XAFS Analysis for Redox Property of SiO_2-Supported Nickel Catalysts Prepared by Impregnation Method

Yusaku Yamamoto, Atsushi Suzuki, Shohei Yamashita,
Misaki Katayama, and Yasuhiro Inada
Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

Abstract

The redox property of SiO_2-supported small Ni particles prepared by impregnation method was investigated by the *in-situ* XAFS measurements. The particle size was successively controlled by the addition of citric acid into the aqueous solution of the Ni precursor. The temperature at which the oxidation reaction occurred for the small Ni(0) particles was lower than that of the larger Ni(0) particles. In contrast, the smaller NiO particles were reduced at the higher temperature. An opposite shift of the temperature suggests that the relatively strong interaction of the NiO species with supporting SiO_2. In addition, the redox property of the supported Ni species was analyzed using the *in-situ* fluorescence XAFS technique by diluting the Ni loading, which is a standard approach to achieve the high dispersion of the supported species. The temperatures at which the redox reactions occurred were found to be shifted in response to the variation of the Ni particle size which was promoted by the dilution of the Ni loading.

1. Introduction

The supported Ni species show a high activity for various reactions such as steam reforming of methane. A lot of researches and developments for higher catalytic performance have been therefore conducted, and one of the important parameters to improve the catalytic activity is well accepted to make the particle size of the active metal species small. The preparations of such small Ni particles have been attempted by applying the sol-gel method [1] and the liquid-phase reduction method [2]. The impregnation technique is a common preparation method for the supported metal catalysts, and the particle size of the metal species is largely affected by the preparation conditions. For example, the particle size decreases with decreasing the loading of the supported metal species. In the case of SiO_2-supported Ni species, the particle size has been reported to be 17 and 54 nm for the Ni loading of 5 and 20 wt.%, respectively [3]. The choice of metal precursor and solvent is known to influence the particle size, and the conditions at the drying and calcination process also contribute to the dispersion of the metal species. Moreover, it has been recently reported that an addition of organic additives such as amino acid and citric acid into the solution of metal precursor promotes the formation of small particles of the active metal species on oxide supporting material [4-7].

The chemical state of the supported metal species is the most important parameter to determine the catalytic property, and the reactant and product gases existing in the catalysis reaction environment frequently modify the chemical state of the active metal species. The evaluation of the chemical state is therefore necessary to understand the catalytic performance and will be a useful guideline for the functional catalyst design. We have been recently reported the chemical state conversion of the supported Ni [3], Co [8], and Pd [9] species in the reactions with H_2 and O_2 by means of the *in-situ* X-ray absorption fine structure (XAFS) technique. It has been revealed that the particle size of supported Ni species increases with an increase of the Ni loading and that such larger metallic Ni particles tend to be oxidized at higher temperature by O_2 [3]. On the other hand, the temperatures at which the reduction of the supported NiO species occurs are almost constant at around 350 °C in the range of the Ni loading between 5 and 20 wt.%. The lower reduction temperature of PdO than those of NiO and CoO is consistent with the more positive redox potential of the PdO/Pd system. The two-step redox processes between Co_3O_4 and metallic Co via CoO have been observed in the case of the supported Co catalyst, which is marked contrast to the cases of the Ni and Pd catalysts, for which only the divalent metal oxide species exists.

The purpose of this research is to clarify the chemical state conversion under the reactive gas environment for the supported small Ni particles prepared by the impregnation method with citric acid. The *in-situ* XAFS measurements have been carried out during the temperature-programmed reduction (TPR) and oxidation (TPO) processes under the dilute H_2 and O_2 gas flow, respectively. In addition, the effect of the Ni loading has been revealed for the supported Ni catalysts with low Ni loadings. The fluorescence XAFS experiments have been conducted to determine the chemical state for dilute samples with the Ni loading less than 1 wt.% using the developed *in-situ* XAFS cell to achieve the fluorescence detection under the reaction gas environment [10].

2. Experimental

2.1. Catalyst Preparation

The SiO_2-supported Ni catalysts were prepared by the impregnation method. To prepare the small Ni particles, a stoichiometric amount of citric acid was added in an aqueous solution of nickel nitrate. SiO_2 powder (Fuji Silysia Chemical Co., Ltd.) with the specific surface area of 192 m^2 g^{-1} was suspended in the aqueous solution and the mixture was stirred for 1 h at 60 °C. The mixture was dried at 70 °C for 72 h in air, and the obtained powder was calcined for 3 h at 600 °C in air. The Ni loading was set to be 5 wt.%. The reduction of the supported Ni species was carried out under a gas flow (200 cm^3/min) of 10 vol.% H_2 diluted by Ar at 700 °C for 3 h. The sample prepared by this procedure is referred to as “5 wt.% IMPCA”.

