Supporting Information

Soot oxidation performance with HZSM-5 supported Ag nanoparticles catalyst and the characterization of Ag species

Hongcheng Ruan¹⁾, Maiko Nishibori¹⁾*, Tomoki Uchiyama²⁾, Kakeru Ninomiya¹⁾, Kazutaka Kamitani³⁾, Kazuo Kato²⁾, Yuko Konishi³⁾, Alexander Haensch⁴⁾, Nicolae Barsan⁴⁾, Udo Weimar⁴⁾ and Kengo Shimanoe¹⁾

1) Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan

2) Japan Synchrotron radiation Research Institute, SPring-8, Sayo, Hyogo, 679-5198, Japan

 Institute for Materials Chemistry and Engineering, Kyushu University, Motooka, Nishi-ku, Fukuoka 819-0395, Japan

4) Institute of Physical Chemistry, University of Tuebingen, Tuebingen D-72076, Germany

List of Figures and Tables

Fig. S1. SEM image (a) and DRIFTs (b) of carbon black at room temperature.

Fig. S2. EDS mapping of different elements of Ag/HZSM-5.

Fig. S3. Schematic of Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs).

Fig. S4. DRIFTs spectra of HZSM-5 (red line) and Ag/HZSM-5 (green line) at room temperature.

Fig. S5. TG-DTA curves of the soot combustion with x Ag/HZSM-5 catalysts in TC and LC modes, respectively, 2% (a), 4.5% (b) and 8% (c).

Fig. S6. In-situ DRIFTs spectra of soot oxidation with 4.5% Ag/HZSM-5 with increasing temperature. All the spectra were divided by the spectrum measured at 149 °C.

Fig. S7. STEM images and size distribution of Ag particles of Ag/HZSM-5 after high temperature (800 °C) treatment.

Fig. S8. In-situ Ag K–edge absorption XANES spectra after normalization for M-TC (a) and M-LC (b) from 25 °C to 250 °C.

 Table S1. Infrared parameters of various modes of HZSM-5.

Table S2. Catalytic performances for soot combustion with catalysts x Ag/HZSM-5 for M-TC and M-LC.

Table S3. Catalytic performance for soot oxidation with various catalysts published already.



Fig. S1. SEM image (a) and DRIFTs (b) of carbon black at room temperature.



Fig. S2. EDS mapping of different elements of Ag/HZSM-5.



Fig. S3. Schematic of Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs).

Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFTs) measurements were performed on an EQUINOX 55 (Bruker, Germany) equipped with a liquid nitrogen cooled MCT detector. N₂ (99.99% purity) is used as chamber blowing gas at a rate of 100 ml/min. Ex-situ DRIFTs spectra were collected at 25 °C in the flowing N₂, the samples were kept in the flowing N₂ for 30 min as a pretreatment at 25 °C. In-situ DRIFTs spectra were collected from 150 to 375 °C with an interval of 1 °C in a sub-chamber with flowing synthetic air (100 ml/min), the temperature was increased at the rate of 1 °C /min and kept at 375 °C for 2 h. The samples were conducted in the synthetic air at 50 °C for 2 h as a pretreatment before measuring. All of the spectra, determined at a resolution of 4 cm⁻¹, were analyzed by OPUS (Bruker, Germany) software.



Fig. S4. DRIFTs spectra of HZSM-5 (red line) and Ag /HZSM-5 (green line) at room temperature.

 Table S1. Infrared parameters of various modes of HZSM-5.

HSZ891HOA(Si/Al= 1500)			
Wavenumbers (cm ⁻¹)	Modes ¹⁻⁵		
3738	Si-OH located at the external surface		
3682	γ(OH)		
3330	H-bonded OH group		
2975	v(CH)		
1996, 1881	lattice vibrations		
1642	δ(HOH)		
1369	δ(OH)		
1217, 811	External linkages between tetrahedral		
1077	Internal vibrations of [Si, Al]O ₄		



Fig. S5. TG-DTA curves of the soot combustion with x Ag/HZSM-5 catalysts in TC and LC modes, (a) 2%, (b) 4.5% and (c) 8%.



Fig. S6. In-situ DRIFTs spectra of soot oxidation with 4.5% Ag/HZSM-5 with increasing temperature. All the spectra were divided by the spectrum measured at 149 °C.



