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Kinetic study of the intercalation process of dimethylsulfoxide in kaolinite

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Abstract

A kinetic study of the intercalation reaction of dimethylsulfoxide (DMSO) into the layers of kaolinite was carried out. Several kaolinite-DMSO mixtures were analyzed at four temperatures (60, 50, 45 and 40 °C). Structural characterization was done by X-Ray diffraction (XRD). The intercalation reaction was followed by XRD of the kaolinite-DMSO intercalates at different reaction times and temperatures. A kinetic analysis of the process was performed considering a two-step simple mechanism for consecutive reactions: ingress of DMSO molecules into the kaolinite galleries and subsequent rotation of DMSO molecules. Finally, the activation energies of the two steps proposed for the global intercalation process were estimated.

Keywords: kaolinite; DMSO; intercalation; kinetic study.

1. Introduction

Intercalation of clays, such as kaolinite ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ or $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), has been of considerable interest to develop materials with different rheological, surface and structural properties. The intercalates of layered silicates are of great interest not only for their potential use as catalyst, catalysts supports, selective sorbents, ion exchange fillers, etc...[1, 2], but also for their application as precursors of further intercalation processes with polymer chains to yield exfoliated or intercalated polymer composite materials [3-5].

Since kaolinite does not present interlayer ions to be exchanged, only a limited number of molecules with high dipole moment can be intercalated directly in the interlayer spaces of kaolinite. Dimethylsulfoxide (DMSO) has been proven to be very efficient to increase the interlayer distance of kaolinite [5, 6, 7] by its easy intercalation due to its high dipole moment ($\mu=3.9\text{D}$) [7]. Basal distances and surface properties of kaolinite-DMSO are essential for intercalation reactions with other organic molecules by substitution reactions. For example, kaolinite-DMSO intercalate has been used as an intermediate in the formation of hydrated kaolinites [8]. Thus, the main objective of this work is to understand the process of intercalation of DMSO and its kinetics to be able to optimize processing conditions in the future. The process was investigated following structural changes by means of X-ray diffraction at different temperatures.

Materials and methods

2. Experimental

2.1. Materials

The kaolin used in this work (Caobar SA) is highly crystalline (>98%) and its chemical composition is as follows (all units are in wt %): 49% SiO₂; 36.5% Al₂O₃. The L.O.I (loss on ignition) and the amount of impurities correspond to the 14.5% remaining. The amount of impurities is not significant, coming from the presence of quartz, mica and smectites [9] and its composition is almost the same as in pure kaolinite. HPLC grade dimethylsulfoxide (DMSO) with 99.8 % of purity was purchased from Scharlau and used without any further purification.

2.2. Preparation of the kaolinite-dimethylsulfoxide intercalation compounds, K-DMSO

K-DMSO intercalation compounds were prepared in a round-bottomed glass flask, by adding 420 mL of DMSO and 39 mL of distilled water to 63 g of kaolinite. The mixtures were heated at four temperatures (40, 45, 50 and 60 °C). The temperature range used for the kinetic study was selected based on the flash point of DMSO, 85 °C, ensuring therefore safe processing conditions.

2.3. Techniques

Structural analysis was done with a diffractometer Philips X'Pert with diffraction and anti-scattering slits of 1°, Ni-filtered Cu radiation ($K\alpha = 1.54056 \text{ \AA}$), a voltage of 40kV and a current of 40mA. The diffraction angle, 2θ , was from 3° to 30°.

To monitor the intercalation reaction, 8-mL aliquots of the K-DMSO suspensions were taken at different reaction times. Samples were centrifuged for 15 minutes at 100 rpm, the sediments were vacuum-dried at room temperature and stored to be analyzed by XRD.

FTIR spectra in the medium range ($4000\text{-}400\text{ cm}^{-1}$) were recorded in a Perkin Elmer Spectrum GX spectrometer, using 10 averaged scans at 2 cm^{-1} resolution. The samples were prepared as KBr disks filled with 0.5 % by mass of the powders to be analyzed.

