



Impact of cerium-based support oxides in catalytic wet air oxidation: Conflicting role of redox and acid–base properties



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ABSTRACT

High surface area ceria is an excellent support of metals (Ru, Pt, etc.) for catalytic wet air oxidation reactions (CWAO). Due to the low solubility of oxygen in water, the rate of transfer of O_2 from the gas phase toward the catalyst has a decisive impact on the whole oxidation process. The role of the ceria support would be to facilitate this oxygen transfer. Redox properties of ceria (generally measured by the oxygen storage capacity, OSC) have a great impact on this step. Attempts were made to modulate the redox properties of ceria by using mixed oxides: CeO_2 – ZrO_2 , CeO_2 – PrO_2 – ZrO_2 or CeO_2 – TiO_2 . In doing so, acid–base properties of the supports are also modified. The role of the redox and acid–base properties on CWAO reactions (acetic acid, aniline and phenol) are reviewed. In most cases, acid–base properties can have a great impact on the catalyst stability (deactivation by carbonates or polymer deposit). Increasing the redox properties may have an adverse effect on the catalytic performances when acid–base properties bias the whole process. In some cases (phenol over CeO_2 – TiO_2 supported catalysts), an adequate Lewis acidity is preferable to a high OSC of the catalyst.

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1. Introduction

Oxidation of organic pollutants in water is a process widely used in water treatment plants for the final purification of drinking water. Even though great efforts should be made to reduce the cost of these treatments [1], powerful oxidants (chlorine, hydrogen peroxide, ozone, etc.) are generally employed to get a high conversion of the pollutants at ambient temperatures [2]. When the nature of the pollutant is clearly identified (as in process water of chemical industry), catalytic oxidation can be used to significantly increase the oxidation rate of the target molecule. Depending on the oxidant used, several processes can be envisaged: (i) catalytic wet air oxidation (CWAO) with air or oxygen, (ii) catalytic wet peroxide oxidation (CWPO) with H_2O_2 and (iii) catalytic wet ozonation (CWO) with O_3 [3–5]. Because of the low price of the oxidant and of its great availability everywhere in the world, catalytic oxidation with air or oxygen (CWAO) has been the subject of intensive researches during the last decades [6–9]. Nevertheless, oxygen is not a powerful oxidant and is not extremely soluble in water, which requires operating at relatively high temperatures and under pressure. Typical reaction conditions are: 140–240 °C, 5–30 bar of

O_2 with a concentration of pollutants comprised between a few grams and several 10 g l^{-1} . The concentration of dioxygen around the catalyst active sites is a key-parameter determining the reaction rate. For the sake of comparison, only the CWAO reactions carried out in an autoclave-type reactor will be considered here, even though more sophisticated reactor technologies (like membrane reactors [10] or monolith catalyst reactors [11]) are possible for water remediation. Mass transfers between the gas phase and the catalyst grains suspended in solution are represented in Fig. 1. Oxygen is dissolved in water by a gas–liquid transfer controlled by the stirrer speed (not shown in Fig. 1). Once dissolved, oxygen should reach the active sites via a liquid–solid transfer, in parallel with a similar process for the pollutant X. Active sites for the oxidation reaction are generally located on metal particles (Ru, Pt, Pd, etc.). However, it has been proven that cerium-based supports can promote the oxygen transfer, which improves the reaction rate of oxidation.

The objective of this paper is to review the literature concerning the use of ceria and related oxides in CWAO of selected compounds (acetic acid, acrylic acid, phenol, aniline). The oxygen transfer is linked to redox properties of ceria. However, oxidation reactions produce great amounts of CO_2 which strongly interact with the catalyst. Acid–base properties of cerium-based oxides are a determining factor of these interactions. The review will be focused on the conflicting roles of redox and acid–base properties of CeO_2 ,

