Synchrotron Radiation Shed Light to In Situ and Dynamic Observation of High-Temperature Processes∗

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I. INTRODUCTION

Synchrotron radiation is extremely bright and naturally collimated X-ray beams with a broad spectral (or energy) range. The most appealing feature of observations that use synchrotron radiation is that the structural changes of a material can be observed in situ during a specific reaction under conditions closely resembling the actual process or environment of interest. In 1982, when Japan’s first full-scale synchrotron radiation facility, the Photon Factory, High Energy Accelerator Research Organization (PF/KEK), was in operation, Nippon Steel (now Nippon Steel & Sumitomo Metal Co.) started research on synchrotron radiation at PF/KEK.

We have developed analytical approaches using synchrotron radiation at a number of facilities: PF/KEK and SPring-8 in Japan, and the National Laboratory of Synchrotron Light Source (NSL) and the Stanford Synchrotron Radiation Light Source (SSRL) in the USA. Our work has clarified various reaction mechanisms relating to iron and steel including recrystallization [1], corrosion [2], and galvanizing [3], and other materials such as titanium [4], and nano-materials [5, 6] (Fig. 1). These have shown that the best usage of in situ and dynamic observation using synchrotron radiation is in analyzing the following phenomena: (1) real-time reaction dynamics, (2) element-selective analysis, (3) surface/interface reactions, and (4) strain/stress analysis (Fig. 1).

II. IN SITU AND DYNAMIC OBSERVATION OF IRON ORE SINTERING [7]

A. Sintering in Iron-Making Process

Iron-ore sinter constitutes the major component of the iron-bearing burden in the blast furnace in most countries in the Asia-Pacific region. Therefore, its quality and consistency have a significant impact on blast furnace performance. It is generally accepted that the quality of iron-ore sinter is governed by its microstructure, which is formed during the sintering process, as well as the properties of individual mineral phases and the size, shape, and distribution of their grains, and mutual interaction among the mineral phases [8–12]. In the industrial sintering process, the fine ores are mixed with limestone flux and coke breeze, and heated by the combustion of coke breeze, resulting in heating up to temperatures of 1450–1600 K (above the eutectic temperature of CaO–Fe2O3: 1478 K) for a few minutes in the region (ca. 10−1 m) near the coke breeze. Consolidation of iron ores progresses with the formation of melt and material transport through the melt, referred to as liquid phase sintering, which is illustrated in Fig. 2 based on the review articles [9, 11, 13–15]. The microstructure of the sinter basically consists of the unmelted ore, bond, pores, and cracks. The bond phases consist of calcium ferrites (CaO–Fe2O3), silico-ferrites of calcium and aluminum (SFCA), glass (CaO–SiO2), and their solid-solution phases [9]. The final structure found in the sinter is critically affected by the way in which various phases develop during heating and cooling in the sintering process [16, 17].
B. In Situ and Dynamic Observation of Changes in both Crystal Structures and Microstructures at High Temperatures up to 1773 K

The formation of calcium ferrites (CFs) in the CaO–Fe₂O₃ system was investigated by in situ and real-time observation of both (a) crystal structures by using a newly developed technique, referred to as “quick X-ray diffraction (Q-XRD),” and (b) microstructures by using an in situ laser microscope. In the new Q-XRD, a specimen was heated up to 1773 K, and X-ray diffraction patterns were measured using a pixel-array area detector with an interval as short as a few seconds (Fig. 3). The heating unit was located at the center of the outer cover of the reaction chamber with a beryllium window for the transmission of incident and diffracted X-ray beams. Q-XRD experiments were conducted on the BL-6C station of the Photon Factory at the High Energy Accelerator Research Organization (KEK) in Japan.

A typical example of obtained X-ray diffraction pattern is shown in Fig. 4 where the specimen CaO:Fe₂O₃ = 25:75 mass% was heated at $T = 1473$ K. The measured Debye-Scherrer ring intensities are discontinuous (Fig. 4(a)), but integration of diffraction intensities along the Debye-Scherrer ring results in a diffraction pattern with a much better-quality (Fig. 4(b)). Figure 4(c) is the diffraction pattern obtained in the same condition with a scintillation detector in place of an area detector, demonstrating the merits of using an area detector for in situ observations of such reactions at high temperature.

The specimens Fe₂O₃; CaO = 64:36, 80:20, and 90:10 (mass%) were heated up from 300 to 1773 K at 5.0
FIG. 4: (a) X-ray diffraction intensities of the specimen CaO:Fe$_2$O$_3$ = 25:75 mass% at $T = 1473$ K measured with the area detector, (b) average intensities along the diffraction angle ($2\theta$), and (c) intensities measured with a scintillation detector.

