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Catalytic removal of chlorinated compounds over ordered mesoporous cobalt oxides synthesised by hard-templating

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ABSTRACT

This work evaluates the catalytic behaviour of a series of mesoporous bulk cobalt oxide prepared by hard-templating using SBA-15, SBA-16 and SBA-3. In addition, a bulk catalyst obtained by silica aquagel confined precipitation is also examined. The oxidation of 1,2-dichloroethane has been selected as a model reaction for determining their suitability for the efficient removal of chlorinated pollutants in gaseous waste streams.

The catalytic behaviour is found to depend on the abundance of surface adsorbed oxygen species and a good low-temperature reducibility. These key physico-chemical properties are optimised for nanocasted Co_3O_4 prepared by using SBA-15 as hard template. This sample is characterised by a relatively high surface area, a nanorod-like morphology and a high quality 2D ordered mesoporous structure. At 375–400 °C this sample attains an efficient oxidation of the chlorinated feed to CO_2 and HCl/Cl_2 while keeping a reasonable stability with time.

1. Introduction

Chlorinated organic compounds, which are emitted from a wide range of industrial processes, such as polymer synthesis and processing, production of pesticides, solvents, insulators or electronic devices, are linked with the formation of low-level ozone and photochemical smog, stratospheric ozone depletion, and are considered greenhouse gases. Catalytic combustion is accepted as an attractive technology for removal at low temperatures when operating with dilute effluent streams. The proper catalyst selection and subsequent optimisation are essential for achieving efficient oxidation.

In order to avoid the use of noble metals in the catalyst formulation, substantial efforts have made in the design of suitable alternatives in terms of activity and cost. In this sense, much interest has been given to the development of Co_3O_4-based catalysts due to their notable performance in comparison with other transition metal oxides [1,2]. The catalytic activity of Co_3O_4 is essentially related to its surface area, pore structure, oxygen nonstoichiometry, and reducibility [3]. These properties in turn are intimately related to the surface morphology and the exposed crystal planes of the spinel. All these physico-chemical features can be optimised by the preparation method [4,5].

As an alternative to conventional and soft-templating synthesis routes, the hard-templating method is an attractive route for the synthesis of mesoporous Co_3O_4. Ordered mesopores silica is especially adequate as solid template for obtaining structured materials owing to

its highly tailorable textural properties [6]. In addition to leading to bulk catalysts with a relatively high surface area and a controllable pore structure, which are derived from replication of the pore system of the template, the nanomorphology can be tuned. Besides the channels of the template may induce a positive confinement effect on the predominantly exposed planes [7,8].

The objective of this work is the synthesis, characterisation and evaluation of a series of mesoporous bulk cobalt oxide catalysts for the oxidation of 1,2-dichloroethane ($C_2H_4Cl_2$, DCE), which has been chosen as a model chlorinated pollutant. More particularly, the effect of the selection of the silica template (SBA-15, SBA16 and SBA-3) on the physico-chemical properties of the nanocasted Co_3O_4 has been analysed.

2. Experimental

2.1. Template preparation

Three different silicas, namely SBA-15, SBA-3 and SBA-16, were synthesised and subsequently used as hard-templates for the preparation of Co_3O_4 catalysts. The SBA-15 and SBA-3 are mesoporous silicas templates with a two-dimensional p6 mm cubic arrangement of pores. SBA-15 shows hexagonal pores in a 2D array with long 1D channels (p6 mm plane group). The channels are interconnected by small micropores. SBA-3 has a uniformly ordered pore structure with a linear

channel array of mesopores, with a 2D hexagonal structure. The SBA-16 matrix is a material with a 3D cubic arrangement of mesopores corresponding to the Im3 m space group. Each mesopore in this body-centred cubic structure is connected with its eight nearest neighbors. These materials were prepared according to the synthesis procedures described in the literature, namely SBA-15 [9,10] and SBA-3 and SBA-16 [5,11].

2.2. Synthesis of hard-templated samples

Using these three silicas as templates (SBA-15, SBA-3 and SBA-16), different Co_3O_4 catalysts were prepared by means of wet impregnation method under reduced pressure using a rotary evaporator. An aqueous solution ($100 \, cm^3$) of cobalt (II) nitrate was used, with a Co/Si molar ratio of 0.25. In an attempt to examine the effect of this parameter, the SBA-15 silica was also impregnated with a more concentrated aqueous solution, with a Co/Si molar ratio of 0.4. In this case, the pores of the silica were expected to be completely filled and some cobalt oxide were likely formed out of the silica structure. This was confirmed by the notable decrease in surface area observed for this sample ($320 \, m^2 \, g^{-1}$) in comparison with that of the impregnated sample with a lower Co/Si molar ratio ($440 \, m^2 \, g^{-1}$). On the other hand, an additional cobalt oxide catalyst was prepared by silica aquagel confined coprecipitation (the so-called SACOP method). Thus, the precursor of the metal oxide was introduced in the cast during the synthesis step of the silica. The catalyst was obtained by mixing sodium silicate, hydrochloric acid, distilled water and cobalt nitrate hexahydrate with a $SiO_2/Co/H^+/H_2O$ molar ratio of 1/0.25/6.54/193.9 for 24 h. Then, the mixture was transferred to an autoclave under hydrothermal conditions at 100 °C for additional 24 h. Next, the metal hydroxide was precipitated with NaOH $3.5 \, mol \, L^{-1}$. Finally, the solid was washed, dried and calcined at 500 °C [12].

