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Journal of Nuclear Materials 329–333 (2004) 1370–1373
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Enhancement of isotope exchange reactions over ceramic breeder material by deposition of catalyst metal

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Abstract

The deposition of catalyst metals in ceramic breeders could enhance the release rate of tritium due to the promotion of isotope exchange reactions taking place at the interface of the breeder surface and the sweep gas. In this work, the authors examined the effects of catalytic active metal deposited on lithium titanate on the isotope exchange reactions. With respect to the virgin lithium titanate, it was found that the rate of the isotope exchange reactions taking place on the surface is quite low. However, the deposition of palladium greatly increased the exchange reaction rate. The effect of the amounts of deposited palladium on the isotope exchange reaction rate was also investigated. The results indicate that the exchange reactions are still enhanced even if the amounts of deposited palladium are as low as 0.04%.

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1. Introduction

In most designs of D–T fusion reactor blankets with solid breeder materials, the extraction of tritium via isotopic exchange reaction is improved by the use of helium sweep gas containing 0.1% of hydrogen [1]. However, these exchange reactions, which take place predominantly on the surface of the ceramic breeders, are rather slow at low temperatures (<500 °C). For this reason, development of methods to promote the isotope exchange reactions on the grain surfaces are of substantial interest, and could accelerate the recovery of bred tritium particularly at moderate temperatures of design inherent.

Over the past few years, studies have been conducted on the isotope exchange reactions and water adsorption at the surface of several ceramic blanket materials. The results indicated that the strong temperature dependence of the exchange reactions leads to the isotope exchange reaction at the breeder gas/solid interface proceeding fast only at relatively elevated temperatures (>700 °C) [2]. A considerable decrease in the reaction rate takes place as temperature is decreased. Taking into consideration that there is a broad temperature distribution within a blanket module [3], it is anticipate that the recovery of the tritium is poor in regions of lower temperature (<500 °C), which could result in an increased overall steady state tritium inventory in the blanket module.

The aim of our study is to accelerate the recovery of tritium from ceramic breeder materials over a broad range of temperatures. For this purpose, studies of the effect of catalytic metal additives on the isotope exchange reactions at the solid breeder/sweep gas interface have been conducted [4]. In our previous studies, out of pile annealing tests were also conducted using the irradiated ceramic breeders impregnated with catalytically active metals [5–7]. The results indicated that the enhancement of tritium release rate from the catalytic

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0022-3115/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2004.04.200

breeder could be attributed to the enhanced isotope exchange reaction by the additive metal. In the present study, the authors investigated the effect of the amount of palladium, a catalytic noble metal, deposited in the Li_2TiO_3 breeder on the rate of isotope exchange reaction taking place on the surface of Li_2TiO_3.

2. Experimental

2.1. Preparation of solid breeder material with catalyst

Palladium was deposited on solid breeder material particles (Li_2TiO_3, 16–24 mesh (0.71–1.00 mm in diameter), >80% TD (theoretical density)) by the incipient wet impregnation method generally used for the fabrication of catalysts. For this purpose, Li_2TiO_3 particles placed in a flask were first dried under air at 150 °C for 24 h. Then, the solution of palladium was poured drop by drop onto the previously dried Li_2TiO_3 particles. The solution was prepared using palladium tetrammonium nitrate $Pd(NH_3)_4(NO_3)$. After the treatment, the wet Li_2TiO_3 pellets were dried in an oven, first at 90 °C for 3 h and then at 150 °C for another 24 h. The obtained precursor was calcined in a quartz tube reactor under a He atmosphere containing 10% O_2 by raising the temperature stepwise to 400 °C. Following the calcination process, the noble metals deposited in the ceramic breeder particles were reduced under a hydrogen atmosphere at 400 °C for several hours. The amount of palladium deposited in the Li_2TiO_3 breeder was controlled by changing the concentration of the metal in the solutions. According to the mass balance in the fabrication process, the concentrations can be estimated to be in the range 0.041–4.0 wt%.

