Tritium Behavior on the Surface of Solid Breeding Materials

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Hydroxyl groups on the surface of Li_2O were studied by using a diffuse reflectance method with Fourier transform infrared absorption spectroscopy at high temperature up to 973K under controlled D_2O or D_2 partial pressure. It was found that hydroxyl groups could exist on Li_2O surface up to 973K under Ar atmosphere. Under D_2O containing atmosphere, only the sharp peak at 2520cm^{-1} was observed at 973K in the O−D stretching vibration region. Below 973K, multiple peaks of the surface -OD were observed and they showed different behavior with temperature and atmosphere. Multiple peaks mean that surface is not homogeneous for D_2O adsorption. Assignment of the observed peaks to the surface bonding structure was also discussed. Tritium release behavior from each observed surface site was discussed. Peculiar tritium release behavior which was observed during temperature increase was also discussed.

1. Introduction

In order to design the fusion reactor fuel cycle, a through understanding of tritium release behavior from the solid breeding materials is required. From the in-pile and the out-of-pile tritium release experiments and modeling studies, it has been pointed out that the surface desorption reaction is often the rate-determining process of tritium release behavior[1,2]. On the surface of lithium oxide, which is a candidate for the solid breeding material, tritium is considered to exist as a hydroxyl group of -OT. The vibration frequency of O-T bonding is affected by the bonding nature of -OT to the surface. Therefore it is possible to study the nature of hydroxyl group on the surface by the observation of O-T stretching vibration.

In the author's previous works, infrared absorption spectra of Li_2O under the controlled D_2O or D_2 partial pressure were observed below 833K by using the diffuse reflectance method[3,4]. Multiple peaks were observed in the O−D stretching vibration and they showed different dependence on temperature and D_2 or D_2O vapor pressure. In addition to these intensive studies on Li_2O, absorption spectra were observed for various lithium ceramics at 673K[5]. In this study, a strong correlation was found between the vibration frequency and Li/O ratio of the sample.

In the present study, we have observed the O-D stretching vibration of -OD on the surface of Li_2O powder under higher temperature up to 973K. Assignment of observed peaks was tried using all experimental results obtained until now. Tritium release behavior in in-situ or out-of-pile experiments from these observed surface sites was qualitatively explained.

2. Experimental

Infrared absorption spectra were recorded using a Shimadzu FT-IR 8100 with a resolution of 2cm^{-1}. In order to observe the absorption spectra of powdered samples, the diffuse reflectance method was used. In this method, the Kubelka-Munk conversion is required to discuss the surface concentration of -OD quantitatively[6].

The sample of Li_2O used in this work was supplied from Furuuchi Chem. Co. Ltd. (purity 99.9 %). Before use, the sample was heated up to 1073K under vacuum to desorb H_2O or carbonate in Li_2O. Then it was sieved into powder (about 45μm) and was placed in the sample holder. The temperature of the sample could be controlled from room temperature to 973K by

the heater attached to the sample holder. The temperature of the surface was evaluated by two ways: firstly by inserting a $0.1mm\phi$ thermocouple directly to the Li_2O powder and secondly by observing the peak at 2696cm^{-1} attributed to precipitated LiOD[3]. Precipitation limit of D_2O vapor pressure at certain temperature is well known. So we can estimate the temperature of the surface from the D_2O vapor pressure when absorption peak of precipitated LiOD was observed. The latter method was mainly used at low temperature below 850K. The results of these methods were well consistent with each other.

The atmosphere in the chamber was controlled by the sweep gas of dry Ar, Ar + D_2O, H_2O (1$\sim$400Pa) or Ar + D_2, H_2 (0 $\sim$1000Pa). At the downstream, the water vapor pressure was checked by a dew point meter. When D_2 containing gas was introduced into the system, the generation of water was confirmed. This was considered to be due to the reaction between D_2 and Li_2O or D_2 and the oxide layers on apparatus components at high temperature. Therefore, the atmosphere near the sample was composed of Ar, D_2O and D_2 when D_2 was added to the sweep gas.

