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Isotope exchange reaction on Li_2ZrO_3

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Abstract

Lithium meta-zirconate, Li_2ZrO_3, is considered as a strong candidate for the tritium breeding material in a D–T fusion reactor. The isotope exchange reaction rate between hydrogen isotopes in the purge gas and tritium on the surface of Li_2ZrO_3 has not been quantified yet, although helium gas with hydrogen or deuterium is planned to be used as the blanket purge gas in the recent blanket designs. The mass transfer coefficient representing the isotope exchange reaction between H_2 and D_2O or that between D_2 and H_2O in the Li_2ZrO_3 is experimentally obtained as $K_{F,ex1} = 1.60 \times 10^2 \exp(-121[kJ/mol]/RT)$ in this work. Discussions about the effect of temperature, concentration of hydrogen in the purge gas or flow rate of the purge gas on the conversion of tritiated water to tritium gas, HT instead of H_2, are also performed. © 1997 Elsevier Science B.V.

1. Introduction

Lithium ceramic materials such as Li_2O, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 are considered as the candidates of tritium breeding materials in a D–T fusion reactor. In early blanket designs, He was used as the purge gas. In this method, however, the time to obtain the steady state conditions in recovery of bred tritium becomes long because the desorption rate of tritiated water is slow. Therefore, it has been proposed to make use of the isotope exchange reaction for enhancement of the tritium release rate from solid breeder materials. For this purpose, hydrogen or deuterium is added to the He purge gas in various in situ or annealing after irradiation experiments [1,2].

In order to understand the release behavior of tritium bred in a solid breeder material, it is necessary to know the contribution of such mass transfer steps as (1) diffusion of tritium in crystal grain, (2) effect of radiation defects on tritium migration in crystal grain, (3) adsorption of tritium on grain surface, (4) absorption of tritium in crystal grain, (5) amount of isotope exchange capacity besides adsorption capacity, (6) isotope exchange reaction between gaseous hydrogen, H_2, in the gas stream and tritium on grain surface, (7) isotope exchange reaction between water vapor, H_2O, in the gas stream and tritium on grain surface, (8) water formation reaction at addition of H_2 to the blanket purge gas, (9) transfer of hydrogen isotopes and water through pores of sintered pellet and (10) transfer of hydrogen isotopes and water through the boundary layer formed on the surface of the sintered pellet to gas stream.

Adsorption or desorption and two types of isotope exchange reactions contribute as the surface reactions. Most results of the in situ experiments so far have been analyzed assuming that the overall release process is mainly controlled by diffusion in the crystal grain. However, it has been pointed out recently that contribution of the surface reactions cannot be ignored [2–5]. The present authors have quantified the amount of water captured in Li_2O, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 in the previous papers [6–9].

However, a quantitative consideration of the isotope exchange reactions has not been done yet except for Li_2O reported by the present authors [10]. In the present work, the isotope exchange reaction between hydrogen isotopes in the purge gas and water adsorbed on the Li_2ZrO_3 surface is studied.

2. Experimental

The schematic diagram of the experimental apparatus is shown in Fig. 1. 40.0 g of Li_2ZrO_3 pebbles made by

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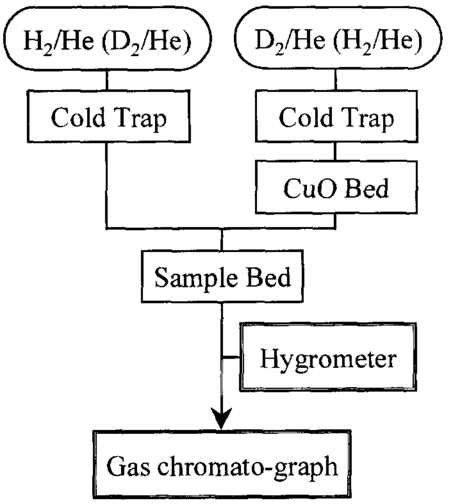

Fig. 1. The schematic diagram of the experimental apparatus.

