Silica-supported Ni_xO_y , Zn_xO_y and Mn_xO_y nanocomposites: physicochemical characteristics and interactions with water and *n*-decane

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Abstract. A series of $\text{M}_x\text{O}_y/\text{SiO}_2$ (where M = Ni, Zn and Mn) nanocomposites were synthesized at different M_xO_y contents (0.2, 1 and 3 mmol per 1 g SiO_2) using a deposition method. The samples were characterized using nitrogen adsorption–desorption, X-ray diffraction, Fourier transform infrared spectroscopy, high resolution transmission electron microscopy and photon correlation spectroscopy. The heat of immersion in water (Q_w) and *n*-decane (Q_d) were measured using a microcalorimetry method, and the corresponding values of the hydrophilicity index $K_h = Q_w/Q_d$ were analysed. The formation of M_xO_y on a silica surface leads to diminishing of the Q_w and Q_d values (calculated per 1 g of nanocomposites) because of the specific surface area reduction. However, the Q_w values calculated per 1 m^2 increase for $\text{Zn}_x\text{O}_y/\text{SiO}_2$ and $\text{Mn}_x\text{O}_y/\text{SiO}_2$ in comparison with the unmodified silica, and it remains unchanged for $\text{Ni}_x\text{O}_y/\text{SiO}_2$. Silica modification with M_xO_y significantly changes the pH dependence of zeta potential and affects the surface charge density. A shift of the isoelectric point (pH_{IEP}) and a character of the zeta potential ζ (pH) curve are affected by the M_xO_y phase, and pH_{IEP} shifts toward higher values as follows $\text{Mn} < \text{Zn} < \text{Ni}$.

Keywords. Oxide nanocomposites; $\text{Zn}_x\text{O}_y/\text{SiO}_2$; $\text{Ni}_x\text{O}_y/\text{SiO}_2$; $\text{Mn}_x\text{O}_y/\text{SiO}_2$; physicochemical properties; heats of immersion.

1. Introduction

During recent decades, nanocomposites based on a combination of two or more oxides of various metals or metalloids have had considerable interest due to their wide application possibilities in various fields of chemistry, physics, materials science and industry [1–3]. High dispersity of these oxides and the presence of various active surface sites are of importance for the use of them as sorbents [4,5], hetero catalysts with an adjustable set and activity of surface acid/base sites [6–9], fillers of polymers [10–12], etc.

To control the morphology and other characteristics of nanoparticles, the synthesis of certain phases (deposits) could be carried out at a surface of nanocarriers with a high-specific surface area [13–17]. Fumed silica is one of the most widely used carriers with a large-specific surface area, high-thermal stability and chemical resistance [14]. The use of fumed silica as a carrier provides the simplicity of the modification methods with easy control of the dispersity of both a deposited phase and whole material as well the structure and surface properties. Some silica-supported nanocomposites with CeO , ZrO and TiO_2 were synthesized by sol–gel or chemical vapour depositions of these oxides on a surface of highly

dispersed fumed silica [15–17]. Such nanosized oxide deposits as Mn_xO_y , Ni_xO_y and Zn_xO_y are promising for the synthesis of highly disperse oxides with improved surface properties, e.g., as catalysts [18–33].

Manganese oxide nanomaterials have been used as catalysts due to their excellent structural flexibility and novel chemical and physical properties [18–20]. It is known that manganese oxide plays an important role in removing of heavy metal ions, degradation of phenolic compounds and catalytic oxidation of volatile organic compounds. It is a suitable candidate for battery and supercapacitor applications [21].

Nanostructured ZnO can be used in nano-electronic and nano-optical devices, energy storage or nanosensors because of unique semiconducting, optical and piezoelectric properties [22–24]. Additionally, ZnO can be found in sunscreens where it plays the role of an UV-ray blocker [25]. ZnO nanoparticles are used in medicine for bioimaging and drug/gene delivery [26]. Zinc oxide exhibits antimicrobial and antifungal activity [27] depending on the size and concentration of nanoparticles. However, there are data on the toxicity of zinc oxide nanoparticles [28] that can be reduced by the use of zinc oxide in nanocomposites.

