

Zirconia doped with La Fe synthesized by sol gel, used in the trichloroethylene catalytic combustion

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Introduction

Zirconia is one of the most studied ceramic materials due to its outstanding thermal, mechanical and chemical stability; in addition, acidic, basic, oxidizing and reducing surface properties make this oxide suitable for many catalytic processes [1-3]. Depending on the preparation method and thermal treatment, monoclinic, tetragonal, cubic, or a mixture of these phases can be obtained. The sol-gel method has attracted considerable attention for the preparation of metallic catalysts, since the constituents are mixed in an atomic scale and this generates a uniform distribution of active metals upon the support [4]. The crystalline phase obtained by the sol-gel method can strongly depend on the starting metallic precursor.

Zirconium oxide is an interesting and useful catalytic support. La, Mn and La-Fe perovskites supported on ZrO₂ have shown good performances during methane combustion and CO oxidation [5]. Doped ZrO₂ catalysts have been prepared by the sol-gel method and have showed a high activity in the low temperature liquid phase cumene oxidation [2]. De Paoli et al. [6] reported that trichloroethylene combustion over LaFeO₃ perovskite presented an inhibition effect caused by the strong adsorption of chlorinated species on the active sites of the catalytic surface but with very good catalytic activity and thermal stability at large using times. In this work, La, Mn and Fe zirconia-supported catalysts were prepared by the sol-gel method employing a zirconium alkoxide and pertinent metallic acetates as precursors. The samples obtained this way were thoroughly characterized with the purpose of evaluating and comparing them as useful catalysts for the combustion of trichloroethylene. The importance of studying the synthesis of new catalysts for destruction of trichloroethylene molecule is that it belongs to the group of chlorinated volatile organic compounds (VOC) that can be seen as a simulation of a pollution of air by an industrial gas emission.

Materials and Methods

For the synthesis; zirconium butoxide was mixed with of 1-butanol. Glacial acetic acid was added under magnetic stirring until reaching pH 3. Acetate solutions of the doping metals were then added dropwise to the butoxide-butanol mixture; the La and Fe doping species represented a 0.5 wt. % of the ZrO₂ mass. The solution was maintained under refluxing conditions at 60 °C until a gel was formed. Xerogels were then obtained by treating the gel samples at 70 °C followed by calcination in an electrical furnace at 800 °C for 8 h. The powders obtained were zirconia pure (Z labeled) and zirconia doped with La and Fe 0.5% wt. of each metal (ZLF labeled). Both powders were characterized by FT-IR, TGA, DTA, XRD

techniques and the microstructure of pores was determined by the isotherms of absorption of N₂ liquid. The catalytic activity was tested using a steady state tubular micro-reactor inserted in a tubular furnace equipped with a temperature controller, employing mixtures of trichloroethylene in air (1% by volume) and the spatial time was of 500 hr⁻¹.

Results and Discussion

The temperature of calcination of gels was determined according to TGA results; the solvent was evaporated totally at 650 C but the temperature was increasing until 800 due to protection at the catalytic tests. The DTA analysis let to see how the doping displaced the temperature transformation peaks to tetragonal phase from 455 to 460 C. The tetragonal phase was favored for the doping species and monoclinic phase was presented in pure zirconia. Figure 1 presents the diffraction patterns of x-ray of both samples.

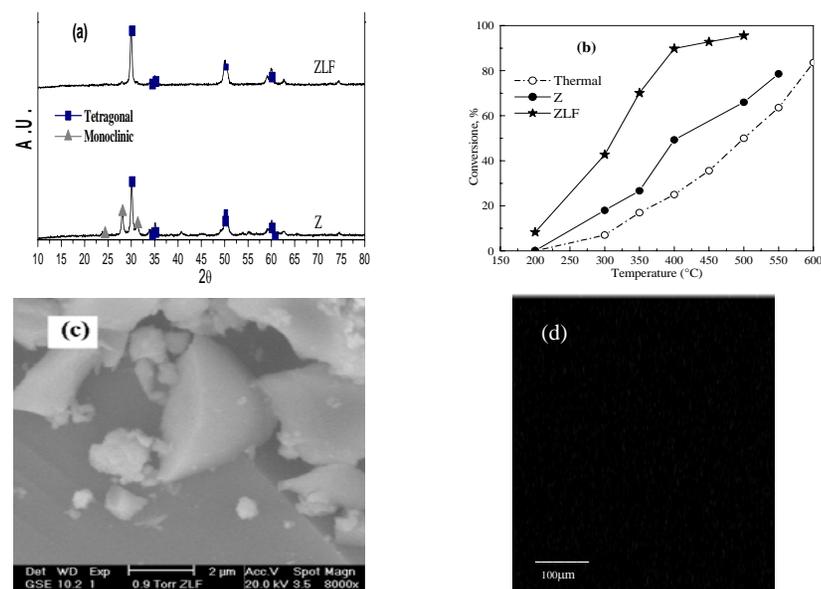


Figure 1. (a) XRD patterns of pure zirconia (Z) and doped La-Fe zirconia (ZLF) calcined at 800 °C, (b) Combustion of trichloroethylene at 1 % in air for Z and ZLF catalysts, (c) SEM micrograph of ZLF catalyst and (d) FeK α signal (white points) for EDAX mapping for ZLF catalyst surface

