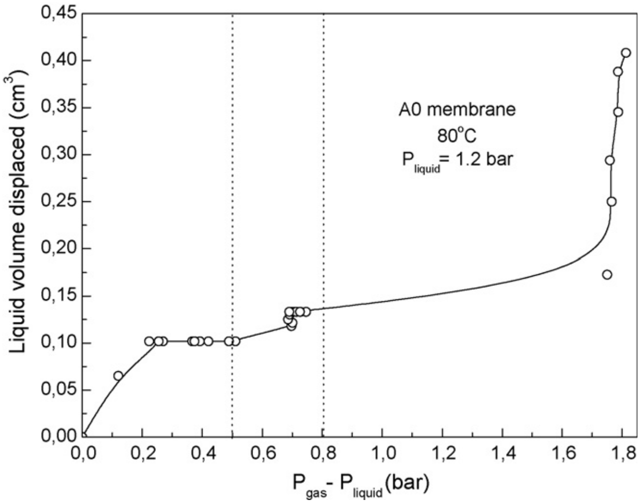


Fig. 2. Typical experimental curve for the G–L contact pressure determination.

Typical experimental conditions for membrane type contactor configuration (see Fig. 1.a) are 3.5–4.5 bar as total oxygen pressure for the gas phase and around 0.5 bar as pressure difference with respect to the liquid phase. This trans-membrane pressure value, which ensures the interfacial gas-liquid contact within the mesoporous catalytic thin layer, is established for each catalytic membrane, previous to the reaction experiments, by a fluidodynamic experiment using a set-up already described in literature [38]. A typical experimental curve for contact pressure determination at 80 °C is shown in Fig. 2 for the starting ceramic supports (A0 membrane). As it can be observed, at 0.25 bar of DP the liquid volume displaced from the membrane corresponds to the macropores volume. Increasing the pressure difference across the membrane up to 0.5 bar displaces the liquid from the mesoposorous thin layer. Further modifications finally provoke the bubbles appearance in the bulk liquid phase. In spite of the experimental difficulties typical of gas-liquid-solid reactions, all the catalytic membrane results here compiled have been obtained from stable operating reaction conditions. As an example, Fig. 3 shows the thermal and fluidodynamic stability thorough a standard catalytic test with a membrane reactor type contactor (A15 membrane).

The membrane reactor results here presented have been obtained working discontinuous for the liquid phase fed to the internal side where the catalytic layer is located (60 ml recirculated at 9 ml/min by an HPLC pump); and continuous for the gas phase (60 ml O_2/min). This configuration has been already proposed by Raeder et al. [21,39,40] for wet oxidation of formic acid.

The bulk catalysts have been studied in two different autoclave type reactors: a commercial one already described in a previous work [30] (see Fig. 1b) and a home-made designed which combines a standard Teflon lined autoclave with a stainless steel porous membrane (purchased from Mott with 500 nm as nominal pore size) for bubbling oxygen in the liquid phase (see Fig. 1c). Both types of reactors are mechanically or magnetically agitated at 800 rpm respectively. The conventional autoclave has been tested at 5 bar of partial O_2 pressure (35 bar as total pressure), whereas for autoclave with membrane diffuser a continuous pure O_2 stream (60 ml/min) is fed to the pressurized vessel at a total pressure of 3.5–4.5 bar. Moreover, it is worthwhile to remark that the experimental procedures used to stabilize the catalytic reaction system at the pressure and temperature conditions in absence of one of the reactants (i.e. oxygen or phenol) clearly differs from one reaction configuration to another due to technical limitations.

For the reaction experiments carried out in the commercial reactor, the catalyst is firstly in contact with oxygen and, once the P, T conditions are stabilized phenol contaminant is added to the liquid volume by pressurized N_2. However, for autoclave with membrane diffuser experiments, phenol is firstly introduced in the pressurized vessel with inert atmosphere once is stabilized at the reaction temperature; afterwards, oxygen is continuously supplied to the reactor. For membrane reactor type contactor, once the system is stabilized at P and T reaction conditions under N_2 atmosphere using DD water; phenol and O_2 streams are fed almost simultaneously to the membrane by opposite sides. Therefore, and for reactor performances comparison, these peculiarities for the reactor start up have to be considered because they might influence the initial activity of the catalysts, in accordance to the reported observations of Masende et al. [33] over Pt/graphite catalysts for phenol oxidation in a slurry-type reactor.