NiO is especially efficient in numerous applications from sensing devices to solar energy conversion, photovoltaic, electrochromic devices, etc. [29]. Nickel oxide has attractive properties to be used in gas sensor applications [30,31] and as a catalyst for wastewater depollution [32,33].

In the above-mentioned applications, the surface structure of oxides, namely the type and concentration of active surface sites (e.g. Brønsted and Lewis acid sites), plays the most important role. The silica-carrier interaction with deposits leads to the appearance of new surface acid sites M1–O(H)–M2, which are absent in individual components [34]. For some systems, the formation of such bridge bonds as M1–O(H)–M1 or M2–O(H)–M2 is preferable than that of M1–O(H)–M2 that can lead to the formation of a separate phase of deposits [34,35]. The surface structure of mixed oxides affects the interactions with polar and nonpolar molecules and electro-surface properties in a liquid medium [35–38].

Thus, the main objective of this study was the synthesis of silica-supported MnO, ZnO and NiO nanocomposites and investigation of their textural and structural properties and peculiarities of interactions with polar (water) and nonpolar (*n*-decane) liquid media.

2. Experimental

2.1 Materials

Unmodified fumed silica (A-380, Degussa) with a specific surface area of $367 \text{ m}^2 \text{ g}^{-1}$ was used as the carrier for deposition of the second phase. Metal acetates as $(\text{CH}_3\text{COO})_2\text{Ni} \cdot 4\text{H}_2\text{O}$ (TU 6-09-3848-87), $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$ (GOST 16538-79) and $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ (GOST 5823-78) were used as precursors to prepare oxide composites.

2.2 Synthesis of oxide nanocomposites

Nanocomposites $\text{M}_x\text{O}_y/\text{SiO}_2$ (table 1) were synthesized by thermooxidation of metal acetates, adsorbed on a surface of nanosilica A-380. The samples were synthesized at a different ratio between components: 0.2, 1.0 and 3.0 mmol of metal acetate per gram of silica. At the first stage, a homogeneous dispersion of silica in the aqueous solution of metal acetate was prepared at a certain ratio of the components. At the second stage, the dispersion was dried at 130°C for 5 h, and then the xerogel was crushed to prepare a fraction $<0.5 \text{ mm}$ in size. At the third stage, the powders were calcined in air at 600°C for 2 h. Nanosilica A-380 alone was treated similarly to nanocomposites at different stages to be used as a control sample.

2.3 Textural characterization

To analyse the textural characteristics of $\text{M}_x\text{O}_y/\text{SiO}_2$ nanocomposites, low-temperature (77.4 K) nitrogen

adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2405N adsorption analyser. The samples were degassed at 110°C for 2 h in a vacuum chamber. The values of the specific surface area (S_{BET}) were calculated according to the standard Brunauer–Emmett–Teller (BET) method [39]. The total pore volume V_p was evaluated by converting the volume of adsorbed nitrogen at $p/p_0 = 0.98 - 0.99$ (p and p_0 denote the equilibrium and saturation pressures of nitrogen at 77.4 K , respectively) to the volume of liquid nitrogen per gram of adsorbent. The nitrogen desorption data were used to compute the pore size distributions (PSDs, differential $f_V \sim dV_p/dR$ and $f_S \sim dS/dR$) using a self-consistent regularization (SCR) procedure under non-negativity conditions ($f_V \geq 0$ at any pore radius R) at a fixed regularization parameter $\alpha = 0.01$ with voids (V) between spherical nonporous nanoparticles packed in random aggregates (V/SCR model) [40]. The differential PSDs with respect to pore volume $f_V \sim dV/dR$, $\int f_V dR \sim V_p$ were re-calculated to incremental PSD (IPSD) at $\Phi_V(R_i) = (f_V(R_{i+1}) + f_V(R_i))(R_{i+1} - R_i)/2$ at $\sum \Phi_V(R_i) = V_p$. The f_V and f_S functions were also used to calculate contributions of micropores (V_{micro} and S_{micro} at $0.35 \text{ nm} < R < 1 \text{ nm}$), mesopores (V_{meso} and S_{meso} at $1 \text{ nm} < R < 25 \text{ nm}$) and macropores (V_{macro} and S_{macro} at $25 \text{ nm} < R < 100 \text{ nm}$).