2.2. Experiments on exchange reactions with H_2 And D_2O mixture gases

The flow diagram of the experimental apparatus is shown in Fig. 1. Pd/Li_2TiO_3 and Li_2TiO_3 particles were placed in a quartz reactor. The temperature of the reactor was controlled by a conventional electric furnace and a temperature controller. The concentrations of H_2, HD and D_2 in the inlet and outlet streams of the reactor were analyzed by gas chromatography. The water vapor content in these streams was analyzed with a hygrometer. The gases employed were purified with a cold trap containing 3A molecular sieve cooled by an ice/water mixture to remove residual water vapor. In order to achieve controlled concentrations of deuterated water in the carrier gas, molecular deuterium D_2 was quantitatively oxidized in a CuO bed held at 350 °C.

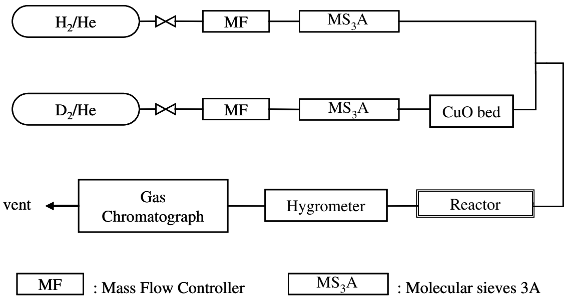

Fig. 1. Flow diagram of experimental apparatus.

As reported in previous papers, water is formed on the surface of breeder materials when heated under an atmosphere containing hydrogen [8]. Although the water formation cannot completely be stopped if hydrogen is present, it is necessary to limit the formation of water by this mechanism during the course of an experiment. For this purpose, the sample bed temperature was raised in steps of 50 °C under a stream of H_2/He gas until the concentrations of water vapor due to the heterogeneous formation reaction became less than a few ppm. Once the maximum experimental temperature was established and the water formation was confirmed to be negligibly small, the actual exchange experiment was started. During the runs, which were carried out under steady state conditions, the reactor temperature was stepwise decreased. The experimental conditions employed are summarized in Table 1. The space velocity (SV) in Table 1 is defined as

$$SV = Q/B, \tag{1}$$

where Q and B are the volumetric velocity of the gas fed into the reactor and the bed volume of the breeder material, respectively. SV) is the reciprocal of the residence time of the process gas, the higher SV, the lower the residence time. As shown in Table 1, the experiments were performed under the conditions where the value of SV was approximately 10 000 h^{-1}.

Table 1
Experimental condition

Sample	Li_2TiO_3 0.041 wt% Pd/Li_2TiO_3 0.41 wt% Pd/Li_2TiO_3 4.0 wt% Pd/Li_2TiO_3
Amount of breeder	0.5 [g]
Flow rate	600 [ml/min]
Bed diameter	5.8 [mm]
Space velocity	10 000 [h^{-1}]
Temperature	50–800 [°C]
Inlet gas composition	
H_2	4000 [ppm]
D_2O	300 [ppm]
He	Balance

3. Results and discussion

In the experiments, the helium gases containing H_2 and D_2O were passed through the reactor packed with the breeder particles. The isotope exchange reactions taking place on the surface of the breeder material are expressed as

$$D_2O + H_2 \leftrightarrow HD + HDO \tag{2}$$

$$HDO + H_2 \leftrightarrow HD + H_2O \tag{3}$$

$$D_2O + HD \leftrightarrow D_2 + HDO \tag{4}$$

The extent of the exchange reactions taking place was obtained from the composition of the outlet stream of the reactor measured by gas chromatography. The conversion ratio R can be defined as

$$R = C_{\mathrm{D,out}}/C_{\mathrm{D,in}}, \tag{5}$$

where $C_{\mathrm{D,in}}$ and $C_{\mathrm{D,out}}$ are the molar concentration of D-atoms in D_2O in the inlet stream and the molar concentration of D-atoms in HD and D_2 in the outlet stream, respectively.

