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ScienceDirect

Ceramics International 41 (2015) 4504–4513

CERAMICS INTERNATIONAL

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Historical hematite pigment: Synthesis by an aqueous sol–gel method, characterization and application for the colouration of ceramic glazes

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Received 8 October 2014; received in revised form 14 November 2014; accepted 18 November 2014
Available online 9 December 2014

Abstract

Synthetic hematite (α-Fe_2O_3) has been synthesized by simple and environmentally benign aqueous sol–gel method. Annealing of the gels at different temperatures in the range of 500–1000 °C yielded the single phase synthetic hematite. Interestingly, the colour of the sol–gel derived hematite can be controlled by annealing temperature of prepared Fe–O nitrate–glycolate gel. It was demonstrated that the heating temperature influences morphology, particle size and shape of pigments. The CIELab values of synthesized pigments have been also determined and revealed different colour of pigments. For comparison, three commercial pigments were also investigated and characterized. Ceramic glazes were prepared with the same pigments and characterized.

Keywords: Synthetic hematite; Ceramic pigment; Sol–gel method; Ceramic glaze

1. Introduction

Hematite (α-Fe_2O_3) is the most stable iron oxide and it is traditionally used as a red pigment from ancient times. Iron oxide pigments, termed ochre, were used for the rock art painting, funerary rituals, cosmetics [1,2], for surface decorations of pottery [2,3], for clothing hides decoration [2]. Nowadays, α-Fe_2O_3 is used for several industrial applications, for instance colouring paints, plastics and enamels, thanks to its low price, low toxicity, and high thermal and chemical stability [4]. Various shades of the hematite appears mainly due to the variation in crystallinity [5], particle size [6,7], shape and degree of aggregation [5]. Thus, the red colour of this pigment depends on synthesis route [4], which influence morphological features of synthesis product. Currently, a lot of methods for synthesizing red ochre are developed among those microemulsion technique [8], microwave synthesis [9], *Pechini* sol–gel method [10], and thermal treatment route [11].

In this work, three different commercial red iron(III) oxide pigments from Kremer Pigmente (Germany) have been investigated by XRD, SEM and DLS methods. Also, we have synthesized red iron(III) oxide pigments by an aqueous sol–gel method in order to reveal its potential for application in the pigmentary field for the colouration of ceramic glazes. Colour properties, phase composition, particle size distribution of pigments have been evaluated and pigments were used for the preparation of ceramic glazes.

2. Experimental part

2.1. Sample preparation

The ceramic pigments Fe_2O_3 were prepared by an aqueous sol–gel method. The Fe–O precursor gels were prepared using $Fe(NO_3)_3 \cdot 9H_2O$ (98.0% Duro-Galvanit-Chemie), CH_3COOH (99.5% Eurochemicals), 1,2-ethanediol $C_2H_6O_2$ (99.5% Aldrich). 2 g of iron(III) nitrate were dissolved in 100 ml 0.2 M CH_3COOH and stirred at 65–70 °C for 1 h. In the following step, 2 ml of 1,2-ethanediol, a complexing agent, was added to this solution and the solution was stirred for an additional 1 h at the same temperature.

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http://dx.doi.org/10.1016/j.ceramint.2014.11.145
0272-8842/

After stirring for 1 h, the obtained solution was evaporated at 65–70 °C. The prepared Fe–O gel was dried in oven at 100–110 °C. Dried gel powders were ground in agate mortar and heated in air at 500, 600, 700, 800, 900 and 1000 °C for 5 h at a heating rate of 3 °C/min.

Ceramic glazes with iron pigments were prepared with Pb_3O_4 (96.0% Kremer Pigmente), SiO_2 (97.0% Kremer Pigmente) in molar ratio of 2.85:1.9 and using 5 wt% of pigment. 1.95 g of Pb_3O_4, 0.11 g of SiO_2 and 0.10 g of pigment were mixed with 2 ml of water and terracotta plates were covered with glaze mass [12]. The glaze samples were fired at 800, 900 and 1000 °C for 1 h.

