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Enhancement of Reducibility and Oxygen Storage Capacity (OSC) of Ce–Fe Mixed Oxides by Repetitive Redox Treatment

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The reduction properties and oxygen storage capacity (OSC) of Ce–Fe mixed oxide (Ce/Fe = 4/1) were investigated. When TPR/OSC cycle was repeated, Ce–Fe mixed oxide gave a new reduction peak at 600 °C, suggesting the enhancement of the reducibility of iron ions. This was accounted by the formation of a solid solution and the participation of Fe_2O_3 as catalyst for the reduction of Ce–Fe mixed oxide.

CeO_2 is one of the most attractive oxides in catalysis because of its ability to release and acquire oxygen through redox processes involving the Ce^{4+}/Ce^{3+} couple, which allows high "oxygen storage capacity (OSC)."[1] However, the OSC of CeO_2 degrades quickly under thermal treatment because of the significant decrease of the surface area.[2] Enhancement of the thermal stability and OSC of CeO_2 and investigation of ceria-based material even with low surface area are, therefore, paid extensive attention.

Addition of smaller Zr^{4+} ions into CeO_2 lattice to form a solid solution is known to greatly enhance the reducibility of Ce^{4+} and delay OSC degradation at high temperatures,[3] while trivalent ions (Pr^{3+} and Tb^{3+}) in CeO_2 could lower the activation energy of oxygen migration.[4] These findings generated considerable interest in introducing undersized lower valence ions such as Fe^{3+} into CeO_2 lattice to improve the activity and stability of catalysts.[5] Recently, we prepared a series of $Ce_{1-x}Fe_xO_2$ ($x = 0.05$–0.95) mixed oxides and investigated their reduction behavior and thermal stability.[6] Strong interaction between iron and cerium oxides was observed, especially for samples preheated at high temperatures, which leads to significant improvement of the reducibility of CeO_2, allowing the material own high OSC notwithstanding the very low surface area. However, the instability of $Ce_{1-x}Fe_xO_2$ under redox conditions is a serious problem from a practical point of view, because iron oxide is completely reduced to iron metal and its reoxidation to iron oxide is difficult. In the present study, we investigated the effect of redox cycling on the reducibility and OSC of Ce–Fe mixed oxide with low surface area and found enhanced reducibility and OSC by repetitive redox treatment.

CeO_2, Ce–Fe mixed oxide (Ce/Fe = 4/1), and Fe_2O_3 were prepared by coprecipitation. The required amounts of $Ce(NH_4)_2(NO_3)_6$ (Wako, minimum purity 95%) and/or $Fe(NO_3)_3 \cdot 9H_2O$ (Wako, minimum purity 99%) were dissolved in distilled water. The hydroxides were precipitated by adding dropwise a 8 wt% aqueous ammonia (Wako, 25 wt% diluted to 8 wt% with distilled water). The mixtures were stirred for 3 h, when the pH increased to 9–10. The precipitates were dried at 110 °C for 24 h, subjected to decomposition at 600 °C for 3 h in air, and then calcined at 800 °C for 3 h in air. BET surface area of each sample prepared here (CeO_2, Ce–Fe mixed oxide and Fe_2O_3) was estimated to be lower than $3.0\,m^2\,g^{-1}$.

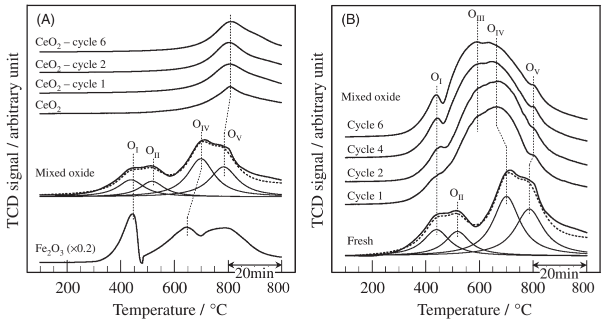

Figure 1. H_2-TPR profiles of (A) Fe_2O_3, Ce–Fe mixed oxide, and CeO_2 and (B) Ce–Fe mixed oxide in the repetitive redox cycle.

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex diffractometer with Cu Kα radiation at 40 kV and 15 mA. The Raman spectra were measured with a JASCO NRS-3100 dispersive Raman spectrometer. Temperature-programmed reduction (TPR) profiles were obtained from room temperature to 800 °C (hold at 800 °C for 20 min) in a $30\,cm^3\,min^{-1}$ flow of 5% H_2/Ar at a heating rate of $10\,°C\,min^{-1}$. After the TPR cycle, the flow was switched to Ar and the sample was cooled down to 600 °C at a cooling rate of $10\,°C\,min^{-1}$. Thereafter, O_2 pulses were injected on the reduced sample at 600 °C, and OSC of this material was obtained by calculating the consumption of oxygen. The reoxidized sample was submitted to a new TPR/OSC cycle.