3. Results and discussion

3.1. Bulk catalyst characterization

The XRD spectra of the bulk catalysts listed in Table 1 are shown in Fig. 4. Neither phase due to pure ceria nor pure zirconia have been observed. The dominant diffraction peaks of all the samples

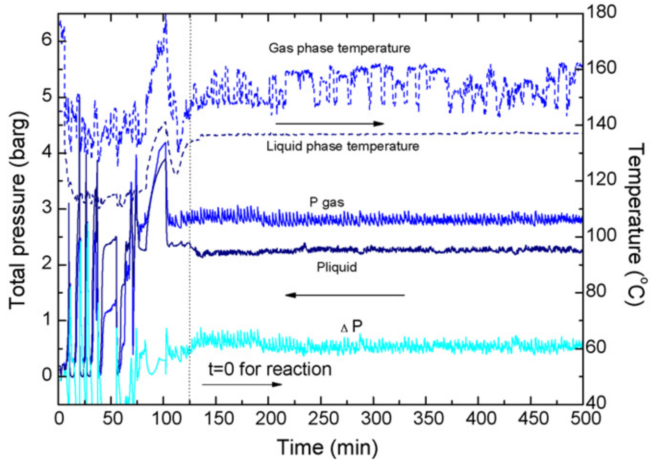


Fig. 3. Thermal and fluidodynamic stability for a standard catalytic membrane reaction experiment (A15 membrane).

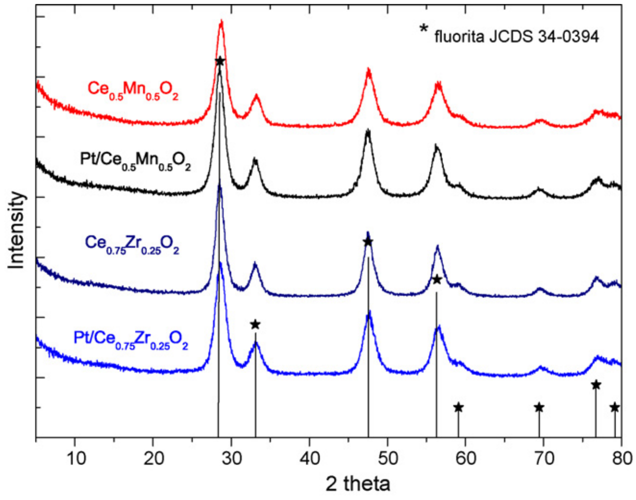


Fig. 4. XRD spectra of the as prepared bulk catalysts.

are the characteristic of cerianite (JCDS 34-0394) corresponding to a face centered cubic cell typical of the fluorite structure in accordance with the published literature [25,26,28,30,31,37].

The specific surface of the as prepared catalysts around 85–90 m^2/g (see Table 1) is similar to the reported values in the literature for mixed oxide Ce–Mn and Ce–Zr [25,37,41] systems. It is noted that after the incorporation of Pt onto mixed oxide Ce–Mn, the surface area decreases by 28% (from 87.1 to 62.4 m^2/g), probably due to the thermal Pt activation process (350 °C for 4 h). This decrease has been also observed by Hamoudi et al. [25] for Pt mixed oxide Ce–Mn catalytic system. However, for Ce–Zr samples, no noticeable textural effects are observed (89.1–86.1 m^2/g) in agreement with the characteristic thermal stability of this mixed oxide [42].

The XPS analysis (not shown here) of the bulk catalysts indicate that the presence of manganese or zirconium species does not alter the chemical environments of cerium; however, the XPS spectra of Mn 2p is clearly shifted to higher binding energies due to the interaction between manganese and cerium oxides [43]. The XPS values of Ce/Mn ratio (calculated from the area of the Ce 3d and Mn 2p core levels) and Ce/Zr ratio (calculated from the areas of the Ce 3d and Zr 3d core levels) are larger than those in the bulk (i.e. 2.6 vs. 1.0 and 4.2 vs. 3.0 respectively); indicating that the surface of the solids is enriched in Ce to some extent.

