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Surface and redox properties of cobalt–ceria binary oxides: On the effect of Co content and pretreatment conditions

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ABSTRACT

Ceria-based transition metal catalysts have recently received considerable attention both in heterogeneous catalysis and electro-catalysis fields, due to their unique physicochemical characteristics. Their catalytic performance is greatly affected by the surface local chemistry and oxygen vacancies. The present study aims at investigating the impact of Co/Ce ratio and pretreatment conditions on the surface and redox properties of cobalt–ceria binary oxides. Co–ceria mixed oxides with different Co content (0, 20, 30, 60, 100 wt.%) were prepared by impregnation method and characterized by means of N_2 adsorption at −196 °C, X-ray diffraction (XRD), H_2 temperature-programmed reduction (H_2-TPR) and X-ray photoelectron spectroscopy (XPS). The results shown the improved reducibility of Co/CeO_2 mixed oxides compared to single oxides, due to a synergistic interaction between cobalt and cerium. Oxidation pretreatment results in a preferential localization of cerium species on the outer surface. In contrast, a uniform distribution of cobalt and cerium species over the entire catalyst surface is obtained by the reduction process, which facilitates the formation of oxygen vacancies though Co^{3+}/Co^{2+} and Ce^{3+}/Ce^{4+} redox cycles. Fundamental insights toward tuning the surface chemistry of cobalt–ceria binary oxides are provided, paving the way for real-life industrial applications.

1. Introduction

Ceria-based transition metal catalysts have recently received considerable attention both in heterogeneous catalysis and electro-catalysis fields, as a result of their unique physicochemical properties and lower cost, compared to noble metals (NMs)-based catalysts [1–3]. Ceria is also an excellent co-catalyst for noble metal materials [4,5]. The combination of ceria with transition metals, results in materials with excellent redox properties and surface oxygen mobility, reflected then on their catalytic activity. In this regard, cobalt–ceria mixed oxides have shown great potential in heterogeneous catalysis field as alternative to NMs-based catalysts, for several applications, such as: oxidation of volatile organic compounds (VOCs) [1,6,7], low temperature CO oxidation [8], soot oxidation [9], hydrocarbons (HCs) oxidation [10–12], NO oxidation [13], preferential oxidation of CO in the presence of H_2 excess (PROX) [14,15], ethanol steam reforming [16,17], iso-octane steam reforming [18], ammonia synthesis [19], among others.

Furthermore, cobalt–ceria materials have been extensively applied in the field of solid oxide fuel cells (SOFCs) as alternatives to the well established Ni/YSZ anodes. Co–Ce oxides offer an interesting combination of electronic conductivity and electro-catalytic activity, which render them as suitable anodes in direct hydrocarbon fed SOFCs [20].

Recent studies have shown that the catalytic behavior of Co–Ce binary systems can be notably altered by adopting several strategies, involving among others, the employment of advanced synthesis procedure [7,15,17], the establishment of a certain Co/Ce atomic ratio [10,11,14], etc. For instance, Liotta et al. [10,11] found that the best catalytic activity for methane oxidation can be attained for a Co/Ce atomic ratio close to 1, due to the well contact of Co_3O_4 particles with ceria. In a similar manner, in our recent study related to the steam reforming of iso-octane over mono- and bimetallic Cu–Co/CeO_2 catalysts, it is shown that Co/ceria composites with a Co content of about 20 wt.% exhibit the optimum characteristics in terms of catalytic activity and carbon tolerance [18]. The high concentration of surface oxygen species was considered to be responsible for the enhanced performance of Co/CeO_2 catalysts [18]. Carabineiro et al. [7] examined the impact of preparation procedure on the VOCs oxidation performance of Ce–Co mixed oxides at a constant Ce/Co ratio of 0.5. The best performance was obtained

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with Ce–Co samples prepared by exotemplating, which resulted to a fine dispersion of oxide phases [7].

Despite the wide application range of cobalt–ceria binary oxides, there is no a systematic study on the impact of Co/Ce ratio and the pretreatment conditions (oxidation or reduction) on the local surface chemistry. To this end, the present study aims to shed some light into the surface chemistry modifications of cobalt–ceria mixed oxides that can be induced by altering the Co/Ce ratio and the pretreatment environment. More specifically, the physicochemical properties of cobalt–ceria mixed oxides of different Co content (0, 20, 30, 60, 100 wt.%) are determined by several complimentary techniques, such as BET, XRD, TPR and XPS. Special emphasis is paid to the impact of oxide composition and pretreatment conditions on elemental chemical states and surface oxygen vacancies, due to their pivotal role on catalytic activity. A direct motivation here it to answer how the oxides composition in conjunction with the pretreatment atmosphere affects the local surface structure (elemental chemical states, surface composition, oxygen vacancies), which finally determines the catalytic activity.

