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Soot Oxidation Activity of Ag/HZSM-5 (Si/Al=40) Catalyst

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Ag/HZSM-5 with Si/Al ratio of 40 was synthesized by the impregnation method. The catalyst materials were characterized by the X-ray diffraction and X-ray absorption spectroscopy by Ag-L_3 edge and Ag-K edge. Three different chemical states of Ag (ZO^-Ag^+, O^-Ag^+ and metallic Ag, here Z represents Si or Al) in the catalyst. The soot oxidation performance was evaluated by the TG-DTA measurement and showed two combustion stages in tight contact mode which indicates the intrinsic soot oxidation activity. This is because that a lot of Ag ion-exchanged with H ions and existed in the pores of HZSM-5 as ZO^-Ag^+, which cannot work for soot oxidation. Additionally, this catalyst has a high thermal stability even after high temperature program at 800 °C.

Keywords: Soot oxidation, Ag species, Catalyst.

1. Introduction

Diesel-engine vehicles are superior to gasoline-engine vehicles in combustion efficiency, fuel economy and emission of CO and CO_2 gases. However, the diesel engine produces more harmful substances of nitrogen oxides (NO_x) and particulate matter (PM) which mainly consists of soot and soluble organic fraction (SOF), compared to gasoline-engine vehicles[1-5]). PM, along with serious environmental and health problems, is one of the main pollutants in air for these two decades. Many researchers have focused on the development of the after-treatment systems for PM. Catalyzed diesel particulate filter (C-DPF), which not only traps the PM but also combusts them with catalyst at low temperatures, is commonly regarded as the most effective technology for reducing PM emission from diesel engines[6-8]). PM are directly combusted in the after treatment system with the presence of oxygen or NO_x, achieving the regeneration of the DPF.

Ag supported catalysts have the explicit advantage in low cost. They have been industrially used in the NO_x abatement[9,10]), carbon monoxide[11]), and organic volatile compounds[12]). For soot combustion, the activity of Ag supported catalysts is found to closely depend on the chemical state, particle size of silver and their dispersion on support. It has been identified that metallic silver is more active in soot oxidation compared to its oxidant. This is because on metallic Ag, the surface oxygen adsorption tends to generate various active oxygen species (O_n^{x-}) that efficiently promote the soot oxidation reactions[13-15]).

HZSM-5 zeolite is widely used as catalyst or support of catalyst for many chemical reactions, such as cracking of alkane[16-19]), dehydration of alcohol[20,21]), disposal of toxic gas[22-26]) and other chemical processes. Specially, the Bronsted acid sites on its pores are known to accommodate ion exchange for metal supported catalysts, yielding strong interactions between Ag and the acid sites (ZO^-Ag^+, Z represents Si or Al). These ion clusters ZO^-Ag^+ are well known as stable and highly-dispersed Ag species on the support[27,28]). However, the soot oxidation activity of Ag/HZSM-5 has not been well understood at present. In this research, we will investigate the soot oxidation activity of Ag/HZSM-5 catalyst with low Si/Al ratio (40) and discuss the correlation between soot oxidation activity and the chemical state of Ag species.

2. Experimental methods

H-type ZSM-5 (HZSM-5, Si/Al = 40, TOSOH Corporation) was selected as catalyst support. Ag/HZSM-5 were synthesized by an impregnation method. In this method, $AgNO_3$ (Kishida Chemical) was simply put into the aqueous solution that contains HZSM-5. The suspended solution was then evaporated under continuous stirring, leaving dark colored precipitates. The residuals were further baked at 350 ºC for 2 h, and calcined at 500 ºC for 5 h in air. The weight ratio of loaded Ag was optimized to be 4.5 wt %.

Commercially available carbon black with an average particle size of 5 µm (CB, Sigma-Aldrich) was used to be substitute for soot. To evaluate the soot combustion performance at differed contact conditions, mixtures of CB and Ag/HZSM-5 catalyst were prepared by grinding them in a mortar using pestle or spatula, which were referred as tight contact mixture (TC mode) and loose Hcontact one (LC mode), respectively.