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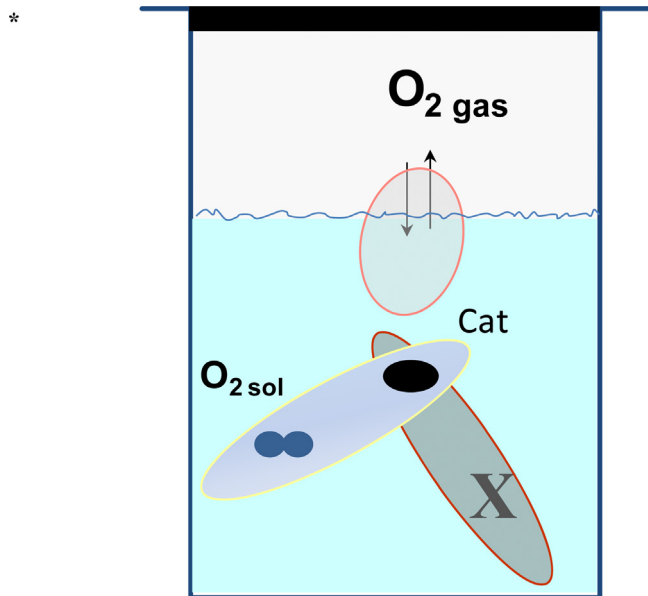


Fig. 1. Mass transfer of O_2 between the gas phase and the active sites of the catalyst grains (Cat). X represents a molecule of pollutant to be oxidized.

CeO_2 – ZrO_2 and CeO_2 – ZrO_2 – PrO_2 supported catalysts for the CWAO reactions.

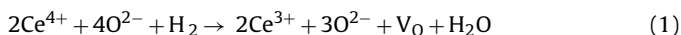
2. Redox and acid–base properties of cerium-based oxides

2.1. Redox properties

Since the pioneer's works of Yao and Yu Yao [12] and of Su et al. [13], redox properties of ceria and related oxides were extensively studied, firstly for applications in automotive converters [14–17], and later for various applications in synthesis chemistry [18], as anti-corrosion agent [19], etc. A detailed analysis of the literature (several hundred papers) is out of the scope of this review. Our main objective is to recall the main results when ceria is doped with Zr or lanthanide cations. Redox properties of cerium-based oxides can be investigated by various techniques, e.g. XPS for the determination of Ce^{3+} content in the solids [20–23], XANES or Synchrotron Radiation Photoelectron Spectroscopy for the electronic state of cerium [23–26], in situ Raman and FTIR of adsorbed probe molecules (oxygen, methanol, etc.) or magnetic susceptibility measurements [20,27–29], EPR for the study of oxygen surface species [20,30], etc. Nanostructures and redox characteristics of cerium-based oxides are detailed in the review by Di Monte and Kašpar [31]. However, H_2 -TPR and OSC measurements were mainly used for characterizing redox properties of ceria-based materials, in the presence or not of metals. The main results of these techniques are analyzed below.

2.1.1. H_2 -TPR of cerium-based oxides

TPR profiles of pure ceria shows two main peaks: a low-temperature peak around 350–550 °C and a large high-temperature peak starting at 550–600 °C [32–35]. The low temperature peak is ascribed to the reduction of surface Ce^{4+} according to the reaction:



One oxygen ion out of four reacts with H_2 to give one molecule of water. For ceria, the theoretical O density would be of 13.7, 9.7 and 15.8 at.O nm⁻² for (1 0 0), (1 1 0) and (1 1 1) crystal planes respectively, which gives a mean surface density of 13.1 at.O nm⁻² or 21.7 $\mu\text{mol at.O m}^{-2}$ [36]. If the reduction of ceria below 500 °C