3.2. Catalytic membranes characterization

All the Ce–Mn, Ce–Zr catalytic membranes tested in CWO of phenol have been prepared by impregnation of a mixed nitrate solution (1.25 M in each metal) during 3 min. The incorporation of catalytic material makes the permeation values to slightly decrease (see Table 2) due to reduction of top layer pore size. For A19 membranes almost no variation on the N_2 flux are observed due to relative low catalyst loading attained (below 2 mg in 5 cm permeable length); whereas for A4 and A18 the influence of high catalytic loadings onto membrane permeation are offset by the repeated thermal treatment due to two impregnation cycles were carried out. It is worthwhile to remark that the amount of catalytic material incorporated to the membrane measured by ICP analysis is always clearly below (circa 50%) the tabulated values estimated by weight difference before and after membrane impregnation.

In Fig. 5a, the Ce/Mn atomic ratio estimated by SEM-EDX analysis across the membrane section of an analogue sample (3 cm in length) to A8 is depicted. The atomic Ce–Mn relationship inside the top layer, 1.8 in average, can be considered, in a first approximation, as the chemical composition of the catalyst responsible for the activity in CWAO of phenol. Moreover, the distribution profile for Ce/Mn based catalytic membranes indicates a preferential location of the catalytic material inside the top layer.

For Ce/Zr based membranes, a cerium enrichment in the top (5 nm in pore size) and intermediate (200 nm in pore size) layers is observed (see Fig. 5b). However, the Zr %atomic values measured are the lowest in comparison with its counterparts; and always below the detection limit inside the membrane thickness. It should be remarked that understanding the solution chemistry of cerium is not a simple task. Cerium ions may undergo complexation and hydrolysis depending on the ion concentration and pH, among others. Such solution parameters are rarely strictly the same when preparing Ce/Mn and Ce/Zr based membranes.

3.3. Catalytic wet oxidation of phenol

3.3.1. Commercial autoclave slurry-type reactor

Catalytic tests were carried at 140 °C using 3.8 $g_{cat.}/l_{solution}$, 5 bar as oxygen partial pressure and different initial phenol concentration (1000–3000 ppm). In Fig. 6a the evolution of phenol conversion with reaction time is shown comparatively for Ce/Mn and Ce/Zr oxides. Although higher phenol removal rates are exhibited by Ce/Mn oxides, the products distribution clearly differs from each other. Table 3 summarizes the selectivity values towards intermediate products (mainly carboxylic acids), carbonaceous deposits and mineralization products (estimated by difference) at final reaction time (420 min). As it can be observed, the carbonaceous deposits yield of Ce–Mn oxides is clearly over (68%) the Ce–Zr counterpart (circa 18%).

