

Studies and Developments of Tritium Recovery System for Blanket of Fusion Reactor in Japan Atomic Energy Agency

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Abstract. A water cooling solid breeder blanket is a prime candidate of the blanket of the fusion reactor in Japan. In this case, the blanket tritium recovery system will be composed of three processes: tritium recovery from the helium sweep gas as hydrogen, that as water vapor and tritium recovery from the coolant water. For these processes, the present authors have proposed a set of advanced systems, and have proved that the proposed systems would be feasible for a DEMO reactor. For tritium recovery as hydrogen, an electrochemical hydrogen pump with a ceramic proton conductor has been proposed. In this work, the correlation between the proton concentration in the ceramic and the hydrogen pressure in the gas phase has been investigated to describe the proton conductivity specifically. A ceramic electrolysis cell has been proposed to process the tritiated water vapor. In this work, the present authors have developed a new electrode that contained the cerium oxide, and it has shown a fairly large current density. For tritium recovery from the coolant water, the reduction of the processing water by tritium concentration is necessary. The present authors have studied about the fixed-bed adsorption process of synthetic zeolite, and the development of the adsorbent that can desorb water vapor easily is required. In this work, the effect of the silica/alumina ratio of the adsorbent on the separation factor was examined. NaY10.0 (faujasite-type, silica/alumina=10.0) showed quite unique characteristics for the water adsorption and desorption.

1. Introduction

Tritium technologies have reached the level where they allow us to design the main fuel cycle for ITER. On the other hand, for the blanket tritium recovery system, a series of fundamental studies have still been carried out even though the system is essential to realize the fusion reactor from the viewpoint of the fuel production. To obtain a large progress in R&D of the blanket tritium system, it is strongly desired to study the tritium behavior systematically in the whole blanket system. In Japan, a water cooling solid breeder blanket is a prime candidate, and the helium sweep gas with hydrogen is planned to use for tritium release enhancement. In this case, the chemical form of released tritium is expected to be hydrogen and water vapor simply. In addition, it has been pointed out that the use of the hydrogen added sweep gases at high temperature region such as a blanket leads to the permeation of tritium into the coolant water. Therefore, the blanket tritium recovery system will be composed of three processes: the tritium recovery from the helium sweep gas as hydrogen, that as water vapor and the tritium recovery from the coolant water. In JAEA, the research and development of each process have proceeded to realize the tritium recovery system for ITER and DEMO. In this report, the recent results of the research and developments of these processes are described.

2. Tritium Recovery System for ITER Test Blanket Module

A water cooling solid breeder blanket (WCSB) is a prime candidate of Japanese Test Blanket Module (TBM). At early of the test, quantification of tritium bred in TBM is

an important subject. Tritium recovery system (TRS) has a role of the recovery and quantification of tritium in the sweep gas. Therefore, we have proposed TRS using the conservative method [1]. It consists with the dryer, the cryogenic molecular sieve bed (CMSB) and the palladium membrane diffuser (PD). At first, the sweep gas is introduced to the dryer (packed bed of synthetic zeolite) to remove water vapor. And then, the gas is introduced to CMSB. CMSB is the packed bed of synthetic zeolite that is kept at 77 K. In CMSB, hydrogen isotopes including tritium are removed from the sweep gas by adsorption, and the gas is returned to the TBM. The water captured by the dryer is released again by the heating and the inert gas circulation. This gas is introduced to the condenser to correct water as liquid. Tritium in the corrected water is measured by calorimeter or liquid scintillation counter. Hydrogen adsorbed on CMSB is also released by the heating. The released gas still includes helium. So, the gas is circulated between CMSB and PD. Hydrogen isotopes only permeate through membrane, and are collected in the measuring tank. Tritium is measured by PVTC (Pressure, Volume, Temperature, Concentration) method. Analysis and measurement system (AMS) is also installed in the glove box with TRS. So, we plan to monitor and quantify tritium based on the chemical form using TRS. The recent activity is the design. FIG.1. shows the schematic of the designed CMSB, and its outline is listed in Table 1. However, the design condition is still not fixed yet. Hereafter, the design change is probable. The design will be continued.

Cooling the sweep gas and the bed to 77K is necessary in CMSB, and this poor thermal efficiency also becomes the weak point in the application of it to the system of the DEMO reactor: it leads to the huge system. Therefore, the development of more effective method is necessary.

