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Structural features of fumed silica and alumina alone, blend powders and fumed binary systems

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ABSTRACT

Fumed silica, initial alumina blend, after mechanochemical activation (MCA), and fumed binary silica/alumina (SA) were studied using infrared spectroscopy, X-ray diffraction (XRD), ultrasoft X-ray emission (USXE) spectroscopy (giving emission bands Si L_α, Al L_α and O K_α related to valence electron transfer onto core levels) and quantum chemistry. The MCA influence on nanoparticle characteristics (sizes, electronic structure) increases with increasing alumina content in the blends due to stronger abrasive effect of alumina nanocrystallites (snagging a surface layer of nanoparticles during MCA) than non-crystalline silica nanoparticles. A difference in Si L_α, Al L_α and O K_α affected by MCA increases with increasing alumina content. It is greater for the top peak of the upper valence band (UVB) than for a lower energy peak in the bottom of the UVB. These spectral changes suggest redistribution of electron density between Si, Al and O atoms depending on alumina content, material type and treatment conditions. The main difference in the properties of the SA blends and binary SA is due to distribution of Si atoms in alumina phase and Al atoms in silica phase in fumed SA (which is amorphous at $C_{Al_2O_3} \leq 30$ wt.%) in contrast to the SA blends with practically separated silica and alumina nanoparticles.

1. Introduction

Physicochemical properties of silica and alumina as main components of numerous natural minerals and synthetic materials are of importance for applications of these materials as fillers, adsorbents, carriers, catalysts, medicinal preparations, *etc.* [1–12]. During simultaneous synthesis of silica/alumina (SA), formation of individual phases of silica and alumina and complex phases containing both cations at various proportions is possible [13–15]. The distributions of the Al and Si atoms in SA materials and the O-coordination numbers of the Al atoms depend strongly on synthesis conditions affecting the formation of individual phases doped by guest cations. For instance, low-temperature sol–gel and high-temperature pyrogenic syntheses can give very different SA materials at the same amounts of the same precursors. This is due to the fact that diminution of the Gibbs free energy is the main factor in the low-temperature synthesis (under equilibrium or quasi-equilibrium conditions) but the kinetic/dynamic factors are the main factors during oxide formation at high temperatures under non-equilibrium conditions. Therefore, the contribution of non-crystalline phases in nanoparticles can be higher in fumed oxides prepared at high temperatures than that in sol–gel microparticles prepared at relatively low temperatures and then calcined.

$SiCl_4$ used as a precursor of fumed silica has higher reactivity and volatility than $AlCl_3$ (forming dimers) upon the pyrogenic synthesis of fumed oxides in the H_2/O_2 flame [1–6,10]. Therefore, the distribution of alumina in fumed binary SA is nonuniform. Typically, alumina tends to be on the surface of complex nanoparticles or capsuled inside silica nanoparticles [10,13–15]. The numbers of four-fold (Al(IV)) and six-fold (Al(VI)) O-coordinated Al atoms depend on alumina content in SA and synthesis temperature. A portion of Al atoms can mutually isomorphically substitute four-fold O-coordinated Si atoms in the silica phase and *vice versa*. However, in pure fumed aluminas, the number of Al(VI) is three to four times greater than that of Al(IV) and this ratio increases with synthesis (treatment) temperature, since there are only Al(VI) in corundum (α-Al_2O_3) as a high-temperature alumina modification. All the mentioned factors can affect the electronic structure and, therefore, other properties of the SA materials. Of course, these properties depend on the alumina (silica) content and can be different in SA in comparison with individual silica and alumina materials [15–38]. Frequently, silicas such as sol–gel and fumed materials are totally amorphous in contrast to alumina-containing materials [1–15, 39–42]. However, fumed binary SA materials are XRD amorphous at a relatively high alumina content up to $C_{Al_2O_3} \leq 30$ wt.% [10,13–15].

