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Catalytic oxidation of toluene by $SrTi_{1-X}B_XO_3$ (B = Cu and Mn) with dendritic morphology synthesized by one pot hydrothermal route

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ABSTRACT

This work is focus in the effect of B-site cations of $SrTiO_3$ perovskites with non-common morphology (dendritic) on the catalytic behavior of the toluene oxidation reaction. $SrTiO_3$ perovskites doped by two different transition metals (Cu or Mn) were synthesized by the one pot hydrothermal method and characterized by several techniques. The perovskite structure and the dendritic morphology were confirmed by XRD and SEM analyses for all catalysts. In addition, similar textural properties were observed among the catalysts. The addition of metal-dopants provides good stability during three catalytic cycles and in the lifetime test. However, segregation of Cu as CuO was observed on the surface of the Cu-doped catalyst. In contrast, the addition of Mn resulted in the incorporation of Mn^{4+} in Ti^{4+} sites present into the structure of the perovskite. This incorporation also enhances the relation O_{ads}/O_{latt} and the catalytic properties. Finally, the catalyst doped by Mn presented the highest catalytic activity with complete conversion of toluene to CO_2 at temperatures below 350 °C.

1. Introduction

Volatile organic compounds (VOCs) are becoming one of the biggest gaseous pollutants, attracting wide attention not only because of their air pollutant effects like photochemical smog and greenhouse effect, but also due to their toxic, mutagenic and carcinogenic properties reported on the human health [1,2]. Therefore, some organizations around the world have been introducing stringent regulations to control their emissions [3–5]. Among the VOCs, toluene has been considered as one of the 189 hazardous air pollutants listed in the 1990 Clean Air Act Amendment (CAAA90) proposed by the US Environmental Agency [5].

Several strategies for the elimination of toluene have been proposed recently such as biodegradation [6,7], adsorption [8,9], photocatalysis [10–12] and oxidative catalysis [13–17]. Among the catalytic alternatives, perovskite-type oxides with ABO_3 structure have been widely used and considered the most promising catalysts for VOCs pollutants removal, due to their low operation temperature, their adequate catalytic activity, high oxygen mobility, redox properties, good thermal stability, adaptability and low cost compared with the precious and transition metal oxides. Moreover, these features can be controlled by partial or total substitution of A- and/or B-site cations with different metals, altering the oxidation state or the redox properties of cations and the surface oxygen vacancies, which have a direct influence on the catalytic performance [18–21]. Thus, these undoped and doped perovskite-type oxides have been extensively studied in last years. Zhang et al. reported the complete catalytic oxidation of toluene below 350 °C without any deactivation of the catalyst using $LaMnO_3$ prepared by three different methods [16]. Ji et al. showed the degradation of 90% of toluene around 305 °C using the perovskite $Eu_{1-X}Sr_XFeO_3$ [17]. Li et al. reported the decomposition of toluene at temperatures below 300 °C introducing Sr and Fe into the perovskite $LaCoO_3$. They attributed the high catalytic activity observed for these catalysts to the increase in the amount of weakly adsorbed oxygen produced by the higher quantity of oxygen vacancies that the introduction of these two metals (Sr and Fe) induce in the perovskites [22]. In addition, the H_2-production by steam reforming of toluene have also been evaluated using the perovskite $LaAlO_3$ as support in a $Ni/LaAlO_3$ catalyst where the 30% of the La sites were replaced by Sr [23]. From these reports we can observe that different type of perovskite have been tested for catalytic abatement of toluene, using

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cations as La, Eu, Sr, etc. in A-site and Mn, Co, Fe, etc. in B-site, being the redox properties of the later an important factor to take into account.

Among the different reported perovskites, strontium titanate perovskite ($SrTiO_3$) doped with different cations has been widely studied as photocatalyst, catalyst and catalytic support for pollution removal and/or environmental protection due to its easily adjustable properties that can be modified by changing the oxygen stoichiometry after doping with foreign elements [24–35]. In particular, the Cu-doped $SrTiO_3$ perovksite prepared by sol-gel method has been reported as an excellent catalyst for the soot combustion and NO_x reduction [26,27]. Białobok et al. [34] and Ura et al. [29] reported the effect over the physico-chemical and catalytic properties in soot combustion of alkalies (Li, K, Cs) incorporation in the A-site of a $SrTiO_3$ perovskite, showing that the altered redox properties after doping have an important role on their catalytic activity and stability. Moreover, Yoon et al. reported the partial substitution of titanium by a transition metal cation promoted the formation of oxygen vacancies and reduced the oxidation state of titanium on the $SrTiO_3$ perovskite, modifying the methane oxidation activity [35]. Recently, Wu et al. reported the photocatalytic degradation of tetracycline under visible light using $SrTiO_3$ doped with Mn in concentration around 3–7 at.% [28]. Therefore, although catalytic properties of raw $SrTiO_3$ perovskites are still limited, one could expect that due to their high thermal stability, adaptability and modifiable oxidative properties they can be applied as promising active catalyst for toluene combustion.

