

Development of a New In-situ XAFS Cell for Fast Gas Injection

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Introduction

Dispersive XAFS (DXAFS) method is a powerful technique to observe irreversible reaction processes with the difficulty on repeating the reaction many times. Especially, it has grasped the overall picture of structural and electronic changes of catalytic metal centers such as transition metals supported on oxides. Those metal supported catalysts have vital and key roles in many industrial processes. Uncovering the reaction mechanisms of the heterogeneous catalysts helps to understand the nature of the catalysis and improve the reactivity and selectivity.

However, there are some problems to study catalytic reactions of powder solid catalysts with gaseous molecules under the working conditions. A main issue is the dead time to start the catalytic reaction, which is triggered by a gas injection into an in-situ reaction cell. It usually takes about 100 ms to complete the gas injection. The dead time at the beginning of reactions may hide the early part of the reaction and then limits the mechanistic evaluation of catalytic reactions. To diminish the dead time by modification of the gas injection procedures leads to further usefulness and importance of the DXAFS method for the mechanistic investigations of the supported catalysts. We have thus designed a new in-situ cell for the fast gas injection and evaluated the injection time.

New In-situ Cell Design

The new reaction cell was designed, focusing on decreasing gas-flow resistance on the way from a gas reservoir chamber to a sample chamber. Conventional in-situ cell is connected to a gas chamber through a stainless pipe, which causes resistance for gas flow into the in-situ cell and increases the dead volume. Fig. 1 shows the schematic design of a new in-situ cell for fast gas injection. The new XAFS cell is divided to two parts; one is an in-situ chamber with X-ray transmission

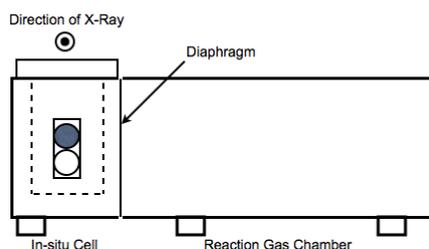


Fig. 1. Schematic diagram of a new in-situ XAFS cell for fast gas injection.

windows and sample heating unit, and the other is a reaction gas chamber. The two parts are separated with a diaphragm at the beginning, and the diaphragm is opened to inject the gas into the sample chamber.

The dead volume is also decreased by the direct connection of the gas chamber to the sample cell. In addition, the in-situ cell with the same radius as the gas chamber also decrease gas flow resistance, leading to the shorter dead time for gas admission.

Performance Evaluation of the New In-situ Cell

The injection time of reaction gas was measured with the DXAFS equipment at NW2A (PF-AR). The Cu-K edge was used for the evaluation. A Si(111) bent crystal polychromator with 2000 mm curvature radius was used and a photodiode array was used as a position-sensitive detector. Several kinds of test gases were used for injection time measurement; Ar, O₂, ethanol, and a mixture gas of ethanol and O₂.

Fig. 2 shows the X-ray absorbance of Ar vs. time. The rapid increase of the X-ray absorbance indicates the injection of Ar gas into the sample chamber, and the gas injection time to the newly developed cell was estimated to be about 50 ms, which is a half of that for the conventional cell. The injection time was independent of the kind of injected gases.

The improvement is attributed to removal of the gas flow resistance between the gas chamber and the sample cell. However, the injection time has not reached our goal (< 10 ms) yet. As it was found that the injection time becomes shorter when the volume of sample chamber decreases, a modified sample cell is now under construction, considering the results mentioned above in order to further shorten the injection time.

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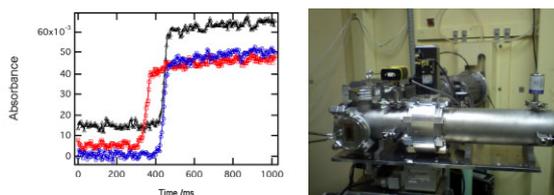


Fig. 2. The X-ray absorption of Ar (left) as a function of time. The gas injection was completed within 50 ms. The right picture shows a newly developed in-situ cell installed in the DXAFS equipment.