Spectroscopic properties of CrOₓ/Al₂O₃ nanopowders synthesized by cw CO₂ laser vaporization

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Abstract. Nanosized 5.0 wt% Cr/nano-Al₂O₃ powders with the particle size of ca. 15 nm were synthesized via laser vaporization using irradiation by a cw CO₂ laser in different gas atmospheres – Ar, Ar+O₂, Ar+H₂. All the investigated nanopowders were studied by XRF, XRD, TEM, UV-vis DRS and PL spectroscopy methods. The nanopowders were found to contain the Cr⁶⁺ ions located on the surface of Al₂O₃ nanoparticles and two types of Cr³⁺ sites. One type is Cr³⁺ ions located in the bulk (Cr³⁺_b-sites) of Al₂O₃ matrix in a strong crystal field. The second type is represented by Cr³⁺ sites residing near the surface (Cr³⁺_s-sites) of CrOₓ/Al₂O₃ nanoparticles in a weak crystal field. It was shown that varying the composition of the buffer gas (Ar, Ar+O₂, Ar+H₂) during laser vaporization makes it possible to control the properties of the obtained 5.0 wt% Cr/nano-Al₂O₃ nanopowders with a change in Cr⁶⁺/Cr³⁺ ratio in the bulk and on the surface of alumina support.

1. Introduction
Today, the development of methods for the synthesis of nanoscale materials has greatly increased interest to them, since the transition from coarse-crystalline materials to nanoscale analogs is often accompanied by a significant change in the physicochemical properties of substances. It was found that the developed surface of individual nanocrystallites affects their bulk structure and thereby contributes to their properties [1, 2]. One of the leading approaches in the synthesis of nanomaterials is the "bottom-up" approach. It consists of the stepwise formation of nanomaterials according to the sequence "atoms → clusters → nanoparticles" [2]. A striking example of this approach is laser synthesis methods, which are based on the Physical Vapor Deposition (PVD) method. Laser methods for the synthesis of oxide nanoparticles are presented mainly by the methods of laser vaporization in the gas phase (LAVA and co-LAVA) [3, 4] and pulsed laser ablation (PLA) in a liquid [5, 6]. Laser synthesis methods make it possible to produce nanoparticles by evaporation of starting materials by exposure to laser radiation and subsequent condensation of the vapor of the evaporated substance in a gas or liquid, the so-called buffer gas or liquid [7-10]. By varying several parameters in the process of laser evaporation such as laser radiation power, the composition of the buffer gas in the evaporation chamber, and gas pressure it becomes possible to control the physicochemical properties of the resulting nanoparticles. Thus, one of the main advantages of laser synthesis methods is high purity, in contrast to, for example, chemical methods, and monodispersity of the obtained samples, as well as the ability to control the size of nanoparticles in the range from 1 to tens of nanometers [11-13]. Laser
synthesis methods are actively used to obtain simple oxides, for example, \( \text{Al}_2\text{O}_3 \), \( \text{ZrO}_2 \), \( \text{TiO}_2 \), \( \text{Y}_2\text{O}_3 \), \( \text{SiO}_2 \), as well as multicomponent compounds such as YSZ, YAG, Eu: \( \text{SrAl}_2\text{O}_4 \), etc. \cite{12, 14-16}.

In the present work, we investigated the physicochemical properties of the nanosized \( \text{CrO}_x/\text{Al}_2\text{O}_3 \) systems synthesized by cw \( \text{CO}_2 \) laser vaporization in different gas atmospheres – \( \text{Ar} \), \( \text{O}_2 \), \( \text{H}_2 \). The samples under consideration are of interest as promising heterogeneous catalysts for isobutane dehydrogenation reaction. A characteristic feature of \( \text{CrO}_x/\text{Al}_2\text{O}_3 \) catalysts is a wide variety of different species of supported chromium oxide particles \cite{17, 18}. This is largely due to the peculiarities of the catalyst preparation, as well as the significant influence of the chemical nature of the initial support on the properties of the final deposited chromium oxides on \( \text{Al}_2\text{O}_3 \) surface. This influence manifests itself in a strong interaction of the supported chromium oxide with the alumina support surface, as a result of which chromium ions are stabilized in different oxidation states and different coordination. There are no data in the literature on the study of the formation of various chromium sites in the nanosized \( \text{CrO}_x/\text{Al}_2\text{O}_3 \) systems prepared by laser evaporation, except for the work of the authors of this paper \cite{19}. The use of various gas atmospheres (oxidative and reductive) during laser synthesis of \( \text{CrO}_x/\text{Al}_2\text{O}_3 \) catalysts should lead to the emergence of different charge states of chromium, a change in their ratio, which, as a result, will make it possible to synthesize chromia-alumina catalysts with a higher concentration of the active component.

