核物理与化学研究所
INSTITUTE OF NUCLEAR PHYSICS AND CHEMISTRY

International Symposium on Fusion Nuclear Technology (ISFNT-15)

Study on the processing of highly tritiated water by the two-stage palladium membrane reactor

Lei Yue

Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics

E-mail: yuelei@caep.cn

Thursday, September 14, 2023

Outline

1 Background

2 Experimental

- **2.1** Experimental device;
- **2.2** Catalyst preparation and characterization;
- **2.3** Impact of operation parameters;
- **2.4** Impact of catalyst;
- **2.5** Processing of tritiated water.

3 Summary

Background

Large amounts of tritiated water (HTO) will be produced during the operation of nuclear power plants and fusion devices. The tritium concentration of tritiated water must be reduced to a very low value before discharge.

Table 1. Processing technology for HTO of different concentrations

Technology	Processing source	Product	Drawback (For highly tritiated water processing)
Water distillation (WD)	Low concentration HTO $< 10^8$ Bq/kg	Concentrated HTO	**Large liquid holdup** is not suitable for processing highly tritiated water
Combined electrolysis catalysis exchange (CECE)	Medium concentration HTO 10^9~10^{13} Bq/kg	Concentrated HT and HTO	**SPE membrane** electrode is unstable in highly tritiated water
Water decomposition on hot metals	High concentration HTO $> 10^{13}$ Bq/kg	Tritium gas	**Strong exothermic** behavior may cause the blockage of pipe, and the used metal is **difficult to regenerate**

A suitable processing technology for highly tritiated water is required !

Background

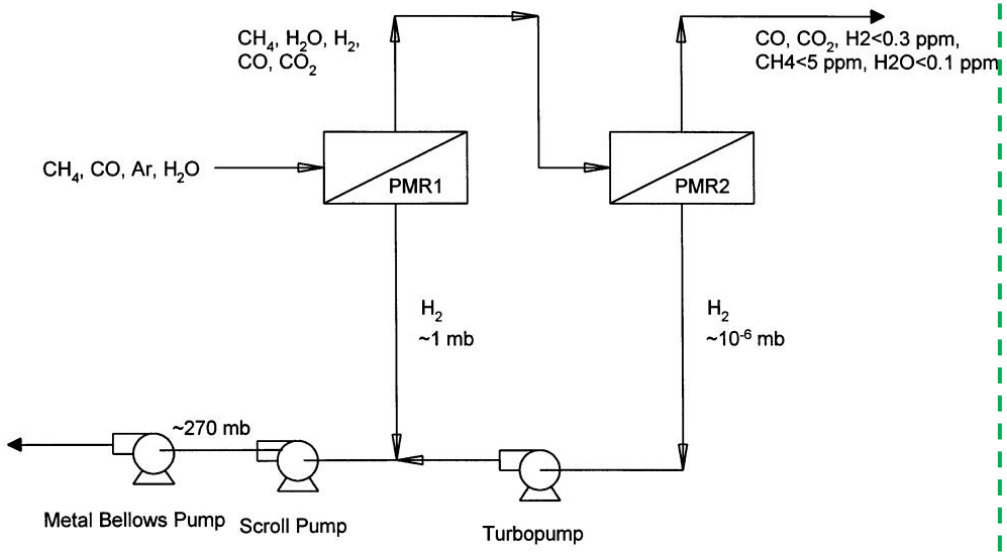


Fig. 1 Membrane reactor proposed by LANL

Principle: CO and HTO are feed into the catalyst side of the membrane reactor, water gas shift reaction (CO + HTO→CO_2 + HT) occurs and the tritium gas permeates to the hydrogen side.

