Advanced Automotive Three Way Catalysts via Solvothermal Reactions

Tsugio Sato, Shu Yin
Institute of Multidisciplinary Research for Advanced Materials,
Tohoku University, Sendai 980-8577, Japan

CONTENTS

- Ceria-based mixed oxides for automobile exhaust gas cleanup
- Tin oxide-based mixed oxides for automobile exhaust gas cleanup

Improvement of OSC of CeO_2 by doping with metal ion

$$CeO_2 \rightleftharpoons Ce^{4+}_{1-x}\, Ce^{3+}_{x}\, O_{2-x/2}\, \square_{x/2} + x/4\, O_2$$

The ideal $r(M^{n+})/r(O^{2-})$ ionic size ratio of MO_8 = 0.732

In the case of fluorite structure ceria: $r(Ce^{4+})/r(O^{2-})$ = 0.703

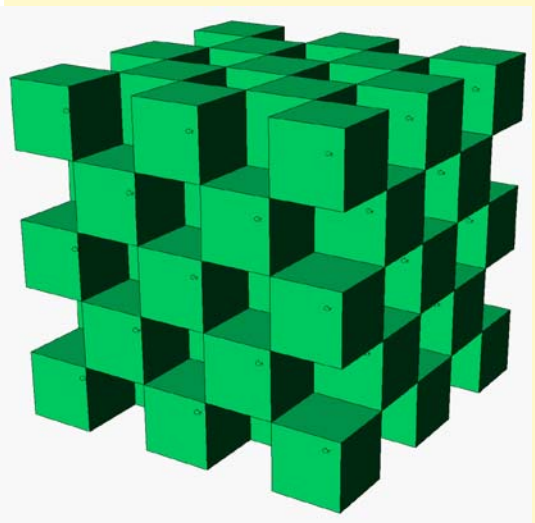
↓

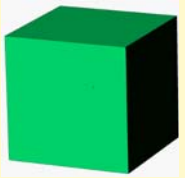
Ce^{4+} is not large enough to stabilize the fluorite structure

