

Adsorption of the selected organic dyes on the functionalized surface of precipitated silica via emulsion route

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Abstract

Physicochemical analysis was performed on silicas precipitated according to a novel method, in an emulsion system. Substrates for the process involved solutions of sodium metasilicate and sulphuric acid while the organic phase consisted of cyclohexane and non-ionic emulsifiers. The silicas were used to obtain hybrid structures of the formed inorganic pigments. For this purpose, the adsorption of organic dyes on the silica surface was preceded by modification of the surface with silane coupling agent containing amine groups. Specific surface area (BET) and porous structure of the raw silicas were estimated. The silicas and pigments were subjected to studies on surface morphology, zeta potential, particle size and distribution of particle diameters were also established. Effects of modification with the aminosilane were appraised using FTIR and ^{29}Si CP MAS NMR techniques.

Stable pigments were obtained on silica core, the surface of which was modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. Particles of the obtained pigment manifested a spherical shape and particle size distribution proved that no agglomerate structures were present. High stability of the obtained pigments proved that the organic dye was chemically bound to the modified silica surface. Mechanisms of inorganic–organic hybrid formation were also suggested.

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1. Introduction

In this paper, we describe the general synthetic mechanism to incorporate selected dyes by covalent interactions or hydrogen bonds into monodisperse, colloidal silica, obtained via precipitation route in emulsion system. In order to effectively introduce organic dyes, silicas are prepared of specific defined hydrophilic–hydrophobic properties and their adsorptive properties are augmented by the surface modification with aminosilane.

Numerous reports have appeared, related to evaluation of interaction of organic dyes, procedures of their

introduction and mechanisms of adsorption on inorganic synthetic oxides, minerals, carbon or its derivatives.

For example, Chun et al. prepared the inorganic hybrid of $\text{TiO}_2/\text{SiO}_2$ with augmented adsorptive and photocatalytic capacity for azo dyes [1]. In turn, numerous groups of aromatic and polyaromatic dyes were “introduced” to the surface of kaolin and aluminium oxide [2]. In the study, general adsorption selectivity was examined as a function of pH for individual adsorbates. Due to the stratified structure of silicates, the high adsorptive capacity reflects charged outer surface as well as the internal (inter-packette) charge. Studies continue on organic dye incorporation to montmorillonites [3–6]. Since the summative montmorillonite charge is negative, it seems more advantageous to modify the mineral with positively charged dyes, e.g., applying Methylene Blue.

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Mechanism of adsorption on activated carbons and carbon derivatives has been described [7,8]. Adsorptive capacity of activated carbon has been examined, establishing adsorption isotherms and changes in zeta potential resulting from interaction between the dye and the carbon adsorbent.

Pigments formed by adsorption of organic dyes on a silica core are of a particular cognitive and technological importance. Pigments of the type can be obtained within a broad range of colours, depending upon the original organic dye used [9,10]. The pigments show many advantages as compared to the conventional pigments [11–13]. Hydrophilic silicas are colourless and carry surface silanol groups ($\equiv \text{Si-OH}$), which react with multiple functional groups forming covalent bonds. The process of colouring the silicas involves first a reaction of silica surface silanol groups with a silane coupling agent (most frequently containing amine groups) to condense molecules of the silane with the surface of silicon dioxide. Subsequently, the organic dye reacts with the bound silane, forming silica particles carrying the dye trapped by a covalent bond [14–19]. Pigments formed by synthesis of silica are also of importance. Pigments of this type are obtained using as a carrier the silica obtained by hydrolysis and condensation of alkoxy silanes (mainly TEOS) in ethanol/water/ammonia mixture and in the presence of appropriate dyes [20–22].

Dispersion and morphological properties of the obtained pigments on the silicon dioxide core strictly depend on the matrix, i.e. on the size and shape of the silica particles, their homogeneity and surface development [9,18,19,23].

In the present study, a novel method has been presented of precipitating silicas of specified properties (spherical shape of particles, low polydispersity, high chemical activity), which may find application as selective carriers of organic dyes. The process of precipitating such silicas is based on a solution of sodium metasilicate.

2. Experimental section

2.1. Materials

In the studies newly synthesized silica was used, precipitated in an emulsion medium from sodium metasilicate and sulphuric acid. Organic phase involved cyclohexane (POCh, Poland). As the emulsifiers, non-ylphenylpolyoxyethyleneglycol ethers with mean oxyethylenation extent 5 (Rokafenol N-5) or 6 (Rokafenol N-6) were tested, both produced by Chemical Works “Rokita” S.A. (Poland). For the silica surface modification *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (UniSil) was applied. Colouration of silica was

conducted using selected organic dyes produced by Boruta-Kolor (Table 1).

2.2. Preparation and modification of silicas

2.2.1. Emulsion preparation

Two emulsions were prepared. The ‘alkaline’ one (E_1) contained 100 cm³ 5 wt% Na₂SiO₃ solution and 110 cm³ cyclohexane, supplemented with an emulsifier. Mass ratio of Rokafenol N-5 to Rokafenol N-6 was 1.0:1.5. The ‘acidic’ emulsion (E_2) consisted of 33 cm³ 5 wt% of H₂SO₄ and 35 cm³ of cyclohexane, supplemented with an emulsifier of the same composition as in E_1 but in appropriately lower amount. The predissolved emulsifiers were diluted in cyclohexane. The aqueous phase (for E_1 5 wt% solution of Na₂SiO₃, for E_2 5 wt% solution of H₂SO₄) was dosed in few portions and the mixture was homogenized at 19 000 rpm for 5 min. The so prepared emulsions were used in precipitation reactions.

2.2.2. Process of formation of colloidal silica

2.2.2.1. *Dispersing (precipitation) using a top stirrer – (E11-Silica)*. Precipitation was conducted in a 0.5 dm³ capacity reaction accompanied with the propeller stirrer EUROSTAR digital type (Ika Labortechnik, Germany). Using the appliance, the system was subjected to intense mixing (2000 rpm). The E_2 emulsion was placed in the reaction vessel and subjected to intense mixing. Emulsion E_1 was dosed to emulsion E_2 at a constant rate using peristaltic pump. As a result of the reaction taking place in the reaction vessel, a silica-containing emulsion was obtained. The emulsion was heated to 80 °C in order to destabilize it. Subsequently, cyclohexane was separated from it by distillation. The subsequent stage involved filtration of the remaining mixture under a lowered pressure. In this way, the obtained sample was washed with hot water and, then, with acetone in order to wash out the remaining surfactants. Acetone was separated by distillation. Subsequently, the sample was subjected to drying for 48 h in a stationary dryer at 105 °C.

2.2.2.2. *Precipitation in an ultrasonic bath – (E19-Silica)*. A reactor of 0.5 dm³ capacity was placed in an ultrasonic bath of INTERSONIG - 102 (30 kHz), 100 W type, in which formation of the silica was conducted using ultrasound. The remaining functions were analogous to those applied in the above method.

2.2.2.3. *Formation (precipitation) using a homogenizer – (E27-Silica)*. The precipitation was conducted in the reactive vessel of 0.5 dm³ capacity. Mixing took place in a homogenizer of ULTRA TURRAX T25 basic type (Ika Labortechnik, Germany) at 19 000 rpm. The remaining

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