Coke formation----degrade the catalyst activity

Radiochemical reaction----convert tritium to other organic matters

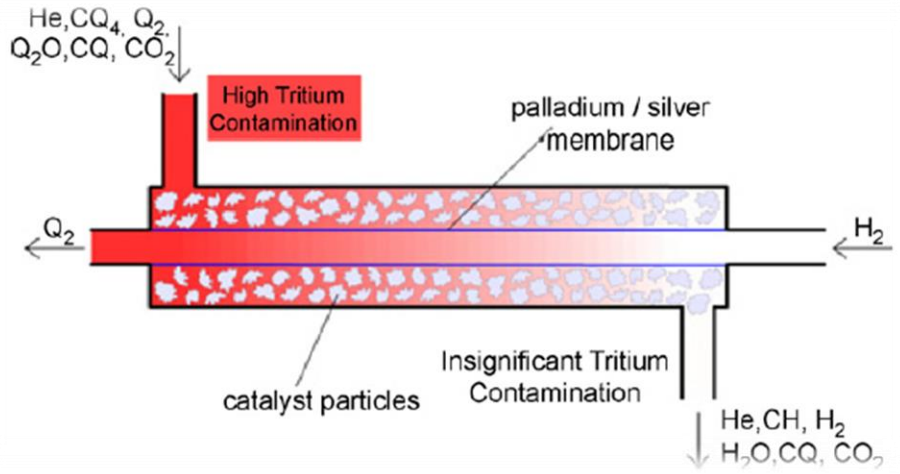


Fig. 2 PERMCAT proposed by KIT

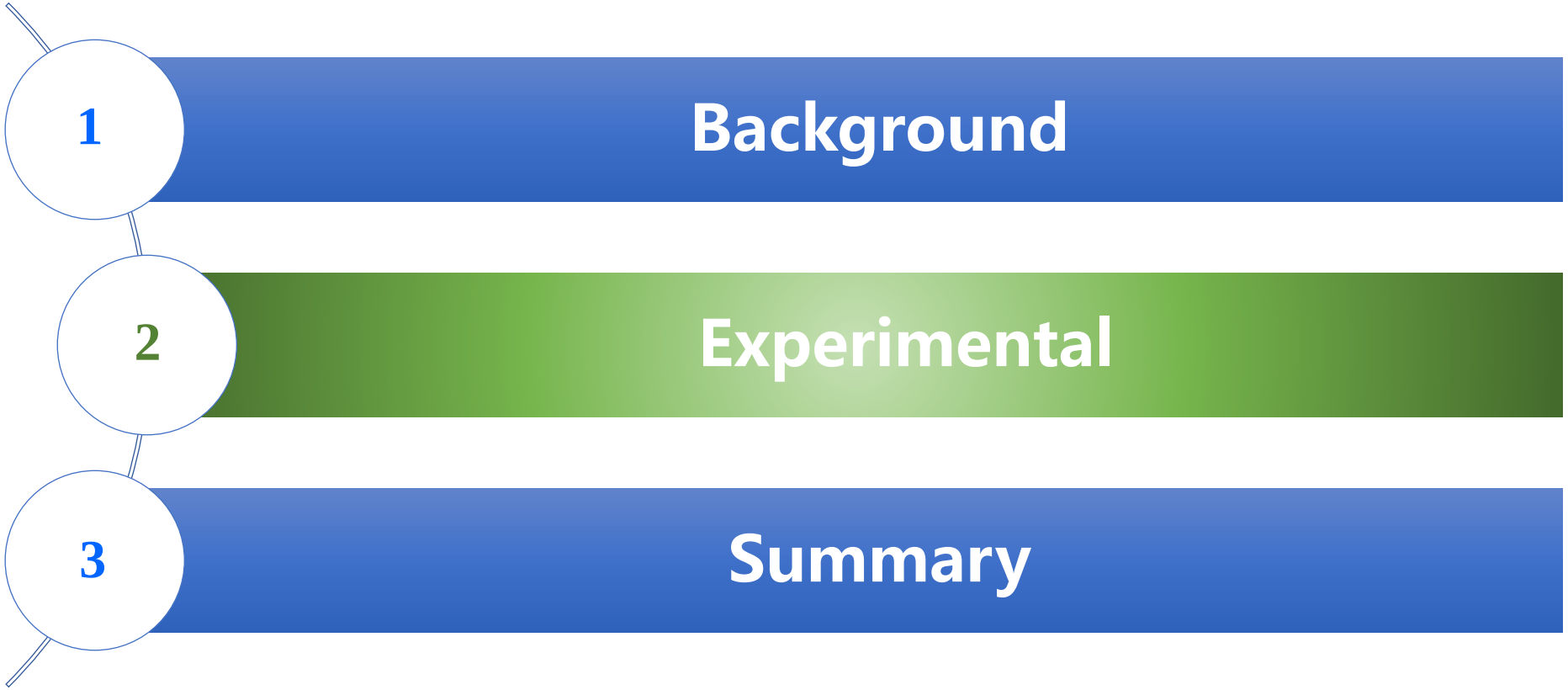
Principle: (1) The pure hydrogen is feed to purge side and permeates to the catalyst side; (2) the isotope exchange reactions (H_2 + HTO→HT + H_2O) happen between hydrogen and tritiated water vapor on the catalyst; (3) tritium gas permeates back to the purge side.

Background

Although PERMCAT technology has been verified to process highly tritiated water successfully, the research is still not enough.

- **The decontamination factors (DF) obtained by different labs varied greatly (DF always less than 10 by ENEA but as high as 100 by KIT), but no one explained the reason. The confused experimental results are disadvantage for the reactor design in the practical application.**
- **Water dissociation on the inert support (Al_2O_3/SiO_2) of Pt-based catalysts is very hard, so the reactor performance may be improved resulted from the co-dissociation of water and hydrogen if an active support (TiO_2 or CeO_2) is used for the catalyst.**
- **Two-stage membrane reactor is more effective than the one-stage, but the report about two-stage membrane reactor is very little.**
- **So the processing of tritiated water by two-stage membrane reactor has been carried out in this work, and try to answer the first two questions.**

