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Catalytic wet oxidation of phenol over lanthanum strontium manganite

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ABSTRACT

The catalytic performances of lanthanum strontium manganite $(La_{0.8}Sr_{0.2})Mn_{0.98}O_3$, in catalytic wet oxidation (CWO) of a phenol solution under milder conditions of temperature (398–498 K) and pressure ($P_{o_2} = 4$ bar), in a batch reactor, have been investigated. Aim of this study is the evaluation of the effect of temperature, catalyst loading, phenol concentration and stirrer speed on phenol conversion. Experimental data obtained from the different test conditions are best-fitted to evaluate the effective reaction order and apparent activation energy.

1. Introduction

The contamination of aqueous streams by organic compounds is a problem of great interest today since the growing demand of quality water resources. As summarized in a recent review [1], the abatement of phenol from fluid streams has been the object of much investigation, because it and/or its derivates are present as pollutants in wastes arising from several industrial and alimentary processes, and also because phenol is frequently taken as a model molecule for bad smelling volatile organic compound water pollutants.

There are different strategies for the remediation of water contaminated with these compounds. Adsorption on activated carbon is a widely used and effective technique for the removal of a broad range of organic compounds including phenols [2]. However, adsorption does not ultimately destroy the pollutants, therefore the active carbons have to be disposed or reactivated, which increases the costs of the method.

The conventional biological treatment is widely applied for the handling of residual wastewaters. The main disadvantage of biological treatment is the incapability of treatment for highly polluted and toxic waste streams in industrial wastewaters. Biological treatment is neither suitable for chemical oxygen demands (COD) above 10 g l^{-1} nor for water which includes toxic compounds [3] due to biomass poisoning.

The wet oxidation (WO) process, in particular the catalytic one (CWO), is considered to be an attractive method for treatment of wastewaters with concentrations of organic loads of about 10–100 g l^{-1} [4–6]. The use of a catalyst results in a significant reduction of the temperature and pressure, an increase of the oxidation rate of refractory compounds and is therefore improving the economy of the process because the oxidation of organic pollutants can be realized under milder conditions compared to the noncatalyzed processes. As usual, a key aspect in this process is the catalyst choice, at the present time those with the best performances are noble metals-based [6,7], whose main drawback is their high cost. In the last decade, significant efforts have been done in finding new materials fulfilling important requirements as cheap cost, activity at low temperature and pressure, stability and that they are environmentally friendly. With regard to this, several groups investigated on Cu-based materials. Pintar and Levec [8–10] worked on Zn–Cu–Al-based systems under 373–403 K and 5–6 bar of P_{o_2}. Cu-based catalysts have also been investigated deeply: Eftaxias et al. [11] worked with a trickle bed reactor at 433 K and $P_{o_2} = 6$ bar employing a γ-Al_2O_3-supported CuO catalyst. The group of Santos tested different copper-based materials as catalysts for phenol wet oxidation [12] in a trickle bed reactor at 413 K and $P_{o_2} = 16$ bar. The same group investigated

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also on the employment of active carbons as catalysts under the same conditions [13].

Recently, interest has been devoted to Mn-based catalysts. Hamoudi et al. investigated on ceria-supported MnO_2 [14,15] obtaining interesting phenol conversion under very mild conditions namely 50 bar of O_2 partial pressure at ca. 373 K. Chen et al. [16] studied the effects of Mn–Ce–O composites on phenol catalytic wet oxidation at low O_2 partial pressure and temperature. The group of Stoyanova published great results [17] in phenol abatement under atmospheric pressure and almost room temperature (308 K) employing a Ni–Mn mixed oxide.

However, it must be taken into consideration that phenol may be not totally directly oxidized to CO_2 by CWO, a range of organic compounds being formed as intermediates or byproducts during the mineralization process. The hydroxylation of phenol to hydroquinone and catechol is considered to be the first step followed by a further oxidation of the dihydroxylbenzenes to benzoquinones [5]. It is also assumed that both dihydroxylbenzenes follow the same oxidation route leading to various C-4 products such as maleic acid or C-2 products like oxalic acid and acetic acid [5]. Since some of the intermediates, in particular hydroquinone and *p*-benzoquinone, are more toxic than the original pollutant [18,19], the identification of the products at the end of the oxidation process is a key point to evaluate the reduction of ecotoxicity actually obtained with the process.

A main drawback of CWO with most impregnated transition metal oxide catalysts is their leaching, which results in solid catalyst deactivation as well as in water contamination by the metal ions. As pointed out by Pintar and Levec [6], to limit leaching, transition metal ions should be incorporated in the solid more than deposed at his surface.