↓

Improve the OSC by doping with metal ion smaller than Ce^{4+}

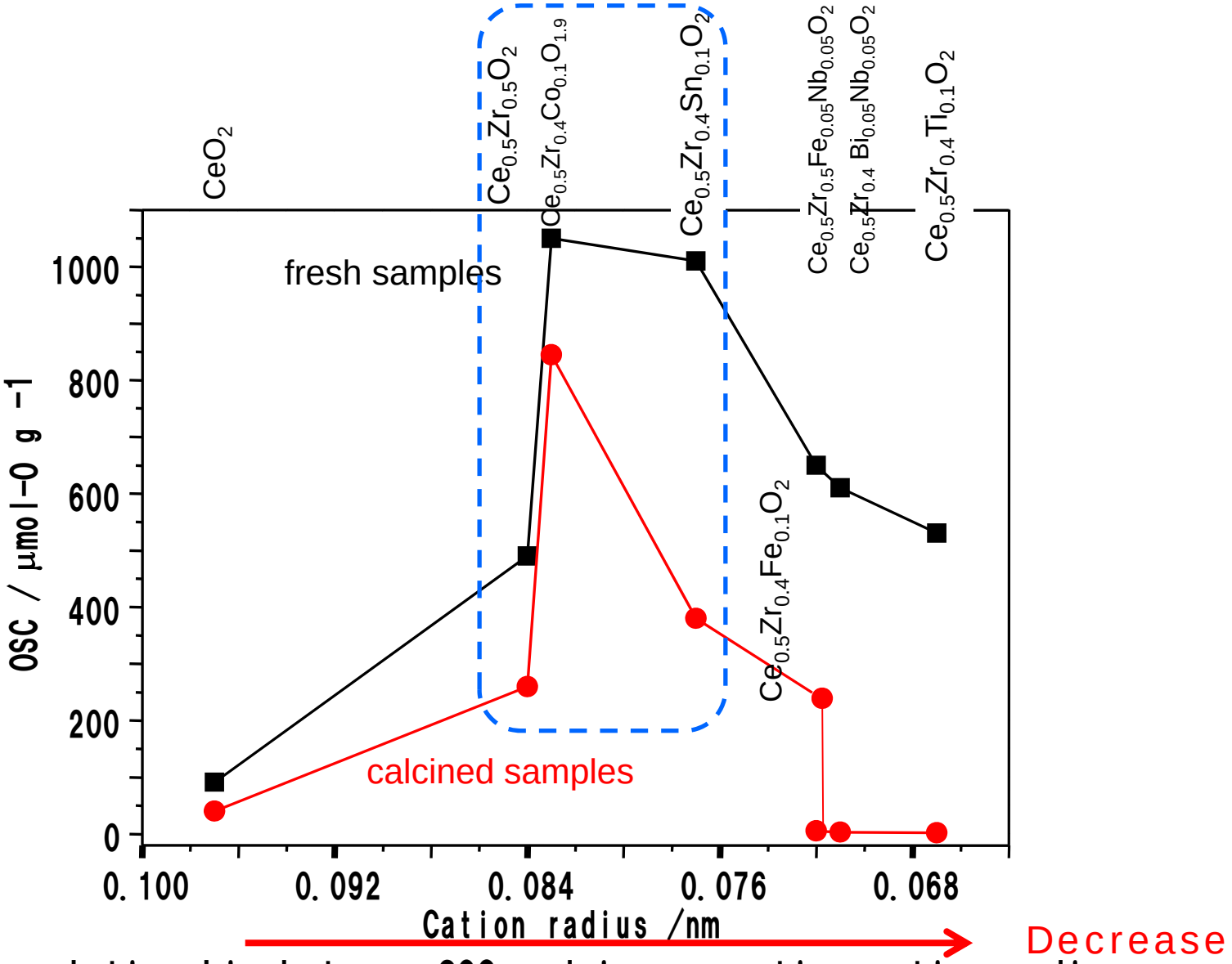
8 cordination ion size (nm)		of various metal ions	
Ce^{4+}	0.097	Ti^{4+}	0.067
Zr^{4+}	0.084	Sn^{4+}	0.077
Ca^{2+}	0.112	Nb^{5+}	0.071
Fe^{3+}	0.072	Bi^{3+}	0.071
Al^{3+}	0.059		





: CeO_8

Crystal structure of CeO_2



The relationship between OSC and incorporating cation radius

Cation radius (nm): Ce^{4+} (0.097) > Zr^{4+} (0.084) > Co^{2+} (0.083) > Sn^{4+} (0.077) > Fe^{3+} (0.072) ≧ Nb^{5+} (0.071) = Bi^{3+} (0.071) > Ti^{4+} (0.067)

