



Effect of cobalt loading on the solid state properties and ethyl acetate oxidation performance of cobalt-cerium mixed oxides



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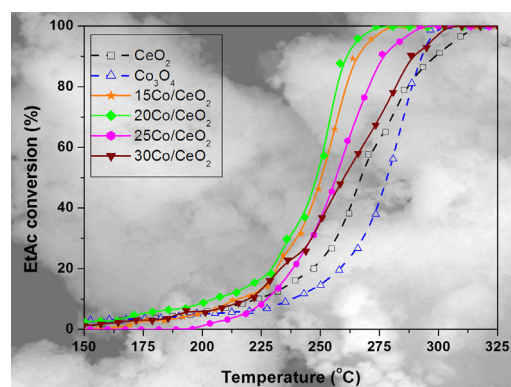
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GRAPHICAL ABSTRACT



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ABSTRACT

Cobalt-cerium mixed oxides were prepared by the wet impregnation method and evaluated for volatile organic compounds (VOCs) abatement, using ethyl acetate (EtAc) as model molecule. The impact of Co content on the physicochemical characteristics of catalysts and EtAc conversion was investigated. The materials were characterized by various techniques, including N₂ adsorption at –196 °C, scanning electron microscopy (SEM), X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS) to reveal the structure–activity relationship. The obtained results showed the superiority of mixed oxides compared to bare CeO₂ and Co₃O₄, demonstrating a synergistic effect. The optimum oxidation performance was achieved with the sample containing 20 wt.% Co (Co/Ce atomic ratio of ca. 0.75), in which complete conversion of EtAc was attained at 260 °C. In contrast, temperatures above 300 °C were required to achieve 100% conversion over the single oxides. Notably, a strong relationship between both the: (i) relative population, and (ii) facile reduction of lattice oxygen with the ethyl acetate oxidation activity was found, highlighting the key role of loosely bound oxygen species on VOCs oxidation. A synergistic Co–Ce interaction can be accounted for the enhanced reducibility of mixed oxides, linked with the increased mobility of lattice oxygen.

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1. Introduction

Volatile organic compounds (VOCs) are hazardous environmental pollutants, precursors of the potential formation of tropospheric ozone (a greenhouse gas) and photochemical smog. They are originated from refineries, fuel storage and loading operations, as well as from motor vehicles, solvent cleaning, printing and painting operations [1]. Common VOCs are ethyl acetate, benzene, ethanol, toluene, and acetone [2]. Some of these compounds are malodorous and/or carcinogenic [3]. In order to minimize their negative impacts on human health and environment, VOCs are worldwide regulated.

Catalytic oxidation is a promising environmental friendly VOC control technology that requires lower temperatures (around 250–500 °C) and is associated with less NO_x formation than conventional thermal oxidation, which operates at much higher temperatures (650–1100 °C) [4,5].

The most common metal oxides used as catalysts in oxidation reactions are: manganese oxides [6–8], copper oxide [5,9,10], nickel oxide [9–11], iron oxide [10,12], cobalt oxide [10,12–14], alumina [15], titania [4], zirconia [16], among others [12]. Zeolites [9] and carbon based materials [5] have also been reported to catalyse the oxidation of VOCs. Noble metal (NM)-based catalysts exhibit high activity at low temperatures and are quite stable. Pt and Pd have been commonly employed [6,17,18], but gold has also been investigated [3,7,11,19–22]. Metal oxides are in general, less active for the oxidation of VOC streams than the precious metal-based catalysts, but are usually more resistant to poisoning phenomena [23,24]. However, mixed metal oxides [11,25–31], perovskites [32–34] and cryptomelane type materials [24,35,36] demonstrate adequate activity in VOC oxidation. In particular, Co-, Cu- and Ce-based mixed oxides, such as CuO-CeO₂ [26,28,37–40], CuO-Co₃O₄ [41–43] and Co₃O₄-CeO₂ [31,44–48] exhibit excellent catalytic performance toward the oxidative abatement of VOCs. This is mainly attributed to the synergistic interactions between the different counterparts leading to an enhanced reactivity of surface oxygen species (catalyst reducibility) [38–40]. The latter is considered as one of the most important factors influencing the VOC oxidation reactivity of catalysts [7,24,36,49–51].