Perovskite-type oxides (ABO_3) containing transition metals such as Mn have been studied as potential combustion catalysts [20–23] ever since it was discovered that some have comparable catalytic activities to conventional Pt/Al_2O_3 catalysts [24]. In particular $LaMnO_{3+\delta}$ is one of the perovskite oxides easier to reduce therefore suitable as catalyst for oxidation reactions; its catalytic activity is strictly related to the nonstoichiometric character of the surface [25,26]. Also, the incorporation of dopant ions, commonly low valent cations such as Sr^{2+}, to the $LaMnO_{3+\delta}$ oxides results in a promotion of the catalytic activity lanthanum strontium manganite $(La_{1-x}Sr_x)MnO_{3+\delta}$ powders, called LSM, is an excellent combustion catalyst in gas–solid processes [20], and is commercially available being, among other applications, used to produce anodes of solid oxide fuel cells by sintering. Perovskite-like oxides recently found application as catalysts in CWO of stearic acid, interesting results were published in [27].

Aim of this work is to investigate on the activity of $(La_{1-x}Sr_x)MnO_{3+\delta}$ as catalyst in phenol CWO, as well as on the optimization of the process parameters as temperature, catalyst load and agitation speed.

2. Experimental

2.1. Catalyst

The catalyst was a commercial (Praxair) perovskite-like $(La_{0.8}Sr_{0.2})Mn_{0.98}O_3$.

X-ray powder diffraction pattern of the sample was carried out with a X-Pert Philips diffractometer using a Co Kα radiation.

The microscopic analysis by scanning electron microscopy (SEM) was carried out in a Jeol SM-840 instrument that allowed to obtain information about the morphology.

2.2. Catalytic activity tests

Catalytic activity test were conducted in a stirred batch reactor (“4563 Mini reactor”, produced by the Parr Instrument Company, IL, USA). It consists of a moveable cylindrical stainless steel 0.6 l vessel with a flat gasket seal. It is equipped with a gas inlet valve, a gas outlet valve, a liquid outlet valve and a rupture disc as a pressure relief device. Temperature and pressure can be checked by an internal fixed thermocouple and by a pressure gauge. The vessel can be heated by a cylindrical heater; inner liquid solution can be stirred by a stirring system.

The reactor was loaded with 0.5 l of phenolic solution at fixed concentration and with the catalyst in powder form. The reactor was then sealed and pressurized with oxygen through gas inlet valve to an initial pressure of 4 bar. Catalytic tests were carried out by varying temperature, phenol concentration, catalyst loading and the stirrer speed. Blank experiments (i.e. with no catalyst) at 423 and 448 K were conducted as well.

The solutions were analyzed by HPLC (Shimadzu 10 A VP system equipped with a diode array detector). The column employed was a Pinnacle II C18 with a length of 250 mm and an inner diameter of 4.6 mm. The stationary phase is C18 or ODS silica supported with a media particle diameter d_p of 5 μm. The mobile phase employed in this work was a mixture of acetonitrile (35%) and water (65%) sent through the column with a flow rate of 0.7 ml min^{-1}. The water employed in the mobile phase was deionized, micro-filtrated and furthermore acidified with 1 ml of H_3PO_4 (3 M) resulting in a pH of 2.8.

3. Results and discussion

3.1. Catalyst characterization

The physical properties supplied by the manufacturer (Praxair) are: $d_{50} = 0.9$ μm, surface area = 5.0 $m^2\,g^{-1}$.

X-ray powder diffraction pattern of the sample, reported in Fig. 1, confirms the perovskite structure of $(La_{0.8}Sr_{0.2})Mn_{0.98}O_3$.

SEM micrograph of the fresh sample, reported in Fig. 2, shows the homogeneity of the microscale crystal size of the powders.

3.2. Catalytic behaviour

Fig. 3 shows the trends of phenol conversion (Fig. 3a) with the temperature and reaction time, as well as the trends of the selectivities to cyclic intermediates, *o*-benzoquinone (Fig. 3b), hydroquinone (Fig. 3c) and *p*-benzoquinone (Fig. 3d). The

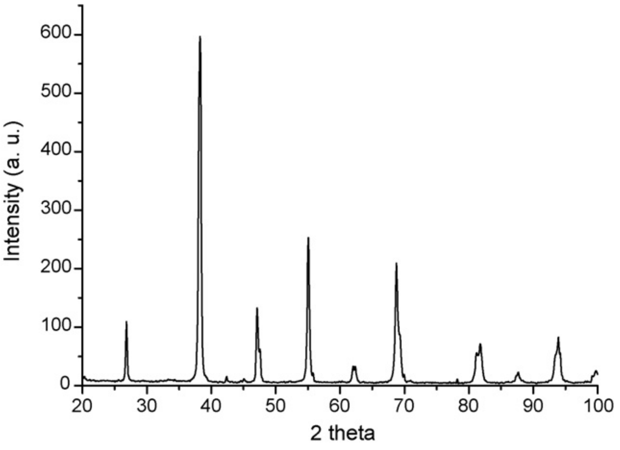

Fig. 1. X-ray powder diffraction pattern of $(La_{0.8}Sr_{0.2})Mn_{0.98}O_3$.