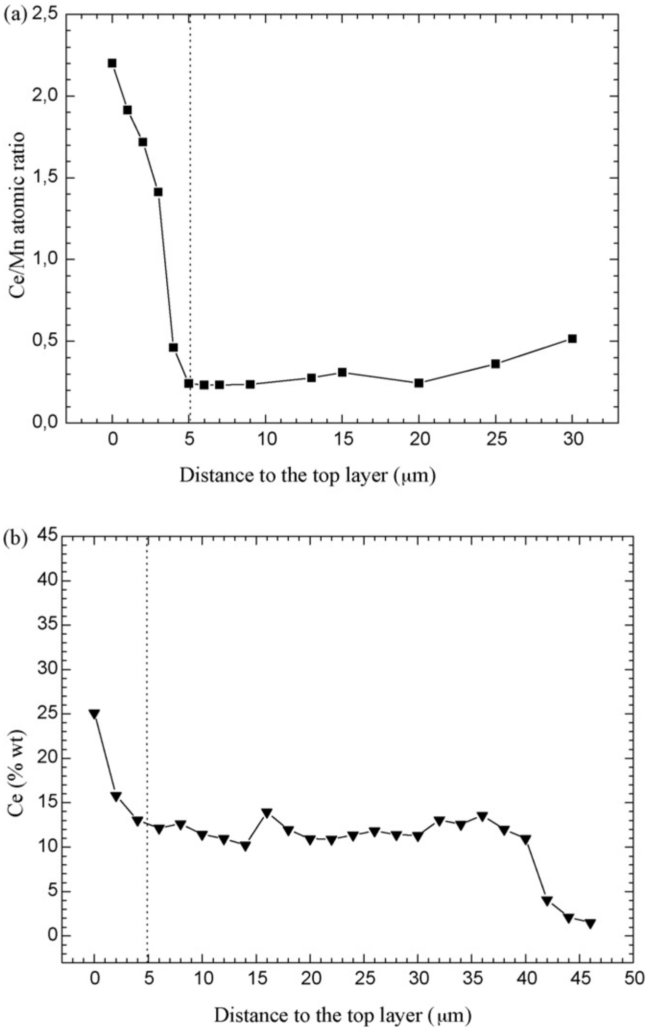


Fig. 5. (a) Atomic distribution profile for Ce/Mn based catalytic membranes. (b) Ce distribution profile for Ce/Zr based catalytic membranes.

The evolution of phenol conversion (3000 ppm) with reaction time is depicted comparatively for Ce/Zr and Pt doped Ce/Zr oxides in Fig. 6b. The addition of Pt up to 1.6 wt% enables nearly total phenol removal after 5 h of reaction time although during the first 2 h of reaction the Pt contribution is almost negligible. The reaction start up for commercial autoclave where oxygen is fed firstly to the reactor is affecting the mechanism of platinum catalysed phenol oxidation as the extent of oxygen coverage on the platinum surface influences the complex reaction pathways. The $Ce_{0.75}Zr_{0.25}O_2/Pt$ sample seems, among the tested, the most adequate for phenol removal given the high percentage towards mineralization even at higher conversion values.

3.3.2. Autoclave with membrane diffuser slurry-type reactor

To assess about the influence of the direct oxidant bubbling in the bulk liquid phase through a macroporous SS membrane,

