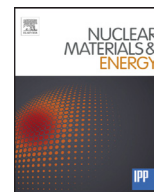




Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

Development of hydrophobic platinum catalyst for oxidation of tritium in JAEA

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ARTICLE INFO

Article history:
Available online xxx

ABSTRACT

To design a recombiner packed with hydrophobic catalyst for passive tritium oxidation, the development of manufacturing technology for hydrophobic platinum catalyst and the following analysis on reaction rate are essential. This presentation deals with the reaction rate for tritium oxidation over a hydrophobic platinum catalyst at temperature between room temperature and 473 K. Two kinds of hydrophobic platinum catalysts; supported with styrene-divinylbenzene and with silica were used for this test. The results indicate that 1) the particle size of platinum affects the reaction rate, 2) the order of reaction is 0.5 of hydrogen concentration at room temperature in case of a hydrogen content below 100 ppm. The rate-determining step approximation method is applied for the discussion on the reaction mechanism of tritium oxidation over platinum catalyst.

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1. Introduction

Precious metal catalysts are fundamental materials for tritium processing to prevent accidental release of tritium into the environment [1]. The system of catalytic reactor for the catalytic conversion of airborne tritium to the oxide in combination with following oxide absorber has been applied in tritium handling facilities to control the tritium release to the environment as low as achievable [2]. Precious metal catalysts are also applied to water detritiation [3]. In a liquid phase catalytic exchange column packed with precious metal catalyst and structured packing, tritium molecules are exchanged from hydrogen to water vapor with hydrogen isotope exchange reacted over precious metal catalyst. In order to improve the efficiency of catalytic reactions mentioned above, there remains an ever-increasing interest and challenge to develop the technology for hydrophobic precious metal catalyst [4]. It is a well-known fact that hydrophobic precious metal catalysts manufactured from hydrophobic polymers have been used all over the world originally for the application of water detritiation [4]. In Japan, a hydrophobic precious metal catalyst manufactured from styrene-divinylbenzene copolymers had been applied to heavy water refinement at Advanced Thermal Reactor “Fugen Nuclear Power

Station” owing to its outstanding hydrophobic property. Typical hydrophobic catalysts were manufactured by platinum deposited on hydrophobic polymer support or made wet-proofed by using Teflon. Compared with conventional hydrophilic catalysts such as Pt/Al₂O₃, the tritium removal from liquid effluent by means of hydrophobic catalyst offers a higher efficiency, lower operation temperature and pressure and energy requirements [4]. The major disadvantage of the existing hydrophobic precious metal catalysts was the low thermal stability to apply them to the catalytic conversion of airborne tritium. On the other hand, tritium safety for handling a kilogram level of tritium stresses the need for a technological countermeasure to consider severe accidents such as complete loss of power supply, technology of hydrophobic catalyst has been drawing intense interest recently because of its potential application of hydrophobic catalyst to passive recombiner for the catalytic conversion of airborne tritium at room temperature. Recently, the Japan Atomic Energy Agency and Tanaka Kikinokogyo K.K developed a new method of manufacturing catalysts involving hydrophobic processing with an inorganic substance base. No performance degradation in response to radiation application of 530kGy and thermal stability at over 600 °C have been demonstrated [5]. It was a great challenge to fabricate a hydrophobic precious metal catalyst with both high thermal stability and high radiation durability.

For the tritium safety of nuclear fusion facility, off normal release of tritium into secondary or final confinement should be considered. In these cases, it is inevitable that the content of tritium

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<http://dx.doi.org/10.1016/j.nme.2016.08.018>

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Table 1
Characteristics of catalysts.

