Thermal synthesis of ultradispersed Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} / γ-Al\textsubscript{2}O\textsubscript{3} and viscosity of its aqueous suspension for catalytic coatings

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Abstract. In the present work, ultradispersed nanostructured powder of Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} / γ-Al\textsubscript{2}O\textsubscript{3} was obtained by thermolysis of a suspension of amorphous boehmite AlOOH in an aqueous solution of maltose C\textsubscript{12}H\textsubscript{22}O\textsubscript{11} and nitrate salts of Zr and Ce at a mass ratio of oxides Ce, Zr : γ-Al\textsubscript{2}O\textsubscript{3} from 1:9 to 1:1. The powders obtained have a high thermal stability which is confirmed by XRD and high specific surface area 40 – 80 m\textsuperscript{2}/g after heating at 1000 °C depending on oxide ratio. Based on the obtained oxide powders, suspensions with a relatively low rotational viscosity are prepared without the use of organic plasticizers by use of protonation and bimodal particle size distribution of solid phase. This allowed us to achieve a gain of catalytic coating 120 g per dm\textsuperscript{3} of substrate and successfully apply this results in the technology of heterogeneous catalysts for automotive pollution control.

1. Introduction

CeO\textsubscript{2}-ZrO\textsubscript{2} mixed oxides are widely used today in automotive pollution control as promoter of the three-way catalyst [1, 2]. Most important role of mixed oxide is related to the redox properties around contacts between this component and the active phases (usually precious metals) deposited on it. Best redox properties have Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} (x = 0.50 – 0.68) mixed oxide with pseudocubic lattice and internal tetragonal symmetry due to oxygen displacement from the ideal sites [3], or so-called t’-phase with ratio of cell parameters c/a = 1,02 – 1,001. This phase is metastable and above a particle size > 20 nm segregated into thermodynamically stable tetragonal Ce\textsubscript{0.2}Zr\textsubscript{0.8}O\textsubscript{2} and cubic Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} phases [4]. Usually for catalytic purposes, Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} is distributed in high specific surface area γ-Al\textsubscript{2}O\textsubscript{3} which does not form solid solutions with Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} and increases the thermal stability and dispersity of the system. Common methods for producing Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} such as the coprecipitation within microemulsions [3], hydrothermal synthesis [5], citrate [6] method, spray prirolysis [7], etc., remain technologically complex. All of these methods usually give mixed oxide with S\textsubscript{BET} ≤ 100 m\textsuperscript{2}/g. We have proposed a simple method for Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} / γ-Al\textsubscript{2}O\textsubscript{3} synthesis by thermal decomposition of Ce and Zr nitrates in a boehmite matrix in the presence of maltose [8, 9]. The boehmite matrix both sets the nanoscale state of the mixed oxide formed and serves as γ-Al\textsubscript{2}O\textsubscript{3} precursor. The reducing medium of maltose and the products of its thermal decomposition leads to high homogeneity of mixed oxide at the stage of crystallite nucleation. This allows to immediately get Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} / γ-Al\textsubscript{2}O\textsubscript{3} composite, rather than a separate Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} oxide for subsequent mixing it with γ-Al\textsubscript{2}O\textsubscript{3} or its precursor.

Catalytic Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} / γ-Al\textsubscript{2}O\textsubscript{3} coatings are applied onto cordierite or annealed steel cellular or honeycomb substrates by suspension method. For high layer strength use boehmite as sintering additive [10]. The key stage of coating is impregnation of the substrate with a suspension with dispersed and / or dissolved coating precursors. It is desirable to use only one impregnation stage for
coating the required thickness due to the hygroscopicity of the primary layer and blockage of the substrate cells at the next impregnation. The efficiency of this stage depends on coating mass yield of the from the precursors and suspension concentration which can be increased by reducing the viscosity $\eta$ of the suspension. To reduce $\eta$ of colloidal systems, surfactants and polyelectrolytes [11, 12, 13, 14], protonation by mineral acid [15] and bimodal particle size distribution [16] are commonly used. At bimodal particle size distribution, particles of a small fraction of the solid phase displace the dispersion medium from the space between the particles of the coarse fraction and increase the amount of unbound liquid and fluidity of the system. The described suspension is a complex system, its rheological properties depend on many factors: high specific surface area of the solid phase, particles of different charge and with different adsorption properties, high content of electrolytes in the dispersion medium. The use of organic plasticizers and protonation in such systems either has little effect, or this effect is unpredictable or not permanent.