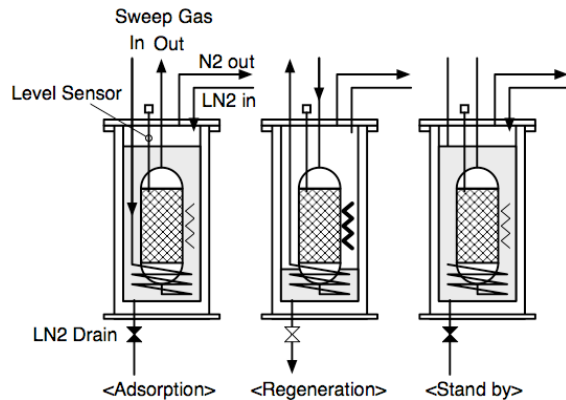


FIG.1. A schematic of CMSB.

TABLE 1: OUTLINE OF CMSB FOR TBM.

Gas	H ₂ (981ppm), HT(19ppm)/He
Flow Rate	34.7 l/min(STP)
Column	3 (x 8hr =24 hr)
adsorbent	MS5A
weight	2.21 kg
bed volume	3.54 L (φ134.2mm x H250mm)
Dewar	
Inner Diameter	260.6 mm
Outer Diameter	318.5 mm
Depth	575 mm
LN2 Consumption	171.4 L/day

3. Tritium Recovery from Helium Sweep Gas as Hydrogen

To overcome these problems, we have paid our attention on the hydrogen pump (HP) with a ceramic proton conductor. HP has proton conductor membrane, and can extract hydrogen selectively by the applying voltage on the membrane. Perovskite-type ceramic has proton conductivity at fairly high temperature, and SrCe_{0.95}Yb_{0.05}O_{3-α} (SCO) is one of the candidates of the ceramic proton conductor for the membrane of HP. Its ionic hydrogen transportation property has been investigated [2-4]. To design HP, the clarification of the hydrogen (proton) transfer process is important. The performance of HP is evaluated by proton conductivity. The proton conductivity is expressed by Nernst-Einstein equation as;

$$\sigma = nD(eZ)^2/kT, \quad (1)$$

where σ is the ion conductivity (S/m), n is the ion concentration in ion conductor (n/m^3), D is the diffusion coefficient of ion in the ion conductor (m^2/s), e is the elementary charge (C), Z is the valence number (-), k is the Boltzmann constant (J/K) and T is the absolute temperature (K). The proton conductivity consists of the diffusion coefficient and the proton concentration in the ceramic, and is similar to the permeation coefficient, but it has been treated as the constant so far. We have pointed out that it depends on the hydrogen pressure in a gas phase [4]. In this work, the proton concentration in SCO was investigated by the impedance measurement under various hydrogen atmospheres.

FIG.2. shows the schematic diagram of the experimental apparatus. The sample used in this work was a disk type SCO made by TYK Co. Its diameter was 15 mm, and thickness was varied between 0.5-2.0 mm. Platinum (Pt) electrode (area: 1.0 cm^2) was pasted on the both surface of the disk. The SCO sample was hanged into the quartz tube by the Pt wires, that were connected with the potentiostat. The sample gas (H_2 : 0.01-100 %, He balanced) was passed through the dryer to remove residual H_2O , and was introduced to the quartz tube with a certain flow rate (0.1-0.4 l/min STP). H_2O in the sample gas (>2 %) was added by the water bubbler. The voltage of alternating current was 100mV in the root mean square. Its frequency was varied below 1.0 MHz. The experimental temperature was 873 K. The conductivities were estimated from the observed impedance plot.

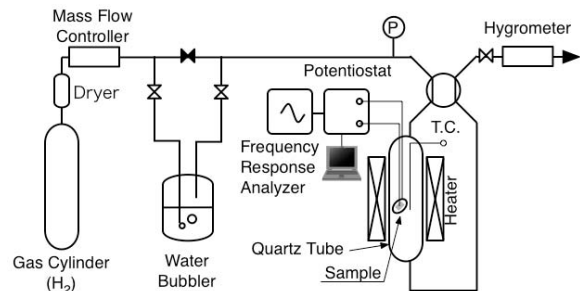


FIG.2. The schematic diagram of the experimental apparatus of the impedance measurement.