The energy distributions of valence electrons and charge states of atoms in metal oxides well characterize interatomic interactions in solids and determine many of the material properties [2,10,22–26,30,33]. Investigations of the energy distributions of valence electrons in silica

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[43] and alumina [44] depending on nanoparticle size showed that the distribution of O 2*p* non-binding electrons narrows down due to a partial return of the electron density to cations. Therefore, the M – O (M = Al, Si) bond order can be greater than unit. It was shown [44] that mechanochemical activation (MCA) of fumed alumina characterized by a coherent-scattering region (CSR) size $d_{CSR} = 17$ nm, corresponding to the average size of crystallites, in the initial state leads to a decrease in d_{CSR} to 12 nm. This affects the electronic structure of the material. Changes in the particle size of nanooxides can cause changes in the binding energy of the valence and core electrons. This can affect all the properties dependent on the electronic structure of the materials. To compare the properties of a series of silica/alumina materials, a set of nanooxides differently prepared but with similar contents of silica and alumina are used here. Three samples of fumed binary SA have $C_{Al_2O_3} = 23$, 30 and 75 wt.%. Simple blends of individual nanosilica PS300 and nanoalumina xAl$_2$O$_3$ + (1 − x)SiO$_2$ were prepared at $x = 0.2$, 0.3, and 0.75. These blends were also mechanochemically activated in a microbreaker for 5 min.

2. Preparation of materials and characterization methods

Amorphous pyrogenic (fumed) silica PS300 (specific surface area $S_{BET} \approx 300$ m^2/g), fumed alumina Al89f ($S_{BET} = 89$ m^2/g), amorphous fumed binary SA23f ($S_{BET} = 347$ m^2/g), amorphous fumed binary SA30f ($S_{BET} = 248$ m^2/g), and SA75f ($S_{BET} = 118$ m^2/g) with amorphous silica and partially crystalline alumina, mainly θ-Al$_2$O$_3$ (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine) were used as the initial materials (Table 1). The type, composition and treatment of all the samples used are described in Table 1.

Fumed binary SA samples (Table 1) were prepared by simultaneous high-temperature hydrolysis of SiCl$_4$ and AlCl$_3$ in the O$_2$/H$_2$/N$_2$ flame. The initial nanooxide materials were described in details elsewhere [1–7,10,13–15]. The fumed alumina Al89f studied is mainly composed of crystalline θ-Al$_2$O$_3$ characterized by the coherent-scattering region (CSR) size $d_{CSR} = 17$ nm. The d_{CSR} value can be considered as the average size of crystallites. Individual silica PS300 and alumina Al89f were used to prepare mechanical blends xAl$_2$O$_3$ + (1 − x)SiO$_2$ at $x = 0.2$, 0.3, and 0.75, where x is the weight coefficient (Table 1). The blends were prepared by simple agitation (without strong mechanical loading) of the powders for 30 min (last symbol "z" in the labels, Table 1). The blend samples were also mechanochemically activated (last symbol "m" in the labels, Table 1) in a stainless steel microbreaker (30 W, volume 10 cm^3 with a stainless steel ball of 0.8 cm in diameter) for 5 min.

XRD investigation was carried out using a DRON-UM1 (Burevestnik, St.-Petersburg) diffractometer with monochromatic Cu K$_\alpha$ radiation and a graphite monocrystal as a monochromator. Diffraction patterns were registered at a step of 0.05° over a 2θ = 10–90° range. XRD data processing was carried out using Powder Cell 2.4 software [ftp://ftp.bam.de/Powder_Cell]. Analysis of diffraction maxima broadening and changes in the coherent-scattering region (CSR) sizes and the lattice strain was carried out using the Williamson–Hall method [45]. In full-profile analysis of diffraction patterns, the texture of samples was taken into account using the March–Dollase model [46].

Table 1
Composition and labels of the studied samples.

Material	Label	Sample type	C_{SiO_2} (wt.%)	$C_{Al_2O_3}$ (wt.%)
Silica	PS300	Fumed individual	99.9	–
Alumina	Al89f	Fumed individual	–	99.8
Silica/alumina	SA23f	Fumed binary	77	23
Silica/alumina	SA30f	Fumed binary	70	30
Silica/alumina	SA75f	Fumed binary	25	75
Silica/alumina	SA20z	Blend of PS300 and Al89f	80	20
Silica/alumina	SA30z	Blend of PS300 and Al89f	70	30
Silica/alumina	SA75z	Blend of PS300 and Al89f	25	75
Silica/alumina	SA20m	Blend of PS300 and Al89f after MCA	80	20
Silica/alumina	SA30m	Blend of PS300 and Al89f after MCA	70	30
Silica/alumina	SA75m	Blend of PS300 and Al89f after MCA	25	75

Ultrasoft X-ray emission (USXE) spectra were recorded using a RSM-500 (SCBXA, Burevestnik, St.-Petersburg) X-ray spectrometer–monochromator with energy of electron beam of $E = 5$ keV, intensity $I = 6 \times 10^{17}$ electrons·cm^{-2}, and pressure of 2.67×10^{-4} N·m^{-2} in an X-ray tube and a spectrometer detector. Emission bands Si L_α, Al L_α and O K_α were analyzed to compare changes in the electronic structure of the valence band of different SA composites. The shape of these bands reflects the distributions of the valence electrons in the Si, Al and O atoms.