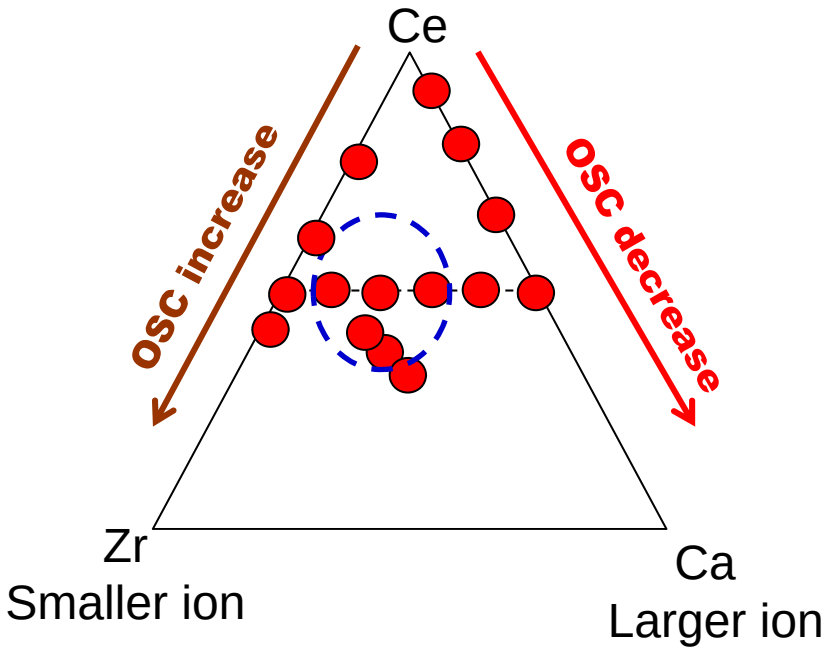
CeO_2-ZrO_2-CaO

$(NH_4)_2Ce(NO_3)_6$: 15 mmol
$ZrO(NO_3)_2$: x mol
$Ca(NO_3)_2$: y mol
H_2O: 60 ml
Conc. NH_3 aq.: 1.5 ml

Heating
at 220°C、24h

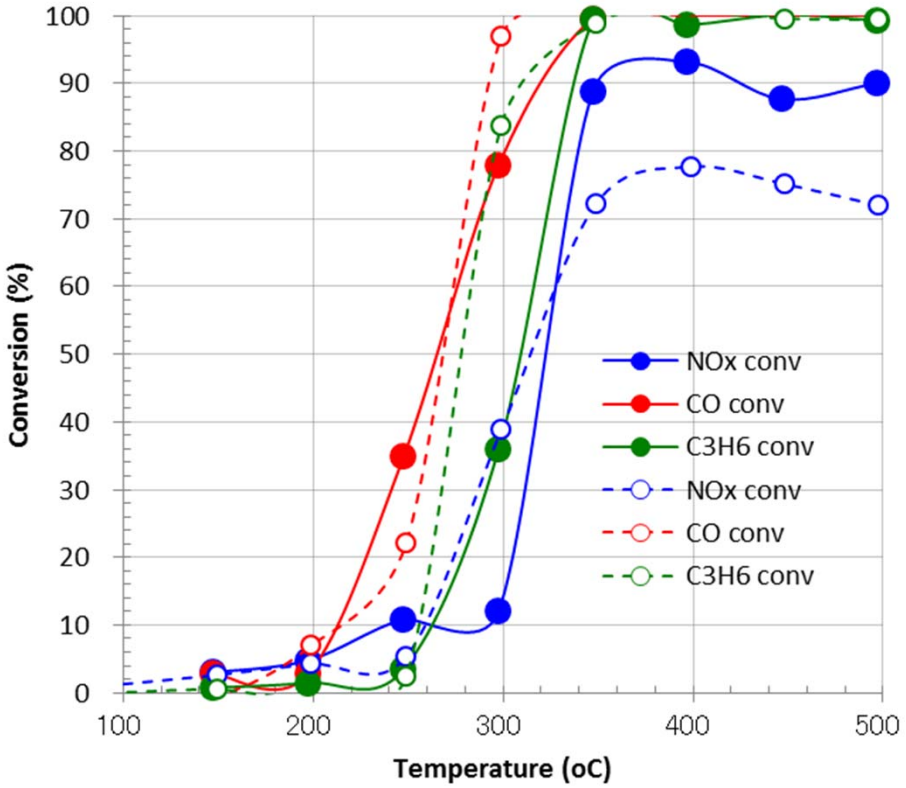
Washing
Water & ethanol）

8 coordination ionic radii
(nm)
Ce^{4+} : 0.097
Zr^{4+} : 0.084
Sn^{4+} : 0.077
Ca^{2+} : 0.112
Mn^{2+} : 0.093

