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전기방전하에서 D_2/H_2O 반응계의 수소 동위원소 교환반응

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Hydrogen Isotope Exchange Reaction in Electrical Discharge through D_2/H_2O System

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초 록

H_2O/D_2, D_2O/H_2O, D_2O/H_2 등의 반응계의 수소동위원소 교환반응은 전기방전을 이용하여 용이하게 일으킬 수 있다. 예를 들어, DC 코로나 방전을 위의 반응혼합물을 통하여 일으키면 여기된 상태의 반응물이 존재하는 플라즈마를 형성하게 된다. 이러한 플라즈마 내에서 반응물들은 양자에너지 준위의 여기, 이온화 그리고 라디칼 형성등을 통하여 매우 큰 반응성을 갖게되므로 실온에서도 용이하게 수소동위원소 교환반응을 일으킨다. 본 연구에서는 H_2/D_2O계의 기상에서의 교환반응에 대한 연구를 실시하였다. 위 반응계는 전기방전하에서 수소(H)와 중수소(D)간의 교환반응에 의하여 HDO와 HD를 생성하게 된다. 이러한 반응생성물을 FTIR 분광법을 이용하여 시간의 함수로 측정을 하였다.

그리고 위 반응계의 수소동위원소 교환반응에 대한 온도의 효과 및 플라즈마 방법과 촉매법과의 비교를 통하여 그 효율성을 비교하였다.

Abstract

Hydrogen isotope exchange in mixtures of H_2O/D_2, H_2O/D_2O, or D_2O/H_2 can be facilitated under electrical discharge. For example, a simple DC corona discharge through the mixture creates a plasma in which the reactants are excited energetically. The reactants in such plasma, due to increase in population of excited quantum levels or due to production of radicals or ions, undergo very rapid chemical reactions even at ambient temperature. The isotope exchange reaction of hydrogen(H) and deuterium(D) produces the third kind of heavy water(HDO) and isotopic hydrogen gas(HD), as shown in

$$D_2 + H_2O \rightarrow HDO + HD \qquad K=11.257(\text{at } 25℃)$$

The reaction products can be detected with temporal resolution using the Fourier transform infrared(FTIR) absorption spectroscopy. Since H_2O, D_2O and HDO are all infrared active with different absorption peaks, FTIR proves to be a useful tool for monitoring the reaction. Experimental results show that the electrical method is indeed a useful means to promote the reaction, showing a better efficiency than traditional catalytic methods.

1. Introduction

Heavy water(D_2O) used as a coolant in nuclear reactors is partly transformed into DTO when the molecules capture neutrons. Among many tritium recovery processes, only catalytic exchange of DTO with D_2 to produce DT and D_2O, or electrolysis of D_2O/DTO to D_2/DT and O_2 followed by cryogenic distillation of the hydrogen isotopes appear feasible or promising.(1) It is well known that many gaseous reactions can be facilitated in electrical discharge. We attempted to apply the discharge method to the exchange reaction instead of using any of type catalyst. For studying kinetics of gaseous reactions, it is necessary to diagnose intermediates or products in real time. Many spectroscopic methods, such as LIF(2-3), OES(4), FTIR(5), MS, etc., are used as a diagnostic tool. Optical emission spectroscopy(OES) or laser-induced fluorescence spectroscopy(LIF) in the UV and visible regions is a useful plasma diagnostic tool for detection of reactive species in the gas phase.(6) But it is difficult to identify molecular species of closed shells by LIF technique. On the other hand, Fourier transform infrared(FTIR) absorption spectroscopy(7) can be applied to any molecular species as long as their characteristic vibrations are infrared active. In this paper, we report some results on the hydrogen isotope exchange reaction in electrical discharge using FTIR spectroscopy. Among various types of the exchange reactions, we selected the reaction of H_2O/D_2 system because the handling of water or hydrogen molecule containing tritium requires special cautions due to its radioactivity. We detected the reaction product species quantitatively with temporal resolution by the spectroscopic method. We also report the efficiency of the plasma method in facilitating the exchange reaction, comparing it with the efficiency of traditional catalytic method.

