Identification of Reactive Sites in Calcined Kaolinite and Montmorillonite from a Combination of Chemical Methods and Solid-State NMR Spectroscopy

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Abstract. Kaolinite and montmorillonite have been examined at heating temperatures from 500–1100 °C. For each sample, the degrees of dissolution in acidic and basic media have been determined, using a 1.0 vol.% HF solution and an 8.0 M NaOH solution, respectively. The solid residues from these experiments are analyzed along with the calcined starting materials by ^{27}Al and ^{29}Si MAS NMR. A comparison of these spectra, before and after dissolution, enables a clear differentiation of the silicon and aluminium environments that are present in each sample, providing direct information about the aluminate and silicate species which are dissolved under basic and acidic conditions, i.e., identification of the active sites in calcined clays. Moreover, this procedure facilitates the structural assignment of the different silicon environments observed by ^{29}Si NMR, shedding light on the dehydroxylation process and on the structural changes that occur for kaolinite and montmorillonite upon heat treatment.

1 Introduction

The use of calcined clays as supplementary cementitious materials (SCMs) may provide a valuable contribution to the reduction in CO_2 emissions associated with cement production since calcined clays can be produced at significantly lower temperatures and do not involve a decarbonation reaction. Thermal activation of clay minerals involves dehydroxylation of the aluminate and silicate sheets which introduces a progressive degree of disorder in the heated material. ^{27}Al and ^{29}Si MAS NMR spectroscopy have the advantage that amorphous and crystalline phases are detected in an equal and unambiguous manner and thus, these tools are ideal in studies of the thermal activation of both pure and impure clay minerals [1–3]. In addition, ^{27}Al and ^{29}Si MAS NMR can provide the degrees of reaction for the principal cement and calcined clay phases which can be utilized in thermodynamic modeling of the hydrate phase assemblages in these blends [4]. Moreover, valuable structural information is also achieved about the calcium-silicate-hydrate phase (C-S-H) [5], formed as the principal hydration product in Portland cement – calcined clay blends.

A common approach to evaluate the reactivity of SCMs is the Chapelle's test which probes the pozzolanic reactivity by measuring the amount consumed $Ca(OH)_2$ in $Ca(OH)_2$ – SCM suspensions. For these experiments, additional information can be

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achieved by studying the solid residues by ^{29}Si and ^{27}Al MAS NMR, which allows identification of the formed hydration products and the remains of SCM in a semi-quantitative manner. In addition to this approach, the present work employs a combination of chemical methods and solid-state NMR to identify the reactive species in clay minerals calcined at different temperatures. Although both kaolinite and montmorillonite have been examined in this work, the paper presents only data observed for kaolinite.

2 Experimental

Premium-grade kaolinite (Imerys Minerals, UK), containing a small impurity of quartz (~2.6 wt%), has been heat-treated in air for 2 h at temperatures between 500 °C and 1100 °C in intervals of 50°C. For each heated sample, one gram was subjected to chemical attack in 100.0 mL HF (1.0 vol.%) at room temperature under stirring for five hours. The same experimental procedure was carried out for a basic medium using 8.0 M NaOH for selected samples, however, the temperature for these experiments was set at 80 ± 2 °C to further facilitate dissolution. After the exposure, the liquid and solid residue was separated by filtration and the residue was rinsed with distilled water until a neutral pH was reached. The mass of the solubilized clay was calculated from the weight difference between the starting material and the dried residue. The Si/Al ratio of the dissolved phase in HF was determined from the Si and Al contents in the filtrate, obtained with a Spectro Arcos ICP-AES instrument. The ^{29}Si MAS NMR spectra were recorded on a Varian INOVA-300 spectrometer using a home-built CP/MAS probe for 5 mm o.d. zirconia (PSZ) rotors and a spinning speed of $\nu_R = 10.0$ kHz. The ^{27}Al MAS NMR spectra were recorded on a Varian Direct-Drive VNMR-600 spectrometer, using a homebuilt CP/MAS probe for 4 mm o.d. zirconia rotors and a spinning speed of $\nu_R = 13.0$ kHz.

3 Results and Discussion

The fraction of dissolved material for the heated kaolinite samples in the 1.0 vol.% HF solution is shown in Fig. 1a as a function of the heating temperature. The fraction of dissolved material increases with temperature until 550 °C where nearly complete dehydroxylation of kaolinite is expected to have occurred. Only minor variations are observed in the range 500 – 900 °C, in accordance with the presence of the metastable metakaolin phase, and it decreases from 900–1100 °C, the latter associated with the transformation of metakaolin into mullite and a spinel-type phase. The decrease in reactivity from 900–1100 °C is accompanied by an increase of the Si/Al molar ratio for the dissolved phase (Fig. 1b), which is ascribed to the formation of the mullite and aluminate-rich spinel-type phases. These phases exhibit a higher degree of structural order than metakaolin and thus, the dissolution of aluminate species from these phases is expected to be lower. Kaolinite has a Si/Al molar ratio of 1.0 whereas slightly lower ratios are observed for the dissolved phase of kaolinite from 500–900 °C. This indicates a preferential dissolution of aluminate species and thereby a slightly incongruent dissolution of silicon and aluminium.