Outline



Experimental

2.1 Experimental device

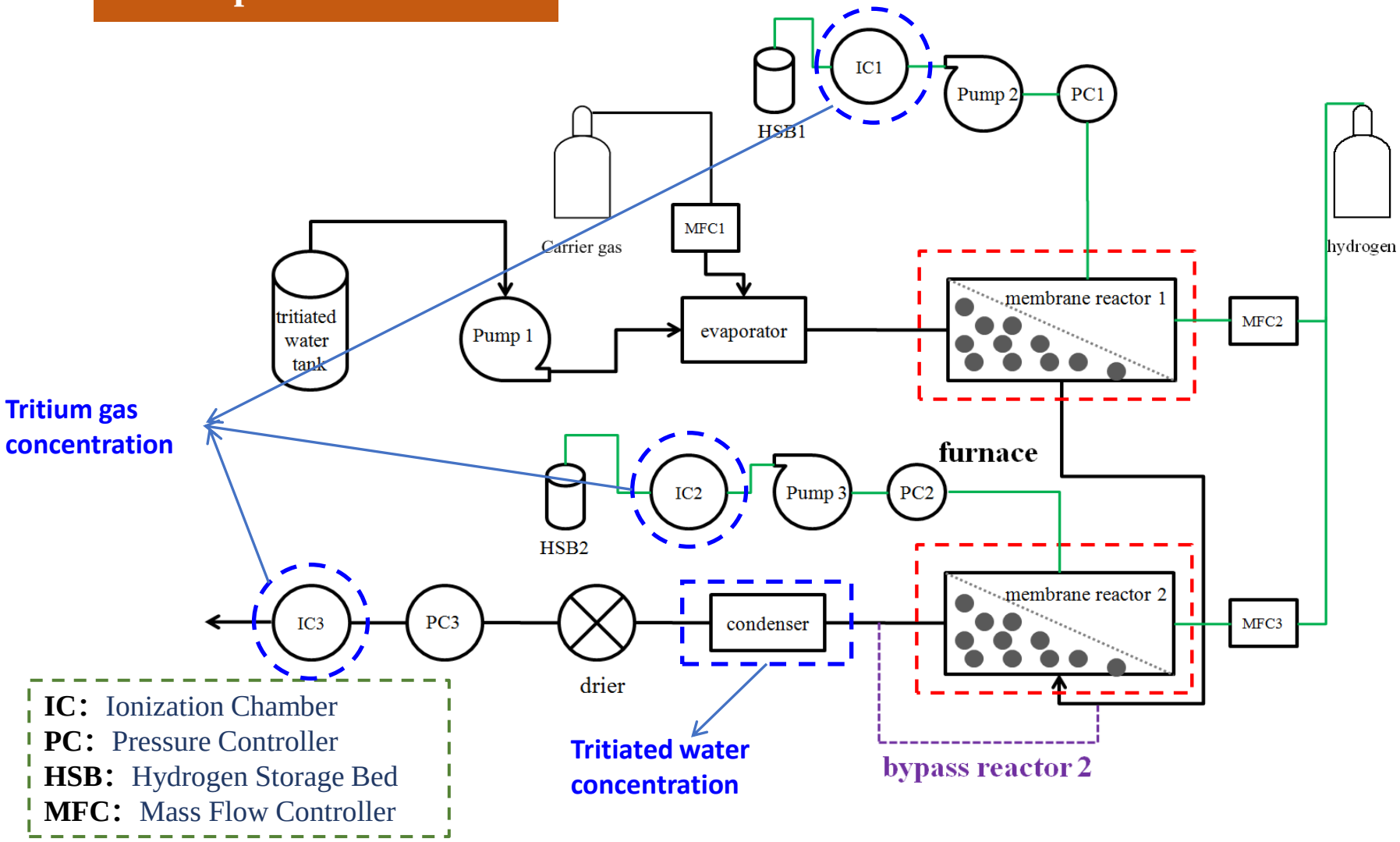


Fig. 3 Schematic of the two-stage membrane reactor

In a typical experiment, tritiated water was feed into evaporator by pump1, and carrier gas helium was also feed to it. The tritiated water vapor and helium was introduced into reactor 1, the hydrogen-water isotope exchange reaction happens and the produced tritium gas was evacuated to store in hydrogen storage bed. The tritiated water vapor is processed again by reactor 2.

The operation modes include one-stage (bypass reactor 2) and two-stage processing mode.

Experimental

Fig. 4 Picture of the two-stage membrane reactor

Table 2. Detailed design information

No.	Parameter	Design Value
1	Processing capacity	0.05~0.5 g water/min
2	Temperature	500 °C
3	Integral leak rate	10^{-9} Pa·m^3·s^{-1}
4	Catalyst side pressure	100~500 kPa
5	Hydrogen side pressure	1~10 kPa
6	Decontamination factor	100~10000

DF = C_{in}/ C_{out}

For tritiated water processing:

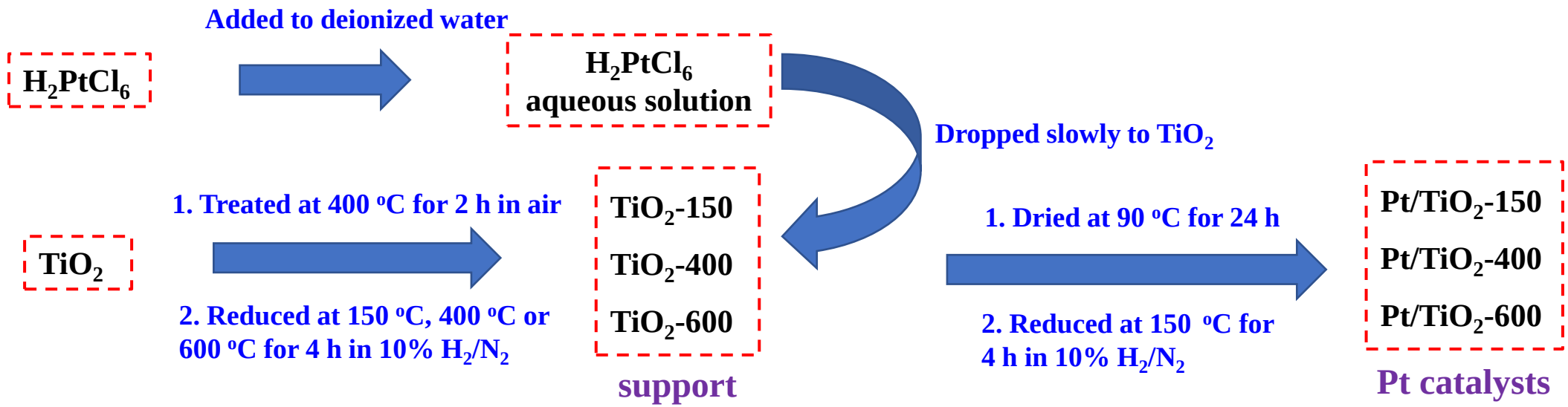
C_{in} is the tritium concentration of tritiated water in the tank (6.9 ×10^9 Bq/kg), C_{out} is the tritium concentration of tritiated water in the condenser. (measured by liquid scintillator)

For heavy water processing:

C_{in} is and C_{out} is the –OD concentration of heavy water. (measured by IR spectrum)