The aim of this work was to suspend of ultradispersed $\text{Ce}_0.5\text{Zr}_0.5\text{O}_2$ / $\gamma$-Al$_2$O$_3$ synthesized by thermal method and plasticization of its aqueous suspension by joint protonation and bimodal particle size distribution.

2. Experimental

As raw materials for synthesis of $\text{Ce}_0.5\text{Zr}_0.5\text{O}_2$ / $\gamma$-Al$_2$O$_3$ oxide composite, commercial boehmite AlOOH (Redkino Catalyst Company, purity 99.5% recount to oxides, $S_{\text{BET}} = 300$ m$^2$/g, water content 18%), salts cerium (III) nitrate $\text{Ce(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}$ and zirconyl nitrate $\text{Zr(NO}_3\text{)}_4 \cdot 2\text{H}_2\text{O}$, maltose $\text{C}_12\text{H}_{22}\text{O}_{11}$, nitric acid (Reachem, purity = 99.9%), distilled water were used. Here and hereinafter, for the compounds Ce, Zr, and Al, we used weight concentrations and ratios converted to oxides, unless otherwise indicated. The oxide composite was prepared in accordance with the scheme (figure 1) by thermal decomposition of a raw suspension of boehmite in an aqueous solution of salts and maltose.

Raw suspension in the amount of 2 kg included 40% of the precursors of the oxide composite which were taken in $\text{CeO}_2$-$\text{ZrO}_2$ : $\text{Al}_2\text{O}_3$ ratio = 1:9, 1:4, 1:2 and 1:1 at an equimolar ratio of Ce, Zr and maltose, the rest was water. Salts and maltose solution adjusted to pH 4.0 by nitric acid was mixed with boehmite in a ball mill and ground within 1 - 4 hours. In addition, a raw suspension with mixed oxide: alumina ratio = 1: 2 without maltose was prepared to observe phase formation in its absence.

Then Raw suspensions were poured on stainless steel plates in a layer of 1–3 mm, dried in a convective oven at 90 °C and thermally decomposed in a furnace at 550 °C with slow exhaust ventilation and trapping NO$_2$ from the exhaust gas with a NaOH solution. Samples of the obtained $\text{Ce}_0.5\text{Zr}_0.5\text{O}_2$ / $\gamma$-Al$_2$O$_3$ composites were taken for XRD and BET studies.

For impregnating suspension mixing, an oxide composite suspensions and raw suspension (line a) were prepared with the same parameters: concentration of the solid phase 40 %, mixed oxide : alumina ratios = 1:4 and pH 4.5. The grinding time of the oxide composite suspension varied from 5 to 20 hours. The content of the raw suspension in the impregnating suspension was varied in the range from 0 to 100%. The resulting impregnating suspensions were diluted with water to a solids content of 35 and 30% to determine the effect of dilution on their viscosity. Optimally-composed impregnating suspensions were applied to surface-oxidized steel Cr23Al5Fe honeycomb carrier with 200 cells per inch$^2$ and a wall thickness of 50 μm, the excess suspension was blown off with compressed air. Then the coatings were dried at 90 °C and annealed at 550 °C for 5 hours, the weight gain of the coatings was determined.

Research methods. Powder XRD patterns were recorded on a Shimadzu XRD-6000 diffractometer using nickel-filtered CuKα radiation and JCPDS card file. BET specific surface area was tested using Micromeritics TriStar 3000 gas adsorption analyzer. Suspended particle size distribution was tested on a Fritsch Analysette 22 laser diffraction analyzer. Dynamic viscosity $\eta$ was measured on a Fungilab Viscolead One rotational viscometer using L3-rotor and 50 rpm rotation speed.
Figure 1. The scheme of synthesis of ultradispersed Ce$_{0.5}$Zr$_{0.5}$O$_2$ / $\gamma$-Al$_2$O$_3$ oxide composite by the thermal method, its suspension and the application of a catalytic coating on steel honeycomb substrate.