FIG.3. shows an example of the impedance plot obtained in this work. In this plot, the smaller value of the intercepts on the real axis corresponds to the resistance of the ceramic bulk. From the results of the direct current experiments in our previous works [2-4], the transport number of proton is expected to be 1.0 under the experimental condition in this work. So, the conductivity obtained in this experiment is considered to be the proton conductivity. The proton conductivity has been obtained under various hydrogen atmosphere. And, the proton concentration in SCO has been obtained from Eq.(1) using the reported diffusion coefficient of hydrogen in SCO crystal grain [5].

FIG.4. shows the correlation between the proton concentration in SCO and the hydrogen concentration in the gas phase. The closed keys and the open keys mean the proton concentration in SCO at the dry conditions and that at the wet conditions, respectively. The maximum value of the proton concentration indicated with the broken line is based on the balance of the valence of SCO (α equals to zero). As shown in *FIG.4.*, the proton concentration in SCO concerns the hydrogen partial pressure in the gas phase. The solid line and the dotted chain line mean the least square approximation of the data at the dry condition and the wet condition, respectively. The slope at the dry condition (1/6) and that at the wet condition (1/16) are much smaller than 1/2 (dissociative absorption). The cause of this difference is not clear, but under the electric field, the proton concentration might be strongly

affected to the balance of the valence. In addition, the water vapor affects the proton concentration. The proton migrates along the oxygen site in the crystal of SCO. In the wet condition, the outflow of oxygen from SCO is prevented by the water vapor, and the proton concentration is kept higher than the dry condition. From above study, it has been shown that the partial pressures of hydrogen and water vapor control the proton concentration in the ceramic as a key parameter of the system.

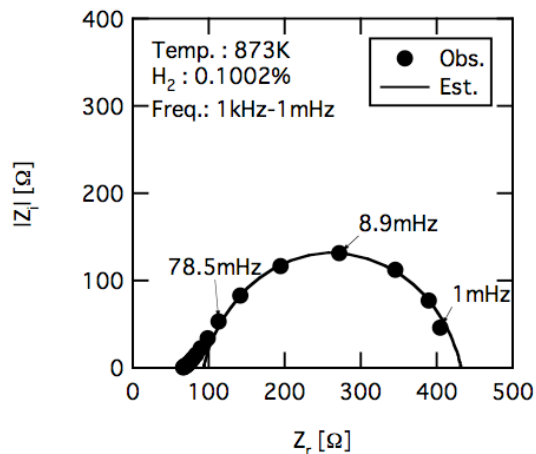


FIG.3. An example of the impedance plot.

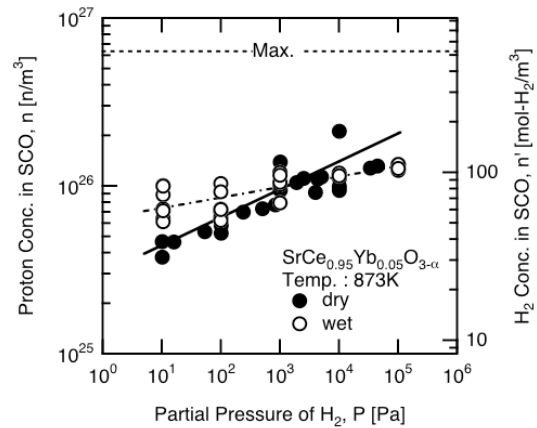


FIG.4. The correlation between the proton concentration in SCO and the hydrogen concentration in the gas phase.

4. Tritium Recovery from Helium Sweep Gas as Water Vapor

A part of tritium bred in the blanket is released as water vapor. Electrolysis is the probable method for the water processing. However, since the tritium level of the water vapor is expected to be extremely high, solid polymer electrolyte (SPE) used for the electrolysis cell of the Water Detritiation System (WDS) in ITER, is not used to avoid degradation by radiation damage. A ceramic electrolysis will be only method to recover tritium from high-level tritiated water. FIG.5. shows the principle of the ceramic electrolysis method. Yttria Stabilized Zirconia (YSZ) is well known material having oxygen ion conductivity over 873 K. As shown in FIG.5., the electrode on YSZ has the porous structure. In this method, voltage is applied to YSZ. Water vapor reached the electrode-YSZ interface is electrolyzed and hydrogen is released. Oxygen ion permeates through YSZ, and is released as oxygen molecule from the counter electrode. We had developed the ceramic electrolysis cell (CEC) for the Tokamak Exhaust Processing (TEP) of ITER, and its reliability had already been proofed [6,7]. The residual problem is the low electrolysis efficiency by use of ceramic.