Fig. 2 shows comparison of the conversion ratios over the Li_2TiO_3 particle beds with different contents of deposited palladium. For the virgin Li_2TiO_3 particles, which did not contain the catalyst, the exchange reaction did not take place at the temperatures ranging from 400 to 750 °C. The conversion ratio was only 4% at 750 °C and 11% even at 800 °C. The equilibrium of the isotope exchange reaction was not attained at temperature as high as 800 °C. In the case of 0.041 wt% Pd/Li_2TiO_3, the catalytic effect appeared even at low temperatures in spite of its very small Pd content; the conversion ratio was about 55% at 400 °C, a temperature where the exchange reaction did not take place over the virgin Li_2TiO_3 breeder. The equilibrium of the isotope exchange reaction in the materials with catalyst was attained at temperatures above 600 °C. When the Pd content was increased to 0.41 wt% (0.41 wt% Pd/Li_2TiO_3), the catalytic effect was further enhanced and the conversion ratio became about 90% at 400 °C, which is almost the equilibrium. When the Pd content was further increased to 4.0 wt% Pd/Li_2TiO_3, which is the maximum amount of Pd deposition, the catalytic effect also took place, but difference in conversions was small in comparison with the case of the 0.41 wt% Pd/Li_2TiO_3 breeder. The results shown above indicate that the catalytic effect of Pd on the isotope exchange reaction increases as the deposition amount of Pd is increased, but concentrations of Pd above 0.41% does not appears to lead to further catalytic effect. It is also suggested that the catalytic effect of Pd takes place even if the deposition amount is as low as 0.041 wt%, and the isotope exchange reaction is increased. The effect of deposition of palladium on a Li_4SiO_4 breeder, reported in previous literature [9], is shown in Fig. 3 for comparison; the experiments were conducted in almost the same experimental condition in terms of the value of SV and the chemical composition of the inlet gas as this study, which enables direct comparison of the experimental results. The comparison of the results shown in Figs. 2 and 3 suggests that without catalysts the exchange reaction over the Li_2TiO_3 breeder is considerably slower than that over the Li_4SiO_4 breeder. Thus, the addition of hydrogen to the sweep gas probably cannot enhance the rate of tritium release from Li_2TiO_3 due to the slow exchange reaction. Furthermore, it is also suggested in these figures that the deposition of palladium in Li_2TiO_3 has a greater effect on the isotope exchange rate than Li_4SiO_4.

The surface of the Li_2TiO_3 and Pd/Li_2TiO_3 breeders were observed with a scanning electron microscope. Fig. 4(a)–(d) show the microphotographs of the surface of virgin Li_2 TiO_3, 0.041 wt% Pd/Li_2TiO_3, 0.41 wt% Pd/Li_2TiO_3, 4.0 wt% Pd/Li_2TiO_3 breeders, respectively. In the figures, scale marks corresponding to 1.0 μm are shown as well. Fig. 4(a) indicates that the grain size of

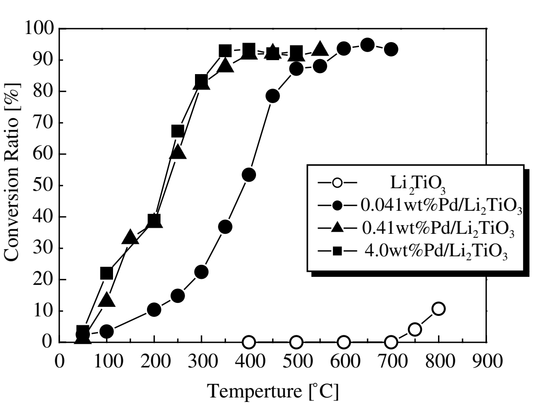

Fig. 2. Conversion ratio of isotope exchange reaction over Li_2TiO_3 as function of temperature.

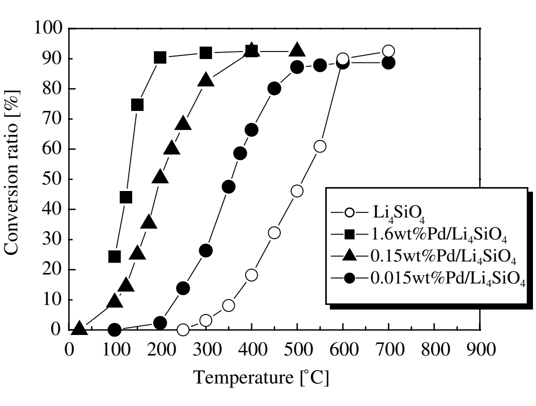

Fig. 3. Conversion ratio of isotope exchange reaction over Li_4SiO_4 as function of temperature.

