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Oxidation of 1,2-dichloroethane over nanocube-shaped Co_3O_4 catalysts

J. González-Prior, R. López-Fonseca, J.I. Gutiérrez-Ortiz, B. de Rivas*

Chemical Technologies for Environmental Sustainability Group, Department of Chemical Engineering, Faculty of Science and Technology, University of The Basque Country (UPV/EHU), PO Box 644, E-48080 Bilbao, Spain

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ABSTRACT

The synthesis of a series of bulk cobalt oxides with different nanostructure (nanocube, nanosheets and nanorods) has been attempted and their performance has been evaluated for the oxidation of 1,2-dichloroethane, one of the most common chlorinated pollutants found in waste streams. Structural, morphological and physicochemical properties have been analysed by X-ray diffraction, Raman spectroscopy, BET measurements, SEM, HRTEM, XPS and temperature-programmed reduction with hydrogen. It has been found that the morphology plays a key role in determining the catalytic behaviour, being the nanocube-shaped oxides the most active catalysts. This catalyst has led the total oxidation of DCE towards CO_2, HCl and Cl_2 at relatively low temperatures (400 °C) without by-products formation. Both activity and selectivity of Co_3O_4 with this morphology are controlled by a high surface area, a low crystallite size, a highly defective structure and a good oxygen mobility within the lattice.

1. Introduction

Industrial emissions containing chlorinated VOCs such as dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane and trichloroethylene require special attention due to high toxicity and stability of these gaseous pollutants. Additionally, these compounds are linked with the formation of low-level ozone and photochemical smog, stratospheric ozone depletion, and are considered greenhouse gases [1]. Catalytic combustion is proposed as an effective technique for the total elimination of chlorinated VOCs from flue gases, owing to its low operating temperatures and high activity and selectivity with a capacity to oxidise completely the pollutants without the production of harmful by-products [2].

Currently, the most active catalysts are those based on platinum and palladium, which are dispersed on a high surface area support. Noble metals are powerful oxidation catalysts but they are very sensitive to poisoning by chlorine and have high costs and limited availability [3]. An alternative to noble-metal based catalysts are cheaper metal oxide catalysts. Particularly, Co_3O_4 with a spinel structure has been shown to be one of the most efficient in the total oxidation of VOCs due to its high content of surface oxygen species and/or the good mobility of oxygen species through the lattice [4,5]. Probably the main drawback is the relatively low thermal stability which frequently results in a substantial decrease in surface area and a marked sintering [6]. Bulk metal oxides can be obtained by various methods, including thermal decomposition, sol-gel processes, microemulsion methods, pyrolysis, precipitation, reduction-oxidation routes, hydrothermal/solvothermal synthesis or template procedures [4,6–9]. Considerable attention has been recently paid to optimising the catalytic properties of the spinel by tuning its nanomorphology [10]. In short, Co_3O_4 nanostructures with well-defined sizes, shapes, and crystallinity are usually prepared following a two-step process. Initially, the precursors with different shapes and novel structures are mainly synthesised by solution-based approaches, and subsequently are transformed to Co_3O_4 by thermal decomposition at elevated temperatures. In this sense it is quite important to control the morphology from the precursors to the final spinel nanostructures while optimising the population of highly active oxygen species. In addition, the achieved morphologies must be thermally stable in the typical temperature window for oxidation of VOC (300–550 °C). The desired bulk metal oxide shapes are typically rods, crystals which grow in one direction preferentially; sheets, which grow in two directions; and three dimensional cubes. Some studies on the viability of these nanoshaped catalysts for oxidation of CO, non-chlorinated VOCs and methane can be found in the literature [11–14] but no reports on their performance for chlorinated VOC abatement are available.

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* Corresponding author.
E-mail address: beatriz.derivas@ehu.eus (B. de Rivas).

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In the present work a variety of Co_3O_4 samples with these predefined morphologies have been prepared, using an organic soft template followed by a hydrothermal treatment. These materials have been tested as catalysts in the total oxidation of 1,2-dichloroethane ($C_2H_4Cl_2$, DCE), which is chosen as a model of chlorinated VOC owing to its widespread presence in the flue gases of polyvinyl chloride plants, in a fixed-bed flow reactor. In order to establish useful relationships between structural, morphological and physiochemical properties of the spinels and their catalytic behaviour the prepared bulk oxides have been thoroughly characterised by X-ray diffraction, Raman spectroscopy, BET measurements, scanning electron microscopy, X-ray photoelectron spectroscopy and temperature-programmed reduction with hydrogen. This study has been further supported by kinetic modelling and evaluation of catalytic behaviour with time on stream.

2. Experimental

2.1. Catalysts preparation

A number of Co_3O_4 samples have been prepared following several routes devoted to synthesis of spinels with a controlled morphology (1D, 2D and 3D structures). Particularly two different methodologies were examined for each selected morphology (rods, sheets and cubes).

2.2.1. Samples with rod-like morphology (R samples – 1D shaped catalysts)

The R1 sample has been prepared mixing cobalt (II) chloride (Sigma-Aldrich, 98%), urea (Fluka, 99.5%) and deionised water with a molar ratio of 1/0.27/300. The mixture has been kept for 12 h at 110 °C in an autoclave [15]. The R2 catalyst has been obtained by dissolving cobalt acetate (Sigma-Aldrich, 98%) 0.45 M with the desired amount of polyethyleneglycol (PEG 10,000, Merck) as surfactant (9/0.1 molar ratio). Then the resulting homogeneous solution has been precipitated adding dropwise an urea solution 0.9 M until a molar ratio cobalt acetate/urea of 1/2 is attained. The mixture has been then transferred to an autoclave and subsequently heated at 100 °C for 6 h [16].