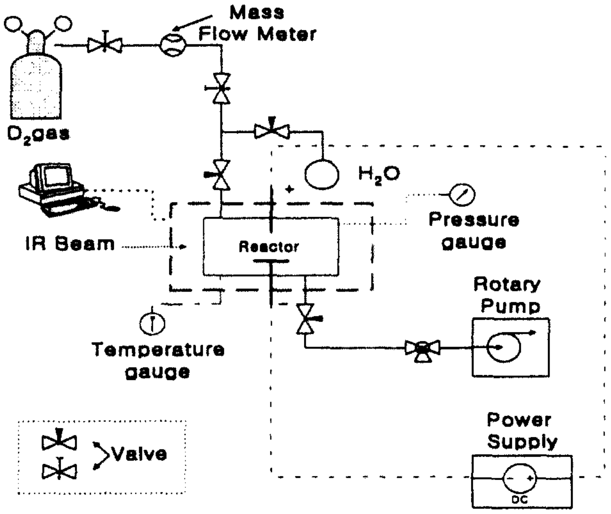

Fig. 1. Experimental set-up for hydrogen-exchange reaction using electrical discharge method

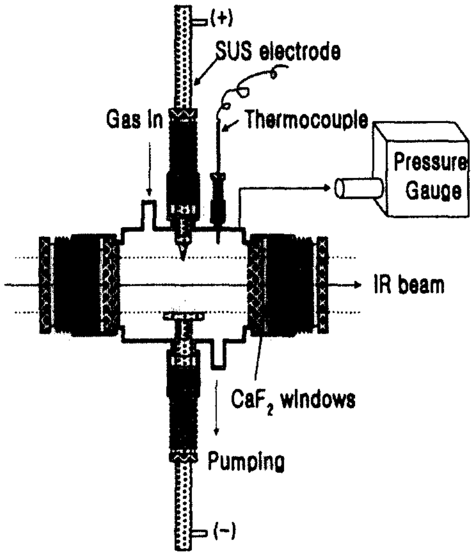

Fig. 2. Schematic of the plasma reactor

2. Experimental

The experimental setup shown in Fig. 1 consists of four parts ; DC power source, plasma reactor chamber, pumping system, and FTIR diagnostic system. The pyrex plasma reactor shown in Fig. 2 includes o-ring-sealed ports for insertion of electrodes, thermocouple and CaF_2 windows for transmitting IR beam. As the discharge electrodes, stainless steel point(+)-plane(-) electrodes were used and the distance between electrodes was kept at 13.5mm. The chamber was pumped down to $\sim 10^{2}$Torr by a cold-trapped rotary pump(Edward E2M1.5 double stage), and then D_2 gas was introduced into the chamber with help of mass flow meter(Sierra series 820 Top-trak^{TM}). Then, a few drops of liquid water was introduced into the chamber. The total pressure of hydrogen and the vapor pressure at the ambient temperature, normally reaching 50 torr, was measured with diaphragm manometer gauge(Varian WV100 model). Electrical discharge was initiated between the electrodes will a DC power source which provides 1~2kV of voltage and 0.5~1mA of current. The discharge time was normally 2 minutes. The reactor was placed inside the FTIR spectrometer(Nicolet Magna-IR), with the resolution of 0.5~16cm^{-1}. The time needed for whole range scanning and for acquiring the data were 2 and 10 seconds, respectively. The infrared data were obtained with a resolution of 2cm^{-1} in infrared region(4000~800cm^{-1}). The detailed conditions for FTIR measurements are summarized in Table 1.

Table 1. Experimental conditions for FTIR measurements

IR range	4000~800cm-1
Resolution	2cm-1
Scan number	1
Optical windows	CaF_2(4000~1000cm-1)
Detection method	Single beam

3. Results and Discussions

3.1. Calculation of equilibrium constants

We first calculated the equilibrium constants of hydrogen isotope exchange reaction using thermodynamic data(8) and Gibbs-Helmholtz equation given by

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \cdots\cdots\cdots \ (1)$$

$$\Delta G^\circ = -RT\ln K_p \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \ (2)$$

The results are summarized in Table 2. The dependence of the K value on temperature are shown in Table 3.

