Reductive Decomposition of Nitrite in a Continuous-Flow Reactor Using Fixed-Bed Structured Pd Catalysts

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Abstract

In order to decompose trace amounts of nitrite in drinking water under mild conditions, a fixed-bed filtering system that used structural catalysts was employed to filter recycled aqueous nitrite. High performance and continuous mass processing are generally accepted as requirements to catalyze the decomposition of aqueous nitrite. However, the use of a fixed-bed operation when recycling aqueous nitrite with palladium catalyst systems could result in either negligible activity when using a carbon monolith impregnated with Pd, or could stop the flow by enhancing the pressure drop when using non-porous alumina spheres coated with Pd/C or structured catalysts consisting of a polyurethane sponge skeleton impregnated with Pd. In the present paper, a Si/SiC ceramic filter was employed as a structured support to prevent pressure drop. When palladium was loaded onto the surface of the filter via electroless plating, continuous flow suitably continued, and the conversion of nitrite was 45% after 60 min. In contrast, when palladium was loaded after the coating of the filter with alumina, complete decomposition was achieved after 60 min under conditions corresponding to those used for the former system. X-ray diffraction, an N_2 adsorption-desorption measurement, scanning-electron microscopy and energy-dispersive X-ray spectroscopy analyses revealed that a higher dispersion of palladium on the latter structured catalyst resulted in the greatest level of activity for the reductive decomposition of aqueous nitrite.

Introduction

Nitrogen-containing compounds such as nitrate (NO_3^-) and nitrite (NO_2^-) are known as harmful contaminations in water since they are causative agents for methemoglobinemia (Titov and Petrenko, 2005; Gladwin et al., 2009), diabetes (Dahlquist et al., 1990) and stomach cancer (Bryan et al., 2012). Since nitrate is present mainly in natural settings (Cantar, 1996), its reduction has received attention for the purification of polluted water, and catalytic reductive decomposition is the most plausible techniques to accomplish this. However, since the reductive decomposition of nitrate results in the formation of nitrite (Eq. 1), the decomposition of nitrite is certainly as important as that of nitrate (Hayashi et al., 2000; Sakamoto et al., 2004; Wang et al., 2007, 2009).

$$NO_3^- \rightarrow NO_2^- \rightarrow N_2 \qquad (1)$$
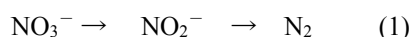
Furthermore, organic nitrogen compounds that are present in the natural world often are decomposed to nitrite via the aerobic bacteria found in soil and groundwater. Therefore, the resultant nitrite is common

on the earth's surface at lower concentrations than that of nitrate. It should be noted that nitrite easily reacts with hemoglobin in the blood, which results in the development of methemoglobinemia (Titov and Petrenko, 2005; Gladwin et al., 2009). Due to the poisonous nature of nitrite, in 2014, the Ministry of Health, Labor and Welfare of Japan revised the water quality standards for its presence in drinking water from 10 mg/L to less than 0.04 mg/L. These problems prompted our group to examine the catalytic reductive decomposition of nitrite (Hayashi et al., 2000, 2004). The catalytic decomposition of nitrate on a Pd catalyst doped with Cu, Ag or Ni is known to favorably proceed under a hydrogen atmosphere (Hörold et al., 1993), resulted in the serious problem of accumulation of nitrite (Hayashi et al., 2000; Hörold et al., 1993; Sakamoto et al., 2004; Wang et al., 2007; Wang et al., 2009). In contrast, single catalyst Pd is suitable as a catalyst for the reductive decomposition of nitrite (Hörold et al., 1993; Hayashi et al., 2000, 2004). Most of the studies on the catalytic decomposition of nitrate or nitrite under a hydrogen atmosphere have used a batch-reactor system. However, a batch reactor is not suitable for the purification of drinking water since it

cannot treat great volumes. Therefore, a fixed-bed operation that recycles an aqueous substrate was used in our earlier study (Hayashi *et al*., 2004) in order to achieve high performance and continuous mass processing. A powder catalyst generates a pressure drop during continuous operation, which has necessitated the use of fixed-bed palladium catalyst systems such as a carbon monolith impregnated with Pd, non-porous alumina spheres coated with Pd/C, or structured catalysts consisting of a polyurethane sponge skeleton impregnated with Pd. Unfortunately, those attempts afforded unsuitable results such as a generation of pressure drops that stopped the flow and low activity. These early attempts demonstrated that the most important factor in a continuous recycling operation involves the selection of a structured support that doesn't involves monolith support, sphere support or a sponge skeleton.