2.4 XRD analysis

X-ray powder diffraction (XRD) patterns were recorded at room temperature using a DRON-4-07 diffractometer (Burevestnik, St.-Petersburg, Russia) with $\text{CuK}\alpha$ ($\lambda = 0.15418 \text{ nm}$) radiation and a Ni filter in the 2θ range from 10 to 70° . The average size of crystallites (D_{cr}) was estimated according to the Scherrer equation [41]. The crystalline structure of samples was analysed using the JCPDS-ICDD database [42]. Silica was totally amorphous in all samples.

2.5 FTIR spectroscopy

Fourier transform infrared (FTIR) spectra of powdered samples (ground with dry KBr at the mass ratio of 1:9) were recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$ using a Thermo Nicolet FTIR spectrometer with a diffuse reflectance mode. Integral intensity of the peaks at 3750 and 1870 cm^{-1} (I_{3750} and I_{1870} , respectively) was calculated from the FTIR spectra to estimate the accessible surface area of silica in all samples.

2.6 Electrophoresis and photon correlation spectroscopy

Electrophoresis studies were carried out using a Zetasizer 3000 (Malvern Instruments) apparatus based on photon correlation spectroscopy ($\lambda = 633 \text{ nm}$, $\theta = 90^\circ$ and software version 1.3). The aqueous suspensions of oxides ($0.1 \text{ wt}\%$ for measuring particle size distribution and $0.02 \text{ wt}\%$ for zeta potential) were prepared using an ultrasonic disperser (Sonicator Misonix Inc., power 500 W and frequency 22 kHz) for 5 min prior to the electrokinetic measurements

Table 1. Textural characteristics of initial silica and M_xO_y/SiO_2 nanocomposites.

Sample	Metal content (mmol g ⁻¹ SiO ₂)	S_{BET} (m ² g ⁻¹)	S_{micro} (m ² g ⁻¹)	S_{meso} (m ² g ⁻¹)	S_{macro} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	V_{macro} (cm ³ g ⁻¹)
SiO ₂	—	367	1.3	366	0.0	1.743	0.001	1.742	0.000
MnO ₂	0.2	306	6.0	300	0.0	0.934	0.003	0.931	0.000
Mn1	1.0	264	2.3	244	18	1.008	0.001	0.776	0.231
Mn3	3.0	186	0.4	185	0.6	1.115	0.000	1.108	0.007
NiO ₂	0.2	329	2.0	327	0.0	1.294	0.001	1.293	0.000
Ni1	1.0	314	8.3	306	0.0	0.865	0.004	0.860	0.001
Ni3	3.0	296	1.0	295	0.0	1.191	0.000	1.191	0.000
ZnO ₂	0.2	335	3.4	332	0.0	1.440	0.002	1.438	0.000
Zn1	1.0	295	0.5	294	0.0	1.446	0.000	1.446	0.000
Zn3	3.0	208	2.0	183	24	0.892	0.001	0.593	0.298

(ζ -potential). The values of pH, measured by a precision digital pH meter, were adjusted by the addition of 0.1 M HCl or NaOH solutions. To evaluate the surface charge density (σ), potentiometric titration was performed using an automatic burette (Dosimat 665, Metrohm) and thermostated Teflon vessel in a nitrogen atmosphere free from CO₂ at 25.0 ± 0.2°C. The solution pH was measured using a pH-meter (PHM240, Radiometer) with G202C and K401 electrodes. The surface charge density of the nanocomposites was calculated by comparison of the potentiometric titration curves of the oxide suspensions and a background electrolyte. The point of zero charge (pH_{PZC}) and the isoelectric point (pH_{IEP}) of samples were analysed vs. sample composition [36].