2. Experimental

2.1. Materials synthesis

Single CeO_2 and Co_3O_4 oxides as well as Co/CeO_2 composites with different cobalt loadings (20, 30 and 60 wt.%) were prepared by wet impregnation. Single oxides were synthesized by diluting the appropriate quantities of the corresponding precursor salts ($Ce(NO_3)_3{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$) in double distilled water. The whole content was next heated under stirring until water evaporation. The resulting samples were dried at 120 °C for 16 h and calcined at 600 °C for 2 h, using a heating rate of 5 °C/min. Following this procedure bare CeO_2 and Co_3O_4 oxides were obtained.

The Co/CeO_2 catalysts were synthesized by impregnation of the CeO_2 oxide in an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich) with appropriate concentration, so as to yield 20, 30, 60 wt.% nominal Co loading. The resulting suspensions were heated under stirring in order to remove the excess of water. The obtained samples were then dried overnight at 120 °C and calcined at 600 °C for 2 h. These samples are hereinafter denoted as *x*Co/Ce, where *x* stands on Co loading. To assess the impact of reduction pretreatment on the mixed oxides characteristics, the 30 wt.% Co/CeO_2 mixed oxide (30Co/Ce sample) is further subjected to a reduction pretreatment at 600 °C for 1 h in a reducing atmosphere (10 vol.% H_2 in He, 100 cm^3/g). This sample is refereed as 30Co/Ce-R.

For binary Co–Ce oxides the Co content was varied in the range of 20–60 wt.% loading. This specific range was carefully selected taking into account the composition of mixed oxides employed in several electro-catalytic applications. More specifically, a relatively high Co loading (usually higher than ca. 20 wt.%) is required in fuel cell applications in order the required electronic conductivity to be accomplished [21]. In a similar manner, sufficient catalytic activity in various applications, such as VOCs oxidation [7,11], CO oxidation [8], etc., is achieved by Co loading higher than ca. 20 wt.%.

2.2. Characterization studies

2.2.1. Textural characterization

The surface area of bare CeO_2, Co_3O_4 as well as Co_3O_4–CeO_2 mixed oxides was determined by N_2 adsorption/desorption isotherms at −196 °C, using the multipoint BET analysis method, in a Tristar Micromeritics 3000 flow apparatus. BET surface area was determined according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.30. The total pore volume was calculated based on the adsorbed nitrogen volume at the highest relative pressure, while the average pore size diameter was determined by the Barrett, Joyner, and Halenda (BJH) method. Prior to the measurements, the samples were degassed at 250 °C overnight.

2.2.2. XRD analysis

The crystalline structure of the catalysts was determined by X-ray powder diffraction (XRD) on a Siemens D 500 diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm) and operating at 40 kV and 30 mA. Diffractograms were recorded in the $2\theta = 10–80°$ range at a scanning rate of 0.04° over 2 s. The Scherrer equation was used to determine the crystal size of different phases based on the most intense diffraction peaks.

2.2.3. TPR analysis

Temperature programmed reduction (TPR) experiments were performed in a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments). In a typical TPR experiment, ∼50 mg of sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated to 1100 °C at 10 °C/min under He flow of 29 cm^3/min and H_2 flow of 1.5 cm^3/min.

2.2.4. SEM analysis

Surface analysis for morphological characterization was carried out by SEM, using a FEI Quanta 400 FEG ESEM (15 keV) electron microscope. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons. EDS confirmed the nature of the components.

2.2.5. XPS analysis

The XPS measurements were carried out in the analysis chamber of MAX200, at room temperature and $\sim 10^{-8}$ mbar pressure, using non-monochromatic MgKα X-rays and a Hemispherical Electron Energy Analyser (SPECS EA200) with Multi-Channel Detection properly calibrated according to ISO15472 and ISO24237. The analyzer operated under conditions optimized for better signal intensity (constant pass energy of 100 eV, maximum lens aperture, analysis along the specimen surface normal). The analyzed specimen area was a 4 × 7 mm^2 rectangle, placed near the center of each specimen surface on an Al plate sample holder.

3. Results and discussion

3.1. Textural/structural characterization (BET and XRD analysis)

Table 1 shows the main textural characteristics (BET surface area and total pore volume) of CeO_2, Co_3O_4 single oxides as well

Table 1
Summary of textural (BET), structural (XRD), surface (XPS) and redox (TPR) characteristics of single and mixed Co_3O_4–CeO_2 oxides.

Samples	BET		XRD		TPR	XPS
	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Phase detected	Crystallite size (nm)	TPR peaks (°C)	Ce (III) %
CeO_2	71.5	0.27	CeO_2	11.9	**500**, **750**	25
20CoCe	34	0.13	CeO_2 Co_3O_4	10.2 37.6	295, **360**	29
30CoCe	45	0.21	CeO_2 Co_3O_4	10.4 37.7	318, **373**	27
60CoCe	15	0.07	CeO_2 Co_3O_4	11.7 39.5	373, **433**	26
Co_3O_4	3.0	0.01	Co_3O_4 CoO	22.1 42.0	370, **433**	–

TPR temperatures: peak maxima (bold), shoulders (plain text).