

Comparison of adsorption properties of $Mg_xO_y-SiO_2$ and $Zn_xO_y-SiO_2$ in the mixed oxide-poly(vinyl alcohol) system



M. Wiśniewska^{a,*}, P. Nowicki^b, V.M. Bogatyrov^c, A. Nosal-Wiercińska^d, R. Pietrzak^b

^a Department of Radiochemistry and Colloids Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

^b Laboratory of Applied Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Umultowska Street 89b, 61-614 Poznań, Poland

^c Chuiko Institute of Surface Chemistry, General Naumov Street 17, 03164 Kiev, Ukraine

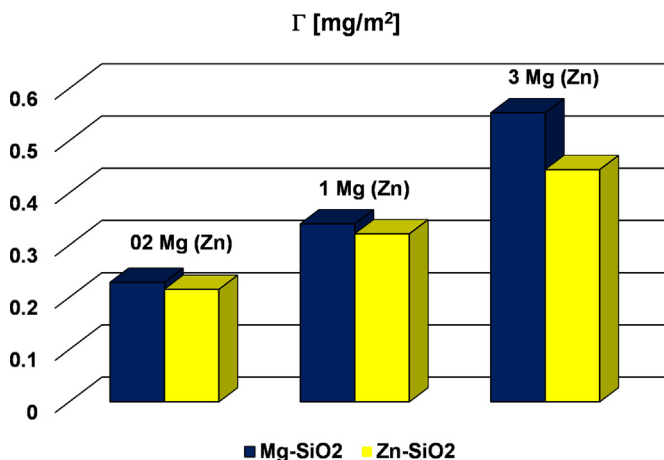
^d Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

HIGHLIGHTS

- Nonionic PVA adsorption mechanism on $Mg_xO_y-SiO_2$ and $Zn_xO_y-SiO_2$ was examined.
- Spectrophotometry, microelectrophoresis and potentiometric titration were applied.
- Mg_xO_y (Zn_xO_y) content in mixed oxide structure affects adsorption properties of solid.
- PVA shows the greater adsorption on $Mg_xO_y-SiO_2$ surface.
- Polymer adsorption does not influence the solid surface charge density.

GRAPHICAL ABSTRACT

Adsorbed amounts of poly(vinyl alcohol) on the surfaces of $Mg_xO_y-SiO_2$ and $Zn_xO_y-SiO_2$ mixed oxides for different contents of Mg and Zn.



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ABSTRACT

The adsorption properties of two silica composite materials: $Mg_xO_y-SiO_2$ and $Zn_xO_y-SiO_2$ in relation to poly(vinyl alcohol)–PVA were examined. For each mixed oxide three solids differing in the metal oxide (Mg_xO_y or Zn_xO_y) content were applied (0.2; 1 and 3 mmol/g SiO_2), respectively. The polymeric sample was characterized with molecular weight 100 kDa and the acetate groups content equal to 14%. Due to solubility of the applied solid at low pH values, the adsorption experiments were conducted at natural suspension pH. The solid surface charge and zeta potential measurements were performed in the pH range 6–11. The obtained results indicated that the PVA shows higher adsorption on the $Mg_xO_y-SiO_2$ surface. Moreover, the adsorbed amount of polymer increases with the increasing Mg_xO_y (or Zn_xO_y) content in the mixed oxide structure. The poly(vinyl alcohol) presence does not cause changes in the solid surface charge, whereas the absolute value of zeta potential of solid particles covered with polymeric layers decreases significantly.

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* Corresponding author.

E-mail address: wisniewska@hektor.umcs.lublin.pl (M. Wiśniewska).

1. Introduction

To obtain the specific surface properties of metal oxides, which are desirable in many technological and ecological applications, the modification of their structure is highly required. One of the innovative ways is the synthesis of mixed oxides, which consists of two or three mineral oxides, such as silica, alumina, zirconia and titania [1–3]. Among many techniques of such compounds preparation, the most important are: sol-gel method, high-temperature hydrolysis and chemical vapor deposition (CVD) [4–6]. These methods enable obtaining solids characterized by different contents of each oxide, which is a significant factor determining the surface properties of the solid particles in aqueous solutions. Our previous studies indicated that changes in percentage composition of mixed oxide affected its adsorption and electrokinetic properties in relation to polymeric macromolecules [7,8].

Metal oxides find a wide practical usage in various branches of industry and many fields of human activity (agriculture, medicine, catalysis, environment protection) [9–12]. For example, magnesium oxide is mainly used as refractory material due to its physicochemical stability at high temperatures. Other applications of this compound are as follows: production of MgO-based cement (reduction of CO₂ emission), as a moisture absorbent, antiacid in heartburn and sore stomach in medicine, optical material, a very good insulator in industrial cables and fireproofing ingredient in construction materials. On the other hand, zinc oxide is widely used as a component of plastic materials, ceramics, glass, cement, paints, food and batteries.

In many cases the application possibilities of metal oxides are limited due to inadequate surface characteristics. The appropriate surface modification leads to obtaining solids with the properties desired in specific processes [13–16]. One of the most important methods of surface modification is adsorption of different substances (both low- and highmolecular) [17–20].

