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Estimation of optimal physico-chemical characteristics of nano-sized inorganic blue pigment by combined artificial neural network and response surface methodology

Shiva Salem[a,*], Saeid Jafarzadeh-Ghoushchi[b]

[a] Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran
[b] Faculty of Industrial Engineering, Urmia University of Technology, Urmia, Iran

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ABSTRACT

The application of response surface methodology combined with artificial neural network was used to estimate the optimal characteristics of nano-sized cobalt based pigment. Firstly, the nano-sized blue powder was synthesized by stoichiometric contents of cobalt and aluminum nitrates using autoignition technique. The study was conducted over a wide range of operating conditions, designed by response surface methodology, in terms of pH, fuel ratio and calcination temperature. The crystallite size, specific surface area, color behavior and crystallinity of powders were determined according to the standard methods. Secondly, several artificial neural networks were designed and then examined for prediction of pigment characteristics. The appropriate model was obtained to achieve better prediction and then the response surface methodology was applied to screen the artificial neural network output data for optimizing synthesis condition. It was concluded that the trained artificial neural network combined with response surface methodology can provide the synergetic pigment synthesis conditions. The additional validations were performed and the results showed acceptable error between the predicted and experimental data. The application of presented algorithm can be important tool for reliable synthesis nano-sized blue powder.

1. Introduction

Recently, the nano-sized cobalt aluminate spinel (CAS) was found extensive application in ceramic, glass, paint industries and color television tubes as a contrast-enhancing luminescent pigment to produce Thenard's blue color [1]. The micro-sized CAS powder is frequently manufactured through a solid-state reaction in which the oxides are mechanically ground at high temperatures about 1300 °C for a long time [2]. Although, this process is relatively inexpensive, undesired products are produced due to a lack of homogeneity. The extensive investigations have been conducted to synthesize nano-sized CAS powder by various novel chemical methods including sol–gel [3], emulsion precipitation [4] and hydrothermal crystallization [5]. Among the wet chemical routes, the self-combustion technique has been regarded as one of the effective and economic methods due to its convenient processing, simple experimental setup, significant time-saving and high purity product [6]. This process is carried out in two stages: combustion and calcination. The combustion stage lasts for a few minutes and is based on the thermochemical reaction of propellants. The appropriate fuel and nitrate salts are dissolved in an aqueous medium and an exothermic redox reaction between the fuel and nitrates determines the quality of the final product. In general, the fuel should produce non-toxic gases during the ignition and act as a reducing agent for metal cations [7–9]. Although, the fuels such as citric acid and urea were also used to prepare CAS [7], the pure powder was synthesized using glycine as fuel [8]. In self-combustion process, pH, fuel content and calcination temperature are the most important factors that control the physico-chemical properties of final product and also have a significant influence on the colorant behavior [8,9]. The crystallite size, specific surface area, colorant property and crystallinity for any given initial condition should be determined to optimize the synthesis condition of powder. Overall, the reaction which is related to the synthesis of blue powder in the presence of glycine (m moles) can be represented as:

$$Co(NO_3)_2.6H_2O + 2Al(NO_3)_3.9H_2O + 8NH_4OH + mH_2NCH_2COOH + (2.25m - 4.00)O_2 \rightarrow MAl_2O_4 + 2mCO_2 + (2.5m + 44)H_2O + (0.50m + 8)N_2 \quad (1)$$

An artificial neural network (ANN) is a computing system, consist-

* Corresponding author.
E-mail address: s.salem@che.uut.ac.ir (S. Salem).

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ing parallel layers with non-linear processing elements linked by weighted interconnections [10]. It comprises an input layer, an output layer and one or more hidden layers. The approach of neural computing is to train the network by experimental data with sets of input and desired output values and to generate a model. After well training, the model is capable to produce an approximated version of real system for given inputs.

The conventional techniques for optimization involve changing one variable at a time and maintaining the others constant. The effects of the interaction of variables cannot be considered in these methods. However, the experimental design method is a powerful technique for studying the effect of several parameters by altering the variables, simultaneously. Also, the optimization of self-combustion process for synthesis blue pigment by the conventional methods is extremely expensive when more than two variables are evaluated. In order to overcome this problem, the central composite design (CCD) can be applied to optimize the final product characteristics. The main use of this method is to reliably guarantee the dependence between the process factors and the outcome of the experiments, crystallite size, specific surface area, colorant behavior and crystallinity with the minimal number of experiments. Moreover, the behavior of each system as function of effective factors can be predicted through CCD.

