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Catalytic reduction of sulfur dioxide using hydrogen or carbon monoxide over $Ce_{1-x}Zr_xO_2$ catalysts for the recovery of elemental sulfur

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Abstract

This study focuses on the direct sulfur recovery process (DSRP), in which SO_2 can be directly converted into elemental sulfur using a variety of reducing agents over $Ce_{1-x}Zr_xO_2$ catalysts. $Ce_{1-x}Zr_xO_2$ catalysts (where $x = 0.2$, 0.5, and 0.8) were prepared by a citric complexation method. The experimental conditions used for SO_2 reduction were as follow: the space velocity (GHSV) was 30,000 ml/$g_{\text{-cat}}$ h and the ratio of [CO (or H_2, H_2 + CO)]/[SO_2] was 2.0. It was found that the catalyst and reducing agent providing the best performance were the $Ce_{0.5}Zr_{0.5}O_2$ catalyst and CO, respectively. In this case, the SO_2 conversion was about 92% and the sulfur yield was about 90% at 550 °C. Also, a higher efficiency of SO_2 removal and elemental sulfur recovery was achieved in the reduction of SO_2 with CO as a reducing agent than that with H_2. In the reduction of SO_2 by H_2 over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst, SO_2 conversion and sulfur yield were about 92.7% and 73%, respectively, at 800 °C. Also, the reduction of SO_2 using synthetic gas with various [CO]/[H_2] molar ratios over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst was performed, in order to investigate the possibility of using coal-derived gas as a reducing agent in the DSRP. It was found that the reactivity of the SO_2 reduction using the synthetic gas with various [CO]/[H_2] molar ratios was increased with increasing CO content of the synthetic gas. Therefore, it was found that the $Ce_{1-x}Zr_xO_2$ catalysts are applicable to the DSRP using coal-derived gas, which contains a larger percentage of CO than H_2.

Keywords: SO_2 reduction; Ce–Zr based catalysts; CO; H_2; Synthetic gas; Coal-derived gas; DSRP

1. Introduction

Due to environmental problems and the need to retain the balance of supply and demand in the petroleum industry, today's researchers are increasingly focusing on the development of clean and efficient energy technology. The utilization and commercialization of clean energies such as solar and hydrogen energy, hydroelectric power, wave power and wind power have been postponed, because of the inefficiency and the disproportion of the supply and demand of petroleum. The integrated gasification combined cycle (IGCC) system has been proposed to develop various energies and chemicals using coal. The IGCC power plant station is a highly efficient modular system designed to produce various energies and chemicals such as hydrogen, dimethyl ether, heat energy, gas turbine and electric power, through the production of coal gas containing synthetic gas by coal gasification. However, the IGCC power plant system has an important problem, in that various toxic and corrosive chemicals are generated, such as hydrogen sulfide and carbonyl sulfide, etc. Therefore, a cleanup process is necessary to treat these pollutants, if an environment-friendly IGCC power plant system is to be realized. The hot gas desulfurization (HGD) process is an efficient way to remove sulfur compounds such as H_2S and COS, etc. The HGD process is composed of the sulfidation and regeneration processes using a sorbent, as described below:

$$MO + H_2S \rightarrow MS + H_2O \quad (\text{sulfidation}) \tag{1}$$

$$MS + O_2 \rightarrow MO + SO_2 \quad (\text{regeneration}) \tag{2}$$

In the regeneration process, SO_2 is generated by regenerating the metal sulfide sorbent with O_2 [1]. SO_2 is a toxic and corrosive sulfur compound which corrodes equipment, generates acid rain and pollutes and acidifies the soil. As environmental regulations are becoming increasingly stricter, developing technologies for the control of SO_x emission is

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important. In order to treat SO_2, throwaway processes such as the lime or limestone scrubbing process, are the prevailing methods of flue gas desulfurization. Furthermore, SO_2 treatment can be performed by the direct sulfur recovery process, in which SO_2 is converted into elemental sulfur with a reducing agent over a catalyst [2–6]. Various reducing agents, such as carbonaceous material, carbon monoxide, natural gas, and hydrogen, have been used in the SO_2 reduction process, as follows [7–13]:

$$SO_2 + C \rightarrow CO_2 + S \quad (3)$$

$$SO_2 + 2H_2 \rightarrow S + 2H_2O \quad (4)$$

$$SO_2 + 2CO \rightarrow 2CO_2 + S \quad (5)$$

$$2SO_2 + CH_4 \rightarrow 2S + CO_2 + 2H_2O \quad (6)$$

Also, various catalysts, such as Ce–Zr, Sn–Zr, Co–Mo, transition metals and Al_2O_3, are used in the DSRP [14,15]. In the DSRP, much effort has been made to find efficient catalysts and reducing agents, in order to reduce SO_2 to elemental sulfur with a high yield. In spite of these efforts, however, no commercial process has been developed, due to the high reaction temperature and low sulfur yield, making it untenable for practical applications.

It has been known that coal-derived gas contains both CO and H_2, and CO has more percentage than H_2 [16]. It seems that the process cost of DSRP can be reduced by using a clean coal-derived gas produced from the gasification process of an IGCC power plant as a reducing agent. Moreover, in a previous study, we reported the development of $Ce_{1-x}Zr_xO_2$ catalysts which are usable in the DSRP, and that coal-derived gas can be used as a reducing agent in the DSRP of $Ce_{1-x}Zr_xO_2$ catalysts [14]. In the present work, by employing CO or H_2 as a reducing agent, the activities of $Ce_{1-x}Zr_xO_2$ catalysts used for the reduction of SO_2 were first examined, and the effect of the composition of the reducing agent on the SO_2 reduction was investigated. Subsequently, we investigated the reaction characteristics of SO_2 reduction over $Ce_{1-x}Zr_xO_2$ catalysts by utilizing coal-derived gas containing simultaneously CO and H_2 as a reducing agent, in order to investigate the possibility of using $Ce_{1-x}Zr_xO_2$ catalysts in DSRP to convert SO_2 to elemental sulfur.

2. Experimental

2.1. Preparation of the catalysts and the reactivity test

The citric complexation method was employed for preparing the $Ce_{1-x}Zr_xO_2$ catalysts with various values of x (0.2, 0.5, and 0.8). In the preparation, the precursors, cerium nitrate hexahydrate [$Ce(NO_3)_2 \cdot 6H_2O$, Aldrich Chem.] and zirconium nitrate oxide dehydrate [$ZrO(NO_3)_2 \cdot 6H_2O$, Aldrich Chem.], with amounts corresponding to a fixed Ce/Zr molar ratio, and citric acid [$C_3H_4(OH)(COOH)_3 \cdot H_2O$, Ducksan Chem.], were dissolved in distilled water with stirring. The solution was dehydrated by a rotary vacuum evaporator at 80 °C for 2 h. After drying the viscous liquid at 110 °C for 24 h, the resulting solid was calcined at 600 °C for 6 h in an electric furnace.