The dilute Ni catalysts with the loading of 1.4 and 0.13 wt.% were prepared by the impregnation method. The SiO_2 powder was suspended in an aqueous nickel nitrate solution, and the suspension was stirred for 1 h at 60 °C. The mixture was dried at 70 °C for 72 h in air, and the obtained powder was calcined at 600 °C in air for 3 h. The sample was reduced under a diluted H_2 gas flow at 600 °C. The sample prepared by this method is referred to as “*x* wt.% IMP”, where *x* denotes the Ni loading.

2.2. Characterization

The X-ray fluorescence analysis was performed with Supermini fluorescence spectrometer (Rigaku Co., Ltd.) to determine the loading of supported Ni species. The Pd Kα radiation was used as the X-ray source and the intensity of the Ni Kα

fluorescence was measured. Transmission electron microscopy (TEM) measurements were conducted using the JEOL-2010 microscope (JEOL Co., Ltd.) for the reduced samples.

2.3. XAFS measurement

The *in-situ* XAFS measurements were carried out at BL-3 of the SR center (Ritsumeikan University) and BL-9C of the Photon Factory (PF, High Energy Accelerator Research Organization) at the Ni K edge. The samples with high Ni loading were measured in the transmission mode, while the fluorescence yield detection was adapted to the dilute samples. For the transmission measurements, the sample powder was mounted in an SUS ring and was set in the flow-type observation cell [11]. The originally developed *in-situ* cell was used for the fluorescence XAFS measurements [10].

The Ni catalyst was heated to 700 °C at 10 °C/min under the diluted H_2 (10 vol.% balanced by He, 200 cm^3/min) during the TPR process. After the sample was cooled to room temperature by keeping the diluted H_2 gas flow, and the reaction gas was switched to diluted O_2 (10 vol.% balanced by He, 200 cm^3/min) to observe the XAFS spectra during the TPO process up to 700 °C. The measurement time of a transmission XAFS spectrum was 1 min and the measurements were conducted with the time interval of 2 min. In the case of the fluorescence XAFS measurements, the temperature was first kept at the target temperature for 25 min, and then the fluorescence measurements were carried out with scanning the incident X-ray energy.

3. Results and discussion

The average diameter of the nickel particles supported on silica was estimated by the TEM images to 4 nm for 5 wt.% IMPCA and 17 nm for 5 wt.% IMP. It is clearly indicated that an addition of citric acid in the precursor solution of the Ni species leads to form the small nickel particles. Such an organic additive binds to the Ni(II) ion in the precursor solution and may inhibit the crystal growth during the evaporation process.

Figure 1 shows the XANES change of IMPCA during the TPO and TPR processes. When the reaction gas was switched from dilute H_2 to dilute O_2 at room temperature, the absorption spectrum of the reduced Ni(0) particle was quickly changed. The X-ray absorbance at the NiO white line increased and the higher energy

