O₂-probe EPR as a method for characterization of surface oxygen vacancies in ceria-based catalysts

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Abstract—Catalytic activity of ceria-based systems is essentially related to the oxygen storage/release characteristics of the surface and, therefore, to the properties of the oxygen vacancies generated upon reduction of CeO₂. EPR analysis of the superoxide species formed upon low temperature oxygen chemisorption on this type of systems is shown to be a very powerful method to characterize such defects. The present work revises results mainly obtained in the authors’ laboratory on this topic and shows the main physicochemical properties of such superoxide species. Situations of practical interest in the field of heterogeneous catalysis are analysed. These include the analysis of defects formed on pure CeO₂, as well as their chemical modification by NO chemisorption or in the presence of chlorine impurities, typically present in supported metal catalysts. Additionally, the characterization of two-dimensional ceria structures in alumina-supported ceria systems with high practical interest is shown to be uniquely provided by this EPR-based method.

Keywords: EPR; CeO₂; oxygen vacancies; oxygen adsorption; NO chemisorption; superoxide; chlorine; alumina-supported ceria.

INTRODUCTION

Cerium oxide (CeO₂) is a very important material from a technological point of view, as it forms part of a number of applications like optical coatings, sensors, ceramics or catalysts [1]. As a catalyst, ceria is included in formulations of systems employed for automobile exhaust gas emission control, removal of SOx and NOx from fluid catalytic cracking flue gases, electrocatalysts over fuel cell electrodes or catalysts for production and purification of hydrogen [1–5]. In most of these processes, the main role of ceria is related to storage/release of oxygen which is facilitated by the particular ability of CeO₂ to undergo redox changes in response to modifications in the gaseous environment [1]. Such redox

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changes are essentially controlled by the characteristics of the oxygen vacancies and reduced/oxidized coordinatively unsaturated cerium cations formed during the course of the respective catalytic processes [1, 6–9]. In particular, surface oxygen vacancies have been directly related to redox processes taking place at relatively low temperatures over ceria [1, 6]. Therefore, knowledge of the nature and redox properties of such defects is essential to understand the catalytic properties of ceria-based materials.

Scanning tunnelling (STM) and atomic force microscopies have certainly provided the most detailed picture (at atomic resolution) so far of defects at the surface of the thermodynamically most stable CeO$_2$(111) surface [8–10]. Alternatively, electron paramagnetic resonance (EPR) analysis of the characteristics of superoxide species formed upon low temperature oxygen adsorption on weakly reduced ceria has been shown to yield important details on the nature and redox properties of surface vacancies formed on more practical high-surface-area CeO$_2$-containing samples [6, 11–13]. The employment of oxygen as an EPR probe of such defects was mainly targeted to overcome the large difficulties found for direct EPR detection of Ce$^{3+}$ cations in this type of samples [14]. The present work collects results obtained by that method for different situations of practical interest. First, the results obtained for pure ceria are analysed and employed as a basis for studying the modifications introduced when the ceria surface is chemically modified by either NO low temperature chemisorption or in the presence of chloride impurities at the sample surface [6, 11–14]. From a practical point of view, it must be noted that chloride ions present in metal precursors employed for preparation of supported metal catalysts are most difficult to eliminate in ceria-related systems due to stabilization of cerium oxychloride phases; this induces significant changes in the redox and catalytic properties of such catalysts [15]. A second practical situation analyzed here corresponds to systems of ceria supported on thermally stable high surface area $\gamma$-Al$_2$O$_3$ of strong relevance to the field of depollution of exhaust emissions in automobiles [1, 16].

**EXPERIMENTAL**

A sample of high-surface-area CeO$_2$ (Rhône-Poulenc, $S_{\text{BET}} = 109$ m$^2$ g$^{-1}$) was used in the experiments. Where so desired, chlorine was incorporated at the surface of this sample (as evidenced by XPS [17]) by impregnating it with an HCl solution at pH 0.1 in order to obtain a Cl$^{-}$ coverage of 1.4 anions nm$^{-2}$, followed by drying and calcination under synthetic air at 673 K. No significant specific area change was produced by this treatment. We will denote this sample hereafter as Cl-CeO$_2$. Alumina-supported ceria samples were prepared by incipient wetness impregnation of a $\gamma$-Al$_2$O$_3$ support (supplied by Condea and showing $S_{\text{BET}} \approx 200$ m$^2$ g$^{-1}$) with aqueous solutions of cerium nitrate. Following impregnation, the samples were dried at 383 K for 24 h and finally calcined in dry air for 2 h at 773 K. The cerium oxide loadings of the thus prepared samples range from 1 to 39 wt% (i.e., from