2.7 Microcalorimetric investigations

The microcalorimetric investigations were carried out by means of a DAC1.1A (Chernogolovka, Russia) differential automatic calorimeter [43]. Glass vials with samples (100 ± 2 mg) were placed in the calorimeter cells with wetting liquid (3 ml) and thermostated at 298 K. Glass vials for immersion wetting studies have a special shape with thin curved tips broken by pressing and surrounding liquid permeated in a vial and wetted a sample studied. Released heat of immersion was registered by the differential calorimeter through the change in the temperature measured by thermopile detectors each composed of 960 thermocouples. The obtained results were recorded in the form of microcalorimetric curves with a typical peak [44] integrated to calculate the thermal effects of immersion. The calorimeter was calibrated against the heat of dissolving of KCl. Since the total heat of immersion depends on the mass and surface area of a sample, the results were normalized to 1 g and 1 m² of surface of samples. For each sample, the measurement of heats of immersion in every liquid was performed 2–3 times and the average value was calculated. The average errors of the Q measurements at multiple repeated measurements were ±7%. To estimate

the hydrophilicity of the samples, the hydrophilicity indexes $K_h = Q_{water}/Q_{decane}$ were calculated.

3. Results and discussion

3.1 Textural characterization

The shape of the nitrogen adsorption–desorption isotherms (figure 1) corresponds to type II with hysteresis loop H3 of the IUPAC classification [45,46] corresponding to the textural porosity of aggregates of nonporous nanoparticles. The hysteresis loop shape indicates dominant contribution of mesopores (filled by adsorbed nitrogen during the measurements). The structural parameters of oxide nanocomposites calculated from nitrogen adsorption isotherms are given in table 1.

The BET surface area and pore volume of composites (table 1) depend on the content and type of M_xO_y . The structural changes in composites increase with increasing M_xO_y concentration and exhibit a similar tendency to a decrease in the specific surface area with increasing M_xO_y concentration for all composites due to filling of inter-particle voids in aggregates by M_xO_y nanoparticles. A possible cause for the decrease in the composite surface area is also the fact that the density of guest oxides is significantly higher than the density of the initial silica namely, the density of NiO is 6.67 g cm⁻³, Mn₃O₄ is 4.86 g cm⁻³ and ZnO is 5.61 g cm⁻³, while the density of the initial silica is 2.65 g cm⁻³. Changes in the pore volume depend on the type of the second oxide due to the peculiarities of the formation of the second phase and a decrease in the empty volume in aggregates of nanoparticles. Thus, despite the fact that for all composites the total pore volume is lower than that of the initial silica, there is a tendency to increase the pore volume with an increase in the concentration of the second phase for manganese oxide composites, whereas for other composites there is an opposite tendency to decrease in the pore volume with increasing M_xO_y phase

Figure 1. Nitrogen adsorption–desorption isotherms for initial silica and M_xO_y/SiO_2 calcined at 600°C: (a) Mn containing samples, (b) Ni containing samples and (c) Zn containing samples; open symbols – adsorption, shaded symbols – desorption.

concentration. This difference could be explained by the difference in the true density of deposited particles of different oxides.

The pore size distribution functions (figure 2) confirm the conclusion based on the isotherm shapes (figure 1) that the

Figure 2. Incremental pore size distributions for initial silica and M_xO_y/SiO_2 calcined at 600°C: (a) Mn containing samples, (b) Ni containing samples and (c) Zn containing samples.

composites are mainly mesoporous, since contributions of micropores and macropores are small (table 1). The first peak of the PSD corresponds to narrow voids between nanoparticles closely located in the same aggregates. Broader voids can

Figure 3. TEM micrographs of (a) Mn3, (b) Ni3, (c) Zn3 samples and (d) initial SiO₂.

occur between neighbouring aggregates. It should be noted that for composites with Mn (1 and 3 mmol g⁻¹) and Zn at the maximum content (3 mmol g⁻¹), two-PSD peaks correspond to mesopores with maxima of 30 and 60 nm, respectively.

