



Infrared spectroscopy as a tool for textural and structural characterization of individual and complex fumed oxides



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ABSTRACT

The effects of nanoparticles size and surface content of pure silica and in complex fumed metal and metalloid oxides (FMO) on the infrared (IR) spectra in the range of Si–O–Si asymmetric stretching vibrations, were analyzed. Correlation functions were obtained linking the integral intensity of a band at $\nu_{\text{SiOSi}} \approx 1200 \text{ cm}^{-1}$ (w_2 , attributed to the surface of silica); or the ratio w_2/w_1 (w_1 corresponds to contribution at $\nu_{\text{SiOSi}} \approx 1100 \text{ cm}^{-1}$ attributed to bulk transverse optical (TO) modes) with the average diameter (d) of silica nanoparticles determined from the specific surface area from nitrogen adsorption isotherms. The results of the IR spectral analyses were compared to Auger electron spectroscopy (AES) results with respect to surface content of silica in complex FMO. The nanoparticulate morphology of FMO analyzed using TEM and SEM images show a relatively broad size distribution of nanoparticles, including core-shell nanoparticles, that can affect the ν_{SiOSi} band intensity and position linked to structural features of the silica phase. Thus, the use of the correlation $w_2(d)$ or $w_2/w_1(d)$ functions give appropriate results for the textural characteristics of fumed silicas and the surface content of silica in complex FMO, compared with nitrogen adsorption and AES data, respectively.

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1. Introduction

Complex fumed metal or metalloid oxides (FMO) synthesized at high temperatures [1–8] are characterized by a non-uniform distribution of different oxide phases in bulk and at the surface of primary nanoparticles [9–14]. This is caused by different precursor reactivities (such as MCl_x), as well as variations in their distribution in the flame characterized by a significant temperature gradient affecting the flame synthesis. The surface/volume structures affect important material properties because the characteristics of surface sites (e.g., Brønsted and Lewis acid sites, basic sites) depend on their composition (e.g., types of M atoms in the $\text{M}_1\text{–O(H)}\text{–M}_2$ and MO_n bonds) and their surroundings over several coordination spheres (e.g., numbers of M_1 and M_2 atoms in the coordination sphere) [9,12,14,15]. The nature and distribution of active surface sites determine catalytic and adsorption properties, the behavior of FMO in aqueous and polymeric media, etc. [1–12]. Therefore, detailed information on the surface/volume structures of complex FMO nanoparticles is important for a deeper analysis of

structure-property relationships characteristic of these materials which is of practical importance.

Infrared (IR) spectroscopy is a powerful tool to study not only surface composition of FMO nanoparticles but also their volume [11–16]; therefore, here we investigate the potential of IR to determine surface/volume structures. IR spectroscopy, including various techniques [17–19], is effectively used to investigate adsorption processes [1,2,13–16,20–23], as well as the morphology, structure, crystallinity, and other characteristics of solid, polymeric, composite, and other materials [24–34]. This is due to strong dependences of the stretching, scissoring, rocking, wagging, and twisting vibrations on the atom masses, bond length, strength, and stress, coordination number of atoms, types of intermolecular bonds, crystallinity, composition, phase organization, electronic and vibrational (thermal) states of the systems, etc. Additionally, all of these factors are sources of useful information for a detailed description of these systems with respect to structure-property relationships. One factor affecting IR spectra is the particle size of nanostructured (for complex nanoparticles) and nanosized systems, such as individual and complex FMO. For example, the position of the Si–O–Si asymmetric stretching vibrations (As_1 transverse optical (TO) mode, ν_{SiOSi}) at 1100 cm^{-1} shifts toward smaller wavenumbers from $\nu_{\text{SiOSi}} = 1150 \text{ cm}^{-1}$ to 1000 cm^{-1} with

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increasing size of silica monodisperse spheres from of 0.1 to 15 μm in diameter, respectively [25]. These microparticles contained nanosized surface structures, which can contribute both TO and LO (longitudinal optical) modes [25], as well as a surface optical (SO) phonon mode [35]. Additionally, the integral intensity of a band of free surface silanols at 3750 cm^{-1} , and an overtone mode at 1867 cm^{-1} (which is the bulk silica overtone mode proportional to the total mass of silica probed by the IR beam and used as the internal standard), can be used to estimate the specific surface area of silicas with relatively small errors [36].

It is of interest to analyze features of the Si—O—Si stretching vibrations at 1100 cm^{-1} for various individual, binary, and ternary FMO composed of silica, alumina, and titania, with respect to the nanoparticle size distribution (NPSD) and silica phase distribution (SPD) at the surface and in volume of nanoparticles. Previously, similar FMO were studied using a variety of methods [9–12,15,16,37–42]. However, the relationships between the NPSD, SPD, and IR spectra was not analyzed in detail for complex fumed oxides. Note that specific conditions (such as high dilution of FMO (0.2–0.3%) in KBr and well distribution of nanoparticles in KBr) are of importance to reduce great absorbance in the spectral range of the Si—O—Si stretching vibrations.

