Application of solid-state electrochemistry techniques to polyfunctional organic–inorganic hybrid materials: The Maya Blue problem

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Abstract

The time evolution of indigo plus palygorskite powdered mixtures during isothermal heating at different temperatures between 120 and 180 °C to form Maya Blue-type materials has been monitored by means of infrared spectrometry, diffuse reflectance spectrometry in the visible region and solid state electrochemical techniques. The kinetics of the formation process of such materials can be described in terms of two consecutive reactions, the first one consisting of the loss of zeolitic water of the palygorskite coupled with clay-indigo attachment and partial indigo to denhydroindigo oxidation. The palygorskite dehydration acts as a rate-determining step fitting to a 3D Avrami-Erofe’ev kinetics. The second step would consist of the diffusion-controlled penetration of the different dye molecules in the palygorskite channel system. This kinetic analysis is consistent with the view of Maya Blue-type materials as organic–inorganic hybrid polyfunctional nanostructured systems.

1. Introduction

Maya Blue (MB), a famous pigment widely used in murals, pottery, codices and sculptures by the ancient Mayas and other people in Mesoamerica has claimed considerable attention because of its singular ethnohistoric value since its discovery by Merwin in 1931 [1]. The interest paid to the chemistry of MB has been reinforced in recent years because of its unique combination of organic and inorganic components at the molecular level making it an antecedent of contemporary organic–inorganic hybrid materials [2]. The historical MB pigment is currently described as a hybrid organic–inorganic material resulting from the attachment of indigo, a blue dye extracted from leaves of Indigofera suffruticosa and other species, to the clay matrix of palygorskite, a fibrous phyllosilicate [3], but this idea, anticipated by Shepard [4], became controversial during years [5]. The structure of palygorskite, of ideal formula Si₈(Mg₂Al₂)O₂₅(OH)₃[(OH)₂₄H₂O]₄, can be described in terms of a multi-layer structure, each layer formed by an octahedral sheet surrounded by two tetrahedral sheets. The tetrahedra in each sheet present a periodic inversion of the apical oxygen, thus resulting in a discontinuous octahedral sheet which defines channels 6.4 × 3.7 Å sized. Such channels are filled by weakly bound, non-structural (zeolitic) water while magnesium and aluminium cations complete their coordination with tightly-bound water molecules (structural water).

In the last decade, the reasons for the peculiar hue and brightness of the pigment, the location of indigo molecules in the palygorskite framework and the nature of the indigo-palygorskite association have been subjects of debate. With regard to the placement of indigo in the palygorskite framework, it has been proposed that dye molecules could be externally adsorbed [6], enter into the palygorskite tunnels [4,7,8–12], remain on surface grooves [8,13], or guard the entrance of the clay tunnels [12,14]. The indigo-palygorskite association has been attributed to the formation of hydrogen bonds between C=O of indigo molecules and structural water molecules [9,11,15,16], with minor contribution of the hydrogen bonding between structural water molecules and N–H units of indigo [15]. Formation of hydrogen bonds between the carbonyl and amino groups of indigo with edge silanol units of the clay [14], bonding to Mg²⁺-coordinated water molecules in the inner surface of the tunnels or the direct bonding to the Mg²⁺ and/or exposed Al³⁺ ions at the edge of palygorskite tunnels [16–20] have been also proposed. The influence of Van der Waals interactions [10] and the possibility of head-to-tail interaction of indigo molecules in the channels of the clay [22] have also been commented.

In this context, we have used the voltammetry of microparticles (VMP) to acquire analytical information on genuine and synthetic MB specimens. VMP is a solid-state electrochemical methodology developed by Scholz et al. [23–26] which provides high sensitivity to detect dye-characteristic signals in the presence of (essentially)
electrochemically silent inorganic hosts. Synergistic combination of VMP with electron microscopy and spectroscopic techniques lead to establish that dehydroindigo, the oxidized form of indigo, accompanies this dye in the palygorskite framework [27]. The dehydroindigo/indigo ratio could be varied by varying the temperature achieved in the thermal treatment during MB preparation, thus yielding different hues for the resulting pigment [27,28]. In the archaeometric domain, VMP permitted to document the most ancient use of MB (Substructure IIC of Calakmul, Late Postclassical period) whereas chemometric analysis of Maya Blue samples from different sites suggested that the preparation procedure of Maya Blue probably changed along time following a ramified pattern [29,30]. More recently, it has been characterized the presence of ‘Maya Yellow’ analogs to MB [31] and characterized the use of indigo plus palygorskite plasters evidencing the use of such materials in non-ritual context [32]. The use of VMP also permitted to characterize the coexistence of different topological redox isomers of dye molecules and to model the possible distribution of such species in the palygroskite grains [33,34] thus providing a more complex view of the MB as a polyfunctional nanostructured material [34,35].