Table 2. Equilibrium constants for hydrogen exchange reactions(K_{calc}) at 25℃

Type of exchange reactions	K_{calc}
$D_2 + H_2O \rightarrow DHO + DH$	11.261
$H_2O + D_2O \rightarrow 2DHO$	3.504
$H_2 + D_2 \rightarrow 2DH$	3.258
$D_2O + H_2 \rightarrow DHO + HD$	1.0138
$DHO + D_2 \rightarrow DH + D2O$	3.212
$H_2O + DH \rightarrow DHO + H_2$	3.461

Table 3. Dependence of the equilibrium constants on temperature

$H_2O_{(g)} + D_{2(g)} \rightarrow HDO_{(g)} + HD_{(g)}$	
Temperature (℃)	K
25	11.261
50	10.201
100	8.712
200	7.023
300	6.103
400	5.530
500	5.140

Table 4. Wavelengths of the characteristic vibrational modes of water molecules

Molecule	Sym.str (cm^{-1})	Bend (cm^{-1})	Antisym. str (cm^{-1})
H_2O	3657	1595	3756
D_2O	2666	1179	2784
HDO	2719	1402	3363

Table 5. The wavenumbers of the bending mode of water molecules used for determining the concentration

Molecule	H_2O	D_2O	HDO
Wavenumber(cm^{-1})	1607.4	1206.3	1434.8

3.2. Determination of the exchange reaction rate

The characteristic IR absorption bands of the species involved in the reaction ($D_2+H_2O \rightarrow HDO+HD$) are summarized in Table 4$^{(9)(10)}$. Both H_2O and HDO molecules have three different vibrational modes. The absorption peak height of these vibrational modes is proportional to the concentration of the water molecules. Of the three modes, the bending mode was selected to determine the concentration of the water molecules like H_2O or HDO. This selection was based on the fact that ,for either water molecule, only the absorption line for the bending mode is not overlapped by any nearby other characteristic lines. But the absorption peak has many branches due to rotational transitions. Thus, the most distinct line was selected for the peak height determination. The selected wavelength for the bending mode of H_2O or HDO was 1607.4cm^{1} or 1434.8cm^{1}, respectively. Thus, the change in the intensity of that absorption line was used as a measure of the progress of the exchange reaction. Total discharge time normally lasted 60 seconds. The IR absorption spectra of the reacting system at different discharge time are shown in Fig. 3. The spectra shows the growth of three characteristic lines of HDO species during the discharge.