The crystalline nature of the catalyst was studied by X-ray diffraction using Cu-Kα radiation (RINT2200, Rigaku Corporation). X-ray absorption spectroscopy (XAS) measurement were conducted at Kyushu University beamline (BL06) in SAGA-LS (Ag L_3-edge) and at BL14B2 in SPring-8 (Ag K-edge). The spectra were recorded at room temperature in fluorescence mode for Ag L_3-edge and transmission mode for Ag K-edge, respectively. The data processing was analyzed using ATHENA and ARTEMIS, a suite of IFEFFIT software programs[29)].

The CB oxidation with prepared Ag/HZSM-5 catalysts were evaluated by a Thermogravimetry–Differential Thermal Analysis system (TG-DTA, STA7300, Hitachi High-Tech Science Corporation) under synthetic air (21 vol. % O_2 and 79 vol. % N_2, 100 ml min^{-1}) using a heating rate of 10 ºC min^{-1} from 30 to 800 ºC. Before the measurement, the catalyst and CB mixtures were preheated at 120 ºC for 1 h to remove the adsorbed water.

3. Results and discussions

The as-prepared Ag/HZSM-5 catalyst shows no diffraction peaks related to Ag, as shown in Fig. 1. This indicates that Ag exists as non-crystalline and highly dispersed particles. In order to understand the chemical state of Ag species in Ag/HZSM-5, Ag-L_3 edge XANES spectra of Ag/HZSM-5 was collected by XAS measurement as shown in Fig. 2. The XANES spectra of as-prepared Ag/HZSM-5 is different from those of Ag foil, Ag_2O and AgO. The edge peak around 3352 eV of as-prepared Ag/HZSM-5 corresponds to the typical peaks of Ag^+ species in Ag/HZSM-5 by previous report[30)]. HZSM-5 and Ag cations would preferentially form at the Bronsted acid sites as ZO^-Ag^+. This is because there is a large amount of Bronsted acid sites in this Si/Al ratio (40) HZSM-5. Therefore, it is inferred that the Ag ions in Ag/HZSM-5 are mainly originated from the exchange with H^+ in HZSM-5.

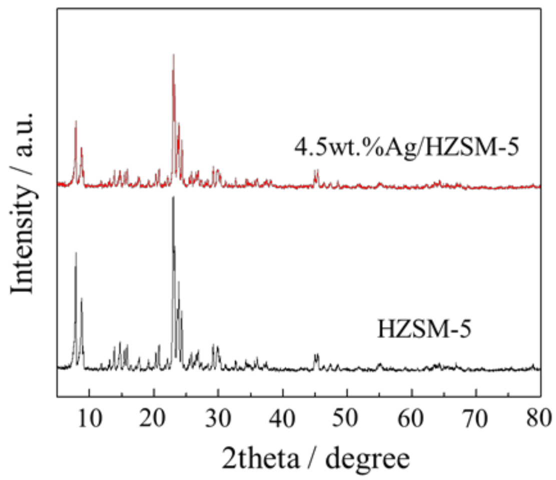

Fig. 1: Diffraction patterns of HZSM-5 and as-prepared Ag/HZSM-5 catalyst.

Here, in order to understand the local structure of Ag in Ag/HZSM-5 clearly, we analyzed the Ag-K edge EXAFS spectra. Fig. 3 shows the corresponding k^3–weighted EXAFS spectra after Fourier transformation of them (k-range of 3.0 to 11.0). The three shell model with Ag-Ag bond and two (short and long) Ag-O bonds was frequently used for ion-exchanged Ag-zeolite materials. When our EXAFS data were investigated with the three shell model, the fitting procedure was successful and the refinement parameters are indicated in Table 1. The bond distance of Ag-Ag in Ag/HZSM-5 was situated at 2.86 Å which is longer than that of Ag foil (2.7 Å), suggesting Ag-Ag bond of Ag/HZSM-5 is weaker than that of Ag foil. Furthermore, the bond distance of Ag-O_1 and Ag-O_2 in Ag/HZSM-5 was situated at 2.27 Å and 2.45 Å, respectively. These results clearly indicated the presence of two kind of Ag-O bonds, originating from the Ag^+ ion-exchange with the Bronsted acid sites of HZSM-5 itself and the OH groups absorbed on the surface of catalyst, denoted as ZO^-Ag^+ and O^-Ag^+, respectively, weaker than that of Ag foil. Furthermore,