3.2 High-resolution transmission electron microscopy (HRTEM)

HRTEM images of M_xO_y/SiO₂ nanocomposites (figure 3) show the formation of M_xO_y particles (dark structures) at a silica surface (light structures). The aggregated structures of grafted oxides of 20 to 30 nm in size are well observed for Ni_xO_y/SiO₂ (figure 3b) and 10–15 nm in size for Mn_xO_y/SiO₂ (figure 3a) and Zn_xO_y/SiO₂ (figure 3c) samples. Composites look like more compacted than initial silica (figure 3d). Therefore, contribution of macropores increases

(figure 2) for samples Mn1 and Zn3, while the total pore volume V_p decreases for composites compared to the initial silica (table 1) due to decreasing empty volume ($V_{em} = 1/\rho_b - 1/\rho_0$, where ρ_0 and ρ_b are the true and bulk density of oxides, respectively) in the nanocomposites. Note that any treatment or modification of fumed silica results in a decrease in the value of V_{em} , i.e. the value of ρ_b increases [47].

3.3 XRD analysis

XRD analysis of M_xO_y/SiO₂ nanocomposites containing different amounts of M_xO_y (figure 4) shows that after calcination (at 600°C) of samples with Ni, Zn and Mn at their content of 0.2 mmol g⁻¹ SiO₂ the deposited oxide phases are amorphous. With increasing concentration of metals to 1 and 3 mmol g⁻¹ SiO₂ (figure 4), nanocrystallites were formed

Table 2. Composition of the M_xO_y phase in M_xO_y/SiO_2 .

Metal	Metal content (mmol g ⁻¹ SiO ₂)	600°C	
		Phase composition	Size (nm)
Ni	0.2	Amorphous	—
	1.0	NiO	16
	3.0	NiO	17
Mn	0.2	Amorphous	—
	1.0	Amorphous	—
	3.0	Mn ₃ O ₄ trace	—
Zn	0.2	Amorphous	—
	1.0	Amorphous	—
	3.0	ZnO trace	—

Figure 4. XRD patterns of composites with 3 mmol M_xO_y/g SiO₂ with M: Ni3 (curve 1), Mn3 (curve 2), Zn3 (curve 3), calcinated at 600°C.

in the case of NiO. For composites with Mn and Zn there are Mn₃O₄ and ZnO traces only at a concentration of 3 mmol g⁻¹ SiO₂. The structure of surface compounds in composites with nickel (table 2) is crystalline at all concentrations, as well for NiO alone (figure 4).

3.4 FTIR spectroscopy

Figure 5a shows FTIR spectra of silica alone and Zn_xO_y/SiO_2 composites with different zinc contents. The intensity of a band at 3750 cm⁻¹ corresponding to the O–H stretching vibrations of the silanol groups decreases with increasing content of zinc oxide in the composite. This is due to coverage of a portion of the silica surface by the deposited phase. A reliable method for estimating the ratio of the free surface with free OH groups to silica volume is the normalizing of the integrated intensity of the 3750 cm⁻¹ band (I_{3750} , i.e., a

fraction of a free surface with free OH groups) to the integrated intensity of a band at 1870 cm⁻¹ (I_{1870}) corresponding to the Si–O stretching vibrations and correlates to the total amount of silica in a sample [48,49]. It can be seen (figure 5b) that the normalized integrated intensity (I_{3750}/I_{1870}) decreases at concentrations of 0.2 and 1 mmol g⁻¹ for all oxides. However, with increasing of the concentration up to 3 mmol g⁻¹ for Ni and Mn, it rises in comparison with lower concentrations, which can be explained by the formation and growth of the particles of the second phase with a decrease in their contact area with the surface of silica. This is confirmed by the presence of the crystal structure of Mn₃O₄ in XRD. For Zn-containing samples, the formation of ZnO traces is observed, and a monotonous decrease in I_{3750}/I_{1870} occurs that shows a greater affinity of zinc oxide to silica up to the formation of silicate and a larger area of contact between the carrier and deposited particles. The normalized integrated intensity I_{3750}/I_{1870} makes it possible to estimate the contribution of silica and second oxide phases to the total surface area of the M_xO_y/SiO_2 composite on the basis of comparison with data on the ratio of components (table 3).

