A heterogeneous mechanism for the catalytic
decomposition of hydroperoxides and oxidation of alkanes
over CeO₂ nanoparticles. A combined theoretical and
experimental study

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Abstract

A nanoparticulate CeO₂ catalyst is presented that is able to oxidize cyclohexane to K/A-oil (a mixture of cyclohexanone and cyclohexanol) using hydroperoxides as oxidizing species. The improvement in selectivity with decreasing particle size suggests the existence of a structure-activity relationship in this process, and points to a preferential activation of cyclohexane at defective corner or edge sites. A detailed theoretical study of the reaction mechanism over three different CeO₂ catalyst models shows that cyclohexane is preferentially activated by bi coordinated oxygen atoms present at the edges of small particles, following a Mars van Krevelen mechanism which has been confirmed by *in situ* IR spectroscopy and ¹⁸O/¹⁶O isotopic exchange experiments. The process is fully heterogeneous, and the catalyst can be reused without loss of activity up to four cycles.

Keywords

Alkane oxidation, heterogeneous catalysis, acid-base, redox, ceria, DFT, *in situ* IR

1. Introduction

The liquid phase aerobic oxidation of cyclohexane to a mixture of cyclohexanone and cyclohexanol, called K/A-oil, is a relevant process in the chemical industry, with more than 10^6 tons of K/A-oil being produced every year. Cyclohexanol and cyclohexanone are precursors of adipic acid and ϵ -caprolactam, which are key intermediates in the production of nylon-6 and nylon-6,6 polyamides. [1,2,3] The actual industrial process for cyclohexane oxidation involves a first non-catalytic reaction of cyclohexane with O_2 to form cyclohexyl hydroperoxide (Cy-OOH) and a second step, called deperoxidation, in which Cy-OOH is catalytically decomposed to cyclohexanol (Cy-OH) and cyclohexanone (Cy=O). The deperoxidation step is currently catalyzed either by an aqueous solution of NaOH containing Co^{2+} cations [4] or by an organic solution containing Cr^{6+} compounds [5, 6, 7] but it is becoming necessary, for environmental reasons, to replace such homogeneous processes that use catalysts in liquid phase with new non-toxic heterogeneous systems involving solid catalysts. Most efforts up to the moment have focused on the use of acid or metal exchanged molecular sieves, [8, 9] polymer and silica-supported transition metal complexes, [10, 11, 12, 13] or transition metal oxides and hydroxides.[14] While most of these materials show relatively good activities and selectivities to K/A-oil, some of them suffer from deactivation and/or metal leaching, thus preventing their industrial application. An additional point in the deperoxidation process is the possibility to use the oxygen in the hydroperoxide to simultaneously oxidize the alkane solvent, thus obtaining selectivities to K/A-oil larger than 100%. Such selectivities have been reported for homogeneous catalysts containing Ru [15, 16] and Os [17] in liquid phase, but not for heterogeneous solid systems.

In the search for an efficient and stable solid catalyst able to oxidize cyclohexane using Cy-OOH as oxidizing species, cerium oxide appears as a promising material. It

combines a well-known catalytic activity for oxidation reactions with not less interesting acid-base properties. [18, 19, 20, 21, 22] The oxidation activity of cerium oxide is often associated to its ability to undergo $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycles that facilitate formation and healing of oxygen vacancy defects, [19] which are the active sites where the oxidizing species, usually O_2 , is activated. According to theory, the formation of oxygen vacancies at some special positions present in small nanoparticles is more favourable than on extended surfaces, and also differs from one crystallographic plane to another one. [20, 21, 23, 24, 25] Thus, the easier formation of oxygen vacancy defects on the (100) planes of CeO_2 has been used to synthesize a highly efficient catalyst for the oxidation of p-xylene to terephthalic acid, which is formed by three-dimensionally self-assembled CeO_2 nanocubes. [26, 27]

In other cases this redox cycle does not participate in the reaction, and the catalytic activity of CeO_2 is then related to acid-base chemistry associated to surface OH groups or Ce^{4+} Lewis type sites. For instance, it has been experimentally and theoretically demonstrated that water dissociation on reduced ceria surfaces producing two surface OH groups does not require the Ce^{3+} cations present, but occurs at Ce^{4+} centers without involving any change in the oxidation state of cerium atoms. [28-31] On the other hand, it has been found in our group that the selectivity of CeO_2 in the case of an acid-base reaction, the carbamoylation of aromatic amines, can be rationally tuned by changing the crystal morphology, that is, the crystallographic facets preferentially exposed.[22]

Based on all these considerations, we present now a nanocrystalline cerium oxide catalyst that is able to decompose Cy-OOH and simultaneously oxidize the cyclohexane solvent, yielding selectivities to K/A-oil larger than 100%. The synthesis procedure, catalyst characterization and catalytic performance in the oxidation of cyclohexane with tBut-OOH (tert-butyl hydroperoxide) and Cy-OOH is described in detail, and the

reaction mechanism is investigated by means of DFT calculations and *in situ* IR spectroscopy. It is found that bi coordinated oxygen atoms present at the edges of small cerium oxide nanoparticles are the active centres catalysing the dissociation of the C-H bond in cyclohexane, and that Cy-OOH preferentially decomposes at oxygen vacancy defects, thus closing the catalytic cycle. The process is fully heterogeneous, and the catalyst can be reused without loss of activity up to four cycles.

2. Experimental Section

2.1. Synthesis and characterization of catalysts

Commercial CeO₂ and ZrO₂ were purchased from Aldrichs (References 202975 and 204994). Commercial TiO₂ (Mirkat-411) was purchased from Eurosuport. High surface CeO₂ was provided by Solvay. A previously reported method was used to synthesize CeO₂ nanostructures with different shape [22, 32].

BET area measurements. Specific surface areas were calculated from dinitrogen adsorption isotherms obtained at 77 K with a Micrometrics ASAP 2420 Accelerated Surface Area and Porosimetry System analyzer, using the Brunauer-Emmett-Teller (BET) equation. The samples were pretreated in vacuum at 673 K for 12 h.