To increase the efficiency of this process, we focused on the electrode. Its structures or compositions are also important factor to determine the efficiency. Pt-YSZ compounds were used as ordinary electrode of CEC. The efficiency of electrolysis is expressed as the current density, and the current density of the Pt-YSZ electrode was around 10 mA/cm² at 1073 K. It was reported that the electrode containing cerium oxide (ceria) improved the efficiency of electrochemical reaction [8,9]. So, we developed new two types of electrodes and tested. One is the ceria double-layer electrode in which ceria is the inner layer and the Pt-YSZ is the outer layer. The other is the Pt-YSZ-ceria electrode using the Pt-YSZ-ceria compound.

The samples prepared were the Pt-YSZ electrode, the ceria double-layer electrode and the Pt-YSZ-ceria electrode. The substrates were the disk type YSZ (22 mm in diameter and 1.5 mm in thickness). The sample gas was argon, and its water concentration was adjusted between 100-2400 ppm. The sample gas was introduced to the CEC with the flow rate of 150 cm³/min (STP). The experimental temperature was 1073 K. The voltage was applied between 0-1800 mV, and the electric current was measured.

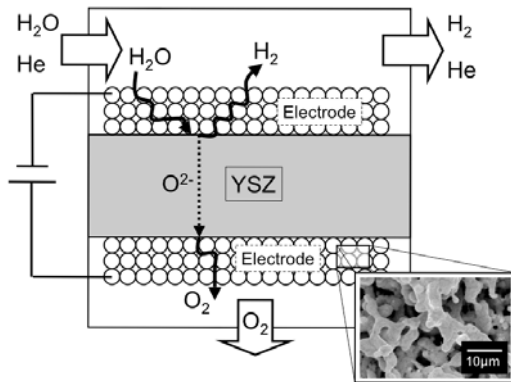


FIG.5. Principle of ceramic electrolysis method.

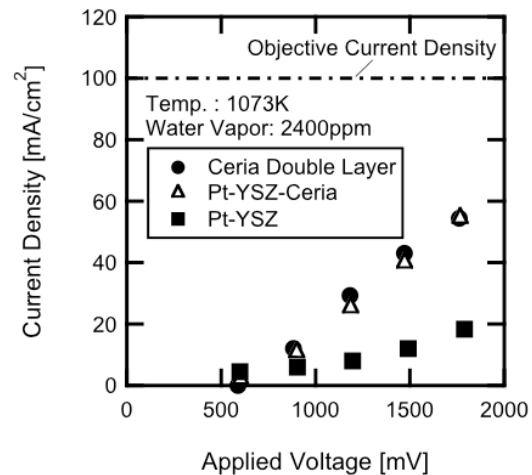


FIG.6. Current density of three types of electrode on different voltage.

FIG.6. shows the comparison of the current density during three types of electrodes. The current densities of each ceria electrodes are three times larger than that of ordinary electrode. This result indicates that electrode strongly affects the electrochemical reaction and that the optimization of electrode may dramatically extend performance of the ceramic electrolysis method. The improvement of efficiency will be caused by ceria that has complex conduction of oxygen ion and electron. Electrochemical reaction is expected to take place by three-phase (the substrate ceramic, the electrode and the gas phase) boundary. Ceria in the electrode can work as double phase (substrate and electrode) due to its complex conduction. Thus, the density of three-phase boundary will be increased by ceria, and this increase leads to enhancement of the electrode reaction. On the other hand, the decrease of the over-potential by use of ceria is also probable. Some additive elements work like catalysis and decrease the over-potential. To clarify the mechanism of the electrolysis efficiency enhancement, the detailed experiments concerning with the dependence of ceria concentration or the measurement of over-potential are required.