It should be noted that currently there is no disposal of direct historical sources that describe the mode of preparation of MB. A variety of methods have been proposed to prepare synthetic analogs to MB. These include embedding palygorskite with a solution of indoxyl acetate, vat dying and dry crushing of indigo with powdered palygorskite [6,36]. This last method is the most extensively used in recent literature, and involves mixing and grinding a mixture of palygorskite and indigo [8–21]. After the ingredients have been combined and dried, a heating process with variable duration (from few minutes to hours or days) and temperature range (90–100 °C, 150–190 °C, or even 250–300 °C) is applied, as recently reviewed [5]. For our purposes it is pertinent to remark that, although it has been reported the possibility of preparing MB-type materials without heating [14,37], in general, it is accepted that a heating step is required for removing zeolitic and, at least partly, structural water in order to prepare MB [5]. Although a variety of MB-type materials have been recently synthesized [38–40], it should be noted that the Mesoamerican people extracted indigo from leaves and twigs of Indigofera tinctoria and other plants by soaking it overnight in a suspension of slaked lime in water, followed by a prolonged mechanical aeration (batido) [27–30]. This means that the composition of genuine MB could differ significantly from contemporary indigo plus palygorskite (or sepiolite) specimens. To the best of our knowledge, however, no kinetic studies on MB formation have been performed.

In this report we describe the application of the VMP methodology to study the kinetics of the formation of synthetic MB-type materials from indigo plus palygorskite mixtures under aerobic heating at different temperatures. Complementary infrared and visible spectroscopic data were used in order to monitor the time evolution of these mixtures. Such data provides a view of the formation of MB as a result of successive solid-state reaction processes consistent with our previous description of MB as a polyfunctional material [35].

2. Experimental

MB-type specimens were prepared by finely grinding and mixing 1.0% (w/w) of synthetic indigo (Fluka) with Palygorskite collected from Yucatán site of Sacalum in an agate mortar and pestle during 60 min. The resulting specimens were separated in different portions and subjected to heating at different temperatures between 120 and 180 °C in furnace for times until 6 h. Aliquots of ca. 5 mg were successively separated in order to perform analyses at different times during the heating process. Blank experiments were performed with pristine palygorskite under identical conditions. In order to avoid complications associated to the use of organic solvents, the prepared specimens were tested, as usually [8–21], without Soxhlet extraction. This means that an undetermined amount of indigo could remain unattached to the clay. In order to ensure minimal excess of non-associated indigo, the proportion of indigo to palygorskite (1% w/w) was taken below the theoretical maximum of ca. 4% w/w [22].

For modified electrode preparation, ca. 0.5 mg of the samples were thoroughly powderred in an agate mortar and pestle and extended forming a spot of finely distributed material. The lower end of the graphite electrode was pressed over that spot of sample to obtain a sample-modified surface. Voltammetry of microparticules experiments were performed at sample-modified paraffin-imregnated graphite electrodes (PIGEs) using a CH 1660 equipment. A standard three-electrode arrangement was used with a platinum auxiliary electrode and a AgCl (3 M NaCl)/Ag reference electrode, separated from the bulk solution by a salt bridge, in a cell thermostated at 298 K. Aqueous 0.50 M acetic acid/sodium acetate at pH 4.75 was used as a supporting electrolyte. Three replicate voltammetric experiments were performed for each sample.

ATR–FTIR spectra of indigo-modified electrodes were obtained with a Bruker Vertex 70 Fourier-transform infrared spectrometer with an FR-DTGS (fast recovery deuterated triglicine sulfate) temperature-stabilised coated detector and an MKII Golden Gate Attenuated Total Reflectance (ATR) accessory. A total of 32 scans were collected at a resolution of 4 cm⁻¹ and the spectra were processed using the OPUS/IR software. Diffuse reflectance spectra were obtained with a Perkin-Elmar lambda35 spectrometer, slit width 1 nm, scan speed 480 nm/min.