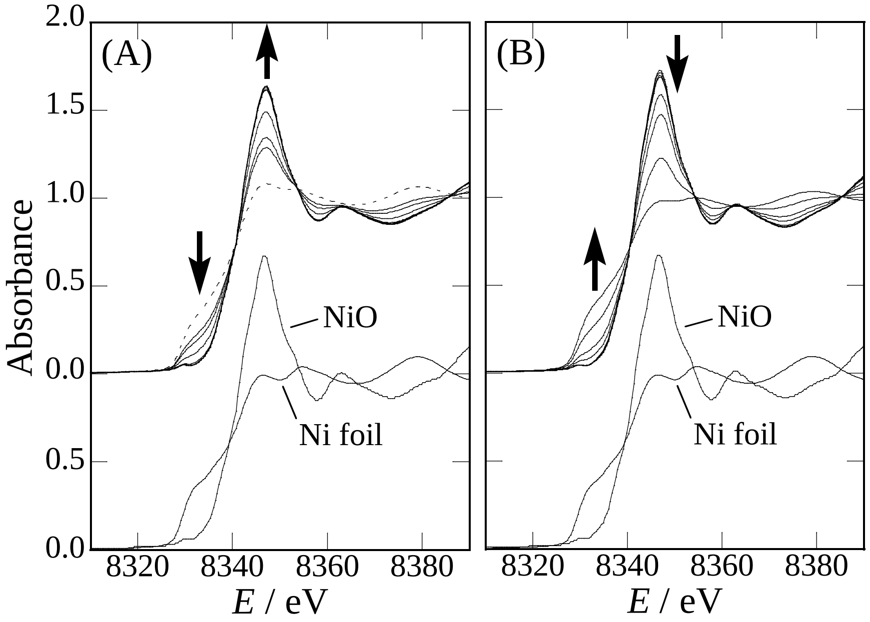

Figure 1. XANES spectrum changes of 5 wt.% IMPCA during the TPO (A) and TPR (B) process. In A, the broken line shows the spectrum before the O_2 injection.

shift of the absorption edge was observed. This spectral change suggests that the O_2 injection causes the partial oxidation of the Ni(0) particle. The Fourier transform functions before and after the O_2 injection are shown in Figure 2. The structure parameters determined by the EXAFS analysis are summarized in Table 1. The weak Ni–O interaction peak at *ca.* 1.6 Å in NiO was clearly observed in the Fourier transform function after the O_2 injection, indicating that the Ni(0) species was partially oxidized. The Ni–Ni peak intensity in metallic Ni(0) was decreased by the partial oxidation, and the average coordination number was reduced from 9.7 to 7.1.

The linear combination fitting analysis of the observed XANES spectrum based on those of NiO and Ni(0) revealed the composition change of the supported Ni

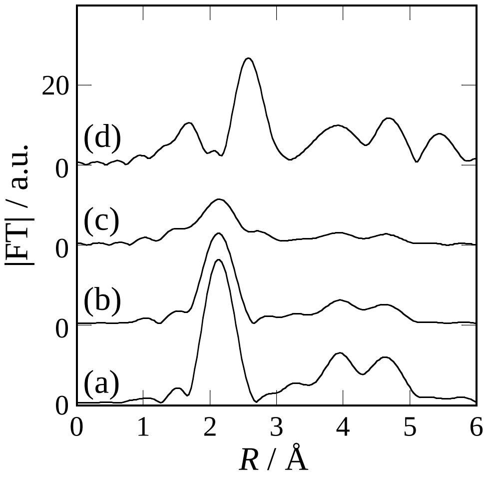

Figure 2. The Fourier transform function of 5 wt.% IMPCA before (b) and after (c) gas switch from H_2 to O_2 are compared with those of reference Ni(0) (a) and NiO (d).

Table 1 Structure parameters around the Ni atom of 5 wt.% IMPCA before and after the environment gas switch.[a)]

Sample	Interaction	N	R / Å	σ^2 / 10^{-3} Å^2	C_3 / 10^{-3} Å^3
Ni foil	Ni–Ni	12[b)]	2.50 ± 0.01	6.3 ± 0.2	0.16 ± 0.08
NiO	Ni–O	6 [b)]	2.06 ± 0.02	6.4 ± 1.3	-0.30 ± 0.66
	Ni–Ni	12 [b)]	2.97 ± 0.02	6.8 ± 0.5	0.18 ± 0.35
r.t. H_2	Ni–Ni	9.7 ± 0.8	2.50 ± 0.01	8.1 ± 0.6	0.27 ± 0.12
r.t. O_2	Ni–O	2.6 ± 0.2	2.04 ± 0.04	11.1 ± 1.1	0.52 ± 0.22
	Ni–Ni	7.1 ± 0.4	2.54 ± 0.04	11.6 ± 0.4	0.77 ± 0.06

[a)] The amplitude reduction factor S_0^2 was set to 0.86 (Ni metal) and 0.97 (NiO). The edge shift energy ΔE_0 was estimated to be 0.5 eV and -0.2 eV for Ni metal and NiO. [b)] The value was fixed.

species during the TPO and TPR processes. The composition analysis revealed that about 40 % of the metallic Ni(0) species was oxidized to NiO for 5 wt.% IMPCA, whereas only 10 % of Ni(0) was oxidized to NiO in the case of 5 wt.% IMP [3]. The larger surface area for the former might increase the surface oxidation of the Ni(0) particles, and thus the larger amount of Ni(0) was oxidized for 5 wt.% IMPCA. If the partial oxidation is assumed to proceed from the particle surface, the oxidation depth is estimated to be about 3 Å for both samples independent on the particle size.

