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Shape-dependency activity of nanostructured CeO_2 in the total oxidation of polycyclic aromatic hydrocarbons

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ABSTRACT

A morphological phase diagram is determined to relate the effect of base concentration and temperature during the hydrothermal synthesis with the final ceria nanostructured morphology. Representative samples of nanoparticles, nanorods and nanocubes have been characterized by XRD, N_2 adsorption, TEM, XPS and Raman and catalytically tested for the total oxidation of naphthalene as a model polycyclic aromatic hydrocarbon. Ceria nanoparticles present the highest surface area and smallest crystalline size, leading to the most active of these structures. However if the catalytic activity is normalized by unit of surface area, the observed reactivity trend (nanorods < nanocubes < nanoparticles) is directly related to the concentration of surface oxygen vacancies as a result of the exposure of the (1 1 0) and (1 0 0) preferential planes.

1. Introduction

Ceria is a well-known rare earth material which presents a highly desirable combination of chemical and physical properties [1]. It has a high oxygen storage capacity (OSC) and high ion conductivity, a high dielectric constant and it shows high transparency in the visible and near IR regions while being a highly efficient UV absorber. As a consequence, it is used in a wide range of applications such as electrochemistry [2], optics [3], and fuel cells [4]. A major application is in the field of catalysis, either as a catalyst itself or as a catalyst support, where its main use is as a component in the three-way catalytic system to reduce automobile exhaust gases [5]. In many of these catalytic applications, a shape-dependency activity of ceria has been observed [6] likely due to the selective exposition of surface planes, being the (1 0 0) surface catalytically more active than the (1 1 1) and (1 1 0) surfaces [7]. Surface plane exposure can be gained by controlling the morphology at the nanoscale, as a way of enhancing the catalytic activity and redox properties at the same time as the surface area is increased [8]. As an example, the dominated surface plane of morphologies such as nanocubes or nanorods is (1 0 0) which make them more active for CO oxidation than conventional ceria [9].

Consequently, different approaches have been followed to synthesize CeO_2 nanostructures including the use of templates [10], complexing agents [6], electrochemical deposition [11], sol–gel method [12], precipitation followed by ageing [13], hydrothermically using mineralizer agents [14]. Among these, the hydrothermal synthesis is considered the simplest, additive-free and economic method. However, the establishment of a robust and normalized hydrothermal manufacturing method remains elusive and a major challenge lies in the controlled manipulation of the nano-morphology in order to carefully tune its properties. Base concentration and temperature treatment have been found to be key parameters determining the final nano-morphology [9,15] during the hydrothermal synthesis. Additionally, the variety of set-ups and even conditions used for the hydrothermal syntheses, often with adventitious temperature inhomogeneities, leads to difficulties in relating defined conditions to morphological structure.

In recent years, nanocrystalline ceria has been identified as one of the most active catalysts for the total oxidation of a polycyclic

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aromatic hydrocarbon (PAH) [16]. PAHs are known to be carcinogenic and are associated with a number of other serious health hazards [17,18]. Therefore, it is important that convenient, practical and cost effective methods are developed for atmospheric PAH abatement. Previous studies have focused on the influence of the ceria nanoparticles' preparation variables, with the aim of determining which catalyst features are required for naphthalene total oxidation as PAH model compound. Factors such as crystallite size, surface area and oxygen defect concentration have been identified as key parameters [19,20]. However, there is no available information in the literature related to the presence of preferential surface planes which can promote the catalytic activity for naphthalene removal.

In this paper, we report on the determination of a morphological phase diagram which relates the effect of base concentration and temperature of the hydrothermal treatment with the final CeO_2 nanostructured morphology. Representative shapes (nanoparticles, nanorods and nanocubes) have been tested for naphthalene total oxidation in order to correlate the physico-chemical properties of ceria with its catalytic oxidation activity.