The main aim of the work is the study of various charge states of chromium in 5.0 wt\% Cr/nano-\( \text{Al}_2\text{O}_3 \) powders, synthesized by cw \( \text{CO}_2 \) laser vaporization. Establishing the effect of the atmosphere (\( \text{Ar} \), \( \text{O}_2 \), \( \text{H}_2 \)) during vaporization on the ratio of the main types of charge states of chromium \( \text{Cr}^{3+}/\text{Cr}^{6+} \) in the investigated nanopowders. This paper is a consistent continuation of our work for the study of different Cr\textsuperscript{III} species in chromia-alumina systems prepared by different methods: zol-gel \cite{20}, laser synthesis \cite{19}.

2. Experimental

2.1. Preparation of samples

The \( \text{Cr}^{\alpha}/\text{Al}_2\text{O}_3 \) ceramic targets for further laser vaporization as pellets (diameter 18 mm, thickness 10 mm, density of the targets 1.8 g/cm\textsuperscript{3}) were prepared using a highly dispersed \( \gamma/\text{Al}_2\text{O}_3 \) powder (99%) as a starting material. \( \gamma/\text{Al}_2\text{O}_3 \) was obtained by calcination of pseudoboehmite (\( \gamma/\text{AlOOH} \times 0.37\text{H}_2\text{O} \)) for 4 h at a temperature of 550°C. To increase the Cr concentration in the targets, the \( \gamma/\text{Al}_2\text{O}_3 \) powder before pelletization was modified using chromium nitrate \( \text{Cr(NO}_3)_3 \times 9\text{H}_2\text{O} \) (99.7%) via incipient wetness impregnation with an aqueous solution of nitrate salt with chromium concentration 5.0 wt\%. The \( \text{Cr}^{\gamma}/\text{Al}_2\text{O}_3 \) powder was then loaded in a vacuum press mold and pelletized at a force of ca. 13–15 t. After that, the \( \text{Cr}^{\gamma}/\text{Al}_2\text{O}_3 \) pellets were calcined in a crucible at 1250 °C for 4 h until \( \text{Cr}^{\alpha}/\text{Al}_2\text{O}_3 \) was formed. According to XRF data, the Cr concentration in \( \text{Cr}^{\alpha}/\text{Al}_2\text{O}_3 \) targets was 4.98±0.04 wt\%.

5.0 wt\% Cr/nano-\( \text{Al}_2\text{O}_3 \) nanopowders were obtained by laser vaporization of \( \text{Cr}^{\alpha}/\text{Al}_2\text{O}_3 \) ceramic targets irradiated by a cw \( \text{CO}_2 \) laser (radiation wavelength 10.6 \( \mu \)m, generation power up to 110 W on one \( \text{TEM}_{00} \) transverse mode, output beam diameter 8 mm, divergence in the far-field region \( 3 \times 10^{-3} \) rad) with subsequent condensation of vapor in a buffer gas flow in a vaporization chamber. Samples of nanopowders were synthesized in argon (99.998%) and argon supplemented with oxygen (99.7%) and hydrogen (99.999%) in the concentration 20 and 30 vol\%, respectively. Laser power on the target surface was 103 W (the power density \( 5.5 \times 10^4 \) W/cm\textsuperscript{2}). After exposure of the target surface to laser radiation, it was heated and the target material was evaporated with subsequent vapor condensation in the low-temperature zone of the chamber. A gas-dust flow with 5.0 wt\% Cr/nano-\( \text{Al}_2\text{O}_3 \) particles was then passed through the filter where the nanoparticles were settled and then collected for further investigation. During all the procedure of laser synthesis, Ar pressure in the vaporization chamber was 0.1 atm. A detailed description of the experimental setup used for the laser vaporization of nanomaterials with different chemical composition can be found in Refs. \cite{12, 21}.
2.2. Characterization of samples