Selected particles with a diameter of 75–150 μm were used as the catalyst in the reactivity test of SO_2 reduction by H_2, CO, and synthetic gas. The experiment for the reduction of SO_2 was performed as follows: a gas mixture with a constant molar ratio of CO (or H_2, $H_2 + CO$): SO_2 (40,000 ppm CO (or H_2, $H_2 + CO$) and 20,000 ppm SO_2 in N_2 balance) of 2.0 and space velocity (GHSV) of 30,000 ml/$g_{\text{-cat}}$ h was fed into the reactor. When a steady state was attained, the concentration of SO_2 in the inlet and outlet gases and that of COS, H_2S and the other reaction by-products in the effluent gas were determined by using a gas chromatograph (Shimadzu-8A) equipped with a thermal conductivity detector. SO_2 conversion, sulfur selectivity, COS selectivity and sulfur yield was calculated as follows:

$$SO_2\ \text{conversion}\ (\%) = \frac{[SO_2]_{in} - [SO_2]_{out}}{[SO_2]_{in}} \times 100$$

$$\text{Sulfur selectivity}\ (\%) = \frac{[SO_2]_{in} - [SO_2]_{out} - [H_2S]_{out} - [COS]_{out}}{[SO_2]_{in} - [SO_2]_{out}} \times 100$$

$$H_2S\ \text{selectivity}\ (\%) = \frac{[H_2S]_{out}}{[SO_2]_{in} - [SO_2]_{out}} \times 100$$

$$COS\ \text{selectivity}\ (\%) = \frac{[COS]_{out}}{[SO_2]_{in} - [SO_2]_{out}} \times 100$$

$$\text{Sulfur yield}\ (\%) = SO_2\ \text{conversion} \times \text{sulfur selectivity}$$

2.2. Analysis of the catalysts

The characterization of the catalysts was conducted by X-ray diffraction (XRD; Rigaku, D/MAX-2500) with Ni-filtered Cu Kα and infrared (IR) spectroscopy (Jasco 7300 FT-IR with an MCT detector at 4 cm^{-1} resolution with 64 scans).

In order to analyze the $Ce_{1-x}Zr_xO_2$ catalyst powders in detail, XPS measurements were performed using an ESCALAB 250 XPS spectrometer fabricated by VG Scientifics and equipped with a focused (spot size 100 Å) monochromatized Al Kα anode ($h\nu$ = 1486.6 eV). The X-ray source power was kept at around 150 W. To analyze the individual contributions of the Ce 3d and O 1s peaks quantitatively, peak decomposition was carried out using a computer program. The binding energies (BE) correspond to the C 1 s peak at 284.6 eV and are given with an accuracy of ±0.2 eV.

In order to investigate the decomposition of the sulfate group on the catalyst using CO, the CO-Temperature-Programmed Reduction (TPR) of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst was evaluated by means of a mass spectrometer (Balzers, QMS 200 Prisma). After pretreating 0.5 g of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst in flowing N_2 for 2 h at 250 °C and then cooling it, the CO-TPR was initiated by the injection of 4 vol% CO and 2 vol% H_2O. At the same time, the sample was heated from room temperature to 600 °C at a ramp rate of 5 °C/min. The signals for the unconverted CO and the SO_2, CO_2, and H_2S produced were analyzed with a mass spectrometer.

3. Results and discussion

3.1. Analysis of the fresh and used catalysts

In this section, only $Ce_{0.5}Zr_{0.5}O_2$ catalyst was characterized because $Ce_{0.5}Zr_{0.5}O_2$ catalyst has the best activity among $Ce_{1-x}Zr_xO_2$ catalysts regardless of Ce/Zr composition, and is similar to other $Ce_{1-x}Zr_xO_2$ catalysts in the physical and chemical properties.

Fig. 1 shows the XPS analysis results of the fresh and used $Ce_{0.5}Zr_{0.5}O_2$ catalysts. The catalysts displayed the principal Ce 3d peaks centered between 880 eV and 884 eV for the fresh and used $Ce_{0.5}Zr_{0.5}O_2$. In the fresh $Ce_{0.5}Zr_{0.5}O_2$ catalyst, the peaks corresponding to Ce 3d and Zr 3d were observed at about 880 eV and 181.8 eV, respectively. From this result, it was inferred that the $Ce_{0.5}Zr_{0.5}O_2$ catalyst is a solid solution containing a mixture of metal oxides, viz. CeO_2 and ZrO_2. In $Ce_{0.5}Zr_{0.5}O_2$ catalyst used for the reduction of SO_2 by CO or H_2, the peak of Ce 3d was shifted to a value of between 882 eV and 883 eV. However, the peak of Zr 3d was not shifted. It was inferred that the binding energy of the Ce–O bond was changed while that of the Zr–O bond was not. From this result, this XPS measurement clearly imply that, contrary to Zr-ion, only Ce-ion is reducible under the conditions of the reduction of SO_2, and this information might be very useful to estimate the role and contribution of Ce-ions redox transformation in the reaction mechanism. These results were consistent with the fact that the O 1s peak of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst was shifted, compared to that of the fresh $Ce_{0.5}Zr_{0.5}O_2$ catalyst. From the above results, it was concluded that the redox properties was caused by the movement of the lattice oxygen from Ce–O of the bulk of $Ce_{0.5}Zr_{0.5}O_2$, and then the evidence was the shift of the peaks corresponding to Ce 3d and O 1s. Fornasiero et al. reported that Ce–Zr mixed oxides have redox properties induced by the movement of the lattice oxygen, due to the crystal structure distortion in the sub-lattice of Ce–Zr mixed oxides [16,17]. We found that the redox properties of the $Ce_{1-x}Zr_xO_2$ catalyst play an important role in the reduction of SO_2 with CO or H_2. In addition, the S 2p peak corresponding to the chemical bond of SO_4^{2-} was observed at about 168 eV in the XPS spectra. This result is in agreement with the formation of the SO_4^{2-} functional group, which was obtained in conventional Redox mechanism of SO_2 reduction reported by Horváth et al. [18].