3. Results and discussion

3.1.- Characterization of the kaolinite-DMSO intercalate

X-Ray diffraction patterns of the kaolinite and the K-DMSO intercalate obtained at 40°C as a function of intercalation time, are presented in Figure 1. Similar changes in the XRD patterns were observed for other temperatures. As can be observed, the original basal spacing of the kaolinite increases from 7.1 \AA ($2\theta = 12.4^\circ$) to 11.22 \AA ($2\theta = 7.9^\circ$) in the kaolinite-DMSO intercalation compound. This result is in accordance with those obtained for similar intercalates [2, 3]. The small peak at $2\theta = 12.3^\circ$, equivalent to a basal spacing of 7.1 \AA observed for the sample labeled as K-DMSO 71h (i.e., K-DMSO after 71 hours of reaction time), corresponds to the remains of kaolinite in this sample.

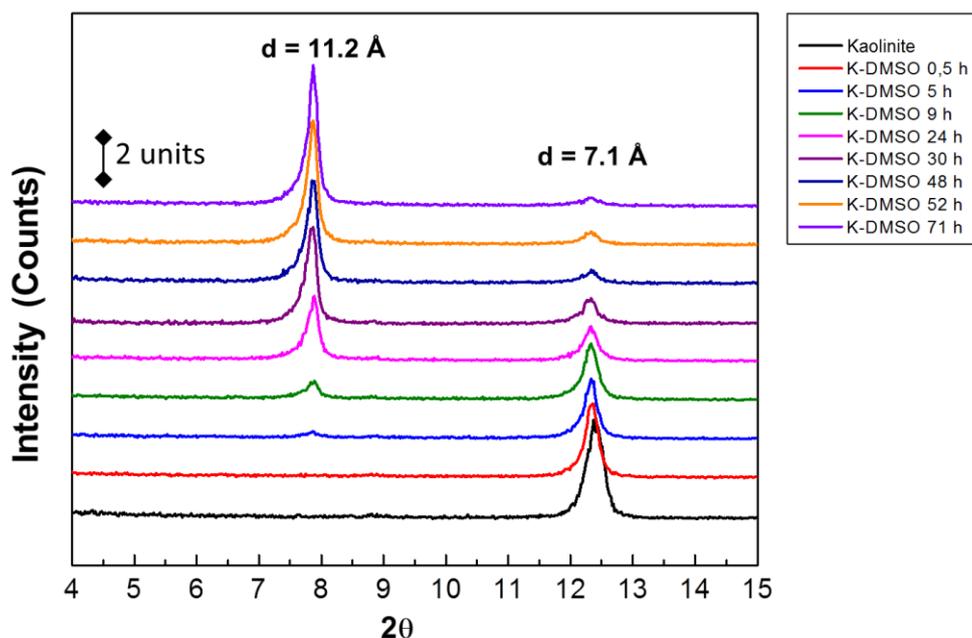


Figure 1

Figure 1. XRD patterns of kaolinite and kaolinite-DMSO intercalate obtained at 40°C as a function of the intercalation time. (The diffraction maximum of quartz ($2\theta = 26.75^\circ$) was used as internal standard). The color code shows the diffractograms obtained at different intercalation times (time given in hours (h)).

In Figure 2, FTIR spectra of the kaolinite, the K-DMSO intercalate (obtained at 40°C) and DMSO are shown. The spectral region where OH-stretching bands appear ($4000\text{--}3000\text{ cm}^{-1}$) was considered. The bands assigned to the O-H stretching of the kaolinite internal surface hydroxyls, centered at 3697 , 3672 and 3652 cm^{-1} , are significantly affected by the presence of DMSO. By contrast, the band centered at 3621 cm^{-1} assigned to the stretching vibrations of kaolinite inner hydroxyl, is not affected by this reaction since, it is located in the bulk [2].

