High temperature stable bismuth vanadate composite pigments via vanadyl-exchanged zeolite precursors

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ABSTRACT

A novel and facile route for synthesising inclusion-stabilised monoclinic bismuth vanadate via solid-state reaction of vanadyl-exchanged zeolites with pentavalent bismuth species is presented. In this report, these new composite materials are extensively analysed and characterised. Most notably, ion scattering spectroscopy is employed as a non-standard and highly surface sensitive characterisation technique to determine surface compositions and to prove that the composites feature alumosilicate protected bismuth vanadate. Thermal stability tests relating to colouristic performance are conducted to demonstrate the superior thermal resilience of these compounds, maintaining better colouristic properties compared to commercial bismuth vanadate even at very high temperatures.

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1. Introduction

In recent years, bismuth vanadate became one of the most extensively investigated materials due to its ability to split water under visible light irradiation [1–5], thus substantially stimulating research in the field of sustainable alternative energy sources. Other interesting applications of bismuth vanadate are, for example, its use as catalyst for photodegradation of pollutants [6–21] or as an inorganic pigment.

In nature, $BiVO_4$ is found in the form of three polymorphs: pucherite (orthorhombic) [22], dreyerite (tetragonal) [23], and clinobisvanite (monoclinic) [24]. Out of these three phases, the tetragonal and especially the monoclinic phase exhibit the best colouristic properties. Monoclinic bismuth vanadate is a bright yellow solid, which has been in use as an inorganic pigment for about 40 years. Due to its excellent brightness of shade, high tinting strength, very good weather fastness, high chemical resistance, and environmental benignity, it has been acknowledged as one of the most popular and customary yellow pigments on the market. Its actual volume now surpasses 1200 t/a [25].

However, the colouristic performance of $BiVO_4$ is known to deteriorate in polyolefine melts above 240 °C and to change colour upon strong heating [26]. In order to improve its thermal stability and chemical resistance properties, numerous attempts have been disclosed in patents and academic publications. In particular, the concept of pigment encapsulation in various oxides, fluorides, and phosphates has been well established [26–29]. Commercial silica encapsulated composite materials are already available under different brand names such as Vanadur®Plus [30].

Further methods of encapsulation comprise e.g. the use of a host-guest system, as is the case with another famous inorganic pigment family, namely the lapis lazuli minerals and derived ultramarine blue based colourants. Their chromophores, predominantly $S_3 \cdot^-$ radical anions, are protected from outer influences due to being located inside of the zeolite [31]. Zeolites are composed of a porous, negatively charged alumosilicate structure that accommodates loosely bound cations inside these pores to guarantee charge neutrality. Due to only being bound electrostatically, these cations may be readily exchanged for others in a contact solution [32] — a property that has been, among numerous other application

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areas, utilised in pigment synthesis. Anthropogenic examples of stabilised pigments via metal-exchanged zeolite precursors include the syntheses of cadmium sulfoselenide or Thénards Blue in zeolite A [33]. For example, heating of a cobalt exchanged zeolite induces the reaction of cobalt with the aluminate part of the zeolite, generating the spinel compound $CoAl_2O_4$ inside of an (alumo)silicate host matrix [33]. In this article, the authors opt to contribute a similar approach. By using vanadyl-exchanged zeolites and reacting them with higher-valent bismuth compounds to generate and concomitantly encapsulate the resulting pigments in alumosilicate matrices, this work reports on their colouristic properties and demonstrates their superior thermal stability in comparison to commercial $BiVO_4$.

2. Experimental

2.1. Materials and methodology

The following starting materials were of reagent grade and used as received: Zeolite 13X, sodium form, powder (Alfa Aesar), zeolite Y, sodium form, powder (Sigma-Aldrich), vanadyl sulphate pentahydrate (Riedel-de Haën/Honeywell), hydrochloric acid 36% (Z.E.U.S. GmbH), sodium bismuthate(V) dihydrate (Sigma-Aldrich), Durovan 5501 (= pigment yellow 184, $BiVO_4$; Habich GmbH) [34].

Bismuth(III,V)oxide was synthesised according to a literature procedure [35], which was modified by a subsequent step in order to yield reproducibly crystalline material: to 11.3 g of $NaBiO_3 \bullet 2H_2O$, 100 ml of 20% HNO_3 with a temperature of 0 °C were added. This mixture was slowly stirred for 10 min, after which the brown product was filtered off and washed with copious amounts of cold water, followed by washing with ethanol and diethyl ether. Finally, the product was dried in high vacuum over P_4O_{10} for 24 h. Afterwards, the amorphous, crude product was placed in an desiccator containing a separate glass beaker charged with deionized water. The closed desiccator was placed in a drying cabinet and held in the equilibrated humid atmosphere at a temperature of 90 °C for 3 days. According to X-ray powder diffraction analysis, the material was completely converted into crystalline Bi_4O_7 [36] during this ageing period. Finally, the product was dried shortly at ambient temperature by means of an oil pump vacuum.