Figure 1A shows the reduction behavior of CeO_2, Ce–Fe mixed oxide, and Fe_2O_3. CeO_2 showed a profile with only high-temperature reduction at 800 °C, assigned as O_V peak, indicating no active surface oxygen on this material due to the low surface area. Fe_2O_3 gave peaks at 450 (O_I), 650 (O_{IV}), and 800 °C, indicating a stepwise reduction of Fe_2O_3 to Fe metal through FeO as an intermediate.[7] In the case of Ce–Fe mixed oxide, a complex TPR profile due to the interaction between cerium and iron oxides was observed. The H_2-TPR profile can be fitted into four peaks (e.g., O_I, O_{II}, O_{IV}, and O_V, Figure 1A) by a Lorentz function. According to the reduction behavior of Fe_2O_3, the O_I peak would be due to the surface reduction of Fe_2O_3 particles dispersed on CeO_2 surface. The O_{II} peak can be related to the reduction of active oxygen of Ce^{4+} in the surface layer, because nanosized CeO_2 gives a reduction peak at around 500 °C,[6] and the crystallite size of CeO_2 in fresh Ce–Fe mixed oxide was found to be small by XRD measurement (Table 1). The reduction peaks at high temperature assigned as O_{IV} and O_V can be ascribed to bulk reduction of Fe_2O_3 particles to FeO and isolated CeO_2 particles without interaction with iron ions, respectively.

When the TPR/OSC cycle was repeated, CeO_2 and Ce–Fe mixed oxide showed quite different reduction behavior. As seen

Table 1. Effect of redox cycling on the structural characteristics and OSC of CeO_2 and Ce–Fe mixed oxide

Catalyst	Number of TPR/OSC cycle	Crystallite size of CeO_2/nm	Lattice constant of CeO_2/nm	OSC /mmol g^{-1}
CeO_2	0	51.3	0.5412	0.30
	6	62.9	0.5411	0.30
Ce–Fe mixed oxide	0	14.4	0.5407	1.08
	1	53.1	0.5404	1.24
	6	69.0	0.5390	1.31

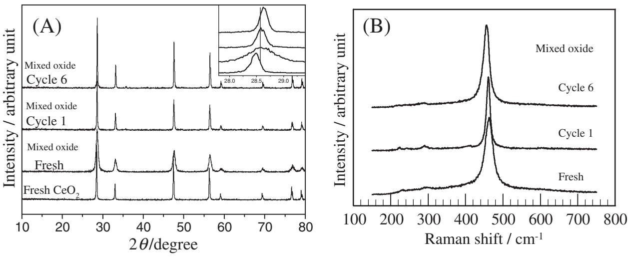

Figure 2. (A) XRD patterns and (B) Raman spectra of Ce–Fe mixed oxide after TPR/OSC cycle.

in Figure 1A, no change in H_2-TPR profile was observed for CeO_2, suggesting that the morphology of CeO_2 is reversibly changed during the redox cycle. On the other hand, as can be seen in Figure 1B, the reduction behavior of Ce–Fe mixed oxide was drastically changed by the TPR/OSC cycle. There are two points which should be highlighted. First, the low-temperature peak (O_I) sharpened. This suggests the growth of the Fe_2O_3 particles dispersed on CeO_2 surface. Since no distinct peaks due to Fe_2O_3 in the XRD patterns of Ce–Fe mixed oxide were detected even after the 6th TPR/OSC cycle, Fe_2O_3 particles seem to be present as amorphous. The second highlight is an appearance of a new peak at a temperature around 600 °C, which was assigned as O_{III}. The O_{III} peak is slightly increased with repeating TPR/OSC cycle, while a slight decrease in the O_{IV} peak was observed. Basically, no significant change in the H_2-TPR profiles of Ce–Fe mixed oxide observed as TPR/OSC cycle was repeated, indicating the reversible change in the morphology of Ce–Fe mixed oxide.