After the sample was introduced into the apparatus, it was dehumidified by heating from room temperature to 973K under Ar atmosphere. During the drying process, a large peak attributed to surface precipitated LiOH at 3662cm^{-1} disappeared around 530K. In the final stage, it was dehumidified for about 24 hours at 973K to remove remaining water adsorbed on the surface.

3. Observed Spectra

Generaly, absorption peak for O$-$D stretching vibration is observed in the range of 3100cm^{-1}- 2400cm^{-1}. Therefore, we payed attention to this region. Fig.1 shows the change of absorption spectra of Li_2O at various temperatures up to 973K. Before measurements, Li_2O sample was exposed to 300Pa D_2O atmosphere at 833K for 8 hours. After this treatment, the sample was dried under Ar atmosphere and the temperature was increased slowly up to 973K. The spectra were measured after at least 12 hours at each temperature, and we confirmed the equilibrium as the peak level did not change. In this figure, sufficiently dried sample at 973K was used as the reference. Several peaks were observed in the O$-$D stretching vibration region (3100 - 2400cm^{-1}). At 833K, broad bands attributed to -OD were observed at 3100 - 2800cm^{-1}and 2700 - 2400cm^{-1}. Intensities of these bands decreased with increasing the temperature, and they disappeared by drying at 973K for more than 12 hours under dry Ar atmosphere. This means considerable amount of -ODs could exist below 973K under Ar atmosphere and these -ODs were desorbed through recombination reaction above 973K. These peaks also disappeared at 833K when the sample was exposed to 3400Pa H_2 containing atmosphere for more than 24 hours. Dissociative adsorption of H_2 is considered to enhance the desorption of -OD as HDO. However these peaks did not disappear by H_2O addition for 24 hours at this temperature.

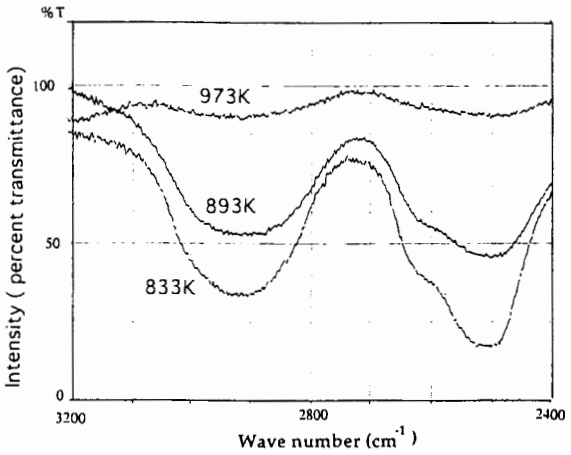

Figure 1: Absorption spectra of Li_2O during drying up to 973K.

We also observed the change of absorption spectra under D_2O containing atmosphere during temperature increase. Fig.2 shows the absorption spectra under 40Pa D_2O vapor from 700K to 900K. As was the case with dry Ar atmosphere, two broad bands were observed in the O$-$D stretching vibration region. These peaks increased in intensity with increasing the temperature up to 833K and then decreased above this temperature. This fact indicates that coverage of -OD on Li_2O surface increases with

increasing the temperature at 723~833K. Enhancement of dissociative adsorption of D_2O onto the surface in this temperatre range might be the reason. This needs further study.

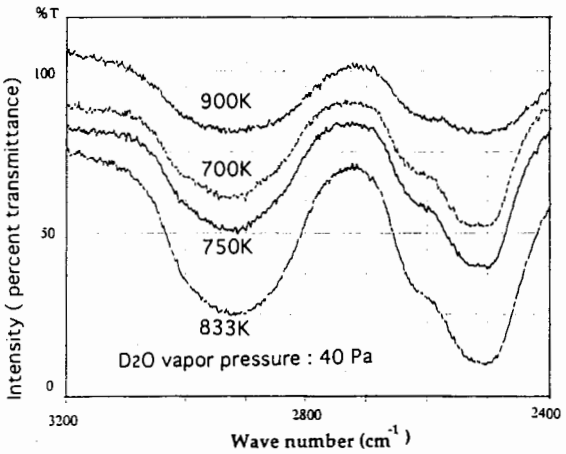

Figure 2: Absorption spectra of Li_2O under 40 Pa D_2O vapor.