	Pt Catalyst A	Pt Catalyst B	Pt Catalyst C
Catalog name	(Trial manufacture)		TKK-H1P
Hydrophilicity	hydrophobic	hydrophobic	hydrophobic*
Substance base	Styrene-divinylbenzene copolymer (SDBC)		Hydrophobic treated SiO ₂ *
Grain diameter	3 mm		
Packed density	220 g/L		490 g/L*
Specific surface area	364 m ² /g		211 m ² /g*
Accumulated pore volume of the catalyst	1.790 cm ³ /g		0.648 cm ³ /g*
Peak top of pore diameter	61 nm		12.3 nm*
Deposited platinum weight per catalyst volume	4.0 g/L		5.0 g/L*
Platinum particle size	2 to 20 nm	fine 2 nm	2 to 20 nm*
Supplier	Tanaka Kikinzoku Kokyo K.K., Japan		

* Ref [6]

taken into account for the design of detritiation system is very small, even though the activity of tritium is evaluated to be quite large. The content of tritium would be smaller than that of hydrogen naturally contained in air. Hence the understanding of the reaction mechanism on oxidation of a very small hydrogen content is quite important. In addition, if we consider the severe accidental scenario such as loss of electric power to heat the catalytic reactor, the passive oxidation of tritium at temperature around room temperature is an engineering option. In order to apply a hydrophobic precious metal catalyst to passive tritium recombiner, the improvement of catalytic activity as much as possible is required from the recombiner design point of view. This is because the activation of catalyst by any heat such as external heat and heat of reaction cannot be taken into account [6]. In order to improve the catalytic activity much more, kinetics data and understanding of the reaction mechanism are essential. It has been demonstrated that the overall reaction rate constant for hydrogen oxidation depends strongly on hydrogen content in feed gas, especially when temperature of catalyst layer is around room temperature [6]. The literature concerning kinetics for tritium oxidation at temperature around room temperature was limited [7]. J.C. Bixel and C.J. Kershner concluded that surface reaction is the rate controlling step for oxidation of hydrogen at 0.5 ppm hydrogen concentration and 296 K with Engelhard #50,088 hydrophilic catalyst [8]. They indicated the first order dependency on hydrogen concentration. However, their system had time delay in response of tritium monitors. In addition, conversion efficiency was quite higher than expected due mainly to absorption of tritiated vapor on the surface of hydrophilic catalyst. The understanding of kinetics with development of hydrophobic precious metal catalysts still remained as an open research issue. The purpose of this study was to examine the oxidation reaction of tritium over hydrophobic precious metal catalyst by kinetics and mass transfer approach, then the main factors for enhance in activity are suggested for better fabrication of hydrophobic precious metal catalyst.

2. Experimental

2.1. Catalysts

In order to evaluate the reaction order for hydrogen oxidation under the wide range of temperature, tritium was mixed in feed gas as tracer due to the analytical difficulties in detecting hydrogen concentrations below 10 ppm. By using tritium, the reaction order for hydrogen oxidation was evaluated even with feed gas accompanied with a low content hydrogen. The adsorption of tritiated water vapor produced by the oxidation reaction causes the error in evaluation of reaction rate. Hence the hydrophobic catalysts were manufactured and applied to the tests. Characteristics of catalysts applied for this research are shown in

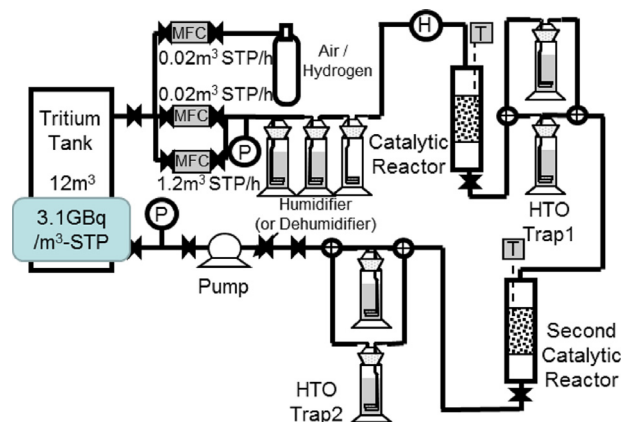


Fig. 1. Experimental flow-through system designed for the evaluation of kinetics of hydrogen oxidation reaction
H: Hygrometer, P: Pressure gauge, T: thermocouple with a PID temperature controller.