3.5 Heat of immersion of M_xO_y/SiO_2 nanocomposites in water and n-decane

The main active sites of an oxide surface are terminal and bridging OH groups. Their concentration and Brønsted acidity determine surface properties of oxides such as interaction strength with polar and nonpolar substances, surface charge density and electric double-layer (EDL) structure in an aqueous medium. In the case of immersion wetting, a liquid/solid interface can be considered as a set of molecules interacting with surface functional groups (which could be modelled by clusters) as well the molecules of gas or vapour [50–52]. The strength of these interactions under the conditions of immersion wetting of powders [53,54] is characterized by the heat of immersion (Q).

The wetting processes implement a variety of types of intermolecular interactions: from universal non-specific intermolecular interactions occurring in all cases in varying degrees, to various specific interactions: orientation electrostatic interactions, hydrogen bond formation, etc. The immersion interaction of the initial silica is described elsewhere [55]. It was indicated that only silanol groups are responsible for the hydrophilic properties of a surface, while the interactions of the siloxane bridges with water are rather weak. A fumed silica surface contains 2.25–2.5 μmol m⁻² of silanol groups [51,55,56]. After modification of silica with Mn, Ni and Zn oxides, the surface of the composites is the sum of the surface of initial silica and amorphous or crystalline second oxide, the ratio between which depends on the surface concentration of the second phase (table 3), while the content of the Si–OH groups decreases in the composite as compared to the initial silica (figure 5). In this case, the diversity of surface centres increases: on the surface of mixed oxides there

Figure 5. FTIR spectra of the (a) initial silica and Zn_xO_y/SiO₂, (b) Mn_xO_y/SiO₂, (c) Ni_xO_y/SiO₂ composites and (d) integrated intensity of bands at 3750 cm⁻¹ normalized to bands at 1865 cm⁻¹ (I_{3750}/I_{1865}) for M_xO_y/SiO₂ nanocomposites with different contents of the M_xO_y phase.

Table 3. The relative contribution of the specific surface area of the M_xO_y phase to the total surface area of M_xO_y/SiO₂ nanocomposites calculated from the nitrogen adsorption data and relative integrated intensity I_{3750}/I_{1865} .

Samples	Metal content (mmol g ⁻¹ SiO ₂)	S_{BET} (m ² g ⁻¹)	S_{BET} (SiO ₂) (m ² g ⁻¹)	S_{BET} (M _x O _y) (m ² g ⁻¹)	S_{BET} (SiO ₂) (%)	S_{BET} (M _x O _y) (%)
SiO ₂	0	367	367	0	100	0
Mn _x O _y /SiO ₂	0.2	306	172	133	56.4	43.6
	1	264	90	174	34.1	65.9
	3	186	157	29	84.3	15.7
Ni _x O _y /SiO ₂	0.2	329	323	6	98.1	1.9
	1	314	263	51	83.9	16.1
	3	296	280	16	94.6	5.4
Zn _x O _y /SiO ₂	0.2	335	266	69	79.3	20.7
	1	295	197	98	66.9	33.1
	3	208	158	51	75.6	24.4

are such active centres as M–OH, Si–OH, M–O(H)–Si, Si–O–Si, M–O–Si and M–O–M. The hydrophilic properties of the surface of mixed oxides depend on their polarity and surface

concentration. Table 4 shows the values of enthalpy change upon wetting as measured heat of immersion in water and *n*-decane calculated per 1 g and 1 m² of nanocomposite surface.

As can be seen from heat of immersion values, Q_{water} is higher than Q_{decane} for all synthesized composites, which indicates their hydrophilic properties. The hydrophilicity index has the highest values for composites containing Zn_xO_y . A decrease in heat of immersion in water and *n*-decane per 1 g for composites compared to the initial silica is associated with a decrease in the specific surface area (table 1).