Experimental

2.2 Catalyst preparation and characterization



1. The different reduction temperatures were used to control the oxygen vacancy amounts of TiO_2 support.

2. The Pt contents in all catalysts were controlled to be 1 %.

Experimental

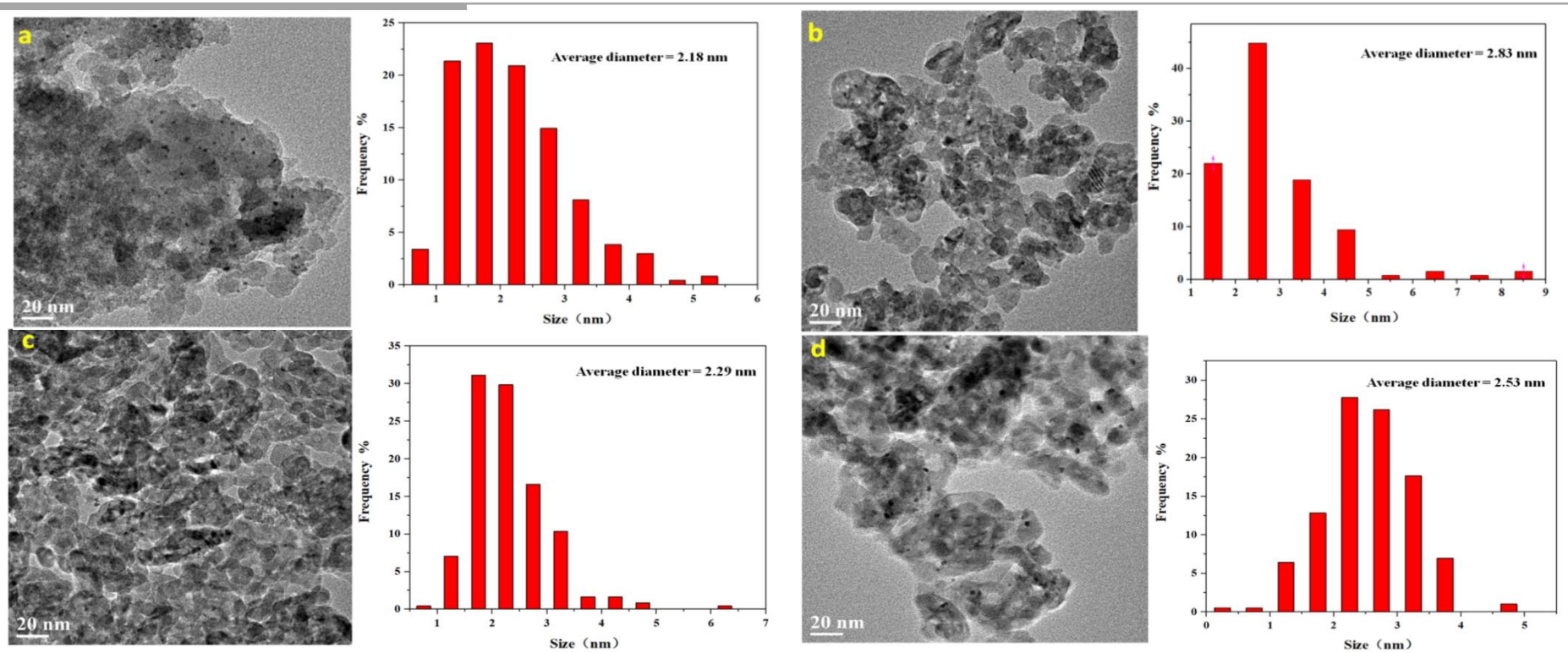


Fig. 5 TEM images and particles size distribution of (a)Pt/Al_2O_3, (b)Pt/TiO_2-150, (c)Pt/TiO_2-400 and (d)Pt/TiO_2-600

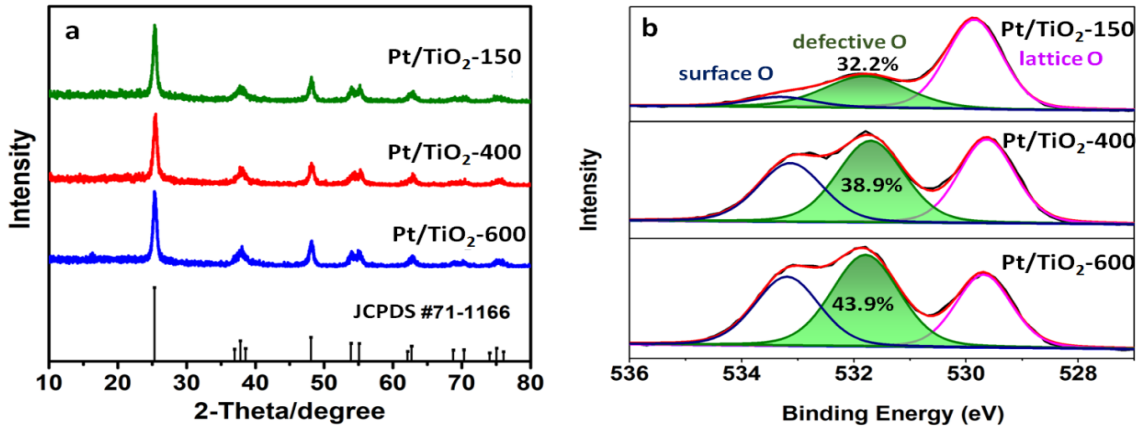


Fig. 6 XRD patterns (a) and XPS O 1s spectra (b) of Pt/TiO2 catalysts

The O 1s core level spectra of Pt/TiO_2 catalysts could be divided to three parts: lattice O (529.8 eV), defective O (531.8 eV) and surface O (533.2 eV).

Experimental

Table 3. Basic parameters of Pt/Al_2O_3 and Pt/TiO_2 catalysts

Catalyst	Pt loading (%wt.)	Pt diameter (nm)	O vacancy proportion(%)
Pt/Al_2O_3	0.94	2.18	/
Pt/TiO_2-150	0.91	2.83	32.2
Pt/TiO_2-400	0.88	2.29	38.9
Pt/TiO_2-600	0.96	2.53	43.9

1. The Pt loading of four catalysts showed little difference.

2. The average size of these catalysts ranged from 2.18 nm to 2.83 nm without significant differences. (The first two parameters with similar values can guarantee the catalysts performance are not influenced by Pt particles)

3. The quantity of O vacancy in Pt/TiO_2-600 was the largest.

Experimental

2.3 Impact of operation parameters （One-stage processing mode）

Table 4. Membrane reactor performance and operation parameters from different labs

No.	*S* / cm^2	*F* / $mL \cdot min^{-1}$	*P* / kPa	*R*	DF	data source
1	550	50	95	4	88.9	TLK[1]
2	325	50	95	4	65	
3	140	50	95	4	58	
4	70	50	95	4	51	
5	550	150	95	4	10	
6	428	100	100	5	14.3	INPC[2]
7	428	200	100	5	10.3	
8	157	186	150	1	1.82	ENEA[3]
9	157	186	150	2	2.52	

operation parameters

***S*: membrane area**

***F*: water flow rate**

***P*: vapor partial pressure**

***R*: H_2/D_2O or H_2/HTO**

Processing source: natural water or heavy water

Catalyst: Traditional Ni/SiO_2 or Pt/Al_2O_3

Ref. 1 S. Welte, et al. ***Fusion Eng Des***, 87 (2012): 1045-1049

Ref. 2 L. Yue, et al. ***J Nucl Radiochem***, 43 (2021): 279-285.