Moreover, it is well known that the synthesis methods greatly influence the physico-chemical and catalytic properties of perovskites [16,36,37]. For this reason, $SrTiO_3$ perovskites have been synthetized by different routes during the last years [29–31,35,38–41]. Among then, the hydrothermal synthesis can be carried out at relative low temperatures and very rapid crystallization rates, allowing to control the morphology and size of this perovskite [38]. Recently, Nishiro et al. prepared $SrTiO_3$ co-doped with rhodium and antimony by hydrothermal route using TiO_2 and $Sr(OH)_2{\cdot}8H_2O$ as precursors. They reported that rhodium species doped in $SrTiO_3$ affects the evolution of H_2 and O_2 during water splitting [30]. Huang et al. also reported the hydrothermal synthesis of $SrTiO_3$ but this time using P25-TiO_2 and $Sr(OH)_2{\cdot}8H_2O$ as starting materials and temperatures from 100 to 180 °C during 24–96 h. They mentioned the promotion of spherical shape of the perovskite by adding NaOH at different concentrations [31]. Zhen et al. achieved the hydrothermal synthesis of $SrTiO_3$ at 180 °C for 6 h using TiO_2 as Ti precursor. This material showed good photocatalytic activity in the photoreduction of Cr (VI) [39]. Jayabal et al. also reported the hydrothermal synthesis of $SrTiO_3$ applying an additional thermal treatment at 900 °C for 6 h to eliminate organic impurities [40]. Mourao et al. reported the rapid hydrothermal synthesis of this perovskite with assistance of mechanical stirring during the hydrothermal process [41].

Taking into account the lot of applications of $SrTiO_3$ in the environmental field and the wide range of advantages that the hydrothermal route offers, in this work the $SrTiO_3$ perovskite and Mn- and Cu-doped $SrTiO_3$ perovskites were prepared by a one pot hydrothermal route, characterized by various techniques and tested on the toluene catalytic oxidation with the aim to evaluate the effect of Mn- and Cu-doping on physico-chemical and redox properties of the B-site (Ti^{IV}/Ti^{III}) in $SrTi_{1\text{-}X}B_XO_3$, as well as on the catalytic performance. To our best knowledge, this is the first report dealing with catalytic performance of synthesized Cu or Mn substitute perovskites oxides $SrTiO_3$ with dendritic morphology in catalytic oxidation of toluene, while there are only a few reports regarding the one pot hydrothermal synthesis of $SrTiO_3$ doped with Cu and Mn.

2. Experimental

2.1. Catalysts preparation

Doped and undoped catalysts of $SrTiO_3$ were prepared by one pot hydrothermal method. Titanium butoxide (>97%, Sigma Aldrich Co.) and $Sr(NO_3)_2$ (>99%, Sigma Aldrich Co.) were used as precursors, which were mixed in stoichiometric ratios with 60 mL of NaOH 0.2 M to obtain an homogeneous solution. For doped-catalysts, calculated amount of $Cu(NO_3)_2{\cdot}3H_2O$ (>99%, Prolabo Fr.) and $Mn(NO_3)_2{\cdot}4H_2O$ (>97%, Sigma Aldrich Co.) to obtain 4%wt. of the metal-doped with chemical formula as $SrTi_{0.89}Cu_{0.11}O_3$ and $SrTi_{0.86}Mn_{0.14}O_3$ were added. After mixing, the final solution was placed into a Teflon vessel with 100 mL of volume and was hydrothermally treated at 180 °C for 24 h. When the thermal treatment was finished the solution was cooled to room temperature. Then, the powder was separate from the solution by decantation and washed gently with distilled water until neutral pH. Finally, the powder was dried at 105 °C for 6 h in room atmosphere and calcinated at 600 °C during 5 h under air flow of 50 mL/min with heating and cooling rates of 5 °C/min.

2.2. Catalysts characterization

The phase composition of the perovskites were evaluated by X-Ray Diffraction (XRD) in a Bruker D5005 diffractometer with CuKα radiation (λ = 1.5418 Å) and a scanning and step size of 0.5 s and 0.02° respectively. The mean crystallite size (d_s) of the perovskites was calculated using the Scherrer equation (Eq. (1)) [42]:

$$d_s = \frac{k \times \lambda}{\beta \times \cos\left(\theta\right)} \quad (1)$$

where d_s is the mean crystallite size, k is the shape factor (0.9), λ is the x-ray wavelength (1.54 Å), β is the broadening at half of the maximum intensity (FWHM), and θ is the Bragg angle. The morphology, particle size and elemental composition were observed by scanning electron microscopy (SEM-EDS) JEOL 6490 LV.

N_2 adsorption-desorption isotherms was carried out at −196 °C on a Micrometrics Tristar 3000 equipment. Before the measurement all catalysts were degassed at 350 °C for 3 h. The specific surface area of each catalyst was obtained by the Brunauer-Emmett-Teller (BET) method.

X-ray photoelectron spectroscopy analyses (XPS) were recorded on a Thermo ESCALAB 250 electron spectrometer with a monochromatized Al Kα X-Ray source (1486.6 eV) and passing energy of 40 eV. C1 s (binding energy 284.8 eV) of formed carbon was used as a reference. XPS spectra were deconvoluted using XPSPEAK 41 program by the curve fitting after the Shirley-type background subtraction.

Finally, temperature-programmed reduction (TPR) experiments were conducted in a commercial BELcat unit with TCD detection. Catalyst (ca. 0.1 g) were loaded into a U-shaped tube and ramped from room temperature to 1173 K (10 K/min), using a reducing gas mixture of 5% v/v H_2/Ar (50 cm^3/min).

2.3. Toluene catalytic test

The catalytic tests were carried out using 100 mg of catalyst and 400 mg of SiC to avoid hot spots, placed in a quartz cell in a U-type reactor. Synthetic air (80/20) was introduced to the reactor and the temperature was increased up to 80 °C using a heating rate of 5 °C/min and then kept at this value for 30 min. When this temperature was reached a mixture containing 1000 ppm of toluene and synthetic air (80/20) at 100 mL/min was introduced to the reactor. Once the 30 min at 80 °C were finished, the temperature

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