Table 1. The hydrophobic precious metal catalysts manufactured from styrene-divinylbenzene copolymer (SDBC) were used [7]. The granular SDBC of 3 mm grain diameter was purchased from Shoko Co. Ltd. Japan. Two types of hydrophobic precious catalyst, Catalyst A and Catalyst B, were manufactured from the purchased granular SDBC by Tanaka Kikinzoku Kokyo, Japan. The catalysts manufactured from SDBC showed the excellent hydrophobic property. However the catalysts were not available under temperature larger than 473 K due to their low thermal stability. Hence another hydrophobic catalyst called Catalyst C manufactured from a hydrophobic processed inorganic substance base was applied especially to check the reaction order for hydrogen oxidation under temperature larger than 473 K [6].

2.2. Test apparatus and experimental procedure

Fig. 1 illustrates the experimental flow-through system designed for the evaluation of kinetics of hydrogen oxidation reaction [6]. A large stainless steel tank which volume is 12 m³ was prepared in order to keep a constant content of tritium in the feed gas. The experimental flow-through system was connected with the tank. To release tritium intentionally in the tank, tritium balanced in air which concentration was approximately 3.1 GBq/m³-STP was prepared in the tank. The unit of m³-STP indicates the equivalent volume under 101.3 kPa and 273 K. The pump started for gas circulation through the experimental flow-through system. Then the hydrogen gas was added from a gas cylinder into the feed gas for hydrogen to be a specified content. The flow rate of a gas was controlled with a gas flow controller (8300MC, KOFLOC, Japan)

over the flow range from 0.018 to 0.144 m³-STP/h. The pressure at the inlet and at the outlet of the tritium tank was monitored with Baratron pressure gauges (Type 626, MKS, Japan). Taking the effect of moisture in feed gas on activity of catalyst into consideration, we kept moisture in feed gas to be a constant content. For the dry condition, dry feed gas was achieved by passing the gas through the prepared two dehumidifiers connected in series. Approximately 200 cm³ of dehydrated silica gel and dehydrated molecular sieve 5A were packed in each dehumidifier, respectively. The dew point of dry feed gas following two dehumidifiers was monitored to be less than 253 K using a capacitance-type dew point hygrometer. For the wet condition, wet feed gas was achieved by passing the gas through the prepared two humidifiers connected in series. The catalytic reactor was packed with hydrophobic catalyst of 20 cm³ in volume. The inner diameter and length of the catalytic reactor were 25.0 mm and 97.2 mm, respectively. The temperature of the catalyst layer was monitored with a thermocouple. The temperature of the layer was controlled by a heater with a PID temperature controller. The tritiated moisture (HTO) in the effluent produced by oxidation reaction in the catalytic reactor was trapped in a water bubbler of HTO Trap 1. The post-catalytic reactor was applied for the purpose to oxidize the unreacted hydrogen and tritium in the effluent from the catalytic reactor. The inner diameter and length of the second catalytic reactor were 56.5 mm and 150 mm, respectively. The post-catalytic reactor was packed with a commercial 0.5 wt% Pt/Al₂O₃ catalyst of 100 cm³ in volume. The Pt/Al₂O₃ catalyst was AP1001 manufactured by N.E. Chemcat, Japan. The volume of the catalyst in the post-catalytic reactor was determined for unreacted hydrogen and tritium from the catalytic reactor to be oxidized completely. The form of a Pt/Al₂O₃ pellet was φ3 mm x 3 mm. The temperature of Pt/Al₂O₃ catalyst layer was controlled to be 473 K. The HTO in the effluent produced by oxidation reaction in the post-catalytic reactor was trapped in a water bubbler of HTO Trap 2. Both catalytic reactors were thermally insulated. The tritiated water vapor produced in each catalyst reactor was collected with a HTO trap and water in each trap was sampled after termination of each run by suspending pump operation, and then the tritium amount was determined with a liquid scintillation counter (Aloka LSC6100, Aloka Ltd., Japan). The gas lines of the system were made of a 316 stainless-steel tube with inner diameter of 6.35 mm and partly of a vinyl chloride tube with inner diameter of 7.0 mm. We confirmed the adsorption of tritiated water on the catalyst and piping was negligibly small by wet purge with tritium free air accompanied with moisture after tritium tests.