Mitsubishi Atomic Power Industries, Inc. was packed in the reaction tube made of quartz, and its specifications are shown in Table 1. Change of H_2, HD and D_2 concentrations at the outlet of the Li_2ZrO_3 bed after introduction of the He gas containing D_2O and H_2 or He gas containing H_2O and D_2 were measured using gas chromatography. The water concentration in the outlet gas of the Li_2ZrO_3 bed was measured with a hygrometer. The gas flow rate was 0.1 to 1.0 l/min and it was controlled by a mass flow meter. Each process gas was passed through a cold trap filled with molecular sieve 5A and cooled with ice water to remove the residual water vapor in the process gas. The water concentration in the process gas is controlled by the hydrogen oxidizing method with a CuO bed of 623 K. As was reported by the present authors [11], water was formed in the Li_2ZrO_3 bed when hydrogen isotopes were added into the He purge gas. To lower the effect of this water formation reaction on estimation of the isotope exchange reaction, the sample bed was stepwise heated up to the experimental temperature by a electric heater in 50 K steps confirming that the vapor concentration from the water formation reaction become below a few ppm. The experimental conditions are shown in Table 2. The experiments were performed under the steady state conditions.

Table 1
Specifications of the Li_2ZrO_3 pellet used in this work

	Sample Li_2ZrO_3
Theoretical density (kg/m^3)	4.15×10^3
Density (kg/m^3)	3.57×10^3 (86% T.D.)
Grain size (μm)	13
Pellet size (mm)	1.0
BET surface area (m^2/g)	0.09
Specific surface area of bed (m^{-1})	2.12×10^5
Void fraction of packed bed (-)	~ 0.34

Table 2
Experimental conditions

Concentration of H_2	2500–10000 ppm
Concentration of D_2O	100–600 ppm
	$M = 6–23$
Concentration of D_2	2100–2900 ppm
Concentration of H_2O	170–550 ppm
	$M = 8–16$
Amount of Li_2ZrO_3	40.0 g
Temperature of Li_2ZrO_3 bed	573–873 K
Gas flow rate	0.1–1.0 l/min

3. Theoretical consideration

The isotope exchange reactions would occur on the grain surface of solid breeder materials. In the present work, H_2 and D_2 are used for the experiment, and therefore exchange reactions concerning hydrogen isotopes (H_2, HD and D_2) and water vapor (H_2O, HDO and D_2O) in the gas phase and adsorbed water (H_2O, HDO and D_2O) on grain surface should be taken into account. If all the exchange reactions are taken into account, the analysis becomes too complex. In addition, it is technically difficult to separate H_2O, HDO and D_2O in the measurement, although H_2, HD and D_2 can be easily separated by a chromatographic method. Therefore, a simplified isotope exchange reaction model is used for the present work. In this model, isotope exchange reactions concerning hydrogen isotopes (H_2 and D_2) and water vapor (H_2O and D_2O) in the gas phase and adsorbed water (H_2O and D_2O) on the grain surface are only taken into account assuming

$$C_{H_2} = C'_{H_2} + \tfrac{1}{2} C'_{HD}, \tag{1}$$

$$C_{D_2} = C'_{D_2} + \tfrac{1}{2} C'_{HD}, \tag{2}$$

$$C_{H_2O} = C'_{H_2O} + \tfrac{1}{2} C'_{HDO}, \tag{3}$$

$$C_{D_2O} = C'_{D_2O} + \frac{1}{2} C'_{HDO}, \tag{4}$$

where C is the nominal concentration in the gas phase (mol/m^3) and C' is the real concentration (mol/m^3). The exchange reactions based on the simplified model are expressed as

$$H_2(g) + D_2O(s) \leftrightarrow D_2(g) + H_2O(s), \tag{5}$$

$$H_2O(g) + D_2O(s) \leftrightarrow D_2O(g) + H_2O(s). \tag{6}$$

Under the steady state conditions, the mass balance in the Li_2ZrO_3 bed is expressed in the same way for Pt–alumina catalysts, Pt–M.S.–5A catalysts and other catalysts beds which were obtained by the present authors [12,13] referring to Perry's 'Chemical Engineering's Handbook' [14],

$$u\frac{\partial C_{\mathrm{H_2}}}{\partial z} = -K_{\mathrm{F,ex1}} a_\nu X_1, \tag{7}$$

$$u\frac{\partial C_{\mathrm{D_2}}}{\partial z} = K_{\mathrm{F,ex1}} a_\nu X_1, \tag{8}$$

$$u\frac{\partial C_{\mathrm{H_2O}}}{\partial z} = -K_{\mathrm{F,ex2}} a_\nu X_2, \tag{9}$$

