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Modification of CeO_2 on the redox property of Fe_2O_3

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ABSTRACT

The modifications of CeO_2 on the reduction behavior, oxygen storage capacity (OSC), and redox stability of Fe_2O_3 were investigated. Combination of Fe_2O_3 with CeO_2 strongly improved the low-temperature reducibility of both Fe_2O_3 and CeO_2, evidencing an obvious interaction between cerium and iron oxides during the H_2-TPR process. Most of the Fe^{3+} in single Fe_2O_3 cannot be restored by the re-oxidation step (OSC step) after the TPR testing, which resulted in a serious decrease in the OSC. On the other hand, the presence of CeO_2 significantly enhanced the redox property of Fe_2O_3: more iron (III) ions were observed in the recycled CeO_2/Fe_2O_3 mixture (Ce/Fe = 1/4, labeled Ce20Fe80 sample), and the OSC was obviously improved by the redox treatment. After the first TPR/OSC cycle, the reduction behavior of the recycled Ce20Fe80 sample is highly reversible, indicating good redox stability. This is attributed to the formation of perovskite-type $CeFeO_3$ with excess CeO_2, Fe_2O_3 and Fe in the recycled Ce20Fe80 sample.

1. Introduction

Iron oxides own broad application potential in material and catalysis areas due to their easy handling, relatively low cost, non-toxicity, and environmentally friendly features [1]. It was reported that iron oxides exhibit good performance as active component or support in many catalytic reactions including decomposition or reduction of NO_x [2–4], elimination of volatile organic compounds (VOCs) [5,6], and methane or CO oxidation [7,8]. The reduction behavior and redox properties of iron oxides were accepted to play an important role in such applications.

Recently, it was reported that iron oxides can be used to hydrogen storage or production by a redox process [9–11]. For hydrogen storage, iron oxide is firstly reduced with hydrogen into iron metal, and then hydrogen is recovered through the oxidation of iron metal with water vapor. When replacing hydrogen to other reductants (e.g., hydrocarbon or coal) to reduce iron oxides, the subsequent re-oxidation process with water vapor can produce pure hydrogen. However, it was also found that repeated redox cycles would result in the deactivation of iron oxide and additives are necessary for improving the redox stability of iron oxides [12–15].

CeO_2 is well known as an oxygen buffer in three way catalyst (TWC) systems due to its outstanding oxygen storage capacity and good redox property [16–18]. CeO_2 has also been widely used as structural and chemical promoters to improve the activity and stability of transition metal catalysts [19–22]. The investigations on the effect of CeO_2 on the redox behavior of iron oxide, therefore, are very important not only from fundamental but also from practical point of view.

In the present work, the modification of CeO_2 on the reduction behavior and redox property of Fe_2O_3 was investigated, and the effect of redox treatment on the structure evolution of the mixed oxides was also examined. According to our knowledge, this is the first report on a strong enhancement on the redox property of Fe_2O_3 due to the reaction between cerium and iron oxides during the redox testing.

2. Experimental section

Material preparation: CeO_2, Fe_2O_3 and CeO_2/Fe_2O_3 mixture with the Ce/Fe of 1:4 (labeled as Ce20Fe80) were prepared by a co-precipitation method. 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, and blended using a magnetic stirrer for 30 min at 25 °C. The hydroxides were precipitated by dropping an ammonia 8 wt% aqueous solution. The mixtures were stirred for 3 h at the pH of 10. The precipitates were dried at 110 °C for 24 h, subjected to decomposition at 600 °C in air for 3 h, and then calcinated at 800 °C for 3 h.

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Characterization: Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex diffractometer with Cu Kα radiation at 40 kV and 150 mA. The microstructures and morphologies were investigated using a JEOL JEM-2100(UHR) transmission electron microscope (TEM) at 200 keV. Raman spectra were measured with a JASCO NRS-3100 Dispersive Raman Spectrometer. The BET surface area was determined by a volumetric adsorption apparatus by nitrogen adsorption at −196 °C using Micromertics TriStar II. 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 gas 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 redox treatment was performed by repeating TPR/OSC couple steps.

3. Result and discussion

Pure CeO_2 and Fe_2O_3 samples showed fluorite CeO_2 and α-Fe_2O_3 phase, respectively, while the Ce20Fe80 sample was identified as a mixture of two phases: CeO_2 and α-Fe_2O_3 (see the XRD of fresh samples in Fig. 5B). The high-resolution TEM micrographs (Fig. 1) give useful information on the microstructure of Ce20Fe80. Two kinds of crystalline particles with ca. 10 nm and ca. 50 nm were observed, and the large particles were closely surrounded by numbers of small particles. Since the XRD data shows that the crystal size of α-Fe_2O_3 is larger than that of CeO_2 (31 versus 13 nm, calculated from peak broadness by Scherrer's equation), the small and large particles can be identified as CeO_2 and α-Fe_2O_3, respectively. Also, the lattice fringe of large particle corresponds to that of α-Fe_2O_3 (Fig. 1B).

The small crystal size of CeO_2 in this material with a calcination temperature of 800 °C is worth being highlighted, because that the nanometer-sized CeO_2 is very useful in many possible catalytic reactions. Also numbers of small CeO_2 particles closely contacting with Fe_2O_3 would result in abundant interface between the two oxides, which may affect the reducibility of this sample, as will be discussed below.