FIG. 5: First continuous cooling transformation (CCT) diagram for sintering of specimen CaO:Fe$_2$O$_3$ = 10:90 mass% [7]. Solid lines show the time-temperature curves for cooling rates: (i) $3\times10^{-1}$ K/s, (ii) $-8.3\times10^{-1}$ K/s, and (iii) $-8.3\times10^{-2}$ K/s. Dotted thin lines (blue) show the temperatures of phase transformation at equilibrium: $L \rightarrow L + W + F$, $L + W + F \rightarrow L + F$, $L + F \rightarrow CF_2 + F$, and $CF_2 + F \rightarrow CF + F$, where $C = CaO$, $F = Fe_2O_3$, and $W = FeO$. Broken lines (red) show those of $L \rightarrow L + W + F$, $L + W + F \rightarrow L + F$ and $L + F \rightarrow CF_2 + CF + F$ un-der non-equilibrium cooling conditions determined in this study. In the case of where liquid co-exists, microstructure observation by laser microscopy clearly showed the phase boundaries. For example, precipitation of oxides in liquid was sometimes more clearly observed by laser microscopy than by XRD. Phase boundaries determined by laser microscopy are shown by diamonds in Fig. 5. The first continuous cooling transformation (CCT) concept for iron ore sintering was proposed to understand overcooling phenomena when the molten oxide cooled down to room temperature and magnetite (Fe$_3$O$_4$), hematite (Fe$_2$O$_3$), and various types of calcium ferrite were formed. The CCT diagram for sintering provides crucial and fundamental information on the sintering accompanying solidification, precipitation, and formation of calcium ferrites from the molten oxide, and can be used as a guideline for controlling sintering processes.

III. IN SITU AND SIMULTANEOUS OBSERVATION OF PALLADIUM REDOX AND OXYGEN STORAGE/RELEASE IN PD/SR–FE–O PEROVSKITE CATALYSTS [19, 20]

A. Three-Way Catalysts for Automotive Emission Control

Gasoline engines generally operate near the stoichiometric air-to-fuel ratio, and three-way catalysts (TWCs) are used to convert pollutant emissions—carbon monox-
We proposed a new analytical technique that enables the simultaneous observation of the redox reaction of palladium and the oxygen storage/release process in the Pd/Sr–Fe–O catalyst. Furthermore, the atomic structure and microstructure of the catalyst are extensively investigated. Based on these results, we proposed reaction mechanisms in terms of the correlation between the redox of palladium and the oxygen storage/release during redox-gas cycles, which is crucial information for understanding the mechanism of the high performance of not only the Pd/Sr–Fe–O catalyst but also other TWCs [19, 20].

B. Atomic Structure and Microstructure of the Pd/Sr–Fe–O Catalyst [19, 20]

We have developed the Pd/Sr–Fe–O catalyst which exhibits high performance for automotive emission control. The Sr–Fe–O oxide support has a unique “multi-phase-domain” structure, where a single grain is composed of nano-sized domains of three phases: SrFeO$_{3-\delta}$, Sr$_2$FeO$_{13-\delta}$, and SrFe$_2$O$_{19-\delta}$ (Fig. 6). The Sr$_2$FeO$_{13-\delta}$ phase is similar to the perovskite phase of SrFeO$_{3-\delta}$, but differs in the stacking sequence of the Fe–O (iron) layer and Sr–Fe–O (perovskite) layers.

Figure 7 shows a series of time-resolved Pd K-edge absorption near edge structure (XANES) spectra of the Pd/Sr–Fe–O catalyst obtained by in situ DXAFS at 673 K during the redox cycles. The virgin Pd/Sr–Fe–O specimen gave a typical singlet white line that is characteristic of Pd$^{II}$ ions, and is similar to that of Pd$^{III}$O. In the reduction cycle, the edge position shifted to a lower energy, and the singlet changed into the doublet of Pd$^{II}$ metal at $t > 10$ s. In the oxidation cycle, the doublet transformed into a singlet, and the edge position shifted to a higher energy. This change proceeded quickly (within 12.0 s), and the spectrum was identical to that of the virgin specimen after 60 s.

