

## Supplementary Materials

### Local Structure Determination of Zn-smectite

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## FTIR spectroscopy

All the synthetic samples showed water-related bands located at 3400–3600  $\text{cm}^{-1}$  (very broad) and 1640  $\text{cm}^{-1}$  (sharp), corresponding to the stretching and bending vibrations of the adsorbed and interlayer water, respectively (Figure S1). Si–O–Si stretching and Si–O–M (M=Zn, Mg) bending vibrations are located at 994–1017  $\text{cm}^{-1}$  and 445–467  $\text{cm}^{-1}$ , respectively (Figure S1) as proposed previously (Kloprogge and Frost, 2000). Some studies also attributed the band at 994  $\text{cm}^{-1}$  to the –OH bending frequencies of  $\text{Zn}_2\text{–OH}$ . The  $\text{M}_2\text{–OH}$  deformation band at 789  $\text{cm}^{-1}$ , corresponding to the 6-coordinated cations in the octahedral sheet, slightly shifted to a lower frequency, in accordance with those of M–OH bending vibrations with the increase of Zn concentration. The absorption of ca. 665  $\text{cm}^{-1}$  could be attributed to the deformation of  $\text{M}_3\text{–OH}$ . These bands were narrower and sharper for S-Zn4 but relatively broader and lower for the samples with coexisting  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  in octahedral sites. No band ca. 695  $\text{cm}^{-1}$ , corresponding to  $\text{M}_2\text{Al–OH}$  deformation, could be seen, confirming that no Al occupied the octahedral sheet, similar to synthetic saponite-like minerals as has been reported previously (Petit and Righi, 2008, Zhang *et al.*, 2016). The presence of the above bands implied that even when octahedral cations were insufficient, the cations were still distributed in such a way so as to abide by the trioctahedral rule locally.

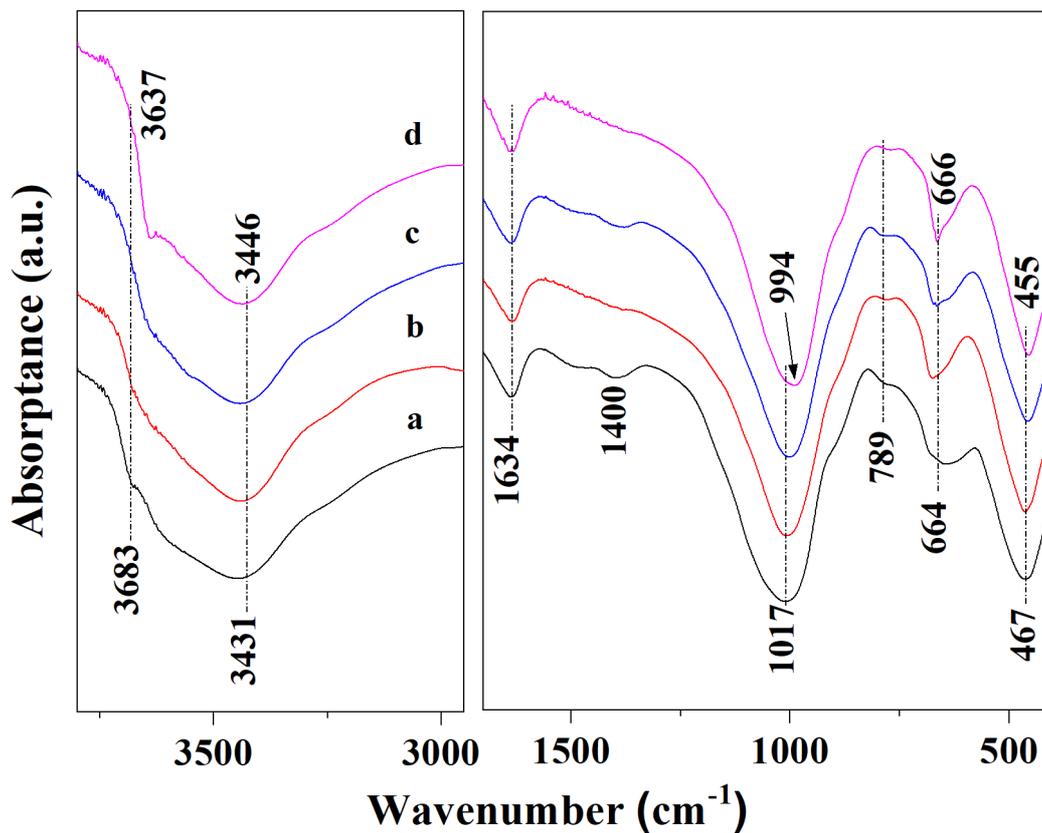


Figure S1 FTIR spectra of synthesized samples: a. S-Zn1, b. S-Zn2, c. S-Zn3, and d. S-Zn4.

The structural  $\text{-OH}$  vibration frequency of the sample reflects octahedral cation coordination and cation substitution environments (Tao *et al.*, 2016). The bands at 3683 and 3637  $\text{cm}^{-1}$  are assigned to  $\text{Mg}_3\text{-OH}$  and  $\text{Zn}_3\text{-OH}$  stretching vibrations (Figure S1a). With an increase in the Zn/Mg ratio, the frequency of the Si-O-M bending vibration in the tetrahedral sheet downshifted from 467 to 455  $\text{cm}^{-1}$ . This resulted apparently from the higher electronegativity of Zn (1.65) than that of Mg (1.31), indicating that Zn was much more feasible to occupy the octahedral sites.