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Development of Pt/ASDBC Catalyst Applicable for Hydrogen Oxidation in the Presence of Saturated Water Vapor at Room Temperature

Yasunori IWAI, Katsumi SATO and Toshihiko YAMANISHI
Tritium Technology Group, Japan Atomic Energy Agency
Tokai - mura, Naka - gun, Ibaraki - ken 319-1195 Japan

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Combined catalytic recombiner and water absorber system has been applied in a tritium handling facility to remove tritium as well as other tritiated components in the atmosphere of a containment. It has been known that the hydrogen oxidation performance of the catalyst packed in the catalytic recombiner considerably decreased at room temperature in the case where the concentration of water vapor is very large. We have developed some hydrophobic Pt catalysts applicable for hydrogen oxidation even in the presence of saturated water vapor at room temperature. A new type of hydrophobic catalyst, Pt/ASDBC, has been prepared by depositing platinum on alkyl-styrene diviyl-benzene copolymer (ASDBC). Pt/ASDBC is more hydrophobic than Pt/SDBC that is the standard catalyst for a water detritiation system. Oxidation tests of the catalysts using 10000 ppm of hydrogen were performed in the presence of saturated water vapor at room temperature. Hydrogen oxidation more than 99% was achieved using Pt/ASDBC catalyst in the range of space velocity from 320 to 3300 h^{-1}. Moreover, radiation technology was applied to extend the pore size of catalyst. Hydrogen oxidation performance has been much improved with Pt/ASDBC catalyst irradiated with electron beams.

Keywords: Fusion, Tritium, Detritiation, Electron beams, Pore size, SDBC, ASDBC, Hydrophobic catalyst, Platinum, Kogel

1. Introduction

In a tritium handling facility, tritium or tritiated components in the atmosphere of a containment should be efficiently eliminated. Combined catalytic recombiner and water absorber system has been applied to remove tritium as well as other tritiated components in the atmosphere of a containment [1]. The typical operating temperatures of catalytic recombiners for the oxidations of hydrogen and tritiated organic compounds were 473 and 773K, respectively [1]. Industrial mature designs of the system are available for a large containment [2]. Recent investigation by Uda *et al.* indicated that honeycomb types of catalyst were a viable alternative to conventional particle catalyst due to its superior low-pressure drop characteristics [3].

Hydrogen oxidation has occurred on the catalytic reacting surfaces coated with platinum or palladium. Hydrogen oxidation reaction normally occurs in a wider species concentration range and over longer times than it would be with a gas combustion [4]. As for a possible poisoning of catalyst, many studies have focused on the hydrogen oxidation performance in the presence of CO, CO_2, and methane [5,6]. Kobayashi *et al.* investigated the poisoning of catalyst by SF_6 that has been used as an electric insulation gas for a negative bream injector in a fusion plant [7]. Negative poisoning of catalyst was observed in the presence of SF_6. Regarding water impact, it has been known that the hydrogen oxidation performance of the catalyst is decreased in the case where the concentration of water vapor is very large. The decrease in hydrogen oxidation performance in the presence of water vapor has been explained as the water layers formed on the noble metal plays the obstruction role of hydrogen transport onto noble metal. Moreover, efficient hydrogen oxidation performance at room temperature is strongly required taking an accident in a fusion plant into consideration. The realization of hydrophobic catalyst with an efficient hydrogen oxidation performance at room temperature even in the presence of saturated water vapor can also reduce the operating cost of catalytic recombiner significantly. Hence, hydrophobic catalysts have been attracted. Over 100 catalysts with hydrophobic properties have been prepared especially for the catalysts of the hydrogen-liquid water isotopic exchange reactions [8,9]. The conventional hydrophobic catalysts were roughly divided into two catalysts, that were coating of the supported platinum catalysts (e.g. Pt/ α Al_2O_3, Pt/Carbon) with polytetrafluoroetylene and supporting Pt directly on styrene diviyl-benzene

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author's e-mail:iwai.yasunori@jaea.go.jp copolymer (Pt/SDBC). Chung *et al.* investigated the hydrogen oxidation performance of a Pt/SDBC catalysts in the presence of water vapor in the temperature range from 303 to 353K [10]. The reported conversion ratio of hydrogen to water for the Korean Pt/SDBC catalyst at 303K was less than 10%. Hence, experiments have been carried out especially for the development and improvement of hydrophobic Pt/SDBC catalyst to have efficient hydrogen oxidation performance at around room temperature even in the presence of saturated water vapor.