2.3. Assessment of overall reaction rate constant for hydrogen oxidation

The conversion rate of tritium by the catalytic reactor is assessed by $X_A = H_1/(H_1 + H_2)$, wherein H_1 and H_2 represent the tritium amount in the first and second trap, respectively. Then, the overall mass transfer coefficient ($k_{overall}$) for the hydrophobic catalyst is theoretically computed from the equation;

$$k_{overall} = \frac{Q}{V_{cat}} \text{LN} (1 - X_A) \quad (1)$$

wherein the Q and V_{cat} represent the volumetric gas flow rate and the volume of catalyst, respectively [9].

3. Theory

3.1. Chemical kinetics analysis

Chemical kinetics with an integral reactor is evaluated by measurement of reaction rate at the outlet of the reactor as a function of flow rate of feed gas under the constant content of hydrogen in the feed gas. Then the reaction order can be determined by

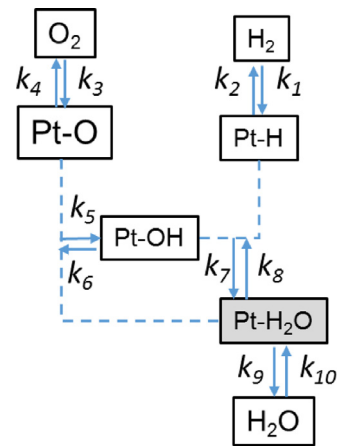


Fig. 2. Reaction route of hydrogen oxidation over catalyst.

the plot of reaction rate vs space time. Space time is defined by V_{cat}/F , where V_{cat} and F are the volume of catalyst and feed gas flow rate, respectively. Generally the oxidation of hydrogen over precious metal catalyst is regarded as pseudo-first-order reaction of hydrogen. In this case, the linear increase of $\text{LN}(1/(1-X_A))$ as a function of τ is obtained, where τ is space time [10]. In the case that the oxidation of hydrogen over precious metal catalyst is 1/2 order of hydrogen, the linear increase of $(1 - \sqrt{1-X_A})$ as a function of τ is obtained [10].

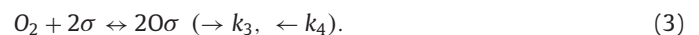
3.2. Rate controlling step

Previous research has indicated that the rate controlling step for the oxidation of hydrogen is pore diffusion at temperature larger than 473 K, where the reaction at active site on the catalyst surface is fast [11]. When the temperature decreases, the rate controlling step will move from pore diffusion to reaction at active site. We would like to focus on the reaction order for the oxidation of hydrogen when the rate controlling step is reaction at active site. Fig. 2 shows a reaction route of hydrogen oxidation over catalyst. Since OH formation by the addition of H to O is highly activated, another mechanism has to account for its formation.

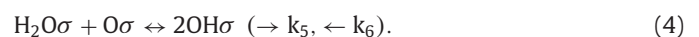
Adsorption of hydrogen on active site



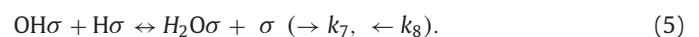
Adsorption of oxygen on active site



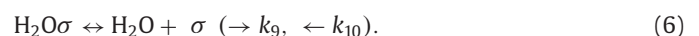
Formation of OH on active site



Formation of water vapor on active site



Desorption of water vapor from active site



Balance of coverage

$$\theta_{Pt} + \theta_{Pt-H} + \theta_{Pt-O} + \theta_{Pt-OH} + \theta_{Pt-H_2O} = 1. \quad (7)$$