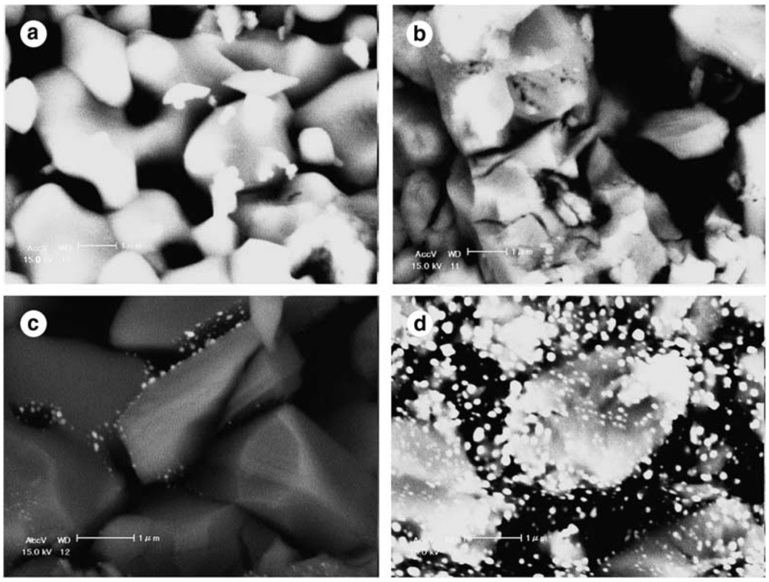

Fig. 4. Microphotographs of surface of Li_2TiO_3 breeders . (a) Virgin Li_2TiO_3, (b) 0.041 wt% Pd/Li_2TiO_3, (c) 0.41 wt% Pd/Li_2TiO_3, (d) 4.0 wt% Pd/Li_2TiO_3.

Li_2TiO_3 particle ranges 1–2 µm. Comparison of Fig. 4(a) and (d) reveals great difference in the surface structures of virgin Li_2TiO_3 and Pd/Li_2TiO_3 breeders. As seen in Fig. 4(d), it was found that Pd particles with size less than 0.2 µm were deposited on the surface of the Li_2TiO_3 grains. These fine Pd particles present on the grain surface of the Li_2TiO_3 breeders probably enhance the isotope exchange reaction. As seen in Fig. 4(c), when the amount of Pd deposited was decreased to 0.41%, much smaller Pd particles appear to be deposited on the surface of the Li_2TiO_3 grains. With regard to the 0.041 wt% Pd/Li_2TiO_3 breeder (see Fig. 4(b)), vary small Pd particles could be identified as white spots, but the number of the Pd particles identified is not many. However, from the experimental results shown in Fig. 2 (catalytic effects took place even with this small amount of Pd deposition), it is expected that far smaller Pd particles were deposited on the surface of the Li_2TiO_3 grains. These observations would suggest that small particles of Pd could be deposited in Li_2TiO_3 particles by the simple incipient wet impregnation method.

4. Conclusions

In order to enhance the isotope exchange reaction rate on breeder gas/solid interface, the effect of the amount of palladium, one of the catalytic noble metals, deposited in the Li_2TiO_3 breeder on the exchange reaction rate was studied. The experimental result on the virgin Li_2TiO_3 breeder suggests that the exchange reaction taking place on the surface of the Li_2TiO_3 breeder is very slow, and it is experimentally confirmed that the deposition of palladium as small as 0.041 wt% greatly enhances the isotope exchange reaction. Observations with a scanning electron microscope reveals that palladium particles with size less than 0.2 µm were deposited on the grain surface of the Li_2TiO_3 breeder, which probably promotes the isotope exchange reaction on the surface of the breeder.

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