In the present study, a Si/SiC ceramic filter (**Fig. 1 (a)**) was employed as the structured support for a Pd catalyst mainly to prevent pressure-drops while attempting the reductive decomposition of nitrite. Pd was loaded onto the filter via electroless plating (Pd/Si/SiC, **Fig. 1 (b)**) that impregnated Pd onto an alumina layer that covered over the filter (Pd/Al$_2$O$_3$/Si/SiC, **Fig. 1 (c)**).
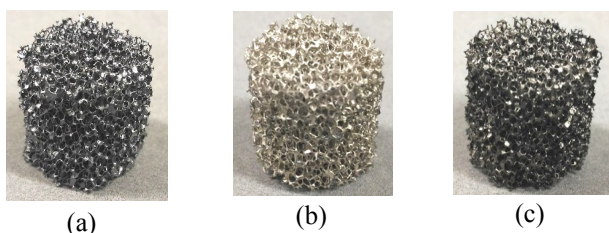

(a) (b) (c)

Fig. 1 Photo images of various filters: (a) Si/SiC, (b) Pd/Si/SiC and (c) Pd/Al$_2$O$_3$/Si/SiC.

1. Experimental

1.1 Catalyst preparation

The structured support, which was a Si/SiC ceramic filter (Si/SiC filter; #20, ϕ 20 mm $\times$ 20 mm, 95.6% of porosity, bulk density 0.12 g/cm^3), was acquired from Nippon Pillar Packing Co. Ltd.

The electroless plating technique that was used to load Pd onto a Si/SiC filter was as follows. The Si/SiC filter was activated and electroless-deposited of palladium (Mardilovich *et al*., 1998; Katoh *et al*., 2006, 2010). The structured support was through a surface activation before the electroless plating. The support was washed using ultrasonic cleaner for 1 h and dried. After the round side of the support was lapped with Teflon tape, the support was immersed in 25 mL of 1.2 M aqueous HCl (Wako) for 5 sec. The support was washed, dried and immersed for 5 min in 25 mL of SnCl$_2$ solution, which was consisting of 1 mL of 1.2 M

aqueous HCl, 0.44 mmol of SnCl$_2$.2H$_2$O (Aldrich) and 100 mL distilled water. The resulting support was washed and immersed into 25 mL distilled water for 5 min. Then the support was immersed for 5 min into 25 ml of PdCl$_2$ solution, which was consisting of 10 mL of 1.2 M aqueous HCl and 0.56 mmol of PdCl$_2$ (Aldrich) diluted with distilled water to the total volume of 1 L. After the support was immersed for 2 min into 25 mL of 0.012 M HCl, it was washed and immersed for 3 min into distilled water. This completed one cycle of the activation process. Next, palladium was deposited onto the filter via an autocatalytic reaction using Pd(NH$_3$)$_4$Cl$_2$·H$_2$O (Tokuriki Honten Co.), H$_2$NNH$_2$ (Tokyo Chemical Industry), and NH$_4$OH (Wako) at 333 K for 1.5 h (electroless-deposition process, Eq. 2).