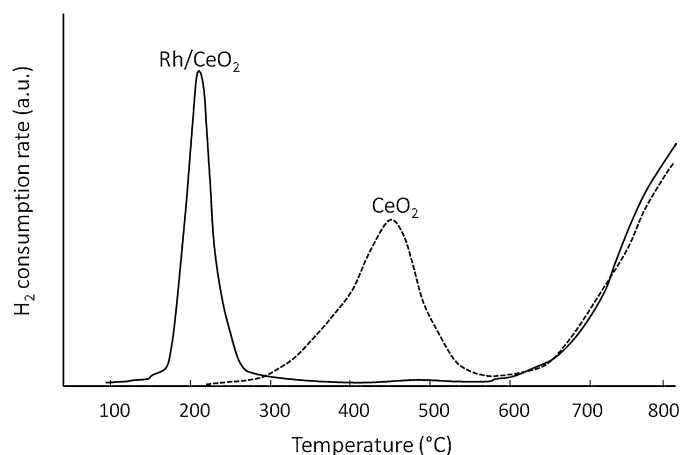


Fig. 2. Temperature-programmed reduction (TPR) profiles for H_2 of CeO_2 and 0.05% Rh/CeO_2 . TPR were carried out by injecting pulses of H_2 (0.231 cm^3) every minute in a stream of Ar ($20 \text{ cm}^3 \text{ min}^{-1}$). Temperature ramp: 4 °C min^{-1} . The TPR profiles are the envelop of the H_2 consumption upon each pulse.

Adapted from Ref. [34].

is strictly confined at the surface, the theoretical amount of hydrogen consumed in the low-temperature peak would be of $5.43 \mu\text{mol } H_2 \text{ m}^{-2}$. The amount of H_2 consumed in the low temperature peak is roughly proportional to the BET area of ceria while the total consumption is virtually independent on the BET area [33]. However, the amount of H_2 taken in TPR can be higher than the theoretical value of $5.43 \mu\text{mol m}^{-2}$. For instance, Johnson and Mooi have reported H/Ce values ranging from 0.005 to 0.141 for CeO_2 samples of 0.7 – $27 \text{ m}^2 \text{ g}^{-1}$, which corresponds to a consumption of 15 – $22 \mu\text{mol } H_2 \text{ m}^{-2}$. Barbier et al. reported a H_2 uptake of $190 \mu\text{mol } H_2 \text{ g}^{-1}$ for a ceria of $19 \text{ m}^2 \text{ g}^{-1}$, i.e. $10 \mu\text{mol } H_2 \text{ m}^{-2}$. By contrast, Perrichon et al. [35] found H_2 consumptions in the first peak (around $4 \mu\text{mol } H_2 \text{ m}^{-2}$) rather in agreement with the theoretical value. It should be noted that pure ceria is sensitive to heat treatment in hydrogen. When the sample is reoxidized and then reduced several times, the low temperature peak tends to vanish. This is due to a collapse of the texture accompanied by a severe BET area decrease [15].

When a metal (Pt, Rh or Pd) is added to ceria, the first peak is shifted to lower temperatures (typically: 150 – 250 °C , Fig. 2). The amounts of H_2 taken in this peak shows that the surface of ceria is reduced at the same time as the noble metal but the high temperature peak (bulk of ceria) is virtually unchanged. H spillover is favored by the noble metal [37] but the reduction of NP/ CeO_2 below 500 – 700 °C does not lead to the classical SMSI effect with metal nanoparticles decoration with reduced oxide moieties, as it is the case for Pt/ TiO_2 [38].

Doping CeO_2 with ZrO_2 can lead to $Ce_xZr_{1-x}O_2$ solid solutions whose crystallographic structure depends on the value of x [15]. For $x > 0.6$, the cubic structure is maintained, even though a tetragonal form named t'' may appear in the region $0.6 < x < 0.8$. However, the structure t'' is very close to the cubic structure and is often indexed in the Fm3m space group. For higher content in Zr ($x < 0.6$), tetragonal structures with c/a axis ratio higher than unity are often observed. However, for medium composition around 50% CeO_2 ($0.4 < x < 0.6$), an adequate preparation of the mixed oxide followed by heat treatment may favor the reformation of a cubic phase. Substituting Ce by Zr drastically changes the reducibility by H_2 . Fig. 3 compares the TPR profiles of ceria and $Ce_{0.5}Zr_{0.5}O_2$. The amount of H_2 taken at low temperature by the mixed oxide is significantly higher than for ceria. And yet, all the characterizations made on $Ce_xZr_{(1-x)}O_2$ oxides show that Zr^{4+} is not reducible by H_2 in the temperature range of the TPR. This TPR result was confirmed on

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