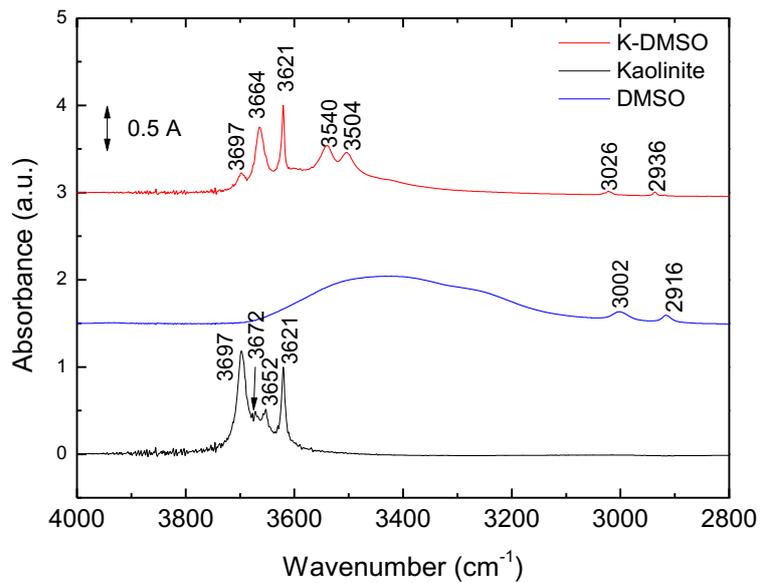


Figure 2

Figure 2. FTIR spectra of the kaolinite, kaolinite-DMSO intercalate (obtained at 40°C) and DMSO.

Three new bands were observed with the intercalation of DMSO centered at 3664, 3540 and 3504 cm^{-1} . These changes reflect a reduction of the electrostatic attractive forces between the kaolinite layers, due to the creation of new, stronger hydrogen interactions between the DMSO and the internal surface hydroxyls of the layers, inducing therefore their separation [10]. Additionally, two more bands in the region of the C-H vibrations, at 3023 and 2936 cm^{-1} were observed, evidencing that the CH-stretching of the DMSO methyl groups is affected by the entrance of the DMSO molecules into the interlayer spaces of kaolinite structure [11].

3.2.- Kinetics of the intercalation process

The intercalation of the DMSO between the kaolinite layers is evidenced by the progressive reduction of the kaolinite original diffraction peak (at 7.1Å) and the enhancement of the K-DMSO intercalate diffraction peak (at 11.2Å) as reaction time increases (Figure 1). The appearance of this new diffraction peak shows the increase of the kaolinite basal distance due to the intercalation of the DMSO between the layers. From the normalized areas of the kaolinite and kaolinite-DMSO intercalate diffraction peaks at different reaction times; kinetic plots like those represented in Figure 3 were obtained according to equation (1):

$$r_{1i} = \frac{A_{Ki}}{A_{Ki} + A_{KDi}} \quad r_{2i} = \frac{A_{KDi}}{A_{Ki} + A_{KDi}} \quad (1)$$

where A_{Ki} A_{KDi} are the diffraction peak areas at a reaction time “i” of the kaolinite and kaolinite-DMSO intercalate respectively (as calculated from XRD patterns shown in Figure 1) and r_{1i} and r_{2i} are the conversion associated to the intercalation process in terms of the disappearance of kaolinite and the appearance of the kaolinite-DMSO intercalate respectively.

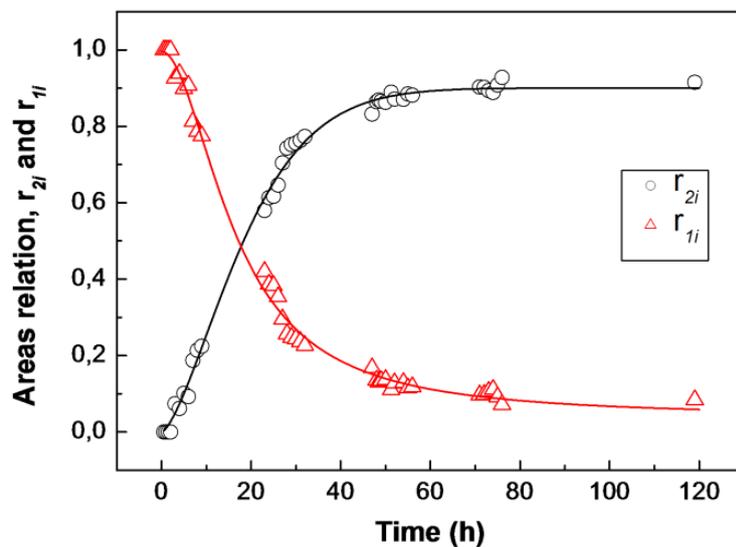


Figure 3

Figure 3. Kinetic curves obtained from the r_{1i} and r_{2i} values for the DMSO intercalation reaction in kaolinite at 40°C.