3. Results and discussion
In this article we consider the preparation of Ce₅₋ₓZrₓOₓ mixed oxide not as the final object of research, but as an intermediate Ce₅₋ₓZrₓOₓ / γ-Al₂O₃ oxide composite in a process line for applying a catalytic coating by a suspension method (figure 1). This composite was obtained by slow thermal decomposition of Ce and Zr nitrates in a boehmite matrix in the presence of maltose [8, 9], as described above. Here and hereinafter, for the compounds Ce, Zr, and Al, we used weight concentrations and ratios converted to oxides, unless otherwise indicated.

The XRD patterns for all sample with mixed oxide: alumina ratio = 1:9, 1:4, 1:2 и 1:1 calcined at 550 °C are broadened due to low crystallite size of this high specific surface area material and not allow a proper assessment of the presence of a single t'-phase. Due to the complexity to characterization of the t'-phase obtained at 550 °C only by XRD, its formation was confirmed by catalytic activity study of composite samples in the oxidation of CO with oxygen [8] and additional annealing of the samples at 800, 1000 and 1200 °C during 5 h was held. Among the considered range of mixed oxide: alumina ratio from 1:9 to 1:1 the most interesting is 1:2 (figure 2A). This ratio gives the highest catalytic activity and is the boundary for the formation of a single t'-phase that does not segregate at 800 °C. An increase in temperature from 550 to 800 °C gives a slight shift of the main reflection (111) to the region of large values of 2θ, which is associated with a change in tetragonality (change in the c/a ratio in lattice) during the enlargement of crystallites. After 1000 °C the main reflection (111) becomes asymmetric which indicates the beginning of phase segregation. At 1200 °C the segregation of the t'-phase in a mixture with γ-Al₂O₃ passes through the phase composition of Ce₀.₆Zr₀.₄O₂ and Zr₀.₄Ce₀.₆O₂ with simultaneous γ-Al₂O₃ to α-phase transformation. With a ratio of < 1:2, the single t'-phase is observed at a temperature of < 1000 °C. When the ratio is > 1:2, the mixture of two phases based on the lattices of Ce and Zr oxides predominates, which is due to insufficient boehmite matrix content in the raw suspension, and starts to form from 800 °C. The sample synthesized in the absence of maltose with mixed oxide: alumina ratio = 1:2 (figure 2B) does not show the formation of a single t'-phase even at 550 °C. This allows us to conclude that the formation of a homogeneous Ce₀.₆Zr₀.₄O₂ in this system is possible only with mixed oxide: alumina ratio ≤ 1:2, joint action of sufficient amounts of boehmite matrix and maltose.

The γ-Al₂O₃ phase is not observed on the XRD patterns with all used compositions of oxide composites and calcination temperatures because of its high dispersion and stronger reflection of heavy Ce and Zr. Only after 1200 °C, α-phase and a small amount of 0-Al₂O₃ (reflex at 2θ = 32.8 °) which is intermediate at the transition of γ-Al₂O₃ to α-Al₂O₃, becomes visible.

**Figure 2.** XRD patterns of oxide composite Ce₀.₆Zr₀.₄O₂ / γ-Al₂O₃ powder samples with CeO₂-ZrO₂ : Al₂O₃ ratio = 1:2 synthesized in the presence (A) or without (B) maltose.
Samples of Ce$_{0.5}$Zr$_{0.5}$O$_2$ / $\gamma$-Al$_2$O$_3$ powders obtained by thermal decomposition of raw suspensions at 550 °C have a high BET specific surface area $S_{BET} = 230 - 130$ m$^2$/g, depending on the mixed oxide: alumina ratio (figure 3). This is 1.5-2 times more than $S_{BET}$ for Ce$_{0.5}$Zr$_{0.5}$O$_2$ obtained by the microemulsion method [3]. The obtained samples exhibit high thermal stability, which is expressed in a $S_{BET} = 140 - 90$ and $80 - 40$ m$^2$/g after heat treatments at 800 and 1000 °C, respectively, for 5 hours. At 1200 °C and $S_{BET}$ reduced to 10 m$^2$/g, the theoretical average particle diameter becomes more than 20 nm, which correlates well with the results of XRD analysis of $t'$-phase segregation at this temperature.