Fig. S7. STEM images and size distribution of Ag particles of Ag/HZSM-5 after high

temperature (800 °C) treatment.



Fig. 8. In-situ Ag K–edge absorption XANES spectra after normalization for M-TC (a) and M-LC (b) from 25 °C to 250 °C.

Table S2. Catalytic performances for soot combustion with catalysts x Ag /HZSM-5 for M
TC and M-LC.

	CB oxidation performance (°C) ^b			
Catalysts xAg/HZSM-5 ^a	M-TC		M-L	.C
	T _{ig}	T _{max}	T _{ig}	T _{max}
2%	308	414	357	534
4.5%	300	366	339	533
8%	307	379	347	563

^a x is the weight percentage of silver in catalyst Ag/HZSM-5; ^b Definition of T_{ig} (ignition temperature of soot combustion) and T_{max} (peak temperature of DTA curves);

Catalysts	Experimental method	T _{so} (°C)	comments	Ref.
$\begin{array}{c} \text{Ag/CeO}_2, \text{Ag/ZrO}_2, \\ \text{Ag/Al}_2\text{O}_3 \\ (1\text{-10 wt\%}) \end{array}$	IW impregnation, Cal. 500 °C for 3 h	334–345 °C (T ₅₀ in TC mode) ^a , 460–436 °C (T ₅₀ in LC mode),	Soot /cata.=1 : 20, T ₅₀ (50% of weight loss)	6
Cu/Mn–Ce mixed oxides	sol–gel method Cal. 500 °C for 3 h	356–390 °C (T _{max} in TC mode) ^b , 503–553 °C (T _{max} in LC mode),	Soot /cata.=1 : 10, T_m (max oxidation rate temp.)	7
$Pt/MO_{x} (MO_{x} = TiO_{2}, ZrO_{2}, Al_{2}O_{3})$	IW impregnation, Cal. 400-600 °C for 3 h.	410–540 °C (T ₅₀) ^b ,	Soot /cata.=1 : 20, T_{50} (50% of weight loss)	8
Ag-loaded sepiolite– Zr–K–O	IW impregnation, Cal. 600 °C for 1 h.	490 °C (T ₅₀ in TC mode) ^a ,	Soot /cata.=1 : 5, T ₅₀ (peak temp. of DTA curve)	9
Ag(1-15 wt%)/perovskite	impregnation, Cal. 500 °C for 4 h.	398–493 °C (T ₅₀) ^b ,	Soot /cata.=1 : 10 T_{50} (50% conversion rate of soot)	10
ZSM5, PtZSM5, PtA1	IW impregnation, Cal. 500-585 °C for 2 h	440–563 °C (T ₅₀) ^b ,	Soot /cata.=1 : 10	11
perovskite	Electrospinning technique, Cal. 800 °C for 6 h	490–505 °C (T _{max, L}), 585–597 °C (T _{max, H}), LC mode ^a	Soot /cata.=1 : 19	12
Co, K and/or Ba supported on MgO, La_2O_3 and CeO_2	impregnation, Cal. 400 °C and 700 °C for 4 h	350–400 °C (T _{max}) ^b	Soot /cata.=1 : 20,	13
Ag-CeO ₂	Co-precipitation method, Cal. 500 °C for 5 h.	315–480 °C (T _{max} in TC mode), 376–596 °C (T _{max} in LC mode) ^b ,	Soot /cata.=1 : 19,	14
Ag/HZSM-5	impregnation, Cal. 500 °C for 5 h	366 °C (T _{max} in TC mode), 533 °C (T _{max} in LC mode) ^a ,	Soot /cata.=1 : 19	this work

 Table S3. Catalytic performance for soot oxidation with various catalysts published already.