Fig.3 shows the D_2O vapor pressure dependence of absorption spectra at 973K. Only the sharp peak at 2520cm^{-1} was observed at this temperatre. Broad peaks around 3100 - 2800cm^{-1}and 2700 - 2400cm^{-1} observed at 833K (Fig.1), did not appear at this temperature. Under D_2 atmosphere at 973K, again only the sharp peak was observed at 2520cm^{-1}.

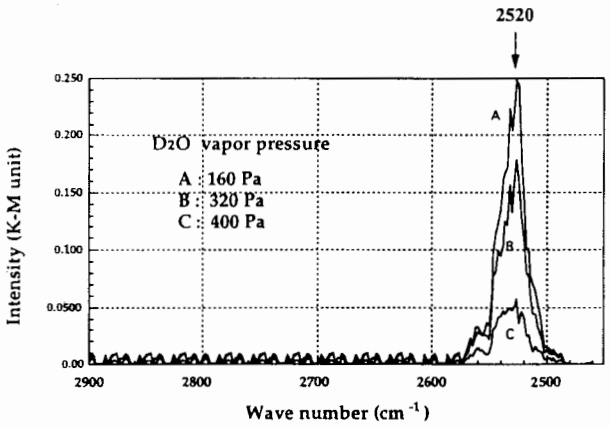

Figure 3: Absorption spectra of Li_2O under D_2O vapor at 973K.

After drying the sample at 973K for 24 hours, 320Pa D_2O was added to the atmosphere. Then the temperature was decreased gradualy down to 723K (Fig.4). At 773K, only the peak at 2520cm^{-1} was observed in the O−D stretching vibration region. At 733K, peaks at 2660cm^{-1}and 2620cm^{-1} appeared and increased in intensity with decreasing the temperature. However, broad bands around 3100 - 2800cm^{-1} and 2700 - 2400cm^{-1} were not observed in this case although these peaks were observed before drying at 973K (Fig.1). This is considered to be due to modification of the surface, which caused the change of reactivity against D_2O molcule. Such a irreversible behavior of water adsorption is also reported for SiO_2[7].

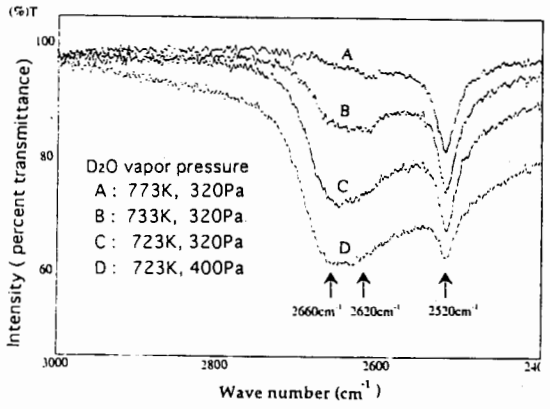

Figure 4: Absorption spectra of Li_2O under D_2O vapor after drying treatment at 973K.

We also observed the absorption spectra under D_2 atmosphere for the sample dried at 973K. In this case, only the peak at 2520cm^{-1} was observed in the region of 973K ~ 733K. Broad bands observed before drying also did not appear.