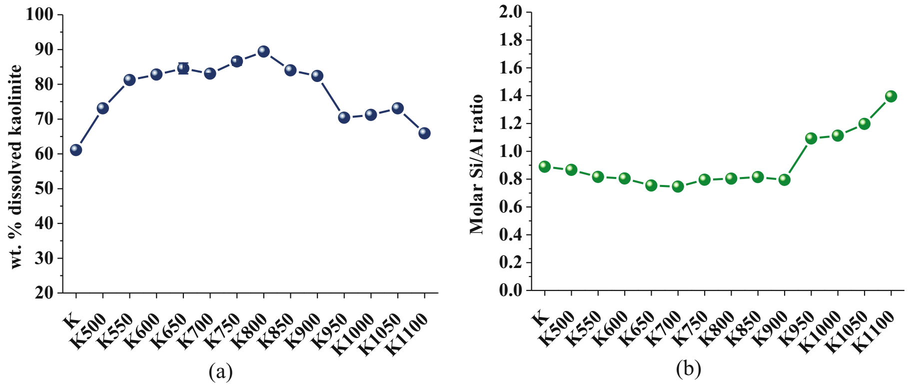

Fig. 1. (a) Fraction (wt%) of dissolved material in the 1.0 vol.% HF solution as a function of the heating temperature. (b) The Si/Al molar ratio of the dissolved phase determined by ICP-AES analyses of the filtrates.

^{29}Si MAS NMR spectra of selected heated kaolinite samples and their corresponding residues from the HF experiments are shown in Fig. 2. The deconvolutions of the individual spectra have been performed using the same number of resonances and only minor variations of their chemical shifts and linewidths. Comparison of the spectra and deconvolutions for the heat-treated samples and their residues reveals that the different silicon sites in the clay material exhibit different reactivities. The contribution to the spectra from metakaolin is simulated by four resonances (Fig. 2) located at −82, −84, −94.5 and −101 ppm and by three resonances at lower chemical shifts than quartz at −108, −115 and −121 ppm. The chemical shifts of the latter three peaks strongly suggest that they originate from Q^4(0Al) silicon sites. From the deconvolutions of the ^{29}Si MAS NMR spectra of the residues, it is apparent that the three Q^4(0Al) peaks give a major contribution to the spectra, demonstrating that these fully condensed SiO_4 units are less reactive than the other components of the metakaolin structure. Moreover, for the samples heated at 950 °C and above, a narrow resonance around −112 ppm appears in the spectra which reflect a partial crystallization of silica and thereby the formation of a less-reactive phase, in agreement with the data in Fig. 2.

^{27}Al MAS NMR spectra of the samples heated at 550 and 800 °C and their residues from the HF solutions are shown in Fig. 3. The spectra contain overlapping centerbands from Al in tetrahedral, fivefold and octahedral coordination. The peak from five-fold coordinated Al (35 ppm) is almost absent in the spectra of the residues, demonstrating that the pentahedral Al sites are highly reactive. In addition, the residues contain at least two different AlO_4 sites, which may also be present in the samples before acid attack, and a rather narrow AlO_6 resonance that may arise from hydroxylated surface sites.