Figure 1 (a) shows the XRD patterns for pure zirconia (Z) and La-Fe doped zirconia (ZLF) catalysts. It can be seen that the tetragonal phase is the dominant one; a similar effect was reported by Navio et al [3] stating that the development of the tetragonal phase by the presence of doping agents could be due to a decrease in the surface free energy of ZrO₂ or to the creation of anionic vacancies. Monoclinic phase is mixed with tetragonal crystalline phase in the Z catalyst. Figure 1(b) shows the conversion as a function of temperature in the combustion of trichloroethylene at 1% in air. The

conversion curve observed in blank run (with silica) and due to homogeneous combustion is shown for comparison (thermal labelled curve), to evidence the contribution of the catalysts. Z catalyst does not present catalytic activity at 200°C and ZLF shows 9% of conversion at the same temperature. Catalyst doped with La and Fe continues with excellent catalytic performance at high temperatures. In this way the ZLF catalyst reaches almost 100% of conversion at 500°C meanwhile Z catalyst reaches 67% of conversion and the thermal combustion only achieves 50% at the same temperature. Morphology of ZLF catalyst is shown in SEM micrograph of Figure 1(c). The particles of ZLF exhibit an estimated size of approximating 5 μm and well defined crystals. The mapping by EDAX (energy dispersive x-ray) microanalysis showed a very well dispersion of the doping agents; Figure 1(d) shows the Fe K α signal on the ZLF catalyst surface.

Table 1. Pore structural parameters of doped and undoped ZrO₂ substrates.

PSD: Pore-size distribution approximated from the adsorption boundary

A_{BET}: Specific area by BET technique

Sample	A _{BET} m ² g ⁻¹	PSD mode nm	Average pore size nm	Total Pore volume mm ³ g ⁻¹
Z	5.1	14.0	10.4	13.2
ZLF	1.5	14.7	12.5	4.8

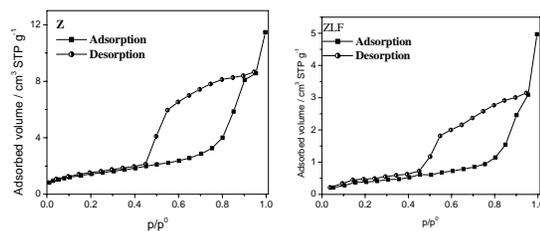


Figure 2.- N₂ sorption isotherms at 77K on pure zirconia (Z) and zirconia-doped (ZLF) catalysts

Figure 2 shows the N₂ sorption isotherms at 77K corresponding to each of the ZrO₂ substrates synthesized in this work. In turn, Table 1 summarizes the values of some of the most important pore structural parameters. All the isotherm shapes can be categorized as Type IV isotherms within the IUPAC classification [7]. In view of the shapes depicted by the N₂ sorption hysteresis loops, the most likely morphology of the undoped Z and doped ZLF systems consists of large chambers delimited by narrow necks. The textural characteristic of Z and ZLF specimens are similar to those found in Gibbsite-205 [9] and which are due to the creation of pore cavities inside the solid mass by water vapor during the hydrothermal dehydration of the precursory gel. The specific surface areas of the ZrO₂ catalysts range from 1 to 5 m² g⁻¹ and the pore size from 10 to 60 nm approximately (Table 1), this means that a low surface area can have a minor contribution on the surface reaction of catalytic combustion of trichloroethylene; on the other hand, the relatively large cavity sizes can facilitate the transport of reactants and products through the porous structure of ZrO₂ catalysts; which is related to percolation and permeability characteristics of the porous materials.

Conclusions

The zirconia crystallization temperature and structural characteristics are affected by metallic doping with La and Fe agents in the synthesis by sol gel. The catalyst doping with La and Fe over zirconia resisted the high concentration of trichloroethylene flow (1% wt in air) and developed a better performance compared with pure zirconia catalyst in the corresponding catalytic test due to the pure presence of the tetragonal zirconia phase. The percolation and the permeability characteristic of the doped zirconia synthesized by sol gel can assist the transport of reactants and products through the porous structure of ZrO₂ catalysts

Significance

The importance of this work is to develop new catalysts to be tested in the destruction of chlorinated VOCs that are very persistent substances in the air with a high reactivity for its chlorine contents.

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