Transmission Electron Microscopy (TEM). TEM images were collected using a JEOL DEBEN AMT JEM-1010 microscope operating at 100 kV.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were collected using a SPECS spectrometer with a 150 MCD-9 detector and using a non-monochromatic AlK α (1486,6eV) X-Ray source. Spectra were recorded using analyser pass energy of 30 eV, an X-ray power of 100W and under an operating pressure of 10⁻⁹ mbar. During data processing of the XPS spectra, binding energy (BE) values were referenced to C1s peak (284,5 eV). Spectra treatment has been performed using the CASA software.

2.2. Procedures for the catalytic reaction and analysis

Preparation of Cy-OOH mixture. Cy-OOH was extracted from a cyclohexane oxidate resulting from the thermal oxidation of cyclohexane by oxygen in an industrial unit. The oxidate was washed with water and then it was extracted with 1 M NaOH. The water phase was then extracted with ether and was neutralized with a chilled aqueous 4 M HCl solution until slightly acidic. The water phase was subsequently extracted 3 times with cyclohexane and dried over Na₂SO₄ or MgSO₄. The solution was concentrated to reach a concentration of 4.7 wt% or 5.6 wt% Cy-OOH.

Preparation of tBut-OOH mixture. The reaction mixture is prepared from a commercial solution of tBut-OOH diluted in water (3:2 tBut-OOH:water) from Fluka, and cyclohexane (>99% purity). The proper amount of tBut-OOH solution and cyclohexane is mixed. Molecular sieves are added to the solution to absorb water and make the mixture anhydrous. The exact amount of tBut-OOH in the final mixture is analyzed by iodometry. The mixture is stored in darkness at low temperature (10°C) until used.

Catalyst pre-treatment. The catalyst is calcined in static air (4 h gradient from room T to 400°C, followed by an isotherm of 400°C for 4 h) and kept inside the oven until used.

Reaction procedure for tBut-OOH. The reaction is performed in a batch reactor consisting of a glass reactor vessel (chemical and thermal shock resistant, 20 mL Volume capacity, Duran Manufacturer), a vent valve (Gas inlet, for pressurizing/depressurizing the system with nitrogen), an outlet micro valve for sample taking, a pressure gauge, a thermocouple, and a magnetic stirring bar, which is stored inside the reaction media in the reactor vessel. To ensure that the reactor is completely clean and no traces of contaminants are present, it is first washed with acetone, then with cyclohexane, and after that dry air is passed through.

The proper amount (160 mg) of catalyst, 200 μ L of internal standard Undecane (99% purity, from Sigma-Aldrich) and 20 mL of the tBut-OOH/cyclohexane solution are introduced in the glass reactor vessel and its exact mass weighted. A magnetic stir bar is introduced and the reactor is closed. An overpressure of nitrogen (4 to 6 atmospheres) is then added in order to increase the boiling point of cyclohexane and keep reaction media at liquid state. An aluminium container for reactors at the desired reaction temperature (100°C), is kept on a hot-stirring plate. Stirring is set to 1400 rpm. The glass reactor vessel is introduced in the container, and the reaction starts.

To follow the reaction progress, samples are taken at different times and their composition analyzed by iodometry and Gas Chromatography. At each time, the reactor is taken off the container and stored in a water bath at room temperature to cool down the reaction media. Once the reactor is at room temperature, three different samples are taken through the outlet micro valve and analyzed.

Reaction procedure for Cy-OOH. The reaction is performed in a Teflon batch reactor consisting of a teflon reactor vessel (40 mL Volume capacity, Bola Manufacturer), an outlet micro valve for sample taking, a pressure gauge, a thermocouple, and a magnetic stirring bar, which is stored inside the reaction media in the reactor vessel. To ensure that the reactor is completely clean and no traces of contaminants are present, it is first washed with acetone, then with water. In case some trace of metal remains on the reactor wall, it is washed with diluted HCl.

The proper amount (160 mg) of catalyst, 0.6 g of internal standard orthodichlorobenzene (99% purity, from Sigma-Aldrich) and about 16 g of the Cy-OOH purified solution are introduced in the reactor and its exact mass weighted. A magnetic stir bar is introduced, the reactor is closed and an overpressure of nitrogen (4 to 6 atmospheres) is then added in order to increase the boiling point of cyclohexane and

keep reaction media at liquid state. The reactor vessel is introduced in a silicon bath at the desired reaction temperature (typically 100°C) placed on a hot-stirring plate. The follow up of reaction and stirring of the mixture begins when temperature reaches 100°C. To follow the reaction progress, samples are taken at different times and their composition analyzed by iodometry and Gas Chromatography. The medium is sampled through a syringe and put in a GC vial when it is cold.

Iodometry. Cyclohexyl hydroperoxide (Cy-OOH) is quantified by iodometry which consists in reacting Cy-OOH with KI to yield cyclohexanol and I₂. The amount of I₂ formed is estimated by potentiometry by reaction of I₂ with Na₂S₂O₃. About 1 g of the solution containing Cy-OOH is weighed in an Erlenmeyer flask. Then, 20 mL of 80% acetic acid, about 1 g of sodium hydrogenocarbonate (NaHCO₃) and about 1g of potassium iodide (KI) are introduced. NaHCO₃ is a weak base and reacts with acetic acid to produce CO₂, so that O₂ is pushed away. Indeed, the presence of O₂ would induce error on the evaluation of Cy-OOH quantity. After mixing, the Erlenmeyer flask is stored 20 minutes in the dark. The Erlenmeyer flask is washed with distilled water and acetonitrile (which avoid the formation of foam). The solution is dosed with a solution of sodium thiosulfate Na₂S₂O₃ (0.1 N). The same method is used to quantify tert-butyl hydroperoxide (tBut-OOH).

Gas Chromatography. Cyclohexanol, cyclohexanone and Cy-OOH are quantified by GC using a Shimadzu GC-2010 chromatograph equipped with FID, with a specific polar column (Permabond FFAP 0.10 µm film thickness, length 20m). For each sample, 30 µL are extracted from the reactor using a syringe and introduced in a vial containing cyclohexane. The amount of Cy-OOH of calibration solution is measured by iodometry.