The rate-controlling step of hydrogen oxidation reaction using a catalyst is generally pore diffusion. Hence, radiation technology was also applied to the Pt/SDBC and our developed Pt/ASDBC catalysts for the purpose to extend the pore size of catalyst.

The paper describes the availability of newly developed hydrophobic catalyst for hydrogen oxidation even in the presence of saturated water vapor at around room temperature.

2. Experimental

2.1 Catalysts

Three kinds of platinum deposited catalysts have been developed for efficient hydrogen oxidation in the presence of water vapor at 293K. Reactivity of these catalysts were compared with that of a conventional Pt / α Al_2O_3 and Pt/SDBC catalysts. Pt / α Al_2O_3 used in this test was commercial 0.5 wt.% Pt / α Al_2O_3 pellets manufactured by N. E. Chemcat cooperation, Japan. A pellet was ϕ 3mm x 3mm. A commercial Pt/SDBC used in this test was 0.5 wt.% Pt/SDBC particles, that have been called Kogel catalyst, manufactured by Showa Engineering Co. LTD., Japan [11]. The mode of particles' diameter was 3.0mm. The packed density was 0.22g/mL. A mercury porosimeter (Model Poresizer 9320, Micromeritics, U.S.A.) was used for determining specific surface area and pore size distribution of catalytic materials. This mercury porosimeter can determine the pore size distribution from 350 microns to about 7 nm. The specific surface area and accumulated pore volume of 0.5 wt.% Pt/SDBC particles were 364.4m^2/g and 1.79cm^3/g, respectively. The peak top of pore diameter evaluated by mercury intrusion porosimetry was 61nm. The deposited platinum of the Pt/SDBC catalyst was 1.8 g/L.

A new type of hydrophobic catalyst, Pt/ASDBC, has been prepared by dipositting platinum on alkyl-styrene diviyl-benzene copolymer (ASDBC). Pt/ASDBC is more hydrophobic than SDBC due to the intended incorporation with hydrophobic alkyl-groups in the molecular structure. An appearance is shown in Fig. 1. A feature of ASDBC was its fine mesoporosity. The mesopore distribution of ASDBC had a keener peek than that of SDBC. The mesopore diameter of ASDBC at the peek top was 163 nm. Pt/ASDBC manufactured for this test was 0.5 wt.% Pt/ASDBC particles. The mode of particles' diameter was 3.0mm. The packed density was 0.20g/mL. The specific surface area and accumulated pore volume were 57.9m^2/g and 1.49cm^3/g, respectively. The deposited platinum of the Pt/ASDBC catalyst was 1.0 g/L. This value was approximately half of the tested commercial Pt/SDBC catalyst. Superior water repellence of Pt/ASDBC catalyst is shown in Fig. 2.

Fig.1 Appearance of Pt/ASDBC catalysts

Fig.2 Superior water repellence of Pt/ASDBC catalyst

In this study, irradiation of the 0.5 wt.% Pt/SDBC and 0.5 wt.% Pt/ASDBC with electron beams at room temperature up to 1500 kGy was conducted for the purpose to extend the pore size of catalyst at the equivalent dose rate to 600 kGy/h using the electron accelerator No.1 facility of the Cockcroft-Walton type in Takasaki Advanced Radiation Research Institute of JAEA under the conditions of the beam energy of 1.99 MeV and the beam current of 2.00 mA. Each catalyst enclosed in a laminate film bag under vacuum was irradiated. A sufficient long interval for every 50 kGy irradiation was taken to prevent the temperature rising of the catalyst. The Pt/SDBC irradiated to 1250KGy and Pt/ASDBC irradiated to 1500kGy were adopted in this study.