2. Materials and methods

2.1. Materials

Individual fumed silicas (A-50, A-100, A-150, A-200, A-300, and A-500, where the numbers roughly correspond to the value of the specific surface area of silicas), binary FMO with silica/titania (STx, where x is the content of titania in mass fraction in%, mf%) and silica/alumina (SAx, x is the content of alumina), and ternary alumina/silica/titania (ASTx, where x is the content of titania) (Table 1) were the powder materials analyzed (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine).

The complex FMO studied demonstrate a strong non-monotonic dependence of surface content of alumina and silica vs. their total content in comparison with the surface content of titania (see electronic Supplementary information (SI) file). Many properties of FMO, especially fumed silicas, were investigated previously [9–16,37–42] (see also SI file). Several FMO with pure silica such as TS-100 (thermal silica prepared with FMO using additional high-temperature treatment), A-300, and OX-50 (Degussa/Evonik), A-150 (Nippon Aerosil), and Cab-O-Sil HS-5 (Cabot Corporation) were used in comparative studies.

2.2. Infrared spectroscopy

The IR spectra of powdered samples over the $4000\text{--}300\text{ cm}^{-1}$ range (at 4 cm^{-1} resolution) were recorded in transmission mode using a Specord M80 (Carl Zeiss, Jena) spectrometer using sample powders mixed with KBr (1:400), treated in a microbreaker (with a stainless steel sphere of 10 cm^3 in volume and a stainless steel ball of 0.8 cm in diameter, 30W, and frequency 50 Hz) for 5 min to prepare a uniform blend, and then pressed at 99 MPa to form thin tablets ($\sim 20\text{ mg}$). This provides a transmittance of $>10\%$ in the range of the Si—O—Si asymmetric stretching vibrations at 1100 cm^{-1} for silica. The transmittance spectra were re-calculated into absorbance spectra.

2.3. SEM and HRTEM

Microscopic images were recorded using a DualBeam Quanta 3D FEG, FEI scanning electron microscope (SEM) in high vacuum (accelerating voltage usually was 5 kV but in some cases 20 or

Table 1
Structural characteristics of FMO studied.

Sample	C_{SiO_2} (mf%)	C_{TiO_2} (mf%)	$C_{\text{Al}_2\text{O}_3}$ (mf%)	S_{BET} (m^2/g)
A-50	100			52
A-100	100			86
A-150	100			134
A-200	100			232
A-300	100			302
A-500	100			492
OX-50*	100			54
TS-100*	100			250
A-300*	100			300
A-150**	100			162
Cab-O-Sil HS-5***	100			326
SA1	98.7		1.3	203
SA3	97		3	185
SA8	92		8	303
SA23	77		23	347
SA30	70		30	238
SA75	25		75	118
SA96	4		96	81
ST2	98	2		77
ST9	91	9		235
ST14	86	14		156
ST20	80	20		84
ST40	60	40		148
ST63	33	63		84
ST65	35	65		34
ST76	24	76		23
AST1	10	1	89	99
AST50	28	50	22	37
AST71	8	71	21	74

Note: Silicas were produced by *Degussa, **Nippon Aerosil, and ***Cabot Corporation.

30 kV). All samples were spread with a thin film of palladium and gold.

High resolution transmission electron microscopy, HRTEM (JEM-2100F, Japan) images were recorded for powder samples. A powder sample was added to acetone (chromatographic grade) and sonicated. A drop of the resulting suspension was deposited onto a copper grid with a thin carbon film. After acetone evaporation, sample particles remained on the film were studied with HRTEM.

2.4. Textural characteristics

To analyze the textural characteristics of FMO degassed at 373 K for several hours (Table 1), low-temperature (77.4 K) nitrogen adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2405N adsorption analyzer. The specific surface area (S_{BET}) was calculated according to the standard BET method [43,44].

3. Results and discussion

FMO powders are characterized by a certain structural hierarchy since primary nanoparticles form aggregates (50–1000 nm in size) and agglomerates of aggregates ($>1\text{ }\mu\text{m}$) (Figs. 1 and S1 in electronic Supplementary information (SI) file) [9,12]. The agglomerates (Fig. 1b) are characterized by lower bulk density than aggregates (Fig. 1a,c). Complex nanooxides can include core-shell nanoparticles, (CSNP, (50–200 nm in size)) with titania or alumina cores and silica or alumina shells (Figs. 1d and S1), in contrast to simple and smaller nanoparticles of individual FMO (Fig. 1c). The presence of CSNP is more characteristic for complex FMO containing crystalline phases with alumina or titania (see Figs. S1–S3 in SI). However, conditions during the flame synthesis (high temperature with significant gradient, flame

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