As shown in Figure 1(A), the NiO white line intensity increased and the absorption edge shifted to the higher energy side during the TPO process. The final XANES spectrum was in consistent with that of NiO. The opposite changes were observed during the TPR process, and the metallic Ni(0) species was quantitatively formed at the end of the TPR process. Some isosbestic points were clearly observed in the XANES changes for both processes. The redox reactions between the Ni(0) and NiO species proceeded without the other stable species with different valence state.

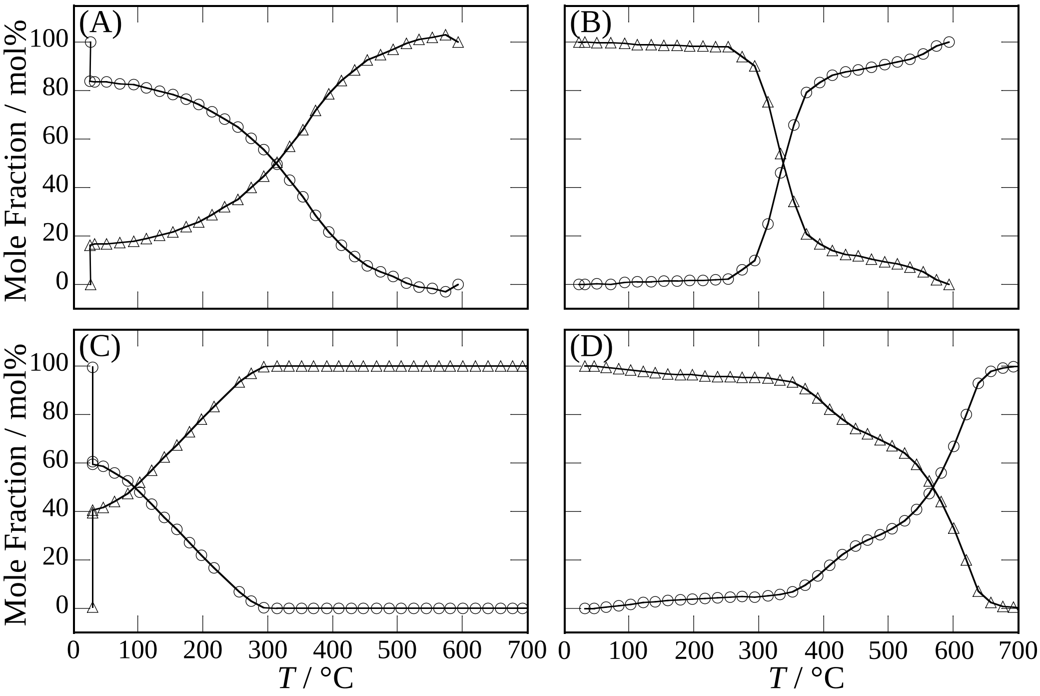

Figure 3. Composition of the supported Ni species as a function of temperature during the TPO processes of 5 wt.% IMP (A) and 5 wt.% IMPCA (C) and during the TPR processes of 5 wt.% IMP (B) and 5 wt.% IMPCA (D). The metallic Ni(0) and NiO species is depicted by circles and triangles, respectively.

Figure 3 shows the composition change of the supported Ni species during the TPO and TPR processes as a function of temperature. The bulk oxidation of the Ni(0) particles for 5 wt.% IMP proceeded around 300 °C. However, the small Ni(0) particles in 5 wt.% IMPCA was oxidized below 300 °C, and the temperature at which the oxidation of Ni(0) occurred was apparently lower for the smaller particle. The similar shift of the oxidation temperature was observed for the small Ni(0) particles with the average particle size of 4 nm supported on silica prepared by the sol-gel method [12]. In contrast, the temperature at which the reduction of the NiO species occurred was around 350 °C for 5 wt.% IMP, whereas the corresponding temperature for the smaller NiO particles in 5 wt.% IMPCA shifted to much higher around 600 °C. It is evident that the particle refinement of the supported Ni species causes the redox temperature shifts.