Reaction rates for formation of Pt-H, Pt-O, Pt-OH, Pt-H₂O and desorption of H₂O,

$$v_1 = k_1 P_{\text{H}_2} \theta_{Pt}^2 - k_2 \theta_{Pt-H}^2, \quad (8)$$

$$v_2 = k_3 P_{\text{O}_2} \theta_{Pt}^2 - k_4 \theta_{(Pt-O)}^2, \quad (9)$$

$$v_3 = k_5\theta_{Pt-H_2O}\theta_{Pt-O} - k_6\theta_{Pt-OH}^2, \tag{10}$$

$$v_4 = k_7\theta_{Pt-OH}\theta_{Pt-H} - k_8\theta_{Pt-H_2O}\theta_{Pt}, \tag{11}$$

$$v_5 = k_9\theta_{Pt-H_2O} - k_{10}P_{H_2O}\theta_{Pt}, \tag{12}$$

where θ , σ , ν , k and P mean the coverage, platinum active site, reaction rate, rate constant and partial pressure, respectively. Generally the coverage of oxygen is larger than that of hydrogen since the content of oxygen in the feed air is larger than that of hydrogen. This leads the adsorption of oxygen is not the rate controlling step. In the case, it is reasonable to consider that adsorption of hydrogen is the rate controlling step. The following steady state approximation is established.

$$v_2 = v_3 = v_4 = v_5 = 0 \tag{13}$$

The numerical analysis with this approximation leads the simple pseudo-first-order reaction of hydrogen in the end. In contrast, it is inferred from the previous result that the reaction for oxidation of a very small hydrogen content at room temperature is not the pseudo-first-order reaction of hydrogen. In this case, desorption of water vapor is likely to be the rate controlling step.

$$v_1 = v_2 = v_3 = v_4 = 0 \tag{14}$$

$$v_{overall} = v_5 = \frac{A P_{H_2} + B}{C P_{H_2} + D \sqrt{P_{H_2} + E}} \tag{15}$$

$$A = \frac{k_1 k_5 k_7^2 k_9}{k_2 k_6 k_8^2} \sqrt{\frac{k_3 P_{O_2}}{k_4}} \tag{16}$$

$$B = -k_{10} P_{H_2O} \tag{17}$$

$$C = \frac{k_1 k_5 k_7^2}{k_2 k_6 k_8^2} \sqrt{\frac{k_3 P_{O_2}}{k_4}} \tag{18}$$

$$D = \sqrt{\frac{k_1}{k_2}} \left(1 + \frac{k_5 k_7}{k_6 k_8} \sqrt{\frac{k_3 P_{O_2}}{k_4}} \right) \tag{19}$$

$$E = 1 + \sqrt{\frac{k_3 P_{O_2}}{k_4}} \tag{20}$$

The equation estimates the apparent order of reaction is between zero to first order of hydrogen, where the order depends strongly on hydrogen content and water vapor content.

4. Results and discussion

4.1. Analysis on rate-controlling step

Fig. 3 illustrates the reaction rate vs space time for tritium oxidation at 473 K with Catalyst C. The oxidation reaction of hydrogen is generally regarded as the pseudo-first-order reaction of hydrogen. In this result, the linear increase of $LN(1/(1-X_A))$ as a function of retention time “t” is clearly obtained, where X_{H_2} means the conversion rate of hydrogen. This result supports the conventional understanding that the hydrogen oxidation is evaluated as the pseudo-first-order reaction of hydrogen. However, our another result indicates an exception of this understanding especially when the hydrogen content is very small and temperature of catalyst layer decreased to temperature around room temperature. For the tritium safety of nuclear fusion facility, off normal release of tritium into secondary or final confinement should be considered. In these cases, it is inevitable that the content of tritium taken into