In impregnating suspension the synthesized Ce$_{0.5}$Zr$_{0.5}$O$_2$ / $\gamma$-Al$_2$O$_3$ composite was used as a filler which increases the mass yield of the coating. It forms the coating frame and reduces shrinkage during sintering. Also, in impregnating suspension, boehmite is needed for durable low-temperature sintering of the coating at 550 °C. But large amount addition of pure boehmite comparable to oxide composite content, would lead not only to suspension viscosity increase due to the impossibility of boehmite suspension plasticification by protonation, but also to the formation of low redox properties centers in the sintered coating and some decrease in promotion of the active component (if present in the coating). Therefore, the use of raw suspension as a precursor to obtain a composite and as a sintering additive turned out to be a simple and convenient method of maintaining not only strength and promotion, but stoichiometry of coating.

For impregnating suspension preparation, oxide composite suspensions and raw suspension with equal concentrations of the solid phase of 40 % and equal mixed oxide: alumina ratio = 1:4 were taken. The oxide composite suspension with a grinding time of 5 and 20 hours, and raw suspensions with a grinding time of 1 and 4 hours were taken in a ratio of 80: 20 % (concentration C of raw suspensions in impregnating suspension = 20 %) and mixed so that the combination of grinding times was 20 to 1 hours, and 5 to 4 hours, respectively. Thus, monodisperse (figure 4A) and bidisperse (figure 4B) compositions of impregnating suspension solid phases were obtained. In fact, both impregnating suspensions are polydisperse, but in a bidisperse impregnating suspensions two fractions of particles are more pronounced, moreover, the small fraction corresponds to the boehmite, and the coarse fraction – to the oxide.

Comparison of particle sizes in impregnating suspensions (figure 4) with approximate particle sizes calculated from BET and XRD suggests that both boehmite and oxide composite in impregnating suspensions are ultrafine agglomerates that exceed the size of crystallites by ca. 2 orders of magnitude. For this reason, using an organic surfactant is difficult.

To study the viscosity of both monodisperse and bidisperse impregnating suspensions, raw suspension and oxide composite suspension was mixed in whole range of C = 0 % - pure oxide composite suspension; 1.5; 10; 30; 70; and 100 % - pure raw suspension. Then, each of the obtained impregnating suspension was diluted to concentrations of a solid phase of 35 and 30 % and their viscosities were measured (figure 5). A pH value of 4.5 provides significant plasticization by

![Figure 3. BET specific surface area – temperature dependence for Ce$_{0.5}$Zr$_{0.5}$O$_2$ / $\gamma$-Al$_2$O$_3$ composites. In brackets – mixed oxide to alumina ratio.](image-url)
protonation of the oxide suspension [15]. Lower pH can lead to the dissolution of boehmite and the untimely acid hydrolysis of maltose.

**Figure 4.** Particle size distribution for impregnating suspension with Ce$_{0.5}$Zr$_{0.5}$O$_2$ : γ-Al$_2$O$_3$ ratio = 1:4, C = 20 %, which is mixed for monodisperse (A) and bidisperse (B) solid phase composition.

**Figure 5.** Viscosity of impregnating suspension with Ce$_{0.5}$Zr$_{0.5}$O$_2$ : γ-Al$_2$O$_3$ ratio = 1:4, in range of concentration C raw suspension in impregnating suspension from 0 to 100 %, which is mixed for monodisperse (A) and bidisperse (B) solid phase composition. In brackets – content of solids in suspension, %.

