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Improvement of Hydrogen Isotope Release on Lithium Orthosilicate Ceramic Pebble by Catalytic Metals

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Lithium Orthosilicate (Li_4SiO_4) ceramic pebble is considered as a candidate tritium breeding material of Chinese helium cooled solid breeder test blanket module（CH HCSB TBM）for the International Thermonuclear Experimental Reactor (ITER). In this paper, Li_4SiO_4 ceramic pebbles deposited with catalytic metals, including Pt, Pd, Ru and Ir, were prepared by wet impregnation method. The metal particles on Li_4SiO_4 pebble exhibit a good promotion of hydrogen isotope exchange reactions in H_2-D_2O gas system, with conversion equilibrium temperature reduction of 200−300 °C. The out-of-pile tritium release experiments were performed using 1.0 wt% Pt/Li_4SiO_4 and Li_4SiO_4 pebbles irradiated in a thermal neutron reactor. The results showed that Pt was effective to increase the tritium release rate at lower temperatures, and the ratio of tritium molecule (HT) to tritiated water (HTO) of 1.0 wt% Pt/Li_4SiO_4 was much more than that of Li_4SiO_4, which released mainly with HTO. Thus, catalytic metals deposited on Li_4SiO_4 pebble may help to accelerate the recovery of bred tritium particularly in low temperature region, and increase the tritium molecule form released from the tritium breeding materials.

Keywords: Lithium Orthosilicate (Li_4SiO_4); Hydrogen Isotope Exchange Reaction; Catalytic Metal; Tritium

1. Introduction

Lithium-containing ceramics，such as Li_2O, $LiAlO_2$, Li_2ZrO_3, Li_2TiO_3 and Li_4SiO_4，are considered as tritium breeding materials for securing an adequate tritium supply to sustain the D-T fusion reaction in a fusion reactor [1-4]. Tritium is produced via $^6Li(n,\alpha)T$ in the lithium ceramic pebbles, and extracted by a helium sweep gas with a fraction of hydrogen or deuterium from the surface of the pebbles. Considering the reduction for the residence time of tritium in the breeder blankets, the bred tritium must be carried out with a fast recovery rate over a broad range of temperatures, so some means shall be developed to accelerate the tritium release rate.

The mass transfer mechanism of tritium released from lithium-containing ceramics is complicated, but it is developed and assumed commonly that tritium is bred in grain interior, diffuses to the surface layer, and then transfer to the surface water layer which consists of physical, chemical and structural adsorbed water. Finally, tritium at the surface water discharges to the purge gas through such surface reactions as desorption, isotope exchange reactions between hydrogen and water vapor in purge gas [5]. However, the isotope exchange reactions at the interface between solid surface and sweep gas are very slow at low temperature, only fast at relatively elevated temperatures (>700 °C) [6, 7]. When isotope exchange reactions contribute strongly to tritium release rate, it is difficult to reflect tritium diffusion in the bulk of grain. Then, platinum and palladium were tried to deposit on lithium-containing ceramics, and exhibited a promotion of hydrogen isotope exchange reactions at low temperatures [6-9]. Considering the practical application of neutron activity materials in a fusion reactor, many problems need systematic study, such as comparison of different metals, the optimization of catalytic metal content and catalyst poisoning.

Now, Li_4SiO_4 ceramic pebble is considered as a candidate tritium breeder of Chinese helium cooled solid breeder test blanket module for the international thermonuclear experimental reactor（ITER）[4]. In order to investigate the energetic tritium moving mechanism in the crystal grain of Li_4SiO_4 ceramic pebble, study the isotope exchange reactions on the gas/solid interface of the pebble, and search some way to enhance the tritium release at low temperaure, it is necessary to investigate the behavior of hydrogen isotope exchange influenced by catalytic active metal. In this work, Li_4SiO_4 ceramic pebbles deposited with four kinds of catalytic metals, Pt, Pd, Ru and Ir, were prepared. The effects of different Pt content and different metal role on the hydrogen isotope exchange reactions were examined in H_2/D_2O gas system. The tritium release behavior of the neutron-irradiated 1.0 wt% Pt/Li_4SiO_4 and Li_4SiO_4 was compared through the out-of-pile tritium release experiments.