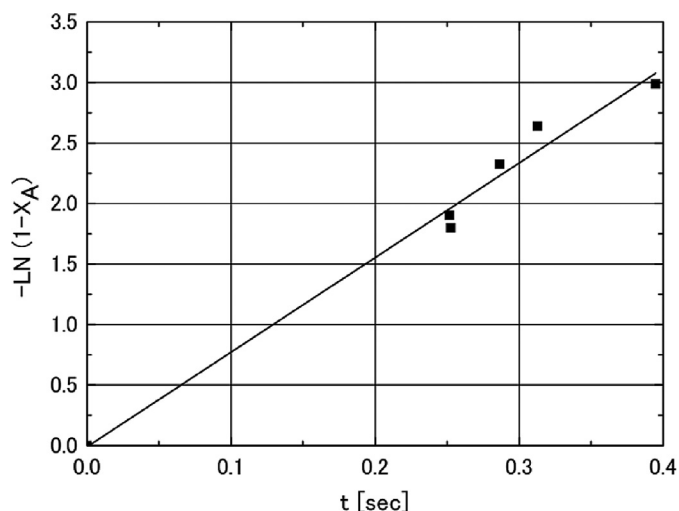


Fig. 3. Reaction rate vs space time for tritium oxidation at 473 K with Catalyst C.

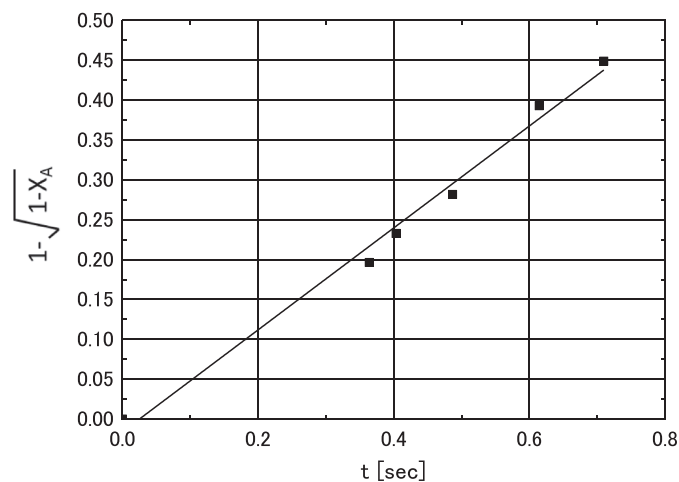


Fig. 4. Reaction rate vs space time for tritium oxidation at room temperature with Catalyst A.

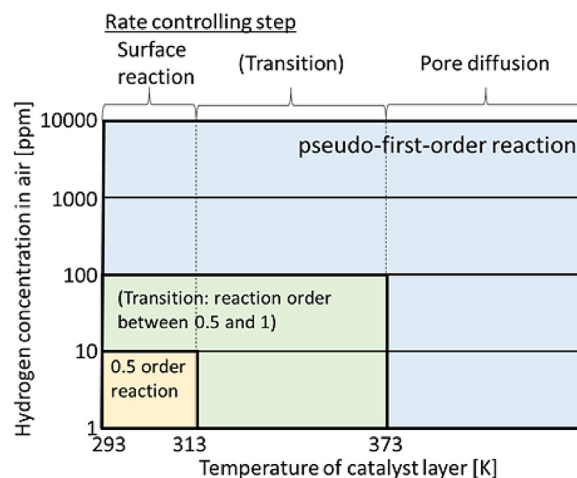


Fig. 5. Change in order of reaction as a function of hydrogen content and temperature of catalyst layer.