The chemical composition of the investigated samples was controlled by X-ray fluorescence (XRF) analysis on an ARL – Advant’x analyzer.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) data were obtained for 5.0 wt% Cr/nano-Al₂O₃ nanopowder synthesized in Ar atmosphere. XRD pattern was obtained on a Bruker D8 Advance diffractometer using CuKα radiation (λ = 0.15418 nm). Measurements were performed in the 2θ range of 10–70° with a step 0.05° and acquisition time 3 s. Phases were identified by comparing experimental diffraction patterns with the data of ICDD, PDF 2 database.

TEM images were collected on a JEM-2010 electron microscope at accelerating voltage 200 kV and resolution 1.4 Å. During TEM measurements all the samples were deposited on a copper grid by dispersing a solid phase suspension in alcohol using an ultrasonic disperser.

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured on a CaryEclipse (Varian) fluorescence spectrophotometer with a Xe lamp as an excitation source. UV-vis DRS measurements were carried out on a UV 2501 PC (Shimadzu) spectrophotometer with an ISR 240A diffuse reflectance attachment. The nanopowders under consideration for PL, PLE, and UV-vis DRS experiments were placed in quartz cuvettes.

3. Results and Discussion

According to XRF data, the Cr concentration in studied nanopowders was 4.8±0.05 wt%. Figure 1 demonstrates the photographs of the initial Cr:α-Al₂O₃ ceramic target and final 5.0 wt% Cr/nano-Al₂O₃ nanopowders synthesized in different gas atmospheres – Ar, Ar+O₂, Ar+H₂. As seen in Fig. 1, depending on the composition of the atmosphere during vaporization, all the resulting powders have a different color.

![Figure 1](image)

**Figure 1.** Photographs of Cr:α-Al₂O₃ ceramic target and laser vaporized 5.0 wt% Cr/nano-Al₂O₃ nanopowders.

Figure 2 displays XRD pattern and TEM images of 5.0 wt% Cr/nano-Al₂O₃ nanopowder synthesized in Ar. X-ray diffraction pattern demonstrates that in terms of phase composition the sample corresponds predominantly to γ-Al₂O₃ with the beginning of the transition to δ-Al₂O₃.

![Figure 2](image)

**Figure 2.** XRD pattern (a) and TEM images (b, c) of 5.0 wt% Cr/nano-Al₂O₃ nanopowder synthesized in Ar.
TEM images demonstrate that the studied sample is represented by faceted spherically symmetric nanoparticles with an average size of $d_{av} = 15\text{ nm}$. It should be noted that the XRD and TEM data for other nanopowders studied in this work are similar to the data for 5.0 wt% Cr/nano-\(\text{Al}_2\text{O}_3\) synthesized in Ar.

Figure 3 shows UV-vis DRS, PL, and PLE spectra of the investigated 5.0 wt% Cr/nano-\(\text{Al}_2\text{O}_3\) nanopowders. The obtained UV-vis DRS spectra demonstrate the presence of four bands with maxima at 16500, 22500, 27100, and 36600 cm\(^{-1}\) in all studied samples. All the PL spectra in each case demonstrate one broad band with a maximum at \(~14300\text{ cm}^{-1}\). PLE spectra contain two broad bands with maxima at \(~17700\text{ and }23400\text{ cm}^{-1}\), respectively.