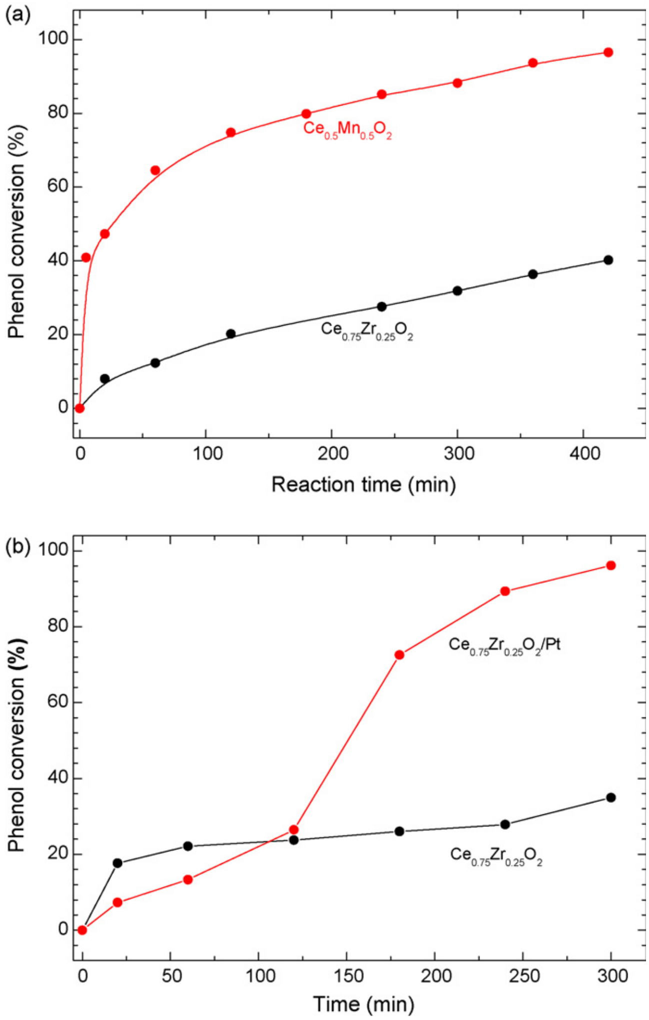


Fig. 6. (a) Comparison of Ce/Mn and Ce/Zr mixed oxides for CWO of phenol at 140 °C, 3.8 $g_{cat.}/l_{solution}$ and 1000 ppm. (b) Comparison of Ce/Zr and Pt–Ce/Zr mixed oxides for CWO of phenol using a commercial autoclave reactor at 140 °C, 3.8 $g_{cat.}/l_{solution}$ and 3000 ppm.

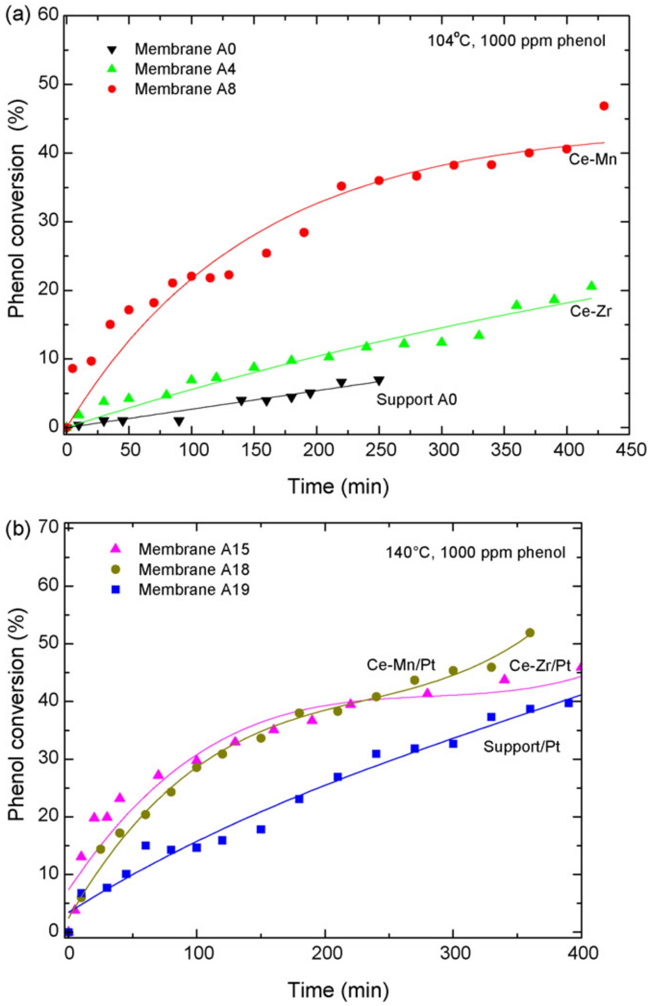


Fig. 7. (a) Comparison of undoped catalytic membranes for CWO of phenol. (b) Comparison of doped catalytic membranes for CWO of phenol.

catalytic tests under similar reaction conditions to the previously described in Section 3.3.1 (140 °C and 3.8 $g_{cat.}/l_{solution}$), have been carried out. Unlike commercial reactor, the operating O_2 pressure in the experiments with the autoclave/membrane diffuser is lower than 5 bar (circa 3.5 bar), but a continuous pure O_2 stream is fed to the reaction vessel enabling the continuous monitoring of the gas phase concentration.

CWO results shown in Table 4 enable the comparison with commercial autoclave reactor performance. For the Ce–Zr system an improvement in the phenol reaction rate is observed as the time necessary for a 25% of phenolic carbon removal decreases in a 33% (112 min vs. 174 min). However, the reaction start up for the autoclave with membrane diffuser where phenol is firstly introduced to the vessel is responsible for the high selectivity to carbonaceous deposits (80.1% vs. 43.7%). For Ce–Mn based catalytic system the differences are not really significant. For $Ce_{0.75}Zr_{0.25}O_2$/Pt catalysts the potential benefits of a membrane diffuser are offset by the poisoning of Pt active centers by polymerized intermediate products fouling during the first stage of reaction. The phenol and polymerized products competition for oxygen becomes the rate controlling step due to the relative low oxygen partial pressure for the elevated phenol loading (initially 3000 ppm) to be removed.