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2. Experimental

2.1 Preparation of Sample

Li_4SiO_4 ceramic pebbles were fabricated by freeze-sintering process[10]. The preparation process included mixing Li_4SiO_4 powder, polyvinylalcohol solution and antifoam agent, dropping the prepared mixture into liquid nitrogen through a nozzle to generate spheres, freeze-drying the spheres in a freeze dry system, and calcinating the spheres programedly to get ceramic pebbles.

Li_4SiO_4 ceramic pebbles (av. 0.9 mm in diameter) were selected to be deposited with noble metals by wet impregnation method. The pebbles were dried in a vacuum drier at 150°C for 3h. Then the metal-containing solution, H_2PtCl_6, H_2IrCl_6, $PdCl_2$ and $RuCl_3$, was dripped on the pebbles respectively, and was adsorbed swiftly by the pebbles. When the pebbles were saturated with the solution, they were dried for 1-2 h by infrared ray. After repeating the above steps until the pebbles had adsorbed a predetermined content, they were transferred to deoxidize in a 5 vol% H_2/N_2 mixture gas at 400-450 ^oC for 3h. Finally Li_4SiO_4 ceramic pebbles with catalyst were obtained.

2.2 Physical Characterization

Powder X-ray diffraction (XRD) patterns of 1.0 wt% Pt/Li_4SiO_4 were determined on a DX-2600SSC diffractometer (Cu Kα radiation at 40 kV and 30 mA) at a scanning speed of $1.2^o\,min^{-1}$ from 15^o to 95^o. Pt particle size was analyzed by Philips- CM30 transmission electron microscope at an acceleration voltage of 200 kV. Pt particles more than 100 were chosen randomly to test the metal particle size by Photoshop CS2 software.

Table1 Experimental conditions

Group	Sample mass (g)	Flow rate of D_2/He	Flow rate of H_2/ He
Li_4SiO_4; 1.0 wt% Pt/Li_4SiO_4	0.2	100	100
0.1~1.0 wt% Pt/Li_4SiO_4	0.35	50	50
0.1 wt% M/Li_4SiO_4 (M = Pt, Pd, Ru and Ir)	0.35	50	50

2.3 Hydrogen Isotope Exchange Reactions

The samples were dried at 150 ^oC for 2h in a vacuum drier, and then installed in a settled reactor (ϕ = 8 mm) made of stainless steel. A mixture gas of 1.08 % H_2/He and 1.12 vol% D_2O/He was introduced into the reactor. The concentration of D_2O was controlled by D_2/He gas passing through a CuO bed of 350 ^oC. The deuterium concentration of HD in the outlet stream was measured by gas chromatogram (Agilent 6890N). 601 column was used as the column material. The HD peak could be obtained depending on the thermal conductivity coefficient when hydrogen was used as a carrier gas. All the experiments were conducted under steady state conditions at ambient atmosphere pressure. The experimental conditions and the expeimental flow chart for hydrogen isotope exchange reactions are shown in Table1 and Fig.1 respectively.

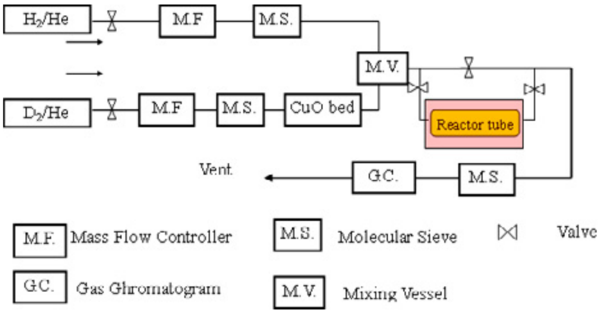

Fig.1 Experimental flow chart for hydrogen isotope exchange reactions

2.4 Tritium Thermal Desorption

Li_4SiO_4 and 1.0 wt% Pt/Li_4SiO_4 ceramic pebbles, which had been dried at 150 ^oC for 2 h in vacuum, were sealed in quartz capsules with He gas less than 10 Pa. Then the encapsulated samples were irradiated in a reactor with a neutron flux of 7.1×10^{12} $cm^{-2}s^{-1}$ for 100min at ambient temperature (29-36 ^oC). Tritium was produced by thermal neutron capture of lithium via the reaction of $^6Li(n, \alpha)T$. After irradiation, the samples were placed at room temperature for two years. The quartz capsules were broken in a glove bag filled with He gas. Some pebbles about 0.01-0.02 g were transferred into a reactor tube made of quartz for tritium thermal desorption, and the others were removed into a small test tube which was stored in a desiccator for stand-by.