Fig. 2 shows the IR spectral analysis of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst. The presence of the peak at 1098 cm^{-1} in the IR spectrum of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst showed that the sulfate group was produced by the reduction of SO_2 by CO over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst. This result is consistent with the result of the sulfate group formation in XPS spectra. In the previous work, it was reported that sulfate group was formulated on the surface of the catalyst because of the side reaction of catalyst surface ($2Cat\text{-}O + SO_2 \leftrightarrow Cat\text{-}SO_4$), which

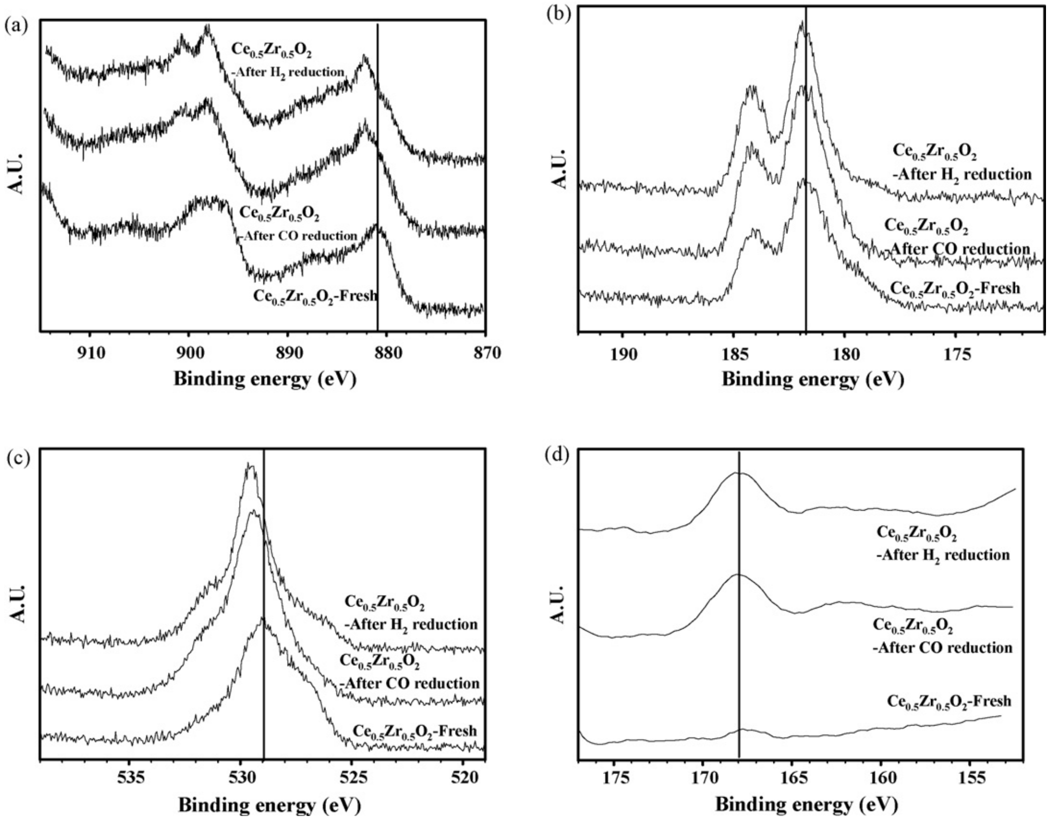

Fig. 1. X-ray photoelectron spectra of the (a) Ce 3d, (b) Zr 3d, (c) O 1s, and (d) S 2p for the fresh and used $Ce_{0.5}Zr_{0.5}O_2$ catalysts.

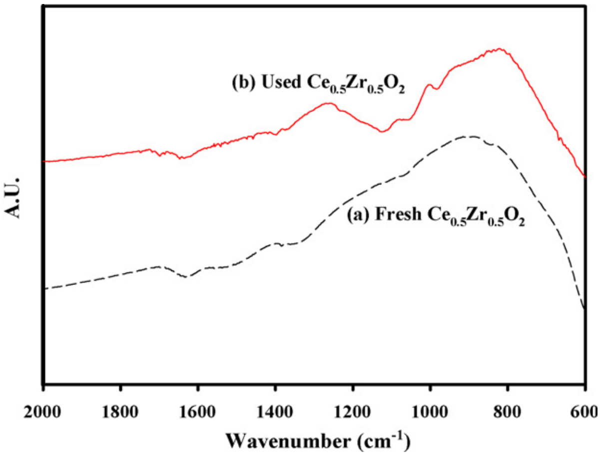

Fig. 2. IR spectrum analysis of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst.

was occurred simultaneously with the various reactions (Cat-[O] ↔ Cat-O, Cat-SO_4 + CO → Cat-O + SO_2 + CO_2) [18]. The sulfate group might be decomposed into SO_2 or CO_2 by CO.

Fig. 3 shows the XRD analysis of the fresh and used $Ce_{0.5}Zr_{0.5}O_2$ catalysts. It was found that the crystalline $Ce_{0.5}Zr_{0.5}O_2$ catalyst was not changed after the SO_2 reduction because the XRD patterns of the used $Ce_{0.5}Zr_{0.5}O_2$ catalyst were similar to that of the fresh catalyst.

Fig. 4 shows CO-TPR profile of the sulfated $Ce_{0.5}Zr_{0.5}O_2$ catalyst. It was observed that the intensities corresponding to SO_2 and CO_2 which were converted from the sulfate group in the CO-TPR profile of the sulfated $Ce_{0.5}Zr_{0.5}O_2$ catalyst increased with increasing temperature. This result is consistent with the decomposition of the sulfate group into SO_2 and CO_2 by CO. Also, H_2 was formulated by water gas shift reaction between H_2O and CO_2 ($H_2O + CO \rightarrow H_2 + CO_2$). The water gas shift reaction using Ceria-based catalyst was reported by Zerva et al. [19]. Therefore, it was found that the activity of the $Ce_{0.5}Zr_{0.5}O_2$ catalyst was not deteriorated by the decomposition of the sulfate group which was produced in the reduction of SO_2 by CO over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst.

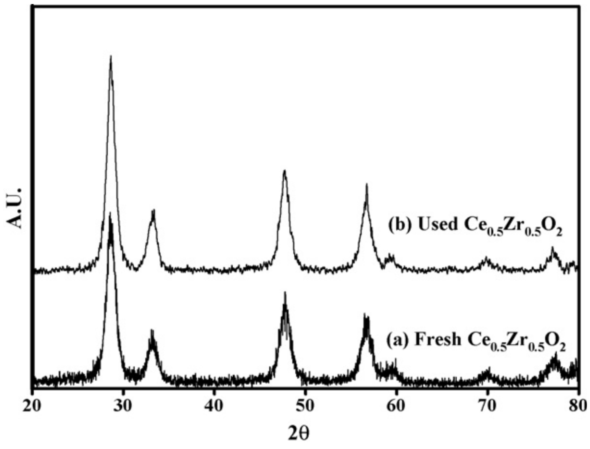

Fig. 3. XRD patterns of the fresh and used $Ce_{0.5}Zr_{0.5}O_2$ catalysts.

