Development of in-situ cell for fluorescence-mode XAFS in BL14B2 of Spring-8

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Abstract. An in-situ cell for fluorescence-mode XAFS was developed in BL14B2 of SPring8. It was confirmed that the cell temperature can be up to 850 °C under atmospheric pressures of reaction gases basing on our firm tests in real experiment. The temperature stability of the cell especially at low temperature region is checked with samples of highly dispersed Pt atoms on FeOx nano-sized supporters by detecting Pt L3 and Fe K edges. The in-situ cell show very good stabilities and the projected temperature on the test position correspond well with that of TPR results.

1. Introduction
In-situ analysis of the materials under reaction conditions has widely been performed together with synchrotron radiation light sources because it is one of the few techniques to obtain the structural and chemical information of catalysts, fuel cells and secondary batteries under well-controlled reaction conditions such as high temperatures and reactive atmospheres. With this motivation and highly demands of industrial users, we developed of the automotive exhaust gas treatment system together with the auto control system in BL14B2 of SPring-8 [1, 2]. Besides time-resolving analytical techniques such as DXAFS and QXAFS, the design of in-situ cell is also crucial, such as the uniform and reproducible temperature around samples, the efficient gas flow to pass the sample, the corrosive attack to the parts of cell and easy to be used in beam line, etc. Basing on the requirements, the in-situ cells for both transmission and fluorescence modes XAFS were designed with quartz. The in-situ cell for transmission mode XAFS measurements have been tested [2] and can be used for user now. However the in-situ cell for fluorescence mode has not been tested yet due to the difficulties in the temperature uniformity and safety consideration coming from the large fluorescence detecting window. In the present work, the in-situ XAFS cell for fluorescence mode developed in BL14B2 of SPring8 will be described. Its performance was evaluated by firm test in real experimental conditions.

2. Experiment
The in-situ XAFS experiment was performed on BL14B2 of Spring-8 - a hard x-ray bending magnet beam line dedicated for XAFS experiments in the wide energy range from 3.8 to 72 keV. A single pair Si (111) or (311) double-crystal monochromator was used to reduce the harmonic component of the monochrome beam with the photon flux of 108~1011 photons/sec and energy resolution of 104 at sample position after focusing with Rh thin films mirrors (standard beam size 5.0mm in horizontal and 0.5mm in vertical directions). For more details please see elsewhere in ref. 1. In the experiment, two
kinds of samples were selected, one is 0.2%wt Pt/Fe₂O₃, in which Pt atoms are mostly dispersed atomically, and the other is 2.5%wt Pt/Fe₂O₃, in which Pt atoms aggregate to several-atom-sized clusters [3]. Pt foil and PtO₂ were used as reference samples and measured in the transmission mode. Before the experiment, the samples were pressed into self-supporting disks with a diameter of 10 mm. To obtain a much better signal-to-noise ratio, an Al foil filter was used to reduce the direct reflection and fluorescence of Fe in addition to extending the integral time for fluorescence measurements. IFEFFIT software was used to calibrate the energy scale, to correct the background signal and to normalize the intensity. A similar approach was used to analyse the EXAFS data at the Pt L₃ and Fe K edges.

Figure 1 The design of in-situ cell for fluorescence mode: (a) the photograph in side view of fully assembled cell for experiment; (b) side and top views as well as the sample holder of cell; (c) the relationship of setting temperature and the temperature on sample position.

3. Results and discussion
The fully assembled in-situ cell for fluorescence mode XAFS with a catalyst sample inserted in is shown in Figure 1 (a). The main body of the cell is a quartz tube with a conical window opened in the middle of it. The cell is sealed with Viton O-ring and stainless flanges. The windows are designed with polyimide adhered to the exterior of the flanges. In order to avoid over-heating of the Viton O-rings and polyimide windows, water-cooling system is used to the stainless flanges. The heating of the cell is accomplished with heating jacket controlled via a programmable temperature controller. A quartz tube was fabricated as the sample holder with a 45° sample pocket along x ray direction in one side as shown in Figure 1 (b). By the design, the cell can be easily heating to 850 °C with good temperature uniformity in sample position. Indeed, the cell was used to conduct catalyst reductions in hydrogen at 850 °C. It is demonstrated that the correspondence of sample temperature against setting temperature is linearly as shown in Figure 1 (c) with a temperature ramp of 10 °C/min, for example. There are many advantages for this design, which can solve the problems mentioned in part 1. Firstly, quartz tube is inert to most gases and solids typically found in catalysis and it is easy to clean, also, its optically transparent is distinct for detecting the changes of samples in color or shape during experiments. Second, the samples can be easily loaded into sample pocket without any damages. Third, the heating jacket is also convenient cooled quickly from high temperature to room temperature after experiment by using a small fan.

Before experiment, the gas distribution and exhaust gas treatment systems as well as emergency shut-off systems were set up as described in ref. 1. In order to test the whole performance of in-situ cells, firstly, Pt L₃ edge EXAFS with fluorescence mode was measured with and without in-situ cell to evaluate the intensity changes effected by in-situ cell. The fluorescence signal did not show differences with and without in-situ cell. It means no shielding from windows of in-situ cell. Then, we
started to test the gas distribution and exhaust system, and no any leakage was detected in 2 hours with the He gas pressure more than one atmosphere. After that, with H₂ flow, we tested the gas distribution and exhaust system to evaluate the gas exchanging time from pure H₂ to pure O₂ detected by a mass spectrometer detector for the gases contribution during the procedure. It was confirmed that 20 minutes is enough for H₂ or O₂ exchanging, which is nearly two times as that of transmission mode owing to the large conical window in fluorescence mode cell [4]. All of the procedures for test were done in nearly 10 hours. The gas flow rate, exhaust gas, QXAFS system and the sample temperature were controlled by the PC with the programs coded by LabVIEW programming language of National Instruments during the procedures [5]. The emergency shut-off system is used during experiments to detect the leak of flammable and/or toxic gasses, fire, earthquake, electric power failure, device failure the abnormal pressure/flow of gases, and so on.