$$u\frac{\partial C_{\mathrm{D_2O}}}{\partial z} = K_{\mathrm{F,ex2}} a_\nu X_2, \tag{10}$$

$$X_1 = C_{\mathrm{D_2}} - \frac{\left(\left(C_{\mathrm{H_2}}/K\right) + C_{\mathrm{D_2}}\right) q_{\mathrm{D_2O}}}{q_{\mathrm{H_2O}} + q_{\mathrm{D_2O}}},$$

$$X_2 = C_{\mathrm{D_2O}} - \frac{\left(C_{\mathrm{H_2O}} + C_{\mathrm{D_2O}}\right) q_{\mathrm{D_2O}}}{q_{\mathrm{H_2O}} + q_{\mathrm{D_2O}}},$$

where u is the superficial gas velocity (m/s), z is the length in the axial direction of the Li_2ZrO_3 bed, $K_{\mathrm{F,ex1}}$ is the overall mass transfer coefficient of the isotope exchange reaction between H_2 in the gas phase and D_2O adsorbed on the grain surface (m/s), $K_{\mathrm{F,ex2}}$ is the overall mass transfer coefficient of the isotope exchange reaction between H_2O in the gas phase and D_2O adsorbed on the Li_2ZrO_3 grain surface (m/s), K is the equilibrium constant of the isotope exchange reaction between H_2 in the gas phase and D_2O adsorbed on the Li_2ZrO_3 grain surface (-), q is the concentration of water adsorbed on the Li_2ZrO_3 grain surface (mol/mol). The rate equation of the isotope exchange reaction between H_2 in the gas phase and D_2O adsorbed on the grain surface is defined from Eq. (8) as

$$r = K_{\mathrm{F,ex1}} a_\nu \left(C_{\mathrm{H_2}}/K + C_{\mathrm{D_2}}\right)\left\{\left(\frac{C_{\mathrm{H_2}}/K}{C_{\mathrm{H_2}}/K + C_{\mathrm{D_2}}}\right) - \left(\frac{q_{\mathrm{H_2O}}}{q_{\mathrm{H_2O}} + q_{\mathrm{D_2O}}}\right)\right\}, \tag{11}$$

where r is an isotope exchange reaction rate between H_2 in the gas phase and D_2O adsorbed on the grain surface (mol m/s m^3).

The boundary conditions at the bed inlet are given as follows in the experimental conditions of this work:

$$C_{\mathrm{H_2}} = C_{\mathrm{H_2,in}} \quad \text{at } z = 0, \tag{12}$$

$$C_{\mathrm{D_2}} = 0 \quad \text{at } z = 0, \tag{13}$$

$$C_{\mathrm{H_2O}} = 0 \quad \text{at } z = 0, \tag{14}$$

$$C_{\mathrm{D_2O}} = C_{\mathrm{D_2O,in}} \quad \text{at } z = 0, \tag{15}$$

where $C_{\mathrm{H_2,in}}$ and $C_{\mathrm{D_2O,in}}$ are the H_2 concentration in the process gas at the inlet and the D_2O concentration at the inlet (mol/m^3), respectively. The mass balance in the Li_2ZrO_3 bed gives

$$C_{\mathrm{H_2}} + C_{\mathrm{D_2}} = C_{\mathrm{H_2,in}}, \tag{16}$$

$$C_{\mathrm{H_2O}} + C_{\mathrm{D_2O}} = C_{\mathrm{D_2O,in}}, \tag{17}$$

$$q_{\mathrm{H_2O}} + q_{\mathrm{D_2O}} = q_{\mathrm{D_2O,in}}, \tag{18}$$

and the mass balance about H-atoms and D-atoms gives

$$C_{\mathrm{H_2}} = C_{\mathrm{H_2,in}} - C_{\mathrm{H_2O}}, \tag{19}$$

$$C_{\mathrm{D_2}} = C_{\mathrm{D_2O,in}} - C_{\mathrm{D_2O}}. \tag{20}$$

The experimental conditions of this work make the following approximation possible:

$$C_{\mathrm{H_2}} \approx C_{\mathrm{H_2,in}}, \tag{21}$$

because $C_{\mathrm{H_2,in}}$ is much larger than $C_{\mathrm{D_2O,in}}$ in this work. It is presumed that the isotope exchange reaction between water vapor and tritium on the surface is much larger than the isotope exchange reaction between gaseous hydrogen and tritium on the surface ($K_{\mathrm{F,ex1}} \ll K_{\mathrm{F,ex2}}$):

$$\frac{q_{\mathrm{D_2O}}}{q_{\mathrm{D_2O,in}}} \approx \frac{C_{\mathrm{D_2O}}}{C_{\mathrm{D_2O,in}}}. \tag{22}$$

