Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2020

Supplementary Material

*

Tuning the Oxygen Release Property of CeO₂-based Catalysts by Metal–Support Interactions for Improved Gasoline Soot Combustion

Ryota Ashikaga, ^a Kazumasa Murata, ^{a, *} Tetsuya Ito, ^a Yuta Yamamoto, ^b Shigeo Arai ^b and Atsushi Satsuma^a,

^aGraduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

^bInstitute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-8603, Japan

*Kazumasa Murata: murata.kazumasa@e.mbox.nagoya-u.ac.jp.

*Atsushi Satsuma: satsuma@chembio.nagoya-u.ac.jp.

Catalyst	Catalytic activity / °C	Catalyst:soot weight ratio	Contact mode	Reaction gas
5wt% Cu/CeO2this work	T ₁₀ / 263	10:1	tight	0.5% O ₂ /N ₂
5wt% Rh/CeO2this work	T ₁₀ / 265	10:1	tight	$0.5\% O_2/N_2$
5wt% Ag/CeO ₂ 1	T ₁₀ / 525	4:1	loose	1% O ₂ /N ₂
La _{0.6} Sr _{0.4} MnO ₃ perovskite ²	T ₅ / 427	4:1	tight	1% O ₂ /He
5wt% Ag/CeO ₂ ³	T ₅₀ / 333	20:1	tight	6% O ₂ /N ₂
4.5wt% Ag/CeO2 nanofibers4	T_{ig} / 292	19:1	tight	21% O ₂ /He

 $T_{\text{ig}} :$ Temperature at which the soot combustion begins.

Table S2. H₂ consumption (50–250 °C) of CeO₂ and Cu-based catalysts.

, =	5
Catalyst	$\rm H_2$ consumption (50–250 °C) / mmol g $^{-1}$
CeO ₂	0
Cu/SiO ₂	0.32
CuO+CeO ₂	0.36
Cu/CeO ₂	$0.44^a, 1.1^b$

^alow-temperature reduction peak at 84 °C, ^bhigh-temperature reduction peak at 148 °C.

Catalyst	H ₂ consumption (< 550 °C) ^{<i>a</i>} / mmol g ⁻¹	Reduction reaction of the supported metal	H_2 consumption of the supported metal ^b / mmol g ⁻¹	H_2 consumption of $CeO_2{}^c$ / mmol g ⁻¹
CeO ₂	0.19	_	_	_
Mn/CeO ₂	0.37	$1/2Mn^{+3}{}_{2}O_{3} + 1/2H_{2}$	0.46	-0.09
		$\rightarrow Mn^{+2}O + 1/2H_2O$	0.40	
Fe/CeO ₂	0.95	$1/2Fe^{+3}2O_3 + 1/6H_2$	0.15	0.80
		$\rightarrow 1/3Fe^{+2}Fe^{+3}_{2}O_{4} + 1/6H_{2}O_{4}$	0.15	
Co/CeO ₂	1.77	$1/3Co^{+2}Co^{+3}{}_{2}O_{4} + 4/3H_{2}$	1 12	0.64
		$\rightarrow Co^0 + 4/3H_2O$	1.13	
Ni/CeO ₂	1.30	$Ni^{+2}O + H_2$	0.85	0.45
		$\rightarrow Ni^0 + H_2O$	0.85	
Cu/CeO ₂	1.54	$Cu^{+2}O + H_2$	0.70	0.85
		$\rightarrow Cu^0 + H_2O$	0.79	
Rh/CeO ₂	0.64	$1/2Rh^{+3}{}_{2}O_{3} + 3/2H_{2}$	0.73	-0.09
		$\rightarrow Rh^0 + 3/2H_2O$	0.75	
Pd/CeO ₂	0.51	$Pd^{+2}O + H_2$	0.47	0.04
		$\rightarrow Pd^0 + H_2O$	0.47	
Ag/CeO ₂	0.19	$1/2Ag^{+}_{2}O + 1/2H_{2}$	0.22	-0.04
		$\rightarrow Ag^0 + 1/2H_2O$	0.23	

Table	\$3	H ₂	consumption	of M/CeOa
1 and	33.	112	consumption	$OI WI/CCO_2$.

^{*a*} Calculated by integrating of the reduction peak (< 550 °C).

^{*b*} Theoretical value calculated based on assumptions that the supported metal species was reduced according to the reduction reaction equation. It is reported that Mn^5 and Fe⁶ oxide species are not reduced to metal below 550 °C.

^c Calculated by subtracting (b) from (a). Positive values indicate that the reduction from CeO₂ occurs below 550 °C.



Figure S1. TEM image of the model soot (PrintexV).



Figure S2. (a) Mn 2p, (b) Fe 2p, (c) Co 2p, (d) Ni 2p, (e) Cu 2p, (f) Rh 3d, (g) Pd 3d, and (h) Ag 3d XPS spectra of asprepared M/CeO₂.



Figure S3. (a) Ce 3d and (b) O 1s XPS spectra of as-prepared M/CeO₂.



Figure S4. TEM image of as-prepared Cu/CeO₂ catalyst.



Figure S5. Low-magnification STEM-EDX mapping images of as-prepared (a) Rh/CeO₂, (b) Pd/CeO₂, and (c) Ag/CeO₂. Red: Rh, Pd, and Ag, Blue: Ce. High-magnification images (Figure 2) are taken in the white frame.