Adsorption of polymers on the surface of solid particles dispersed in the liquid medium is essential for such system stability. Depending on molecular weight and concentration of a macromolecular compound, the stabilization or destabilization effect can be observed [21]. The low concentration of polymer (usually with a high molecular weight) favor the occurrence of bridging flocculation (leading to polymer bridges formation and suspension destabilization). Higher concentration of polymer (often with low molecular weight) promotes the steric stabilization process. Further increase in the polymer concentration causes depletion flocculation. At the highest concentrations of macromolecular substance, the depletion stabilization becomes possible. The adsorbed macromolecules assumed specific conformation at the solid-liquid interface. Thus the structure of polymeric layers covering colloidal particles determines their stability behavior in the dispersion medium.

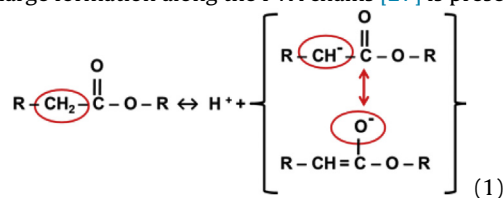
Considering the high demand for new solid materials and wide possibilities of their surface modification by the adsorbed polymer, the main aim of the present study is determination and comparison of adsorption mechanisms of poly(vinyl alcohol)–PVA on the surfaces of two mixed oxides (Mg_xO_y–SiO₂ and Zn_xO_y–SiO₂). The effect of metal oxide content in the hybrid silica material was examined. Excellent biodegradability and high biocompatibility of the applied polymer prejudged about its choice as an adsorbate. Moreover, PVA finds an extensive usage in the production of adhesives, coatings, pharmaceuticals, paints, oils, fibers and hydrogels [22–24]. Based on the adsorption and electrokinetic (solid surface charge density, zeta potential) results, the more probable way of poly(vinyl alcohol) binding with the mixed oxide surface was proposed.

2. Experimental

2.1. Materials

Two mixed oxides: Mg_xO_y–SiO₂ and Zn_xO_y–SiO₂, consisting of silica and metal oxide (magnesium or zinc oxide), were used as adsorbents. They were characterized by different contents of metal oxide, i.e., 0.2; 1 and 3 mmol/g SiO₂ and they were designated as: 0.2 Mg–SiO₂, 1 Mg–SiO₂, 3 Mg–SiO₂; 0.2 Zn–SiO₂ and 3 Zn–SiO₂, respectively. The solid BET surface areas and average pore volumes (BET method, Micromeritics ASAP 2405 analyzer) were placed in Table 1 (discussions on these results are provided in references [25] and [26]). All nanocomposites with nanosilica and grafted metal oxide were prepared at the Institute of Surface Chemistry of the National Academy of Sciences of Ukraine in Kiev. For this purpose magnesium (zinc) acetate–Mg(CH₃COO)₂·4H₂O (Zn(CH₃COO)₂·2H₂O) and nanosilica A-380 (Degussa) were used. The applied SiO₂ material was totally amorphous and composed of nanoparticles with mean diameter about 5 nm. The dispersion of silica in the aqueous solution of metal acetate was treated at 600 °C. As a result the metal oxides (Mg_xO_y and Zn_xO_y) were formed on the nanosilica surface. The detailed characteristics of their structural and surface properties was included in separate papers [25,26]. They contain results of the following methods: FTIR spectroscopy, thermogravimetry, XRD, HRTEM, UV–vis spectroscopy and XPS. Their analysis leads to the conclusion that amorphous MgO (or ZnO) was mainly formed on the surface of composite materials. Additionally, a small amount of MgO (ZnO) crystallites was present. It was also found that the portion of surface silanol groups interact with the metal-containing compound forming Si–O–Mg and Si–O–Zn bonds. The number of these bonds increases with the increasing metal content.

Poly(vinyl alcohol) – PVA (Fluka) was applied as an adsorbate. PVA is a water soluble polymer prepared in the hydrolysis of poly(vinyl acetate) in methanol solution. The polymer sample was characterized with the weight average molecular weight of 100 kDa and the degree of its acetate groups hydrolysis equal to 86%. In such a case 14% of the acetate groups (–OCOCH₃) in the poly(vinyl acetate) chains do not hydrolyze to hydroxyl ones (–OH). Despite the fact that poly(vinyl alcohol) belongs to the nonionic polymer group, due to the formation of the resonant structure, their macromolecule can gain a negative charge. The mechanism of negative charge formation along the PVA chains [27] is presented below:



All measurements were performed at 25 °C. The NaCl solution with the concentration of 0.01 mol/dm³ was used as a supporting electrolyte. Adsorption measurements were performed at the natural pH value of aqueous suspension of mixed oxide (changing in the range 6–7). The potentiometric titrations and zeta potential measurements were performed in the pH range 6–11. This results from solubility of magnesium and zinc oxides at more acidic values of pH.

2.2. Apparatus

The UV/vis spectrophotometer Cary 100 (Varian) was applied for determination of the poly(vinyl alcohol) concentration in the solution.

The potentiometric titration was performed by the use of a set consisting of: thermostated Teflon vessel, glass and calomel elec-

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