Fig.5 shows the absorption spectra of Li_2O under D_2O vapor at 833K without a drying treatment at 973K. Sufficiently dried sample at 833K was used as the reference sample. Several absorption peaks attributed to surface hydroxyl groups were observed in the region of O−D stretching vibration region. Under a low D_2O vapor pressure, only the peak at 2520cm^{-1} were observed. This peak became larger with increasing D_2O vapor pressure up to 76Pa and peak intensity at 2520cm^{-1} was saturated above 76Pa. Peak at 2660cm^{-1}appeared only under higher

D_2O vapor pressure. This peak was not observed under low D_2O pressure below 76Pa, but higher D_2O pressure above 157Pa, this peak appeared and increased in intensity with increasing D_2O vapor pressure. Broad band around 3100 - 2800cm^{-1} was also observed under high D_2O vapor pressure and its intensity was saturated under higher D_2O vapor pressure. However, broad band around 2700 - 2400cm^{-1} was not observed under this condition. This could be attributable to the difference in the temperature for drying sample to obtain the reference spectra. In fig.5, the spectrum for the sample dried at 833K was used as the reference because once sample was dried at higher temperature than 833K, reactivity of surface against D_2O was changed. Therefore it was considered that there existed considerable amount of -OD which gave absorption band at 2700 - 2400cm^{-1} on the surface of the reference sample, so that these peaks were not observed.

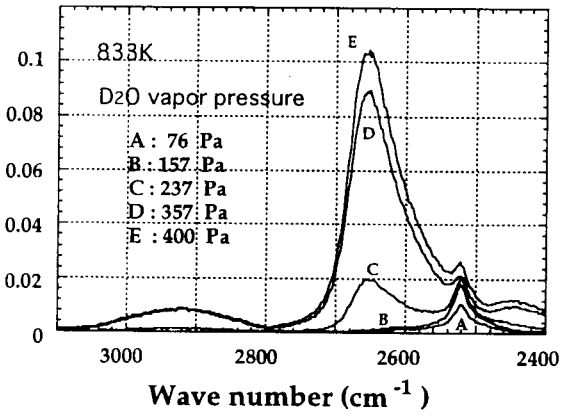

Figure 5: Absorption spectra of Li_2O under D_2O vapor at 833K.

Fig.6 shows the absorption spectra under various D_2 partial pressures at 833K using the dried sample at 833K as a reference. When D_2 containing gas was introduced into the system, the generation of water was confirmed by a dew point meter at the down stream of the sample. This is considered to be due to the reaction between D_2 and Li_2O or D_2 and the oxide layers on apparatus components at high temperature. Therefore, the atmosphere near the sample is composed of Ar, D_2O and D_2 when D_2 is added to the sweep gas. The D_2O partial pressure was roughly proportional to the D_2 partial pressure, about 500Pa at 833K when 1000Pa D_2 was added to the sweep gas. We can observe considerable difference between D_2 added and D_2O added sweep gas. Firstly, the intensity of the peak at 2660cm^{-1} reduced compared with that of Ar + D_2O sweep gas under the same D_2O vapor pressure. In particular, peak at 2660cm^{-1} was not observed at 833K although appreciable amount of D_2O vapor exists under this condition. Secondly, a broad band was observed around 2700 - 2400cm^{-1}. The shape of this peak was similar to that observed at 2700 - 2400 cm^{-1} during the drying process (Fig.1). This band is considered to be due to the overlap of three peaks. 2540cm^{-1}, 2520cm^{-1}, 2490cm^{-1}. It is considered that the increase of the peaks at 2540cm^{-1} and 2490cm^{-1} caused the broadness of this band. Thirdly, peak around 3100 - 2800cm^{-1}was not saturated under experimented D_2 partial pressure up to 1000Pa. This tendency is different from that under D_2O atmosphere.

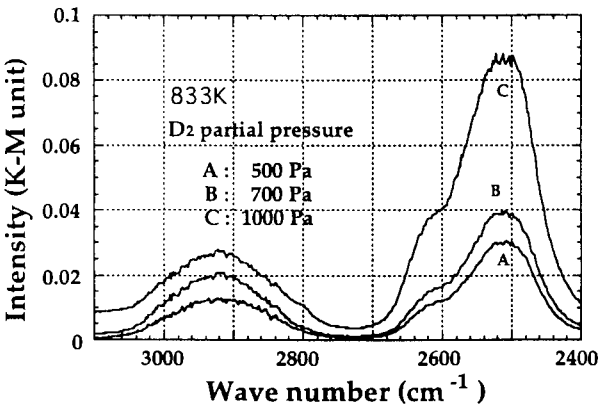

Figure 6: Absorption spectra of Li_2O under D_2 at 833K.