3. Results and discussion

3.1. Electrochemical monitoring

Fig. 1a shows a typical voltammetric response for unheated MB-type specimens attached to PIGEs in contact with aqueous acetate buffer. As previously reported [27,28], using square wave voltammetry (SWV, a technique recommended for its inherently high sensitivity and reluctance to capacitive effects) two sharp peaks at ca. –300 (I) and +450 mV vs. AgCl/Ag (II) are recorded, superimposed
to broad background signals in the +350 to −100 mV range. Peaked background responses can be associated to quinone-type functionalities generated in the graphite surface [41,42]. In agreement with studies on the electrochemistry of solid indigo [43,44] and MB samples [27,28], the processes II and I correspond to essentially reversible proton-assisted electron transfer processes that can be represented, respectively, as the oxidation of indigo (H2IN) to dehydroindigo (DHI) and the reduction of indigo to leucoindigo (H4IN), as:

\[
\begin{align*}
H_2IN & \rightarrow DHI + 2H^+ + 2e^- + 2H_2O \\
H_2IN + 2H^+ + 2e^- & \rightarrow H_4IN
\end{align*}
\]

where \( i \) represents clay-associated species. Charge conservation is ensured in such processes by the coupled issue/entrance of protons and electrons in the solid. As previously described, the variation with temperature of peak potentials for such couples allows us to determine several thermochemical parameters for the dye attachment to palygorskite [27,28]. This voltammetry can be described on the basis of theoretical modeling for the electrochemistry of immobilized microparticles due to Bond, Lovric, Scholz, Oldham and co-workers [45–50]. In this model, the redox process initiates at the solid particle/electrode/electrolyte three-phase junction and extends to the solid particle via electron hopping between adjacent, immobile redox centers and ion transport through the solid.

Upon heating, the voltammetric response changes with variation of the relative height of peaks I and II and even the appearance of peak splitting [34]. In order to monitor the kinetics of the MB formation, the peak current (or peak area) ratio for the processes I and II, \( i_{p(II)}/i_{p(I)} \), and the processes II (or I) relative to the background peak \( i_p \), can be used. Such peak current ratios should depend on the electrochemical parameters (starting potential, potential step increment, square wave amplitude and frequency) and the composition of the specimen. Thus, the \( i_{p(II)}/i_{p(I)} \) ratio can be assumed to be representative of the dehydroindigo/indigo proportion in the specimen whereas the \( i_{p(II)}/i_{p(B)} \) ratio should be representative of the total dye concentration in the sample. An important aspect to be considered is that both peak current ratios become particularly sensitive to changes in the square wave frequency (vide infra).

There is another factor to be considered in order to properly analyze voltammetric data. As described in studies on zeolite-type systems, guest molecules/ions entrapped into microporous aluminosilicates can be located in different positions, thus defining different topological redox isomers [51,52] and can be differently distributed in the grains of the inorganic host [53]. The presence of different topological redox isomers could explain the broadening and splitting of voltammetric peaks while the variation of the peak current ratios with the square wave frequency can be associated to the distribution in depth of the dye molecules. The idea, based on the models on the electrochemistry of ion-insertion solids [45–50], is that in voltammetric experiments under diffusive conditions, the current/time response is controlled by the advance of the diffusion layer through the crystals [54]. As previously described [33,34], this means that at short times, the response will be representative of the composition of the solid in the more external layers of the palygorskite grains; while at longer times, the composition of more depth regions will be also influential on the electrochemical response. Accordingly, for a given set of electrochemical parameters, the \( i_{p(II)}/i_{p(I)} \) and \( i_{p(II)}/i_{p(B)} \) ratios would be representative of the dehydroindigo/indigo and total dye/palygorskite ratios averaged to the region of the palygorskite crystals attained by the diffusion front.