5. Tritium Recovery from Coolant Water

Under the WCSB blanket concept, a problem we have to face is that considerable part of bred tritium will be continuously permeated into the coolant so far as sound permeation barrier technique has not established. Even in case when the permeation barrier reduces tritium permeation to 1/100 in comparison with no barrier, tritium will permeate at the rate of 1.3 g/day from blanket to the coolant [10]. Tritium that has permeated into the coolant is evaluated to be HTO. To keep the tritium level of

the coolant to be acceptable, tritium recovery from the coolant is essential even if the permeation barrier technique would be established. The throughput required is assessed to be more than 100 kg/h to maintain the coolant tritium level less than 3.7×10^{11} Bq/kg. In ITER, WDS is installed to process the tritiated water produced mainly through the regeneration process of dryers in the Atmospheric Detritiation System (ADS). Since the expected throughput is estimated to be no more than 20 kg/h, the concept of the Combined Electrolysis Catalytic Exchange (CECE) process was selected for the ITER-WDS [11]. The application of CECE type WDS to the tritium recovery from the blanket coolant is difficult. The reasons are that 1) a huge SPE system corresponding to the large throughput becomes severe problem from the viewpoint of economics, and that 2) the scale-up of water-hydrogen exchange towers is difficult from the viewpoint of water distribution in the tower. It is supposed that the value of throughput is limited for the CECE type WDS. Therefore, it is inevitable to install tritium pre-concentration system at the front of CECE type WDS to reduce throughput to the acceptable level.

Water distillation (WD) is an established tritium concentration process, although its separation factor is practically small. Considering applying WD to the tritium pre-concentration process, the scale of WD will become unacceptably huge and it leads to the undesirable scale enlargement of ADS because of enlargement of the housing of WD [12]. Therefore, development of advanced tritium concentration process of the large throughput instead of WD process has been essential. So, we have proposed to apply pressure swing adsorption (PSA) which uses zeolite to the tritium pre-concentration process. PSA system needs the additional functions to the established dryer system, which are the isotope separation in the adsorption operation and the quick dehydration in the regeneration operation. Though there are some reported data concerning HTO/H₂O separation factor with commercial zeolite, fundamental data of zeolite on not only the isotope separation but also the dehydration characteristics are essential to design the PSA system for WDS. We focused on the understanding of the influence of silica/alumina ratio of faujasite-type (X-, Y-type) zeolite on water adsorption/desorption properties and on the isotope effect systematically in the H₂O-HTO system.

FIG.7. shows the conceptual diagram of a PSA. Basically, the system is composed of a pair of columns: when one is in adsorption, the other is in dehydration using a vacuum pump. Both columns are operated at room temperature. As to the column in adsorption, the dry gas is discharged from the column before the breakthrough of H₂O. This gas is used as the purge gas to dehydrate the other column. We encountered difficulties when we used the zeolite with low framework silica/alumina ratio since considerable amount of dry purge gas was necessary to dehydrate the zeolite at room temperature. To solve the insufficiency of amount of purge gas, we focused on the effect of the silica/alumina ratio on the dehydration. *FIG.8.* shows dehydration performance of zeolite with various framework silica/alumina ratios. In a

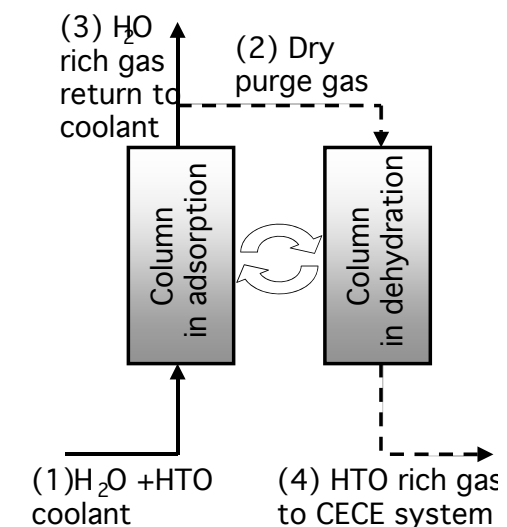


FIG.7. Conceptual diagram of a PSA.