2.2. Sample characterization

Thermogravimetry/differential scanning calorimetry (TG/DSC) measurements of the precursor Fe–O gel was carried out in air at a heating rate of 10 °C/min using Simultaneous Thermal analyser STA6000 from PerkinElmer. Malvern Nano ZS (Malvern Instruments, GB) was used for measurements of particle size distribution. The crystal structures of the powdered materials were studied by X-ray diffraction (XRD) analysis. The diffraction patterns of the samples were obtained with Rigaku MiniFlex II diffractometer working in the Bragg–Brentano ($\theta/2\theta$) geometry. The data were

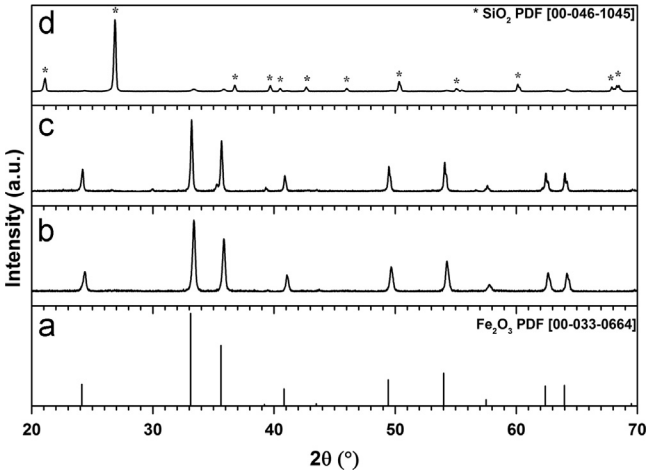

Fig. 1. Powder XRD patterns of standard synthetic hematite (a) and commercial iron(III) oxide pigments purchased from Kremer Pigmente: light red iron(III) oxide (b), dark red iron(III) oxide (c) and burnt red iron(III) oxide (d).

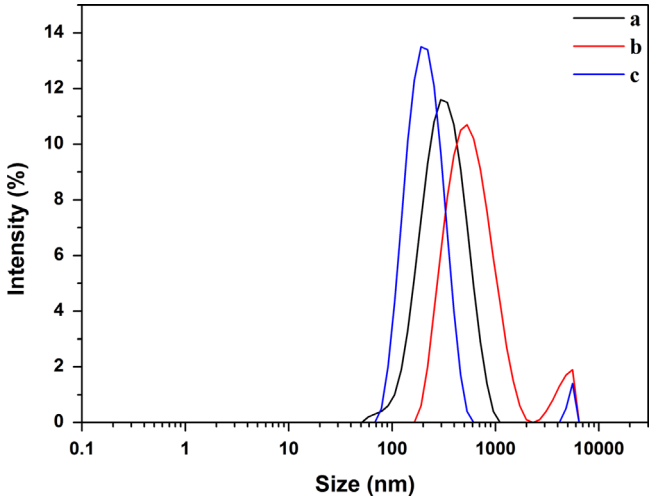

Fig. 3. Particle size distribution of light red iron(III) oxide (a), dark red iron (III) oxide (b) and burnt red iron(III) oxide (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

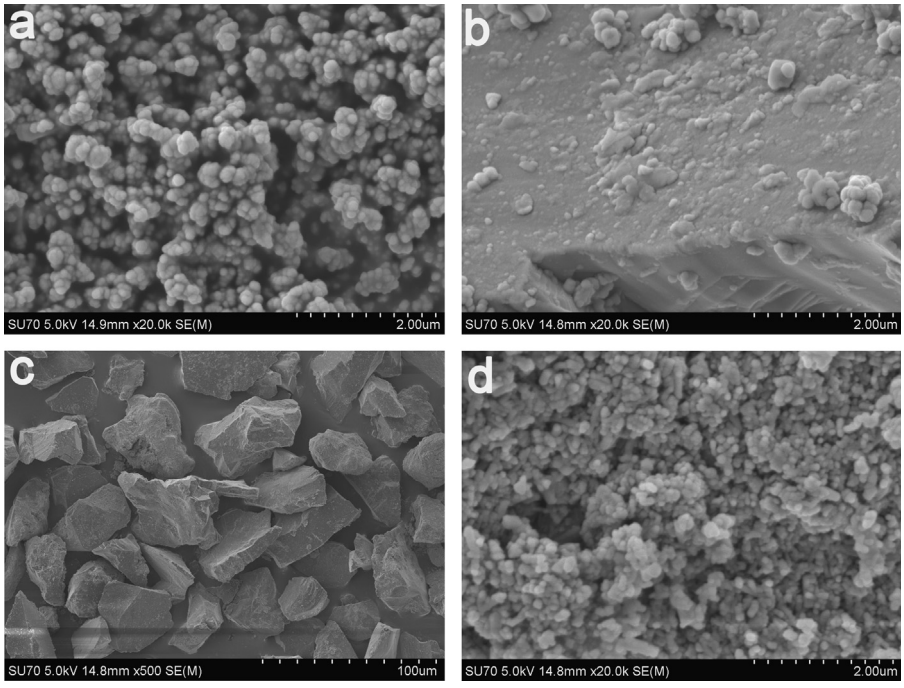

Fig. 2. SEM micrographs of light red iron(III) oxide (a), dark red iron(III) oxide (b) and burnt red iron(III) oxide (c and d).