2.2 Hydrogen Oxidation Performance Test

The experimental apparatus is shown in Fig. 3. An experimental gas mixture containing approximately 10000ppm of hydrogen in dry air (21%O_2 and 79% N_2) was fed to the reactor packed platinum catalysts. The water vapor concentration of the experimental gas was negligibly small. The flow rate of a gas was controlled with a gas flow controller (8300MC, KOFLOC, Japan). The inner diameter and length of the catalytic reactor were 56.5mm and 150mm, respectively. The catalytic reactor was not thermally insulated. The temperature of catalyst was monitored with a thermocouple. The oxidation tests were carried out at room temperature around 293K. The pressures at the inlet and outlet of the reactor were measured with Baratron pressure gauges (Type 626, MKS, Japan). The water concentration at the inlet of the reactor was measured with a capacitance-type dew point hygrometer (M Series [dew point: 213-293 K], Panametrics, Japan). The process gases were sampled at the inlet and outlet of the reactor and the concentrations of hydrogen were measured using a micro gas chromatograph with a thermal conductivity detector (Micro-GC CP-2002, CHROMPACK, Holland). The detectable sensitivity of hydrogen with the micro gas chromatograph was more than 10ppm. When the reactivity of a platinum catalyst in the presence of water was investigated, an experimental gas with saturated water vapor was made by passing the experimental gas through two water bubblers and a water mist trap in series. In this case, the water vapor in the process gas discharged from the reactor was removed by passing two silica gel absorbers in series prior to the sampling of process gas.

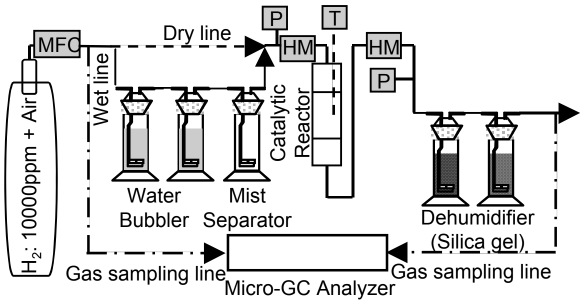
The conversion factor of hydrogen oxidation, CF (-), was defined by the following equation:

$$CF = C_{in}/C_{out} \qquad (1)$$

where C_{in} and C_{out} were the hydrogen concentrations at the inlet and the outlet of the reactor, respectively. The space velocity, SV (h^{-1}), was defined by the following equation:

$$SV = Q/V_{cat} \qquad (2)$$

where V_{cat} and Q were the volume of catalyst (cm^3) and the volumetric flow rate (cm^3-STP/h), respectively.



MFC: Gas flow controller, P: Pressure gauges, HM: Hygrometer, T: Temperature monitor, Micro-GC: Micro gas chromatograph with a thermal conductivity detector

Fig. 3 Experimental apparatus for Hydrogen Oxidation Performance Test

2.3 Thermal Stability Test

Thermogravimetric analysis (TGA) of catalytic materials was carried out on a TG-DTA-2000S analyzer (Mac Science, Japan). Since the non-repeatable results due to combustion of the catalysts in air obscured the difference of thermal stability, helium atmosphere was selected to prevent any combustion of the sample and any adsorption of moisture. The repeatable results obtained in a helium atmosphere showed clearly the difference of thermal stability between Pt/SDBC and Pt/ASDBC. An aluminum pan was used for each sample, and it was flamed prior to each analysis. The weight of a sample was approximately 6.0 mg. The temperature ramp rate was 1 K/min.

3. Results and Discussion

3.1 Hydrogen Oxidation Performance of Pt/ASDBC catalyst

The CF *v.s.* SV for tested platinum catalysts in the absence of water vapor in the experimental gas at 293K was shown in Table 1. The CF for hydrophilic Pt / α Al_2O_3 catalyst was quite low even in the absence of water vapor at 293K. The gradual decrease in reactivity was observed for Pt / α Al_2O_3 catalyst. The low reactivity was observed especially at approximately 250 h^{-1} of SV. At the low SV, it was pointed out that the laminar layer resistance decreased in reactivity [12]. Moreover, the deactivation by adsorption of produced water molecules on platinum surface should be considered. Small part of the adsorbed water molecules was purged from the platinum surface with a dry air. However in the light of our previous study on the water desorption from porous aluminate materials, it is quite difficult to remove most of adsorbed water molecules from platinum surface with a dry air of low SV [13, 14]. The heat of reaction led to the temperature increase of up to 3 K in the Pt / α Al_2O_3 catalyst bed. The CFs for Pt/SDBC and Pt/ASDBC were more than 1000. The CF more than 1000 indicated

Table 1 Conversion factor *v.s.* space velocity in the absence of water vapor at 293K