Absorption spectra was also measured at 673K[3]. Three sharp peaks were observed at 2748, 2717 and 2520cm^{-1} under D_2O atmosphere. The shape of the absorption spectra under D_2 was similar to that under D_2O atmosphere. In these observations, dried sample at 673K was used as the reference. Peaks at 2748, and 2717cm^{-1} decreased in intensity with increasing the temperature, and at 723K

these peaks were completely vanished although large amount of D_2O was added to the atmosphere.

4. Discussion

4.1. Assignment of the observed peaks to the surface nature

From the experiments described above, we observed plural peaks attributed to the surface hydroxyl group of -OD. These peaks showed different dependence on temperature and partial pressures of D_2O or D_2. The study of Peri[8] is suggestive to assign these peaks to the surface nature. In his experiments on the hydroxyl group on alumina surface, five absorption peaks were observed attributed to O-H stretching vibration. He explained these five peaks by considering the number of O^{2-} around the noticed OH. Similarly, O−D stretching vibration of surface -OD will be affected by the chemical species (O^{2-}, Li^+, oxygen vacancy, OD^-) around the noticed -OD. Table 1 shows our assignment of the observed peaks which was considered from experimental results shown above. In the present chapter, we show the basis of these assignments.

Table 1: Tentative assignment of observed peaks to the surface nature

observed peaks	surface nature
$2900cm^{-1}$	many O^{2-} exist around the -OD, on modified surface by heat treatment at 973K
$2748cm^{-1}$ $2717cm^{-1}$	"isolated" deutroxyl groups with several adjacent O^{2-}
$2660cm^{-1}$	-OD with several adjacent -OD
$2540cm^{-1}$ $2490cm^{-1}$	-ODs with small number of O^{2-} in the neighbor
$2520cm^{-1}$	adsorbed on the most active site

Considerable assignment is shown for peak at $2900cm^{-1}$, while further experiment is needed (See text).

At 833K, deutroxyl group attributed to peak at 2900 cm^{-1} was removed only when H_2 was added to the atmosphere. When H_2O was added, there was no change in this band. In order to remove surface -OD as HDO, another -OH must exist in adjacent site. Therefore this experimental fact indicates that only H_2 can be dissociatively adsorbed on the ajacent site for deutroxyl group attributed to $2900cm^{-1}$. Taking these facts into consideration, surface -OD which was surrounded by many O^{2-} could be considered. The local surface of Li_2O with many O^{2-} is thought to be more reactive with D_2 than with D_2O because dissociative adsorption of D_2 requires two adjacent oxygen ions while D_2O adsorption needs adjacent oxygen ion and oxygen vacancies. This band increased in intensity when D_2 was added to the atmosphere at 833K. On the other hand, when D_2O was added, intensity of this peak became saturated at high D_2O pressure. This experimental results contradict with the above explanation. The difference in coordination number of Li ion around -OD or hydrogen bonded -OH due to the H_2O which inevitably exists in the system could also be considered to be the reason for this peak. The assignment of this band needs further study.

Peak at $2660cm^{-1}$ could not be observed under low D_2O vapor pressures. But above a certain pressure, this relatively broad peak appeared and increased in intensity with increasing D_2O pressure as shown in Fig.5. From this result, this peak can be assigned to the -OD which was adsorbed on such a site as several -ODs exist closely in the neighbor. Under low D_2O vapor pressures, this peak could not exist because the coverage of -OD on the surface is relatively low. Furthermore, this peak disappered under the D_2 containing atmosphere (Fig.6). When D_2 was added to the atmosphere, desorption of -OD as D_2O is considered to be enhanced by the reaction of D_2 with the surface. Therefore, coverage of -OD became relatively small, causing disappearance of this peak.