Definition of terms. The reaction of interest is the oxidation of cyclohexane (Cy-H) with Cy-OOH yielding cyclohexanol (Cy-OH):

But the hydroperoxide can also directly decompose into cyclohexanone (Cy=O) and water according to:

Moreover, Cy-OH can be further oxidized to Cy=O, producing a mixture of both molecules (K/A oil). The selectivity of the reaction, which measures the degree of alkane oxidation, is calculated as:

$$\text{Selectivity} = \frac{[\text{mol}(\text{Cy} - \text{OH}) + \text{mol}(\text{Cy} = \text{O})]_{\text{formed}}}{[\text{mol}(\text{Cy} - \text{OOH})]_{\text{converted}}} \times 100$$

When selectivity is lower or equal to 100%, the catalyst only decomposes Cy-OOH without oxidizing cyclohexane, and when it is higher than 100%, the catalyst is able to decompose the peroxide and oxidize cyclohexane at the same time. In the reaction between tBut-OOH and cyclohexane, all Cy-OH and Cy=O detected come from the oxidation of cyclohexane:

The selectivity in this case is calculated as:

$$\text{Selectivity} = \frac{[\text{mol}(\text{Cy} - \text{OH}) + \text{mol}(\text{Cy} = \text{O})]_{\text{formed}}}{[\text{mol}(\text{tBut} - \text{OOH})]_{\text{converted}}} \times 100$$

And takes values between 0 if the catalyst decomposes tBut-OOH without oxidizing cyclohexane, and 100 if all tBut-OOH decomposed is used to oxidize cyclohexane.

Calculation of Turnover Frequencies (TOF). The turnover frequencies for the reaction of tBut-OOH with Cy-H were calculated as:

$$\text{TOF} = \frac{[\text{mol}(\text{tBut} - \text{OOH})]_{\text{converted}}}{[\text{mol}(\text{surfaceCe sites})]} \times \frac{1}{t}$$

The number of surface Ce sites in each sample, with the exception of CeO₂-Rods and CeO₂-Cubes, was estimated assuming a surface density of $7,8876 \times 10^{18}$ Ce atoms per

m^2 , that is, $1,3096 \times 10^{-5}$ moles of Ce atoms per m^2 , which was obtained from the periodic slab model of the extended (111) surface used in the DFT study. For CeO_2 -Rods that preferentially expose (110) facets the estimated surface density is $1,4490 \times 10^{19}$ Ce atoms per m^2 , that is, $2,4068 \times 10^{-5}$ moles of Ce atoms per m^2 , and for CeO_2 -Cubes preferentially exposing (100) facets the values are $6,8307 \times 10^{18}$ Ce atoms per m^2 , that is, $1,1341 \times 10^{-5}$ moles of Ce atoms per m^2 .

2.3. Computational details

All calculations in this work are based on periodic density functional theory (DFT) and were performed using the Perdew–Wang (PW91) exchange-correlation functional within the generalized gradient approach (GGA) [33, 34] as implemented in the Vienna Ab-initio Simulation Package (VASP) code. [35] The valence density was expanded in a plane wave basis set with a kinetic energy cutoff of 450 eV, and the effect of the core electrons in the valence density was taken into account by means of the projected augmented wave (PAW) formalism. [36] All calculations are spin polarized. Integration in the reciprocal space was carried out at the Γ k-point of the Brillouin zone. Charge distributions were estimated using the theory of atoms in molecules (AIM) of Bader using the algorithm developed by Henkelman. [37, 38]

Small CeO_2 nanoparticles were simulated by means of a $\text{Ce}_{21}\text{O}_{42}$ and a $\text{Ce}_{40}\text{O}_{80}$ model systems previously described by Migani et al. [23] (see Figure S1 in the Supporting Information). These models contain two-coordinated O atoms at the edges between {100} and {111} facets, and three-coordinated O atoms in the {111} terraces, as well as Ce atoms in different coordination environments. The $\text{Ce}_{21}\text{O}_{42}$ and a $\text{Ce}_{40}\text{O}_{80}$ models were placed in cubic boxes of $20 \times 20 \times 20$ and $30 \times 30 \times 30 \text{ \AA}^3$, respectively, large enough to avoid interactions between periodically repeated nanoparticles or adsorbates. During geometry minimizations, the positions of all atoms in the systems were fully relaxed

without any restriction, and vibrational frequencies were calculated numerically. Larger CeO₂ nanoparticles were simulated by means of a CeO₂(111) slab model containing 36 Cerium and 72 Oxygen atoms in four CeO₂ layers, that is, twelve atomic layers. During the geometry optimizations the atoms in the two bottom layers were not allowed to relax.

The accurate description of the electronic structure of CeO₂, and in particular of the Ce³⁺ cations present in the reduced material, is a challenging task due to the lack of cancelation of the self-interaction error in DFT that leads to over-delocalized electrons. This can be solved either by using the so-called DFT+U approach, which consists of adding a Hubbard-type U term to the Ce 4f states that destabilizes the delocalized solutions, or by using hybrid functionals. A major drawback of the DFT+U approach is its non-universality, that is, the strong dependence of geometrical and electronic properties on the value of U, while the high computational cost of hybrid methods limits their application to reactivity studies such as that presented here [21]. We recently investigated the influence of the U value in the DFT+U approach on the theoretical description of the acid-base and redox properties of CeO₂ nanoparticles of ~1 nm diameter, and we found that only the energy of formation of an oxygen vacancy defect varies by ~ 0.8 eV when the value of U increases from 0 to 4 eV. [24] For this reason, and taking into account the slower convergence of calculations with U=4 as compared to U=0, no Hubbard parameter has been used in this study.