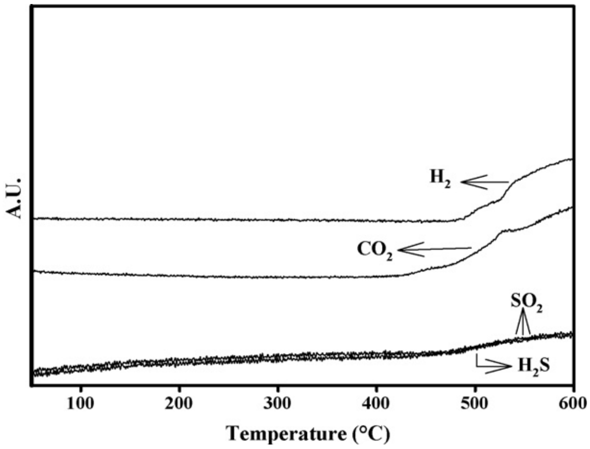

Fig. 4. CO-TPR profiles of sulfated $Ce_{0.5}Zr_{0.5}O_2$ catalyst by mass spectrometry.

3.2. SO_2 reduction by CO over $Ce_{1-x}Zr_xO_2$ catalyst

In order to investigate the reaction characteristics of the SO_2 reduction by CO over $Ce_{1-x}Zr_xO_2$ catalysts, a performance test for each Ce–Zr based catalyst was conducted. Fig. 5 shows the effect of the temperature on the reduction of SO_2 by CO over $Ce_{1-x}Zr_xO_2$ catalysts with x values of 0.2, 0.5, and 0.8. In this experiment, the space velocity (GHSV) was 30,000 ml/$g_{\text{-cat}}$ h and the [CO]/[SO_2] molar ratio was 2.0.

In conducting the performance test of the $Ce_{0.8}Zr_{0.2}O_2$ catalyst, the range of the reaction temperature was from 400 °C to 550 °C. The light-off temperature was 425 °C, and the reactivity increased with increasing reaction temperature below 500 °C. The generation of COS started at 450 °C and was not increased in spite of the increase in the reaction temperature. In addition, an SO_2 conversion of about 87–91% and sulfur yield of about 86–89% were obtained and did not increase with increasing temperature above 475 °C, which was consistent with the thermodynamic equilibrium. The COS yield was very low, ranging from about 1.2% to 2.6%, above 450 °C. The highest reactivity in the SO_2 reduction by CO over the $Ce_{0.8}Zr_{0.2}O_2$ catalyst was an SO_2 conversion of about 89.9% and a sulfur yield of about 88.4% at 500 °C. The generation of CO_2, which is an essential by-product in the production of elemental sulfur from the reduction of SO_2 by CO, was observed in the range of temperature above 450 °C with high reactivity. Even when the reaction temperature was increased from 450 °C to 550 °C, the emission CO_2 was maintained.

In the case of $Ce_{0.5}Zr_{0.5}O_2$, the conversion of SO_2 into elemental sulfur started at 450 °C. The optimal reaction temperature was approximately 550 °C, at which point the SO_2 conversion and sulfur yield were about 92.4% and 91.2%, respectively. The reactivity for the SO_2 reduction increased dramatically with increasing temperature in the range of reaction temperature below 475 °C, whereas no apparent variation of the reactivity was observed, even when the reaction temperature was increased above 475 °C. The emission of CO_2 started at 475 °C and the COS yield of about 1.0–3.0% was maintained, despite the change of the reaction temperature. The generation of CO_2 began at 425 °C and the emission of CO_2

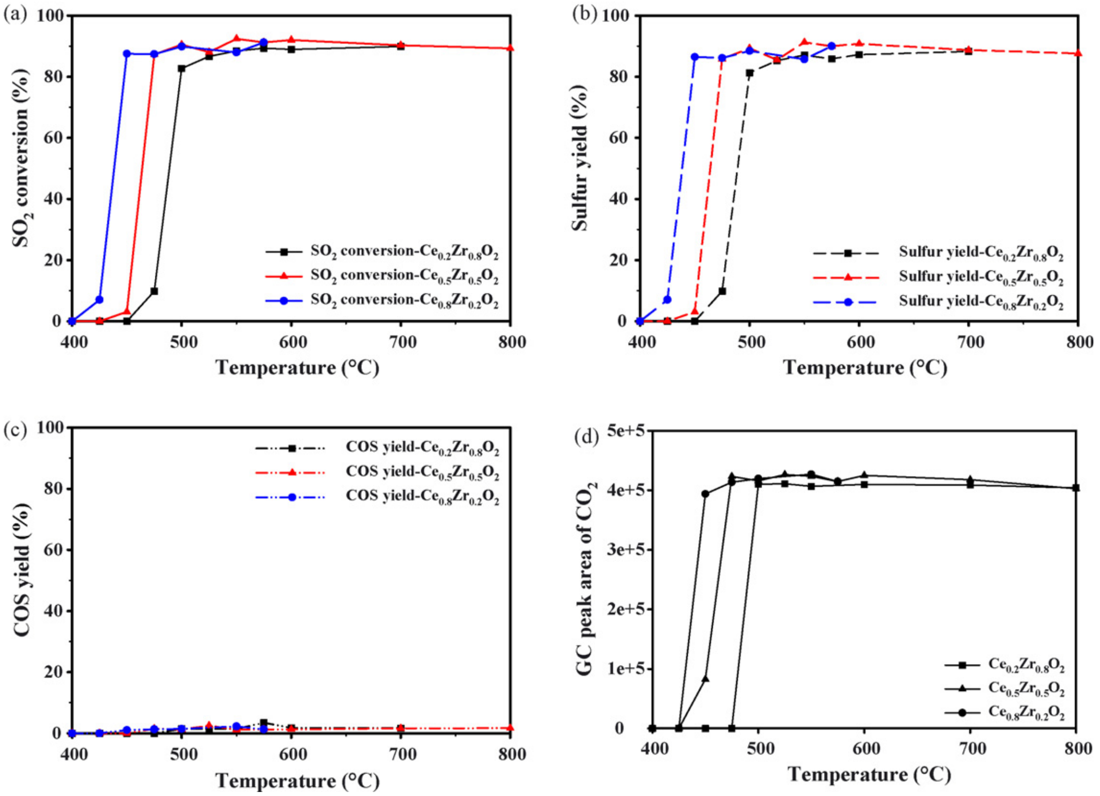

Fig. 5. SO_2 reduction by CO over $Ce_{1-x}Zr_xO_2$ catalysts: (a) SO_2 conversion, (b) sulfur yield, (c) COS yield, and (d) GC peak area of CO_2.

increased with increasing temperature in the range from 425 °C to 475 °C. However, when the reaction temperature was increased above 500 °C, no increase in the CO_2 emission was observed.

