Evidence of Local Heating of Catalyst during Soot Oxidation

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During carbon black oxidation over Ag catalyst, the local temperature of the catalyst surface reached more than 1073 K, although observed oxidation peaks were around 650 and 750 K.

During catalytic reaction, the local temperature of the catalyst bed sometimes dramatically increases as a hot spot, which significantly influences catalytic activity. Hot spot formation has been observed frequently in chemical synthesis processes, such as partial oxidation and hydrogenation.[1] The hot spot is one reason for local deactivation of catalysts and reaction runaway. Therefore, to obtain information on hot spot formation, formation was observed by IR imaging and detailed simulation in the catalyst bed.[2–4] Catalytic oxidation of particulate matter (PM) emitted from diesel engines is an exothermic reaction. PM is mainly composed of solid carbonaceous material, soot, which can be captured using a catalyzed diesel particulate filter (DPF). The distribution of the accumulated soot is inhomogeneous on the catalyzed DPF, namely, some parts of the catalyzed DPF that contact soot and other parts do not. During regeneration of DPF, it is expected that temperature distribution in the catalyst bed will differ significantly from part to part. It is anticipated that the contact points will undergo severe heating, so that partial deactivation of catalysts should occur. Obtaining information on the real temperature of the catalyst surface during soot oxidation helps design practical catalysts with respect to thermal durability. To our knowledge, there is no report that confirms real temperature of the local area, especially contact points with soot. In this paper, we attempted to confirm the temperature of a local area in catalyst surface by using a material having highly ordered arrays of a cylindrical 1D mesoporous structure as an indicator of temperature. This material is composed of SiO_2 and the mesoporous structure is preserved at around 1073 K. When the mesoporous structure is broken, we can distinguish that the local area temperature reaches above 1073 K. We found that the local temperature must have reached more than 1073 K.

The catalyst used was a mesoporous SiO_2 (m-SiO_2) loaded with 10 wt% Ag and 10 wt% ZrO_2, expressed here as Ag/Zr/m-SiO_2. The details of the preparation procedure of m-SiO_2 have been described elsewhere.[5,6] Specific surface area, pore volume, and mean pore radius of mesopores were $853 m^2 g^{-1}$, 196 $cm^3 g^{-1}$, and 3.1 nm, respectively. The m-SiO_2 was impregnated with an aqueous solution of $ZrO(NO_3)_2$ (Kishida Chemical), followed by drying and calcination at 873 K for 4 h. The Zr/m-SiO_2 thus prepared was further impregnated with an aqueous solution of $AgNO_3$ (Wako), followed by drying and calcination at 773 K for 4 h. The activity test of catalytic soot oxidation was carried out with a fixed-bed flow reactor system at atmospheric pressure. Carbon black (CB: 7350F, Nippon Tokai Carbon, primary particle size 28 nm) was used as a model soot. 0.2 g of

Ag/Zr/m-SiO_2 and 2 mg of CB were mixed with an agate mortar, then pelletized and sieved in 0.15–0.25 mm, thus forming tight contact between CB and the catalyst as described previously.[7] The mixture was set in a quartz tube reactor with an inner diameter of 8 mm, and thermocouple was located at the center of catalyst bed. Temperature-programmed reaction (TPR) was performed from 373 to 923 K at a heating rate of 10 $K min^{-1}$. The reactant gas with a flow rate of $300 mL min^{-1}$ was composed of 10% O_2 and 10% H_2O with N_2 as a balance gas. The product gases were analyzed with an FT-IR spectrometer (Magna 560; Nicolet) equipped with a multireflectance gas cell (Gemini Specialty optics; Mercury Series, optical path length = 2 m). A sheath thermocouple with a diameter of 0.5 mm was set in the center of the catalyst bed, and the temperature was monitored continuously. Morphology of the catalysts was observed by transmission electron microscopy (TEM: EM-002B, TOPCON), using an accelerating voltage of 120 kV.

Figure 1a shows TEM photograph of fresh Ag/Zr/m-SiO_2. Highly ordered arrays of mesopore channels in m-SiO_2 are recognized, and Ag particles having sizes of approximately 2 and 10–20 nm are observed. The smaller Ag particles are situated in the mesopores, and the larger Ag particles are situated on the outer surfaces of m-SiO_2. ZrO_2 particles were not observed. Since for Zr/m-SiO_2, pore volume and specific surface area dramatically decreased to $102 cm^3 g^{-1}$ and $444 m^2 g^{-1}$, respectively, ZrO_2 presented both inside and outside of m-SiO_2, and part of the mesopores were blocked.[8] Figure 1b shows TEM photograph of Ag/Zr/m-SiO_2 after using for CB oxidation. The striped pattern of the mesopore channels of m-SiO_2 has partly disappeared, suggesting that the mesoporous structure in some parts of m-SiO_2 was destroyed by local heating during the CB oxidation reaction. Many 4–8-nm Ag particles were observed in the nonmesoporous area. Small Ag particles originally situated in the mesopore channels of fresh Ag/Zr/m-SiO_2 had migrated and were somewhat agglomerated, and
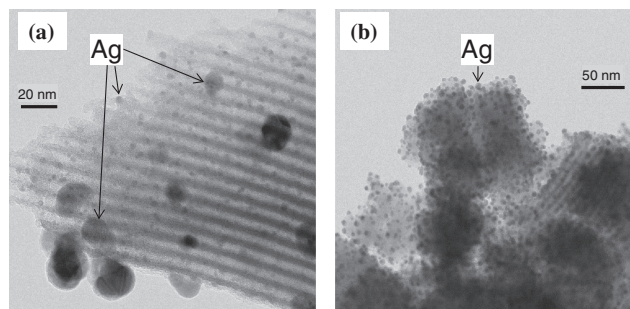