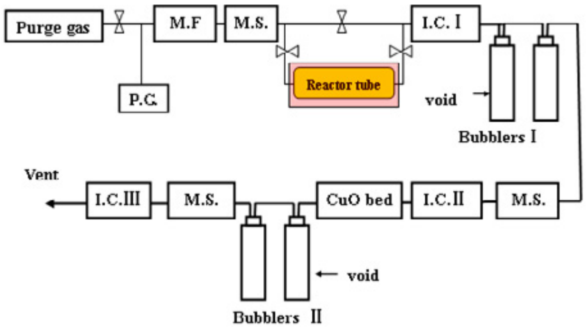

Fig.2 Experimental flow chart for tritium release

Tritium release experiments were performed by applying the out-of-pile temperature programmed desorption technique. The flow chart of the experimental system is shown in Fig.2.The reactor tube was heated in a tube furnace at a heating rate of 5 ^oC min^{-1} from room temperature to 800 ^oC, while a purge gas of He containing 1vol% H_2 carried the released tritium (HT and HTO) through the experimental system at a flow rate of 50 ml min^{-1}. The first ionization chamber measured total tritium released from the ceramic pebbles, the second ionization chamber measured tritium released as HT. The amount of tritium in the bubblers, which were used to adsorb HTO (T_2O) with glycol solution as adsorbent, was measured by liquid scintillation counting. Details of the experiments were cited in the previous literature[11,12].

3.Results and Discussions

3.1 Preparation of Sample

As the data shown in Table 2, Li_4SiO_4 ceramic pebble fabricated by freeze-sintering process has good sphericity, high density and material phase purity .

Table 2 Characteristics of Li_4SiO_4 ceramic pebble

Raw materials	Density (%T.D.)	Phase purity of Li_4SiO_4 (%)	Sphericity	Diameter (mm)	Grain size (μm)
Li_2CO_3+SiO_2	80~85	>97	1.04(a.v.)	0.5~1	4.5(a.v.)