Fig. 2 shows the TPR profiles of prepared CeO_2, Fe_2O_3 and Ce20Fe80 samples. It is generally accepted that CeO_2 owns a TPR profile with two peaks at low and high temperatures, evidencing the surface and bulk reduction processes, respectively [23]. In the present work, CeO_2 sample represented a profile with only high-temperature reduction process at 800 °C, indicating no surface oxygen on this material due to its low surface area (see Table 1). The TPR profile of single Fe_2O_3 represented three peaks (α, β and γ) at ca. 438, 700 and 800 °C, showing a stepwise reduction of Fe_2O_3 to Fe metal through FeO as an intermediate [24]. For the Ce20Fe80 sample, a similar TPR profile with single Fe_2O_3 was observed. It should be noted that a small new peak at 340 °C was detected on the mixed oxide and the α and β peaks shifted to lower temperatures compared with the single Fe_2O_3. Since the α, β and γ peaks were attributed to the stepwise reduction of Fe_2O_3, the new peak at 340 °C should be related to the reduction of CeO_2 on Fe_2O_3. Taking the TEM observation (Fig. 1) into account, the enhancement on the low-temperature reducibility of CeO_2 must be related to its small particle size on the mixed oxides. On the other hand, the shift of α and β peaks suggests that CeO_2 as an additive on Fe_2O_3 could enhance the surface reducibility of Fe_2O_3, which should be attributed to the appearance of abundant interface between two oxides because this intergranular layers possess very high adsorption ability [25]. In summary, the synergism between cerium and iron oxides in an initial Ce20Fe80 sample give the CeO_2/Fe_2O_3 material with relatively high reducibility at low temperature.

After the TPR/OSC redox testing, the reduction behavior of single Fe_2O_3 was drastically changed, as shown in Fig. 3. The redox treatment obviously reduced the intensity of the reduction peaks, indicating that the oxygen species in single Fe_2O_3 consumed in the TPR process cannot be totally restored after the re-oxidation by oxygen. This is in accordance with its decrease in OSC from 0.67 mmol/g to 0.2 mmol/g after six redox cycles (Table 1). In addition, it is also observed that the high-temperature peaks gradually disappeared with the successive cycles. Since the high-temperature peaks for iron oxides are related to the reduction of bulk Fe^{3+}, this phenomenon suggests the absence of Fe^{3+} in the recycled iron oxide. This could be

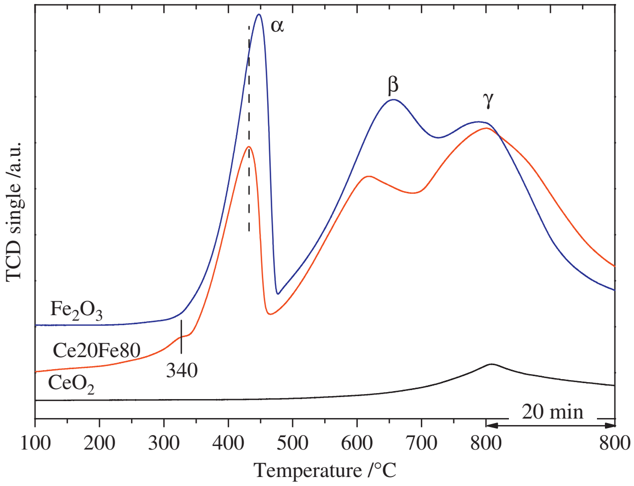

Fig. 2. TPR profiles of CeO_2, Fe_2O_3 and Ce20/Fe80 samples.

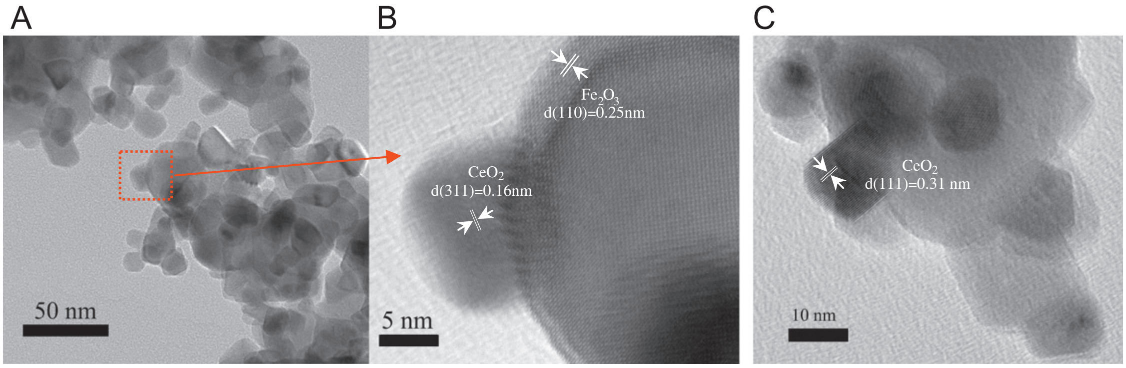

Fig. 1. High-resolution TEM micrograph of Ce20Fe80 sample.