Ref. 3 A. Santucci, et al. ***Fusion Eng Des***, 109–111 (2016): 642-646.

1. DF measured by three labs varied greatly. (why ?)

2. Of course, we know the membrane reactor performance is influenced by *S*, *F*, *P* and *R*, but the quantitative relationship is not clear. (two or more parameters change simultaneously→difficult to predict the variation trend of the DF)

Experimental

A new combined parameter $S^{0.5}P^{1.5}R/F^2$ was used for correlating with DF values

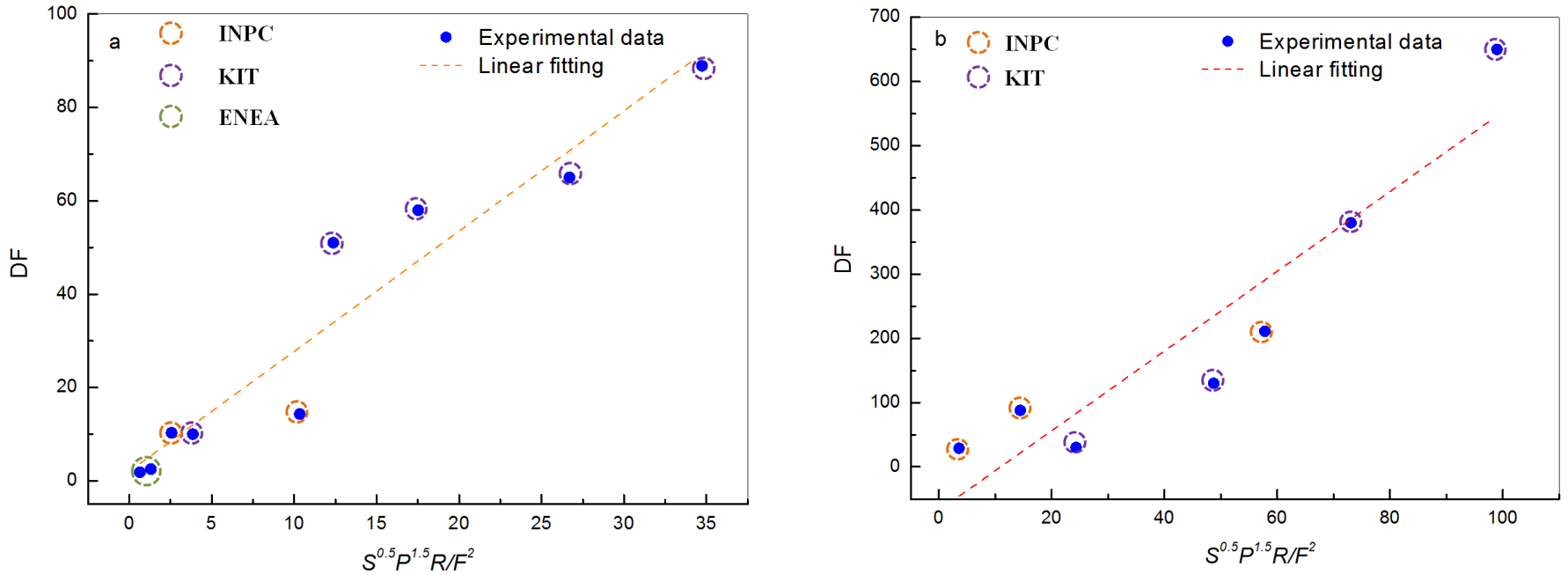


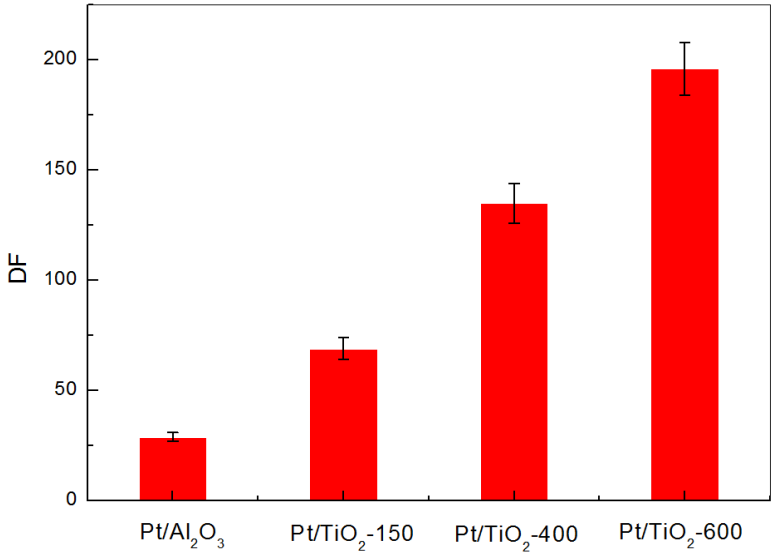
Fig. 7 DF values as a function of the parameter $S^{0.5}P^{1.5}R/F^2$ for processing of natural/heavy water (a) and tritiated water (b)

1. **The experimental data showed an approximate linear relationship with $S^{0.5}P^{1.5}R/F^2$, which meant increasing *S*, *P* and *R* were beneficial to enhance the reactor performance and increasing *F* led to reactor performance degradation.**
2. **The impact of *F* is the most remarkable, and the impact of *S* is the most slight.**