In spite of the wide application range of cobalt-cerium binary oxides on VOCs abatement, there are still several controversial issues regarding: (i) the impact of surface (e.g., oxygen vacancies) and bulk (e.g., lattice oxygen) properties of Co-Ce mixed oxides, (ii) the specific role of each component as well as of their synergistic interaction on the catalytic activity. Therefore, the main purpose of this study is to develop a better understanding on the effect of the Co/Ce ratio on the surface/redox properties and VOC oxidation activity of Co₃O₄/CeO₂ mixed oxides, employing ethyl acetate as a model compound. Several characterization techniques were used to better understand the influence of the Co content on the solid state properties of Co-Ce mixed oxides and their impact on the VOCs oxidation performance.

2. Experimental

2.1. Materials synthesis

Single CeO₂ and Co₃O₄ oxides as well as Co₃O₄/CeO₂ mixed oxides with different cobalt loading (15, 20, 25 and 30 wt.%) were prepared. Bare oxides were synthesized by diluting the appropriate quantities of the corresponding precursor salts (Ce(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O) in double distilled water. The solutions were heated under stirring until water evaporation. The resulting samples were dried at 120 °C for 16 h and calcined at 550 °C for 2 h,

using a heating rate of 5 °C/min. Following this procedure, bare CeO₂ and Co₃O₄ oxides were obtained. The Co₃O₄/CeO₂ catalysts were synthesized by impregnation of the resulting ceria with an aqueous solution of Co(NO₃)₂·6H₂O (Sigma Aldrich) at stoichiometric concentration, in order to yield Co loadings in the range of 15–30 wt.% (corresponding to a Co/Ce atomic ratio in the range of 0.5–1.25, Table 1). The resulting suspensions were heated under stirring in order to remove the excess water. The obtained samples were then dried overnight at 120 °C and calcined at 550 °C for 2 h. These samples are hereinafter denoted as xCo/CeO₂, where x is the Co weight percent content (wt.%) (Table 1).

2.2. Characterization studies

2.2.1. Textural characterization

The surface area of as prepared samples was determined by N₂ adsorption isotherms at –196 °C, using the multipoint BET analysis method, in a Tristar Micromeritics 3000 flow apparatus. The total pore volume was calculated based on the adsorbed nitrogen at the relative pressure of 0.99, while the average pore size was determined by the Barrett, Joyner, and Halenda (BJH) method using the N₂ desorption isotherm. Prior to the measurements, the samples were degassed at 250 °C overnight.

2.2.2. X-ray diffraction

The crystalline structure of the catalysts was determined by X-ray powder diffraction (XRD) on a Siemens D 500 diffractometer using Cu K_α radiation ($\lambda = 0.154$ nm) and operating at 40 kV and 30 mA. Diffractograms were recorded in the $2\theta = 10$ – 80° range at a scanning rate of 0.04° over 2 s. The DIFFRAC plus Basic data evaluation software was employed to identify the diffraction peaks and through the Scherrer equation to calculate the crystallite sizes of the detected phases within an experimental error of 10%.

2.2.3. Temperature programmed reduction

Temperature programmed reduction (TPR) experiments were performed in a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments). In a typical TPR experiment, ~50 mg of sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated to 1100 °C at 10 °C/min under He flow of 29 cm³/min and H₂ flow of 1.5 cm³/min.

2.2.4. Scanning electron microscopy

The surface analysis for morphological characterization was elaborated by scanning electron microscopy (SEM), using a FEI Quanta 400 FEG ESEM (15 keV) electron microscope. The sample powders were mounted on double sided adhesive tape and observed at different magnifications under two different detection modes: secondary and backscattered electrons. Energy-dispersive X-ray spectroscopy (EDS) confirmed the nature of the components.

2.2.5. X-ray photoelectron spectroscopy

The surface composition of the samples was determined by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra HSA with VISION software for data acquisition and CASAXPS software for data analysis. The effect of the electric charge was corrected by the reference of the carbon peak (284.6 eV).

2.3. Catalytic activity measurements

The catalytic evaluation was performed in a U-shaped quartz fixed-bed reactor with 6 mm internal diameter, placed inside a temperature controlled electrical furnace. The amount of catalyst used was 50 mg, mechanically mixed with inert SiC (carborundum, 0.2–0.5 mm), resulting in a total bed volume of ca. 0.5 cm³. A total air flow rate of 500 cm³/min, corresponding to a gas hourly space

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