The typical XANES changes during the TPO and TPR processes are shown in Figure 4 for the dilute Ni catalysts supported on silica. The XANES spectrum before the TPO process was in agreement with that of metallic Ni(0), and it was changed to that corresponding to NiO, indicating that the supported Ni(0) species quantitatively oxidized to NiO during the TPO process. The formed NiO species was then

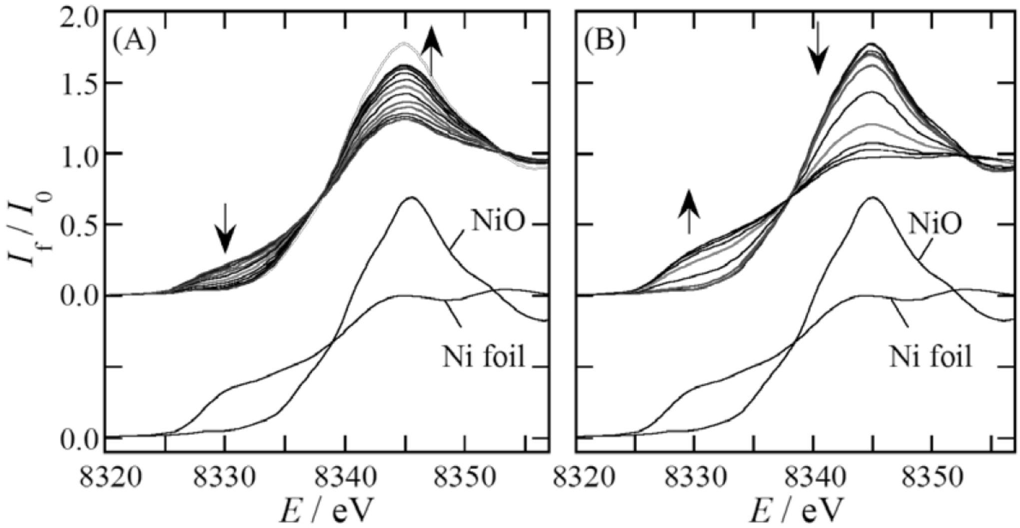

Figure 4. XANES change of 0.13 wt.% IMP during the TPO (A) and TPR (B) process observed by *in-situ* fluorescence XAFS measurements.

quantitatively reduced to metallic Ni(0) species by the TPR process. The existence of isosbestic points indicates that the redox reactions proceeds with only two component species (metallic Ni(0) and NiO) also for the dilute Ni catalysts.

The composition change of the supported NiO species in dilute Ni catalyst is shown in Figure 5 as a function of temperature by comparing the corresponding change for 5 wt.% IMP. The oxidation of the metallic Ni(0) species completed at 300 °C (see Figure 5(A)), and the lower shift of the oxidation temperature was observed by diluting the Ni loading. The average diameter of the Ni(0) particle was 7 nm and 3 nm for 1.4 wt.% IMP and 0.13 wt.% IMP, respectively, according to the TEM observations, and they are almost comparable to that of the Ni species in 5 wt.% IMPCA. The dispersion of the Ni species in the dilute sample makes the particle size smaller, and then the oxidation of such Ni(0) particles proceeds at lower temperature. The surface oxidation of the Ni(0) particles also observed at room temperature at the beginning of the TPO process, and the amount of the formed NiO species was increased with decreasing the particle size. In addition, it was found that the reduction temperature of the supported NiO species was higher shifted when the particle size became small. The observed change of the redox temperatures for the dilute samples containing small Ni particles is in agreement with that for 5 wt.% IMPCA.

The small Ni particles supported on silica show the specific redox property, that is, the lower oxidation temperature of metallic Ni(0) and the higher reduction temperature of NiO. The low temperature oxidation for small Ni(0) particles suggests the easy oxygen migration in the small particle. In addition, the higher shift of the