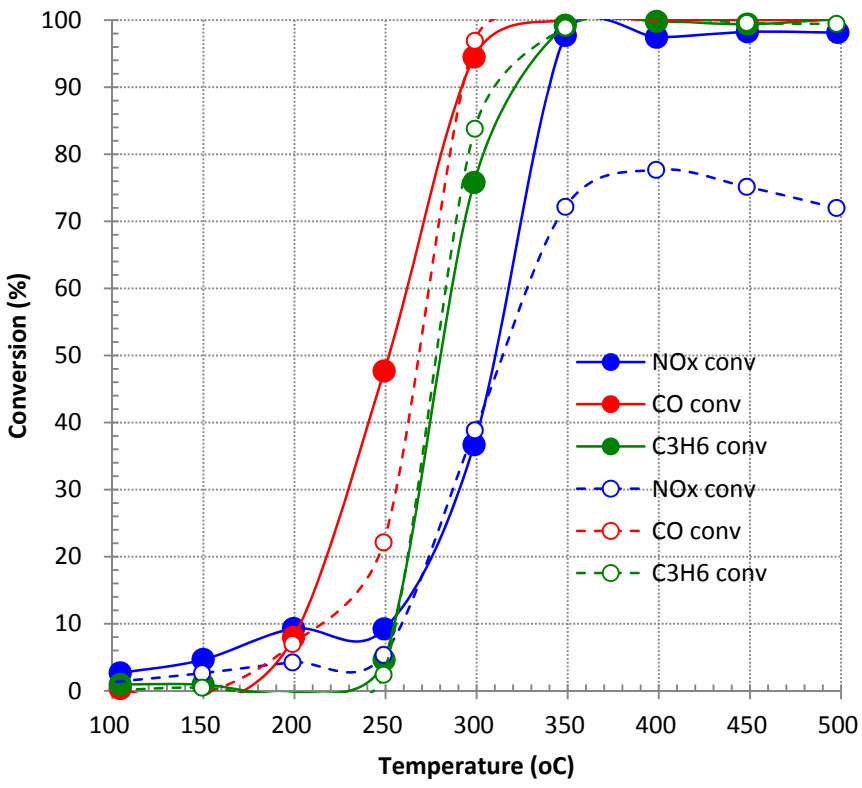


Three-way catalytic property

Weight	60mg (including Pd/Al_2O_3)
Mixed gas	250 ml/min, NO (500ppm), CO (5000ppm), C_3H_6 (400ppm), H_2 (1000ppm), O_2 (5000ppm), CO_2 (14%), H_2O (7%) , weak lean



$Al_2O_3/Pd/Ce_{0.5}Zr_{0.42}Sn_{0.08}O_2$



$Al_2O_3/Pd/Ce_{0.5}Zr_{0.4}Ca_{0.1}O_2$

Full line: Samples prepared in our work

Dotted line: $Al_2O_3/Pd/CeO_2$ of a standard sample

Conclusions for the ceria-based mixed oxides for the automobile exhaust gas cleanup

- The OSC of CeO_2 could be improved by co-doping of Zr^{4+} with Sn^{4+} and/or Ca^{2+}.
- γ-Al_2O_3/Pd/$Ce_{0.5}Zr_{0.4}Ca_{0.1}O_2$ exhibited the excellent three way catalytic performance superior to γ-Al_2O_3/Pd/ $Ce_{0.5}Zr_{0.4}Sn_{0.1}O_2$ and γ-Al_2O_3/Pd/$Ce_{0.5}Zr_{0.5}O_2$

- Ceria-based mixed oxides for the automobile exhaust gas cleanup
- Tin oxide-based mixed oxides for the automobile exhaust gas cleanup