$$2Pd(NH_3)_4Cl_2 + H_2NNH_2 + 4NH_4OH \rightarrow$$
$$2Pd + N_2 + 8NH_3 + 4NH_4Cl + 4H_2O \quad (2)$$
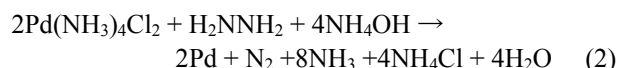
The process optimized for this system was as follows. The round side of the activated support was again lapped with Teflon tape. The support was immersed in 28 mL of the electroless palladium-plating solution, which was consisting of 1.44 mol NH$_4$OH, 15.2 mmol Pd(NH$_3$)$_4$Cl$_2$·H$_2$O and 0.11 mol 2NA(EDTA・2Na) (Wako) diluted with distilled water to 1 L but used after kept for more than 12 h of the preparation. Then 0.1 mL of 0.5 M aqueous H$_2$NNH$_2$ was added into the solution using micro syringe. The solution was kept at 333 K for 90 min. During this step, bubble formed in the support was removed every 15 min. The support was finally washed using distilled water. The resultant catalyst can be expressed as x%Pd/Si/SiC, wherein the loading (x%) of Pd is expressed as a weight percentage. The loading was controlled via changes in the number of passages through the activation and electroless-deposition processes. Pre-seeding with palladium nuclei during the activation process can reduce the introduction period of the autocatalytic process at the beginning of the deposition.

In order to cover the Si/SiC filter with an alumina layer, a boehmite sol was used. The boehmite sol was prepared by hydrolyzing aluminum isopropoxide (Wako) (Sugiyama *et al*., 2007). Boehmite sol was prepared by hydrolyzing aluminum isopropoxide (9.42 g; 46.1 mmol) in 75 mL of distilled water at 353 K for 24 h. After the hydrolysis, the alcohol was removed from the solution and then HNO$_3$ (0.34 mL; 5.38 mmol) (Wako) was added into the solution for the peptization of the hydroxide at 363 K for 24 h to form boehmite sol. The final sol pH was 3.8. The boehmite sol was then dip-coated onto the surface of the Si/SiC filter, followed by drying for 24 h at a room temperature and calcination at 876 K for 3 h, which was adjusted from a room temperature at a rate of 1K/min. It has been already reported that, during this calcination step, boehmite is converted to γ-Al$_2$O$_3$ that is stable at a higher

temperature up to 1073 K (Sugiyama *et al.*, 2003). Aqueous $Pd(NO_3)_2$ (24.41% by weight, N. E. Chem-cat Co.) was impregnated into the alumina-coated Si/SiC filter followed by drying and calcination at 473 K for 3 h. This impregnation process was repeated to control the Pd loading. After impregnation, formalin reduction was carried out at 347 K for 2 h followed by drying at 347 K under atmospheric pressure for 24 h, then drying at 347 K under vacuum. The resultant catalyst was expressed as $x\%Pd/y\%Al_2O_3/Si/SiC$, wherein the loadings ($x\%$ and $y\%$) of Pd were expressed as the weight percentage of Pd and Al_2O_3, respectively.

The structured catalysts thus obtained, Pd/Si/SiC and Pd/Al_2O_3/Si/SiC, were characterized using X-ray diffraction (XRD; SmartLab/RA/INP/DX, Rigaku Co.), N_2 adsorption-desorption measurement (BELSORP-max12, MicrotracBEL), CO pulse method (BELCAT II, MicrotracBEL) and scanning electron microscope together with energy dispersive X-ray spectroscopy (SEM and EDX; JSM-6510A, JEOL ltd.). The powder XRD patterns of the catalysts were obtained using monochromatized Cu Kα radiation (40 kV, 40 mA). Before the N_2 adsorption-desorption measurement at 77 K, the catalysts were pretreated at 473 K for 5 h under vacuum. The BET surface area was calculated from an obtained isotherm. The loading of Pd was analyzed using ICP-AES (SPS3520UV, SII Nanotechnology Inc.) after the complete dissolution of Pd from the structured catalysts using aq. HNO_3.

1.2 Catalytic activity testing

Catalytic activity testing was carried out in the continuous recycling operation using fixed-bed structured catalysts.
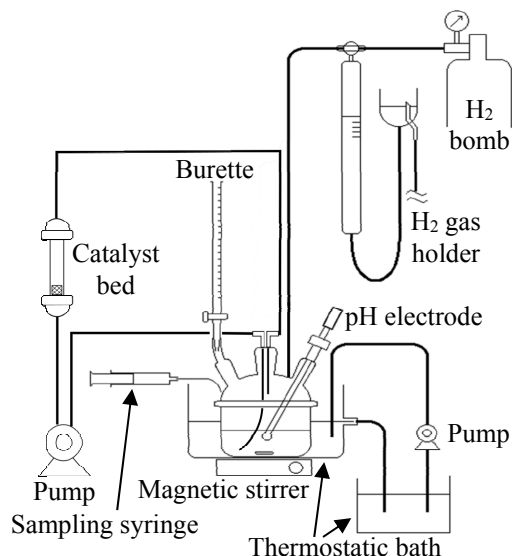