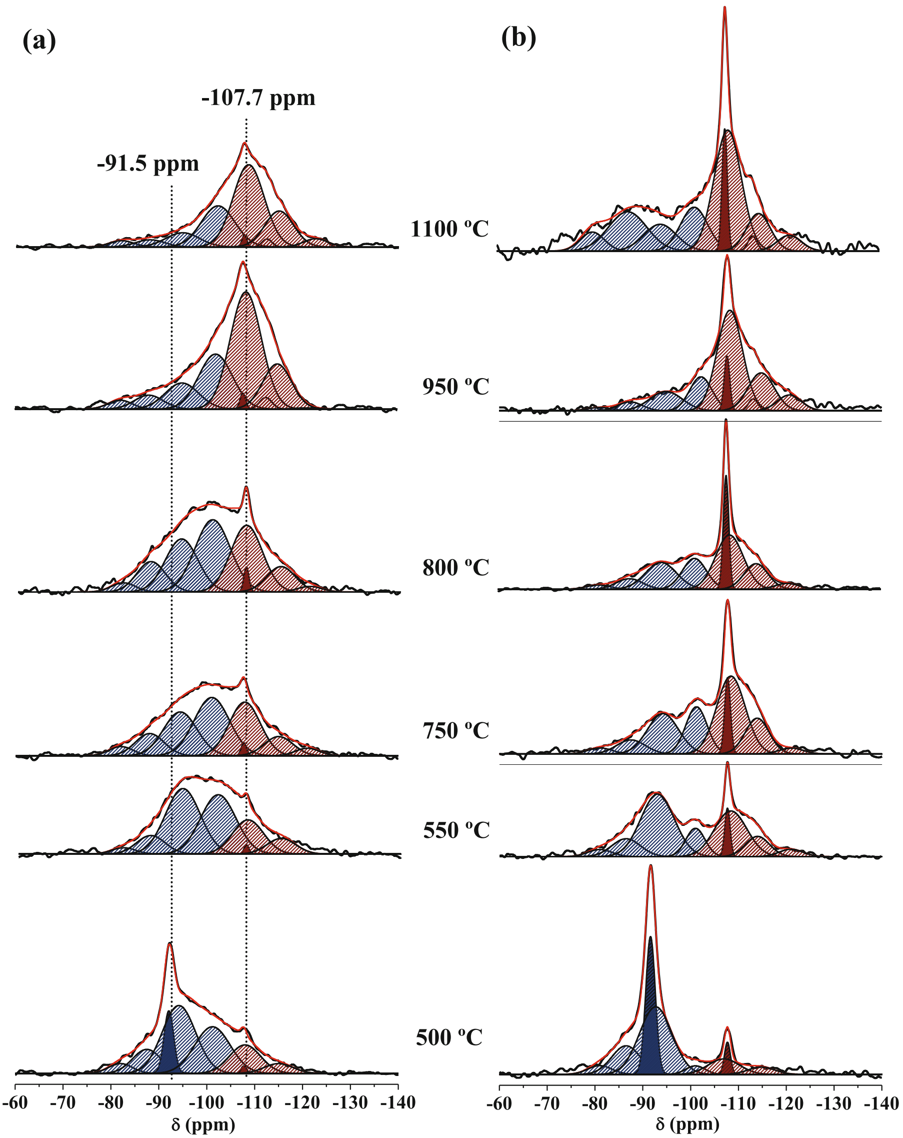

Fig. 2. ^{29}Si MAS NMR spectra (7.1 T, $\nu_R = 10.0$ kHz) of (a) selected heat-treated kaolinite samples and (b) their corresponding residues from the HF acid-attack experiments. The quartz impurity is observed at −107.7 ppm.

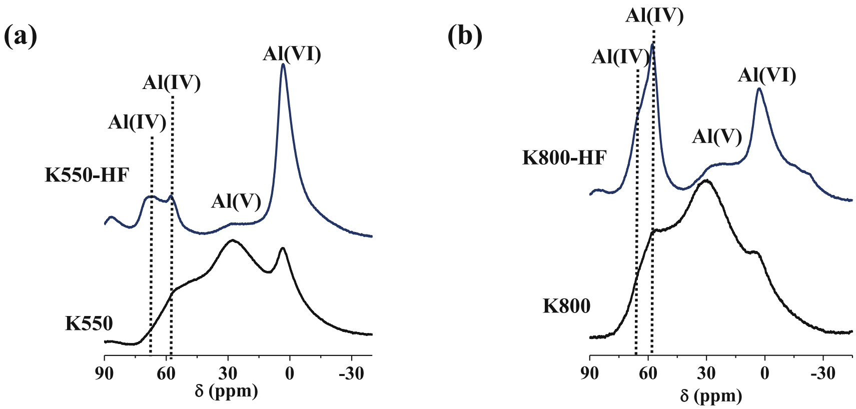

Fig. 3. ^{27}Al MAS NMR spectra (14.1 T, $\nu_R = 13.0$ kHz) of kaolinite heated at (a) 550 °C and (b) 800 °C and of the corresponding residues from the HF solution (upper row spectra).

4 Conclusions

The combination of chemical procedures and solid-state MAS NMR represents a valuable approach to gain new information about the nanostructure and reactivity of heat-treated kaolinite samples. Comparison of the ^{29}Si NMR spectra for the heated clays and their residues allow identification of different silicate environments in metakaolin and characterization of the chemical reactivity for these silicate species. ^{27}Al MAS NMR spectra of the heated samples and their residues have shown that the fivefold coordinated Al sites in metakaolin is the most reactive Al sites and that almost a full degree of reaction is observed for these sites in the chemical attack experiments.

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