According to the experimental results reported by Salem [11] the color of inorganic blue pigment is strongly related to the synthesis conditions. Regardless crystallinity and crystallite size, the colorant behavior is related to spinal phase transformation. The green powder is characterized by an inverse spinel structure whereas a normal spinel, corresponding to blue color, is produced at higher temperatures. It is very difficult to analyze the effects of operational factors on colorant behavior by conventional methods, simultaneously. Though, ANN is a flexible mathematical structure which is capable to identify complex nonlinear relationships between input and output data sets, the calibration model based on ANN is more unstable. On the other hands, the trained network model is not applicable for optimization of limited number of experimental data. In order to overcome this problem it seems that the combination of ANN and CCD is the appropriate method which can be considered to identify relationships between the inputs, synthesis conditions, and outputs, physico-chemical characteristics of nano-sized inorganic blue pigment. Therefore, this article presents a new approximation approach for estimation of blue powder characteristics using ANN and CCD techniques. Firstly, the work experimentally studies the relationship between the synthesis conditions and colorant behavior of powder by changing pH, fuel ratio and calcination temperature and measuring crystallite size, specific surface area, colorant behavior (b^*) and crystallinity by CCD thereafter, the obtained results were used for training a neural network model for a wider range of applicable operating conditions and the pigment characteristics. Finally, CCD methodology and the desirability function were used to better predict the optimal condition for synthesis nano-sized blue powder.

2. Experimental

2.1. Materials and synthesis method

All chemicals mentioned hereafter were of reagent grade and used as received. All water used in the experiments was previously de-ionized. Typical synthesis of the blue pigment has been described in our previous work [11]. A mixed solution of cobalt and aluminum nitrates (Sigma-Aldrich Company, purity > 99.0 wt%) was prepared by dissolving the salts in de-ionized water with a Co/Al molar ratio of 1:2. The obtained mixtures were divided to different parts to prepare the samples at different conditions. The appropriate amount of glycine (NH_2CH_2COOH, 99.5 wt.%, Sigma-Aldrich) was added to solution and the level of pH was controlled by nitric acid or ammonia solutions. The following ranges of variables were chosen in this work: $0.36 \le fuel/NO_3 \le 0.75$ and $2.5 \le pH \le 10.5$. All of the above operating ranges have been considerably extended in comparison with previous studies. Thus, more operating conditions, such as the very lean or rich fuel, can be covered. In addition, the authors have taken into consideration the state of self-combustion either as flame ignition or smoldering combustion. In order to achieve the viscous gels, the mixed solutions were heated on a hot plate kept at a steady temperature of 110 °C. The viscous precursors were then heated rapidly in a pre-heated furnace kept at 300 °C. The obtained voluminous and foamy ashes were easily crushed and were further calcined at different temperature, 600–1200 °C, over 1 h.

2.2. Pigment characterizations

X-ray diffraction measurements (XRD) were carried out on calcined powders using a conventional Bragg–Brentano diffractometer (X′PERT PRO; Philips, Eindhoven, The Netherlands) with Ni-filtered Cu-Kα radiation. The patterns were recorded in the 10–80° range with a scanning rate of 0.001 °s^{-1} and a step interval of 0.02°.

The quantitative X-ray analyses of the synthesized powders were determined by the Rietveld-RIR (Reference Intensity Ratio) method that allows both the crystalline and the amorphous fractions to be determined in a polyphase mixture. In fact, the scattering contribution of any amorphous component eventually existing in the sample is a part of the background and allows its quantification using an internal standard, suitably chosen, which is added in a known amount to the investigated mixture and treated as a mixture component itself. At the end of the Rietveld process, the refined phase fractions are converted into weight fractions and rescaled to the values of the original mixture by the ratio between the refined and the known amount of added standard. Whenever, an amorphous phase exists in the system, the values of the weight fractions are overestimated to satisfy the normalization condition. The percentage of the amorphous phase in the original mixture can be calculated directly from the weight of the internal standard. For all the samples, the powder diluted with 10 wt% corundum (NIST SRM 674a) as internal standard, was side loaded into an aluminum flat holder to minimize preferred orientation. Data were recorded in the 5–140 °2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld-RIR refinements, using GSAS and EXPGUI, were rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized. All the agreement indices ($R_{wp} < 2\%$ and $R_P < 1.5\%$) and the additional statistical indicators supplied by GSAS ($\chi^2 < 1.2$) are indicative of the very good quality of the refinements and testify the accuracy of the estimated weights.

The X-ray diffraction technique was used not only to identify the phases in the powders but also to evaluate the average crystal size by using Sherrer equation [9]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where D is the crystallite size, λ is the wavelength of the X-ray (Cu-Kα, 0.15418 nm), β is the full width at the half height of peak and θ is the diffraction angle of peak.

In order to observe the morphology of particles, the powders were dispersed into water, and then a drop of the suspension was put on a grid covered with carbon film for the observation by transmission electron microscopy (TEM, Philips CM30, Netherlands).

Brunauer–Emmett–Teller specific surface area of powders (BET, Gemini 2360 Apparatus, Micromeritics, Norcross, GA, USA) was determined by nitrogen adsorption apparatus after degassing the samples at 100 °C. Finally, the optical properties of calcined powders were studied by UV–vis spectroscopy (Lambda 19; Perkin Elmer, Shelton, CT) using the CIELab method to obtain b^* value.