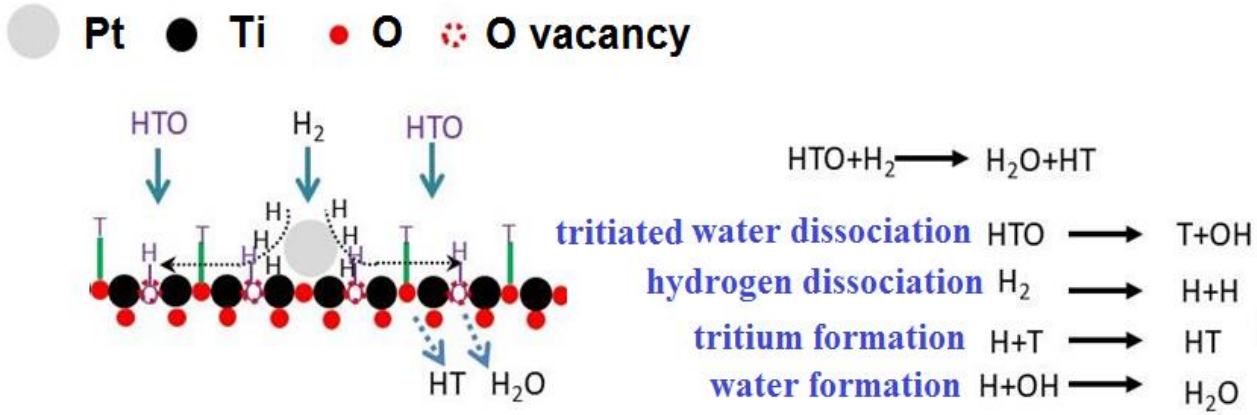
Experimental

2.4 Impact of catalysts（One-stage processing mode）

Fig. 8 DF values determined by using different catalysts (Experimental condition: S = 428 cm^2, F = 200 mL/min, P = 125 kPa, R = 5)



1. Compared with Pt/Al_2O_3, the DF value of Pt/TiO_2-600 exhibited a most significant increase of 5.7 times. For Pt/TiO_2-150 and Pt/TiO_2-400, the DF value increased by 1.4 times and 3.6 times, respectively.
2. The experimental results confirmed that Pt catalysts with O vacancies were more conducive to hydrogen-water isotope exchange.



Water molecule can be dissociated easily on oxygen vacancy of catalysts, so the exchange reaction is promoted.

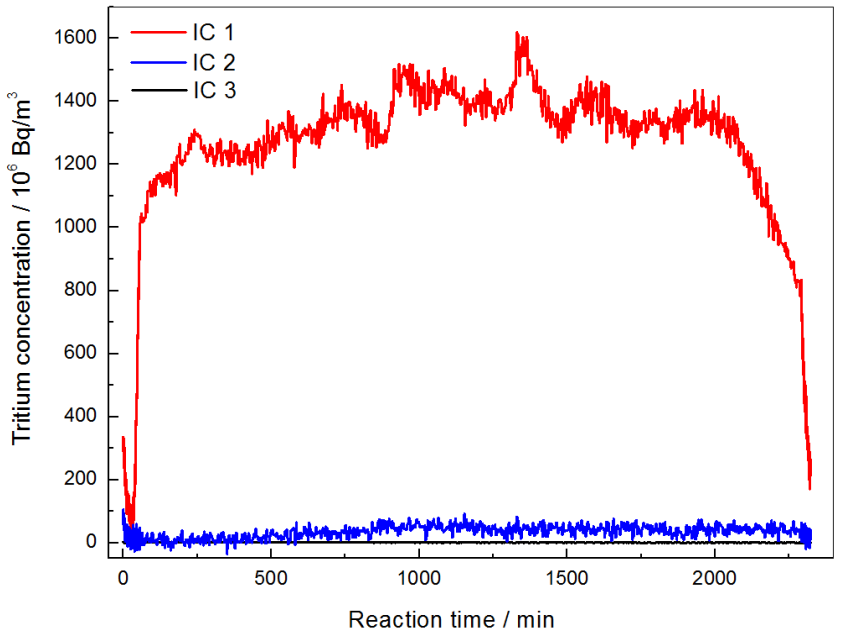
Fig. 9 Proposed mechanism for hydrogen-water isotope reaction on Pt/TiO_2 catalyst