Substitution of Eqs. (20)–(22) into Eq. (8) gives the change of D_2 concentration in the gas phase as

$$-u\frac{\partial C_{\mathrm{D_2}}}{\partial z} = K_{\mathrm{F,ex1}} a_\nu \left(C_{\mathrm{H_2,in}}/K\right) \times \left\{1 - \left(\frac{K}{C_{\mathrm{H_2,in}}} + \frac{1}{C_{\mathrm{D_2,in}}}\right) C_{\mathrm{D_2}}\right\}. \tag{23}$$

Then, the following equation is obtained by integration of Eq. (23):

$$K_{\mathrm{F,ex1}} a_\nu = \frac{1}{\tau}\frac{-K}{M+K}\ln\left[1 - \frac{M+K}{M}X\right], \tag{24}$$

$$M = \frac{C_{\mathrm{H_2,in}}}{C_{\mathrm{D_2O,in}}}, \qquad X = \frac{C_{\mathrm{D_2}}}{C_{\mathrm{D_2O,in}}},$$

where τ is the average residence time in the Li_2ZrO_3 bed (s) which is given by the bed height divided by the superficial gas velocity z_b/u, and M is the molar ratio of H_2/D_2O at the inlet (-) and X is the conversion ratio of D_2O into D_2 (-).

The value of a_ν is the specific surface area of the Li_2ZrO_3 grain in packed bed (m^2/m^3), and is given as

$$a_\nu = (1 - \varepsilon_b)(1 - \varepsilon_p)\rho A_{\mathrm{BET}} = 6(1 - \varepsilon_b)(1 - \varepsilon_p)/d_p \quad (\mathrm{m^2/m^3}), \tag{25}$$

where ε_b is void fraction of the packed bed (-), ε_p is void fraction of the pellet (-), ρ is theoretical density of grain (g/m^3), d_p is the grain diameter (m) and A_{BET} ($= 6/\rho d_p$) is the BET surface area (m^2/g).

4. Results and discussion

The observed values for the overall mass transfer capacity coefficients representing the isotope exchange reaction on Li_2ZrO_3 are shown in Fig. 2 where evaluation using Eq. (24) is performed assuming K is unity. Agreement of data under various experimental conditions implies that equations for the isotope exchange reaction on Li_2ZrO_3 would be proper. The open circles in Fig. 2 indicating the isotope exchange reaction between H_2 in the gas phase and D_2O on the grain surface, shows the same tendency as the solid circles indicating the isotope exchange reaction between D_2 in the gas phase and H_2O on the grain surface. Therefore, the value of K in Eq. (24) decided to be 1. This observation implies that there is no isotope effect in the isotope exchange reaction between gaseous hydrogen isotopes in the purge gas and water adsorbed on the grain surface. Accordingly, it can be said that the following correlative equation can be applied to the tritium–hydrogen or tritium–deuterium system. The following equation is obtained from Fig. 2 as the mass transfer capacity coefficient representing the isotope exchange reaction on the Li_2ZrO_3 surface of this work:

$$K_{\mathrm{F,exl}}a_{\nu} = 3.4 \times 10^7 \exp(-121\ (\mathrm{kJ/mol})/RT)$$
$$(\text{for } Li_2ZrO_3)\ (\mathrm{s}^{-1}). \tag{26}$$

The value of a_{ν} is $2.12 \times 10^5\ \mathrm{m}^{-1}$ for the Li_2ZrO_3 bed in this work. Therefore, the isotope exchange reaction $K_{\mathrm{F,exl}}$ for Li_2ZrO_3 is obtained as

$$K_{\mathrm{F,exl}} = 1.60 \times 10^2 \exp(-121\ (\mathrm{kJ/mol})/RT)$$
$$(\text{for } Li_2ZrO_3)\ (\mathrm{m/s}). \tag{27}$$

Fig. 3 shows the comparison of $K_{\mathrm{F,exl}}$ obtained for Li_2ZrO_3 in this work with $K_{\mathrm{F,exl}}$ for Li_2O which is evaluated in the same way for Li_2ZrO_3 in this work using data reported in the previous paper [10]. The value of $K_{\mathrm{F,exl}}$ for Li_2O is obtained as

$$K_{\mathrm{F,exl}} = 8.55 \times 10^3 \exp(-143\ (\mathrm{kJ/mol})/RT)$$
$$(\text{for } Li_2O)\ (\mathrm{m/s}), \tag{28}$$

and it is about the same as that for Li_2ZrO_3 in the temperature range shown in Fig. 3.

