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Reactions of kaolinites and metakaolinites with NaOH—comparison of different samples (Part 1)

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Abstract

Reactions with aqueous sodium hydroxide of eight different kaolinites and of metakaolinites derived from them were studied under hydrothermal conditions. All the kaolinites gave basic hydrosodalite 8:2:2 ($8Na^+/2OH^-/2H_2O$) as the primary product. The metakaolinites reacted to produce mainly zeolite A, in some of the samples associated with minor amounts of zeolite X. After 5 days, all the metakaolinites were converted to hydrosodalite. The kinetics of the reactions of the samples differed, but no correlation could be established between the rates of the reactions and the crystallinity of the kaolinites, the impurities present or any other observed feature of the starting material.

Keywords: Kaolinite; Metakaolinite; Zeolite A; Zeolite X; Hydrosodalite; Precursor gel

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1. Introduction

The conversion of kaolinite and metakaolinite to zeolite by alkali attack is a well known and widely practiced procedure. When kaolinites or metakaolinites are used without additives, zeolites with a Si/Al ratio of 1, like that of the parent material, are the main products. Alternatively, the Si/Al ratio may be increased by addition of silica gel or other forms of silica to the reactants. In strongly alkaline environments, some Al may be leached from the reactant. The processes have been studied in considerable detail, but at least one basic question remains unanswered: to what extent do reactions of individual kaolinite samples differ from each other? In most previous studies, the reactions of one kaolinite were investigated, with a view to establishing the reaction mechanism or, more frequently, to optimize the conditions for exploitation of a particular raw material pragmatically. By implication, the results were regarded as representative for the reactions of other kaolinites and metakaolinites under similar experimental conditions. The importance of the experimental conditions comprising the thermal pretreatment of the samples, particularly of metakaolinites, the concentration and proportion of the reagents, the ageing period and the temperature and time of reaction have all been emphasized, but relatively little attention was paid to the characteristics of the starting material.

Reactions of raw kaolinite with NaOH were studied by many investigators dating back to 1892 and were reexamined in detail by Engelhardt et al. (1992 and references therein). Using an unidentified kaolinite, they

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found that the primary product of both hydrothermal synthesis and reactions in open systems was always the basic hydrosodalite $Na_8[SiAlO_4]_6(OH)_2{\cdot}2H_2O$. Four other hydrosodalites were identified, but these were secondary phases produced by washing the basic form. In some studies prolonged treatment led to zeolite P, but hydrosodalite was the primary product (Madani et al., 1990; Rees and Chandrasekhar, 1993), which was formed without any intermediate phases (Buhl et al., 1997). It appears that hydrosodalite is the product obtained whenever raw kaolinite is reacted with NaOH of sufficient concentration, independent of the kaolinite used. The effect of specific features of the initial kaolinite on the reaction kinetics or on the stability of the product has not been determined.

Conversion of kaolinite to metakaolinite by heating above the dehydroxylation temperature activates the clay. The reactivity of metakaolinite varies with the thermal treatment (Rocha and Klinowski, 1990) and the course of zeolitization is affected by it. When metakaolinite was reacted with NaOH at 70–100 °C, the product most commonly obtained was zeolite A, with a Si/Al ratio of 1, like that of the starting material (e.g. Breck, 1974; Barrer, 1982; Madani et al., 1990; Rocha et al., 1991; Rees and Chandrasekhar, 1993; Chandrasekhar, 1996; Gualtieri et al., 1997; Benharrats et al., 2003 and numerous patents). On more prolonged treatment, other zeolites sometimes appeared (Madani et al., 1990; Rees and Chandrasekhar, 1993; Benharrats et al., 2003). Only in very few studies has zeolitization of two or three metakaolinites derived from different kaolinites been compared. Murat et al. (1992) studied the reactions of metakaolinites obtained at different temperatures from a well-crystallized and a poorly crystallized kaolinite, which contained different amounts of impurities. They observed differences not only in the reaction kinetics, but, with kaolinites calcined at 900 °C and above, also in the type of zeolite formed: zeolite A or P, or a mixture of the two. They attributed differences in the nucleation process to the effect of impurities, specifically to potassium or silica derived from mica. They also suggested that the rate of zeolite formation could be used to characterize the degree of crystallinity of kaolinite. In contrast, Gualtieri et al. (1997) did not observe any significant differences in zeolite formation from metakaolinites derived from the CMS kaolinites KGa1 and KGa2, which were heated at 600 and at 800 °C. As these kaolinites are of very different crystallinity, the authors concluded that the reactions of metakaolinites are independent of the defects in the original crystals. Comparing two Spanish kaolinites, Granizo et al. (2000) found a faster reaction of the sample with larger specific surface. Sanhueza et al. (1999) studied the reactions of two Chilean kaolinites, but their interest focused on optimizing the conditions of zeolitization of each, rather than on a comparison of the samples. In their summary of parameter design (Table 2 of their paper), at least two parameters were changed at each stage, which renders direct comparison of the reactions of the two samples very difficult. Costa et al. (1988) investigated zeolitization of three Spanish kaolinites, with the objective of establishing the optimum process variables for synthesizing detergents. The conditions finally selected for the three samples differed only in the time of calcination of the kaolinites at 900 °C and in the time allowed for zeolite crystallization. No correlation with any features of the reactants was reported.

Although kaolinites resemble each other in bulk chemical composition more than most other clay minerals, there are yet significant differences between individual samples. These include crystal structure and perfection, particle size and particle size distribution, minor amounts of isomorphous substitution, different kinds and amounts of adsorbed and admixed impurities and, in commercially supplied samples, sometimes acid activation or other unspecified pretreatment. With so many variables, it is evident that the causes of any differences in the course of zeolitization cannot be established by comparison between two or three samples. Moreover, because the reactions are very sensitive to experimental conditions, results obtained by different investigators cannot be directly compared.

In the present study, the reactions with NaOH of eight samples of kaolinite and of the metakaolinites derived from them were investigated. Great care was taken to ensure that the experimental conditions in any one set of experiments were identical for all the samples. The aim was to ascertain whether zeolitization of kaolinite or metakaolinite could, indeed, be correlated with crystallinity of the original kaolinites or with the presence of impurities, as suggested by Murat et al. (1992). The experimental conditions were chosen following Murat et al., to be most sensitive to differences between the product assemblages. In view of the large number of variables involved, it is questionable from the outset whether eight samples suffice to establish unequivocally which parameters affect the course of the reactions. It should be possible, however, to determine whether any given parameter, such as crystallinity, plays a decisive role.

2. Materials and methods

2.1. Materials

Kaolinite samples from eight different localities were used without pretreatment other than light crushing where necessary