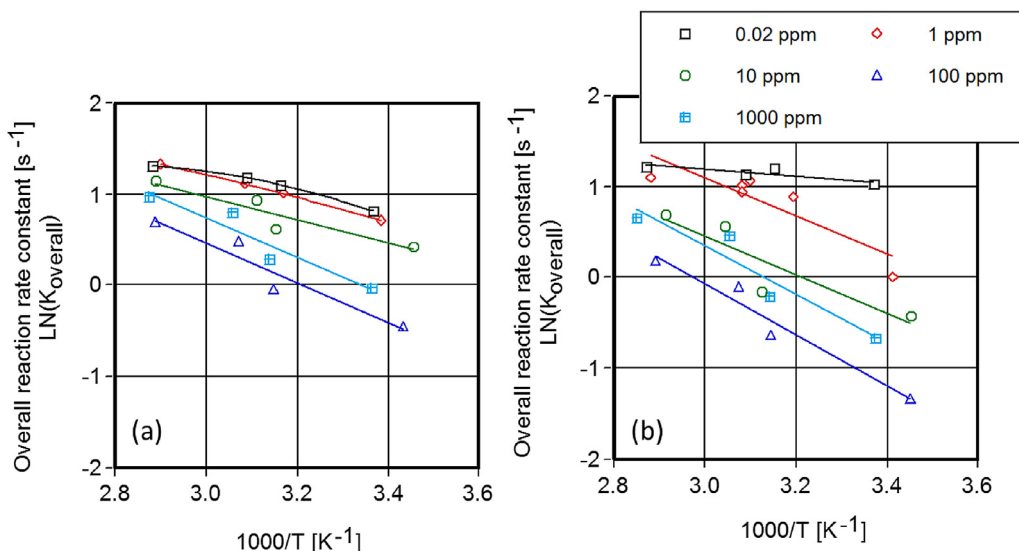


Fig. 6. Variation in natural logarithm of overall reaction rate constant for tritium oxidation as a function of reciprocal temperature $1000/T$ at different hydrogen content under the dry condition (a) for Catalyst A and (b) for Catalyst B.

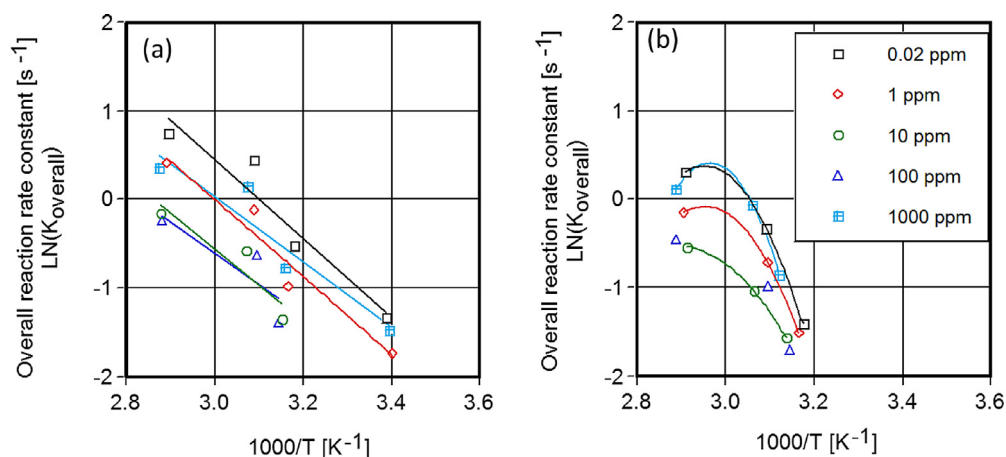


Fig. 7. Variation in natural logarithm of overall reaction rate constant for tritium oxidation as a function of reciprocal temperature $1000/T$ at different hydrogen content under the moisture concentration of 22,000 ppm (a) for Catalyst A and (b) for Catalyst B.