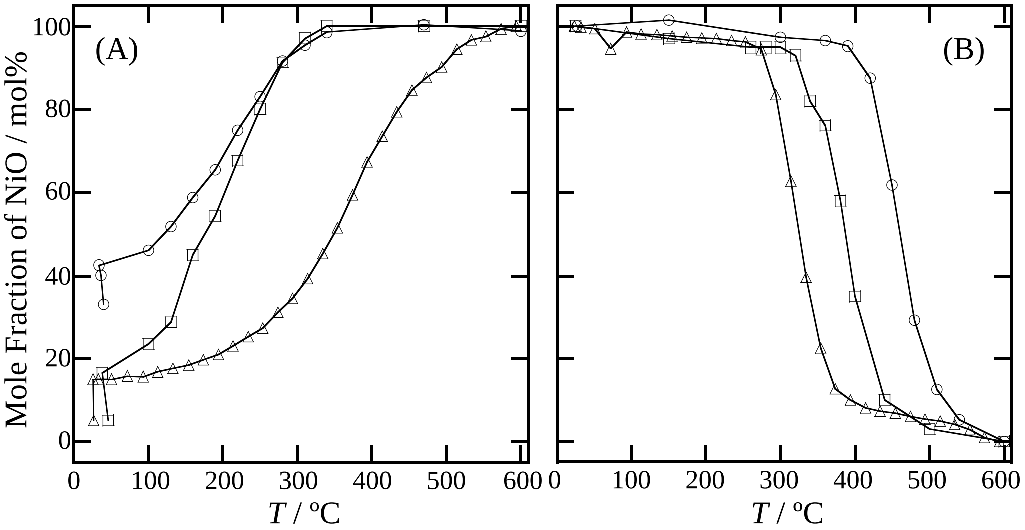

Figure 5. The composition of NiO as a function of temperature during the TPO (A) and TPR (B) processes for 0.13 wt.% IMP (triangles), 1.4 wt.% IMP (squares), and 5 wt.% IMP (circles).

reduction temperature is ascribed by the stronger interaction between the smaller NiO particle and SiO_2 support. The similar oxygen arrangement at the particle surface of NiO and SiO_2 contributes to the stabilization of NiO on SiO_2, and it is thus considered that the flatting deformation of the smaller NiO particle enhances the thermodynamic stability of the smaller NiO particles.

4. Conclusion

The particle size effect of the redox properties for the SiO_2-supported Ni particle has been investigated by the *in-situ* XAFS measurements. The refinement of the Ni(0) particle size promotes the oxidation temperature lower, on the other hand, the small NiO particle is reduced at higher temperature. The specific redox property is explained by the interaction between NiO and SiO_2. The active Ni species is exposed to the reaction gas environment under the catalytic reaction conditions, and thus the chemical state of the Ni species is potentially varied by the redox reactions. This study reveals the different redox property of the supported Ni species depending on the particle size. To achieve high catalytic activity and to optimize the catalytic reaction conditions, the systematic knowledge of the chemical state conversion for the supported Ni species is the most important and essential information.

Acknowledgement

The *in-situ* XAFS measurements at Photon Factory (KEK) were performed under the approval of the Photon Factory Program Advisory Committee (Proposal Nos. 2013G596 and 2015G544).

References

[1] C. Wu and P. T. Williams, *Environ. Technol.*, **33**, 631 (2012).

[2] N. Ichikuni, O. Tsuchida, J. Naganuma, T. Hara, H. Tsunoyama, T. Tsukuda, and S. Shimazu, *Trans. Mater. Res. Soc. Jpn.*, **37**, 177 (2012).

[3] S. Yamashita, Y. Yamamoto, M. Katayama, and Y. Inada, *Bull. Chem. Soc. Jpn.*, **88**, 1629 (2015).

[4] F. Bentaleb, M. Che, A. Dubreuil, C. Thomazeau, and E. Marceau, *Catal. Today*, **235**, 250 (2014).

[5] C. C. Culross, U. S. Patent 5 928 983 (1999).

[6] C. H. Mauldin, U. S. Patent 5 968 991 (1999).

[7] C. H. Mauldin, U. S. Patent 6 331 575 B1 (2001).

[8] S. Chotiwan, H. Tomiga, S. Yamashita, M. Katayama, and Y. Inada, *J. Phys. Conf. Ser.*, in press.

[9] M. Katayama, Y. Niwa, K. Doi, S. Yamashita, and Y. Inada, *J. Phys. Conf. Ser.*, **430**, 012053 (2013).

[10] A. Suzuki, S. Yamashita, K. Furusato, M. Katayama, and Y. Inada, *Memoirs of the SR Center*, **16**, 135 (2014).

[11] M. Kimura, K. Uemura, T. Nagai, Y. Niwa, Y. Inada, and M. Nomura, *J. Phys. Conf. Ser.*, **190**, 012163 (2009).

[12] Y. Yamamoto, S. Yamashita, N. Afiza, M. Katayama, and Y. Inada, *J. Phys. Conf. Ser.*, in press.