The conversion ratio from tritiated water to gaseous tritium is expressed as follows from Eq. (23) considering that K is unity as observed in this work:

$$X = \frac{M}{M+1}\left[1 - \exp\{-\tau(M+1)K_{\mathrm{F,exl}}a_{\nu}\}\right] \quad (-). \tag{29}$$

The value of X also indicates the fraction of gaseous tritium in the total tritium leaving the breeding blanket purged by dry He purge gas with hydrogen.

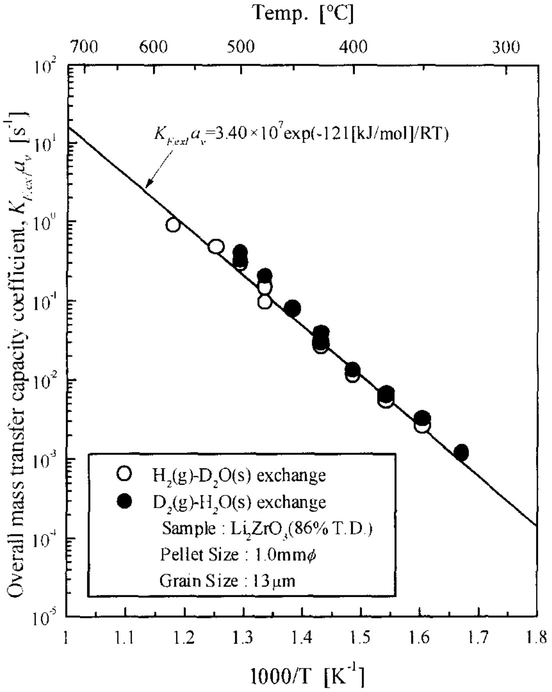

Fig. 2. The overall mass transfer coefficient of representing isotope exchange reactions on Li_2ZrO_3.

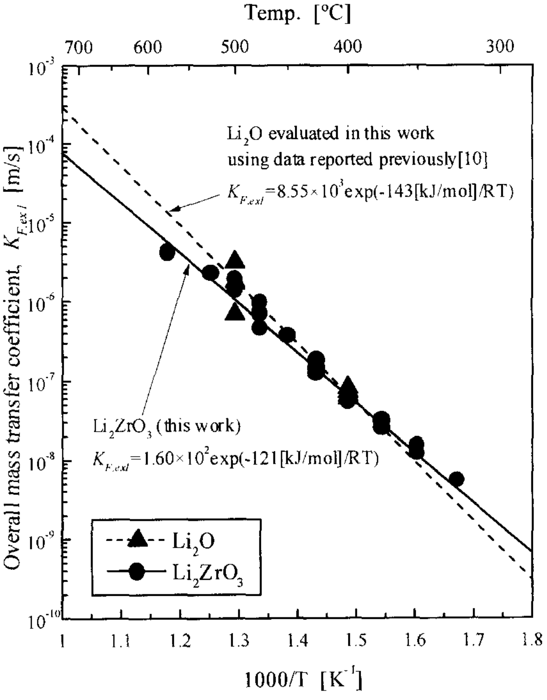

Fig. 3. The comparison of $K_{\mathrm{F,exl}}$ obtained for Li_2ZrO_3 in this work with $K_{\mathrm{F,exl}}$ for Li_2O which is evaluated in the same way for Li_2ZrO_3 in this work using data reported in the previous paper.

The change of X with M under various blanket temperatures is compared in Fig. 4a and b, where M means the ratio of the partial pressure of hydrogen added to the purge gas to nominal partial pressure of the tritiated water P_{T_2O} corresponding to the tritium generation rate. When all tritium bred in the grains of the solid breeder material is considered to be released in the chemical form of water to the He purge gas, P_{T_2O} is obtained as

$$P_{T_2O} = P_{He} G_T / G_{He} \text{ (Pa)}, \qquad (30)$$

where P_{He} (Pa), G_T (mol/s) and G_{He} (mol/s) are the total pressure of the He purge gas, tritium generation rate in the blanket and flow rate of the He purge gas, respectively.