Fig. 2 Apparatus for nitrate reduction using fixed-bed operation with recycling of aqueous substrate

As shown in Fig. 2, 400 mL of aqueous nitrite (100 ppm $NaNO_2$ solution: 0.87 mmol/400 mL) was added to a 4-necked flat-bottom separable flask that was connected to a hydrogen gas-holder, 0.25 M HCl burette in order to adjust the pH, of both the catalyst bed and the electrode. A given number of Pd/Si/SiC or Pd/Al_2O_3/Si/SiC filters were loaded into the catalyst bed, in which the solution flowed from the bottom to the top. The reaction temperature was controlled using double thermostatic baths to be adjusted to 298 K. In this operation, aqueous nitrite saturated with hydrogen using a magnetic stirrer was supplied to the catalyst bed and recycled via a pump. Unless otherwise stated, the flow rate was set at 1,166 or 1,048 mL/min for one or five filters, respectively, which was corresponded to 370 or 330 cm/min of linear velocity, respectively. In the present study, the concentration of the nitrite and the hydrogen volume that was consumed were monitored in order to detect the decomposition behavior. An aliquot of the liquid sample was taken intermittently using a sampling syringe and was analyzed for nitrite composition via ion-chromatography (DKK-TOA Co., PCI-230).

2. Results and Discussion

2.1 Pd/Si/SiC

XRD analysis of Pd/Si/SiC (**Fig. 3** for 2.59% Pd/Si/SiC) showed that the structured catalyst prepared in the present study consisted of metallic Pd (PDF 00-0056-0681), Si (PDF 00-005-0565), and SiC (PDF 01-075-0245), which indicated that a much greater particle size of Pd had formed on the structured catalyst prepared via electroless plating. Structured catalysts with various loads of Pd on Si/SiC filter via electroless plating (Pd/Si/SiC) were set in the apparatus for 60 min in order to accomplish the reductive decomposition of nitrite.
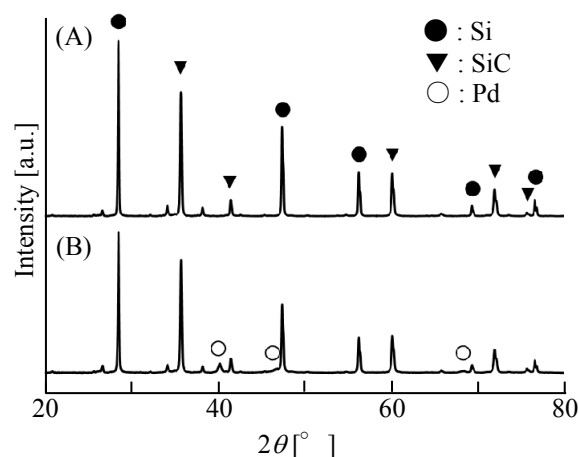

Fig. 3 XRD of Si/SiC (A) and 1.98% Pd/Si/SiC (B) filters

Fig. 4 shows a reduced amount of $NO_2{}^-$ at various level of Pd loading after the reaction starting

with 100 ppm (0.87 mmol/400 mL) of NO_2^- aqueous solution. This result indicated that the favorable decomposition of NO_2^- was observed at rather lower loadings of Pd, while that an excess loading of Pd resulted in a decrease in the reduced amount of NO_2^- to 0.022 mmol/400 mL from NO_2^- decomposed using 13.1%Pd/Si/SiC.
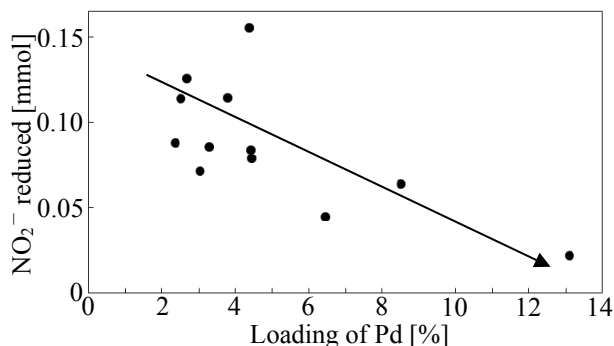