Fig.3 Appearance of 1.0 wt% Pt/Li_4SiO_4 pebble

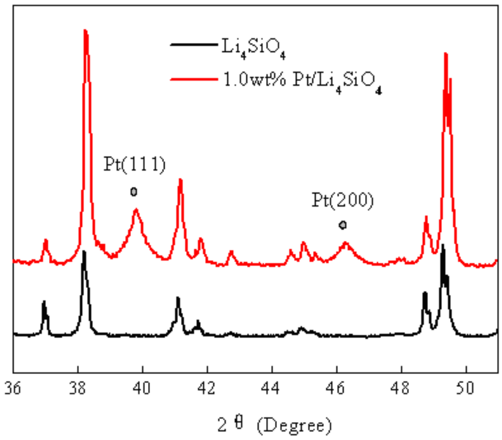

Fig.4 XRD patterns of Li_4SiO_4 and 1.0 wt% Pt/Li_4SiO_4

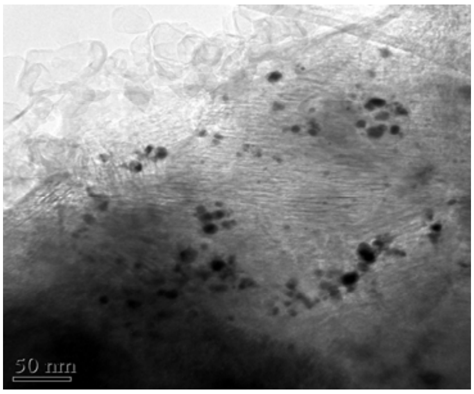

Fig.5 TEM micrograph of 1.0 wt% Pt/Li_4SiO_4 pebble

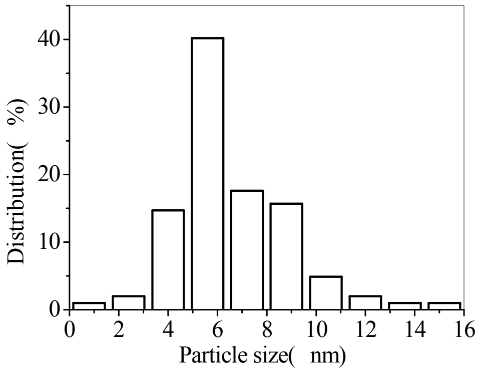

Fig.6 Distribution of Pt particles on the surface of 1.0 wt% Pt/Li_4SiO_4 pebble

0.1−1.0 wt% Pt/Li_4SiO_4 and 0.1 wt% M/Li_4SiO_4 (M =Pd, Ru, Ir) ceramic pebbles were obtained by the wet impregnation method. When the catalytic metals were deposited on Li_4SiO_4, the surface color changed from white to grey（0.1 wt% Pt）, brown (0.5 wt% Pt) or black（1.0 wt% Pt） as shown in Fig.3. It is determined by X-ray diffraction that Pt particles on the pebble surface belong to face centered cubic structure with the crystalline planes of Pt (1 1 1) and Pt (2 0 0) in Fig.4. TEM analysis in Fig.5 shows that the agglomeration of Pt particles is obvious, but the maximal size of Pt particles is less than 20 nm as shown in Fig.6. The mean size of Pt particles is 6.7 nm.

3.2 Isotope Exchange Reactions on pebble

The mixture gas of H_2, D_2O and He was feeded into the reaction bed, D_2O was adsorbed on the grain surface of the sample, and then the isotope exchange reactions took place over the grain surface between the adsorbed D_2O and H_2 in the gas. The exchange reactions on the basis of the simplified model were expressed as

$$D_2O(s) + H_2(g) \Leftrightarrow HD(g) + HDO(s) \qquad (1)$$
$$HDO(s) + H_2(g) \Leftrightarrow HD(g) + H_2O(s) \qquad (2)$$

The deuterium concentration in the outlet stream was measured with gas chromatogram, and the conversion of D-atoms for the isotope exchange reaction was defined as the formula (3) , where $C_{D,out}$ was the concentration of HD in the outlet stream, and $C_{D,in}$ was the concentration of D-atoms in the inlet stream.

$$R = \frac{C_{D,\ \text{out}}}{C_{D,\ \text{in}}} \qquad (3)$$

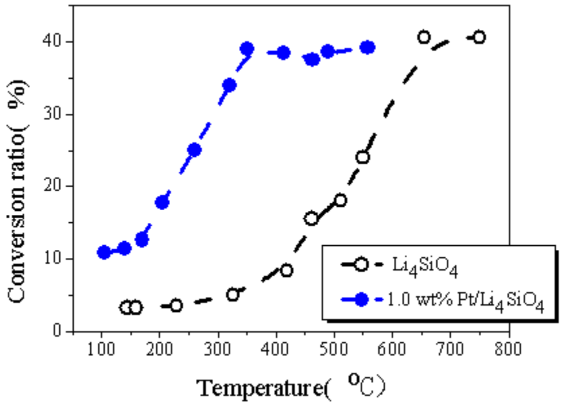

Fig.7. Conversion ratio of hydrogen isotope exchange reactions

With respect to the virgin Li_4SiO_4, the rate of the isotope exchange reaction taking place on the surface was quite slow, and the conversion ratio reached equilibrium above 650 °C. However, the conversion ratio of 1.0 wt% Pt/Li_4SiO_4 ceramic pebble increased rapidly between 200 °C and 300 °C, and reached equilibrium above 300 °C. The experimental curves in Fig.7 indicate that the conversion equilibrium temperature decreased about 300 °C if 1.0 wt% Pt was deposited on the surface.