Taking into account these considerations is difficult to ascertain about the real influence of the improved gas/solid/liquid interfacial area from the catalytic tests carried out in this work.

3.3.3. *Catalytic membrane reactor type contactor*

Fig. 7a and b, show the phenol conversion profiles with reaction time for undoped an doped Pt membranes respectively evaluated at 140 °C and 1000 ppm of initial phenol concentration. Although the total liquid volume, continuosly recirculated by means of a

Table 3
CWO of phenol in commercial autoclave slurry-type reactor at 7 h of reaction time.

Sample	$[phenol]_0$ (ppm)	X_{phenol} (%)	Sel_{CO_2} (%)	$Sel_{deposit}$(%)	Sel_{acetic} (%)	Sel_{formic} (%)
$Ce_{0.75}Zr_{0.25}O_2$	1000	40.2	52.4	43.7	1.7	2.2
$Ce_{0.5}Mn_{0.5}O_2$	1000	96.5	26.8	70.2	1.3	1.6
$Ce_{0.75}Zr_{0.25}O_2$	3000	42.9	85.9	13.1	0.4	0.6
$Ce_{0.75}Zr_{0.25}O_2$/Pt	3000	96.1	77.8	18.9	2.4	0.9

Table 4
CWO of phenol in autoclave with membrane diffuser slurry-type reactor at 7 h of reaction time.

Sample	$[Phenol]_0$ (ppm)	Total P_{O_2} (bar)	X_{phenol} (%)	$Sel_{deposit}$ (%)	$t_{25\%}$ (min)[a]
$Ce_{0.75}Zr_{0.25}O_2$	1000	3.5	43.7	80.1	112
$Ce_{0.5}Mn_{0.5}O_2$	1000	3.5	92.4	100.0	25
$Ce_{0.75}Zr_{0.25}O_2$/Pt	3000	3.3	42.7	26.3	79

[a] Extrapolated from the phenol reaction curve at 25% conversion level.

HPLC pump, remains constant for all the reaction tests, the catalyst/liquid volume ratio differs from one membrane to another (from 0.02 to 1.88 g/l) due to the differences in catalytic material loadings (see Table 2). Moreover, it is worthwhile to emphasize that the real liquid volume for reaction purposes might be the corresponding to the porous volume of the thin layer (less than 0.1 cm^3) rendering to two orders of magnitude higher catalyst/liquid volume ratio values.

The reaction system has proven to be very challenging due to the deactivation phenomena that have emerged as a result of the unwanted reaction of polymerization, also observed in the catalysts powder, but highly notorious in the catalytic membrane reactor type contactor.

For undoped membranes, Ce–Mn supported oxides outperform their Ce–Zr counterparts in agreement with the bulk catalysts results. It is worthwhile to remark the residual activity of the γ-Al_2O_3 layer from the starting ceramic supports (up to 7% of phenol conversion). Pt based catalytic membranes exhibit higher activity towards phenol degradation, although less noticeable for Ce–Mn supported oxides due to the high deactivation by carbonaceous deposits. A promising catalytic behaviour is exhibited by A19 membrane, Pt supported on γ-Al_2O_3 layer; although fluidodynamic stability issues associated to the starting asymmetric structure of the support are hindering its deployment.

Table 5 summarizes the products distribution obtained at final reaction time. The selectivity towards deposits formation has been calculated from the TPO-MS analysis of spent catalytic membranes. The permeation measurements before and after such analysis, carried out at 350 °C for 3 h with a 6% O_2 in Ar, compiled in Table 6 are indicating the total removal of the carbonaceous solids blocking the mesoporous thin layer.

