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Lanthanum-based perovskites as catalysts for the ozonation of selected organic compounds

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ABSTRACT

The ozonation of two model compounds (oxalic acid and dye C. I. Reactive Blue 5) was carried out in the presence of La containing perovskites prepared by the citrate method. With the exception of $LaFe_{0.9}Cu_{0.1}O_3$, all samples are active in the catalytic ozonation of oxalic acid, some of them allowing fast degradation of the compound. The presence of lattice vacancies on the perovskites surface and tuning of oxidation ability by the B cation play a key role in oxalic acid removal. Sample $LaCoO_3$ was considered the best catalyst in oxalic acid degradation; in addition to its high activity, no metal leaching was observed. Regarding colour removal from the dye solution, single ozonation was slightly more efficient than catalytic ozonation in the presence of $LaCoO_3$. On the other hand, ozonation catalyzed by $LaCoO_3$ improved the TOC removal, allowing almost complete mineralization of the solution after 3 h of reaction under the conditions tested.

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1. Introduction

Perovskite have a general formula ABO_3, where A is usually a rare earth cation and B a transition metal cation [1]. This kind of material can tolerate substitutions at both cation sites without modification of the crystal structure. The substitution at A site with ions having lower valence can allow the formation of structural defects such as anionic or cationic vacancies and/or a change in the oxidation state of the transition metal cation to maintain the electroneutrality of the compound. When the oxidation state of B cation increases, the redox process generates larger amounts of available oxygen at low temperature and the overall oxidation activity is enhanced. Moreover, the oxygen vacancies favour the catalytic activity in oxidation reactions because they increase the lattice oxygen mobility [2]. The preparation method of perovskites is important both in defining suitable textural characteristics for catalysis and in achieving phases of great purity. The literature describes numerous synthesis methods, most of them producing materials for applications other than catalysis, and allowing incorporation of cations into the functional perovskite structure due to the high calcination temperatures used. The most commonly technique used to overcome the problem of purity is the sol–gel citrate method. This method allows to obtain catalysts with high surface areas, but it has the drawback of sintering, which depends on the temperature [3]. Metal oxides with a perovskite structure have been consistently proposed during the last two decades as alternative catalysts for the total oxidation of methane and volatile organic compounds. The use of these materials has been especially promoted in applications involving high temperatures and oxygen steam-rich atmospheres, where their thermal stability comes into play [4].

Heterogeneous catalytic ozonation is gaining an increasing interest in the drinking water and wastewater treatment field [5]. The main advantages of this technique are the ability to enhance the rate of oxidation of organic compounds and especially to improve the mineralization degree achieved at the end of the process [6]. Carbon materials, metal oxides and supported metal oxides have been proposed as effective heterogeneous ozonation catalysts, but only a few studies adressed the catalytic activity of perovskites in ozonation processes. Perovskite $LaTi_{0.15}Cu_{0.85}O_3$ was successfully used in the ozonation of pyruvic acid, a refractory substance typically generated after oxidation of phenol-like compounds [7], and in the ozonation of gallic acid [8]. The same perovskite was evaluated in the ozonation of different phenolic wastewaters, and the catalytic stability were confirmed by consecutive experiments [9]. More recently, a perovskite containing copper was appointed as a very efficient catalyst to improve TOC removal in the ozonation of sulfamethoxazole, a sulfonamide type synthetic antibiotic [10].

In this work, a wide range of La-containing perovskites prepared by the citrate method and characterized by different techniques were used to investigate the catalytic ozonation of

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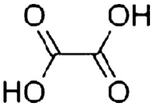
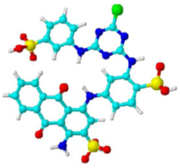
Table 1
Main characteristics of selected pollutants.

Compound		M (g mol^{-1})	pKa	$\lambda_{max.}$(nm)
Oxalic acid ($C_2H_2O_4$)		90.04	1.23, 4.19	–
CI Reactive Blue 5 Cibacron Blue BR ($C_{29}H_{20}ClN_7O_{11}S_3$)		74.16	–	597

oxalic acid and the reactive dye C. I. Reactive Blue 5 for the first time.

2. Experimental

2.1. Catalysts preparation and characterization

Perovskites were prepared by the citrate method as described by Merino et al. [1]. Briefly, aqueous solutions of the metal nitrates were added to the solution of citric acid, and then stirred for 15 min. The resulting solution was concentrated by slowly evaporating water under vacuum in a rotavapor at 75 °C until a gel was obtained. The gel was dried in an oven, slowly increasing the temperature to 200 °C and maintaining this temperature overnight, in order to produce a solid amorphous citrate precursor, which was then milled and calcined in air at 700 °C for 2 h.