In Table 1 are summarized OSC of CeO_2 and Ce–Fe mixed oxide after the repetitive TPR/OSC cycle. It appears that Ce–Fe mixed oxide showed quite larger OSC than CeO_2. It is also noteworthy that OSC of Ce–Fe mixed oxide increased with repeating TPR/OSC cycle, although a significant sintering of Ce–Fe mixed oxide was detected. No obvious change in OSC of CeO_2 was observed. The crystal size, which was estimated from the X-ray diffraction peak due to the (111) plane ($2\theta =$ ca. 28.6°) using Scherrer's equation, of Ce–Fe mixed oxide increased from 14.4 to 69.0 nm after the 6th cycle (Table 1). Nevertheless, the fact that the reducibility and OSC were enhanced indicates that Ce–Fe mixed oxide is a good candidate as oxygen storage material.

Crystallite structure of Ce–Fe mixed oxide before and after the repetitive TPR/OSC cycle was measured by XRD (Figure 2A). Fresh Ce–Fe mixed oxide before use in the TPR/OSC cycle showed distinct XRD peaks ascribed to a fluorite-type structure, and each peak slightly shifted to a higher angle compared with that for CeO_2, indicating a slight lattice contraction (Table 1). No other peaks due to Fe_2O_3 were observed. We also measured the Raman spectra of Ce–Fe mixed oxide to clarify the status of iron species, because Raman spectroscopy is a more sensitive technique to identify changes in M–O bond arrangement. As shown in Figure 2B, on the fresh Ce–Fe mixed oxide, a sharp Raman band at 457 cm^{-1} as well as weak bands in the region of 200–400 cm^{-1} were observed. The former band is due to the F_{2g} mode of the fluorite structure, while the latter ones to Fe_2O_3.[6] The results of XRD and Raman spectroscopy suggest that amorphous Fe_2O_3 is mainly present on the CeO_2 surface and that a part of iron ions is incorporated into the CeO_2 lattice to form a solid solution. This is also supported by the fact that the fresh Ce–Fe mixed oxide gave a similar H_2-TPR profile with that of Fe_2O_3 (Figure 1A). The appearance of O_{IV} peak at a slightly higher temperature for Ce–Fe mixed oxide, compared with that for Fe_2O_3, is probably due to amorphous Fe_2O_3 with disordered structure.

When the TPR/OSC cycle was repeated, the lattice constant of Ce–Fe mixed oxide was gradually decreased from 0.5407 to 0.5390 nm after the 6th cycle (Table 1). Furthermore, as can be seen in Figure 2B, a red shift of the Raman band at ca. 457 cm^{-1} was clearly observed. These results suggest that the formation of a solid solution is accelerated by the repetitive redox treatment. As can be seen in Figure 1B, it should be noted that the repetitive redox treatment caused an appearance of a new reduction peak assigned as O_{III} at 600 °C. In addition, the O_{III} peak was slightly increased with repeating TPR/OSC cycle. Taking into account the results of XRD and Raman spectroscopy, the appearance of the O_{III} peak is ascribed to the enhancement of the reducibility of Fe^{3+} ions incorprated into the CeO_2 lattice as a solid solution. This also causes an increment of OSC as given in Table 1. It is also noteworthy that Fe^{3+} ions in the CeO_2 lattice are reduced at lower temperature (O_{III}), than the bulk reduction of Fe_2O_3 (O_{IV}), meaning an increase in the reduction rate. Since the growth of Fe_2O_3 particles on CeO_2 surface was suggested by an increase of a well-defined O_I peak (Figure 1B), Fe_2O_3 particles are considered to catalyze the reduction of Fe^{3+} ions in the solid solution of Ce–Fe mixed oxide by H_2.

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References

1 C. T. Campbell, C. H. F. Peden, *Science* **2005**, *309*, 713.
2 A. Trovarelli, *Catal. Rev., Sci. Eng.* **1996**, *38*, 439.
3 I. Atribak, A. Bueno–López, A. García–García, *J. Catal.* **2008**, *259*, 123.
4 A. Trovarelli, *Comments Inorg. Chem.* **1999**, *20*, 263.
5 a) F. J. Pérez–Alonso, M. L. Granados, M. Ojeda, P. Terreros, S. Rojas, T. Herranz, J. L. G. Fierro, M. Gracia, J. R. Gancedo, *Chem. Mater.* **2005**, *17*, 2329. b) H. Bao, X. Chen, J. Fang, Z. Jiang, W. Huang, *Catal. Lett.* **2008**, *125*, 160.
6 a) K. Li, H. Wang, Y. Wei, D. Yan, *Appl. Catal., B* **2010**, *97*, 361. b) O. H. Laguna, M. A. Centeno, M. Boutonnet, J. A. Odriozola, *Appl. Catal., B* **2011**, *106*, 621.
7 Z. Zhong, J. Highfield, M. Lin, J. Teo, Y.-f. Han, *Langmuir* **2008**, *24*, 8576.