Peaks at $2540cm^{-1}$ and $2490cm^{-1}$ were assigned to surface hydroxyl group with O^{2-} vacancies in the neighhbor. Difference in the number of ajacent O^{2-} was considered to cause the two peaks. Schematic configuration of these hydroxyl groups is shown in Fig.7. This assignment is supported by the following experimental results. (1)These peaks increased in their in-

tensities when D_2 was added to the sweep gas (Fig.6). When D_2 was added to the sweep gas, oxygen potential near the surface is considered to be relatively low. Under this condition, the number of O^{2-} near the -OD is thought to be small. (2)These peaks existed at higher temperature compared with other peaks (Fig.1). In order to remove the surface -OD as D_2O by recombination reaction, another -OD must exist on an adjacent site. Therefore, desorption of -OD with small number of O^{2-} in the neighbor is considered to be more difficult than that with large number of O^{2-} because of the difference in mobility between OH^- and H^+. (Migration of -OD with large number of O^{2-} could occur through D^+ transfer from a hydroxyl group to adjacent O^{2-} but -OD with small number of adjacent O^{2-} requires -OD movement).

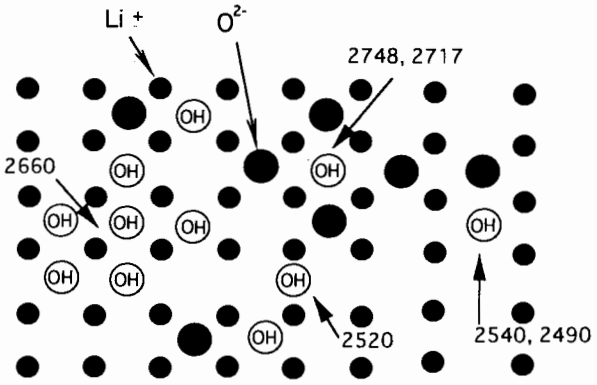

Figure 7: Plausible configuration for each -OH on Li_2O.

Peaks at 2748 and 2717cm^{-1} were observed at 673K and could not exist at high temperature, indicating that the activation energies for desorpion of these -ODs are small. From the reason mentioned above, these peaks are considered to be isolated -OD with several O^{2-}s in the neighbor as shown in Fig.7.

The hydroxyl group of -OD which gives the absorption peak at 2520cm^{-1} was observed under low D_2O vapor pressure in the range 673K $\sim$ 973K. Especially at 973K, only this peak was observed under D_2O or D_2 atmosphere. This fact indicates that the adsorption site attributed to this peak is most stable. Such a site as shown in Fig.7 is suggested to be a stable site for D_2O adsorption by ab-initio study[9]. Surface defect structure such as corner or edge in the crystal could also be considered for this active site.

4.2. Desorption of each hydroxyl group in in-pile or out-of-pile tritium release experiments

We observed the hydroxyl groups on the surface of lithium oxide and showed that there are several kinds of adsorption sites which differ in microstructure around them. In the actual blanket system, H_2 or H_2O will be added to the sweep gas in order to enhance the tritium recovery. Under this condition, surface tritium which exists as -OT is considered to be desorbed by one of the following reactions:

(1) surface recombination reaction

$$\text{-OT} + \text{-OH} \rightarrow \text{HTO} + O^{2-},$$

(2) surface exchange reaction

$$\text{-OT} + H_2 \rightarrow \text{-OH} + \text{HT},$$
$$\text{-OT} + H_2O \rightarrow \text{-OH} + \text{HTO}.$$

Furthermore, under low surface oxygen potential, desorption of tritium as HT by following reaction is also considered to be possible,

(3) $\text{-OT} + \text{-OH} \rightarrow \text{HT} + 2O^{2-}$.