Catalytic metal deposited on Li_4SiO_4 ceramic pebbles would provide active adsorption sites for H_2 in the gas, and had a tendency to decompose H_2(ads) into H(ads). The H(ads) atom had higher reactivity and quicker transfer capability, so the activation energy for the exchange reaction was reduced, and it's easy to occur hydrogen isotope exchange between the H(ads) atom and D_2O molecule adsorbed on the surface of ceramic pebbles [6-9]. The hydrogen isotope exchange reaction process may be expressed as follows.

$$H_2(g) + 2M(s) \Leftrightarrow 2M\text{-}H(s) \qquad (5)$$

$$M\text{-}H(s) + D_2O(ads) \Leftrightarrow M\text{-}H(D_2O) \Leftrightarrow M\text{-}D(HDO) \Leftrightarrow M\text{-}D(s) + HDO(ads) \qquad (6)$$

$$M\text{-}H(s) + M\text{-}D(s) \Leftrightarrow 2M(s) + HD(g) \qquad (7)$$

, where M(s) is the catalytic metal deposited on solid surface.

To investigate the catalytic effect depended on different metal content, the Li_4SiO_4 ceramic pebbles were deposited with 0.1 wt%, 0.5 wt% and 1.0 wt% content of Pt respectively. According to the experimental results shown in Fig.8, the content of Pt on the surface could influence the enhancement of the isotope exchange reactions. The conversion ratio of 0.1 wt% Pt/Li_4SiO_4 reached equilibrium after 350 °C, and that of 0.5-1.0 wt% Pt/Li_4SiO_4 reached around 300 °C. It indicates that more content of Pt on the pebble surface would provide more active adsorption localities, and the lower equilibrium temperature for the isotope exchange reaction would be obtained. However, the efficiency of noble metals of the surface should depend on the surface coverage for the samples having different specific surface area. Y. Narisato and K. Mochizuki reported that the better content range of Pd on lithium ceramic pebbles was 0.15-1.6 wt% or 0.02-0.2 wt% [5, 13].

Pd, Ru, and Ir were also deposited on Li_4SiO_4 respectively, and exhibited to enhance the isotope exchange reactions as shown in Fig.9. It is suggested that many catalytic metals could be used to promote hydrogen isotope exchange reactions on Li_4SiO_4 ceramic pebble.

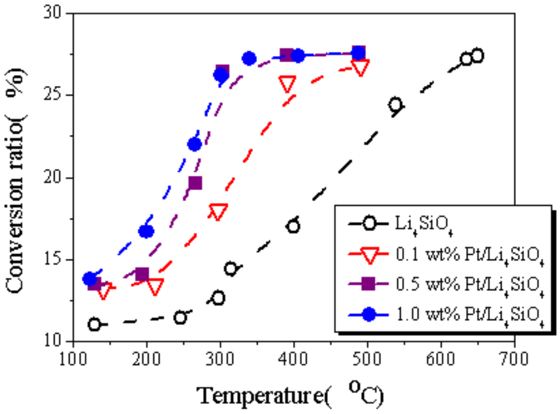

Fig.8. Conversion ratio of isotope exchange reactions on Pt/Li_4SiO_4 pebble

According to the thermodynamic functions, hydrogen isn't adsorbed on catalytic active metal surface in intact molecule, and it combines with metal atoms in single atom [13, 14]. Water vapor molecule exists in intact molecule on Pt surface, but has a tendency to be dissociated to OH(ads) and H(ads) on Ir or Ru surface. So there were different hydrogen isotope exchanging processes on the surface of M/Li_4SiO_4 pebbles. It indicates that if Pt or Pd with rational intermingles of Ru, Ir or Fe, deposited on Li_4SiO_4 pebbles together, would incease the catalytic activity. In that case, the amount of the noble metal could be reduced in the tritium breeder materials.