Catalyst	Conversion Factor			
	SV=294 h^{-1}	SV=588 h^{-1}	SV=1176 h^{-1}	SV=2941 h^{-1}
Pt / α Al_2O_3	9.51	4.53	4.69	3.75
Pt/SDBC		>1000	>1000	>1000
Pt/ASDBC	>1000		>1000	

that the hydrogen was practically not detected in the sample gas from the outlet of the catalytic reactor by a micro gas chromatograph. The key factor to achieve such a large CF was the water repellence of the polymers. The deactivation by adsorption of produced water molecules on platinum surface was negligibly small. The heat of reaction led to the temperature increase of up to 10 K in the Pt/SDBC and Pt/ASDBC catalyst beds due to high reactivity.

The CF *v.s.* SV for tested platinum catalysts in the presence of saturated water vapor in the experimental gas at 293K is shown in Table 2. In the presence of water vapor, the CF for hydrophilic Pt / α Al_2O_3 catalyst was considerably low. The increase of temperature was not observed in the Pt / α Al_2O_3 catalyst bed. Pt / α Al_2O_3 catalyst cannot be applied as hydrogen oxidation catalyst for a catalytic recombiner operated at room temperature. On the other hand, Pt/SDBC and Pt/ASDBC maintain a large CF even in the presence of saturated water vapor. Although the deposited platinum used to prepare Pt/ASDBC catalyst was reduced to 1.0 g/L which value was approximately half of a commercial Pt/SDBC catalyst, hydrogen oxidation more than 99% was achieved using Pt/ASDBC catalyst in the range of SV from 320 to 3300 h^{-1}. The increase in CV was evaluated especially for Pt/SDBC catalyst even as the SV was increased. The CF is generally decreased as the SV is increased. The primary consideration in understanding this increase of CV should be the thermal effect. The increase in CV must be due to the temperature rising by heat of reaction, since the Pt/SDBC and Pt/ASDBC catalyst have high reactivity. The increase in temperature was measured as the SV was increased. At the SV=1290 h^{-1}, the temperature increase reached 12 K in the Pt/SDBC catalyst bed. ASDBC is more hydrophobic than SDBC and has superior water repellence. Hence, the CF of Pt/ASDBC at the lower SV was significantly improved as expected. The decrease in adsorption of produced water molecules on platinum surface was achieved. This result reveals our developed Pt/ASDBC is a promising catalyst for a catalytic recombiner operated at room temperature.

Table 2 Conversion factor *v.s.* space velocity in the presence of saturated water vapor at 293K

Catalyst	Conversion Factor		
	SV=323 h^{-1}	SV=1290 h^{-1}	SV=3226 h^{-1}
Pt / α Al_2O_3	1.70	1.08	1.27
Pt/SDBC	37.00	130.70	228.75
Pt/ASDBC	91.45	202.40	127.00

3.2 Effect of Irradiation on the Hydrogen Oxidation Performance of Pt/ASDBC

Figure 4 shows the CF *v.s.* SV for irradiated platinum catalysts in the presence of saturated water vapor in the experimental gas at 293K. The validity of radiation technology was well demonstrated. Radiation technology was applied to extend the pore size of catalyst, since the rate-controlling step of hydrogen oxidation reaction is generally pore diffusion. Hydrogen oxidation performance has been much improved with Pt/ASDBC catalyst irradiated with electron beams. Figure 5 shows the pore size distribution of unirradiated catalytic materials measured by mercury porosimeter. A feature of

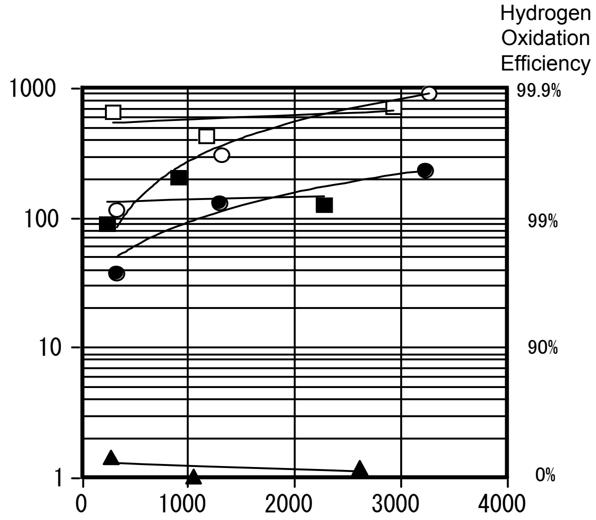


Fig. 4 Conversion factor *v.s.* space velocity for irradiated platinum catalysts in the presence of saturated water vapor at 293K.