Fig. 4 Relationship between NO_2^- reduced and loading of Pd
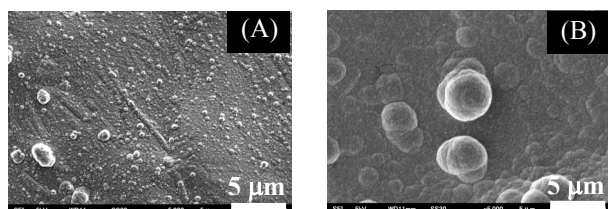

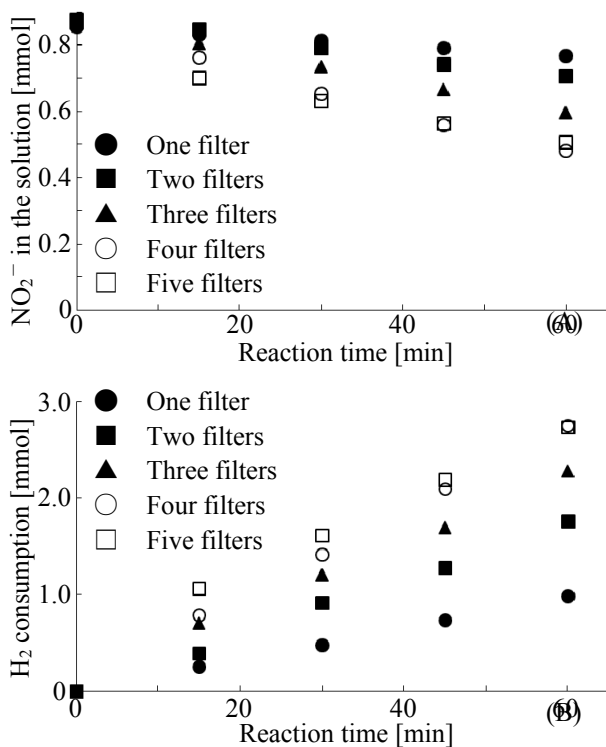**Fig. 5** SEM images of 4.4% Pd/Si/SiC (A) and 13.1% Pd/Si/SiC (B)

Fig. 6 The effect of numbers of Pd/Si/SiC filters on the decomposition of NO_2^- and H_2 consumption

The specific surface areas of all the catalysts shown in Fig. 4 were estimated to be less than 1 m^2/g while Pd dispersions on all the samples detected in the CO pulse method were estimated at 0.1%, or less, as suggested using XRD. This information, however, cannot explain the greater activity that was attained when using a smaller loading of Pd on Pd/Si/SiC. A comparison of the SEM image of 4.4% Pd/Si/SiC (**Fig. 5 (A)**) with that of 13.1%Pd/Si/SiC (**Fig. 5 (B)**) revealed that the greater activity was the results of using a structured catalyst covered with a smaller particle size of Pd. In order to decompose NO_2^- more effectively, the effect that the number of Pd/Si/SiC filters exerted on the reduction activity was examined using easily reproducible 2.68% Pd/Si/SiC (**Fig. 6**). **Figs. 6 (A)** and **(B)** show increases in the reduced NO_2^- and in the hydrogen that was simultaneously used according to the number of the filters, which reached to plateau at four and five filters probably due to insufficient concentration of hydrogen in the solution for rather lower dispersion of Pd species on the structured support. In order to improve the dispersion of Pd on the structured support (Si/SiC), an impregnation of Pd onto an alumina layer covering over the filter was examined