2.4. IR spectroscopy

IR studies were performed on a Bruker V70 FTIR spectrometer using an MCT detector and acquiring at 4 cm⁻¹ resolution. A glass IR cell allowing in situ studies in controlled atmospheres and temperatures from 25 °C to 600 °C has been connected to a vacuum system with gas dosing facility. For IR studies the samples were pressed into self-

supported wafers and treated at 250 °C in O₂ flow (15 ml/min) for 2 h followed by evacuation at 10⁻⁵ mbar at 300 °C for 1.5 h. After activation the samples were cooled down to 25°C under dynamic vacuum conditions followed by cyclohexane adsorption at 12 mbar. Spectra were recorded at increasing temperatures from 25 °C to 110 °C. Gas phase spectra have also been collected at each temperature. At 110°C tBut-OOH was co-adsorbed at 2 mbar. For IR band assignation Cy-OH (0.2-4 mbar) and tBut-OOH (0.2-4 mbar) were adsorbed separately on fresh activated CeO₂ samples. For mechanistic studies an isotopic exchange experiment was performed where the CeO₂ surface was exchanged with O-18 by activating the catalyst “in situ” in the IR cell in the presence of 400mbar ¹⁸O₂ at 375°C for 2h. After activation, the sample was cooled down to 25°C in vacuum and Cy-H (12mbar) and tBut-¹⁶O¹⁶OH (2mbar) were simultaneously co-adsorbed, followed by increasing temperature to 110°C. The required temperature for ensuring surface isotopic 18-O exchange was obtained according to the ¹⁸O₂/¹⁶O₂ isotopic oxygen temperature programed profile displayed in Figure S2 in the Supporting Information.

3. Results and discussion

3.1. Catalytic activity of CeO₂.

Taking into account all the considerations about the influence of particle size and morphology on the catalytic performance of cerium oxide mentioned in the introduction, the deperoxidation of tBut-OOH was initially studied using two commercial samples of CeO₂ with very different surface area, namely 13 m²/g for the low surface area sample (CeO₂-LSA) and 222 m²/g for the sample with high surface area (CeO₂-HSA). The presence of Ce³⁺ cations in these systems was determined by XPS (see Figure S3 in the Supporting Information) and a similar concentration, ~8-12%

Ce^{3+} , was found. Both samples were found active in the decomposition of the hydroperoxide and in the oxidation of cyclohexane (see Table 1). As expected, tBut-OOH conversion was considerably lower on the material with less surface area, but calculation of turnover frequencies (TOF) (see Table S1 in the Supporting Information) revealed a higher intrinsic reactivity of the active centres present in the CeO_2 -LSA sample. To confirm this trend, three new catalysts were prepared by calcining the CeO_2 -HSA sample at increasing temperatures (600, 700 and 900°C), so that their particle size increased and their surface area decreased accordingly. While conversion continuously decreased with decreasing surface area, TOFs followed the opposite tendency. Interestingly, the selectivity to K/A-oil was also found to vary with the catalyst particle size. The data summarized in Table 1 clearly indicate that the lower the surface area the higher the TOF and the worse the selectivity to K/A-oil. The role of surface morphology was explored by comparing the catalytic performance of CeO_2 nanostructures, namely octahedra, rods and cubes, preferentially exposing the (111), (110) and (100) crystallographic facets, respectively (see TEM images in Figure 1). Nano-rods were found more selective than nano-octahedra, and the worse catalytic behaviour was obtained with nano-cubes.

Figure 1. TEM images of a) CeO_2 -octahedra, b) CeO_2 -rods, and c) CeO_2 -cubes.

Table 1. Cyclohexane oxidation with tBut-OOH catalysed by CeO₂. Surface area S.A. in m²/g of the CeO₂ catalysts, conversion of tBut-OOH and selectivity to K/A-oil (Cy-OH + Cy=O) in % at 9 hours reaction, and calculated turnover frequencies TOF^a in s⁻¹.

Catalyst	S.A. (m ² /g)	Conversion (%)	Selectivity (%)	TOF (s ⁻¹)
CeO ₂ -LSA	12,7	33	21	0,044
CeO ₂ - HSA	221,9	88	34	0,005
CeO ₂ - HSA-600	159,8	81	29	0,010
CeO ₂ - HSA-700	115,9	78	29	0,011
CeO ₂ - HSA-900	37,0	42	27	0,026
CeO ₂ -Rods	111,0	86	29	0,004
CeO ₂ -Octahedra	64,9	67	26	0,008
CeO ₂ -Cubes	31,2	31	25	0,028
TiO ₂	292	18	25	
ZrO ₂	104	12	2	

^aTOFs calculated at low tBut-OOH conversion. Details in Table S1 in the Supporting Information.

The evolution of tBut-OOH conversion with time, plotted in Figure 2, clearly shows the different reactivity of the eight CeO₂ catalysts considered, with CeO₂-HSA and CeO₂-rods being the most active from the beginning of the reaction, and with activity continuously decreasing as a function of surface area. Figure 3 shows, however, that the intrinsic reactivity of the active sites, determined by the calculated TOFs, is higher on the samples with lower surface area. As mentioned before, the most interesting result from the point of view of industrial application is that selectivity clearly improves with

increasing surface area, following an almost linear relationship (see Figure 3). And this trend is maintained if only the experiments with significant conversion (larger than 65%) are considered. These results lead to the conclusion that there exists a structure-activity relationship in this process. The selectivity to K/A-oil is larger on smaller CeO_2 particles irrespective of the preferential facets exposed, suggesting that cyclohexane activation occurs at defective corner or edge sites, whose relative concentration increases with decreasing particle size. On the other hand, the active centres present in larger particles are intrinsically more reactive towards decomposition of tBut-OOH. Commercial TiO_2 and ZrO_2 were also tested for comparison, and despite their large surface area, they were found almost inactive and with a low K/A-oil selectivity (see Table 1).

Figure 2. Conversion of tBut-OOH as a function of time for the different CeO_2 catalysts investigated.

Figure 3. Turnover frequency (left) and selectivity to K/A-oil (right) in the reaction of tBut-OOH with cyclohexane as a function of surface area of CeO₂ catalysts.