To explain these results the following model was proposed. First, the DMSO molecules enter through the kaolinite galleries with the most favorable configuration, that means, lie on position (see scheme of Figure 4) for which, in one dimension, z direction for instance; it acquires a minimum thickness of about 2 Å (estimated by computational methods, [1]). In this case, a complex without favorable interactions is formed, complex B. Then, in a second step, DMSO molecules might rotate inside the galleries due to favorable interactions (> S=O and –OH) to form the hydrogen bonds above mentioned, to yield the final kaolinite-DMSO intercalate. In fact, if DMSO rotates so that the oxygen could interact with kaolinite internal surface hydroxyls, the thickness throughout the z direction would be about 4 Å (estimated by computational methods). This interpretation matches with the increase of the original basal spacing (from 7.2 Å

to 11.2 Å). The last configuration for the DMSO in the galleries is based on that model proposed by other authors with the aid of experimental data and simulation [8]. The most stable complex would be formed after this rotation, leading to a structure where the S=O group will be oriented towards the octahedral layer yielding to hydrogen bonding interactions with the hydroxyl groups of the surface [6, 8]. This increase in the basal spacing of 4 Å due to the intercalation of DMSO molecules may be attributed to the formation of a monolayer complex [12].

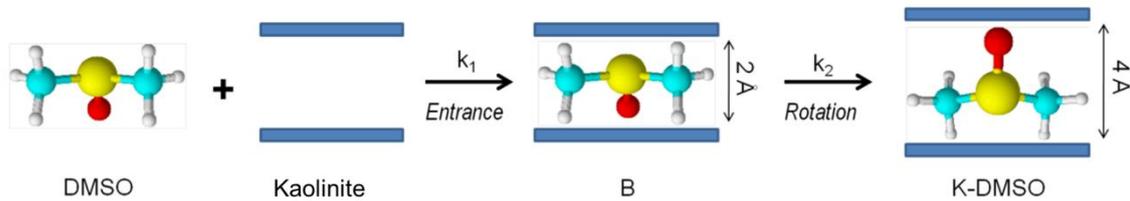
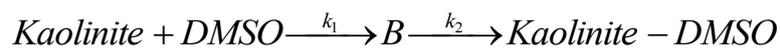


Figure 4

Figure 4. Scheme of the model proposed to explain the mechanism of the DMSO intercalation in kaolinite.

From this model, a mechanism for the intercalation process based on consecutive reactions might be considered for which the conversion can be expressed in terms of the following sequence:



where B represents K-DMSO without rotation of the DMSO. The initial normalized amount of kaolinite ($r_{1i,0}$) should be equal to 1; therefore $r_{1i,0} = 1$. The initial amount of B intermediate (B_0) as well as the initial normalized amount of the K-DMSO intercalate

($r_{2i,0}$) should be zero, therefore $r_{2i0} = 0$. The variations of r_{1i} , B_i and r_{2i} with time are given by [13] (Note that the subscript 'i' refers to the concentration of each of the species at a given time):

$$\frac{dr_{1i}}{dt} = -k_1 r_{1i} \quad (2)$$

$$\frac{dB}{dt} = k_1 \cdot r_{1i} - k_2 \cdot B_i \quad (3)$$

$$\frac{dr_{2i}}{dt} = k_2 \cdot B_i \quad (4)$$

Separating variables and integrating:

$$r_{1i} = r_{1i0} \cdot e^{-k_1 \cdot t} \quad (5)$$

Substituting (5) in (3) it is obtained (6)

$$\frac{dB}{dt} = k_1 \cdot r_{1i0} \cdot e^{-k_1 \cdot t} - k_2 \cdot B_i \quad (6)$$

Solving this differential equation it is obtained (7)

$$B = r_{1i0} \cdot \frac{k_1}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (7)$$

Finally the expression for r_{2i} is obtained from simple mass balance:

$$r_{1i} + B_i + r_{2i} = r_{1i0} = 1 \quad (8)$$

$$r_{2i} = 1 - r_{1i} - B_i \quad (9)$$

Substituting (7) and (5) in the equation (9) it is obtained:

$$r_{2i} = 1 + \frac{1}{k_1 - k_2} \cdot (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \quad (10)$$

The curves obtained from the r_{2i} values at the different temperatures are represented in Figure 5a. The solid lines in Figure 5a represent the non-linear curve fitting using the

function represented by the equation (10). It is shown that the model based on consecutive reactions fits the experimental data quite well. From the non-linear square fit, the kinetic constants k_1 and k_2 can be obtained as fitting parameters (Table 1).