**Figure 3.** UV-vis DRS spectra (a) and PL, PLE spectra (b) of 5%Cr/nano-\(\text{Al}_2\text{O}_3\) nanopowders synthesized in different gas atmospheres during vaporization: black curve – Ar; pink curve – Ar + H\(_2\); green curve – Ar + O\(_2\). PL/PLE: $\lambda_{ex} = 532\text{ nm} (18800\text{ cm}^{-1})/\lambda_{em} = 700\text{ nm} (14400\text{ cm}^{-1})$.

Based on the analysis of spectroscopic data, it was concluded that in the studied 5.0 wt% Cr/nano-\(\text{Al}_2\text{O}_3\) nanopowders, chromium is stabilized mainly in the charge states of Cr\(^{3+}\) and Cr\(^{4+}\) in different coordination. Thus, according to the UV-vis DRS data (see Fig.3 a), the absorption bands at 16500 and 22500 cm\(^{-1}\) correspond to $d$-$d$ transitions in Cr\(^{3+}\) ions located in octahedral oxygen coordination in the matrix of nanosized \(\text{Al}_2\text{O}_3\) (\(4\text{A}_{2g} \rightarrow 2\text{T}_{2g}\) and \(4\text{A}_{2g} \rightarrow 2\text{T}_{1g}\) electron transitions, respectively) [22, 23]. The bands at 27100 and 36600 cm\(^{-1}\) in UV-vis DRS spectra correspond to the ligand-metal CT bands for Cr\(^{6+}\) ions in tetrahedral coordination of oxygen ions [23]. An increase in the intensity and a change in the ratio of the corresponding bands at 27100 and 36600 cm\(^{-1}\) in the UV-vis DRS spectra for the sample obtained by laser vaporization in the presence of O\(_2\) indicates an increase in the concentration of water-soluble forms of Cr\(^{6+}\) in tetrahedral coordination. The variety of different chromium compounds, the defectiveness of the structure of the obtained nanopowders, most likely, is responsible for their differences in color.

Chromium ions in the trivalent state, that are located in the bulk of alumina matrix, exhibit intense luminescence in the red spectral region [24-27]. Thus, the band at \(~14300\text{ cm}^{-1}\) in the PL spectra (Fig. 3 b) is identified with the radiative $d$-$d$ transition $2\text{E}_g \rightarrow 4\text{A}_{2g}$ in octahedrally coordinated Cr\(^{3+}\) ions in \(\text{Al}_2\text{O}_3\) lattice. The broad bands in the PLE spectra correspond to the $4\text{T}_{2g} \rightarrow 4\text{T}_{1g} \rightarrow 4\text{A}_{2g}$ electron transitions for Cr\(^{3+}\) ions in octahedral coordination [19].

Earlier, in x\(\text{Cr}/\text{Al}_2\text{O}_3\) (zol-gel synthesis; \([x] = 0.25, 0.5, 1.0\text{ wt\%}) and x\(\text{Cr}/\text{nano-}\text{Al}_2\text{O}_3\) (laser synthesis; \([x] = 0.0, 0.05, 0.5, 1.0, 2.5, 5.0\text{ wt\%}) samples, along with the emission of Cr\(^{3+}\) ions ($\text{E}_g \rightarrow 4\text{A}_{2g}$ electron transition) located in the bulk of \(\text{Al}_2\text{O}_3\) lattice, we revealed the PL of Cr\(^{3+}\) sites located in more disordered structural positions, which are situated in the subsurface layers of \(\text{Al}_2\text{O}_3\) nanocrystallites [19, 20]. This PL corresponds to the $4\text{T}_{2g} \rightarrow 4\text{A}_{2g}$ electron transition in Cr\(^{3+}\) ions, which are in a weak crystal field, where $Dq/B \ll 2$. Electron transition $4\text{T}_{2g} \rightarrow 4\text{A}_{2g}$ becomes possible when the octahedron in which the Cr\(^{3+}\) ion is located undergoes significant distortion, leading to the position of
the $^4T_2$ state on the Tanabe-Sugano energy diagram appears at lower energies than the $^2E$ state [28, 29]. Figure 4 shows the PL spectra ($\lambda_{\text{ex}}=532 \text{ nm (18800 cm}^{-1})$) of 5.0 wt% Cr/nano-Al$_2$O$_3$ nanopowders deconvolved into Gaussian components.