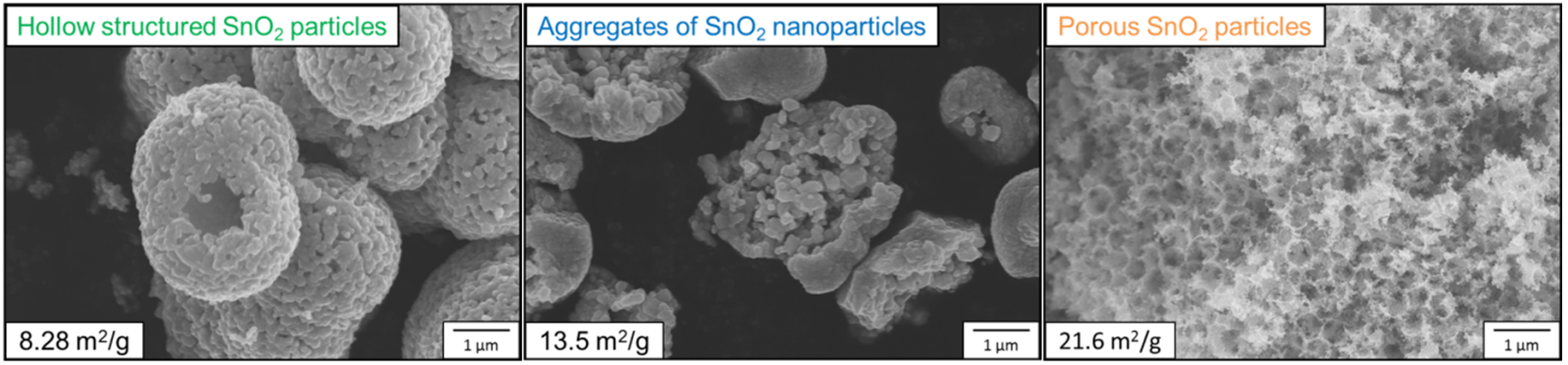
1. Morphologies control of SnO_2

   Preparation of various morphologies of SnO_2 particles to evaluate the OSC.

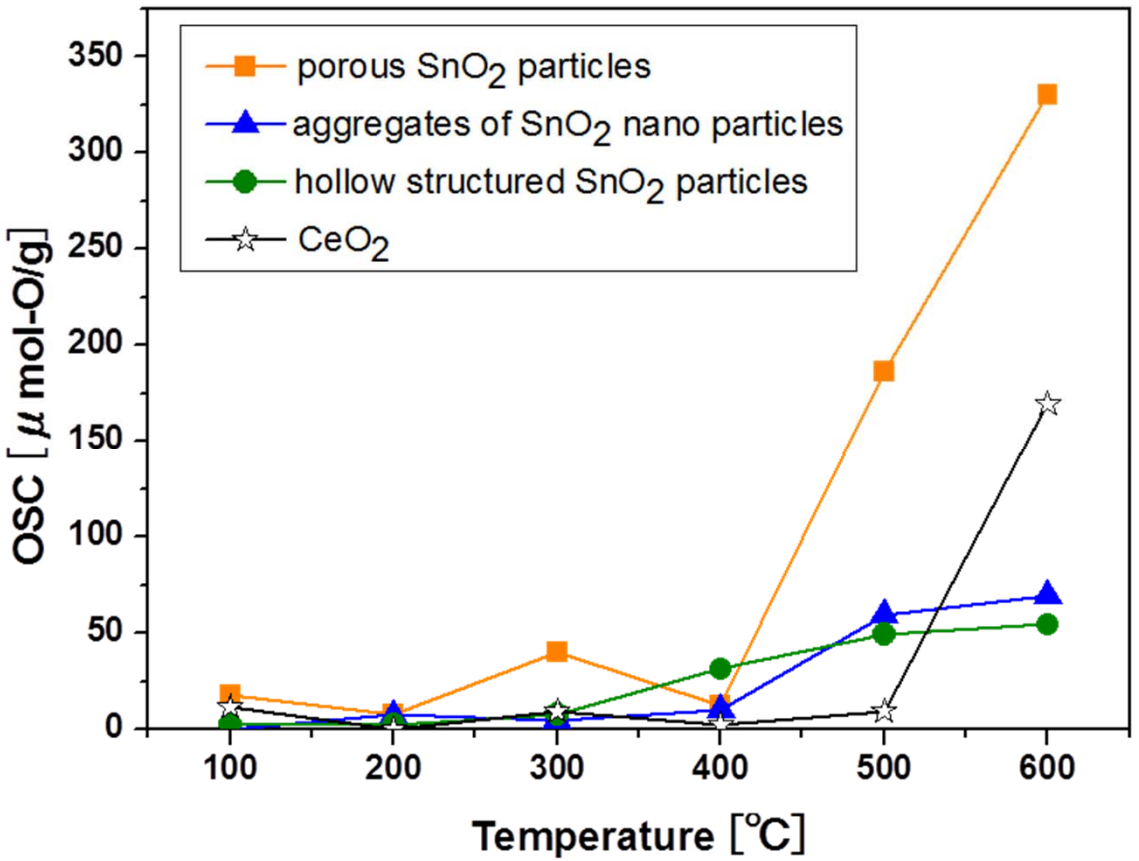
2. Alkali earth metal ion doping with SnO_2

   Effect of alkali earth metal ion doping on the thermal stability and OSC of SnO_2.