3.6 Electro-surface properties

The phase composition of the composite particles and the nature and concentration of active sites on their surfaces are the main factors determining such electro-surface properties as surface charge density and zeta potential in the aqueous media. Surface hydroxyls of different types, mentioned above, are the active centres responsible for the surface charges [55]. The silanol groups on a silica surface can dissociate to provide negative charges in aqueous medium at $\text{pH} > \text{pH}_{\text{PZC}}$:

On a surface of complex oxides, the active sites characteristic of individual oxides $\text{M}-\text{OH}$ as well the bridges $\text{M}-\text{O}(\text{H})-\text{Si}$ (where $\text{M} = \text{Ni}, \text{Zn}, \text{ or } \text{Mn}$) are present. The last ones could be more acidic than the individual oxides [57,58]. The reactions of the surface groups at the mixed oxides responsible for the surface charges are as follows:

Figures 6 and 7 show the surface charge density and zeta potential as functions of pH for the aqueous suspensions of silica and $\text{M}_x\text{O}_y/\text{SiO}_2$. Both pH_{IEP} and pH_{PZC} are important characteristics of the EDL. For initial silica, the surface charge density vs. pH is characterized by values close to 0 in a broad range (up to pH 8.5) and a sharp increase at $\text{pH} > 8.5$. Composites containing nickel oxide exhibit a similar dependence of the surface charge density on pH (figure 6). This can be explained by a low contribution of the nickel oxide surface (table 3) with no significant effect on the surface charge density. Nevertheless, its influence on the EDL and zeta potential values is quite noticeable (figure 7). In the acidic region, the zeta potential values are positive indicating a significant difference in the acidic properties of $\text{Ni}-\text{OH}$ and $\text{Ni}-\text{O}(\text{H})-\text{Si}$ compared to $\text{Si}-\text{OH}$ and the implementation of the proton attachment mechanism according to equation (3). For the 3Ni composite, $\text{pH}_{\text{IEP}} = 3.4$ and $\text{pH}_{\text{PZC}} = 7.8$. The positive values of the surface charge density and zeta potential in the acidic pH range indicate the basic properties of Ni_xO_y . However, the positive values of the surface charge density are small. It does not exceed 4.5 mC cm^{-2} in the entire range, whereas in the alkaline pH region the 3Ni sample shows high values of the surface charge density

Figure 6. Surface charge density of mixed oxides as a function of pH: (a) Ni containing samples and (b) Mn containing samples and (c) Zn containing samples.

up to -60 mC cm^{-2} . With an increase in the concentration of the second oxide, the pH_{PZC} shifts toward lower pH for both $\text{Ni}_x\text{O}_y/\text{SiO}_2$ and other composites. For manganese and

zinc composites, positive values of the surface charge density in the acidic pH range are also observed, the pH_{PZC} values (figure 6) are comparable with those in the literature for individual Mn_xO_y ($\text{pH}_{\text{PZC}} = 7.5\text{--}8.7$) and ZnO ($\text{pH}_{\text{PZC}} = 8.0$) [59]. The differences in the surface charge density vs. pH are practically not observed at different Zn_xO_y concentrations in $\text{Zn}_x\text{O}_y/\text{SiO}_2$. This was confirmed previously [60], and they are insignificant for $\text{Mn}_x\text{O}_y/\text{SiO}_2$. This is due to the fact that even at a small concentration of $0.2 \text{ mmol g}^{-1} \text{ SiO}_2$, the second oxide particles occupy a significant part of the $\text{M}_x\text{O}_y/\text{SiO}_2$ surface (table 3). Despite the positive values of the surface charge density in the acidic pH range, zeta potential values for $\text{Mn}_x\text{O}_y/\text{SiO}_2$ and $\text{Zn}_x\text{O}_y/\text{SiO}_2$ are negative in the pH range studied, $\text{pH}_{\text{IEP}} = 1.5$ for composites with Zn.

Figure 7. Zeta potential of mixed oxide particles as a function of pH.

An increase in the absolute value of the zeta potential with increasing pH is observed for initial silica as well for the composites. For the latter, a change in the zeta potential is smaller than that for the initial silica and the values correspond to low-charged surfaces. This does not provide a sufficient contribution of electrostatic components to the colloidal stability of the systems. It should be noted that the zeta potential depends on a number of factors [36], among which are the dispersity and particle shape. Upon modification of the silica nanoparticles by the second oxide, the particle size increases and the shape differs from the spherical one. Therefore, a decrease in the absolute value of the zeta potential of the composites in comparison with silica can be related to both the changes in the surface charges and the mobility in the particles due to an increase in their size and change in the shape.