▲; Pt/ α Al_2O_3 [Pt:5.3g/L],
●; Pt/SDBC [Pt:1.8g/L],
○; Pt/SDBC (Irradiated to 1250kGy with EBs)[Pt:1.8g/L],
■; Pt/ASDBC [Pt:1.0g/L],
□; Pt/ASDBC(Irradiated to 1500kGy with EBs)[Pt:1.0g/L].

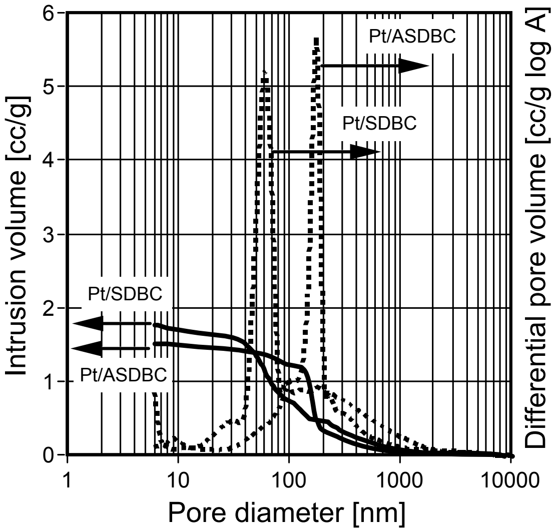


Fig. 5 Pore size distribution of unirradiated catalytic materials measured by mercury porosimeter.

Table 3 Specific surface area and pore size distribution of catalytic materials

Catalyst	Irradiation	Specific Surface [m2/g]	Peak Top Diameter [nm]	Accumulated Pore Volume [mL/g]
Pt/SDBC	unirradiated	364.4	61	1.79
	1250kGy	77.2	240	1.84
Pt/ASDBC	unirradiated	57.9	163	1.49
	1500kGy	43.4	170	1.55

unirradiated Pt/ASDBC catalyst is a designed fine pore size distribution and larger peak top pore diameter than that of unirradiated Pt/SDBC. The peak-top pore diameter of unirradiated Pt/ASDBC catalyst can be controlled to be in the range from 100 to 220 nm. The manufacturing of ASDBC beads needs a lot of know-how. We have established the fabrication technology of ASDBC beads ranged from 1.0 to 5.0mm in diameter. Specific surface area and pore size distribution of catalytic materials are shown in Table 3. It is clear that irradiation of Pt/SDBC catalyst with electron beams caused a considerable enlargement of peak-top pore diameter and the following decrease in specific surface area. Though unirradiated Pt/ASDBC has originally fine pore size distribution and larger peak top pore diameter than that of unirradiated Pt/SDBC, enlargement of peak top pore diameter and the following decrease in specific surface area of irradiated Pt/ASDBC was also measured as expected. The rate-controlling step of hydrogen oxidation reaction is generally pore diffusion. The improvement of hydrogen oxidation performance of irradiated Pt/SDBC and irradiated Pt/ASDBC was due accordingly to the enlargement of pore size by irradiation.

The degradation in mechanical strength of irradiated SDBC series catalysts is a debatable point that should be cleared. Figure 6 shows the result of compression test of irradiated Pt/SDBC catalyst based on Japanese Industrial Standard K 6254-1993 using a PC-controlled Strograph VE5D (Toyoseiki Co. Ltd., Japan). The crosshead speed adopted was 10mm/min. SDBC beads with 5.0mm of diameter was selected. Multiple measurements using more than 5beads were made on all conditions. SDBC beads with 5.0mm of diameter had an increase in mechanical strength with increase in radiation dose. Both chain scission and bridging were admittedly competing for the structural change of the beads by irradiation. The reason for the increase in load at break is that the bridges of the polymer were predominant over chain scission on the structural change of polystyrene divinyl- benzene beads by irradiation. The degradation in mechanical strength of irradiated ASDBC beads was not tested with the same method due to the insufficient amount of catalyst available for the test. The backbone structure of ASDBC is similar to that of SDBC. It is reasonable to suppose that the degradation in mechanical strength of irradiated ASDBC is similar to that of SDBC. The result of degradation in mechanical strength of irradiated SDBC strongly supports that radiation technology is applicable to improve the hydrogen oxidation performance of Pt/SDBC and Pt/ASDBC catalysts.