Specific surface areas of the various morphologies of SnO_2

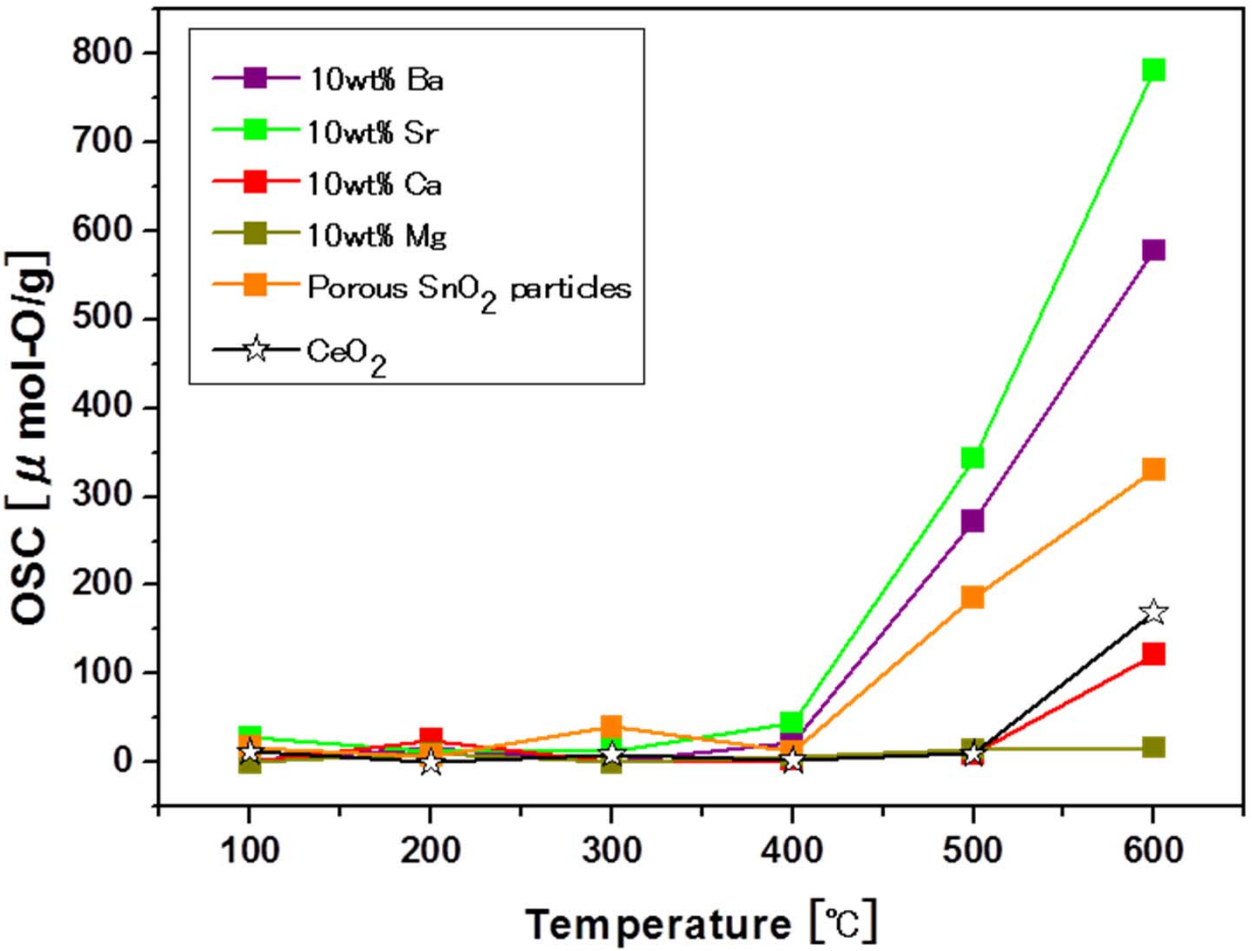


- Specific surface area:
  Porous SnO_2 (21.6 m^2/g) >
  Aggregates of SnO_2 (13.5 m^2/g) >
  Hollow structured SnO_2 (8.28 m^2/g)



OSC of the annealed SnO_2 samples and CeO_2.

- ☞ SnO_2 showed the OSC superior to CeO_2 below 500°C.
- ☞ The OSC of the SnO_2 samples changed depending on the specific surface area in the order porous SnO_2 particles > aggregated SnO_2 nanoparticles > hollow structured SnO_2 particles.
- ☞ The porous SnO_2 particles showed the OSC superior to CeO_2 even at 600°C



OSC of the doped SnO_2 samples and CeO_2

- As expected, the OSC of porous SnO_2 particles could be greatly improved by doping with alkali earth metal ions such as Sr^{2+} and Ba^{2+}, but degraded by doping with Ca^{2+} and Mg^{2+}.