Next, the catalytic activity of the best sample, CeO₂-HSA, was tested in the deperoxidation of Cy-OOH, using a solution containing 4.7wt% Cy-OOH in cyclohexane. After 6h reaction Cy-OOH conversion was 97%, and selectivity to K/A oil was 113%. These values indicate that the catalyst is decomposing the hydroperoxide and at the same time oxidizing cyclohexane. The TOF estimated for Cy-OOH decomposition at 27% conversion is 0,014 s⁻¹, better than those reported for mesoporous Co-TUD-1 (~0,003 s⁻¹) [9] or silica-supported Ti- (~0,008 s⁻¹) and Ta- (~0,010 s⁻¹) complexes [11,12]. The reaction mixture was left overnight and after 21h 30 min reaction full conversion was reached with a maintained selectivity of 113%. The evolution of the reactant Cy-OOH and products Cy-OH and Cy=O with time is shown in Figure 4. Cy-OH is formed from the beginning of the reaction and its concentration increases continuously with time until all Cy-OOH is decomposed. Formation of Cy=O is slower, but its evolution with time is similar to that of Cy-OH. No induction period was observed at short times suggesting that both Cy-OH and Cy=O are primary products.

Figure 4. Evolution of Cy-OOH (blue rhombus, $\blacklozenge$), Cy-OH (red squares, $\blacksquare$), Cy=O (green triangles, $\blacktriangle$), and total K/A oil (yellow circles, $\bullet$) over CeO_2 -HSA with time.

Finally, recycling tests were done to determine the stability and reusability of the CeO_2 catalyst. A standard reaction was stopped at 80% Cy-OOH conversion. Then, the catalyst was allowed to deposit on the bottom of the reactor, the supernatant liquid was removed, and fresh reaction mixture was added for a new catalytic test. This procedure was repeated up to four times without loss in activity or selectivity (see Figure 5).

Figure 5. Reusability of CeO_2 -HSA in the deperoxidation of Cy-OOH. Conversion (blue) and selectivity (red) for four consecutive cycles.

3.2. DFT study of the reaction mechanism. In order to understand the structure-activity relationship suggested by the experimental data and to identify the active centers participating in the activation of cyclohexane and in the decomposition of the hydroperoxide, the mechanism of cyclohexane oxidation with Cy-OOH was theoretically investigated using Density Functional Theory. Small CeO₂ nanoparticles were simulated by means of the Ce₂₁O₄₂ and Ce₄₀O₈₀ models described in the Computational Details Section, while large CeO₂ particles were simulated by means of an extended CeO₂(111) surface model.

3.2.1. Cyclohexane activation. Cyclohexane is the less reactive molecule present in the reaction medium, and the dissociation of its C-H bond is in principle the most difficult step in the process. A **previous** DFT study [24] showed that the bi-coordinated O atoms on top of the Ce₂₁O₄₂ nanoparticle are the most reactive sites on this model, and consequently we first explored the adsorption and dissociation of cyclohexane at this site. The optimized geometry of the structures involved in this process and the relative energies with respect to separated reactants (Cy-H and Cy-OOH) and CeO₂ catalyst model are shown in Figure 6. Cyclohexane interacts weakly with the most reactive O atoms on top of the Ce₂₁O₄₂ nanoparticle (structure R1), and the dissociation of the C-H bond through transition state structure TS1 involves a large activation energy barrier of 30,1 kcal/mol. A metastable intermediate species very similar to TS1 and only 3,6 kcal/mol more stable was obtained (not shown) that evolved without energy barrier to the most stable intermediate species II, in which the cyclohexoxy fragment is covalently bonded to a surface oxygen atom. For comparison, cyclohexane dissociation at a different edge position was investigated and found 6 kcal/mol less stable. Also, C-H dissociation yielding either a hydrogen atom or a cyclohexyl fragment directly attached

to Ce were considered, and found 56,2 and 36,8 kcal/mol, respectively, less stable than structure I1 (see Figure S4 in the Supporting Information).

Then, a proton transfer through transition state TS2 converts intermediate I1 into a cyclohexanol molecule adsorbed on the catalyst surface (product structure P1) with an activation energy barrier of 23,9 kcal/mol, and subsequent desorption of cyclohexanol from this P1 structure leaves a Ce₂₁O₄₁ nanoparticle model with an oxygen vacancy defect. Reduction of the nanoparticle produces an elongation of the Ce-Ce distance from 3,556 Å in the stoichiometric Ce₂₁O₄₂ system to 4,146 Å in the Ce₂₁O₄₁ model.

The next step in the proposed mechanism is the interaction of the oxidant species, that is, CyOOH, with the oxygen vacancy defect generated by desorption of the first cyclohexanol molecule. In this highly exothermic process the O-O bond in CyOOH is dissociated without activation barrier generating an adsorbed cyclohexoxy fragment and a hydroxyl group that heals the vacancy (reactant structure R2). Then, a proton transfer from the hydroxyl to the alkoxy fragment through transition state TS3 with an activation energy barrier of 18 kcal/mol yields cyclohexanol, which after desorption leaves the stoichiometric Ce₂₁O₄₂ nanoparticle thus closing the catalytic cycle.

Figure 6. Optimized structures of all structures involved in cyclohexane oxidation to cyclohexanol over a $\text{Ce}_{21}\text{O}_{42}$ nanoparticle. Bond lengths (in Å) and relative stability with respect to $\text{Ce}_{21}\text{O}_{42}$ model and separated reactants (in kcal/mol) are given. Ce, O, C and H atoms are depicted as blue, red, orange and white balls, respectively.

Figure 7. Calculated energy profiles for cyclohexane oxidation to cyclohexanol over a $\text{Ce}_{21}\text{O}_{42}$ nanoparticle (blue line) and over an extended $\text{CeO}_2(111)$ surface (red line).