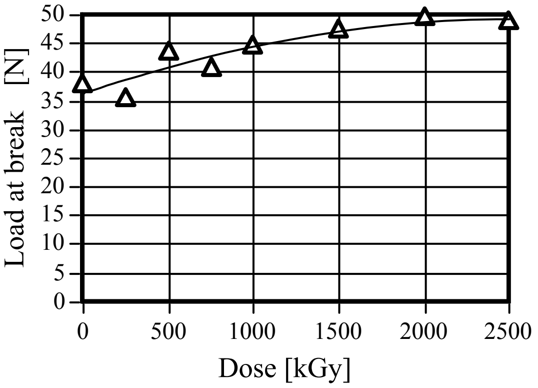


Fig.6 Result of compression test of irradiated Pt/SDBC catalyst

3.3 Thermal Stability of Irradiated Pt/ASDBC Catalyst

The intended incorporation with hydrophobic alkyl-groups in the molecular structure of ASDBC suggests the degradation in thermal stability of Pt/ASDBC catalyst by comparison with Pt/SDBC catalyst. Figure 7 shows the result of thermogravimetric analysis of catalytic materials in a helium atmosphere. Slight decrease in thermal stability was observed for Pt/ASDBC catalyst by comparison with Pt/SDBC catalyst as expected. Unirradiated Pt/SDBC is the standard catalyst

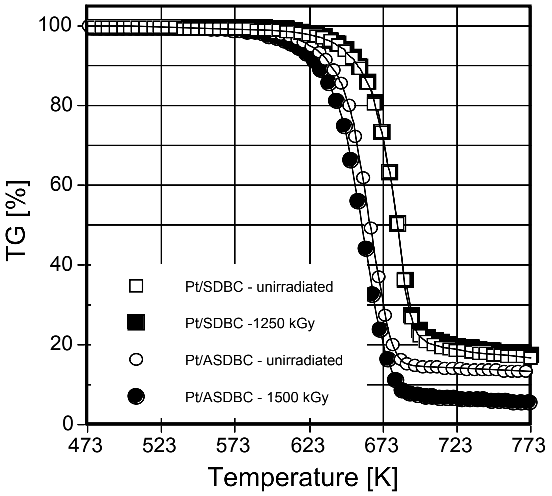


Fig. 7 Result of thermogravimetric analysis of catalytic materials.

for a water detritiation system normally operated at 343 K. The thermal stability of unirradiated Pt/SDBC has been acceptable for the use in a tritium facility. Hence, it is reasonable to suppose that such a slight decrease in thermal stability of irradiated Pt/ASDBC is not a debatable issue against its validity as a promising catalyst for a catalytic recombiner operated at room temperature. Moreover, negligible decrease in thermal stability was observed for irradiated catalyst by comparison with unirradiated catalyst. This result strengthens our understanding that irradiated catalysts are also promising catalysts for a catalytic recombiner operated at room temperature.

4. Conclusions

We have developed some hydrophobic Pt catalysts applicable for hydrogen oxidation in the presence of saturated water vapor at room temperature. A new type of hydrophobic catalyst, Pt/ASDBC, has been prepared by dipositting platinum on alkyl-styrene diviyl-benzene copolymer (ASDBC). Pt/ASDBC is more hydrophobic than Pt/SDBC that is a promising catalyst for a water detritiation system. The deposited platinum used to prepare Pt/ASDBC catalyst was 1.0 g/L. The value was approximately half of a commercial Pt/SDBC catalyst. Oxidation tests of the catalysts using 10000 ppm of hydrogen were performed in the presence of saturated water vapor at room temperature. Hydrogen oxidation more than 99% was achieved using Pt/ASDBC catalyst in the range of space velocity from 320 to 3300 h^{-1}. Moreover, radiation technology was applied to extend the pore size of catalyst, since the rate-controlling step of hydrogen oxidation reaction is pore diffusion. Hydrogen oxidation performance has been much improved with Pt/ASDBC catalyst irradiated with electron beams.

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