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Interaction of NO and NO_2 with the surface of $Ce_xZr_{1-x}O_2$ solid solutions – Influence of the phase composition

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Abstract

Structural (XRD) and spectroscopic (EPR, IR and Raman) investigations were performed to elucidate the influence of CeO_2 content on the phase composition and surface chemistry of $Ce_xZr_{1-x}O_2$ solid solutions ($x = 0.10$–0.85), interacting with NO and NO_2 in the absence and presence of oxygen. Strong influence of ceria loading on the adsorption modes of both nitrogen oxides and the nature of the resultant surface species was revealed. Adsorption of NO led to formation of mononitrosyl complexes, dimers and N_2O, whereas interaction of NO_2 with the ceria–zirconia catalyst resulted in the adsorbate disproportionation or coupling, depending on the sample composition.

Keywords: $Ce_xZr_{1-x}O_2$; Phase composition; NO_x adsorption; EPR; RS

1. Introduction

One of the most important industrial application of CeO_2–ZrO_2 solid solutions is related with the automobile three-way catalyst, where the support extensively assists in catalytic performance of the deposited active phase, constituted by noble metals such as Pt, Rh or Pd [1,2]. The redox properties of the solid solution, controlled by the CeO_2/ZrO_2 ratio and its phase composition [3], are intimately associated with easy oxygen shuttling between the catalyst and the gas phase under oxygen lean or rich conditions, respectively. The resultant oxygen storage capacity of $Ce_xZr_{1-x}O_{2-y}$ is directly related to facile reduction of cerium component, accompanied by concomitant creation of oxygen vacancies. Apart from playing the role of a good oxygen buffer, the CeO_2–ZrO_2 support can directly participate in the reduction of nitric oxides [4–6]. For instance, in the case of the three way catalyst, it has been found that at temperatures higher than 400 K, NO can be dissociatively adsorbed on the zirconia–ceria support, following a mechanism involving oxygen vacancies [6].

Paramagnetic NO and NO_2 molecules adsorbed on the surface of CeO_2–ZrO_2 solid solutions can play the role of probe molecules while examined by IR and EPR, providing important information not only about coordinatively unsaturated sites of different reducibility and acid–base properties [7–9], but also about occurrence of zirconia-enriched and ceria-enriched domains, which cannot be revealed by powder diffraction [10,11].

At temperatures below 1273 K, the CeO_2–ZrO_2 solid solutions may exist in three different phases, depending on the molar ratio of both oxide components. Thus, for CeO_2 contents lower than 10%, a monoclinic ($P2_1/c$) phase, whereas for CeO_2 contents higher than 80%, a cubic phase ($Fm3m$) have been identified [6,12]. In the intermediate concentration region, both stable (t) and metastable (t′ and t″) tetragonal phases ($P4_2/nmc$) have been postulated. The t′ structure can be derived from the cubic phase by the cation diffusionless phase transition, whereas the t″ phase characterized by the lattice parameter ratio $a/c = 1$, is an intermediate one between the tetragonal t′ and the cubic phase [6]. Actually, the phase boundaries are rather vague due to a fact that for the metastable tetragonal forms, distortions from the fluorite-type structure are rather easy and highly sensitive to particles size.

For bare ZrO_2 and zirconia-based materials, the stability of a particular polymorph is strongly size-dependent

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($\Delta G(r < r_o)_{m\rightarrow t} = 4/3\pi r^3 \Delta G_{bulk} + 4\pi r^2(\gamma_t - \gamma_m) < 0$) [13,14]. The monoclinic form is much more stable than the tetragonal one, in the case of coarse-grained samples. However, if the particle size r is lower than the critical value of $r_o \sim 30$ nm [15], the tetragonal polymorph becomes thermodynamically more stable, because it exhibits considerably lower surface energy than the monoclinic counterpart ($\gamma_t < \gamma_m$).

The aim of present work was to characterize the $Ce_xZr_{1-x}O_2$ solid solutions of various compositions from the view point of their bulk and surface properties, to find the correspondence between the ceria content and the adsorption modes of NO and NO_2. Particular attention was devoted to the formation and thermal evolution of the resultant surface complexes and their reactivity with dioxygen.

2. Experimental

The investigated binary CeO_2–ZrO_2 solid solutions, containing 10–85 mol% CeO_2, were commercially produced by *RHODIA* by hydrothermal synthesis from nitrate precursors, dried at 373 K for 1 h and then calcined at 873 K for 6 h. The single phase zirconium and cerium dioxides, used in these studies as reference systems, were obtained from aqueous solutions of the corresponding $ZrOCl_2$ and $Ce(NO_3)_3{\cdot}6H_2O$ (Aldrich 99.99%) precursors by precipitation with 25% solution of ammonia. After drying, the samples were calcined in air at 873 K for 6 h.

