

Observation of hydrogen transfer reactions via radical species in chibaite

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In 2011, new mineral named “chibaite” was discovered in Chiba prefecture (Momma et al., 2011). Chibaite is one of the silica clathrate minerals and has a framework structure of silica with cage-like voids occupied by guest species. The structures of silica clathrates are very similar to those of clathrate hydrates. There are three types of structures which are called structure I, II, and H in clathrate hydrates, and chibaite is isostructural with structure II. Chibaite can include methane, ethane, propane, and iso-butane (2-methyl-propane) in the cages as guest species. This means that 6 organic radicals (methyl, ethyl, n-propyl, iso-propyl, iso-butyl, and tert-butyl radicals) could be formed in gamma-irradiated chibaite. The preliminary electron spin resonance (ESR) measurements of the gamma-irradiated chibaite at 110 K and 290 K showed that four radicals (methyl, iso-propyl, iso-butyl, and tert-butyl radicals) were observed at 110 K, whereas only two radicals (methyl and tert-butyl radicals) were observed at 290 K. Since the kinds and amounts of the observed radicals are different at the measurement temperatures between 110 K and 290 K, hydrogen picking process would occur in chibaite. The hydrogen picking process (atomic hydrogen transfer reaction) in this presentation is an intermolecular reaction where atomic hydrogen is transferred from guest organic species to radicals formed by gamma-ray irradiation. This process was observed in clathrate hydrates such as propane hydrate and iso-butane hydrate with structure II (e.g. Ohgaki et al., 2008). The activation energy of this process was evaluated and may be caused by the potential barrier through the shared hexagonal face between adjacent cages which is composed by hydrogen bonds. If activation energy of hydrogen picking process in chibaite is estimated, the properties of framework structure of silica and hydrate could be compared and discussed. In this study, we performed isochronal annealing experiments to investigate whether hydrogen picking process was observed in chibaite.

We gently crushed chibaite samples in a mortar into several pieces with about 1 mm in diameter and irradiated at 77 K by gamma-rays with 60-Co source. ESR signals of the gamma-irradiated samples were measured at 120 K after annealing the samples for 15 min at each temperature (120, 140, 170, 200, 230, 260, and 290 K). The ESR signals of 5 organic radicals were observed and the amount of these radicals showed the different thermal behavior; especially around 260 K, tert-butyl radical increased, whereas methyl radical decreased. This may indicate that hydrogen picking process also occurs in chibaite.

Keywords: silica clathrate, chibaite, hydrogen transfer reaction, radical species, electron spin resonance