Stabilised bismuth vanadate was synthesised via a two-step procedure: first, sodium forms of zeolites X and Y were metathesised to their vanadyl-exchanged analogues [37]. This was accomplished by stirring the zeolites in 0.1 M $VOSO_4$ solutions at 90 °C for 24 h (due to the basic nature of zeolite X, the pH for the zeolite X exchange reaction was adjusted to 3.5 using hydrochloric acid in order to avoid formation of anionic vanadium species [38]), followed by filtration, washing with copious amounts of hot water and acetone, and finally drying the green products at 100 °C for 24 h.

In a second step, the dried precursors (from now on denoted VO-X or VO-Y) were mixed with $NaBiO_3$ or Bi_4O_7, ground in an agate mortar, and calcined in a muffle furnace at 850 °C for 1 h (heating rate 5 °C min^{-1}) to give the products **1**–**4**. Higher-valent bismuth species were necessary for oxidation of the vanadium cations, as they were expected to be in the tetravalent state. However, there have been reports that in vanadyl-exchanged zeolites, some vanadium ions are already oxidised to the pentavalent state before calcination, forming clusters inside of the zeolithic structure [39]. Since there was no certainty that all vanadium would be accessible for reaction to $BiVO_4$, bismuth amounts were increased incrementally until optimal colouristic properties were achieved. Table 1 shows sample notation and preferred mixing ratios.

2.2. Characterisation techniques and instrumentation

Identification and phase purity determination were carried out by X-ray powder diffraction (XRPD) using a Stoe Stadi P powder diffractometer with Ge(111)-monochromatised Mo$K_{\alpha 1}$ ($\lambda = 70.93$ pm) radiation operated in transmission geometry. The silicon microstrip solid-state detector Mythen 1K was used. All data were measured in 2θ with steps of 0.030° from 2 to 41.9° each with a 12 s counting time.

Fourier transformed infrared (FT-IR) spectra of the powdered products were recorded at room temperature using the Bruker ALPHA Platinum ATR single reflection diamond module in attenuated total reflection (ATR) mode.

Electromagnetic spectra in the range between 360 and 830 nm were recorded on an Agilent Cary 5000 UV−Vis−NIR spectrophotometer (version 2.23), equipped with a DRA2500 integrating sphere. All compounds were transferred in a powder cell holder and measured in reflection mode with a resolution of 1 nm. For reference baseline acquisition, a barium sulfate standard was used. Colour coordinates were determined using CIE 1976 *Lab* as recommended by the Commission Internationale de l'Éclairage (CIE). For that, the Cary WinUV Colour software, a D65 (noon, solar emission) standard illuminant, and a 10° complementary observer were employed. According to the colour coordinate system, L^* represents the lightness axis (black = 0, white = 100), while the axis a^* (green = negative, red = positive) and the axis b^* (blue = negative, yellow = positive) correspond to the coordination axes of the colour space. In addition, the colour parameters of the compounds were calculated in cylindrical colour space coordinates $L^*C^*h°$ [$C^* = [(a^*)^2 + (b^*)^2]^{1/2}$; $h° = \tan^{-1}(b^*/a^*)$]. In this system, L^* is the lightness mentioned before, C^* represents the saturation of the colour, and $h°$ the hue angle expressed in degrees from 0° to 360°. For orange, $h°$ is in the range 35−70° and for yellow it's in the range of 70−105°. Apparent band gap energies were determined by the extrapolation method from the absorption edge of the corresponding absorbance spectra and employing the formula $E(eV) = h \bullet c/\lambda = 1239$ (eV nm)/λ (nm).

X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) measurements were conducted with a Thermo Scientific MultiLab 2000 spectrometer with a base pressure in the low 10^{-10} mbar regime, equipped with an Alpha 110 hemispherical sector analyser (suitable for the detection of electrons as well as ions), a switchable Al K_α/Mg K_α X-ray twin source and an ion source. Charging of the samples was prevented by the use of a flood gun, providing electrons with a kinetic energy of 6 eV to keep the surface charge constant. For ISS, helium ions were employed (2 keV) and the scattering angle was approximately 127°.

For scanning electron microscopy (SEM) images, back-scattered

Table 1
Sample numbering and synthesis conditions of zeolite stabilised bismuth vanadate.

Sample	Precursor type	Precursor amount/mg	Bi source	Bi source amount/mg
1	VO-X	100	$NaBiO_3 \cdot 2H_2O$	55
2	VO-X	100	Bi_4O_7	45
3	VO-Y	100	$NaBiO_3 \cdot 2H_2O$	35
4	VO-Y	100	Bi_4O_7	25