**Figure 2** Pt L₃ XANES spectra of 2.5%wt Pt/Fe₂O₃ (a) and 0.2%wt Pt/Fe₂O₃ (b) samples against temperature; H₂-TPR profiles of Fe₂O₃, 0.2%wt and 2.5%wt Pt/Fe₂O₃ (c).

To test the temperature uniformity, the samples were reduced with in-situ cell from room temperature (RT) to 850 °C with a PC program by transition mode at a temperature-increasing rate 10 °C/min for several times to detect the reproducibility of sample temperature. After that, Pt/Fe₂O₃ samples were reduced by H₂/He flow (H₂ 10%, He 90%, flow rate 100 ml/min) with a PC programmed temperature from RT to 850 °C as shown in Ref. 4. The Pt L₃ edge XAFS were measured at certain temperatures during reduction by transition mode for 2.5%wt Pt/Fe₂O₃ and fluorescence mode for 0.2%wt Pt/Fe₂O₃ samples respectively. Since the fluorescence signal is weak, the spectra were measured several times by fix temperature at certain values. The exhaust gases contribution is detected with mass spectrometer detector during experiments. Pt L₃ XANES spectra of 0.2%wt and 2.5%wt Pt/Fe₂O₃ were presented in Figures 2 (a) and (b). We can find that Pt L₃ white line suffers gradually changes by variation of temperature and the Pt L₃ white line intensity changes combined well with the H₂ consumption peak and the produce of water [4]. By the knowledge that difference between the area of the L₃ edge resonance (white line) in the 5d pure metals and their compounds can be related to the amount of d electron vacancies [6-8], one can detect the amount of charge transferred to the ligands by the changes of white line intensities. So, the abrupt changes of Pt L₃ white line intensity correspond to the reduction or alloying of Pt atoms. To fully understand the changes of Pt L₃ white line intensity, the ex-situ temperature progammed reduction (TPR) results (after Ref. 3) of Fe₂O₃, 0.2%wt and 2.5%wt Pt/Fe₂O₃ samples were presented in Figure 2 (c). The H₂ consumption peaks at certain temperature give the information of sample reduction. Such as for Fe₂O₃, the small peak from 300–400 °C indicates the reduction of Fe atoms from Fe₂O₃ to FeO, while the broad peak from 420 °C to750 °C is due to the reduction of Fe atoms from Fe₂O₃ to FeO and finally to Fe metal [9]. For Pt/Fe₂O₃ samples, besides the two peaks related with the reduction of Fe mentioned above, an additional sharp peak appears, which should correspond to the reduction of Pt atoms [10]. Besides, the temperatures for
reduction of Fe atoms from Fe$_2$O$_3$ to Fe$_3$O$_4$ are shift to low temperature side due to the Pt interaction with Fe$_2$O$_3$ supporters. With the knowledge, now, we can discuss the sample temperatures by combining Pt L$_3$ white line intensity changes and the H$_2$-TPR profiles. The abrupt changes of Pt L$_3$ white line intensity start around 107 °C, 237 °C, 552 °C for 2.5%wt Pt/Fe$_2$O$_3$ and 182 °C, 215 °C for 0.2%wt Pt/Fe$_2$O$_3$, respectively. While, the H$_2$ consumption peaks in H$_2$-TPR profiles, are around 90 °C, 220°C, 580 °C for for 2.5%wt Pt/Fe$_2$O$_3$ and 160 °C and 210 °C for 0.2%wt Pt/Fe$_2$O$_3$, respectively. It means that the temperature on the samples is nearly the same as that corrected by thermocouples, if we thinking about the temperature-increasing rate of 10 °C/min, the differences of temperature in the different measuring methods are reasonable, since the temperature on the sample should be a little delayed due to the bad thermo conductance of samples during experiments.

4. Conclusions

In this work, the in-situ cell for fluorescence mode EXAFS at BL14B2 was tested successfully. The on-line test of exhaust gas treatment systems and the in-situ cells showed no leakage during experiment even up to 850 °C. The in-situ cell can be used both transmission and fluorescence modes and temperature can be up to 850 °C basing on our firm test in the experiment. The automatic temperature control system can work well with the designed program. But due to the weak signal of 0.2%wt Pt samples, only the temperature-increasing rate of 10 °C/min was tested. Even though, the temperature on real sample and that on the test position correspond well by in-situ test of standard samples comparing with that of ex-situ TPR experiments. This test of in-situ fluorescence mode XAFS will introduce a new method for BL14B2 and compensate the demands of industrial users for in-situ XAFS. After this whole performance test and evaluation, we think that the system can be opened for users of industrial applications now. As described in part 3 of this work, the mass spectrometer detector was used to detect the gases contributions by connected with in-situ cell in the gas outlet. Even though, a true operando test is not done for the system, we think that the operando mode can be used to monitor the states of the catalyst during the catalytic reactions by determining the conversation and selectivity with the additional mass spectrometer detector to the gas outlet of in-situ cell. And further work will be done for that.

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