Experimental

2.5 Processing of tritiated water

About 96 g tritiated water of 6.9×10^9 Bq/kg was processed b

1.
re
2.
sic
3.
ou
Bc
4.
tri



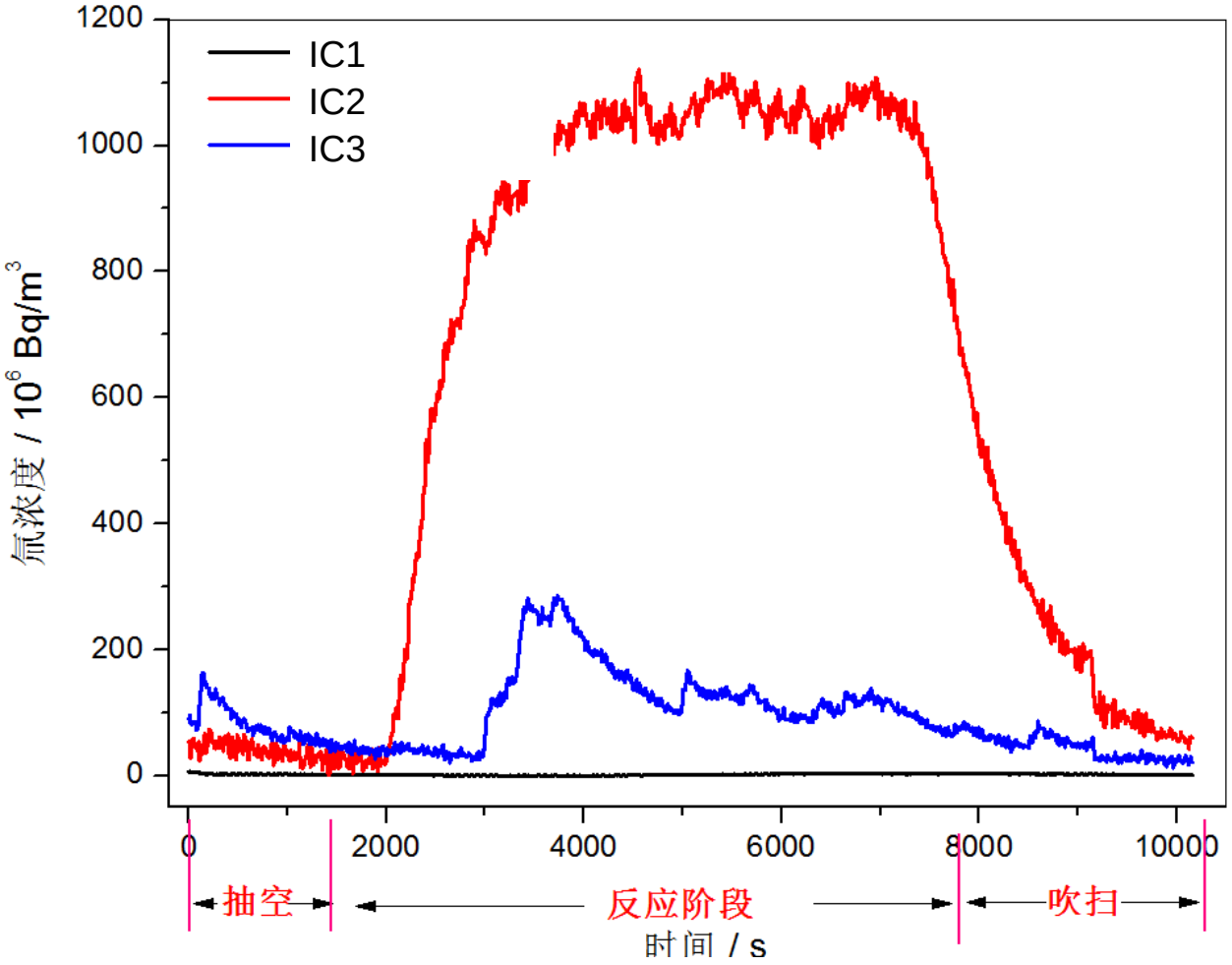
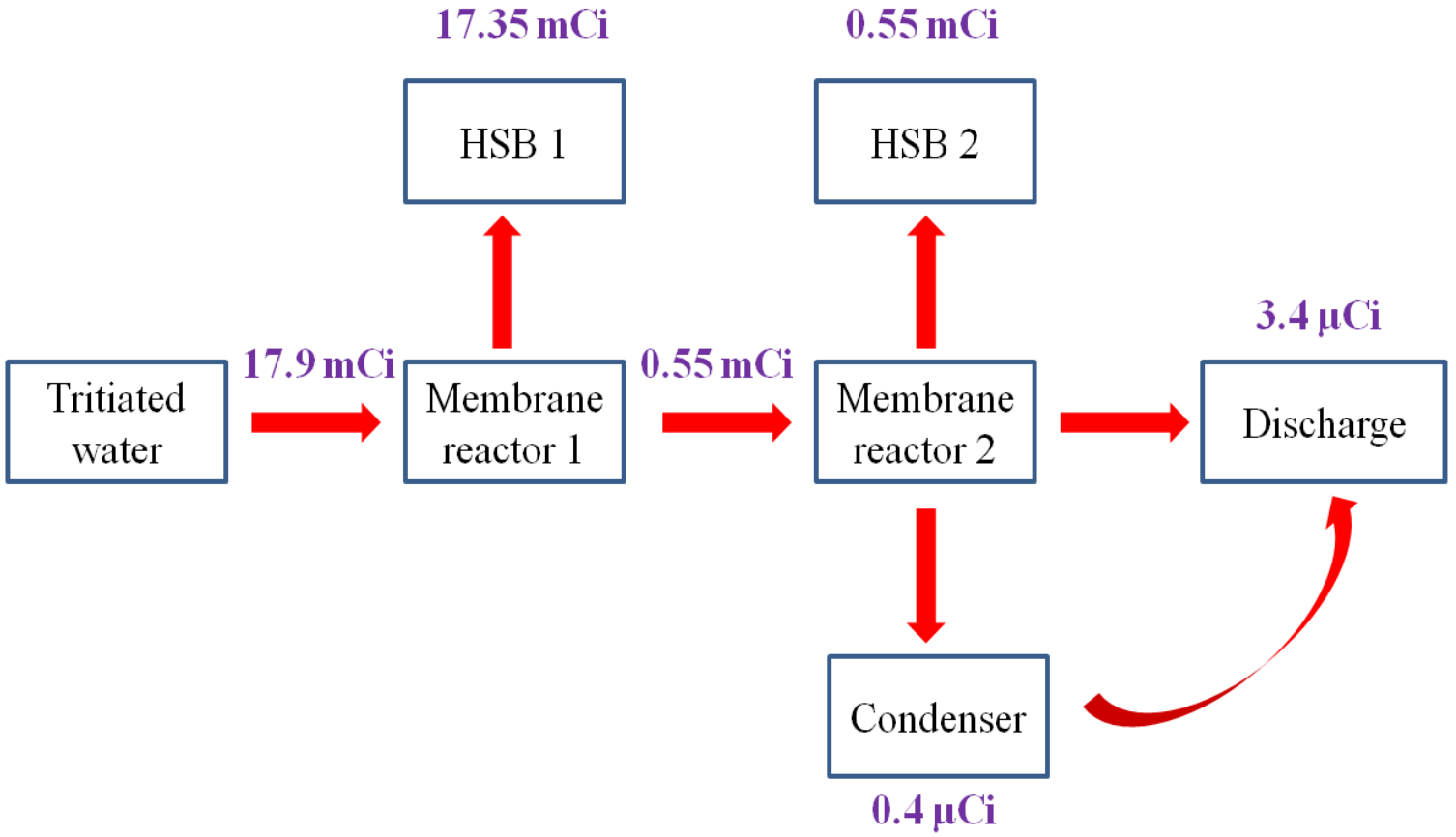


