Aluminum ion occupancy in the structure of synthetic saponites: Effect on crystallinity

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ABSTRACT

Two series of saponites with fixed (Si+Al)/Mg and Si/Mg ratios, respectively, were synthesized by using hydrothermal methods. The obtained products were characterized by XRD, XRF, 27Al, and 29Si MAS NMR, SEM, and TEM. XRD patterns showed that well-ordered saponites were obtained in the initial Si/Al ratio range of 5.43–7.89. Beyond this Si/Al ratio range, poorly crystallized saponites were obtained with small crystallized particles, which can be seen from TEM images. When intercalating saponite with surfactant, the intercalated products displayed strong and well-ordered (00l) reflections, indicating that layered saponite has been successfully synthesized in the present study. 27Al MAS NMR spectra demonstrated that well-crystallized synthetic saponites had a higher Al(IV)/Al(VI) ratio than the poorly crystallized samples, which is an important factor affecting the crystallinity of synthetic saponite. A one-to-one substitution (i.e., 1 Al3+ → 1 Mg2+) actually occurred in the octahedral sheet and this substitution had a negative effect on the crystallinity of the synthetic saponites. After grafting the synthetic saponites with silane, the decreased intensity of the 29Si NMR signal at ca. –86 ppm and the increased intensity of Q2 Si(0Al) and Q3 Si(1Al) signals strongly suggested that the signal at ca. –86 ppm corresponded to Q2 Si at the layer edges of saponite.

Keywords: Synthetic saponite, occupancy of aluminum ion, crystallinity, 27Al and 29Si MAS NMR, isomorphous substitution

INTRODUCTION

Saponite is a 2:1 type trioctahedral phyllosilicate of the smectite group of clay minerals. The saponite structure is composed of a central octahedral sheet with essentially a brucite [Mg6(OH)12] structure, in which four out of six OH- groups are replaced by oxygen atoms. These oxygen atoms are connected to two tetrahedral sheets consisting of Si4+ and O2- situated on both sites of the central octahedral sheet. The ideal structural formula of saponite can be presented as M2+M4+[Si4+xAlx]O10(OH)2nH2O, where M is the exchangeable interlayer cation (Brigatti et al. 2006).

Natural saponites are usually formed from weathering of Mg-containing rocks. Due to the complexities of the chemical compositions of the mother rocks and physical-chemical conditions in the geological process of saponite formation, isomorphous substitution of Al3+ for Si4+ in the tetrahedral sheet and Mg2+ by metals with different valences (e.g., Al3+, Fe3+, Li+, Mn2+, Ni2+, Zn2+) in the octahedral sheet extensively occurred (Mackenzie 1957; Vicente Rodriguez et al. 1994). Generally, the isomorphous substitution of Al3+ for Si4+ in the tetrahedral sheet is dominant and saponite is negatively charged, in which the net negative charges are compensated by exchangeable interlayer cations.

Because of its high surface acidity and thermal stability, saponite has been widely used as a heterogeneous catalyst and catalyst support (Varma 2002; Casagrande et al. 2005; Vogels et al. 2005a) as well as a filler in the preparation of polymer nanocomposites (Giannelis et al. 1999; Alexandre and Dubois 2000; Zanetti et al. 2000). The surface properties (e.g., acidity, interlayer swelling) of clay minerals are also highly dependent on their chemical composition which, in turn, is strongly affected by the extent of isomorphous substitution in their layer structure (Moronta 2004).

For industrial applications, it is very important that the composition and properties of clay materials can be adjusted for different industries. But for a specific field, the composition and property are demanded to be homogeneous. The chemical composition and property of natural saponites can be extremely variable, which strongly depend on the chemical composition of the mother rock, the genesis process and the provenance (Utracki et al. 2007). This variability represents a strong limitation in their applications especially when surface properties have to be strictly controlled, such as in catalysis.

For this reason, different methods have been developed to prepare synthetic saponites with well-controlled chemical composition and property (Farmer et al. 1991, 1994; Kloprogge et al. 1993, 1994a, 1994b; Vogels et al. 1997, 2005b; Kawi and Yao 1999; Yao et al. 2005; Higashi et al. 2007; Bisio et al. 2008; Vicente et al. 2010; Xue and Pinnavaia 2010). For instance, Farmer et al. (1991, 1994) synthesized well-formed saponite in hydrazine-water mixtures and found that the presence of Fe3+ in a calcareous environment may promote the formation of saponite. Different NH4+ saponites with variable crystallinity, platelet dimensions, specific surface areas and cation exchange capacities were obtained by varying synthesis gel composition and crystallization temperature (Kloprogge et al. 1993). Bisio et al. (2008) reported that different H2O/Si molar ratios of the gels...