3.3 Tritium Thermal Desorption

Fig.10 and 11 present the tritium release behavior of neutron-irradiated Li_4SiO_4 and 1.0 wt% Pt/Li_4SiO_4 pebbles under the 1.0 vol% H_2/He purge gas flow. After

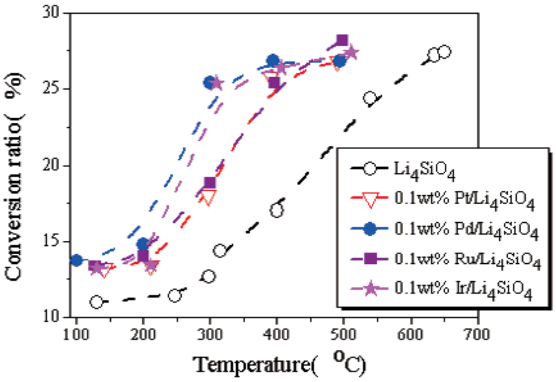

Fig.9. Conversion ratio of isotope exchange reactions on M/Li_4SiO_4 pebble

the specimens were swept by pure He gas to wipe off the tritium adsorbed physically on the pebble, the purge gas was changed to 1.0 vol% H_2/He, and then the reactor tube was heated at a rate of 5 °C /min. The blue curve represents the total tritium concentration denoted as HT&HTO released from the pebbles, and the red curve represents the molecular form of tritium denoted as HT.

Fig. 10 shows the tritium release curves of virgin Li_4SiO_4. There are two large peaks of total tritium from R.T to 800 °C. One peak, appeared at around 259 °C, and the second one, relatively larger than the former, appeared at 418 °C. It's evidently that tritiated water, denoted as HTO, is much more than HT in the annealing course, especially at low temperature less than 400 °C. As shown in Table 3, the fraction of HTO was 96.2 % of the total tritium, but HT was 3.8 %. It indicated that tritium was released mainly as the chemical form of tritiated water in the experimental conditions of this paper.

Fig.11 shows the tritium release curves of 1.0 wt% Pt/Li_4SiO_4. There are two peaks for both the total tritium and the tritium molecular form during the annealing course. With regard to the total tritium curve, the larger peak was observed at 218 °C, and the smaller peak appeared at 468 °C. It means that most of tritium was released at lower temperature less than 400 °C. The tritium release curve of HT had a similar shape as that of the total tritium. Table 3 shows that the fraction of HTO was 36.9 %, but HT was increased to 63.1%. The fraction of chemical forms was quite different from that of the virgin Li_4SiO_4. It indicates that the tritium molecular form (HT) became the main component when noble metal deposited on the surface of Li_4SiO_4.

To compare the tritium release amount of Li_4SiO_4 and 1.0 wt% Pt/Li_4SiO_4, 37.4% of the total amount of tritium was released at 350 °C for Li_4SiO_4, but 66.9% for 1.0 wt% Pt/Li_4SiO_4. The largest peak of total tritium was at 418 °C for Li_4SiO_4, but 218 °C for 1.0 wt% Pt/Li_4SiO_4. So the catalytic effect of Pt was evidently. Even at temperature less than 200 °C, the tritium concentration in the outlet stream of the reactor tube increased rapidly