Fig. 10 Real-time monitoring curve of tritium concentration during the
(Experimental condition: S = 428 cm^2, F = 50 mL/min, P = 125 kPa, R = 5)

Experimental



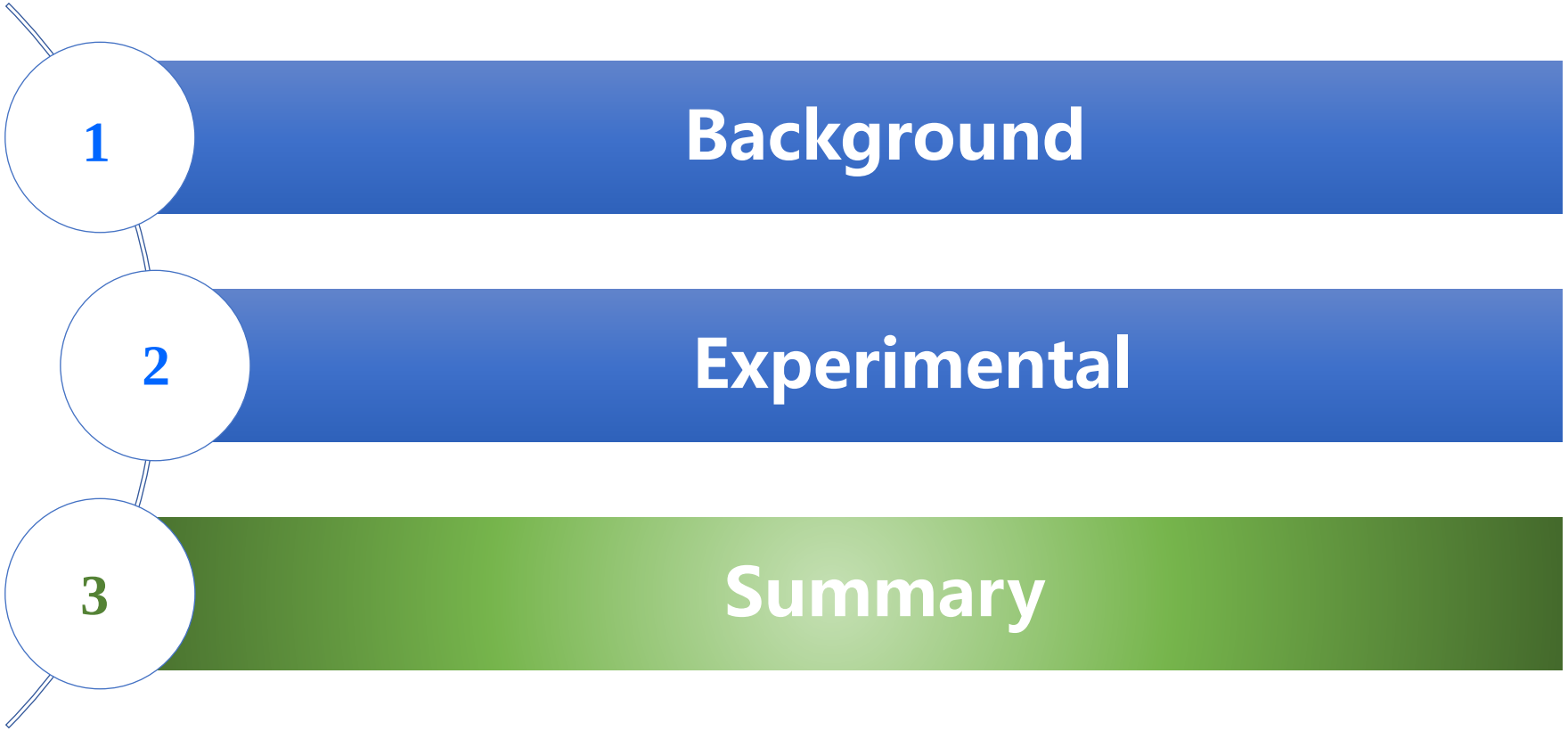
1. Almost all the tritium (99.99 %) in tritiated water could be converted to tritium gas and separated from helium and water vapor by Pd membrane to be pure products and stored in the hydrogen storage bed.

2. 97 % of the tritium was recovered by the first membrane reactor.

Fig. 11 Tritium balance data of the two-stage membrane reactor for processing tritiated water

More information can be found in this paper: L. Yue, et al. International Journal of Hydrogen Energy 2023 In Press,https://doi.org/10.1016/j.ijhydene.2023.07.226

Outline



Summary

In this work, a two-stage membrane reactor has been established and the catalytic activities of Pt/Al_2O_3 and Pt/TiO_2 catalysts have been investigated. Some conclusions can be summarized as follows:

- **The DF values show an approximate linear relationship with a new combined parameter $S^{0.5}P^{1.5}R/F^2$, and the impact of *F* is the most significant.**
- **The catalytic activity of Pt/TiO_2 is better than that of Pt/Al_2O_3, because Pt/TiO_2 realizes the co-dissociation of hydrogen (Pt sites) and tritium water (O vacancy of TiO_2).**
- **The DF values of two-stage membrane reactor can reach 40588, which means tritium concentration of tritiated water can decrease by 4 orders of magnitude (from 10^9 Bq/kg to 10^5 Bq/kg).**

Future plan: We will use membrane reactor to process tritiated heavy water (DTO produced in the China Mianyang Research Reactor), and give a detail comparison for reactor performance of H-D, H-T and D-T system.

核物理与化学研究所
INSTITUTE OF NUCLEAR PHYSICS AND CHEMISTRY

责任 执行 创新 卓越
自主创新 军民融合 三元发展

Thanks for your attention !