tested condition, amount of dry gas discharged from the column in adsorption was approximately 30 NL [12]. The NaY (Cation: Na, Y-type) zeolite with the framework silica/alumina ratio of 10.0 (NaY10.0) showed the characteristic dehydration: The amount of H₂O desorption from NaY10.0 by 30 NL of dry purge gas was approximately three times as large as those of other zeolites. This is mainly due to the considerable change in pore size distribution of the faujasite-type zeolite when the framework silica/alumina ratio was changed from 7.0 to 10.0 [12]. FIG.9. shows the separation factors of HTO/H₂O observed with static and breakthrough methods. The large separation factor means enrichment of HTO. The NaY10.0 showed the distinctively large separation factor. The difference of the pore-diffusion rate between H₂O and HTO strongly affects the factor due to the larger pore size of NaY10.0. More investigation is necessary to evaluate the separation factor of NaY10.0 under various conditions. To reduce the volume of tritiated water to 1/6 (100 kg/h from blanket coolant and 20 kg/h from ADS to 20 kg/h for CECE feed through) using PSA, a cascade of several pair of columns are essential. The size of the largest column are evaluated as 2.30 m I.D. x 2.77 m H with 15000 kg of adsorbent.

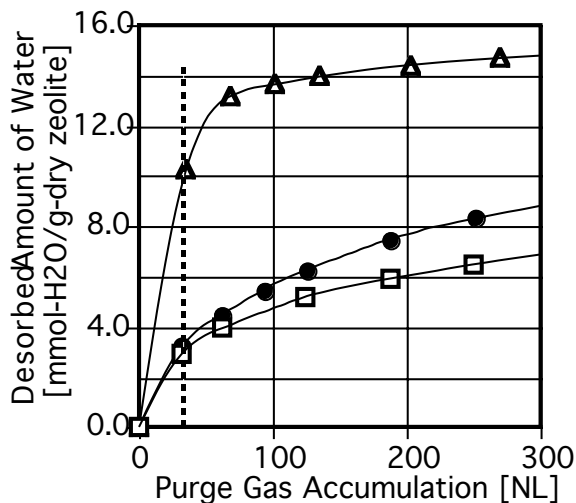


FIG.8. Dehydration performance of zeolite with various framework SiO₂/Al₂O₃ ratios (Symbols; □ for SiO₂/Al₂O₃=2.0, ● for 5.0, △ for 10.0)

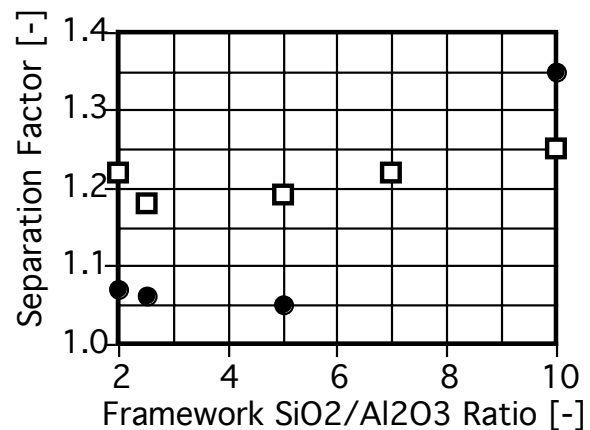


FIG.9. Separation factors of HTO/H₂O observed with static and breakthrough methods (Symbols; □ for static method, ● for breakthrough method).

6. Conclusion

The recent results of the research and development of tritium recovery system for blanket are follows;

- (1) Tritium recovery system for ITER-TBM of Japan is the complex system of dryer, cryogenic molecular sieves bed and palladium membrane diffuser. Its design has been revised. However, TBM design is still not fixed yet. Minor design change may be carried out hereafter.
- (2) Hydrogen pump has been proposed as the process that recovers tritium from helium sweep gas as hydrogen, and the correlation between the proton concentration in the ceramic and the hydrogen partial pressure in the gas phase has been quantified. The partial pressures of hydrogen and water vapor control the proton concentration in the ceramic as a key parameter of the system.

- (3) Ceramic electrolysis cell has been proposed as the process that recovers tritium from water vapor in the helium sweep gas, and new electrodes using ceria have been developed and tested. Their electrolysis efficiency were three times as large as the ordinary electrode. The optimization of electrode may dramatically extend performance of the ceramic electrolysis method.
- (4) For the tritium recovery from the coolant water, the pressure swing adsorption process using zeolite has proposed as the tritium pre-concentration process of the water detritiation system, and the effect of the silica/alumina ratio of faujasite-type zeolite on its water desorption properties were investigated. When the silica/alumina ratio was 10.0, water desorption rate was dramatically enhanced and HTO was also enriched. The prospect of the development of the zeolite optimized to this system was indicated.

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