MnO _x -CeO ₂	Citric acid complex	299–387 °C	Soot /cata.=1 : 9.	15
	method. Cal. 550 °C for 5 h	(T _{CO2} , max in LC mode) ^a	Two types O-vacancies favored to the migration and transformation of active species	
Manganese oxide (MnO ₂ , Mn ₂ O ₃ and Mn ₃ O ₄)	Commercially obtained or FSP method	305–390 °C (T _{CO2, max} in LC mode) ^a	A strong contribution of bulk oxygen (ca. 60%) occurred for tight as well as loose contact.	16
MnCeO	Hydrothermal method, impregnation method	MnO_x/CeO_2 nanorod 317 °C (T ₅₀ in TC mode) ^a	MnO _x /CeO ₂ nanorods exhibits better catalytic activity due to its larger surface area and higher oxygen release rate	17
Ag/CexNd _{1-x} O ₂	Hydrothermal method,	394–458 °C (T _{CO2, max} in LC mode) ^a	Soot /cata.=1 : 10, Introduction of Nd can lower soot oxidation activity but improve the catalysts' thermal stability effectively	18
Co-CeO ₂	Sol-gel method.	335 °C (without H ₂ O, T _{CO2,} max in TC mode) ^a , 310 °C (with H ₂ O, T _{CO2,} max in TC mode) ^a	Co in Co-Ce- O_x can improve its catalytic activity for NO oxidation. Ce in Co-Ce- O_x can promote its capacity for NO ₂ storage.	19

^a Temperature of soot oxidation measured by temperature programmed combustion; ^b Temperature of soot oxidation measured by thermogravimetric methods.

References

(1) F. Wakabayashi, J. Phys. Chem., 1996, 100, 1442-1444.

(2) I. O. Ali, M. S. Thabet, K. S. El-Nasser, A. M. Hassan, T. M. Salama, *Microporous Mesoporous Mater.*, 2012, **160**, 97–105.

- (3) K. Hadjiivanov, J. Saussey, J. L. Freysz, J. C. Lavalley, Catal. Lett., 1998, 52, 103–108.
- (4) M. Mhamdi, S. Khaddar-Zine, A. Ghorbel, Appl. Catal., A, 2009, 357, 42-50.
- (5) A. Kudasheva, S. Sorribas, B. Zornoza, C. Téllez, J. Coronas, J. Chem. Technol. Biotechnol., 2015, 90, 669–677.
- (6) E. Aneggi, J. Llorca, C. D. Leitenburg, G. Dolcetti, A. Trovarelli, *Appl. Catal. B*, 2009, **91**, 489–498.
- (7) Q. Liang, X. D. Wu, D. Weng, H. B. Xu, Catal. Today, 2008, 139, 113–118.
- (8) J. Oi-Uchisawa, A. Obuchi, R. Enomoto, J. Y. Xu, T. Nanba, S. T. Liu, S. Kushiyama, *Appl. Catal.*, B 2001, **32**, 257–268.
- (9) N. Güngör, S. Işçi, E. Günister, W. Miśta, H. Teterycz, R. Klimkiewicz, Appl. Clay Sci., 2006, 32, 291–296.
- (10) Z. M. Liu, Z. P. Hao, H. P. Zhang, Y. H. Zhuang, J. Chem. Technol. Biotechnol., 2002, 77, 800–804.
- (11) S. Liu, X. D. Wu, D. Weng, M. Li, R. Ran, ACS Catal., 2015, 5, 909-919.
- (12) C. Lee, Y. Jeon, S. Hata, J. Park, R. Akiyoshi, H. Saito, Y. Teraoka, Y. J. Shul, H. Einaga, *Appl. Catal., B*, 2016, **191**, 157–164.

- (13) M. L. Pisarello, V. Milt, M. A. Peralta, C. A. Querini, E. E. Miró, *Catal. Today*, 2002, **75**, 465–470.
- (14) K. Yamazaki, T. Kayama, F. Dong, H. Shinjoh, J. Catal., 2011, 282, 289-298.
- (15) X. T. Lin, S. J. Li, H. He, Z. Wu, J. L. Wu, L. M. Chen, D. Q. Ye, M. J. Fu, *Appl. Catal., B*, **2017**, *in press*.
- (16) S. Wagloehner, M. Nitzer-Noski, S. Kureti, Chem. Eng. J. 2015, 259, 492-504.
- (17) K. Mori, Y. Miyauchi, Y. Kuwahara, H. Yamashita, Bull. Chem. Soc. Jpn., 2017, 90, 556–564.
- (18) Y. X. Gao, A. Q. Duan, S. Liu, X. D. Wu, W. Liu, M. Li, S. G. Chen, X. Wang, D. Weng, *Appl. Catal.*, *B*, 2017, **203**, 116–126.
- (19) J. N. Xu, G. Z. Lu, Y. Guo, Y. L. Guo, X. Q. Gong, Appl. Catal., A 2017, 535, 1-8.