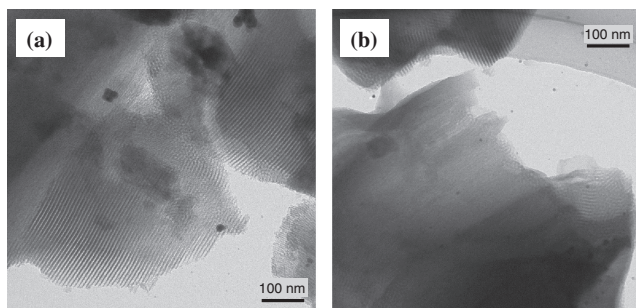**Figure 1.** TEM photograph of (a) fresh Ag/Zr/m-SiO_2 and (b) Ag/Zr/m-SiO_2 used in CB oxidation.

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Figure 2. TEM photograph of Ag/Zr/m-SiO$_2$ calcined at (a) 1073 and (b) 1173 K for 1 h.

Figure 3. Catalytic activity of Ag/Zr/m-SiO$_2$ for CB oxidation. The weights of the catalyst and CB in catalyst bed were 0.2 g and 2 mg, respectively. The flow rate was 300 mL min^{-1}. The feed gas was composed of 10% O$_2$ and 10% H$_2$O.

large Ag particles situated outside of channels were redispersed. Since another part of m-SiO$_2$ in the used catalyst maintains the mesoporous structure, the area exposed to high temperatures of exothermic reaction was limited. The broken area is suspected to be near the contact point with CB.

To estimate the temperature for the occurrence of destruction of the mesoporous structure, fresh Ag/Zr/m-SiO$_2$ was heated in air up to 1073 and 1173 K with a heating rate of 10 K min^{-1}, then kept at each temperature for 1 h. Figure 2 shows a TEM photographs of the calcined samples. At 1073 K, there is no indication of destruction (Figure 2a), but at 1173 K the striped pattern of the mesopore channel structure has mostly disappeared (Figure 2b). These results suggest that destruction of the mesoporous structure of m-SiO$_2$ starts in the range of 1073–1173 K. From these results, it is suggested that the local temperature reached more than 1073 K during CB oxidation.

Figure 3 shows the CO$_x$ (CO + CO$_2$) formation profile in a TPR experiment. Two peaks of CO$_x$ formation were observed. Since Ag/ZrO$_2$ demonstrated a high CB oxidation activity and Ag/SiO$_2$ a lower activity than Ag/ZrO$_2$,[9] CO$_x$ formations at the low and high temperatures were attributable to catalytic CB oxidation over Ag/ZrO$_2$ and Ag/m-SiO$_2$, respectively. The temperature of the catalyst bed was measured by the thermocouple, and the profile of deviation of the bed temperature from programmed-temperature is also shown in Figure 3. The bed temperature increased along with CO$_x$ formation. However, the increment of bed temperature was much lower than that expected from TEM observation.

Based on the fact that the specific heat of combustion of graphite is 393.5 kJ mol^{-1}, the calorific value of CB in the catalyst bed was estimated to be 65.6 J, and from the intensity of the peaks the calorific values of CO$_x$ formation at 650 and 750 K were estimated to be 42 and 24 J, respectively. Since the increment of catalyst bed temperature measured by thermocouple indicated the heating of both catalyst and feed gases, the calorific values for heating only catalyst were estimated to be 29 and 14 J, respectively. These calorific values correspond to the increment of total m-SiO$_2$ temperature by 142 and 61 K from 650 and 750 K, respectively. If the heat of combustion influences only contact point CB and its neighborhood, the temperature of the limited area should increase progressively. We estimated the
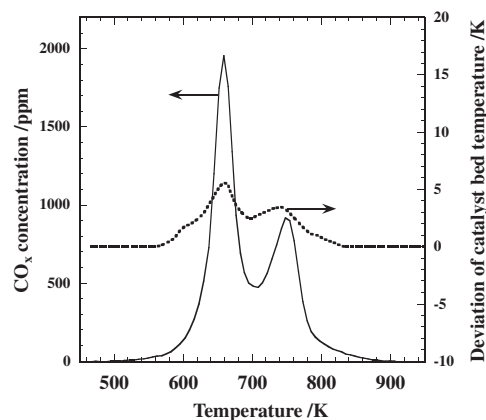
ratio of the limited area whose temperature can reach 1100 K by the calorific heat of CB oxidation. When approximately 31% and 18% of m-SiO$_2$ are adiabatically heated by the heat values of 29 and 14 J, the temperature of m-SiO$_2$ can rise to 1100 K from 650 and 750 K, respectively. This calculation agreed with the fact that the mesoporous structure of m-SiO$_2$ was partly destroyed. Therefore, it is impossible to detect local substantial heating by the thermocouple. In conclusion, we have obtained evidence that the local temperature reached 1073 K or more during CB oxidation.

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