Unlike conventional reactor, the contactor membrane alters the distribution of reaction products due to only CO_2 and carbonaceous deposits are detected. This may be related to the influence of the solid–liquid ratio on the formation of carbonaceous deposits [5]. In the slurry-type reactors, where a low catalyst-to-liquid volumetric ratio is found, the formation of polymers in liquid phase is favoured. However, for reactors where this relationship is high, i.e. trickle-bed reactors, homogeneous reactions in the liquid phase are suppressed, leading to an almost quantitative transformation of phenol to CO_2 [5]. This observation is particularly interesting for the scope of this work where membrane contactors with elevated values for the effective catalyst-liquid volumetric ratio have been studied.

For the different catalytic membranes tested, those based on γ-Al_2O_3/Ce–Zr/Pt are in terms of activity and selectivity the most adequate for phenol mineralization. As it has been already pointed out, the promising catalytic behaviour of γ-Al_2O_3/Pt membrane is offset by the difficulties associated to the stabilization of contact pressure.

In order to check the efficiency of membrane reactor type contactor, additional autoclave with membrane diffuser experiments have been carried out under identical reaction conditions. For the system of Pt/Ce–Zr, the comparison of results (Fig. 8a) shows the improvement of G–S–L contact imposed by the use of a catalytic membrane. A slurry reactor experiment with Pt supported on ceria bulk catalyst is also included for comparison purposes due to the lower Zr contents estimated by SEM-EDX analysis of the as prepared membranes. Considering that the membrane catalytic loadings estimated by ICP are approximately 50% of the value used to calculate the nominal catalyst-volumetric liquid ratio, the comparison with new slurry-type reactor

Table 5
CWO of phenol in membrane reactor type contactor at final reaction time.

Membrane	Active phase	P_{O_2} (bar)	X_{phenol} (%) ($t=\infty$)	mg $C_{deposits}$[a]/g $C_{converted}$	mg $C_{deposit}$[a]/$g_{mixed\ oxide}$	Sel_{CO_2} (%)[b]
A0	γ-Al_2O_3	3.5	7.0	328	–	67.2
A4	γ-Al_2O_3/Ce–Zr	4.5	20.5	246	41.4	75.4
A8	γ-Al_2O_3/Ce–Mn	4.0	46.8	464	142.3	53.6
A15	γ-Al_2O_3/Ce–Zr/Pt	3.8	45.8	333	100.4	66.7
A18	γ-Al_2O_3/Ce–Mn/Pt	4.0	51.9	556	167.6	44.4
A19	γ-Al_2O_3/Pt	3.8	40.0	131	–	86.9

[a] Estimated from CO_2 desorption during TPO-MS analysis.
[b] Estimated by difference.

Table 6
Total removal of the carbonaceous solids blocking the mesoporous thin layer.

Membrane	Active phase	Permeation (mol N_2/m^2 s Pa)[a]	Permeation (mol N_2/m^2 s Pa)[b]	Permeation (mol N_2/m^2 s Pa)[c]
A0	γ-Al_2O_3	6.0×10^{-6}	8.3×10^{-6}	8.1×10^{-6}
A4	γ-Al_2O_3/Ce–Zr	8.3×10^{-6}	8.4×10^{-6}	1.1×10^{-5}
A8	γ-Al_2O_3/Ce–Mn	1.5×10^{-6}	2.2×10^{-7}	2.8×10^{-6}
A15	γ-Al_2O_3/Ce–Zr/Pt	3.8×10^{-6}	1.3×10^{-6}	5.4×10^{-6}
A18	γ-Al_2O_3/Ce–Mn/Pt	4.4×10^{-6}	3.2×10^{-7}	4.7×10^{-6}
A19	γ-Al_2O_3/Pt	5.3×10^{-6}	4.7×10^{-7}	4.6×10^{-6}

[a] Before CWO of phenol reaction test.
[b] After CWO of phenol reaction test.
[c] After TPO-MS regeneration analysis.