The same catalytic cycle was investigated over a $\text{CeO}_2(111)$ surface representing large CeO_2 nanoparticles. The optimized geometries and relative stability of the structures involved are depicted in Figure S5 in the Supporting Information, and the calculated energy profiles for the complete mechanism over $\text{Ce}_{21}\text{O}_{42}$ nanoparticle and $\text{CeO}_2(111)$ surface are plotted together in Figure 7. On both systems the dissociation of the C-H bond in cyclohexane is the rate determining step, with the activation barrier being 3 kcal/mol larger on the extended surface. From this point, the dissociated I1 intermediate and the adsorbed cyclohexanol P1 product, as well as the transition state for proton transfer TS2, are significantly less stable on the extended surface. Also, desorption of the first cyclohexanol molecule generating a oxygen vacancy defect is energetically more difficult on the $\text{CeO}_2(111)$ surface model. The healing of the oxygen vacancy defect by Cy-OOH is energetically favored on both systems, so that it seems that the higher capacity of small ceria nanoparticles to oxidize cyclohexane is related to the

enhanced reactivity of bicoordinated oxygen atoms at corner or edge positions and to the higher reducibility of smaller nanoparticles.

The cycle described up to now corresponds to the optimum process in which all oxygen atoms of the hydroperoxide are used to oxidize cyclohexane:

However, the decomposition of Cy-OOH yielding cyclohexanone and water also happens, leading to an observed efficiency lower than 200%. Therefore, we have investigated other possible routes for cyclohexanone formation, either from direct decomposition of Cy-OOH or from further oxidation of initially formed cyclohexanol.

3.2.2. Cyclohexyl hydroperoxide decomposition. The adsorption and dissociation of Cy-OOH was studied at different sites on the CeO₂ particles, including the highly reactive two-coordinated O atoms present in the Ce₂₁O₄₂ and Ce₄₀O₈₀ models, as well as low coordinated Ce cations present in the Ce₄₀O₈₀ model and three-coordinated O atoms present in the terraces of the CeO₂(111) slab model. As depicted in Figure 8, Cy-OOH interacts strongly with the basic oxygen atoms present in the Ce₂₁O₄₂ and Ce₄₀O₈₀ models, and is deprotonated through transition state TS4 with an activation energy barrier of only 2,5 kcal/mol. The stable intermediate structure I2 formed in this step consists of one cyclohexylperoxo fragment directly attached to a low coordinated Ce⁴⁺ cation. Dissociation of the O-O bond in this peroxo intermediate through transition state TS5 produces a cyclohexyl alkoxide fragment and an oxygen atom that immediately forms a new bond with a surface oxygen generating a surface peroxo group (intermediate structure I3). The stability of both intermediates, I2 and I3, is similar, but the activation energy necessary to interconvert them is really high, 42,1 kcal/mol, suggesting that another pathway must exist for Cy-OOH decomposition. Further protonation of the alkoxy intermediate through transition state TS6 with an activation

energy of 10,7 kcal/mol produces cyclohexanol and leaves an oxidized $\text{Ce}_{21}\text{O}_{43}$ nanoparticle, in a process that is globally exothermic by -16 kcal/mol.

Figure 8. Optimized geometries of all structures involved in Cy-OOH decomposition over a $\text{Ce}_{21}\text{O}_{42}$ nanoparticle. Bond lengths (in Å) and relative stability with respect to $\text{Ce}_{21}\text{O}_{42}$ model and separated reactants (in kcal/mol) are given. Ce, O, C and H atoms are depicted as blue, red, orange and white balls, respectively.

Taking into account the experimental indication that larger particles are intrinsically more reactive towards hydroperoxide decomposition, the process described above was calculated over the $\text{CeO}_2(111)$ slab model. The optimized geometries and relative stability of the structures involved are depicted in Figure S6 in the Supporting Information, and the calculated energy profiles for the complete mechanism over $\text{Ce}_{21}\text{O}_{42}$ nanoparticle and $\text{CeO}_2(111)$ surface are plotted together in Figure 9. Cy-OOH

deprotonation over $\text{CeO}_2(111)$ surface is not as exothermic as on the $\text{Ce}_{21}\text{O}_{42}$ nanoparticle due to the lower basicity of three-coordinated O atoms, but involves a low activation barrier of 3,7 kcal/mol. The I2 intermediate resulting from deprotonation evolves to a more stable structure I2b (see Figure S6) in which the proton interacts with the O atom directly bonded to the C atom of the cyclohexyl ring. This interaction facilitates the dissociation of the O-O bond in I2b through transition state TS5, with an activation energy barrier of 17,2 kcal/mol, significantly lower than that obtained on the $\text{Ce}_{21}\text{O}_{42}$ system, 42,1 kcal/mol. Further protonation of the cyclohexoxy fragment through TS6 produces adsorbed cyclohexanol and a superoxide adsorbed species (P4 in Figure S5) with an activation energy barrier of only 2,3 kcal/mol. Alternatively, a H transfer from the carbonyl C atom to the O atom in the superoxide species via TS7 would produce cyclohexanone and an adsorbed hydroperoxide group (P5 in Figure S6). However, the higher value of the calculated activation energy, 23,3 kcal/mol, suggests that cyclohexanol route will be preferred.

Figure 9. Calculated energy profiles for Cy-OOH decomposition yielding cyclohexanol over a $\text{Ce}_{21}\text{O}_{42}$ nanoparticle (blue line) and over an extended $\text{CeO}_2(111)$ surface (red line), and yielding cyclohexanone over a $\text{CeO}_2(111)$ surface (dotted red line).

Another possibility explored is the direct dissociation of the O-O bond in Cy-OOH at low coordinated Ce^{4+} Lewis acid sites present in the $\text{Ce}_{40}\text{O}_{80}$ model. The interaction of the O-O bond with the Ce^{4+} cationic sites is strong, with a calculated adsorption energy of -13,8 kcal/mol (reactant R4 in Figure 10). The rupture of the O-O bond through transition state TS8 is assisted by formation of a new Ce-O bond, leading to structure I4 consisting of one alkoxide and one hydroxyl groups directly attached to the same Ce^{4+} centre. The process is thermoneutral, and the activation energy involved is 18,1 kcal/mol, significantly lower than that previously found over $\text{Ce}_{21}\text{O}_{42}$ model and similar to that obtained over the extended $\text{CeO}_2(111)$ surface. From I4 intermediate, a transfer of the H atom bonded to the carbonyl C atom to one surface O atom through transition state TS9 yields cyclohexanone (P5 in Figure 10) together with two surface hydroxyls. This process is highly exothermic and requires an activation energy of only 3 kcal/mol. Desorption of water and cyclohexanone leaves the $\text{Ce}_{40}\text{O}_{80}$ nanoparticle unaltered and ready to start a new catalytic cycle.