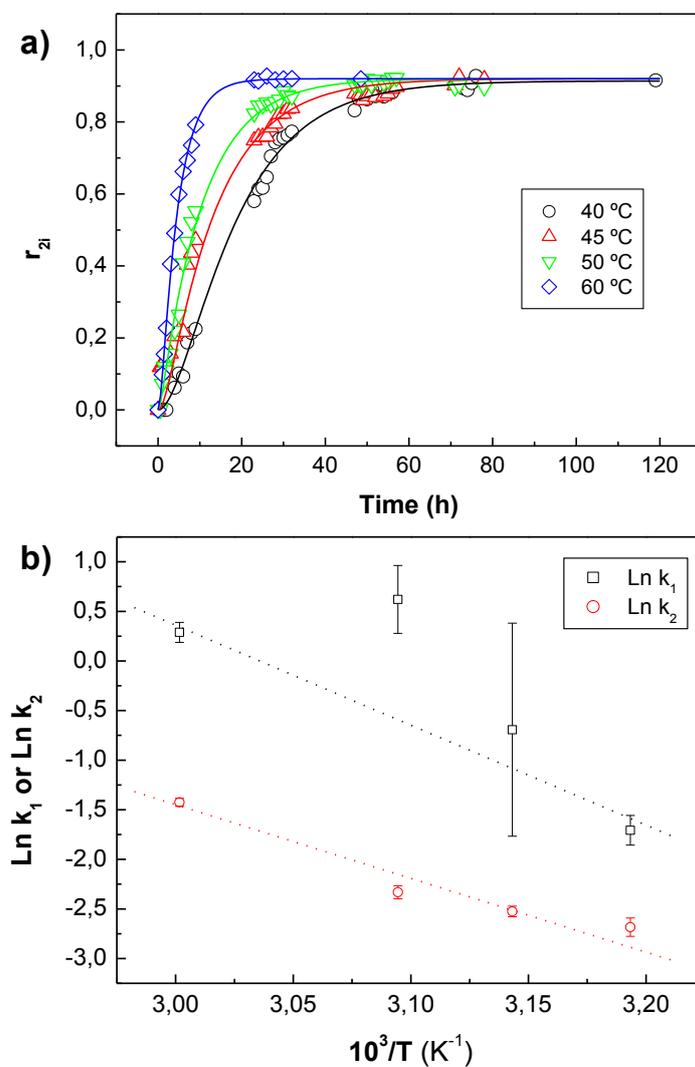


Figure 5

Figure 5. (a) Kinetic curves obtained from the r_{2i} values, of the DMSO intercalation reaction in kaolinite at 40°C (circles), 45°C (upright triangles), 50°C (downright triangles) and 60°C (diamond); (b) Arrhenius plots of the rate constants (k_1 , k_2).

Table 1.- Values of rate constants for the two steps considered in the modeled intercalation process.

T (°C)	k₁ (h⁻¹)	k₂ (h⁻¹)
40	0.18 ± 0.03	0.068 ± 0.006
45	0.50 ± 0.33	0.080 ± 0.004
50	1.86 ± 0.54	0.097 ± 0.006
60	1.33 ± 0.13	0.241 ± 0.009

Assuming an Arrhenius-like behavior for both kinetic constants ($k = Ae^{-E_a/RT}$), where A is a pre-exponential factor, E_a the activation energy, T the absolute temperature and R the gas constant, the activation energies associated to the process of real intercalation of DMSO (E_{a1}) and subsequent rotation of the DMSO molecules (E_{a2}) may be estimated. Plotting the natural logarithm of the kinetic constants (k_1, k_2) vs. the inverse of temperature, the activation energy can be obtained from the slope.

From the corresponding fitting the following activation energy values were calculated: $E_{a1} = 84 \pm 20$ kJ/mol; $E_{a2} = 62 \pm 8$ kJ/mol. As expected the first process or the real intercalation process is energetically more hindered. The value of the activation energy obtained for the first step assigned to the entrance of the DMSO is in good agreement with the relatively high activation energies obtained for the thermal decomposition of the kaolinite-DMSO intercalates [2, 14, 15].

4. Conclusions

The intercalation process of DMSO into the galleries of kaolinite was successfully monitored by XRD. A kinetic analysis of the intercalation process was carried out considering a mechanism of simultaneous reactions based on a model in which the intercalation process occurs in two steps: ingress of DMSO into the kaolinite galleries and subsequent rotation of the DMSO molecules to finally form a most stable structure where the S=O group interacts with the –OH of the inner-surface of the kaolinite by the formation of strong hydrogen bonds.

Acknowledgements

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