



Highly dispersed silica-supported ceria–zirconia nanocomposites: Preparation and characterization



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ABSTRACT

Ternary CeO₂-ZrO₂/SiO₂ nanocomposite oxides were synthesized by a liquid-phase method and subjected to thermal treatment at 550 °C. The physicochemical characterization of the obtained nanosized systems was carried out by various techniques, namely: X-ray diffraction (XRD), nitrogen adsorption–desorption, Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). The XRD measurements revealed the presence of cubic phase Zr_{0.4}Ce_{0.6}O₂ in CZS1 (CeO₂:ZrO₂:SiO₂ = 3:10:87) and CZS2 (CeO₂:ZrO₂:SiO₂ = 10:10:80) samples. The crystallinity of this phase slightly increased with increasing ceria content in nanocomposites. Raman spectra indicated the presence of oxygen vacancies in the case of CZS2 and an absence displacement of oxygen ions from their normal lattice positions in both of the samples. XPS data indicated a significant quantity of Ce³⁺ ions present in the composites, which is greater in the CZS2 composite. In the case of CZS systems the TEM–HRTEM results showed well-dispersed nanosized Zr–Ce–oxides over the surface of amorphous SiO₂. All the characterization techniques revealed that silica does not form any compounds with the dispersed Zr–Ce–oxides. The prepared materials were tested in catalytic reaction of CO oxidation in the presence of H₂ and it was shown that CZS2 system had better performance than CZS1 one.

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1. Introduction

Nowadays, ceria and ceria-based composite oxides, particularly ceria–zirconia, in different stoichiometries, are effective supports or catalysts for important industrial reactions and reactions directed towards environment protection, such as oxidation of CO with O₂ in the presence or absence of H₂ [1–4], cracking of heavy oils [5], cracking and reforming of methane with CO₂ and/or with steam [6], water-gas shift reaction [7], catalytic combustion of hydrocarbons [8] et al. The wide application of CeO₂ is due to its unique acid–base and redox properties. It is well known that ceria can affect: (a) a thermal and structure stability of the catalyst supports [9]; (b) a dispersion of active component [10]; (c) a facile oxidation and reduction of noble metals [11]; (d) a storage and release of oxygen in ceria containing catalysts [12] and (f) the decrease of carbon formation on the catalyst surfaces [13]. The high oxygen storage capacity (OSC) of CeO₂ is a result of high mobility of O²⁻

ions inside the ceria lattice [5,14]. The substitution of other metal in the ceria lattice can increase the concentration of oxygen vacancies or change the bulk composition of CeO₂, which expedites the diffusion of lattice oxygen and improves the oxygen storage–release capacity [1,14,15]. Recent studies suggest that the formation of mixed oxides of ceria with cations such as Zr⁴⁺, Cu²⁺, Mg²⁺, Al³⁺ and La³⁺ enhances the thermal stability, redox and oxygen storage properties of ceria-based systems [1,16,17]. In this sense, ceria–zirconia mixed oxides are known to bear a high thermal resistance and increased OSC. Incorporation of zirconia into the cubic CeO₂ framework with formation of a solid solution results in increased thermal stability and improved redox properties due to the high efficiency of the Ce⁴⁺ ↔ Ce³⁺ redox cycle [18].

The catalytic performance of ceria–zirconia composite oxides is strongly influenced by a crystal structure, particle size, balance between structural defects and Ce content, the degree of reducibility, and the mobility of oxygen in the bulk of mixed oxides [4,19]. Despite all these implications, insufficient textural/structural stability and mechanical strength and decrease of specific surface area at high temperatures are some of the problems encountered in the case of unsupported ceria–zirconia solid solutions because many

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applications require high temperatures [20]. Therefore, there are some attempts to disperse ceria-based nanocomposites on different supports and exploit them for various catalytic reactions [7,21]. Silica is one of the most widely used inert carriers with excellent chemical inertness, high thermal stability and high specific surface area, which can enhance the dispersion and catalytic activity of most deposited active oxides [2,14,21].

In the present investigation, highly dispersed silica-supported ceria–zirconia nanomaterials with various compositions were synthesized by a liquid-phase method employing fumed silica and subjected to thermal treatment at 550 °C to study the influence of changes in phase composition on the structural properties of CeO₂–ZrO₂/SiO₂ nanocomposites and on their catalytic performance in CO oxidation in the presence of H₂. These effects were characterized using X-ray diffraction (XRD), nitrogen adsorption–desorption, Raman spectroscopy (RS), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The catalytic activity of prepared materials was tested in the selective oxidation of CO in the presence of H₂.

2. Experimental

2.1. Materials

Initial fumed silica (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine), zirconium acetylacetonate (Aldrich, >98% Zr(acac)₄) and cerium acetylacetonate (Sigma–Aldrich, Ce(acac)₃·xH₂O) were used as base materials for preparing the samples.