X-ray photons were registered (intensity *I*, impulses per second, im/s) using a channel electron multiplier KBL1505 (Dr. Sjuts Optotechnik GmbH, Germany). The photon energy distribution functions related to the O K_α emission bands correspond to transition of valence O 2*p* electrons to vacant O 1*s* levels with energy of emitted photons $h\nu = E_{O_{2p}} - E_{O_{1s}}$. According to a rule of selection, Al L_α (Al L_{23}) emission band corresponds to photon energy $h\nu = E_{Al_{3s3d}} - E_{Al_{2p1s}}$ due to transition of valence electrons Al 3*s* (and Al 3*d*) to vacant level Al 2*p*. The Si L_α emission band has a similar origin. Vacancies in the core levels are formed as a result of interactions of the electron beam with these atoms. An excitation mode at $I = 6 \times 10^{17}$ electrons·cm^{-2} does not lead to formation of radiation defects in oxides studied since the defects appear only at $I > 5 \times 10^{20}$ electrons·cm^{-2}.

Samples were rubbed into a copper anode etched and rinsed in ethanol cooled by water. To prevent overlap of the O K_α bands of adsorbed oxygen and O K_α bands of nanooxides, the spectra were recorded at different intensity values of the electron beam (1.5×10^{17}, 3×10^{17}, 4.5×10^{17} and 6.0×10^{17} electrons·cm^{-2}). After four records at the beam intensity of 1.5×10^{17} electrons·cm^{-2}, the shape and half-width of the O K_α band stabilized and did not change in subsequently recorded spectra. Stabilization of the O K_α band shape is due to removal of adsorbed oxygen and water. The O K_α band shape and I_{max}(O K_α)/$I_{background}$ ratio did not change with increasing intensity of the electron beam from 6×10^{17} to 15×10^{17} electrons·cm^{-2}. Therefore, the intensity of the electron beam at 6×10^{17} electrons·cm^{-2} was selected as optimal. Diffraction grating with groove density of 600 mm^{-1} and curvature radii of 6 m (O K_α), and 2 m (Al L_α and Si L_α) was used with filtering gold and polystyrene mirrors, respectively. The instrumental errors were smaller than ±0.2–0.3 eV for Si L_α, Al L_α, and O K_α, and the accuracy of spectra recording was ±0.1 eV.

The infrared (IR) spectra of the powdered samples over the 4000–300 cm^{-1} range (at 4 cm^{-1} resolution) were recorded in a transmittance mode with a Specord M80 (Carl Zeiss, Jena) spectrometer using samples ground and pressed in a blend with KBr (Merck) (1: 100 or 1: 400 for PS300 alone, tablets of ~20 mg in weight). The transmittance spectra were re-calculated into the absorbance spectra.

Quantum chemical calculations were carried out by *ab initio* and density functional theory (DFT, functional B3LYP) methods with the 6-31G(d,p) basis set using the Gaussian 09 [47] program suit. Silica and silica/alumina clusters were calculated to full geometry optimization. The GaussView 5.0.9 program [48] was used for visualization of the calculation results. Oxide structures were also calculated by the PM7 method with periodic boundary conditions and total geometry optimization with the MOPAC 2012 package [49,50]. The number of polyhedrons in expanded cells was 16 (gibbsite), 24 (α-quartz, sillimanite), 32 (β-tridymite), and 36 (corundum). Substitution for Si by Al in the lattice of α-quartz (Si: Al = 23:1) and β-tridymite (Si:Al = 31/1 and 26/6) was isomorphic but with addition of the bridged H atoms in ≡Si – O(**H**) – Al≡ (to compensate the system charge to be zero) with subsequent total optimization of the geometry.