Fig. 2 compares the time variation of the \( i_{p(II)}/i_{p(I)} \) ratio for MB specimens treated at 130, 150 and 180 °C from SWVs at a frequency of 5 Hz. In the initial heating stage the \( i_{p(II)}/i_{p(I)} \) ratio increases with time until a maximum value is reached, then decreasing monotonically to an essentially time-independent value larger than the initial \( i_{p(II)}/i_{p(I)} \) ratio. A similar variation was observed for the \( i_{p(II)}/i_{p(B)} \) ratio (see Fig. 3) as well as for the corresponding peak area ratios. Upon prolonging the heating treatment for days, there are additional variations of the \( i_{p(II)}/i_{p(I)} \) ratio. These long-time variations, that could parallel those indicated for the spectral properties of MB-type specimens [55], will not be treated here. The time variation of both \( i_{p(II)}/i_{p(I)} \) and \( i_{p(II)}/i_{p(B)} \) ratios varied significantly with the square wave frequency, as can be seen in Fig. 3. Interestingly, the \( i_{p(II)}/i_{p(I)} \) ratio varies slightly with time at frequencies above 50 Hz whereas the

![Fig. 2](image-url)  
**Fig. 2.** Variation of the \( i_{p(II)}/i_{p(I)} \) ratio with time for MB-type specimens treated at 130, 150 and 180 °C. From SWVs of sample-modified PIGEs immersed into 0.50 M HAc/NaAc, pH 4.75. Potential scan initiated at −0.75 V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

![Fig. 3](image-url)  
**Fig. 3.** Time variation of the \( i_{p(II)}/i_{p(I)} \) and \( i_{p(II)}/i_{p(B)} \) ratios for MB-type specimens heated at 130 °C. From SWVs of sample-modified PIGEs immersed into 0.50 M HAc/NaAc, pH 4.75. Potential scan initiated at −0.75 V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV.
The differences between peak current ratio vs. time plots in Figs. 2 and 3 can be discussed on considering the different size of the photoactive regions of the palygorskite grains. On the basis of the value for the diffusion coefficient for electrons ($D_e$) and protons ($D_h$) previously calculated for MB [33,34], respectively $2 \times 10^{-9}$ and $2 \times 10^{-8}$ cm$^2$/s, the thickness of the electrochemically active region would be estimated as $d = (D \tau)^{1/2}$, $D$ being the diffusion coefficient of the rate-controlling diffusive process and $\tau$ the measurement time characteristic of the experiment. Under our experimental conditions, with $\tau$ values between 10 and 0.01 s, the values of $d$ would range between $10^{-4}$ and $10^{-6}$ cm.

If this in depth distribution of dye species is considered, voltammetric data in Figs. 2 and 3 can be rationalized on assuming that: (i) the formation of MB-type materials involve two consecutive reactions, as clearly suggested by the time variation of the $i_d(II)/i_d(I)$ ratio with time; (ii) along the entire process there is an apparent decrease of the total dye concentration in the external regions of the palygorskite grains, as suggested by the depletion of the $i_d(II)/i_d(B)$ ratio at high square wave frequencies.

3.2. VIS spectroscopy monitoring

Fig. 4 shows the normalized diffuse reflectance spectra for 1% indigo + palygorskite specimen treated at 180 ºC for times $t = 0$, 10 and 60 min. Such spectra are close to those repeatedly described in literature [8,27,29,34,35,55,56] and present spectral features attributable to indigo plus dehydroindigo. It should be noted, however, that, in view of the crushing preparation procedure used for the preparation of the material, a certain amount of indigo remains as solid indigo grains rather than as palygorskite-associated units. Accordingly, the ill-defined absorption maximum at 650–675 nm recorded for pristine indigo + palygorskite specimens, is followed by a relatively high absorption between 600 and 400 nm, consisting of a succession of shoulders with no defined absorption bands, almost identical to that obtained for solid indigo blanks where the absorption maximum is located at 650 nm. These spectra clearly differ from that of indigo dissolved in organic solvents, consisting of a main absorption band at ca. 600 nm [57–59]. Upon heating, the spectra of MB-type specimens present a fast decrease of the absorption in the 450–550 nm region relative to that at $t = 0$, attributable to the disappearance of solid indigo. In fact, the spectra of heated specimens show bands centered at 675, 525 and 440 nm. The first absorption maximum corresponds to palygorskite-associated indigo [55] whereas the last two wavelengths are coincident with the absorption maxima reported for dehydroindigo in solution (440 nm [55,56]) and in solid state (525 nm) [55]. Remarkably, the difference spectrum between spectral curves for $t = 0$ and $t = 10$ min, also shown in Fig. 4, presents the above dehydroindigo spectral features in the 400–550 nm region accompanied by a peaked difference at ca. 740 nm. This last could be associated to a certain indigo–indigo interaction, as suggested by studies in solution [60] and indigo plus sepiolite specimens [22]. In view of the similarity of the spectra of other indigoids [58,59], the formation of minority secondary indigoid products such as indirubin cannot be discarded, as previously noted [34].