Yamaki and co-workers have constructed the model of surface adsorption/desorption considering these reactions and succeeded in explaining the tritium release behavior observed in in-situ tritium release experiments[10]. In this section, we will try to discuss qualitativery the desorption of -OT adsorbed on each site observed by FT-IR study.

Hydroxyl groups adsorbed on the sites corresponding to peaks at 2540, and 2490cm^{-1} could not be desorbed under Ar atmosphere at 833K as shown in Fig.1. In order to recover tritium trapped on these sites at this temperature, addition of H_2 or H_2O to the sweep gas was needed. Surface -OD corresponding to peaks at 2540 and 2490cm^{-1} is considered to be hard to be desorbed by recombination reaction under

H_2 atmosphere. These -ODs are thought to have small numbers of O^{2-} in the neighbor. In this case, adsorption of H_2 on an adjacent site is considered to be difficult because dissociative adsorption of H_2 requires two neighboring oxygen ions on the surface. Therefore, recovery of these -OTs is considered to requires exchange reaction (2).

Peaks at 2748 and 2717cm^{-1} are assigned to hydroxyl group with several adjacent oxygen ions. Surface -OT trapped at these sites is considered to be mobile by T^+ transfer from one O^{2-} to adjacent O^{2-}. Therefore under dry Ar sweep gas, these -OTs could be desorbed as T_2O by recombination reaction (1). It is also possible to desorb these -OTs as HTO by adding H_2O or H_2 to the sweep gas.

Peak at 2660cm^{-1} was observed only under high D_2O vapor pressure and was assigned to -OD with many -ODs in the neighbor. From this fact, surface tritium could exist at this site only when surface tritium concentration is high or H_2O pressure in the sweep gas is high. In this case, desorption of tritium as T_2O by recombination of two adjacent -OTs in pure He sweep gas or as HTO by recombination of -OT and -OH which was produced by dissociative adsorption of H_2 or H_2O is considered to be easy.

Peak at 2520cm^{-1} was observed mainly under D_2O atmosphere and assigned to surface -OD on an active site like corner or edge in the crystal. H_2O adsorption on adjacent site to this -OT is considered to be easy. Therefore, under H_2O atmosphere, surface -OT trapped at this site could be desorbed by reaction (1) as HTO.

We have observed many sites with different wavenumber, or with different -OD bonding strength to the surface. If the mobility of -OD on the surface is same, activation energy for tritium desorption should have a strong correlation with the bonding strength.

From the discussion in this section, we can conclude qualitatively that activation energy for desorption of surface -OT varies according to the adsorption sites which is affected by the chemical composition of the sweep gas. In order to compare the result of this FT-IR study with that of in-situ tritium release test or out-of-pile TPD experiments, we have to evaluate the activation energy of -OT desorption for each site quantitatively. For this purpose, more work using different approaches such as quantum chemical calculation are essential. This will be the next step of our work.

4.3. Peculiar tritium release behavior in temperature increase

In tritium release experiments, strange behavior of tritium release is reported by several groups. In the CRITIC tritium release experiments, using the He + H_2 sweep gas, when the temperature of the sample was increased from 708K to 888K, tritium release exhibited a sharp decrease followed by an increase to a maximam, then a deline to steady state[11]. Kopasz and coworkers succeeded in explaining this phenomena by considering the multiple activation energies for HTO desorption[12] as shown in fig.8. The same tendency is also observed by TTTEx tritium release experiments (Fig.9 [13]) and it was shown that larger decrease in tritium release was found for higher H_2O partial pressure (40 $\sim$ 80 Pa) in the sweep gas.

