

LETTER

A comment on “Mechano-chemical effects on surface properties and molybdate exchange on hydrotalcite”, *Clay Minerals* (2009) 44, 311–317

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Bonifacio-Martínez *et al.* (2009) recently reported a study of the mechano-chemical effects on the surface properties and molybdate exchange on hydrotalcite. These authors reported that milling of hydrotalcite leads to a sharp decrease in the specific surface area and a simultaneous decrease in the particle size and pore volume, which they attributed to compaction/shrinkage. The samples had been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive (EDX) and Fourier transform infrared (FTIR) spectroscopy. The ability of the samples to intercalate molybdate after calcinations at 500°C by the so-called reconstruction method was also tested.

However, the results reported in that paper lack proper interpretation on scientific grounds, and the reconstruction process with simultaneous incorporation of molybdate in the interlayer of the hydrotalcite phase seems to have failed; I will try to demonstrate why in this letter.

The first (at low angle) XRD line recorded for these solids around 2θ values close to 10° is usually ascribed to diffraction by (003) planes. Spacing for

this line corresponds to the sum of the width of the brucite-like layers, $\sim 4.8 \text{ \AA}$ (Drezdson, 1988), and the gallery height, which depends on the size and orientation of the intercalated species. Carbonate is located with its molecular plane parallel to the brucite-like layers, and the corresponding gallery height result of $\sim 3.0 \text{ \AA}$ provides a space for the (003) planes close to 7.8 \AA .

However, when carbonate is substituted by anions with a different molecular size, changes in the spacing of the (003) planes are expected. Quite surprisingly, the position of this peak in patterns (a), (b), (d) and (e) included in their Fig. 1 are coincident, suggesting that the spacing is the same in all four cases, a rather surprising result bearing in mind that the thermochemical diameter of the molybdate anions, MoO_4^{2-} , is 5.08 \AA (Waddington, 1959). This leads to an expected spacing of 9.88 \AA , which corresponds, for Cu- $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$), to $2\theta = 9.88^\circ$, while in Fig. 1 this first peak is always recorded well above 10° . We can assume that MoO_4^{2-} is the most probable species in solution under the experimental conditions used for the reconstruction process (a basic pH, provided by calcined hydrotalcite and the Na_2MoO_4 solution), although the formation of species with different polymerization degrees, depending on the pH, is well known for oxomolybdate species. In other words, it is difficult

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to accept that molybdate has been hosted in the interlayer space of the reconstructed hydroxalcite. We could assume that the molybdate anion is somewhat constrained within the interlayer space, distorting from tetrahedral to a near-to-square-planar geometry, thus giving rise to a smaller width, thereby allowing hosting without any detectable swelling of the layers from the value measured for the carbonate sample. However, in such a case, the change in molecular symmetry of molybdate anions would give rise to splitting of some of the IR bands of molybdate, and this has not been observed. As the position of this XRD band is recorded in almost the same position for the exchanged sample, I assume that hydroxyl groups have probably become intercalated, instead of molybdate, giving rise to the phase known as meixnerite, leading to a spacing very similar to that of a carbonate-containing phase, as the width of both species (hydroxyl and carbonate) is that of the oxide anion.

Further hints can be drawn from the EDX results, shown in their figures 3 and 4. From the weight content for C, Mg and Al deduced from EDX displayed in figure 3 for sample HT_m-CO₃, and the atomic masses of these elements, the C/Al molar ratio is close to one (0.91). This is also unexpected, as such a ratio should be 0.5 for a carbonate-hydroxalcite if carbonate is located exclusively in the interlayer, balancing the positive charge due to the isomorphic Mg/Al substitution in the brucite-like layers. In other words, the sample contains more carbonate (almost 80% more) than that required for balancing the positive charge due to the Mg/Al isomorphous substitution.

Again, the EDX results for sample HT_m-MoO₄ are difficult to understand. The sample contains a large amount of carbonate; the molar C/Al ratio is close to 1.38, even greater than for the parent compound. In both cases it is possible that carbonate is formed through adsorption of atmospheric CO₂, forming surface-adsorbed carbonate species. No mention is given in the manuscript about caution being taken to avoid the presence of atmospheric CO₂ during synthesis and post-synthesis.

It should be also noted that the IR spectrum of sample HT_m shows a weak shoulder around 3000 cm⁻¹ (not discussed in the text) which is usually ascribed to the O-H stretching mode of hydroxyl groups hydrogen-bonded to interlayer carbonate anions. This shoulder is absent in the

spectrum of sample HT_m-MoO₄, suggesting the presence of hydroxyl groups in the interlayer, partially (or totally) substituting carbonate species (thus accounting for the lower intensities of the IR carbonate bands mentioned by the authors), and that the existing carbonate species are probably adsorbed on the external surface of the crystallites during handling of the samples. Moreover, the Mo content for sample HT_m-MoO₄ indicates an Al/Mo molar ratio close to 50, while it should be 2 if only molybdate species in the interlayer are responsible for balancing of the positive charge; in other words, the amount of molybdate in the sample is negligible. As the authors state, from the EDX analysis results (see page 314), molybdate anions are assumed to be “adsorbed” on the grain surfaces contrary to the statement in the title, which mentions “exchange”.

In other words, neither the chemical analysis data nor the XRD patterns provide any convincing evidence for the presence of molybdate in the interlayer of the hydroxalcite sample following a carbonate/molybdate exchange process.

Results concerning the effect of milling are also surprising. Usually one would expect a decrease in the average particle size and an increase in the specific surface area as the samples are milled for longer periods of time. If milling is prolonged, then aggregation of the particles should be observed because of the increase in the surface energy of the samples. Unfortunately, in the current case, only one milling time (2 h) has been used, giving rise to a sharp decrease in particle size (from 21 to 8 nm), specific surface area (from 97 to 6 m² g⁻¹) and total pore volume (from 0.41 to 0.01 cm³ g⁻¹). Despite the smaller particle size, a larger specific surface area would be expected. Similar trends are observed for the corresponding samples calcined for 5 h at 500°C in air.

If one assumes spherical, compact, non-porous, particles, the relationship (specific surface area) × (specific gravity) × (particle diameter) = 6 should be maintained. From the particle-size values included in their table 1 for sample HT_c and taking a specific gravity of 2 g cm⁻³ for hydroxalcite, the calculated specific surface area would be ~150 m² g⁻¹, ~50% larger than the value reported. The surface area would be even larger if the sample is mesoporous. In other words, these results confirm that the particle size in table 1 actually should correspond to “crystallite size” and that the primary crystallites should be aggregated, forming larger particles.

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