In order to monitor the progress of the reactions operating in the heating process, the relationships between the absorbances at 440, 525 and 675 nm, $A_{440}/A_{675}$ and $A_{525}/A_{675}$, respectively, were taken. These absorbance ratios can be associated to the dehydroindigo/indigo ratio, both species being associated to the palygorskite framework, existing in the material. As in the case of voltammetric data, such absorbances would be representative of the average composition of the region of the palygorskite grains effectively contributing to the absorption spectrum under our experimental conditions. Fig. 5 shows the time variation of the $A_{525}/A_{675}$ ratio for MB-type specimens treated at 130, 150 and 180 ºC. Consistently with SWV data in Fig. 2, the above absorbance ratio decreases initially with time further increasing to a value different from that of the pristine material. Similar results were obtained using the $A_{440}/A_{675}$ ratio. Again, a reaction scheme involving two consecutive reactions appears to occur.

3.3. FTIR spectroscopy monitoring

The infrared spectra of MB and MB-type materials is dominated by the palygorskite absorption bands that appear in the 3700–3200, 1700–1600 and 1000–900 cm$^{-1}$ regions associated at the stretching and bending vibrations of OH groups (3614, 3542, 3373, 3273 cm$^{-1}$) and (1652, 1628 cm$^{-1}$), respectively, and the stretching vibrations of Si–O groups (971 cm$^{-1}$) [61].

![Fig. 4. Diffuse reflectance spectra for 1% (w/w) indigo + palygorskite specimen treated at 180 ºC for times $t = 0$, 10 and 60 min and difference spectrum between spectral curves for $t = 0$ and $t = 10$ min. The spectra are normalized to a common absorption maximum.](image)

![Fig. 5. Time variation of the $A_{525}/A_{675}$ ratio in the VIS spectra of 1% (w/w) indigo + palygorskite specimens treated at 130, 150 and 180 ºC.](image)
A spectral region of particular interest is that between 3200 and 3700 cm\(^{-1}\) where the stretching vibrations of O–H groups are found. IR spectrum of non-heated MB exhibits a sharp band at 3614 cm\(^{-1}\) ascribed to the OH-stretching mode in Al\(_2\)–OH groups. As can be seen in Fig. 6, upon heating, this band shifts toward higher frequencies (3623 cm\(^{-1}\)) and increases intensity. In contrast, temperature rise in MB sample causes the red-shift to 3512 cm\(^{-1}\) of the IR band that appears at 3542 cm\(^{-1}\) and the appearance of a new feature at 3500 cm\(^{-1}\) forming a doublet with the previous one. Following literature [62], this band can be assigned to stretching vibrations of OH groups of coordinated water in combination with the stretching modes in Al–Mg–OH, Fe–Mg–OH and Fe–OH groups. A monotonic decrease in intensity of this band with time is also observed during the heating treatment, which is consistent with a partial loss of coordinated water molecules [63].

Bands at 3373 and 3273 cm\(^{-1}\) have been ascribed to stretching vibrations of OH groups associated with coordinated and zeolitic water. The broad band at 3261 cm\(^{-1}\) ascribed to the stretching vibrations of N–H groups, which is found in pristine indigo, is probably contributing to this last band that appears at 3273 cm\(^{-1}\) in the unheated MB. Heating of MB samples results in the significant and monotonic decrease of intensity with time of these two bands, which is associated with the loss of zeolitic and coordinated water. Interestingly, a red-shift to 3215 cm\(^{-1}\) is observed in the weak IR band that remains during the heating process, which is ascribed to the stretching vibrations of N–H groups. This last result is consistent with the idea that palygorskite/indigo interaction has taken place during the thermal treatment.

For our purposes, the relevant point to emphasize is that the evolution of bands at 3614 and 3542–3500 cm\(^{-1}\), in the following, OH1, OH2, should be representative of the loss of zeolitic water and structural water, respectively. The variation of the area ratio of such bands, A(OH1)/A(OH2), with time is depicted in Fig. 7.