4. Conclusion

Novel binary fumed silica-supported M_xO_y nanocomposites were synthesized by thermooxidation of metal acetates adsorbed on the nanosilica surface. The phase composition and average size of crystallites were determined from XRD data. The NiO phase in $\text{Ni}_x\text{O}_y/\text{SiO}_2$ has crystallite sizes of 16–17 nm. There are amorphous phases in $\text{Mn}_x\text{O}_y/\text{SiO}_2$ and $\text{Zn}_x\text{O}_y/\text{SiO}_2$ nanocomposites with traces of Mn_3O_4 and ZnO crystallites at the maximum concentration of Mn and Zn of $3 \text{ mmol g}^{-1} \text{ SiO}_2$. The analysis of the nitrogen adsorption–desorption data and HRTEM shows that the deposition of new oxide phases strongly changes the textural characteristics of the powders. The incremental pore size distribution functions show predominantly the mesoporosity of nanocomposites, but the average pore size increases in comparison with the initial nanosilica. For $\text{Mn}_x\text{O}_y/\text{SiO}_2$ (at 1 mmol g^{-1}) and $\text{Zn}_x\text{O}_y/\text{SiO}_2$ (3 mmol g^{-1}), mainly meso/macroporosity is observed in the incremental pore

Table 4. Heat of immersion in water and *n*-decane for $\text{Mn}_x\text{O}_y/\text{SiO}_2$, $\text{Ni}_x\text{O}_y/\text{SiO}_2$ and $\text{Zn}_x\text{O}_y/\text{SiO}_2$ with different concentrations of the second phase.

Samples		Metal content (mmol g ⁻¹ SiO ₂)		M _x O _y /SiO ₂				
				<i>Q_w</i>		<i>Q_d</i>		<i>K_h</i>
				J g ⁻¹	J m ⁻²	J g ⁻¹	J m ⁻²	
SiO ₂	0	57.0	0.155	28.0	0.076	2.0		
Mn _x O _y /SiO ₂	0.2	37.1	0.121	16.5	0.054	2.2		
	1	39.9	0.151	15.7	0.059	2.5		
	3	28.8	0.155	16.0	0.086	1.8		
	0.2	55.3	0.168	17.9	0.054	3.1		
Ni _x O _y /SiO ₂	1	39.0	0.124	16.3	0.052	3.0		
	3	43.2	0.146	11.0	0.037	3.9		
	0.2	56.7	0.169	17.8	0.053	3.2		
Zn _x O _y /SiO ₂	1	52.1	0.177	10.8	0.037	4.8		
	3	45.0	0.217	10.7	0.051	4.2		

size distributions. For $\text{Ni}_x\text{O}_y/\text{SiO}_2$, HRTEM images show the presence of well-dispersed Ni-oxide nanocrystallites of $\sim 15\text{--}50$ nm in size on the amorphous silica matrix. The XRD results showed that silica did not form any compound with Ni and Mn, but it formed silicate with Zn. According to the hydrophilicity index K_h , the surface of all synthesized nanocomposites is hydrophilic and hydrophilicity of $\text{Zn}_x\text{O}_y/\text{SiO}_2$ nanocomposites is significantly higher than that of initial nanosilica that could be due to the formation of more polar Si–O–Zn bonds that intensively interacting with polar molecules of water. Investigation of the electro-surface properties of the nanocomposites shows that modification of the silica surface with M_xO_y leads to significant changes in the pH dependence of zeta potential, and affects the surface charge density and pH_{PZC} . A shift of the isoelectric point and the behaviour of the $\zeta(\text{pH})$ curves are determined by the M_xO_y phase. As a whole, pH_{IEP} shifts toward higher values in series $\text{Mn} < \text{Zn} < \text{Ni}$ -containing composites.

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