Finally, once the cobalt oxide was inside the pores of the various silicas, the matrix was removed using NaOH $2 \, mol \, L^{-1}$. This step was repeated four times allowing for obtaining nanocasted pure cobalt oxide. All samples were then washed several times with distilled water to remove the remaining NaOH and then dried at 110 °C overnight. Thus, the Co-S15 sample was obtained from the cobalt oxide impregnated on the SBA-15 silica. When using a higher Co/Si molar ratio (0.4) the sample was labelled as Co-S15(0.4). Similarly, the Co-S3 and Co-S16 oxides were prepared using SBA-3 and SBA-16 silicas, respectively while the Co-SP oxide was the sample synthesised by the SACOP method.

2.3. Characterisation techniques

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

X-ray diffraction (XRD) studies were carried out on a X'PERT-MPD X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) and Ni filter. The X-ray tube was operated at 30 kV and 20 mA. Samples were scanned from 5° < 2θ < 80° and the X-ray diffraction line positions were determined with a step size of 0.02° and counting time of 2.5 s per step. Phase identification was conducted by comparison with ICDD (International Centre for Diffraction Data) database cards.

Transmission electron microscopy (TEM) investigations were performed using a Philips CM200 microscope equipped with LaB6 crystal as electron source and operating at 200 kV. Bright field images were acquired using a high resolution CCD camera. 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 with a 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 sample was 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.

X-ray photoelectron spectroscopy studies were performed using in a SPECS system with equipped with Phoibos 150 1D analyzer and DLD-monochromatic radiation source.

The IR spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer in the range of $4000–400 \, cm^{-1}$. The skeletal characterization was carried out diluting 1 mg of each powder with 100 mg of IR-grade KBr powder finely mixed in an agate mortar and subjected to a pressure of 2 ton to obtain suitable self-supporting disks for the IR analysis.

Redox behaviour was examined by temperature-programmed reduction experiments (TPR) with hydrogen. These experiments were conducted on a Micromeritics Autochem 2920 instrument. Firstly, all the samples (20 mg) were pre-treated in an oxygen stream ($5\%O_2$/He) at 400 °C for 1 h, and then cooled down to room temperature. The reducing gas used in all experiments was $5\%H_2$ in Ar, with a flow rate of $50 \, cm^3 \, min^{-1}$. The temperature range explored was from room temperature to 600 °C with a heating rate of 10 °C min^{-1}. This temperature was held for 0.5 h. The water produced by the reduction process was trapped into a cold trap. The consumption of H_2 was quantitatively measured by time integration of TPR profiles. The calibration sample for quantitative analysis of H_2 uptake was silver oxide.

The total acidity of the catalysts was evaluated by NH_3 adsorption at 100 °C followed by thermogravimetry. These experiments were carried out with a Setaram Setsys Evolution thermobalance under atmospheric pressure coupled to a Pfeiffer Prisma mass spectrometer. Prior to adsorption experiments, the samples were first pretreated in a helium stream at 500 °C (10 °C min^{-1}) and then cooled to 100 °C (40 °C min^{-1}). Later, the NH_3 adsorption step was performed by admitting a flow of 10% NH_3/He at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of helium ($50 \, cm^3 \, min^{-1}$) for 2 h at 100 °C to remove reversibly and physically bound ammonia from the surface. The mass variation and the sample temperature were continuously recorded by a computerised data acquisition system. The net weight gain was considered as the total acidity of the samples. Then, the temperature was increased from 100 to 500 °C at a constant heating rate of 10 °C min^{-1}. The exit stream was analysed by on-line mass spectrometry.

2.4. Catalyst activity determination

Catalytic tests were performed in a bench-scale fixed bed reactor (Microactivity modular laboratory system provided by PID Eng & Tech S.L.) operated at atmospheric pressure and fully monitored by computer. The reactor is made of quartz with an internal diameter of 10 mm and a height of 300 mm, in which the temperature is measured with a thermocouple placed in the catalyst bed. Typically, 0.85 g of catalyst in powdered form (0.3–0.5 mm) was loaded. No quartz sands mixed with the catalyst were used. The reaction feed consisted of 1000 ppm of DCE in dry air with a total gas flow of $500 \, cm^3 \, min^{-1}$. The corresponding gas hourly space velocity was 30,000 h^{-1}. The amount and particle size of catalyst and the total gas flow rate were chosen in order to be out of the internal and external diffusion limits. Catalytic activity was measured over the range 150–500 °C and conversion data were calculated by the difference between inlet and outlet concentrations. Conversion measurements and product profiles were taken at steady state, typically after 30 min on stream. Either product selectivity was calculated based on either chlorine or carbon atoms present in that product divided by the total chlorine or carbon atoms present in the product stream