Remarkably, blank experiments on palygorskite reproduced essentially the above spectral features but the dehydration process is clearly faster than for indigo plus palygorskite specimens at all temperatures. This means that in MB-type specimens the presence of indigo decelerates significantly the loss of zeolitic water presumably by blocking the channel access. This result is in agreement with the fact that in rehydration experiments MB-type specimens do not recuperate their initial degree of hydration [12]. These features indicate that the amount of indigo relative to palygorskite and the type of grinding are crucial with regard to the synthesis of genuine MB-type materials and support the use of pristine indigo plus palygorskite mixtures with no rinsing nor Soxhlet extraction.

![Fig. 6. ATR–FTIR spectra of indigo plus palygorskite specimens treated at 150 °C for different times.](image)

**Fig. 6.** ATR–FTIR spectra of indigo plus palygorskite specimens treated at 150 °C for different times.

**Fig. 7.** Time variation of the A(OH1)/A(OH2) ratio in the ATR–FTIR spectra of 1% (w/w) indigo + palygorskite specimens treated at 130, 150 and 180 °C.

On comparing experimental data in Figs. 2, 3, 5 and 7, one can observe that the time variation of the different experimental parameters is quite similar, at each temperature, for the initial reaction process. However, whereas voltammetric and visible spectral data clearly show a second reaction step, infrared spectra only show, apparently, the first reaction stage. This can be explained by considering that such infrared data correspond to palygorskite-associated water so that only the dehydration process is monitored using this technique.

### 3.4. Reaction kinetics

In principle, the above experimental data could be used to quantitatively analyze the kinetics of the reaction process on the basis of disposable models describing solid state kinetics [64,65]. In such models, the advance of the reaction, for the case of a single interconversion reaction, is expressed in terms of the conversion fraction, \( \alpha \) (0 < \( \alpha \) < 1), defined as the molar fraction of obtained product. Then, the kinetics of the reaction process can be obtained by testing different integrated reactions of the type \( \dot{x} = k \tau \), where \( k \) is the rate constant for the process.

Application of this scheme is particularly difficult in the studied system by three main reasons. The first one is that the composition of the system and the reaction kinetics would vary significantly with the depth so that no homogeneous reaction models would be applied. The second is that at least two consecutive reactions occur, so that available models for single-reaction kinetics are not directly usable. The third problem deals with the characteristics of the measured signals and will be detailed in the Appendix.

For our purposes, the relevant point to emphasize is that, under favorable conditions, one can estimate an apparent conversion fraction, \( \alpha_{\text{app}} \), from experimental data in Figs. 2, 5 and 7 using the values of the \( i_i(II)/i_i(I) \), \( A_{440}/A_{675} \), \( A_{525}/A_{675} \), and \( A(OH1)/A(OH2) \) ratios (generalized as \( \xi_2/\xi_1 \)) using the relationship (see Appendix):

\[
\alpha_{\text{app}} = \frac{\xi_2/\xi_1}{\xi_2/\xi_1} - \frac{\xi_2/\xi_1}{\xi_2/\xi_1}
\]

(3)

In this equation, \( \xi_2/\xi_1 \) represent the signal ratio at a time \( t \).

\( \xi_2/\xi_1 \) is the initial value (\( t = 0 \)) of this ratio, and \( \xi_2/\xi_1 \) the limiting value of this quantity, corresponding to the conditions where it can be assumed a complete conversion of the reagent into the reaction product.
Application of this approach produced the more satisfactory results for infrared data. As can be seen in Fig. 8, use of the $x_{\text{app}}$ values calculated from $A(\text{OH1})/A(\text{OH2})$ ratios in Fig. 7, leads to an excellent linear fit for:

$$g(x_{\text{app}}) = \left[ -\ln(1-x_{\text{app}}) \right]^{1/3} = k_{\text{app}} \cdot t \quad (4)$$

an integrated kinetic equation that corresponds to Avrami-Erofe’ev model for random nucleation with 3D growth as described, for instance, for the dehydration of $\text{MoO}_3\cdot2\text{H}_2\text{O}$, an example of topotactic reaction where the lattice structure is maintained [68].

Using the values of the apparent rate constants calculated at different temperatures ($T$), one obtains linear Arrhenius plots of $\ln k_{\text{app}}$ vs. $1/T$. The value of the apparent activation energy, $E_{\text{app}}$, was of $56.3 \pm 0.5 \text{kJ/mol}$. Remarkably, this value is close to the average binding energy of zeolitic water calculated in optimized Maya Blue molecular models ($\approx 66.5 \text{kJ/mol}$) [11,15].

