## Measuring the Local High Temperature on Metal Nanoparticles under Microwave Irradiation using *in situ* XAFS

Microwaves often promote catalytic reactions by directly heating the catalysts. A local "hot spot" has been proposed that promotes catalytic reactions by microwaves, however, its local temperature has not been directly observed. Here we demonstrate the local temperature of metal nanoparticles supported on metal oxides using microwave *in situ* XAFS. The temperature-dependent Debye-Waller factor is used to estimate the local temperature of Pt nanoparticles on  $Al_2O_3$  and  $SiO_2$ . We revealed that the local temperature of Pt is 26–132 K higher than that of bulk catalysts. The efficient propagation of microwave energy to the active sites of the catalysts promotes catalytic reactions due to microwave irradiation.

The development of energy-saving chemical processes is required to replace conventional chemical processes that consume large amounts of fossil resources. The electrification of chemical processes that use renewable energy is one of the key technologies to reduce energy consumption and  $CO_2$  emissions [1]. Microwaves can selectively heat materials and enable a rapid temperature rise with high energy efficiency, therefore, industrial applications of microwave chemical processes are attracting increasing attention. Catalytic reactions are an important process in the chemical industry, and microwaves have been reported since the 1990s to effectively promote various catalytic reactions. It has been proposed that the formation of so-called "hot spots" at the catalyst particles promotes the catalytic reactions by microwaves. However, how the local high temperature of hot spots is generated inside the packed catalyst bed is not well understood.

Our group has reported that microwaves form multiscale temperature gradients in mm to nm scales in the catalyst bed (**Fig. 1**). The core of the packed bed often reaches a higher temperature than its surface [2]. Using a coupled simulation of the electromagnetic field and heat transfer revealed that a concentrated electromagnetic field at the contact points of the catalyst particles forms local high temperatures on a  $\mu$ m scale. *In situ* luminescence analysis confirmed a local temperature increase at the contact point of spherical SiC particles. Moreover, local heat generation can occur even at smaller nm scales, such as supported metal nanoparticles on the metal oxide support. Microwaves can efficiently propagate energy to metal nanoparticles that work as an active site of the catalysts. A chemical process that dramatically saves energy can be achieved by effectively utilizing the formation of a local high temperature at the catalytic active sites. We performed microwave in situ X-ray fine structure (XAFS) analysis to demonstrate the formation of a local high temperature at Pt nanoparticles. The temperature-dependent Debye-Waller factor was determined by extended X-ray fine structure (EXAFS) analysis. The temperature of the supported Pt nanoparticles under microwaves was calculated using the Debye-Waller factor obtained under heating in an electric furnace as a calibration curve.

Microwave *in situ* XAFS measurements were performed using the BL-9C. The microwave conditions were precisely controlled from outside the hatch during XAFS measurement using a single-mode microwave cavity resonator and semiconductor microwave amplifier. **Figure 2(A)** shows the FT-EXAFS spectra of the Pt-L<sub>III</sub> edge of Pt/Al<sub>2</sub>O<sub>3</sub> during microwave heating and conventional heating using an electric furnace. A prominent peak of 2.77 Å, which is attributed to Pt-Pt bonding, gradually decreased with increasing temperature by us-



Figure 1: Multi-scale temperature gradient formed in a catalyst bed in mm to nm scales as "hot spots" that promote catalytic reactions [2-4].



Figure 2: Measurement of the local high temperature at Pt nanoparticles of  $Pt/Al_2O_3$  and  $Pt/SiO_2$ . (A) *In situ* FT-EXAFS (Pt-L<sub>III</sub> edge) under electric furnace and microwave heating. (B) Temperature-dependent changes in the Debye-Waller factor. (C) The overall temperature gradient in the packed catalyst bed of  $Pt/Al_2O_3$  and  $Pt/SiO_2$  [4].

ing the electric furnace. On the other hand, microwave heating rapidly decreased the peak intensity even at a low temperature of 368 K. Then the Debye-Waller factor was obtained by curve fitting [3] and plotted against temperature [Fig. 2(B)]. Since the Debye-Waller factor ( $\sigma^2$ ) is affected by temperature ( $\sigma_T$ ) and structural ( $\sigma_S$ ) factors, we have confirmed that there is no structural change of Pt nanoparticles due to microwave heating by TEM and EXAFS spectra after microwave heating. From this, we concluded that the intense increase in the Debye-Waller factor by microwave heating is attributed to the local high temperature at the Pt nanoparticles.

Next, the Debye-Waller factor was used to calculate the local temperature of Pt nanoparticles using the calibration curve of the same sample obtained using an electric furnace [4]. **Figure 2(C)** summarizes the temperatures of Pt nanoparticles ( $T_{Pt}$ ), surface ( $T_{ex}$ ), and core ( $T_{in}$ ) of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>. When  $T_{ex}$  was 376 K and 378 K,  $T_{in}$  reached 453 K and 471 K while  $T_{Pt}$  obtained by *in situ* EXAFS was 479 K and 603 K, respectively. From this, the temperature difference between the Pt nanoparticles ( $T_{Pt}$ ) and the bulk average temperature ( $T_{in}$ ) where the X-rays pass through was calculated to be 26 K and 132 K, respectively. SiO<sub>2</sub> was more efficient for generating local high temperatures probably due to the lower dielectric loss of SiO<sub>2</sub> and effective collection of microwaves at the Pt nanoparticles. In the future, we will be able to control the local temperature of supported metal nanoparticles by precisely controlling the microwave irradiation conditions and catalyst materials to maximize the concentration of microwaves at the nanoparticles. It will be possible to apply microwave catalytic reactions to industrial processes as an innovative energy-saving catalytic process that is driven by renewable energy.

## REFERENCES

- K. M Van Geem, V. V. Galvita and G. B. Marin, *Science* 364, 734 (2019).
- [2] N. Haneishi, S. Tsubaki, M. M. Maitani, E. Suzuki, S. Fujii and Y. Wada, *Ind. Eng. Chem. Res.* 56, 7685 (2017).
- [3] N. Haneishi, S. Tsubaki, E. Abe, M. M. Maitani, E. Suzuki, S. Fujii, J. Fukushima, H. Takizawa and Y. Wada, *Sci. Rep.* 9, 222 (2019).
- [4] T. Ano, S. Tsubaki, A. Liu, M. Matsuhisa, S. Fujii, K. Motokura, W.-J. Chun and Y. Wada, *Commun. Chem.* 3, 86 (2020).

## BEAMLINE

BL-9C

S. Tsubaki<sup>1, 2</sup>, T. Ano<sup>3</sup>, A. Liu<sup>3</sup>, W. -J. Chun<sup>4</sup>, K. Motokura<sup>5</sup>, S. Fujii<sup>6</sup>, Y. Wada<sup>3</sup> (<sup>1</sup>JST-PRESTO, <sup>2</sup>Osaka Univ., <sup>3</sup>Tokyo Tech., <sup>4</sup>ICU, <sup>5</sup>Yokohama National Univ., <sup>6</sup>Toyohashi Univ. Technol.)