An alternative pathway starting from intermediate I4 consists of transferring a proton from the hydroxyl group to the cyclohexoxy fragment, generating cyclohexanol and leaving an extra O atom on the particle. The structure obtained (I5 in Figure S3 in the Supporting Information) is almost 11 kcal/mol less stable than I4, and 7 kcal/mol less stable than the transition state TS9 leading to cyclohexanone formation. Consequently, this alternative route was discarded.

Figure 10. Optimized geometries of all structures involved in Cy-OOH decomposition over a low-coordinated Ce^{4+} centre in $\text{Ce}_{40}\text{O}_{80}$ nanoparticle. Bond lengths (in Å) and relative stability with respect to $\text{Ce}_{40}\text{O}_{80}$ model and separated reactants (in kcal/mol) are given. Ce, O, C and H atoms are depicted as blue, red, orange and white balls, respectively.

3.2.3. Cyclohexanol oxidation to cyclohexanone. Another possible pathway for cyclohexanone formation is the further oxidation of the cyclohexanol formed in the oxidation of cyclohexane. The interaction of cyclohexanol with small CeO_2 nanoparticles is strong, and involves a hydrogen bond between the alcohol proton and a basic surface oxygen atom, as well as a Lewis acid-base interaction between the lone

pair in the alcohol oxygen atom and a Ce^{4+} Lewis acid centre (reactant structure R5 in Figure 11). This conformation polarizes the O-H bond that is easily dissociated through transition state TS10 with an activation energy barrier of only 4,3 kcal/mol, generating a highly stable cyclohexoxy intermediate (structure I6). Then, a second hydrogen transfer from the cyclohexoxy fragment to a basic oxygen atom of CeO_2 produces cyclohexanone and a reduced $\text{CeO}_2\text{-HH}$ nanoparticle (structure P6). The process is highly exothermic, but involves an activation energy of 32.7 kcal/mol, as large as that found for cyclohexane activation.

Figure 11. Optimized structures of all structures involved in cyclohexanol oxidation to cyclohexanone over a $\text{Ce}_{21}\text{O}_{42}$ nanoparticle. Bond lengths (in Å) and relative stability with respect to $\text{Ce}_{21}\text{O}_{42}$ model and CyOH (in kcal/mol) are given. Ce, O, C and H atoms are depicted as blue, red, orange and white balls, respectively.

Figure 12. Calculated energy profiles for Cy-OOH decomposition over $\text{Ce}_{21}\text{O}_{42}$ nanoparticle (blue line), $\text{CeO}_2(111)$ surface (red line) and over Lewis acid sites in $\text{Ce}_{40}\text{O}_{80}$ nanoparticle (yellow line), and for cyclohexanone formation by oxidation of cyclohexanol over a $\text{Ce}_{21}\text{O}_{42}$ nanoparticle (cyan line).

The energy profiles obtained for Cy-OOH decomposition over basic O atoms on $\text{Ce}_{21}\text{O}_{42}$ (blue line) and $\text{CeO}_2(111)$ (red line) models and over Lewis acid Ce^{4+} cations in $\text{Ce}_{40}\text{O}_{80}$ system (yellow line) are compared in Figure 12, which also includes the energy profile for Cy-OH oxidation to Cy=O (cyan line). Dissociation of the O-O bond is the most difficult step in the decomposition of Cy-OOH, but the activation energy involved when the process occurs over Ce^{4+} centres in $\text{Ce}_{40}\text{O}_{80}$ or over $\text{CeO}_2(111)$ surface is half the barrier required in the pathway starting with Cy-OOH deprotonation over $\text{Ce}_{21}\text{O}_{42}$ nanoparticle. These data agree with the experimental observation that the TOF for hydroperoxide decomposition decreases with increasing surface area of CeO_2 catalysts, and suggests that in the case of very small nanoparticles Cy-OOH will also decompose over low-coordinated Ce^{4+} cations generating cyclohexanone.

3.3. IR study of cyclohexane activation. The mechanism proposed according to the DFT study involves, on one hand, the decomposition of Cy-OOH over CeO₂(111) terraces or at Ce⁴⁺ Lewis acid sites generating cyclohexanol and cyclohexanone and, on the other hand, the activation and dissociation of the C-H bond in cyclohexane at the most reactive bi-coordinated O atoms at the edges between {100} and {111} facets. Cyclohexane oxidation follows therefore a Mars van Krevelen mechanism, and the role of the Cy-OOH oxidant species is to heal the oxygen vacancy defects generated in the formation of cyclohexanol. In order to confirm this proposed mechanism we studied, using *in situ* IR spectroscopy, the interaction of cyclohexane with the CeO₂-HSA sample that was found to be the most active in the catalytic tests. Figure 13 shows the IR spectra of the clean CeO₂-HSA sample (black line), after adsorption of cyclohexane (red line) and after co-adsorption of cyclohexane and tBut-OOH (blue line) together with the corresponding gas phase spectra.

After cyclohexane adsorption on CeO₂-HSA at 110°C, the appearance of IR bands at 1190, 1133, 1097 and 1040 cm⁻¹, corresponding to surface alkoxy species, is clearly observed (Figure 13A, red line). The assignment is confirmed by the detection of similar IR bands after cyclohexanol adsorption on a clean CeO₂ sample (see Figure S7 in the Supporting Information). Moreover, the corresponding IR gas phase spectrum (Figure 13B, red line) shows the presence of cyclohexanol (IR band at 1140 cm⁻¹), as a consequence of a fast cyclohexoxy transition to adsorbed cyclohexanol species and further desorption into the gas phase. Notice that the above discussed IR data have been collected in the absence of any oxidizing species, and therefore they confirm the theoretical proposal that the C-H bond activation in cyclohexane involves the participation of surface oxygen atoms and results in formation of adsorbed cyclohexoxy fragments. According to the theoretical study, the role of the oxidant is the healing of

the vacancies, that is, the reoxidation of the surface. In order to proof this reaction mechanism, TBHP was co-adsorbed at 110°C after cyclohexane dosing. An increase in the intensity of the IR band at 1133, 1097 and 1040 cm^{-1} corresponding to adsorbed alkoxy species is clearly observed (Figure 13A, blue line), supporting the Mars van Krevelen mechanism discussed previously. In parallel, gas phase cyclohexanol is also detected (Figure 13B, blue line).