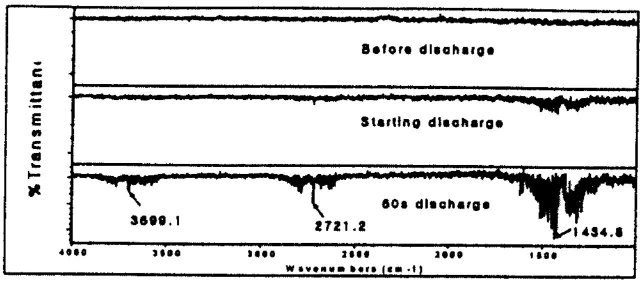

Fig. 3. IR spectrum for the whole range of HDO before and after the discharge

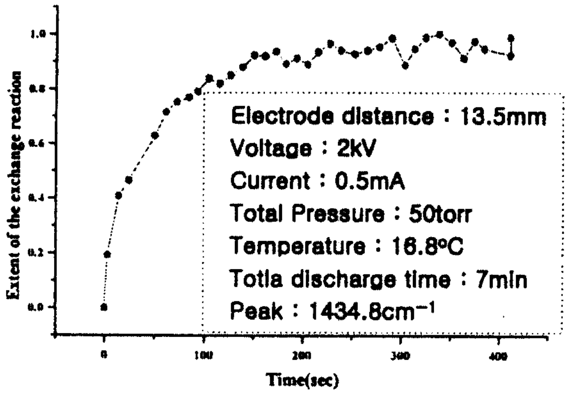

Fig. 4. Advance of the D_2/H_2O reaction as a function of the discharge time

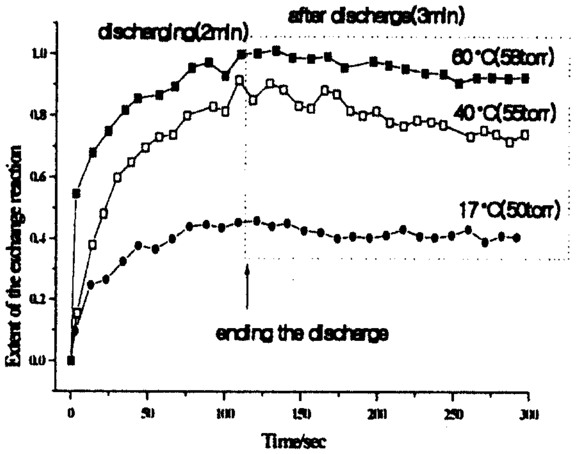

Fig. 5. Advance of the D_2/H_2O reaction as a function of temperature

3.3. Measurement of the reaction progress

Fig. 4 shows the progress of the reaction with time determined by the peak height change of the HDO species. Total discharge time was 7 minutes. The wavenumber for HDO detection was 1434.8cm^{-1}. The detailed discharge conditions are shown in this figure. To prove the efficiency of the plasma method, the quantity of hydrogen isotope transferred per electrical energy was calculated. The amounts of H_2O and D_2 injected into the reactor were 1.1×10^{4}mol and 3.1×10^{-4}mol, respectively. The fraction of H_2O converted into DHO and DH after the 2 minutes discharge was 0.34, which is equivalent to 3.7×10^{-5}mol of H_2O. Thus, the transferred quantity per electrical energy was evaluated as 1.2×10^{-3}mol · (W · hr)$^{-1}$.

3.4. Temperature effect

Fig. 5 shows the progress of the exchange reaction as a function of the discharge time and temperature. The detailed conditions for the experiment are summarized in Table 6. The absorption measurements were done continuously for 5 minutes even though the discharge was terminated 2 minutes after the onset of the discharge. Fig. 5 shows that the progress of the reaction was clearly enhanced by raising the temperature. This temperature effect is of kinetic origin rather than of thermodynamic one. Table 3 indicates that higher temperature can suppress the forward reaction.

Table 6. Electrical discharge parameters for D_2/H_2O reaction carried out at different temperature

Temperature(℃)	17	40	60
Water vapor pressure(torr)	13	13	13
Total pressure at ambient temperature(torr)	50	50	50
Total pressure after temperature increase(torr)	50	55	58
Total discharge time(minutes)	2	2	2
Discharge voltage(kV)	1.5	2	2
Discharge current(mA)	0.5	0.5	0.5
Electrode Distance(mm)	13.5	13.5	13.5

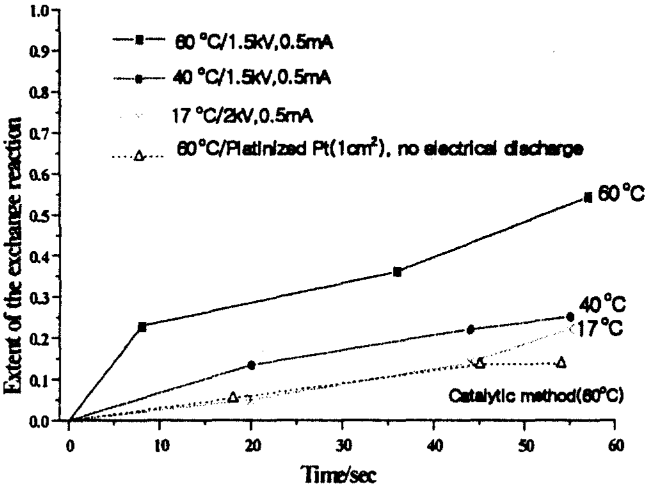

Fig. 6. Advance of the exchange reaction with the help of platinum catalyst is compared with that using electrical discharge method. The catalyst method at 60℃ shows almost the same efficiency as the plasma method at 17℃

Therefore, the enhanced reaction with increasing temperature reflects the temperature effect on the reaction rate predicted by the Arrhenius equation. The fact that the degree of the progress in the reaction remains the same even 3 minutes after termination of the discharge implies that the system did not reach the thermal equilibrium readily. In Fig. 6, progress of the reaction with the help of platinum catalyst is compared with that by the plasma method. It shows that the efficiency of the electrical discharge method at 17℃ was as high as that of the catalytic method at 60℃. This trend remained the same even when the reaction time was extended from 60 to 120 seconds.

4. Conclusion

The hydrogen exchange fraction of H_2O/D_2 system was facilitated by a DC electrical discharge. The progress of the reaction was studied using Fourier transform infrared spectroscopy which easily detects the transfer reaction product, HDO. A DC electrical discharge through the (D_2+H_2O) reacting system at room temperature shows the transfer efficiency is as high as that manifested by platinum catalytic method at 60℃. If the system temperature remains the same, the plasma chemical method is three times more efficient than that by the catalytic method. The exchange reaction does not proceed readily without any external means such as plasma or catalytic method. The amount of the transferred deuterium during the discharge is about 1.2×10^{3}mol · (W · hr)^{1}.

Acknowledgement

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