As can be seen in Fig. 4a and b, the higher blanket temperature or the longer residence time is required to obtain the higher conversion at a certain value of M and the temperature to give the theoretical maximum conversion, $M/(M+1)$, becomes lower for the longer residence time. For example, 873 K is necessary to obtain the theoretical maximum conversion for all M when τ is 1 s as shown in Fig. 4a though 773 K is enough when τ is 10 s as shown in Fig. 4b. It can be seen from these figures that the high conversion can be obtained when M becomes larger although that is smaller than the theoretical

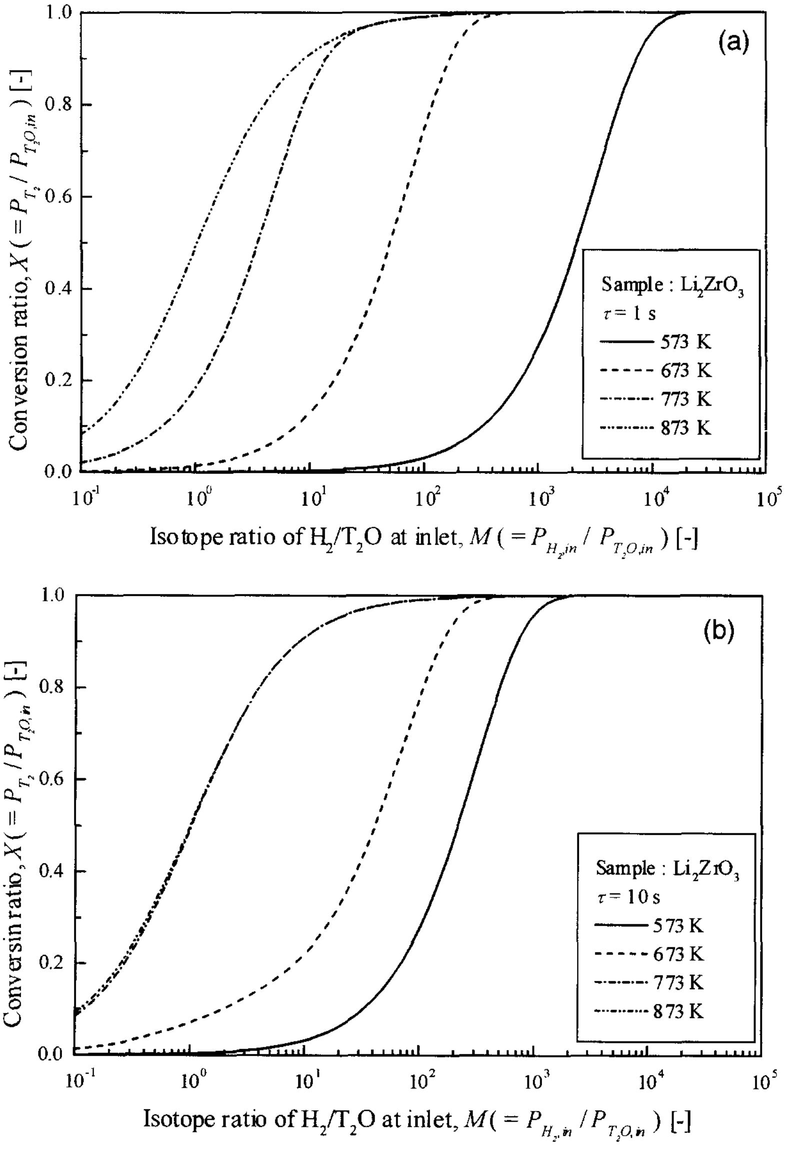

Fig. 4. (a) Change of X and M under various temperatures when τ is 1 s. (b) Change of X and M under various temperatures when τ is 10 s.