2. Experimental

2.1. Synthesis and characterization of materials

The standard hydrothermal method was based on that previously reported [9]. 0.6 g of $Ce(NO_3)_3 \cdot 6H_2O$ were added to a 40 mL NaOH solution in the range of 1–15 M and stirred magnetically for 10 min in a PTFE beaker. The solution was placed in a 45 mL Teflon lined autoclave inside an air-circulating oven which allows gradientless temperature to be achieved throughout the autoclave. The temperature range studied is 70–180 °C at a set synthesis time of 10 h. Following hydrothermal synthesis, the autoclave was allowed to cool to ambient temperature. The powder obtained was filtered, washed several times with deionised water and dried at 120 °C overnight. Large particles of agglomerated dry powder were broken in a mortar prior to further investigation. The phase identification of the samples was done by X-ray diffraction (XRD) analyses using an X'Pert PRO diffractometer by PANalytical with a Cu Kα radiation, operated at 40 kV and 40 mA. Low temperature nitrogen adsorption measurements at 77 K were done using a Micromeritics ASAP 2020 apparatus. Specific surface area was calculated by the BET method (associated error of ±0.5%) and pore size distributions were calculated from the desorption data using the BJH model. Samples were degassed at 150 °C prior to analysis to calculate specific surface area. A JEOL 2010 microscope was used for transmission electron images and a JSM6400 microscope for scanning electron images. X-ray photoelectron spectroscopy (XPS) measurements were made on an Omicron ESCA+ photoelectron spectrometer using a non-monochromatized MgKα X-ray source ($h\nu = 1253.6$ eV). Analyser pass energy of 50 eV was used for survey scans and 20 eV for detailed scans. Binding energies are referenced to the C1s peak from adventitious carbonaceous contamination, assumed to have a binding energy of 284.5 eV. XPS data were analyzed using CasaXPS software. Shirley background subtraction was applied to all the raw data. All the peaks of the corrected spectra were fitted with a Gaussian–Lorentzian shape function to peak fit the data. Iterations were performed using the Marquardt method. Standard deviations were always lower than 1.5%.

2.2. VOC catalytic oxidation

Catalytic activity tests for naphthalene oxidation were carried out in a fixed bed laboratory micro-reactor. Blank tests were conducted by passing naphthalene (450 vppm) through an empty reactor that was heated from 100 °C to 350 °C at a rate of 10 °C $\min^{-1}$ showing no conversion. Catalysts (pelletized to 0.1–0.2 mm particle size without any binder) were tested using a 3/8″ o.d. quartz tube as the reactor. The reaction feed consisted in all cases of ca. 450 vppm naphthalene in a mixture of 20 vol.% oxygen and 80 vol.% helium. A total flow rate of 50 ml $\min^{-1}$ was used and the catalysts occupied a constant volume, giving a GHSV of ca. 25,000 h^{-1} for all the catalysts. Analyses were performed by an on-line gas chromatograph with thermal conductivity and flame ionization detectors. The catalytic activity was measured over the temperature range of 100–275 °C, in incremental steps of 25 °C, and temperatures were controlled by a thermocouple, placed in the catalyst bed. Data were obtained at each temperature after the naphthalene adsorption equilibrium was accomplished and steady state activity attained. Four consistent analyses were made at each temperature and average values were calculated. The reaction temperature was increased and the same procedure followed to determine each data point. Oxidation activity was expressed as a yield of carbon dioxide closing the mass balance within ±10%. The associated error for the conversion values is ±5%.

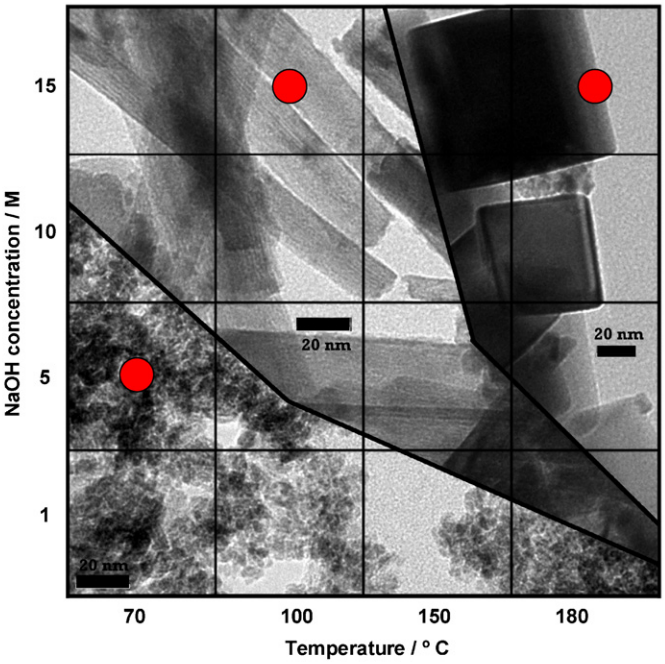

Fig. 1. Morphological phase diagram of CeO_2 after 10 h of hydrothermal treatment. Phase boundaries shown do not imply sharp transitions to pure phases. Circles show the conditions of the representative samples of each morphology taken for the catalytic study.

3. Results and discussion

3.1. Morphological phase diagram

Transmission electron microscopy (TEM) images of samples synthesized at different temperatures (between 70 °C and 180 °C) and a range of NaOH concentrations (from 1 to 15 M) for 10 h of hydrothermal treatment were used to determine the morphological phase diagram (Fig. 1). The phase boundaries were estimated taking into consideration the relative concentration of different nanostructures at given conditions but they did not imply a sharp transition to a pure phase. At low temperatures (<100 °C), no formation of nano-structured ceria is observed when the concentration of base is lower than 10 M. Under these conditions, nanoparticulated ceria is observed with dimensions >5 nm (Fig. 2). Increasing