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Ceria and cerium-based mixed oxides as ozonation catalysts

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HIGHLIGHTS

- Ceria and cerium-based mixed oxides were tested as catalyst in the ozonation of organic pollutants.
- For oxalic acid the catalytic activity increases with the increase of Ce(III) on the surface.
- The surface oxygen vacancies play an important role in the mineralization of aniline.
- All catalysts allowed a complete or near complete mineralization of the dye solution.

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ABSTRACT

Ceria (CeO_2) and cerium-based mixed oxides (Ce–Sm, Ce–La and Ce–Zr with different compositions) were prepared by the precipitation method from aqueous solutions of nitrate precursors. The materials synthesized were tested as catalysts in the ozonation of oxalic acid, aniline and the textile dye C. I. Reactive Blue 5.

Different performances were obtained depending on the type of organic compound and catalyst involved. In the case of oxalic acid, cerium–zirconium catalysts with more zirconium presented the best catalytic activities, allowing a total removal after 3 h of reaction. The good performance of these samples was justified by the increase of Ce(III) species on their surfaces. In the catalytic ozonation of aniline, the highest mineralization degree was achieved with CeO_2 and $Ce_{0.75}Zr_{0.25}O_2$, the latter being the sample with the largest amount of oxygen vacancies on its structure. All the prepared catalysts significantly improved the mineralization rate in the ozonation of the dye solution relatively to single ozonation (no catalyst). By itself, adsorption on the surface of catalysts is not relevant in the removal of organic compounds.

1. Introduction

Ozonation processes are used in the decontamination of drinking water and wastewater, since they promote high COD (chemical oxygen demand) reduction, increase the biodegradability and, in general, the secondary products are not toxic for the environment. On the other hand, ozone alone presents limitations in the mineralization of organic compounds and in the removal of refractory pollutants. The ozonation of several hazardous organic compounds such as pesticides, dyes and aromatic hydrocarbons originates significant amounts of saturated organic compounds such as aldehydes, ketones and carboxylic acids. Due to the low reactive nature towards ozone, these compounds tend to accumulate in solution. Hence, single ozonation is not sufficient to achieve a high mineralization degree [1]. To overcome this drawback, ozonation processes are being modified in order to increase their oxidizing capability [2]. Some studies have shown that several metals in solution or in the solid phase under various forms (metal oxides, supported metals) may catalyse ozonation reactions, being able to destroy some very recalcitrant pollutants [3]. Heterogeneous catalytic ozonation, which is one of the most attractive alternatives, aims at enhance the removal of more refractory compounds by the transformation of ozone into more reactive species such as hydroxyl radicals and/or by adsorption and reaction of the pollutants on the surface of the catalyst [4]. The efficiency of the catalytic ozonation depends on the surface properties of the catalyst as well as on the solution pH and on the chemical nature of the reactants. Oxides of transition metals, such as manganese [5], titanium [6] or cobalt [7], are amongst the most frequently studied ozonation catalysts.

Ceria (CeO_2) is a cubic fluorite-type oxide, and is considered as the most important of rare-earth oxides, hence it has been extensively investigated and used in several industrial applications. However, the main applications of cerium oxide are as catalysts, catalyst promoters or catalyst supports. The importance of ceria

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