Another slight, but significant, change in the spectrum was observed for the background absorbance at energies lower than the absorption edge. The absorbance, corresponding to the specimen density, decreased and increased reversibly during the redox cycles. The reversible change in the density can be attributed to the change in the density of the Sr–Fe–O oxides. It is reasonable to consider that the density change during the redox cycles is caused by chemical expansion and contraction of the perovskite-type SrFeO$_{3-\delta}$ and Sr$_2$FeO$_{13-\delta}$ phases in response to changes in the oxygen deficiency ($\delta$), which is typically found in oxides with perovskite-type structures, such as La$_{1-x}$Sr$_x$MnO$_{3+\delta}$ [29], SrCo$_{0.5}$Nb$_{0.5}$O$_{3-\delta}$ [30], Nd$_{2-x}$Sr$_x$NiO$_{4+\delta}$ [31], and Ca$_{0.5}$Sr$_{0.5}$Mn$_{1-x}$Fe$_x$O$_{3-\delta}$ [32]. The observed change in the normalized density, $\rho_{\text{norm}}$, can be concluded to indicate the change in the oxygen deficiency $\delta$ that is located in the perovskite-type SrFeO$_{3-\delta}$ or Sr$_2$FeO$_{13-\delta}$. Thus, it can also be concluded that we succeeded in the simultaneous observation of the redox reaction of palladium and the oxygen storage/release process during redox-gas cycles using dispersive XAFS with a time resolution of less than 20 ms, when we measured the change in absorbance at an energy lower than the edge energy, as well as the change in the XANES and EXAFS spectra.

In situ X-ray absorption fine structure (XAFS) analysis is a powerful technique for characterizing catalysts in a reactive atmosphere [22–24]. In situ XAFS analysis with a shorter time resolution (less than a second) was conducted using a reaction cell with an energy-dispersive XAFS (DXAFS) technique [25–28].

FIG. 6: Atomic structures of the co-existing phases in the Pd/Sr–Fe–O catalysts: (a) SrFeO$_{3-\delta}$, (b) Sr$_2$FeO$_{13-\delta}$, and (c) SrFe$_2$O$_{19-\delta}$. The red, orange, and blue spheres indicate strontium, iron, and oxygen, respectively. A gray octahedron shows the FeO$_6$ unit.

FIG. 7: Spectral changes obtained by in situ DXAFS measurements during the RedOx reactions for an MPD-structured catalyst with 3.0 mass% Pd that was measured under gas-closed conditions at $T = 673$ K (a) in H$_2$, $P = 18.5$ kPa, and (b) in O$_2$, $P = 47.2$ kPa. The arrows in the figures show the time evolution of the spectra.

ide (CO), unburned total hydrocarbons (THC), and nitrogen oxides (NO$_x$)—into carbon dioxide (CO$_2$), water (H$_2$O), and nitrogen (N$_2$) [21]. In TWCs, precious metals are added to oxide supports with a high oxygen storage capacity (OSC), such as CeO$_2$–ZrO$_2$ or perovskite-type oxides [21]. Thus, the change in the structure and chemical state of the precious metals during the redox cycles, and the relationship of that change with the oxygen storage/release properties of the supporting oxides in TWCs, are pivotal for revealing the reaction mechanisms of these catalysts, which have been investigated using various approaches.

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FIG. 8: Schematic illustration of the reaction mechanisms that provides a clear understanding of the difference in the reaction mechanisms for the different reaction periods: Red-I, II, and Ox-I, II, and III. For simplicity, the Fe–O structure is symbolized by a square of oxygen atoms with an iron atom at its center. Pink broken circles show oxygen vacancies. The illustration is drawn in 2D, and does not indicate the exact atomic configuration.

Detailed analysis of in situ and simultaneous observation of palladium redox and oxygen storage/release revealed a strong correlation between the redox of palladium and the oxygen storage/release in the Pd/Sr–Fe–O catalyst as follows. Reduction from Pd$^{II}$ to Pd$^{0}$ begins just after the introduction of H$_2$/He gas, with a simultaneous increase in the oxygen deficiency ($\delta$) in perovskite-type SrFeO$_3.5$ and Sr$_4$Fe$_6$O$_{13.5}$. After the completion of the Pd reduction, the recovery (decrease) of $\delta$ follows. Contrary to this sequence, oxidation from Pd$^{0}$ to Pd$^{II}$ begins after an incubation period, after which the change in $\delta$ precedes. The palladium oxidation and the increase of $\delta$ then progress simultaneously (Fig. 8) \cite{19, 20}.

IV. SUMMARY

We showed that unique analytical techniques using special reaction cells for in situ and dynamic observation using synchrotron radiation gives us crucial information on reaction mechanisms by showing the latest research topics: iron ore sintering and Pd/Sr–Fe–O perovskite catalysts for automotive emission control. The obtained information gave us a guideline principle for designing materials and processes.

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