2.2 Pd/Al₂O₃/Si/SiC

The most important factor for improving the low activity when using Pd/Si/SiC seemed to be an enhancement of the Pd dispersion. Therefore, to improve the low surface area of the Si/SiC filter, an alumina layer, Al₂O₃/Si/SiC, was formed on the surface of the filter, followed by an impregnation of Pd, which was referred to as Pd/Al₂O₃/Si/SiC. Covering the Si/SiC with alumina increased the surface area to 2.4 m^2/g from less than 1 m^2/g. Pd/Al₂O₃/Si/SiC catalysts with various loadings of Pd were prepared via changes in the impregnation times, which showed that an impregnation of more than 5-fold did not improve the activity. A 5-fold impregnation increased the surface area to 8.2 m^2/g and the Pd and Al₂O₃ loading rates to 0.55 and 8.0%, respectively. After the impregnation of Pd on Al/Si/SiC, no peaks due to Pd species were detected by XRD, which indicated that Pd must impregnate via high dispersion (**Figure 7**). This was supported by a CO pulse method that showed a Pd dispersion of 9.9%, which was approximately 100 times greater than that for 13.1%Pd/Si/SiC (0.1%).
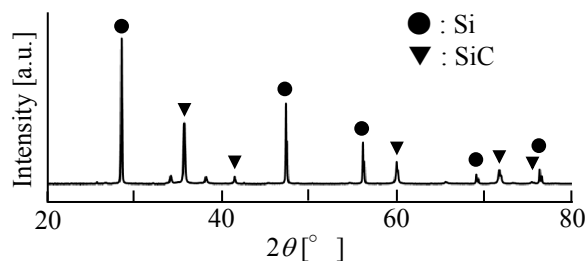

Fig. 7 XRD of 0.55%Pd/8.0%Al₂O₃/Si/SiC filter

The high dispersion of Pd was further supported using SEM and the corresponding element mapping images of the $Pd/Al_2O_3/Si/SiC$. As shown in **Fig. 8 (A)**, a greater size of the Pd species was not detected in the SEM image of the structured catalyst which showed greater concentrations of Si and Al, as shown in **Figs. 8 (B)** and **(C)**, respectively. In contrast, a much lower concentration of Pd was detected in the element-mapping image of Pd over the surface of the structure catalyst.
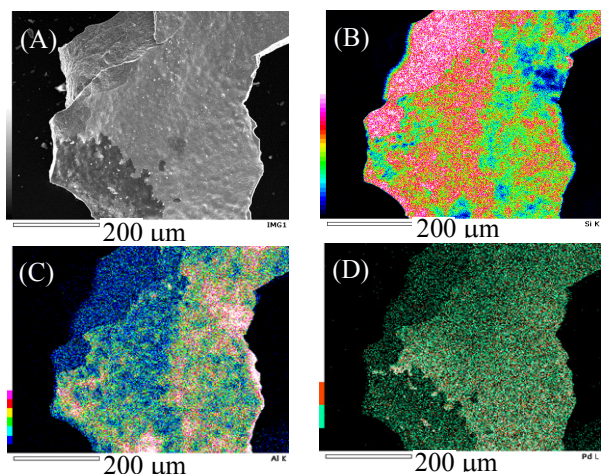

Fig. 8 SEM image of $0.55\%Pd/8.0\%Al_2O_3/Si/SiC$ (A) and the corresponding element mapping images of Si (B), Al (C) and Pd (D), respectively

Four or five $0.55\%Pd/8.0\%Al_2O_3/Si/SiC$ filters were used for the decomposition of NO_2^- (**Fig. 9**). When using four filters, flow rates of 913 and 1,048 mL/min were used, the former of which corresponded to 290 cm/min of the liner velocity. It was evident that the much rather greater flow rate of 1,048 mL/min was more suitable than the lower flow rate of 913 mL/min, and a complete decomposition of NO_2^- was achieved after 60 min. It should be noted that the loading of $Pd/Al_2O_3/Si/SiC$ was 1/4 times that of $Pd/Si/SiC$. Therefore, as expected by the greater Pd dispersion on $Pd/Al_2O_3/Si/SiC$ than that on $Pd/Si/SiC$, the incorporation of Al_2O_3 between Pd and Si in $Pd/Si/SiC$ resulted in a great improvement in the catalytic activity and the decomposition of NO_2^-. Further increasing the filter number to five resulted in a slight enhancement in the decomposition activity. It is of interest to note that such a slight enhancement of the decomposition using $Pd/Al_2O_3/Si/SiC$ filters was not observed using $Pd/Si/SiC$ filters (Fig.6 (A)). This indicates that a high dispersion of Pd on $Pd/Al_2O_3/Si/SiC$ filters may be more suitable for the consumption of low concentration of hydrogen in the solution than $Pd/Si/SiC$ filters consisting of lower dispersion of Pd. It may be strange that the greater flow rate (1048 mL/min using four filters in Fig. 8), that is, shorter residence time resulted in the complete decomposition of NO_2^- while the lower