Figure S6. Raman spectra of as-prepared M/CeO₂.



Figure S7. (a) Soot conversion versus temperature and (b) T_{10} values for M/CeO₂ under 10% O₂/N₂.



Figure S8. (a) Soot conversion versus temperature and (b) T_{10} values for M/SiO₂ under 0.5% O₂/N₂.

XAFS measurement

The structure and oxidation sate of Cu species on Cu/CeO₂ were investigated by Cu K-edge XAFS measurement. Figure S9 shows the Cu K-edge XANES spectra and the fourier transformed (FT)-EXAFS spectra of Cu/CeO₂ after each treatment and Cu reference compounds. Since Cu/CeO₂ showed the two reduction peaks at 84 °C and 148 °C in H₂-TPR (Figure S6), Cu/CeO₂ was reduced by H₂ at 100 °C and 200 °C. The Cu K-edge XANES spectra clearly demonstrate the presence of Cu²⁺ species in Cu/CeO₂ (Fresh). The Cu K-edge FT-EXAFS spectra exhibited the peaks due to Cu–O contribution at 1.5 Å and due to Cu–Cu in copper oxide contribution at 2.5 Å. The intensity of peak due to the Cu-Cu contribution of Cu/CeO₂ (Fresh) was lower than that of the reference CuO. Thus, Cu species on Cu/CeO₂ exist as small CuO_x clusters, which is consistent with XRD, STEM-EDX, and Raman results. The Cu K-edge XANES spectra of Cu/CeO₂ (Red. 100 °C) showed no change compared to Cu/CeO₂ (Fresh). On the other hand, Cu species on Cu/CeO₂ (Red. 200 °C) were reduced to metallic Cu. It was indicated that the reduction of Cu²⁺ species occurred mainly at 100–200 °C.



Figure S9. Cu K-edge (a) XANES and (b) FT-EXAFS spectra of Cu/CeO₂. Fresh: as-prepared, Red. 100 and 200 °C: after H₂ reduction at 100 and 200 °C.

The oxidation state of Ce was also investigated by Ce L_{III} -edge XAFS measurement. Figure S8 shows the Ce L_{III} -edge XANES spectra and FT-EXAFS spectra of Cu/CeO₂ after the reduction at 100 °C or 200 °C and Ce reference compounds. As the reduction temperature increased, the broad peak at 5720–5730 eV in Ce L_{III} -edge XANES spectra of Cu/CeO₂ shifted to lower energies. By linear combination fitting (LCF) analysis, the ratios of reduced Ce were estimated to be 1.2% at 100 °C (Red. 100 °C) and 3.2% at 200 °C (Red. 200 °C). In the Ce L_{III} -edge EXAFS spectra, the intensity of the peak due to the first shell of Ce–O contribution at 1.9 Å was also lower. This means that oxygen was released from CeO₂ surface as the reduction temperature increased, i.e., a part of Ce⁴⁺ was reduced to Ce³⁺.



Figure S10. Ce L_{III} -edge (a) XANES and (b) FT-EXAFS spectra of Cu/CeO₂. Fresh: as-prepared, Red. 100 and 200 °C: after H₂ reduction at 100 and 200 °C.



Figure S11. Relationship between soot combustion activity under $0.5\% O_2/N_2$ and BET surface area of M/CeO₂.



Figure S12. Weight change of Cu/CeO₂ under switching a flowing gas between 5% H_2/N_2 and 10% O_2/N_2 at 300°C.



Figure S13. Relationship between soot combustion activity under 0.5% O_2/N_2 and OSC of M/CeO₂. The coefficient of determination $R^2 = 0.67$.



Figure S14. Relationship between soot combustion activity under 10% O_2/N_2 and oxygen release rate of M/CeO₂. The coefficient of determination $R^2 = 0.69$.



Figure S15. H₂-TPR profiles of M/CeO₂.



Figure S16. Raman spectra of M/CeO2 after H2 reduction at 300 °C



Figure S17. Relationship between peak temperature of H₂-TPR and metal–oxygen bond energy.

References

- 1 S. Wu, Y. Yang, C. Lu, Y. Ma, S. Yuan and G. Qian, *Eur. J. Inorg. Chem.*, 2018, 2018, 2944–2951.
- 2 W. Y. Hernández, M. N. Tsampas, C. Zhao, A. Boreave, F. Bosselet and P. Vernoux, *Catal. Today*, 2015, 258, 525–534.
- E. Aneggi, J. Llorca, C. de Leitenburg, G. Dolcetti and A. Trovarelli, *Appl. Catal. B Environ.*, 2009, **91**, 489–498.
- 4 C. Lee, J. Il Park, Y. G. Shul, H. Einaga and Y. Teraoka, *Appl. Catal. B Environ.*, 2015, **174–175**, 185–192.
- 5 L. Xing, Y. Yang, C. Cao, D. Zhao, Z. Gao, W. Ren, Y. Tian, T. Ding and X. Li, *ACS Sustain. Chem. Eng.*, 2018, **6**, 16544–16554.
- 6 Z. Zhang, D. Han, S. Wei and Y. Zhang, J. Catal., 2010, 276, 16–23.