$Ce_{0.2}Zr_{0.8}O_2$ catalyst has the highest light-off temperature among Ce–Zr based catalysts in SO_2 reduction by CO. The conversion of SO_2 into elemental started at 475 °C. As the reaction temperature increased, SO_2 conversion as well as sulfur yield was increased dramatically in the temperature range of below 500 °C. Above 525 °C, both SO_2 conversion and sulfur yield were not steeply increased despite increasing the temperature from 525 °C to 800 °C. These tendencies of reaction characteristics depending on the reaction temperature were consistent with the tendency of CO_2 formulation with temperature. As the result of the best performance, SO_2 conversion and sulfur yield were around 89.9% and 88.2%, respectively.

From the above results for the reduction of SO_2 by CO over $Ce_{1-x}Zr_xO_2$ catalysts, it was inferred that the reactivity is not directly dependent on the Ce/Zr molar ratio and the reaction temperature after the activation of the $Ce_{1-x}Zr_xO_2$ catalysts in the reduction of SO_2 by CO. However, it was found that the light-off temperature was related to the Ce/Zr molar ratio given that the light-off temperature decreased with increasing Ce/Zr molar ratio. The profile of the starting temperature, at which the saturation of the reactivity was observed, was similar to that of the light-off temperature. The best performance in the reduction of SO_2 by CO over the $Ce_{1-x}Zr_xO_2$ catalysts was an SO_2 conversion of about 94.4% and a sulfur yield of about 91.3% in the case of the $Ce_{0.5}Zr_{0.5}O_2$ catalyst.

3.3. *SO_2 reduction by H_2 over $Ce_{1-x}Zr_xO_2$ catalyst*

The effect of the temperature on the reduction of SO_2 by H_2 over the $Ce_{1-x}Zr_xO_2$ catalysts was investigated. Fig. 6 shows the SO_2 conversion, sulfur yield, H_2S yield and GC peak area of H_2O depending on the temperature. The reactivity test was performed in the reaction temperature range of 400–800 °C under the conditions of a space velocity of 30,000 ml/$g_{\text{-cat}}$ h and an $[H_2]/[SO_2]$ molar ratio of 2.0. First, in terms of the variation of the reactivity with the x value, the light-off temperature was 575 °C in the SO_2 reduction over the $Ce_{0.8}Zr_{0.2}O_2$ catalyst, and both the SO_2 conversion and sulfur yield were increased dramatically with increasing temperature, in the temperature range below 700 °C. However, the SO_2 conversion and sulfur yield were increased gradually with increasing temperature in the range of temperature above 700 °C. In this experiment, H_2S was generated as a by-product due to the reaction between H_2 and elemental sulfur. H_2S formation started at 625 °C and was increased with increasing reaction below 700 °C. The generation profile of H_2O as a by-product in the reaction between SO_2 and H_2 is similar to that of H_2S.

In the reduction of SO_2 by H_2 over $Ce_{0.5}Zr_{0.5}O_2$, the conversion of SO_2 into elemental sulfur started at a lower temperature than the reduction of SO_2 over the other $Ce_{1-x}Zr_xO_2$ catalysts. The light-off temperature was 500 °C, and both the SO_2 conversion and sulfur yield were increased steeply below 700 °C. The rate of increase in the reactivity with temperature for the reduction of SO_2 by H_2 over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst was higher than that over the other

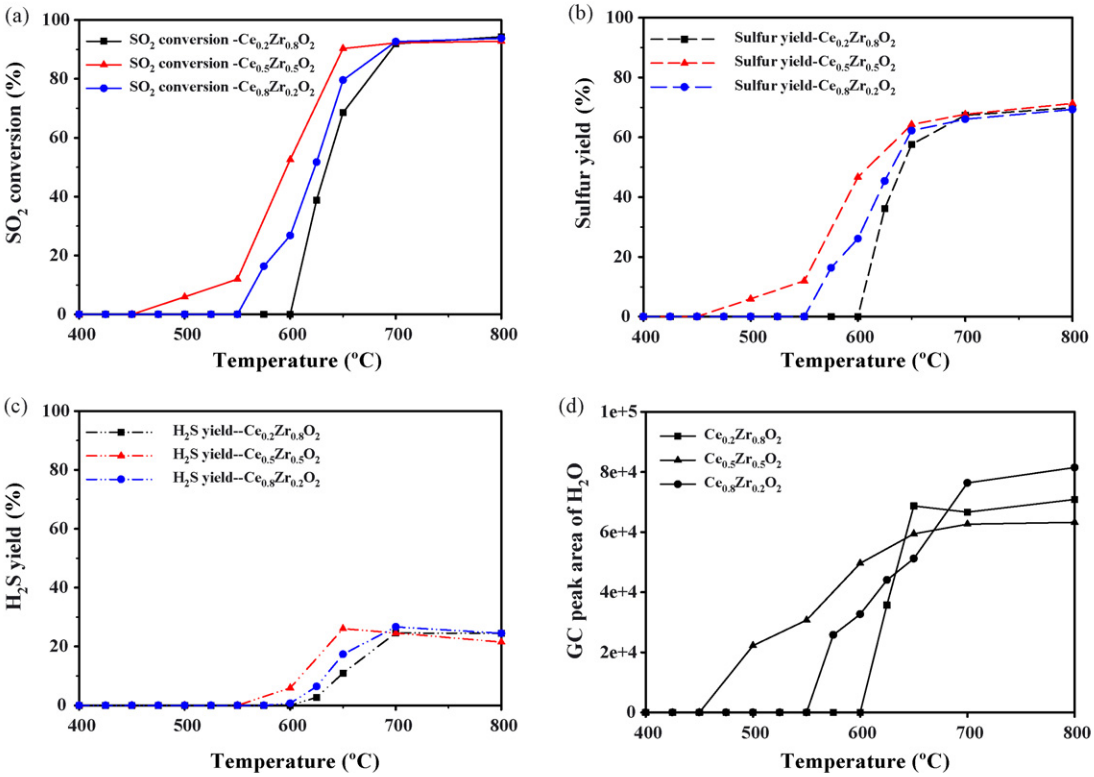

Fig. 6. SO_2 reduction by H_2 over $Ce_{1-x}Zr_xO_2$ catalysts: (a) SO_2 conversion, (b) sulfur yield, (c) H_2S yield, and (d) GC peak area of H_2O.

catalysts, while, above 650 °C, no increase in the reactivity with increasing reaction temperature was observed for the reduction of SO_2. Also, in the range of temperature above 650 °C, the sulfur yield reached 71% at 800 °C due to the decrease of the H_2S selectivity, as well as the increase of the sulfur yield. The best catalytic performance was exhibited at 800 °C, at which point the SO_2 conversion and sulfur yield were about 92% and 71%, respectively. The generation of H_2S as a by-product started at around 600 °C and then decreased a little in the range of temperature above 700 °C. The increasing profile of H_2O generation was similar to that of H_2S.