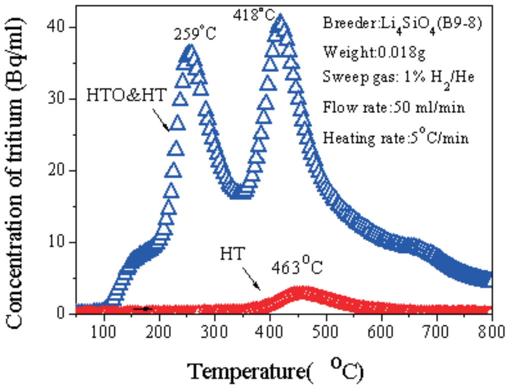

Fig.10 Tritium release of neutron-irradiated Li_4SiO_4 pebble

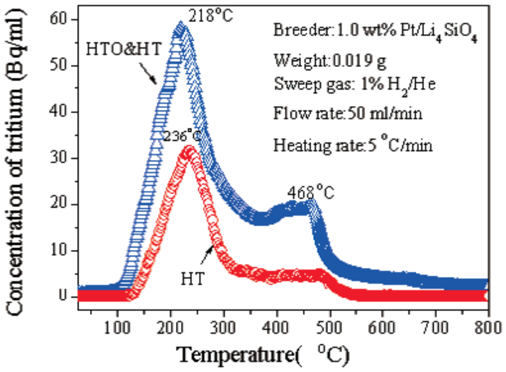

Fig.11 Tritium release of neutron-irradiated 1.0 wt% Pt/Li_4SiO_4 pebble

Table 3 Fraction of tritium released from samples

Sample	Fraction of Chemical forms in TDS process (%)		Fraction of tritium (HTO&HT) released in TDS process (%)		
	HTO	HT	25-350 °C	350-550 °C	550-800 °C
Li_4SiO_4	96.2	3.8	37.4	44.0	18.6
1.0 wt% Pt/Li_4SiO_4	36.9	63.1	66.9	25.8	7.3

from 1.0 wt% Pt/Li_4SiO_4. It means that when catalytic metal was deposited on the surface of Li_4SiO_4, the hydrogen isotope exchange reactions were enhanced between H_2 in the purge gas and tritium adsorbed on the solid surface.

With regard to the tritium chemical form, 3.8 % of the total tritium was released as HT from room temperature to 800 °C for Li_4SiO_4, and a small peak of HT appeared at 463 °C. However, the fraction of HT was 63.1 % for 1.0 wt% Pt/Li_4SiO_4 with only one large peak at 236°C. The HT curve strongly influenced the shape of the total tritium curve for 1.0 wt% Pt/Li_4SiO_4. It indicated when 1.0 wt% Pt was deposited on Li_4SiO_4, the hydrogen isotope exchange reactions, expressed as (5)-(7),were easy to proceed at the temperatures less than 460 °C.

The isotope exchange reactions on 1.0 wt%

Pt/Li_4SiO_4 proceeded much faster than that on virgin Li_4SiO_4 , and the chemical forms of the released tritium changed. It was attributed to the catalytic effect of noble metal on the solid surface. Without the effect of catalyst, the exchange reaction rates of (1) and (2) were far smaller than the desorption rate or the rate of isotope exchange reaction (8), then the conversion of tritium (HTO into HT) was quite slow.

$$H_2O(g) + HTO(s) \Leftrightarrow HTO(g) + H_2O(s) \qquad (8)$$

With the help of catalyst, it's easy to occur hydrogen isotopes exchanging between H(ads) atoms and T adsorbed on the surface of ceramic pebbles at lower temperature as the formula(6). As soon as T exchanged with H(ads) and migrated to the active adsorption locality, it would discharge quickly combined with another H(ads).

Considering the high neutron activity in practical application, the content of noble metals should be reduced on lithium ceramic pebble, and some new metal with low neutron activity need to discover.

Conclusions

Wet impregnation method has been used to fabricate Li_4SiO_4 ceramic pebbles deposited with catalytic active metals including Pt, Pd, Ru and Ir.

Lithium orthosilicate pebble deposited with noble metals exhibite a promotion of hydrogen isotope exchange reactions in H_2/D_2O gas system. With respect to virgin Li_4SiO_4, the rate of the isotope exchange reaction taking place on the surface was quite slow, and the conversion ratio reached equilibrium after 650 ^oC. However, the conversion ratio of M/Li_4SiO_4 was increased obviously from 200 ^oC and 300 ^oC. More content of the catalytic metal provided more active adsorption localities on the pebble, so the conversion ratio of 0.1 wt% M/Li_4SiO_4 reached equilibrium after 350 ^oC, and that of 0.5-1 wt% M/Li_4SiO_4 reached equilibrium after 300 ^oC.

Most tritium was released at lower temperatures from neutron-irradiated 0.1 wt% Pt/Li_4SiO_4, and the chemical form of HT was increased remarkably compared with that of Li_4SiO_4. The result indicates that catalytic metal deposited on Li_4SiO_4 ceramic pebble could reduce activation energy, facilitate H-T(D) isotope exchange reaction, and influence the tritium release mechanism. Consequently, the deposition of catalytic metal on Li_4SiO_4 is an effective way to promote the tritium release from the breeder materials, and is in favor of the design of tritium cycle system about extracting, separating and purifying in a D-T fusion reactor.

Acknowledgements

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