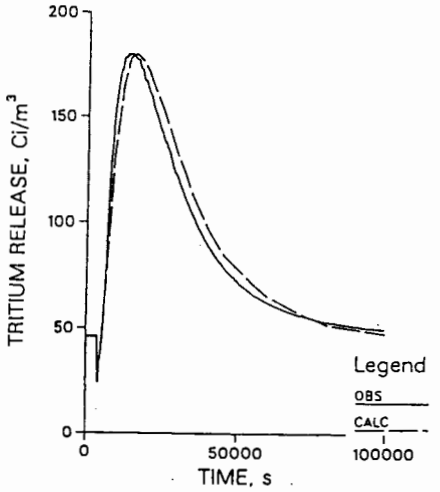

Figure 8: Calculated and observed tritium release for a temperature increase from 708K to 888K for Li_2O[12]

According to our FT-IR srudy, increase in intensity of the peak at 2700 - 2400cm^{-1} was observed with increasing the temperature from 723K to 833K under low D_2O atmosphere (Fig.2). This experimental result indicates that coverage of surface hydroxyl group increases with increasing temperature in this range. From

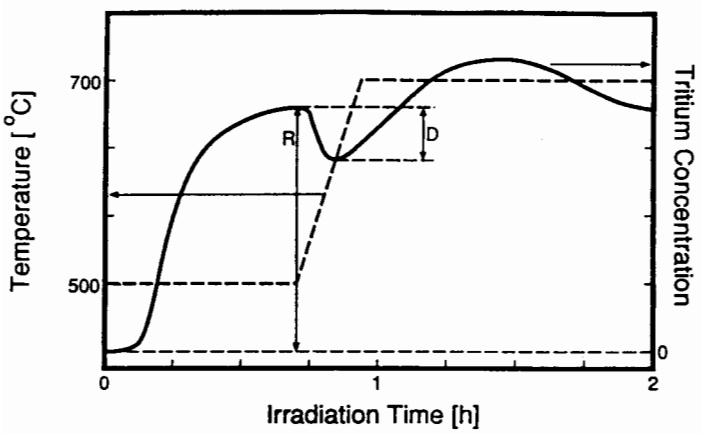

Figure 9: A typical tritium release observed in TTTEx

these facts, strange tritium release behavior observed in tritium release experiments could be explained as follows: When temperature of the sample was increased, coverage of surface -OT also increases. This means that tritium inventry at the surface increases with increasing the temperature. Therefore, desorption of -OT by recombing reaction once decreases for a short time. After the coverage of surface -OT becomes maximam at this temperature, desorption of -OT begins to increase because of the higher tritium concentration compared with that of at the initial temperature. The amount of tritium migration to the surface becomes larger for a while at higher temperature, because tritium diffusivity is lower and tritium diffusion inventry is large at lower temperature. So tritium release rate has a maximam. However tritium production rate is constant, so that tritium concentration on the surface gradually decreases, leading to a decrease of tritium release to a steady-state level.

5. Conclusions

Absorption spectra from -OD on the surface of Li_2O were studied by using the diffuse-reflectance Fourier transform infrared spectroscopy under the controlled atmosphere and temperature up to 973K. Following conclusions were obtained.

It was observed that hydroxyl groups of peaks at 3100 - 2800cm^{-1} could exist on Li_2O surface up to 973K under Ar atmosphere. Reactivity of Li_2O surface against D_2O was changed after drying treatment at 973K. This is considered to be due to the modification of the surface by desorbing hydroxyl groups.

Under D_2O or D_2 atmosphere, only the sharp peak at 2520cm^{-1} was observed at 973K in the O−D stretching vibration region. Below 973K, multiple peaks due to the surface -OD were observed and they showed different behavior with temperature or atmosphere.

These results show that surface is not homogeneous for D_2O adsorpion and that bonding structure is affected by atmosphere. Observed peaks were tentatively assigned considering the surface species around the -OD.

Desorption of tritium in in-situ or out-of-pile tritium release experiments from each surface site observed by FT-IR study was qualitatively disscused by considering the mobility of surface -OT and adsorption behaviors of H_2 or H_2O on adjacent sites of -OT.

Peculiar tritium release behavior during temperature increase which was observed in in-situ tritium release experiments were explained by using the results of FT-IR study.

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