In the reduction of SO_2 by H_2 over the $Ce_{0.2}Zr_{0.8}O_2$ catalyst, the light-off temperature was around 625 °C, above which the SO_2 conversion and sulfur yield were increased with increasing temperature. In the range of temperature below 700 °C, the SO_2 conversion and sulfur yield were increased sharply with increasing temperature. On the other hand, the SO_2 conversion and sulfur yield remained constant when the reaction temperature was increased above 700 °C. The generation of H_2S as a by-product started at around 625 °C and then decreased a little in the range of temperature above 700 °C. The increasing profile of H_2O generation was similar to that of H_2S.

From the above-mentioned results, we can infer the following: in the reduction of SO_2 by H_2 over Ce–Zr based catalysts, the reactivity increases dramatically with increasing reaction temperature below 700 °C, but not above 750 °C. At this time, an SO_2 conversion of about 93% and a sulfur yield of about 70% are obtained above 700 °C or 750 °C. In comparing the maximum performance of each of the Ce–Zr based catalysts, it can be concluded that they exhibit similar reaction characteristics. However, the best catalyst was $Ce_{0.5}Zr_{0.5}O_2$ since it has the lowest light-off temperature and highest performance at the same temperature.

3.4. SO_2 reduction by synthetic gas over $Ce_{0.5}Zr_{0.5}O_2$ catalyst

The reduction of SO_2 by synthetic gas containing both CO and H_2 over a $Ce_{0.5}Zr_{0.5}O_2$ catalyst was conducted in this experiment. As the catalyst having the best performance, $Ce_{0.5}Zr_{0.5}O_2$ was chosen among the various Ce–Zr catalysts. In this experiment, we investigated the effect of temperature and the $[CO]/[H_2]$ molar ratio of the synthetic gas on the reduction of SO_2 by synthetic gas. The reactant gas mixture containing 2 vol% SO_2 and 4 vol% synthetic gas was fed into the fixed bed catalytic reactor packing the $Ce_{0.5}Zr_{0.5}O_2$ catalyst. Under the reaction condition of a space velocity of 30,000 ml/$g_{\text{-cat}}$ h, and an $[H_2 + CO]/[SO_2]$ molar ratio of 2.0, the reaction temperature was varied from 375 °C to 600 °C at a fixed $[CO]/[H_2]$ molar ratio. The results are shown in Fig. 7 in the form of the SO_2 conversion, sulfur yield, H_2S yield, COS yield and GC peak areas of CO_2 and H_2O.

In the case where a $[CO]/[H_2]$ molar ratio of 1/3 was used, the dependence of the reaction temperature in the reduction of SO_2 by synthetic gas was investigated over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst. The conversion from SO_2 into elemental sulfur started at around 475 °C. The SO_2 conversion and sulfur yield were increased steeply with increasing reaction temperature in the

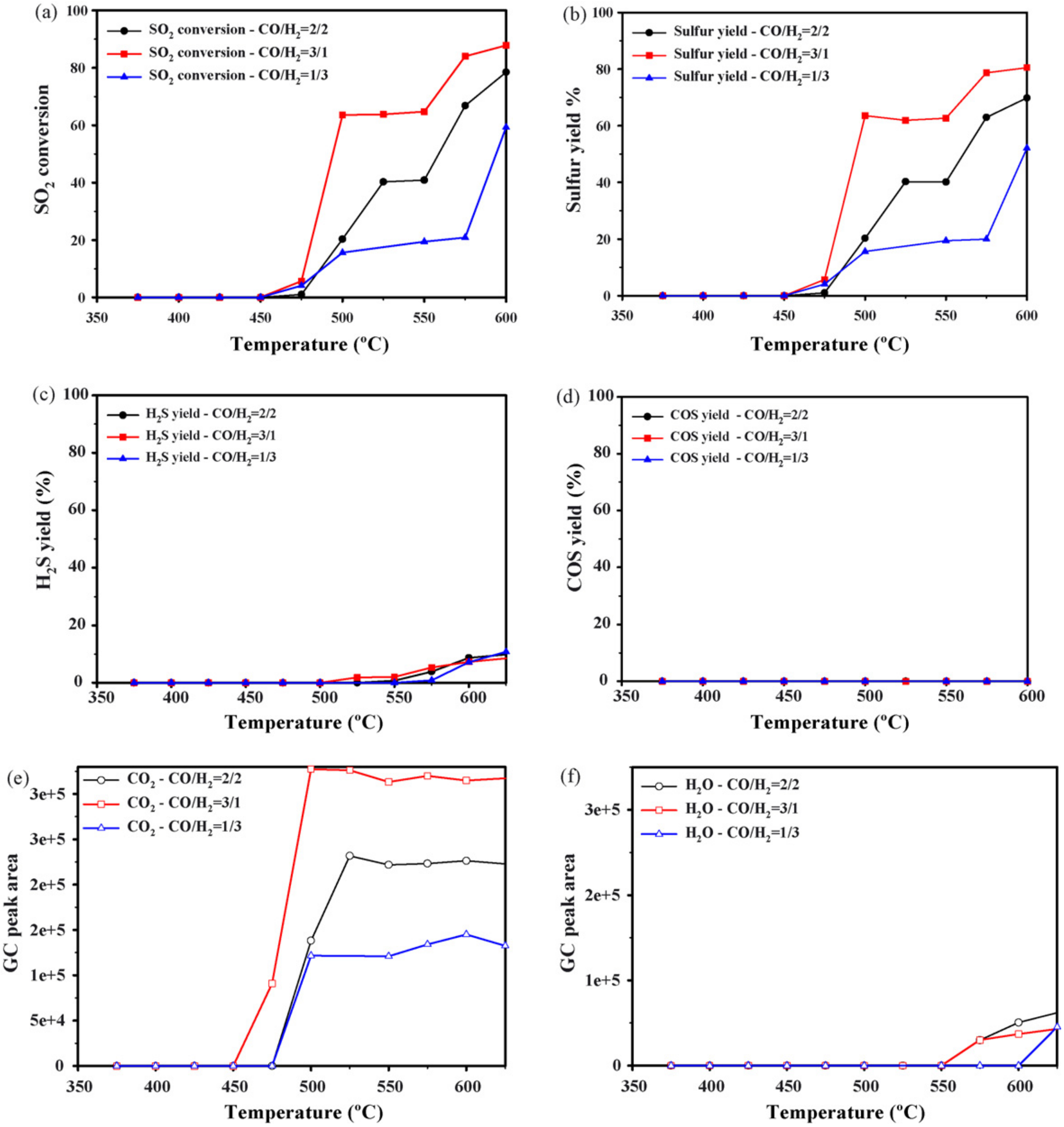

Fig. 7. SO_2 reduction by synthetic gas with a variety of [CO]/[H_2] molar ratios over $Ce_{0.5}Zr_{0.5}O_2$ catalysts: (a) SO_2 conversion, (b) sulfur yield, (c) H_2S yield, (d) COS yield, (e) GC peak area of CO_2, and (f) GC peak area of H_2O.