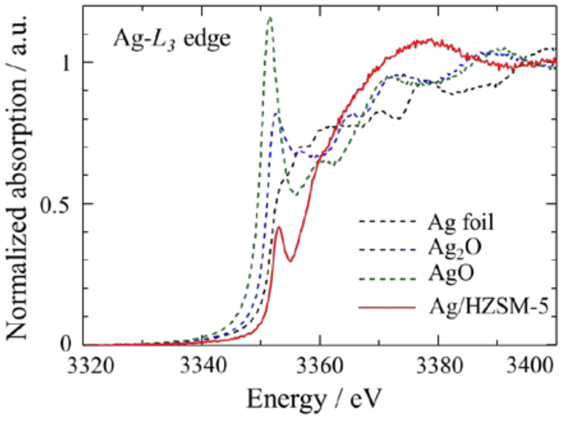

Fig. 2: Comparison of Ag-L_3 edge XANES spectra of Ag foil, Ag_2O, AgO and Ag/HZSM-5.

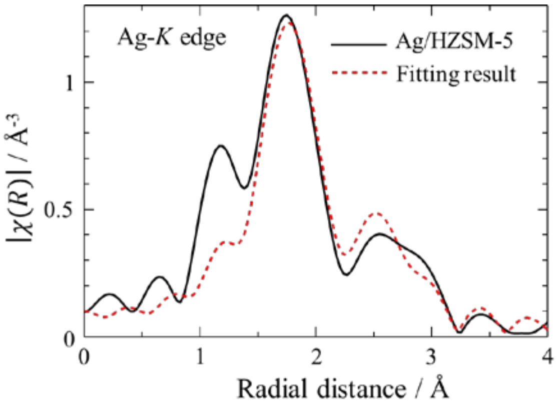

Fig. 3: Fourier transformed K^2–weighted Ag-*K* edge EXAFS spectra of them in Ag/HZSM-5.

the bond distance of Ag-O_1 and Ag-O_2 in Ag/HZSM-5 was situated at 2.27 Å and 2.45 Å, respectively. These results clearly indicated the presence of two kind of Ag-O bonds, originating from the Ag^+ ion-exchange with the Bronsted acid sites of HZSM-5 itself and the OH groups absorbed on the surface of catalyst, denoted as ZO^-Ag^+ and O^-Ag^+, respectively.

To examine the soot oxidation activity of Ag/HZSM-5 catalysts, we conducted the TG-DTA measurements of the mixture of CB and Ag/HZSM-5 in TC mode and LC mode at the temperature range from 30 °C to 800 °C, as shown in Fig. 4. In TC mode, the weight loss of mixture, which corresponds the CB oxidation, processed in two steps and started at around 300 °C and 500 °C (ignition temperature, denoted as T_{ig}). Moreover, the maximum heat-release temperature of CB oxidation was at 404 °C and 630 °C (peak temperature of DTA curves, denoted as T_{max} hereafter). The higher exothermal peak (630 °C) is inferred as the spontaneous combustion of the CB with free-catalyst. On the other hand, in LC mode, the weight loss of mixture processed in one step. The T_{ig} and the T_{max} are around 400 °C and 640 °C, respectively. This exothermal peak of 640 °C (T_{max}) is also inferred as the spontaneous oxidation of the CB with free-catalyst.

