Investigation on radiation-induced radicals in primary alkylamines in silica clathrates

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Introduction

Silica clathrates have polyhedral cages formed with SiO_2. A silicon atom exists in each vertex and an oxygen atom is in the middle between the silicon atoms. The cages are occupied with guest species like hydrocarbon molecules. Chibaite, one of silica clathrates, was found in Chiba prefecture, Japan [1]. As shown in Fig. 1, the structure is composed of two different cages: larger one with 16 faces and smaller one with 12 faces. These cages enclathrate methane, ethane, propane, and isobutane. Since questions when and where the chibaite crystalized are unsolved, we have tried to estimate an ESR age using radiation-induced radicals in the chibaite [2]. However, ESR observation of the gamma-irradiated chibaite showed the overlapped signals attributed to several organic radicals and it is not easy to investigate the detailed thermal stability of them.

For further understanding, it is worthwhile to use a synthetic silica clathrate with a single gaseous molecule. Nevertheless, it is quite difficult to synthesize silica clathrates with propane or isobutane because of almost no solubility in water. Here, we focused on primary alkylamines instead of alkane molecules. Silica clathrates with primary alkylamines were successfully synthesized with orthosilicic acid solution [3].

In this study, we have synthesized isopropyl amine silica clathrate which would have the same clathrate structure with chibaite and investigated the thermal stability of the radiation-induced radicals.

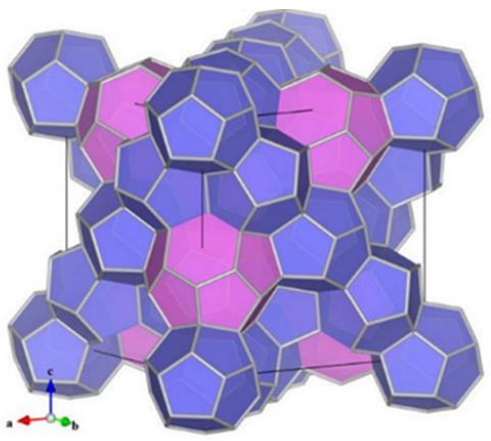

Fig. 1 Polyhedral structure of chibaite [1].

Experimental

We prepared orthosilicic acid solution with isopropyl amine and sealed it in quartz glass tubes (Fig. 2), followed by the literature [3]. After the tubes were kept at 180 ºC for 1 month, small crystal particles were found on the glass tube as shown in Fig. 3. Since the shape of the particles was symmetric and looked like cubic, we considered that these particles were silica clathrate including isopropyl amine. We cut the tubes and irradiated them by gamma-rays (6.3 kGy) at 77 K using liquid nitrogen because the particles on the surface of the tube were not detached at all.

ESR spectra of the synthetic crystal together with quartz glass tube were observed at 120 K and 210 K using X-band ESR spectrometer. In addition, ESR spectra were also measured during annealing at 150, 180, 210, 240, 270, 300, 330, and 360 K. Annealing time was 15 minutes in each step.

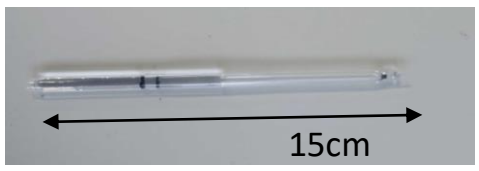

Fig. 2 Orthosilicic acid solution with isopropyl amine sealed in quartz glass tube.

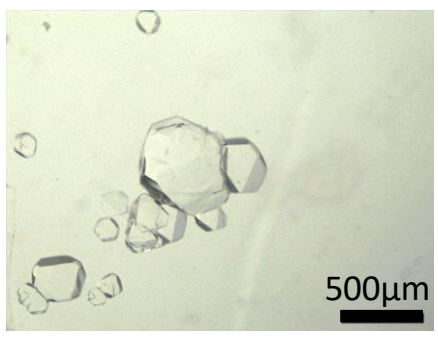

Fig. 3 Synthetic particles of isopropyl amine silica clathrate.

Results and discussion

ESR spectra observed at 120 K and 360 K were shown in Fig. 4-a and b, respectively. A few peaks observed around g = 2 at 120 K were due to radiation-induced defects in the quartz glass because almost the same peaks were observed in the gamma-irradiated quartz glass without silica clathrate. Once measurement temperature increased, sharp peaks appeared only in the tube with the silica clathrate particles as shown in Fig. 4-b. It may be caused by free rotation of the radicals at higher temperature. This phenomenon was not observed in chibaite.