The boundary values of the viscosity curves in figures 5A and 5B, corresponding to a pure oxide suspension and a pure raw (boehmite) suspension of monodisperse composition is equal to those values for bidisperse composition. This shows that the viscosity of these suspensions is influenced by the specific surface area of the agglomerates, and not by agglomerate sizes. At $C = 0$ and 100% and pH = 4.5, the oxide suspension is plasticized by protonation, but in raw (boehmite) suspension protonation does not observed because of a positive charge of boehmite particles. A monodisperse impregnating suspension linearly increases the viscosity with increasing C (Figure 5A), which is expected when a component added to its solid phase is not affected by plasticization. On the contrary, the viscosity of a bidisperse impregnating slurry decreases slightly with increasing C, reaches a minimum at $C = 50\%$, and then increases sharply (figure 5B). The initial decrease in viscosity can be explained by a competing dominance of the plastification due to bimodal particle size distribution against the solidification due to decrease of protonation plastification when boehmite is added. Theoretically, the optimum content of the fine fraction is 1/3 of the volume of the coarse fraction, and corresponds to the complete filling of the voids of the densest packing of the coarse fraction, but in this case the minimum viscosity falls to 50%. This may be due to the following facts: C is a mass concentration and not a volume one include the content of Ce and Zr salts in the dispersion.
medium, the fractions of particles in the suspension are not monodisperse and their shape is not spherical.

For coatings on honeycomb substrates, impregnating suspensions with Ce0.9Zr0.1O2 : γ-Al2O3 ratio = 1: 4 and C = 20% were chosen. These values were sufficient for high strength and promoting ability [8]. It is practically established that for easy penetration of the suspension into a substrate cell with a diameter of 1 – 1.5 mm (200 cells per inch2 of substrate), the optimum viscosity is 1000 centipoise. Using the bidispersed composition, while maintaining this viscosity, the suspension was concentrated from 30 to 35% (figure 5 A against B), which increased the weight of the catalytic coating after sintering from 100 to the required 120 g per dm3 of substrate. The annealed coating on the substrate has an equal phase composition to figure 2A. In accordance with the bimodal particle size distribution theory, we could achieve greater plastification of the suspension due to enlargement of coarse fractions up to hundreds of microns, this can be achieved by increasing temperature at the thermal decomposition stage (figure 1), but then the specific surface area of the oxide composite and its promoting ability will fall.

The scheme (figure 1) reflects the full cycle of obtaining the Ce0.9Zr0.1O2 : γ-Al2O3 catalytic coating and allows to involve of precious metal salts at the preparation stage of impregnating suspension. This scheme allows to return the residual suspensions to the cycle, because if suspension contain precious metal salts or nanoparticles, they are subjected to precipitation or agglomeration in a liquid suspension medium during prolonged storage. The residues impregnating suspensions, wastes or suspensions, whose viscosity cannot be returned to the working range, return to the cycle through the stage of their thermal decomposition (line b) with the formation of an oxide composite having a long shelf life without aggregation of the active component.

4. Conclusions

The method of thermal synthesis of highly dispersed Ce0.9Zr0.1O3 / γ-Al2O3 oxide composite eliminating the expensive stages of production has been developed. The formation of a homogeneous t’-phase, not segregating at 800 °C, occurs with mixed oxide: alumina ratio ≤ 1 : 2 and the joint action of a sufficient amount of the matrix of boehmite and maltose. At the moment of formation of the t’-phase, the boehmite agglomerates are covered by it and the entire active component (if present) is in contact with the promoter particles, in contrast to the common methods in which the t’-phase is mixed with γ-Al2O3 or its precursor.

The high-plastic organic surfactant-free oxide composite-based impregnating suspension allowing to involve of precious metal salts or nanoparticles into its composition has been developed. One immersion of steel honeycomb substrate with 200 cells per inch2 in this suspension allows after subsequent annealing to obtain a gain of catalytic coating of 120 g per dm3 of substrate. A crucial role in achieving this was played by the viscosity of the suspension, a low value of which was achieved due to the plastification and bimodal particle size distribution.

The composition of the impregnating suspension allows even large deviations of any parameters for the preparation of suspension, except for the equimolar ratio Ce to Zr, which do not lead to significant or irreversible properties of the suspension and catalytic coating. The developed method allows the use of raw materials of variable composition and properties and takes into account their long-term storage and their return to the cycle of residues and wastes.

5. References

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