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

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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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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 $Ce(NO_3)_3{\cdot}6H_2O$, $ZrO(NO_3)_2{\cdot}xH_2O$, and $Mn(NO_3)_2{\cdot}xH_2O$ (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 $H_2PtCl_6{\cdot}xH_2O$ (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.