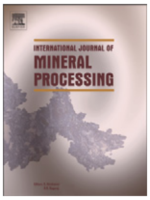
International Journal of Mineral Processing 144 (2015) 70–74

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro



# Kinetic study of the intercalation process of dimethylsulfoxide in kaolinite

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ARTICLE INFO

*Article history:*
Received 24 April 2014
Received in revised form 15 August 2014
Accepted 5 October 2015
Available online 9 October 2015

*Keywords:*
Kaolinite
DMSO
Intercalation
Kinetic study

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.

## 1. Introduction

Intercalation of clays, such as kaolinite ($2SiO_2.Al_2O_3.2H_2O$ or $Al_2Si_2O_5(OH)_4$), 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. (Michalková et al., 2002; Cordeiro Lopes et al., 2003), but also for their application as precursors of further intercalation processes with polymer chains to yield exfoliated or intercalated polymer composite materials (Cabedo et al., 2004; Komori et al., 1999; Gardolinski et al., 2000).

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 (Gardolinski et al., 2000; Olejnik et al., 1968; Zhang and Xu, 2007) by its easy intercalation due to its high dipole moment ($\mu = 3.9$ D) (Zhang and Xu, 2007). 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 (Thompson and Cuff, 1985). 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.

## 2. Materials and methods

### 2.1. Experimental

### 2.1.1. 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% $SiO_2$; 36.5% $Al_2O_3$. 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 (Galán-Huertos and Martín-Vivaldi, 1972) 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.

### 2.1.2. 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.

### 2.1.3. Techniques

Structural analysis was done with a diffractometer Philips X'Pert with diffraction and anti-scattering slits of 1°, Ni-filtered Cu radiation

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http://dx.doi.org/10.1016/j.minpro.2015.10.001
0301-7516/

(K$\alpha$ = 1.54056 Å), a voltage of 40 kV and a current of 40 mA. 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 min at 100 rpm, the sediments were vacuum-dried at room temperature and stored to be analyzed by XRD.

FTIR spectra in the medium range (4000–400 $cm^{-1}$) 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 Fig. 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 Å (2θ = 12.4°) to 11.22 Å (2θ = 7.9°) in the kaolinite–DMSO intercalation compound. This result is in accordance with those obtained for similar intercalates (Cordeiro Lopes et al., 2003; Cabedo et al., 2004). The small peak at 2θ = 12.3°, equivalent to a basal spacing of 7.1 Å observed for the sample labeled as K–DMSO 71 h (i.e., K–DMSO after 71 h of reaction time), corresponds to the remains of kaolinite in this sample.

In Fig. 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 (4000–3000 $cm^{-1}$) 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 (Cordeiro Lopes et al., 2003).

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 (Jacobs and Sterch, 2000). 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 (Frost et al., 1999).

### 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 7.1 Å) and the enhancement of the K–DMSO intercalate diffraction peak (at 11.2 Å) as reaction time increases (Fig. 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 Fig. 3 were obtained according to Eq. (1):

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

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 Fig. 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.

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 Fig. 4) for which, in one dimension, z direction for instance; it acquires a minimum thickness of about 2 Å (estimated by computational methods). 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

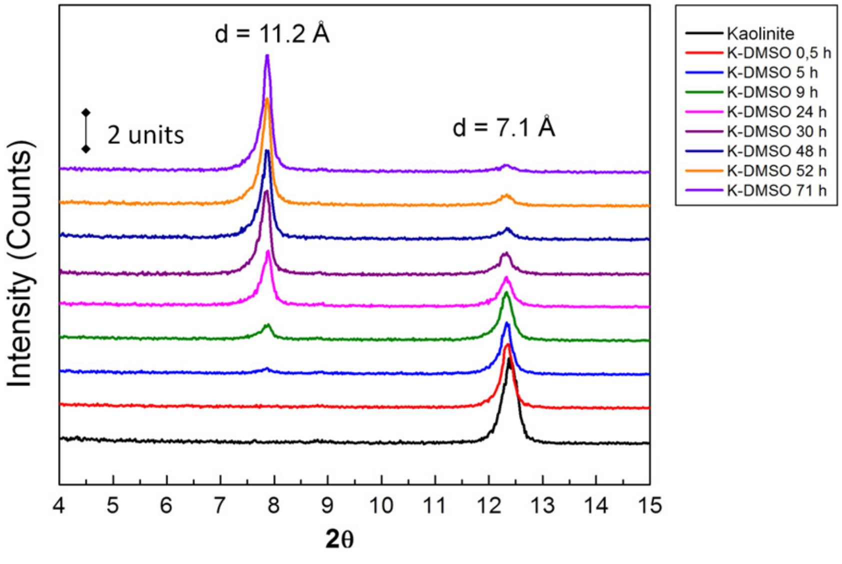

**Fig. 1.** XRD patterns of kaolinite and kaolinite–DMSO intercalate obtained at 40 °C as a function of the intercalation time (the diffraction maximum of quartz (2θ = 26.75°) was used as internal standard). The color code shows the diffractograms obtained at different intercalation times (time given in hours (h)).