account for the design of detritiation system is very small, even though the activity of tritium is evaluated to be quite large. The content of tritium would be smaller than that of hydrogen naturally contained in air. Hence the understanding of the reaction mechanism on oxidation of a very small hydrogen content is quite important. In addition, if we consider the severe accidental scenario such as loss of electric power to heat the catalytic reactor, the passive oxidation of tritium at temperature around room temperature is an engineering option. Hence, the understanding of the reaction mechanism on hydrogen oxidation at temperature around room temperature is also quite important. Fig. 4 reveals the reaction rate vs space time for tritium oxidation at room temperature with Catalyst A. Concerning on hydrogen oxidation at room temperature, the linear increase of $\text{LN}(1/(1-X_A))$ as a function of retention time is not obtained. This indicates the hydrogen oxidation under a very small hydrogen concentration and room temperature never assessed as the pseudo-first-order reaction of hydrogen. Instead the linear increase of $(1 - \sqrt{1-X_A})$ as a function of retention time is obtained. This indicates the oxidation of hydrogen is 1/2 order of hydrogen in this case. Similar results are evaluated with the following combined condition which is a hydrogen content below 10 ppm and catalytic temperature lower than 313 K. Fig. 5 shows our understanding; the change in order of reaction as

a function of hydrogen content and temperature of catalyst layer. In case of a hydrogen content below 10 ppm, the order of reaction at catalytic temperature between 313 and 373 K shows the transition state where the apparent order of reaction increases from 1/2 to 1 with an increase in temperature of catalyst layer. In case of a hydrogen content above 10 ppm, the hydrogen oxidation reaction is evaluated as the pseudo-first-order reaction of hydrogen over the entire temperature range. This is because the pseudo-first-order reaction of hydrogen is applied in both rate-controlling cases of pore diffusion at a high temperature and adsorption of hydrogen on active site at a low temperature.

4.2. Effect of platinum particle size

Fig. 6(a) and (b) show the variation in natural logarithm of overall reaction rate constant for tritium oxidation as a function of reciprocal temperature $1000/T$ under the dry condition for Catalyst A and Catalyst B, respectively. Both hydrophobic catalysts show the dependence of overall reaction rate constant on hydrogen content. With an increase in hydrogen content from tracer level, the overall reaction rate constant decreases over the whole temperatures. Then the overall reaction rate constant reaches the bottom value with the hydrogen content of 100 ppm. The decrease in

overall reaction rate constant with an increase in hydrogen content is mainly attributed to the increase in content of water vapor produced by oxidation reaction. With a hydrogen content above 100 ppm, the overall reaction rate constant increases reversely with an increase in hydrogen content. This reverse suggests the change in rate controlling step. It is also clear the platinum particle size deposited on the catalyst surface affects the catalytic activity. With a decrease in platinum particle size, water vapor can considerably cover the active sites. Compared with the catalyst A, the catalyst B significantly decreases the catalytic activity due mainly to the contribution of covered water vapor. Since the adsorption of water vapor is a key factor for the oxidation of tritium especially at temperature around room temperature, adsorption of water vapor affects considerably in case of the wet oxidation. Fig. 7(a) and (b) show the variation in natural logarithm of overall reaction rate constant for tritium oxidation as a function of reciprocal temperature $1000/T$ under the wet condition for Catalyst A and Catalyst B, respectively. Under the moisture concentration of 22,000 ppm, the catalyst B which has a fine platinum size shows the considerable decrease in overall reaction rate constant due to the effect of water vapor. When a hydrophobic platinum catalyst is designed for a passive recombiner, platinum particle size is a dominant factor.

5. Conclusions

To design a passive recombiner packed with hydrophobic catalyst for tritium oxidation, the development of manufacturing technology for hydrophobic platinum catalyst and the following data on reaction rate are essential. This presentation deals with the reaction rate for tritium oxidation over hydrophobic platinum catalyst at temperature between room temperature and 473 K. The re-

sult indicated that the particle size of platinum affects the reaction rate. Catalyst with a fine platinum size showed the considerable decrease in overall reaction rate constant due to the effect of water vapor. Concerning the order of reaction for hydrogen combustion, it is 0.5 of hydrogen concentration at room temperature when the hydrogen concentration is below 10 ppm.

Acknowledgment

Part of this work was supported by JSPS KAKANHI Grant-in-Aid for Scientific Research C (Grant Number 25420894). The authors wish to acknowledge this funding support.

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