![Figure 4](image)

**Figure 4.** PL spectra of 5.0 wt% Cr/nano-Al$_2$O$_3$ nanopowders synthesized in different gas atmospheres – Ar, Ar + O$_2$, Ar + H$_2$. $\lambda_{\text{ex}}=532 \text{ nm (18800 cm}^{-1})$ (with deconvolution into Gaussians).

Deconvolution of the PL spectra into Gaussian components made it possible to reveal two types of Cr$^{3+}$ sites in all the studied samples. The first type is Cr$^{3+}$ ions located in the bulk (Cr$^{3+}$b) of Al$_2$O$_3$ matrix, in a strong crystal field. Cr$^{3+}$b sites correspond to the PL band with $\lambda_{\text{max}} \sim 14400 \text{ cm}^{-1}$ ($^2E_g \rightarrow ^4A_2g$ electron transition). Whereas Cr$^{3+}$ ions in nonequivalent positions corresponding to a weak crystal field ($^4T_2 \rightarrow ^4A_2$ electron transition) are responsible for the shoulders with $\lambda_{\text{max}} \sim 12500, 13600, 14100 \text{ cm}^{-1}$ for 5.0 wt% Cr/nano-Al$_2$O$_3$ (Ar, Ar+O$_2$) and 12700, 13300, and 14200 cm$^{-1}$ for 5.0 wt% Cr/nano-Al$_2$O$_3$ (Ar+H$_2$). These are Cr$^{3+}$ sites that are located in the subsurface (Cr$^{3+}$s) layers of Al$_2$O$_3$ nanocrystallites.

4. Conclusion

The nanostructured powders Cr/nano-Al$_2$O$_3$ with the Cr concentration 5.0 wt% were synthesized via laser vaporization using a radiation by a cw CO$_2$ laser in flowing argon and in Ar with the addition of O$_2$ and H$_2$. Laser synthesized Cr/nano-Al$_2$O$_3$ nanopowders can be used as the promising catalysts for isobutane dehydrogenation.

As follows from TEM images investigated nanopowders are represented by faceted spherically symmetric nanoparticles with an average size of $d_{\text{av}}=15 \text{ nm}$. XRD data demonstrate that in terms of phase composition the samples correspond predominantly to low-temperature $\gamma$-Al$_2$O$_3$ with the beginning of the transition to high-temperature $\delta$-Al$_2$O$_3$. The electronic states of various chromium ions were investigated by means of UV-vis DRS and PL spectroscopy methods. It was shown that Cr ions in the 5.0 wt% Cr/nano-Al$_2$O$_3$ samples are stabilized predominantly in Cr$^{3+}$ and Cr$^{6+}$ states in octahedral and tetrahedral coordination, respectively. The PL properties of all the studied nanopowders are caused by the luminescence of octahedrally coordinated Cr$^{3+}$ ions in Al$_2$O$_3$ matrix. The analysis of the acquired data allowed us to separate the observed PL into luminescence of Cr$^{3+}$ sites located in the bulk of Al$_2$O$_3$ lattice (Cr$^{3+}$b-sites; the case of a strong crystal field) and Cr$^{3+}$ sites located near the surface of Al$_2$O$_3$ nanocrystallites (Cr$^{3+}$s-sites; the case of a weak crystal field).

Varying the composition of the buffer gas (Ar, Ar+O$_2$, Ar+H$_2$) during laser vaporization makes it possible to control the properties of the obtained 5.0 wt% Cr/nano-Al$_2$O$_3$ nanopowders with a change in Cr$^{6+}$/Cr$^{3+}$ ratio in the bulk and on the surface. This is particularly important in catalytic studies on the dehydrogenation of alkanes using laser vaporized CrO$_x$/Al$_2$O$_3$ nanosized powders as novel catalytic systems.

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