Perovskites were characterized by a wide range of techniques as reported elsewhere [1]. Briefly, BET specific surface areas were calculated from N_2 adsorption isotherms at −196 °C, obtained in a Micromeritics Accusorb 2100E apparatus. The elemental composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). XRD patterns were recorded at room temperature with a Rigaku diffractometer operated at 30 kV and 20 mA and Ni-filtered Cu-Kα radiation (λ = 0.15418 nm). Temperature-programmed reduction (TPR) experiments were performed in a quartz reactor with a TCD detector; samples were pretreated in helium and the temperature was increased from room temperature to 700 °C under a reducing atmosphere of 5% H_2/N_2. XPS spectra were recorded on a VG Scientific ESCALAB 200A spectrometer and XPS data were fitted using the software XPSpeak.

2.2. Kinetic experiments

Two organic molecules were selected for this study: a carboxylic acid (oxalic acid, 99%, Sigma–Aldrich) and a textile dye (CI Reactive Blue 5). Their main characteristics are shown in Table 1.

Ozonation of pollutants was investigated in a slurry lab-scale reactor equipped with agitation under optimal operation conditions, previously determined. In each experiment the reactor was filled with 700 cm^3 of pollutant solution ($C_{0,\text{oxalic acid}}$ = 1 mM, $C_{0,\text{ dye}}$ = 50 mg L^{-1}) at the natural pH ($pH_{0,\text{ oxalic acid}}$ = 3.0, $pH_{0,\text{ dye}}$ = 5.5). In the catalytic ozonation experiments, 100 mg of catalyst (dp < 100 μm) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow rate (150 cm^3 min^{-1}) and constant inlet ozone concentration (50 g m^{-3}). The concentration of ozone in the gas phase was monitored with a BMT 964 ozone analyzer. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with iodide potassium solution. The agitation was maintained constant in order to keep the reactor content perfectly mixed. In adsorption experiments, the ozone-containing stream (mixture of ozone and oxygen) was replaced by an oxygen stream, in order to maintain the experimental conditions and to remove the effect of ozone. In the experiments carried out in the presence of *tert*-butanol, a concentration of 10 mM of this radical scavenger was used [11]. All experiments were carried out at room temperature and atmospheric pressure.

The concentration of oxalic acid was followed by a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was an Aminex HPX-87H column (300 mm × 7.8 mm), working at room temperature under isocratic elution with H_2SO_4 4 mM. The concentration of dye in the solution was followed by UV–vis spectrophotometry with a JASCO V-560 UV/Vis spectrophotometer. The degree of mineralization was determined by total organic carbon (TOC) analysis in a Shimadzu TOC-5000A Analyser.

3. Results

3.1. Catalysts characterization

Table 2 presents the BET surface areas and the percentages of lattice oxygen species (O^{2-}) on the surface of the prepared perovskites. La-containing perovskites have BET surface areas between 7 and 15 m^2 g^{-1}. $LaFeO_3$ presents the highest BET surface area, which decreases with the introduction of Cu. The study of the catalysts by XPS was carried out as described in [12]. XPS analyses of selected samples allow to conclude that oxygen vacancies are present on perovskite surfaces, except in the case of $LaFeO_3$. Sample $LaAl_{0.9}Cu_{0.1}O_3$ has the largest amount of lattice oxygen species on surface.

Fig. 1 shows the TPR profiles of La-containing perovskites. $LaMnO_3$ has a splitted signal with a maximum at around 400 °C. $LaCoO_3$ has two reduction stages, one between 350 and 450 °C and the other at around 600 °C [1]. Sample $LaNiO_3$ presents two peaks, the first corresponding to the reduction of Ni^{3+} to yield the $La_2Ni_2O_5$ phase, with a loss of oxygen from the structure, and the second with

Table 2
BET surface areas and percentage of lattice oxygen species of La-containing perovskites.

Perovskite	S_{BET} (m^2 g^{-1})	% O^{2-} (lattice)[a]
$LaFeO_3$	15.2	0
$LaNiO_3$	9.8	N.D.
$LaCoO_3$	7.4	39.4[b]
$LaMnO_3$	14.6	N.D.
$LaFe_{0.9}Cu_{0.1}O_3$	10.5	46.3
$LaFe_{0.7}Cu_{0.3}O_3$	11.5	41.8
$LaAl_{0.9}Cu_{0.1}O_3$	6.9	57.4
$LaAl_{0.7}Cu_{0.3}O_3$	8.4	48.1

[a] Determined by O 1s XPS peak deconvolution.
[b] Value from [12].

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