2.2.2. Samples with sheet-like morphology (S samples – 2D shaped catalysts)

The S1 sample has been prepared by dissolving cobalt(II) nitrate (Sigma-Aldrich, 98%) and polyvinylpyrrolidone (PVP40, Sigma-Aldrich) (1/0.01 molar ratio) in a mixture of 50% v/v of formaldehyde (Sigma-Aldrich, 37%) and deionised water, with a Co/H_2O molar ratio of 1/65. Then, 0.4 M NaOH (Panreac, 99%) (Co/NaOH 1/0.2) has been slowly added to the solution. Finally, the mixture has been heated at 120 °C for 12 h [17]. For synthesising the S2 sample, cobalt(II) nitrate (Sigma-Aldrich, 98%) has been dissolved in deionised water (with a molar ratio of 1/1000). Triethylamine (TEA, Panreac, 99.5%) has been added to attain a Co/TEA of 1/0.366 molar ratio. The mixture has been maintained at 140 °C for 12 h [18].

2.2.3. Samples with cube-like morphology (C samples – 3D shaped catalysts)

The C1 sample has been synthesised from a mixture of cobalt (II) acetate tetrahydrate (Sigma-Aldrich, 98%), PVP and deionised water with a molar ratio of 1/0.02/445. Once the mixture is heated at 90 °C an ammonia solution (Panreac, 25%) is added dropwise until the pH reaches 8.5. Finally, 1.35% of hydrogen peroxide solution (Sigma-Aldrich, 30%) has been added while maintaining a Co/H_2O_2 molar ratio of 1/0.05. The final solution has been kept at 90 °C for 5 h [19]. The C2 sample has been prepared from cobalt(II) acetate, using polyethyleneglycol (PEG 20,000, Merck) as template (1/0.04 molar ratio) and a mixture of 50% v/v of formaldehyde and deionised water, with a Co/H_2O molar ratio of 1/275. Then, the mixture has been precipitated by adding KOH (Panreac, 85%) until the pH reaches 8.5. Finally, a hydrogen peroxide solution (Sigma-Aldrich, 30%) has been added with a Co/H_2O_2 molar ratio of 1/8. The final solution is kept at 90 °C for 5 h [20].

All the mixtures have been cooled down to room temperature after the hydrothermal treatment. The resulting precipitates have been filtered and washed with deionised water. The samples have been then dried in an oven at 110 °C overnight followed by a calcination step in static air with a heating ramp of 10 °C min^{-1} and held for 4 h at 500 °C. Next, catalyst pellets with a 0.3–0.5 mm diameter have been prepared by a process of compressing the oxide powders into flakes in a hydraulic press (Specac), crushing and sieving.

2.2. Characterisation techniques

Textural properties have been evaluated from the nitrogen adsorption–desorption isotherms, determined at −196 °C with a Micromeritics TRISTAR II apparatus. The specific areas of the samples were determined in line with standard BET procedure. Mean pore size was calculated using the BJH method. The samples have been previously degassed overnight with N_2 flow.

X-ray diffraction (XRD) studies have been carried out on a X'PERT-MPD X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) and Ni filter. The X-ray tube is operated at 30 kV and 20 mA. Samples have been scanned from $5^\circ < 2\theta < 80^\circ$ and the X-ray diffraction line positions have been determined with a step size of 0.02° and counting time of 2.5 s per step. Phase identification has been conducted by comparison with JCPDS (Joint Committee on Powder Diffraction Standards) database cards. The structural analysis the Co and Si species were evaluated with their electronic transitions by diffuse reflectance UV–vis and near infrared spectroscopy (DR-UV–vis-NIR) with a Jasco V-570 apparatus in the 2300–200 nm wavenumber range.

Raman spectra, acquired using a Leica 50 x N Plan (0.75 aperture) lens, have been recorded with a Renishaw InVia Raman spectrometer coupled to a Leica DMLM microscope. The spectrometer is equipped with a 514-nm laser (ion-argon laser, Modu-Laser) with a nominal power at the source of 50 mW and a maximum power at the sample of 20 mW. Ten seconds are employed for each spectrum, and 20 scans are accumulated with 10% of the maximum power in the spectral window from 150 to 1200 cm^{-1}.

X-ray photoelectron spectroscopy studies have been performed using in a SPECS system with equipped with Phoibos 150 1D analyzer and DLD-monochromatic radiation source. Scanning electron microscopy (SEM) images have been studied using Schottky (JEOL JSM-7000F) equipment with a resolution of 30 kV. Drops of emulsions, created by sonication of the powder samples in ethanol, were deposited on C coated Cu grids and left in air to dry.

HRTEM measurements were carried out at FEI Titan Cubed G2 60-300 electron microscope at 300 kV equipped with a high-brightness X-FEG Schottky field emission electron gun and a monochromator and CEOS GmbH spherical aberration (Cs) corrector on the image side. The images were recorded on a charge-coupled device (CCD) camera (2kx2k Gatan UltraScanTM 1000). The samples were prepared by dispersion into ethanol solvent and keeping the suspension in an ultrasonic bath for 15 min, after a drop of suspension was spread onto a TEM copper grid (300 mesh) covered by a holey carbon film followed by drying under vacuum.

Redox behaviour has been examined by temperature-programmed reduction experiments (TPR). These experiments have been conducted on a Micromeritics Autochem 2920 instrument. Firstly, all the samples (20 mg) have been pre-treated in an oxygen stream ($5\%O_2/He$) at 400 °C for 1 h, and then cooled down