temperature ranges below 500 °C and above 575 °C, whereas between 500 °C and 575 °C they remained constant with increasing temperature. As regards the generation of the various by-products, the generation of H_2S started at 575 °C, but no COS was generated. The best performance of the $Ce_{0.5}Zr_{0.5}O_2$ catalyst was obtained at 600 °C, at which point the SO_2 conversion and sulfur yield were about 60% and 52%, respectively. At that time, the H_2S yield was very low, being only about 7%, and COS was not detected due to the high selectivity of elemental sulfur in the conversion of SO_2 The generation of CO_2 was increased within the temperature range of 475–500 °C, and remained constant above 500 °C. It was supposed that when the synthetic gas with a [CO]/[H_2] molar ratio of 1/3 was used as the reducing agent, the main reducing agent was CO in the range of temperatures below 500 °C, but was H_2 in the range of temperatures above 550 °C. It might be due to the fact that the amount of CO_2 was increased below 500 °C, and that of H_2O was decreased above 550 °C.

In the case where a [CO]/[H_2] molar ratio of 2/2 was used, the conversion of SO_2, during which H_2S, CO_2, and H_2O were generated, started at 500 °C. The best performance in the reduction of SO_2 by synthetic gas over $Ce_{0.5}Zr_{0.5}O_2$ was obtained at 600 °C, at which point the SO_2 conversion was about 78.5% and the sulfur yield was about 69.8%. Both the SO_2 conversion and sulfur yield were simultaneously increased with increasing reaction temperature within the temperature ranges of 450–525 °C and 550–600 °C. The generation of H_2S started at 550 °C, but no COS was generated even though the amount of CO contained in the gas mixture was more than that in case where a [CO]/[H_2] molar ratio of 1/3 was used. The H_2S

yield reached about 7% at 600 °C. The generation of CO_2 started at 500 °C, and increased with increasing reaction temperature within the temperature range of 475–525 °C. The GC peak area of CO_2 remained constant in the temperature range above 525 °C and the GC peak area of H_2O increased in the temperature range above 550 °C. From this result, it was inferred that CO acted as the main reducing agent within temperature range of 475–500 °C, whereas H_2 acted as the main reducing agent in the temperature range above 550 °C in the reaction generating elemental sulfur through the reduction of SO_2 by CO or H_2.

In the case where a [CO]/[H_2] molar ratio of 3/1 was used, the beginning point of the SO_2 conversion was 475 °C. The SO_2 conversion and sulfur yield were increased with increasing reaction temperature within the temperature ranges of 475–550 °C and above 550 °C. Though synthetic gas, which contained more than three times as much as CO than H_2, was used as a reducing agent, no COS was generated, but only H_2S. The amount of CO_2 generated increased abruptly with increasing reaction temperature in the range from 450 °C to 500 °C, but decreased with increasing reaction temperature above 500 °C. The generation of H_2O picked up above 550 °C. It was presumed that below 500 °C CO acted as the main reducing agent in the reduction of SO_2 by the synthetic gas with a [CO]/[H_2] molar ratio of 3/1, whereas above 550 °C the main reducing agent was H_2.

When examining the yields of COS and H_2S in the results described above, given that COS but not H_2S was generated as a by-product and that better performance was achieved in the reduction of SO_2 by CO than that by H_2, it was inferred that CO plays a more effective role than H_2 as a reducing agent in the reduction of SO_2 over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst. However, when using CO, less COS was generated than H_2S when using H_2, in spite of the fact that higher SO_2 conversion was obtained using CO than using H_2 as a reducing agent in the reduction of SO_2. It was assumed that the sulfur selectivity was higher in the case where CO was used in the reduction of SO_2 than in the case where H_2 was used. Particularly, when the synthetic gas was used as a reducing agent, COS-free gas composition products were generated and even higher sulfur selectivity was obtained than in the case where only CO was used. In comparing the performance and reaction characteristics in the case where the synthetic gas with a variety of [CO]/[H_2] molar ratios was used in the reduction of SO_2 over $Ce_{0.5}Zr_{0.5}O_2$, the following conclusions could be drawn: from the viewpoint of the reaction temperature, the light-off temperature in the case where only CO was used was lower than that in the case where the synthetic gas or only H_2 was used in the reduction of SO_2 over the $Ce_{1-x}Zr_xO_2$ catalysts. At this time, we obtained the different light-off temperatures according to the sort of reducing agent in the range from 400 °C to 425 °C in the reduction of SO_2 using only CO. In the case where H_2 was used, the conversion of SO_2 began in the high temperature range of between 500 °C and 625 °C, whereas a higher onset temperature was observed in the case where CO or synthetic gas was used. In comparing these results, which were attributed to the reduction of SO_2 by the synthetic gas containing both CO and H_2, it was found that the temperature, at which CO or H_2 play the predominantly role as the main reducing agent, varied with the temperature. For example, CO played the main role as the reducing agent in the temperature range below 500 °C, while H_2 was the dominant reducing agent above 550 °C. Also, despite the high SO_2 conversion obtained using the synthetic gas containing more CO than H_2, COS was never generated in the reduction of SO_2 because of the high sulfur selectivity. And then and the H_2S yield was increased slightly with increasing reaction temperature. It seems that these results were consistent with the following results: the COS yield was increased below 450 °C, but then was diminished above 450 °C in spite of the increase in temperature in the reduction of SO_2 using only CO. In the case where only H_2 was used in the reduction of SO_2, the H_2S yield increased with increasing reaction temperature within the temperature range of 550–700 °C, but the H_2S yield fell off in the temperature range above 700 °C, regardless of the reaction temperature. These results are in agreement with the GC peak areas corresponding to CO_2 and H_2O which were inevitably produced as by-products in the conversion of SO_2 into elemental sulfur by CO and H_2. We confirmed that the linear growth of the GC peak area corresponding to the amount of CO_2 or H_2O generated was continuous before or after the saturated reactivity was attained, in spite of the increase in both the SO_2 conversion and sulfur yield with increasing reaction temperature, by comparing the changes in the CO_2 or H_2O peak area according to the [CO]/[H_2] molar ratio in the reduction of SO_2 by the synthetic gas. It was found that different temperature ranges existed in which CO or H_2 acted as the main reducing agent in the reduction of SO_2 over $Ce_{1-x}Zr_xO_2$ catalysts. For example, when the [CO]/[H_2] molar ratio was 1/3, 2/2, and 3/1, CO acted as the main reducing agent in the temperature ranges below 600 °C, 575 °C and 575 °C, respectively, as determined by the increase in the amount of CO_2 generated, and H_2 played the role of the main reducing agent above 600 °C, 575 °C, and 575 °C, respectively, as determined by the increase in the amounts of both H_2S and H_2O generated in the reduction of SO_2 by the synthetic gas over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst. From the above-mentioned results, it was confirmed that the gas composition of the reducing agent containing more CO than H_2 is more favorable in the reduction of SO_2 over the $Ce_{1-x}Zr_xO_2$ catalysts.