Representative Three Way Catalytic Performance

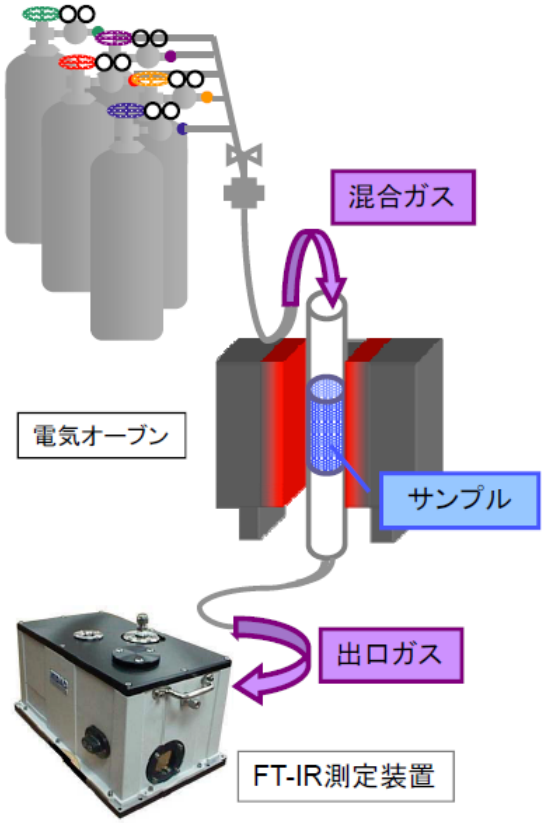
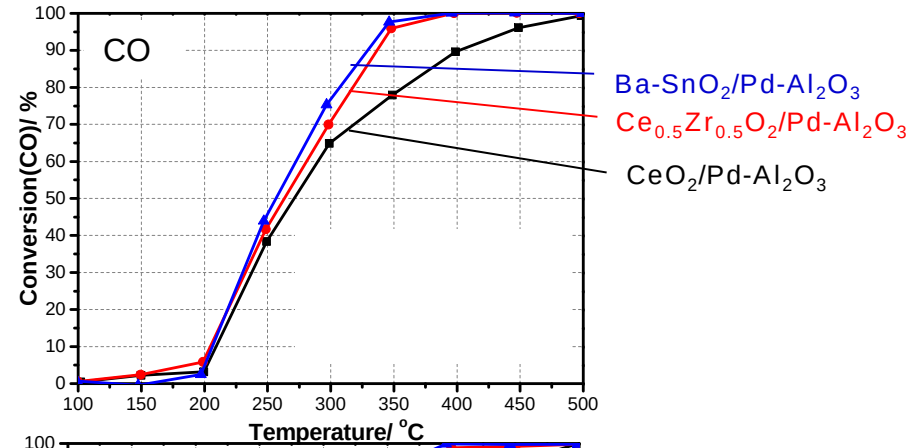
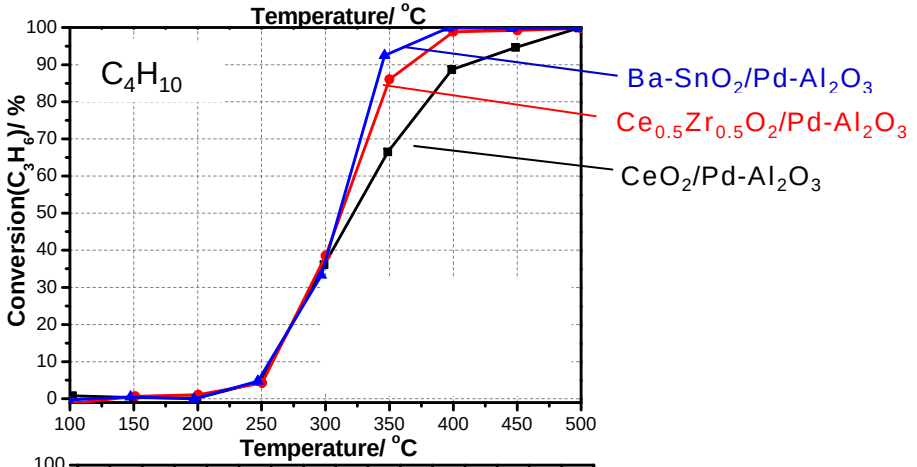
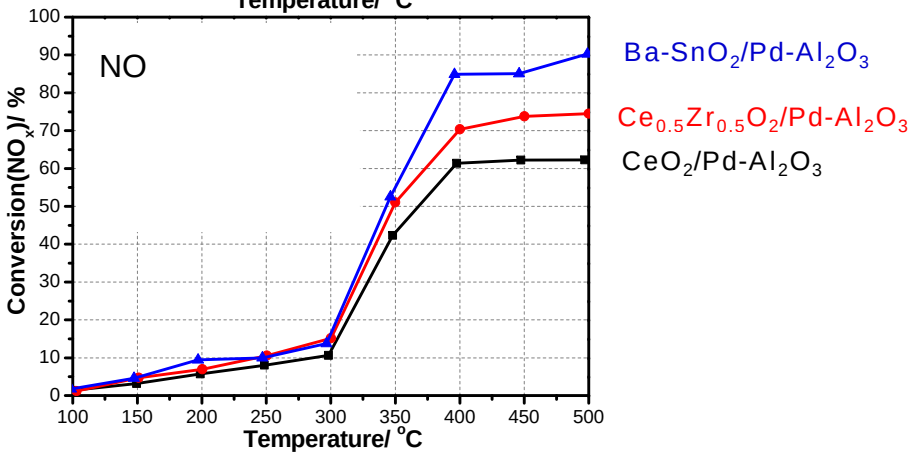


Fig. CO – NO - n-C_4H_{10} ガス浄化活性測定装置

ガス流量	1L/min
ガス組成	O_2 : 3000ppm
	CO : 3000ppm
	NO : 500ppm
	n-C_4H_{10} : 700ppm
	N_2 : balance







Conclusions for the tin oxide-based mixed oxides for the automobile exhaust gas cleanup

- ☞ Porous SnO_2 particles possessing the OSC superior to CeO_2 could be prepared by solvothermal reaction, where the large specific surface area seemed to be useful to improve the OSC property.
- ☞ The OSC of SnO_2 was greatly improved by doping with alkali earth metal ions such as Sr^{2+} and Ba^{2+}.
- ☞ Ba-SnO_2/Pd/γ-Al_2O_3 exhibited the excellent three way catalytic performance superior to CeO_2/Pd/γ-Al_2O_3 and $Ce_{0.5}Zr_{0.5}O_2$/Pd/γ-Al_2O_3