Application of this scheme to voltammetric and visible spectroscopy data is complicated by the difficulty in properly defining the $\varphi^2/\xi^4$ ratio because the initial reaction process is followed by consecutive reaction. In spite of this, kinetic analyses of such data were close to that from ATR–FTIR spectroscopy. Again, Avrami-Erofe’ev model for random nucleation with 3D growth applies. The values of the apparent activation energies, which are similar to that determined from ATR–FTIR data, are listed in Table 1.

The second reaction could in principle be treated as a single reaction assuming that the first process is completed before the second progress advances significantly. Using this rough approach, the kinetics of that process can be described in terms of the time interval $t - t_1$ since the first reaction is completed, $t_1$. Then, plots of $g(x_{\text{app}})$ vs. $t - t_1$ can be used in order to test possible kinetic models for the second reaction. Although these data are non-conclusive, it appears that the second reaction could be attributed to diffusion-controlled reactions. Thus, VIS spectral data can be satisfactorily fitted to a Jander-type 3D diffusive model ($g(x_{\text{app}}) = [1-(1-x_{\text{app}})^{1/3}]^2 = k(t-t_1)$) as can be seen in Fig. 9, where $g(x_{\text{app}})$ vs. $t - t_1$ plots extracted from diffuse reflectance spectra data at $150^\circ C$ for this model are compared with those for 2D and 3D Avrami-Erofe’ev and 2D diffusive models. In the case of SWV data, however, the 2D diffusive model ($g(x_{\text{app}}) = (1-x_{\text{app}})\ln(1-x_{\text{app}}) + x_{\text{app}} = k(t-t_1)$) provides the best fit to experimental data (see Fig. 10), but other models also approach to linear $g(x_{\text{app}})$ vs. time representations.

The above kinetic results allow to draw a reaction scheme based on:

a) The reaction is initiated by the loss of zeolitic (and possibly partly of coordinated water) coupled with the attachment of indigo to the palygorskite matrix and the partial oxidation of indigo to dehydroindigo.

b) The loss of palygorskite zeolitic water would be rate-determining following Avrami-Erofe’ev kinetics with 3D growth. The apparent activation energy for this process, $56.3 \pm 0.5 \text{kJ/mol}$, is close, as previously noted, to the average binding energy of zeolitic water calculated in optimized Maya Blue molecular models ($\approx 66.5 \text{kJ/mol}$) [11,15] but clearly far from the calculated lattice energy of indigo ($133 \text{kJ/mol}$, [67]). This means that the palygorskite dehydration rather than the disintegration of the indigo grains to yield palygorskite-attached dye molecules would be the rate-controlling process. In this scheme, the palygorskite-associated indigo oxidation to palygorskite-associated dehydroindigo should be relatively fast, in agreement with the large spontaneity for this process derived from previous thermodynamic calculations [27,28].

c) A second reaction step occurs involving the relatively slow penetration of indigo plus dehydroindigo in the palygorskite framework. This process would be controlled by diffusion and would determine the apparent depletion of the dyes in the external region of the palygorskite grains.

d) This reaction scheme is consistent with the previously discussed consideration of MB as a polyfunctional nanostructured material where different topological isomers of different dye molecules are attached to the palygorskite framework [33–35]. The overall two-step process could be tentatively explained on assuming that there is a first dye attachment to the tunnel entrances (possibly with participation of silanol units) followed by a second, more depth attachment within the channels (now directed by bonding to Mg$^{2+}$-coordinated water molecules).

This scheme, however, should be taken with caution. In particular, several aspects can be underlined:

i) The measured signal ratios are representative of averaged quantities for the composition of the system that should be regarded as a multicomponent one. In particular, the indigo plus palygorskite mixtures contain undetermined amounts of indigo crystals, thus contributing to the measured signals.

ii) The measured signals are representative of the composition of the system at a given reaction time averaged in the region of the palygorskite grains that become responsive to the applied (optical, electrochemical) external input. For instance, visible spectra and electrochemical data in Figs. 2 and 4 suggest that the dehydroindigo/indigo ratio first increases and subsequently decreases. These results can be rationalized on considering that the ability of dehydroindigo to penetrate into the palygorskite channels should be larger than that of indigo by reasons of molecular flexibility (indigo possesses C=C double bond with introduces a significant structural rigidity). This is consistent with previous results [33,34] indicating that the dehydroindigo/indigo ratio is maximum not in the surface but at a certain nominal depth in the palygorskite crystals.