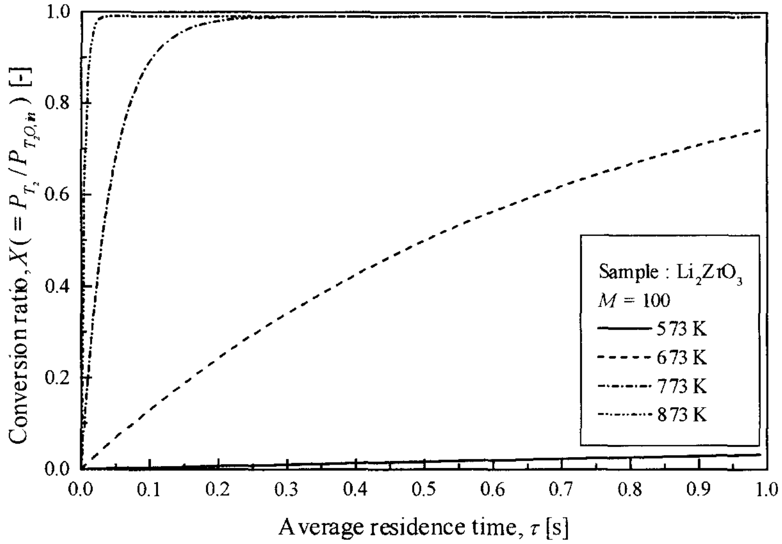

Fig. 5. Change of X and τ under various temperatures when M is 100.

maximum conversion. For example, τ is 1 s can give a conversion as high as 0.97 when M is 1000 though X is 0.3 when M is 100 and 0.03 when M is 10.

Change of X with τ when M is 100 is compared in Fig. 5 for various blanket temperatures. This figure tells that the bed height of Li_2ZrO_3 to give the theoretical maximum conversion, 0.99 in the case shown in Fig. 5, is very small when the blanket temperature is higher than 773 K and that the required bed height to give the theoretical maximum conversion becomes rapidly larger when the blanket temperature becomes lower.

The change of X with τ when the blanket temperature is 573 K is compared in Fig. 6 for various M. Increase of the bed height gives rather small efficiency in improvement of the conversion though the high conversion can be obtained by addition of hydrogen of a large partial pressure to the purge gas as stated above.

Though several models to estimate the tritium release behavior from solid breeder blankets have been reported (Refs. [15,16] for example), the isotope exchange reaction is not taken into account in the models in spite of the addition of several percent of H_2 to He purge gas used in

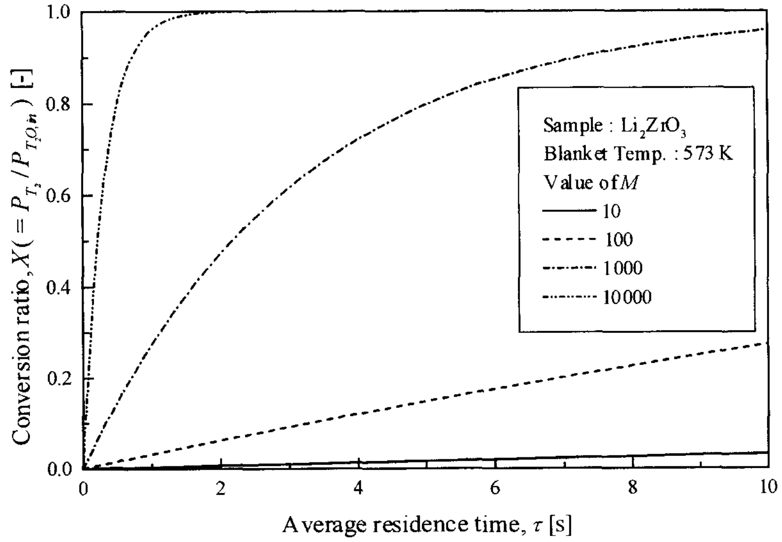

Fig. 6. Change of X and τ under various M when the blanket temperature is 573 K.

the referred in situ experiments to their models. The effect of the isotope exchange reaction is not being excluded in the model formation because strong dependency of the isotope exchange reaction rate on temperature is observed in this work.

5. Conclusions

The overall mass transfer coefficients of the isotope exchange reaction between H_2 and D_2O or that between D_2 and H_2O on Li_2ZrO_3 are obtained as

$$K_{F,ex1} = 1.60 \times 10^{2} \exp(-121\ (\mathrm{kJ/mol})/RT)\ (\mathrm{m/s})$$

in steady state experimental methods assuming the pseudo first order reaction in this work. An isotope effect for the isotope exchange reaction between H_2 and D_2O or that between D_2 and H_2O on Li_2ZrO_3 is not obtained in this work.

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