Although two radicals were formed from isopropyl amine by irradiation (Fig. 5) [4], simulated ESR spectra of them in Fig. 4-c and d indicated that only the carbon-centered radical in Fig. 5-a was detected. The nitrogen-centered radical in Fig. 5-b should be formed during irradiation and might change to the carbon-centered radical or non-radical species even at low temperature.

Hydrogen atom was also observed in the isopropyl amine silica clathrate at low temperature. It disappeared around 240 K. Similar behavior was observed in the gamma-irradiated chibaite [5].

Synthetic silica clathrate showed simple ESR spectrum caused by only the carbon-centered radical. This radical was stable at least up to 360 K. Further annealing experiments will be performed in near future to investigate the stability of the radical.

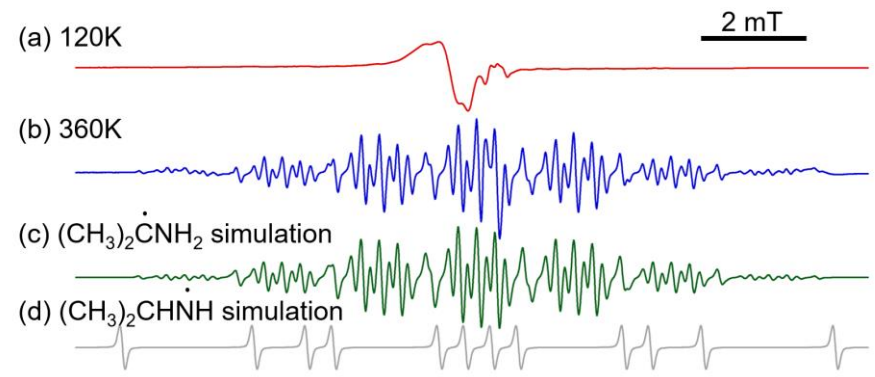

Fig. 4 ESR spectra of the gamma-irradiated synthetic isopropyl amine silica clathrate in (a) and (b) together with simulated spectra for the two radicals from isopropyl amine in (c) and (d).

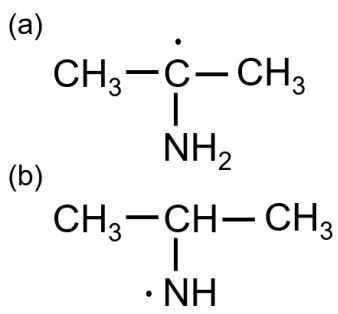

Fig. 5 Two radicals from isopropyl amine.

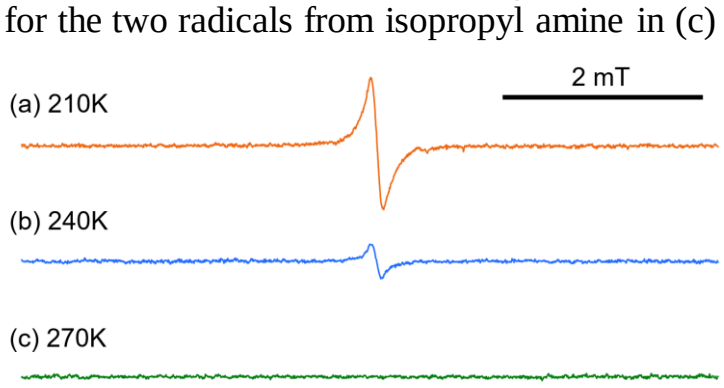

Fig. 6 ESR spectra of hydrogen atom at 210 K in the synthetic silica clathrate. Annealing temperatures were displayed.

Conclusion

We synthesized silica clathrate with isopropyl amine and investigated the radiation-induced radicals by ESR. In comparison with the results in chibaite, silica clathrate with methane, ethane, propane, and isobutane [5], we revealed the followings in this study.

1. The carbon-centered amine radical was formed and stable at least up to 360 K, whereas hydrogen transfer reaction between the alkyl radicals and alkane molecules occurred in chibaite around 240 K.
2. The motion of the radical was restricted within the large cage at low temperature, whereas the alkyl radicals in chibaite were freely rotated even at 120 K.
3. The thermal stability of hydrogen atom was similar to that in chibaite.

References

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