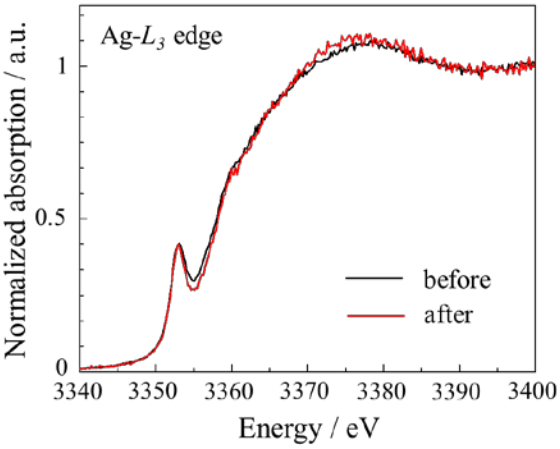

Fig. 4: TG-DTA curves of the mixture of CB and Ag/HZSM-5 in TC mode and LC mode

These results suggest that Ag in HZSM-5 zeolite acts the active species for the CB oxidation. In this catalyst, a lot of Ag ions exchange with the Bronsted acid sites of HZSM-5 and exist in the pores of HZSM-5. And the Ag ions existed in the pores of the HZSM-5 are difficult to work as active species for the CB oxidation since most of Ag cannot contact with the CB, resulting in a huge reduction of the contact points between the CB and the Ag active species. So it is thought that just a few Ag active species on the surface of HZSM-5 could produce the CB oxidation. Therefore, the spontaneous oxidation of the CB with free-catalyst occurred in TC mode as well as LC mode which indicates the non-contact oxidation with catalysts.

The change of chemical state of Ag before and after the CB oxidation was also investigated by XAS measurement, as shown in Fig. 5. There are no obvious difference of Ag L_3-XANES spectra before and after the CB oxidation till 800 °C. This result suggests that Ag species in Ag/HZSM-5 have no change and the

Table 1: Fourier transformed K^2–weighted Ag-*K* edge EXAFS spectra of them Ag/HZSM-5.

Sample	Scattering path a)	*N* b)	*R* c) / Å	σ^2 d) / Å^2	ΔE_0 e) / eV	R_f f) / %
Ag-840	Ag-O_1	0.96	2.290	0.0319	5.9	1.4
	Ag-Ag	0.45	2.866	0.0093	1.2	
	Ag-O_2	0.78	2.475	0.0319	5.9	

*fixed value

a) Amplitude reduction factor for all paths are fixed to be the value for Ag-Ag single scattering.

b) Coordination number, c) bond distance, d) Debye-Waller factor, e) Edge shift (E_0 = 25476 eV),

f) Residual factor denoted as $100\times\sqrt{\frac{\sum\left(k^2\chi_{obs}-k^2\chi_{calc}\right)^2}{\left(k^2\chi_{obs}\right)^2}}$, where χ_{obs} and χ_{calc} indicates the experimentally measured EXAFS oscillation and theoretically calculated one, respectively.

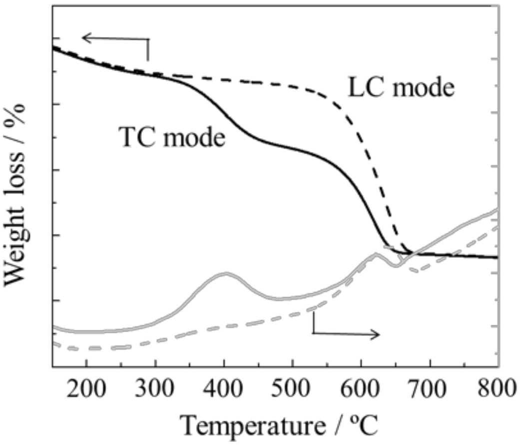

Fig. 5: Difference of chemical state of Ag in Ag/HZSM-5 between before and after the CB oxidation.

interaction between Ag and HZSM-5 is kept even after the CB oxidation. Therefore, it is suggested that the Ag/HZSM-5 catalyst has a high stability for soot oxidation.

4. Conclusion

In this research, we discussed the soot oxidation activity with the Ag/HZSM-5 catalysts (Si/Al = 40). Three kind of chemical states of Ag (ZO^-Ag^+, O^-Ag^+ and metallic Ag) were formed in this Ag/HZSM-5 catalyst. A large amount of Ag ions exchanged with the Bronsted acid sites of HZSM-5, existing inside the pores of HZSM-5 as ZO^-Ag^+ which almost has no contribution for soot oxidation. And it is thought that just a few metallic Ag are dispersed on the surface of the HZSM-5 support, which are the active species for the soot oxidation. Furthermore, the chemical state of Ag in Ag/HZSM-5 do not change even after the CB oxidation.

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