iii) Experiments in this report are restricted to relatively short times. At longer times, subsequent variations in the composition of the system occur. Similarly, re-hydration of MB-type materials under exposure to ambient conditions yields
4. Conclusions

The kinetics of the formation of Maya Blue-type materials by heating indigo (1% w/w) plus palygorskite powdered mixtures at temperatures between 120 and 180 °C and reaction times until 6 h can be monitored by infrared and visible spectroscopies and solid state electrochemistry. Using several simplifying assumptions, different signal ratios allow us to quantify the relative amount of different species thus allowing to monitor the advance of the reaction.

The reported data suggest that the formation of the Maya Blue-type materials occurs through at least two successive reactions each one consisting, probably, of parallel processes. The first step can be described in terms of the simultaneous loss of zeolitic water and the concomitant attachment of indigo molecules to the clay framework coupled with the partial indigo-to-dehydroindigo oxidation, the dehydration of the clay being the rate-determining process following a 3D Avrami-Erofe’ev kinetics. The second step would consist of the penetration of the different dye molecules in the palygorskite channel system, this process being under diffuse control. The overall reaction scheme becomes consistent with the view of Maya Blue-type materials as organic–inorganic hybrid polyfunctional nanostructured systems.

Although further research is needed to properly elucidate the structure and mechanism of formation of Maya Blue-type systems, synergistic use of available techniques, in particular the voltammetry of microparticles, can provide significant information on this matter.

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Appendix Analysis. of reaction kinetics

In the most single case, one can assume that a single interconversion reaction occurs between two forms, A, B, that contribute differently to the values of two signals, $\zeta_1$, $\zeta_2$. This situation can be applied (vide infra) to the absorbances and peak areas of visible or infrared absorption bands so that while A is increasingly converted into B, the signal $\zeta_1$ is enhanced while the signal $\zeta_2$ is depleted. It should be emphasized that, in the absence of an adequate standard for calibration, the kinetic study must be based in the variation of the signal ratio ($\zeta_2/\zeta_1$), rather than in the individual values of the signals.

We further assume a linear response of both signals relative to the concentrations/amounts of A and B. As is usual in solid state kinetics, we can represent the advance of the interconversion reaction in terms of the conversion fraction, $\alpha$ ($0 < \alpha < 1$), defined as the molar fraction of obtained product and assuming that at the end of the reaction the reactant is quantitatively converted into the product. Accordingly, one can write:

$$\zeta_1 = b_{1A}(1 - \alpha) + b_{1B}\alpha$$

(A.1)

$$\zeta_2 = b_{2A}(1 - \alpha) + b_{2B}\alpha$$

(A.2)

Here, and $b_{1A}$, $b_{2A}$, $b_{1B}$, $b_{2B}$, represent the specific coefficients of response of each species relative to the signals 1 and 2. Inserting the initial ($\zeta_1^0$, $\zeta_2^0$) and limiting values of the signals ($\zeta_1^t$, $\zeta_2^t$), one can write:
\[ \frac{a_1}{b_1} = \frac{b_2}{a_2} ; \frac{c_1}{b_1} = \frac{b_2}{c_2} ; \frac{c_2}{a_2} = \frac{a_1}{c_1} \]

Combining the above expressions one can arrive to the relationship:

\[ \alpha = \frac{(c_2/c_1) - (c_2/c'_1)}{(c_2/c_1) + (c_2/c'_1)} \left[ 1 - \frac{c_2/c'_1}{c_2/c'_1} \right] \]

(A.3)

In favorable cases where the \( c_2/c_1 \) ratio approaches to one; i.e., when one of the signals remains essentially unchanged along the experiment, the above equation reduces to:

\[ \alpha = \frac{(c_2/c'_1) - (c_2/c'_1)}{(c_2/c'_1) + (c_2/c'_1)} \]

(A.4)

Accordingly, the values of the conversion factor \( \alpha \) can be calculated from the experimental ones measured for the signals, \( c_1 \), \( c_2 \), and then used to elucidate the reaction kinetics. Interestingly, since only the \( c_2/c_1 \) signal ratio is used, this method is applicable to experimental situations where it is difficult to control the amount of sample used for measuring the signals, just occurring in the experimental techniques in this study.

References