flow rate (913 mL/min using four filters in Fig. 8) resulted in incomplete decomposition of NO_2^-. It should be noted that the lower flow rate, that is, longer residence time may result in the deep reduction from NO_2^- to NH_3 or NH_2OH which needs an excess hydrogen, compared to decomposition of NO_2^- to N_2. Furthermore, the short residence time also results in the enhancement of recycling time. This indicates that the contact time of the reaction solution with the structured catalyst also increase, resulting in the enhancement of the decomposition. Therefore it may be suggested that a suitable decomposition of NO_2^- to N_2 needs great dispersion of Pd on the structured support and short residence time in the reactor system. The study on the deep reduction of NO_2^- using the present system is now in progress.
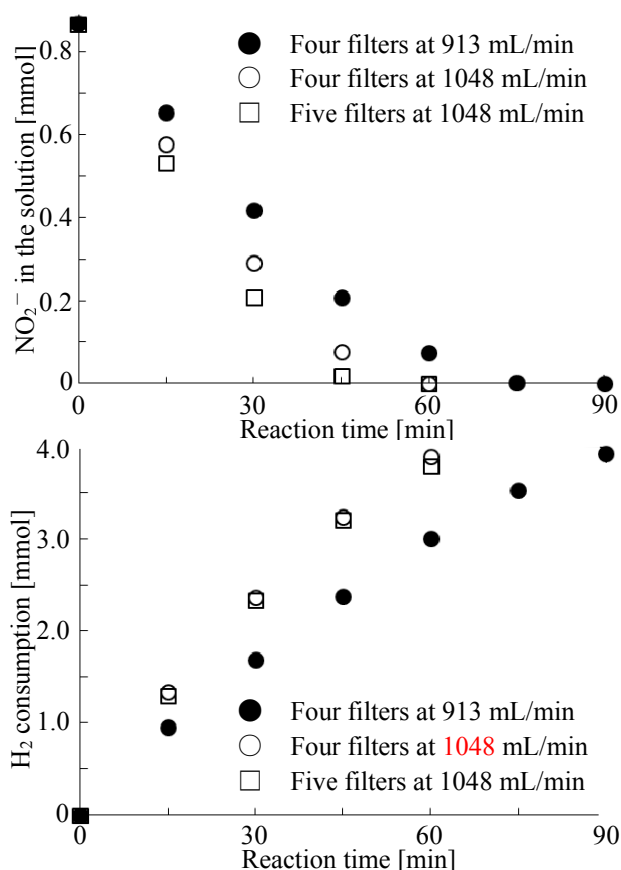

Fig. 9 The effect of flow rate and numbers of $Pd/Al_2O_3/Si/SiC$ filters on the decomposition of NO_2^- and H_2 consumption

Conclusions

Previous reports show that fixed-bed nitrite filtering systems that use a palladium catalyst to recycle an aqueous substrate resulted either in negligible activity or in enhanced pressure drops that stopped the flow. These systems consisted of various structured supports such as a carbon monolith, non-porous alumina spheres or a polyurethane sponge skeleton. However, the employment of a Si/SiC ceramic filter coated with

an Al_2O_3 layer as the structured support for a Pd catalyst revealed suitable results for a fixed-bed operation while recycling aqueous NO_2^-. This setup showed that a greater dispersion of Pd together with the use of a Si/SiC filter was an important factor in the suitable decomposition of aqueous NO_2^-.

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