The investigated samples were structurally and texturally characterized by XRD, SEM/TEM, and N_2-porosimetry. Their spectroscopic characterization by EPR, IR and Raman was also performed. X-ray diffraction patterns were recorded with Philips X'Pert (PW1710) diffractometer using monochromatized Cu Kα radiation. Raman spectra were measured by means of a FTS 6000 spectrometer equipped with a BIORAD accessory. The samples were excited with the 1064 nm line of a diode-pumped Nd:YAG laser (Spectra Physics Model T108S) and the scattered radiation was collected at 180°, using 4 cm^{-1} resolution. The IR spectra were registered with the resolution of 2 cm^{-1} using an Equinox 55 spectrometer equipped with a MCT detector. The samples placed in the IR cell on a silicon wafer were treated *in situ*. The CW-EPR X-band spectra were recorded at room and liquid nitrogen (77 K) temperatures with a Bruker ELEXSYS E-500 spectrometer operating at the 100 kHz field modulation. EPR parameters were determined by simulation using the EPRsim32 program [16].

In all cases described below, nitrogen oxides were adsorbed at pressure of 20 Torr (non-equilibrium pressure) on the samples previously outgassed under vacuum at $p \leq 10^{-5}$ Torr and activated at 623–673 K for 0.5 h. All samples were contacted with NO and NO_2 at 77 K for 1 min and next gradually exposed to room temperature or to 333 K, to follow the adsorption progress monitored by EPR. Once the NO_x evolution was accomplished, the samples were outgassed and oxygen was introduced under the pressure of 2 Torr at 77 K. The exposure to room temperature was then repeated.

3. Results and discussion

3.1. Phase composition analysis

Due to the strong mutual dependence between the bulk structure and the surface properties of the CeO_2–ZrO_2 solid solutions, a detailed phase analysis in the whole concentration range is an indispensable step of samples characterization. Introduction of less than 10 mol% of CeO_2 into m-ZrO_2 matrix did not involve any appreciable phase modification at room temperature. However, a phase transition was observed above 1470 K, when the monoclinic phase is transformed into the stable tetragonal form. The m → t phase transition can be followed easily by XRD, because the maxima corresponding to (1 1 1) and $(1\,1\,\bar{1})$ reflections, diagnostic of the monoclinic zirconia, were replaced by a single (1 1 1) reflection characteristic of the tetragonal phase. At CeO_2 loadings exceeding 10 mol%, metastabilization of the high-temperature tetragonal and cubic phases takes place already at room temperature. Thus, the (1 1 1) reflection of t-ZrO_2 was clearly visible in the diffraction pattern of the $Ce_{0.75}Zr_{0.25}O_2$ solid solution (Fig. 1a). Because the metastable tetragonal phase can exists in two t′ and t″ variants depending on the CeO_2 content [6], distinguishing between them required a detailed insight into XRD data in the 2θ region of 70–71.5° (Fig. 1a, inset). The (4 0 0) reflection, which is crucial for making the phase discrimination, splits into (0 0 4) and (4 0 0) components (usually for $0.20 \leq x \leq 0.65$) in the case of the t′ phase, or it remains intact (for $0.70 \leq x \leq 0.90$), when the t″ phase is dominant [5,12]. Due to the low sensitivity of the XRD method to small shifts in the position of oxygen atoms and relatively weak intensity of those lines, such analysis is rather difficult. Contrary to this, the nuances in the phase composition of the CeO_2–ZrO_2 solid solutions were much better pronounced in the Raman spectroscopy, which is more sensitive to the short-range oxygen displacement, owing to the large polarizability of oxygen ions. The factor group theoretical analysis predicts 18 ($9A_g + 9B_g$) Raman-active modes for the monoclinic ZrO_2 form, 6 ($A_{1g} + 2B_{1g} + 3E_g$) for the tetragonal one and only 1 F_{2g} mode for the cubic phase [17,18]. The number of components observed in the Raman spectra decreased continuously with CeO_2 loading, from at least 10 bands observable for $Ce_{0.10}Zr_{0.90}O_2$ (m), 8 for $Ce_{0.20}Zr_{0.80}O_2$ (m + t′), 4 for $Ce_{0.50}Zr_{0.50}O_2$ (t′) and $Ce_{0.70}Zr_{0.30}O_2$ (t″) to 1 band for $Ce_{0.85}Zr_{0.15}O_2$ (c), making the distinction between the t″ and cubic phases possible. The representative spectra, recorded for $Ce_xZr_{1-x}O_2$ solid solutions, with $x = 0.20$, 0.70 and 0.85, respectively are presented in Fig. 1b. They obviously differed in the number of resolved bands, but in all cases the most intense ones occurred between 465 and 490 cm^{-1}. A single band at 469 cm^{-1} observed for $Ce_{0.85}Zr_{0.15}O_2$ was attributed to the symmetrical F_{2g} mode, characteristic of the cubic phase with the fluorite-like structure. In the case of the solid solutions with an intermediate ceria content (but higher than 50 mol%), such as $Ce_{0.70}Zr_{0.30}O_2$, weaker bands at ~170 and 310 cm^{-1} along with a broad feature centered at ~632 cm^{-1} (A_{1g}), revealed the presence of the t″ phase. The last band is usually ascribed to