2.1.1. Synthesis of silica-supported ceria–zirconia nanocomposites

Silica-supported ceria–zirconia nanocomposites (CeO₂–ZrO₂/SiO₂) were prepared using a liquid-phase method. The synthesis was performed in a glass double-throat reactor equipped with a propeller agitator and a reflux condenser. Zr(acac)₄ and Ce(acac)₃ solutions in dry CCl₄ were added to fumed silica (15 g; previously calcined at 500 °C; S = 283 m² g⁻¹) at 76 °C. The reaction mixture was stirred in the refluxing tube for 1 h. Then CCl₄ and acetylacetone as reaction product were removed from the mixture by evacuation. Then the solid product was dried and calcined at 550 °C for 1 h. According to [22] the temperature range 500 – 550 °C corresponds to the destruction of acetylacetonates ligands and complete removal of the volatile carbon components upon oxide formation. The content of ZrO₂ was 10 wt. % and the contents of grafted CeO₂ was 3 and 10 wt. %. Thus, compositions of the prepared materials were CeO₂: ZrO₂: SiO₂ = 3:10:87 (CZS1) and CeO₂: ZrO₂: SiO₂ = 10:10:80 (CZS2).

2.2. Methods

2.2.1. X-ray diffraction powder analysis

X-ray diffraction patterns were recorded at room temperature using a DRON-3 M diffractometer (Burevestnik, St.-Petersburg, Russia) with Cu K_α (λ = 0.15418 nm) radiation and a Ni filter in the 2θ range from 10° to 70°. The average size of nanocrystallites (D_{cr}) was estimated according to the Scherrer equation [23]. Crystalline structure of the samples was analyzed using the JCPDS Database (International Center for Diffraction Data, PA, 2001) [24].

2.2.2. Textural characterization

To analyze the textural characteristics of CeO₂–ZrO₂/SiO₂ nanocomposites, low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were recorded using an automatic gas adsorption analyzer ASAP 2405 N (Micromeritics Instrument Corp.) after outgassing the samples at 110 °C for 2 h in a vacuum chamber. The specific surface areas (S_{BET}) of the nanocomposites were

calculated according to the standard BET method [25]. The total pore volume (V_p) was evaluated by converting the volume of adsorbed nitrogen at p/p₀ = 0.98 – 0.99 (p and p₀ denote the equilibrium pressure and the saturation pressure of nitrogen at 77.4 K, respectively) to the volume of liquid nitrogen per gram of the adsorbent. The nitrogen desorption data were used to compute the pore size distributions (PSD_S, differential f_V ~ dV_p/dR and f_S ~ dS/dR) using a self-consistent regularisation (SCR) procedure under non-negativity condition (f_V ≥ 0 at any pore radius R) at a fixed regularisation parameter α = 0.01 with voids (V) between spherical nonporous nanoparticles packed in random aggregates (SCV/SCR model) [26]. The incremental pore size distributions (IPSD) at Φ_V(R_i) = (f_V(R_{i+1}) + f_V(R_i))(R_{i+1} – R_i)/2 at ΣΦ_V(R_i) = V_p) were calculated from the differential PSD_S with respect to pore volume f_V ~ dV/dR, ∫f_VdR ~ V_p. The f_V and f_S functions were also used to calculate contributions of nanopores (V_{nano} and S_{nano} at 0.35 nm < R < 1 nm), mesopores (V_{meso} and S_{meso} at 1 nm < R < 25 nm), and macropores (V_{macro} and S_{macro} at 25 nm < R < 100 nm). The average pore radius (R_{p,V}) was determined from the differential pore size distributions with respect to the pore volume.

2.2.3. Raman spectroscopy

The Raman spectra were recorded over the 150 – 3200 cm⁻¹ range using an InVia Reflex Microscope DMLM Leica Research Grade, Reflex (Renishaw, UK) with Ar⁺ ion laser excitation at λ₀ = 514.5 nm. For each sample, the spectra were recorded at several points in order to ascertain the homogeneity of the sample, and the average of all these spectra were presented in this study.

2.2.4. X-ray photoelectron spectroscopy

The XPS measurements were performed on a VG Scienta R4000 electron analyzer with a MX650 monochromatized Al K_α (1486.6 eV) radiation source. The binding energy (BE) were referenced to Si 2p (BE = 103.5 eV) with an accuracy of ±0.1 eV. Peak fitting was done using Casa XP5 with Shirley background and 10:90 Lorentzian:Gaussian convolution product shapes. The atomic concentration ratios were achieved by determining the elemental peak areas, following a Shirley background subtraction by the usual procedures documented in [27].

2.2.5. High-resolution transmission electron microscopy

The particulate morphology was analyzed using Transmission Electron Microscope (TEM) employing Tecnai G2 T20 X-TWIN (FEI Company, USA) apparatus operating at a voltage of 200 kV with LaB6 electron source. The presence of metals and their elemental composition were recorded by using energy dispersive X-ray (EDX). The samples were supported on holey carbon copper grids by dropping ethanol suspensions containing uniformly dispersed oxide powders.

2.2.6. CO oxidation in the presence of h₂

The catalytic performance of the synthesized CeO₂–ZrO₂/SiO₂ nanocomposites was investigated in selective CO oxidation in presence of H₂ (reaction gas mixture 1 vol.%CO + 2 vol.%O₂ + 65 vol.%H₂ + 32 vol.%He). A sample (0.2 g) previously split up to 0.25 – 0.5 mm granule size was merged to a flow reactor and catalytic measurements were carried out over the temperature range 20 – 400 °C under the atmospheric pressure at gas flow rate of 0.1 l/min. The outlet gas stream was analyzed by a gas chromatograph “SHIMADZU” (Japan) equipped with thermal conductivity detector; gas separation (O₂, CO, CO₂, H₂) was conducted in a column filled with CARBOXEN-1000 (USA). The CO conversion and selectivity towards CO were calculated as follow:

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