OBSERVATION BY SCANNING ELECTRON MICROSCOPY OF GLOBULAR PARTICLES OF CALCIUM-MONTMORILLONITE AND OF MONTMORILLONITE EXCHANGED WITH METHYL VILOLOGEN OR TRIS (BIPYRIDYL) RUTHENIUM (II)

Key Words—Globular particles, Methyl viologen, Montmorillonite, SEM, Tris (bipyridyl) ruthenium (II).

The intercalation of organic (Barrer, 1989a, 1989b, Lao et al., 1991), organometallic (Giannelis et al., 1988) or inorganic (Yamagishi, 1987) species into the interlamellar spaces of smectites is a subject of great interest. It is known that the nature of the intercalated cation has a dramatic effect on the size of smectite particles in aqueous suspension. For example, the number of layers per tactoid increases from one to three for Na+ to 6–8 for Ca2+-montmorillonite (Ca-M) (van Olphen, 1977; Schramm and Kwak, 1982). Exchanging Na+ with Ca2+ causes an increase of the aggregation of the clay particles. An even more dramatic effect on the clay configuration is expected if Na+ or Ca2+ are exchanged for a large inorganic cationic complex such as tris (bipyridyl) ruthenium (II) [Ru(bpy)32+] (Ghosh and Bard, 1984; Villemure, 1991) or for an aromatic organic dication, such as methyl viologen (MV2+) (Villemure et al., 1986, 1991). We have shown previously (Villemure et al., 1987) that this process takes place for each interlamellar space, so that, in the case of incompletely exchanged Ca-M, Ru(bpy)32+ or MV2+-exchanged layers coexist with non exchanged layers.

We report in this Note the study by scanning electron microscopy (SEM) of the configuration of isolated montmorillonite particles. When part or all of the clay’s interlamellar calcium cations were replaced by Ru(bpy)32+ or MV2+, large globular aggregates were observed. Such large globular aggregates could also be observed in the case of calcium montmorillonite when long evaporation times were used.

RESULTS AND DISCUSSION

Two types of clay particles coexisting on the same sample, the typical corn-flake structure of a smectite and large globular aggregates, were observed on the scanning electron micrograph of Ca(II)-montmorillonite partially exchanged for Ru(bpy)32+ or for methyl viologen. Figures 1A and 1B give a close look at almost spherical aggregates for 50% Ru(bpy)32+—(Figure 1A) and 50% MV2+—(Figure 1B) exchanged Ca(II)-montmorillonite. The diameters of the particles shown are respectively 5 μm (MV2+) and 10 μm [Ru(bpy)32+].

Some aggregation was expected by intercalating Ru(bpy)32+ or MV2+ into the montmorillonite interlamellar spaces (Villemure and Bard, 1990). However, the observation of large globular aggregates after evaporation of dilute aqueous suspensions of smectites has no precedent in the literature, to the best of our knowledge. It is known that the use of spray-drying preparation methods could result in the formation of quasi-spherical hydroxy-Al-montmorillonite particles (Tsvetkov et al., 1990). In this study, the samples were prepared by evaporation, a method which is not ex-
Figure 1. SEM micrographs of montmorillonite partially exchanged with tris (2,2'-bipyridyl) ruthenium (II) [Ru(bpy)$_3^{2+}$] and methyl viologen (MV$_2^{2+}$). (A) 50% of the exchangeable calcium cations have been replaced with Ru(bpy)$_3^{2+}$. (B) 50% of the exchangeable calcium cations have been replaced with MV$_2^{2+}$.

Contrary to the case of the exchanged montmorillonites, one could not detect any large aggregate when Ca-M suspensions were evaporated under the same conditions as those described above (Figure 2A). Large, globular, aggregates (Figure 2B) formed only if the evaporation time was long (two days or more).

The effect of the organic or complex cations on the aggregation process can be interpreted in the following manner:

1. Tactoids (typically 8 lamellae) are present in the suspension of Ca-M (van Olphen, 1977).
2. In the presence of MV$_2^{2+}$ or Ru(bpy)$_3^{2+}$, the calcium cations are exchanged. In this process, one can logically expect that the external sites of the tactoids will be exchanged first.
(3) The presence of MV$^{2+}$ or Ru(bpy)$_3^{2+}$ on the external sites of the tactoids is expected to favour the tactoid aggregation to larger aggregates. The aggregates observed in Figure 1 are composed of several thousands of the original Ca(II) tactoids.

(4) When long evaporation times are used, globular aggregates are also found in the Ca-M samples. This observation suggests that the aggregation process is a normal evolution of the particle morphology in concentrating smectite aqueous suspensions. The process is accelerated in the presence of organic or complex cations such as MV$^{2+}$ or Ru(bpy)$_3^{2+}$.

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