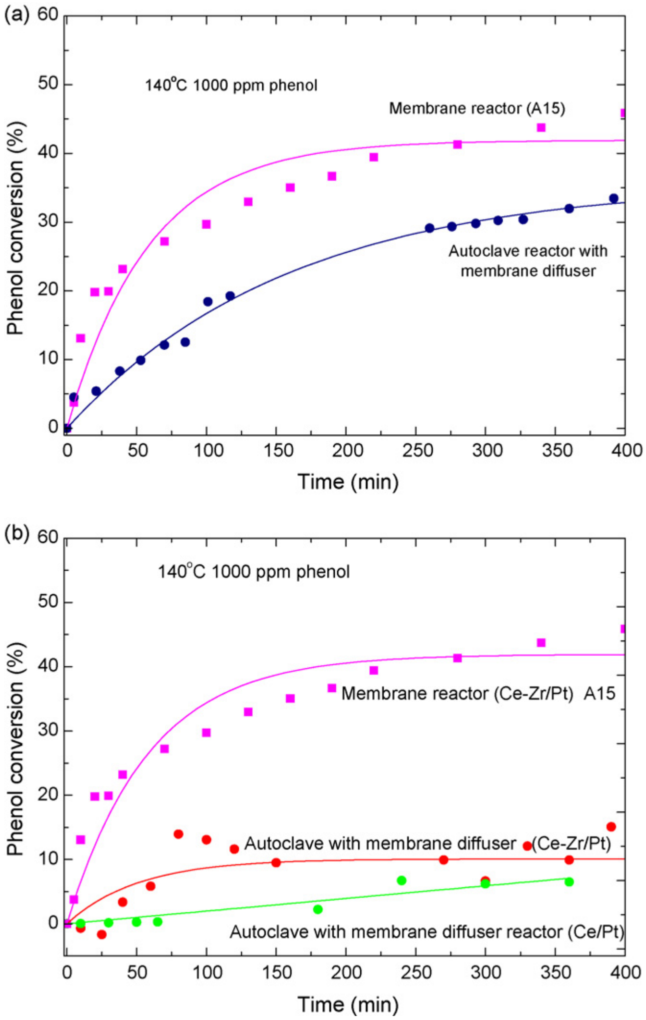


Fig. 8. (a) Reactor performance comparison for Pt/Ce–Zr based catalytic systems using nominal catalyst-volumetric liquid ratio. (b) Reactor performance comparison for Pt/Ce–Zr based catalytic systems using the catalyst-volumetric liquid ratio estimated by ICP analysis of the membrane digestion solution.

experiments is shown in Fig. 8b. As it can be noticed, the conclusions before drawn are greatly reinforced (see Fig. 8b), even more when the Pt/Ce bulk sample behaviour is analyzed.

4. Conclusions

The improvements of GSL contact by use of a catalytic membrane reactor type contactor over two different slurry-type reactors have been demonstrated in the case of wet oxidation of phenol at 1000 ppm, since it is not only a common pollutant in industrial waste streams, but also it is considered as a worst-case model compound for water pollution studies. However, a proper location of the gas–liquid interphase, which is in the thin catalytic internal top layer, has to be ensured thorough the experiment to take advantage of the interfacial membrane contactor.

For the three catalytic Ce mixed oxide systems, the catalyst based on Pt/Ce–Zr has been the most adequate in terms of phenol removal towards mineralization products whatever the reactor configuration used. The reaction system has proven to be very challenging due to the deactivation phenomena by carbonaceous deposits onto the catalyst surface as a result of the unwanted reaction of polymerization. This is one of the main drawbacks, particularly noticeable for Ce–Mn based oxides and requires new catalysts formulation (e.g. Ce–Mn/K or Ce–Mn/Ag). Moreover, the deactivation process seems critical for membrane reactor operation due to the progressive blocking of the catalytic top layer is hindering the complete phenol removal. Unlike slurry-type reactors, the contactor membrane alters the distribution of reaction products because no intermediate products are observed at the elevated values for the effective catalyst-liquid volumetric ratio attained.

Acknowledgment

Mirella Gutiérrez gratefully acknowledges to the Universidad Autónoma Metropolitana (México) for the predoctoral fellowship.

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