While these experiments demonstrate the feasibility of a Mars van Krevelen mechanism, an alternative pathway involving the initial dissociation of the hydroperoxide on the catalyst surface generating adsorbed oxidizing species, these being responsible for cyclohexane oxidation, cannot be excluded yet. Therefore, an additional experiment was performed in which the CeO_2 surface was first exchanged with $^{18}\text{O}_2$, and then interacted with a reactant mixture of cyclohexane and tBut-OOH. Figure 14 shows the IR spectra of the CeO_2 -HSA (black line) and the isotopically exchanged 18-O CeO_2 -HSA (blue line) samples after co-adsorption of cyclohexane and tBut-OOH together with the corresponding gas phase spectra. Both $\text{Cy-}^{18}\text{O}$ (solid lines) and $\text{Cy-}^{16}\text{O}$ (dashed lines) alkoxy species were observed on the 18-O CeO_2 -HSA (blue line) sample, confirming the Mars van Krevelen mechanism where oxygen lattice species are involved in the oxidation process and further replenished by 16-O species coming from tBut- $^{16}\text{O}^{16}\text{OH}$. The identification of gas phase Cy^{18}OH is challenging due to the overlapping by gas phase Cy^{16}OH , which shows a broad and asymmetric IR band.

Figure 13. A (top) IR spectra of CeO₂-HSA sample a) before adsorption (black line) b) after 12 mbar cyclohexane adsorption at 110°C (red line) and c) followed by 2 mbar tBut-OOH co-adsorption at 110°C (blue line). *IR bands due to tBut-OOH. B (bottom) shows the corresponding gas phase spectra.

Figure 14. A (top) IR spectra recorded at 110°C of the CeO₂-HSA (black line) and 18-O CeO₂-HSA (blue line) samples after co-adsorption of cyclohexane (12mbar) and tBut-OOH (2mbar). Solid lines corresponds to isotopic ¹⁸O-alcoxy species. B (bottom) shows the corresponding gas phase spectra. Reference spectra of Cy-H and tBut-OOH in light grey.

3.4. Addition of a radical inhibitor. Finally, to unambiguously discard the possibility that the reaction follows a radical mechanism, 2,4,6-tritertbutylphenol was added as a radical inhibitor. The choice of this inhibitor was based on the fact that the presence of the bulky tert-butyl groups should sterically hinder the reaction of the phenolic hydrogen with the basic O atoms of the catalyst, so that the Mars van Krevelen mechanism proposed should not be affected. However, free peroxy and/or alkoxy radicals present in the reaction media could easily react with the phenolic hydrogen atom, inhibiting the radical chain by formation of a resonance stabilized phenoxy radical. No significant differences are observed in conversion nor efficiency when 2,4,6-tritertbutylphenol is added to the reaction media (see Figure 15), confirming the non-radical nature of the mechanism of Cy-OOH deperoxidation.

Figure 15. Conversion (left) and efficiency (right) as a function of time for the deperoxidation of Cy-OOH over CeO₂-HSA catalyst in the absence (blue lines) and presence (red lines) of 2,4,6-tritertbutylphenol as radical inhibitor. Full and dashed lines correspond to two equivalent experiments.

4. Conclusions

In the search for an efficient and stable solid catalyst able to oxidize cyclohexane using hydroperoxides as oxidizing species, a number of CeO₂ catalysts with different particle size and shape have been synthesized and characterized. Analysis of their catalytic performance in the oxidation of cyclohexane with tBut-OOH evidences that the selectivity to K/A-oil improves with increasing surface area of CeO₂ particles, irrespective of the preferential facets exposed. This finding suggests the existence of a structure-activity relationship in this process, and points to a preferential activation of cyclohexane at defective corner or edge sites, whose relative concentration increases with decreasing particle size.

A detailed theoretical study of the reaction mechanism shows that the dissociation of the C-H bond in cyclohexane is catalysed by bi-coordinated oxygen atoms present at the edges of small CeO₂ nanoparticles. Cy-OH is formed in this step as primary product, generating oxygen vacancy defects that are healed by the subsequent decomposition of Cy-OOH, thus closing the catalytic cycle. On the other hand, direct decomposition of Cy-OOH occurs at CeO₂(111) terraces in larger particles preferentially forming Cy-OH and at low coordinated Ce⁴⁺ Lewis acid centres present in small CeO₂ nanoparticles generating Cy=O. The lower activation energy found for Cy-OOH decomposition on CeO₂(111) surfaces explains the higher intrinsic reactivity (TOF values) obtained for the sites present in samples with lower surface area. The theoretical proposal that cyclohexane oxidation follows a Mars van Krevelen mechanism involving the oxygen atoms of the catalyst surface is confirmed by *in situ* IR spectroscopy and isotopic exchange experiments performed on ¹⁸O isotopically exchanged CeO₂ samples. In this last case, ¹⁸O and ¹⁶O labelled surface cyclohexoxy intermediates are identified by IR after cyclohexane and tBut-¹⁶O¹⁶OH co-adsorption. Finally, a conventional radical

mechanism can be excluded according to the catalytic results performed in the presence of a radical inhibitor and the *in situ* IR studies.

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Graphical Abstract

Highlights

CeO₂ nanoparticles catalyze cyclohexane oxidation to K/A-oil using hydroperoxides

Cyclohexane activation is structure-sensitive and preferentially occurs at particle edges

Both acid-base and redox properties of CeO₂ play a role in the mechanism

A Mars van Krevelen mechanism is proposed based on DFT and in situ IR spectroscopy