In comparing the performance for the reduction of SO_2 as a function of the [CO]/[H_2] molar ratio at the same temperature, the reactivity obtained using the synthetic gas was higher than that obtained using only H_2 and lower than obtained using only CO. Also, using synthetic gas with a higher CO content than H_2 content results in a higher SO_2 conversion, a higher sulfur yield and a lower light-off temperature in the reduction of SO_2 by the synthetic gas. In the reduction of SO_2 by the synthetic gas, the sulfur selectivity was higher than that obtained using only CO or H_2. Consequently, the reducing agent containing a higher CO content than H_2 content was more effective in the reduction of SO_2 over the Ce–Zr based catalysts and it was confirmed that the coal-derived gas containing a higher CO content than H_2 would be more favorable as a reducing agent in the DSRP of an IGCC power plant system.

3.5. Catalytic redox properties and reaction characteristics of SO_2 reduction according to reducing agent

As previously stated, the effect of the x value and reaction temperature on the reaction characteristics of the reduction of SO_2 by H_2 and CO was investigated. In the case where H_2 was used as a reducing agent, $Ce_{0.5}Zr_{0.5}O_2$ was the best catalyst, and the SO_2 conversion and sulfur yield were about 92.8% and 71.3% at 800 °C, respectively. No direct relationship between the reactivity for the reduction of SO_2 by H_2 and the Ce/Zr molar ratio was observed in the above results. It could be supposed that the activity of the $Ce_{1-x}Zr_xO_2$ catalyst with the optimal Ce/Zr molar ratio was dependent upon the reaction temperature, because the reactivity of the SO_2 reduction increased as the reaction temperature increased. The light-off temperature was around 550 °C and the optimal temperature was 800 °C in this case. This dependence of the reduction of SO_2 by H_2 on the reaction temperature might be related to the redox properties of the Ce–Zr catalysts. These reaction characteristics were consistent with the redox properties of Ce–Zr catalysts. In accordance with the research result which was reported by Chen et al., the redox properties obtained in the H_2-TPR experiment started at 550 °C, and were strongest at 800 °C [20]. It is believed that this result concerning the redox properties of the $Ce_{1-x}Zr_xO_2$ catalysts obtained in the H_2-TPR experiment is consistent with the reaction characteristics of the reduction of SO_2 by H_2 over the $Ce_{1-x}Zr_xO_2$ catalysts. In this reduction of SO_2 by CO, the optimal temperature varied with the Ce/Zr molar ratio. The higher the Ce content of the Ce–Zr based catalyst, the lower the light-off temperature. At this time, the light-off temperature ranged from 425 °C to 450 °C and the optimal temperature for the performance of the reduction of SO_2 by CO over the Ce–Zr based catalysts was in the range from 500 °C to 550 °C. Madier et al. reported that $Ce_{1-x}Zr_xO_2$ catalysts exhibited vigorous redox properties in the relatively low temperature range of 300–600 °C in a CO-TPR experiment over $Ce_{1-x}Zr_xO_2$ [21]. The present result for the reduction of SO_2 by CO over Ce–Zr based catalysts might be related to the redox properties of the $Ce_{1-x}Zr_xO_2$ catalysts which were reported by Madier et al. Regardless of the increase of Ce/Zr ratio of the $Ce_{1-x}Zr_xO_2$ catalyst, the reactivity for the reduction of SO_2 by CO did not appear to be increased, even when the reaction temperature was increased after the Ce–Zr catalyst was activated. An SO_2 conversion of about 94.4% and a sulfur yield of about 91.3% were obtained at 500 °C as the best performance for the reduction of SO_2 by CO over the $Ce_{0.5}Zr_{0.5}O_2$ catalyst. This performance is higher than that obtained using H_2 as a reducing agent. The dependence of the reduction of SO_2 upon the reaction temperature over Ce–Zr based catalysts was less for CO than for H_2. Also, a much lower COS yield was obtained in the reduction of SO_2 by CO than the H_2S yield in the reduction of SO_2 by H_2. Consequently, it was inferred that the reactivity for the reduction of SO_2 using CO was higher than that using H_2 and that the $Ce_{0.5}Zr_{0.5}O_2$ catalyst and a reducing agent with a high CO content are more favorable in the reduction of SO_2 by a reducing agent containing both CO and H_2 over $Ce_{1-x}Zr_xO_2$ catalysts.

4. Conclusion

In order to investigate the feasibility of using coal-derived gas in the DSRP of an IGCC power plant, the reaction characteristics for the catalytic reduction of SO_2 and the performance of $Ce_{1-x}Zr_xO_2$ catalysts were investigated by using reducing agents containing H_2 or CO. It was found that the reaction characteristics for the reduction of SO_2 over the $Ce_{1-x}Zr_xO_2$ catalysts were dependent on the type of reducing agent. When the dependence of the reaction temperature on the reduction of SO_2 was investigated with the various reducing agents, a lower light-off and reaction temperature were obtained when using CO than when using H_2 for the same performance in the reduction of SO_2 over the $Ce_{1-x}Zr_xO_2$ catalysts. As regards the performance, the $Ce_{1-x}Zr_xO_2$ catalyst using CO has a higher activity at a lower temperature for the reduction of SO_2 than the same catalyst using H_2. Therefore, we inferred that a reducing agent which contains more CO than H_2 was necessary for obtaining higher performance from the $Ce_{1-x}Zr_xO_2$ catalyst in the DSRP. It was concluded that $Ce_{1-x}Zr_xO_2$ catalysts can be used in the DSRP using coal-derived gas containing a higher CO content than H_2 content in an IGCC power plant system.

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