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Methane reforming and water splitting by zirconia-supported cerium-tungsten composite oxides for cyclic production of syngas and hydrogen

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ABSTRACT

Redox cycles of methane reforming (MR) and water splitting (WS) of cerium-tungsten composite oxides were investigated at 1223 K for the cyclic production of syngas and hydrogen. Among various composite oxides tested having different Ce/W ratios, the sample with the Ce/W molar ratio of 1, CeW1/Zr, showed the best performance. When the sample was stabilized after several cycles, most of the Ce was present as Ce³⁺ and thus only W participated in the redox process. Production of CO₂ during MR by the cerium-tungsten composite sample was much less than that by the WO₃-only sample, yielding a H₂/(CO + CO₂) ratio much closer to the desired value of 2. The extent of reduction of W by MR remained nearly constant during repeated cycles, but re-oxidation by WS was not complete during the first several cycles. However, the re-oxidation extent increased to full re-oxidation during repeated cycles; the redox system became very stable after the sixth cycle. These are both beneficial effects owing to the presence of Ce.

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Introduction

Steam reforming of CH₄ is currently the most widely used process for the production of syngas and H₂. As an alternative to this process, cyclic production of syngas and H₂ by redox of metal oxides is attracting great attention. The cycle typically consists of reduction of a metal oxide by CH₄ (i.e., methane reforming: MR) followed by re-oxidation of the reduced metal or metal oxide by H₂O (i.e., water splitting: WS). Many metal oxides have been investigated for use in this process [1–19].

Concentrated solar heat may be utilized for this redox operation, making it particularly interesting in light of the current global attention to sustainable energy and environmental issues. Direct thermal reduction of stable metal oxides which generates O₂ typically requires temperatures higher than 1573 K [20–26]. However, reduction of those metal oxides by CH₄ which produces syngas can be achieved below 1300 K, constituting a considerable advantage over direct thermal reduction. The H₂ and syngas thus produced can be used for fuel cells and for synthesis of ammonia, methanol, synthetic fuels, etc.

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Among the metal oxides, cerium oxide and tungsten oxide are promising for use in this process [3–5,7,12–18,22,25,26]. The reasons are as follows: (i) the temperature of reduction by CH_4 is comparatively low: ~ 1073 K for cerium oxide [13] and ~ 1223 K for tungsten oxide [14]; (ii) these two oxides are thermally stable at the operating temperatures; (iii) the H_2/CO ratio in syngas produced during MR is nearly 2, which is desirable for synthesis of hydrocarbon fuels and methanol, and can be maintained by properly controlling the reduction temperature and time to prevent carbon deposition by methane decomposition, an undesirable side reaction [13–18]; (iv) all oxygen in the WO_3 can be used to produce syngas, by means of the reduction of WO_3 to WO_2 and then to metallic W, making the yield of syngas per mole of WO_3 much greater than that of other oxides [14]. However, to make use of these oxides, improvements are needed to prevent the present problems of gradual decrease in the syngas and H_2 yields during repeated cyclic operations, and of carbon deposition.

Several studies have been reported on the use of either cerium oxide or tungsten oxide as the metal oxides in MR-WS, but to the best of our knowledge, there have been no reports on the use of composite oxides of cerium and tungsten. A recent study on ceria-zirconia stabilized tungsten oxides reported a lower reduction temperature (1123 K) and greater stability compared to the use of WO_3 alone [12]. Because ceria-zirconia solid solutions [3,17] and some composite oxides such as Ni-, Zn-, Mn-, and Cu-containing ferrites [6,8,9,11] show better performance than single-metal oxides, composite oxides of cerium and tungsten are expected to exhibit improved performance.

The purpose of this study is to investigate the synergistic effects of composite oxides of cerium and tungsten compared with each oxide used alone. Samples with different ratios of Ce/W were prepared. The samples were first subjected to temperature-programmed reduction (TPR) experiments to quickly obtain a general understanding of the reduction characteristics. Appropriate reaction times were investigated by means of experiments conducted at a constant temperature, and the cyclic redox reactions were carried out to evaluate the composite oxides' long-term stability.

Experimental

Sample preparation

Samples of cerium-tungsten oxides supported on ZrO_2 were prepared by following the procedure detailed in our previous studies on the $\text{CeO}_2/\text{ZrO}_2$ and WO_3/ZrO_2 systems [13,14]. The ZrO_2 powder employed (Alfa Aesar, 99.5% purity) was of monoclinic phase and had a particle size of 0.5–1 μm , and a surface area of 6.40 m^2/g . An aqueous solution of cerium nitrate was prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical, 99.99% purity) in distilled water; ZrO_2 powder was then added to this solution. To precipitate Ce species, the solution was adjusted to pH 9.5 by adding aqueous ammonia under stirring. After 2 h, the solid precipitate was filtered using an aspirator (Joie-Tech., VE-11), washed with distilled water and acetone, and then suspended in distilled water using a sonicator for 30 min. An aqueous solution of

$(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$ (Fluka, 99% purity) was added to the suspension. The water in the mixture was evaporated to dryness while stirring at 343–353 K for one day, followed by calcination of the dried solid in air at 1273 K for 2 h. The calcined solid was crushed and sieved to obtain powder samples of particle size 106–250 μm .

To match the stoichiometries of several crystalline cerium-tungsten oxides listed in the JCPDS database, namely $\text{Ce}_2\text{W}_3\text{O}_{12}$, $\text{Ce}_2\text{W}_2\text{O}_9$, Ce_2WO_6 , Ce_4WO_9 , and $\text{Ce}_6\text{WO}_{12}$, the molar ratios of Ce/W in the calcined samples were adjusted to 2/3, 1, 2, 4, and 6 during preparation. (Note: those oxides may be alternatively expressed as $\text{Ce}_2\text{O}_3(\text{WO}_3)_3$, $\text{Ce}_2\text{O}_3(\text{WO}_3)_2$, $\text{Ce}_2\text{O}_3\text{WO}_3$, $(\text{Ce}_2\text{O}_3)_2\text{WO}_3$, and $(\text{Ce}_2\text{O}_3)_3\text{WO}_3$, respectively.) The oxidation states of Ce and W in these oxides are +3 and +6, respectively; hence the oxides may be considered as composites of Ce_2O_3 and WO_3 . In the calcined samples, the amounts of ZrO_2 and WO_3 (assuming that W were present as WO_3) were typically fixed at 9.0 and 1.0 g, respectively. Thus, the weight percentages of WO_3 in the calcined samples were 9.55, 9.34, 8.76, 7.79, and 7.02, respectively. The prepared samples were labeled using the convention CeWX/Zr, where X is the Ce/W molar ratio.

TPR experiment

To identify the main and side reactions occurring during the reduction of cerium-tungsten composite oxides by CH_4 , reduction experiments were carried out, employing the TPR apparatus and procedure described in our previous study [14]. Briefly, the reactor used was made of a quartz tube with the internal diameter of 8 mm. This tube was narrowed in the middle to the diameter of 5 mm diameter, and quartz wool was packed into this narrowed zone to support the sample. The CeWX/Zr powder was mixed with 2-mm zirconia balls to prevent pressure build-up and fluctuation; this mixture was loaded into the reactor tube, and additional quartz wool was added and used to pack the mixture. The packed reactor was placed in a temperature-programmable electric furnace. The amounts loaded into the reactor tube were typically 2.7 g of the zirconia balls and 0.1 g of WO_3 in the CeWX/Zr sample; thus the amounts of CeWX/Zr loaded were 1.05, 1.07, 1.14, 1.28, and 1.43 g for X = 2/3, 1, 2, 4, and 6, respectively.

CH_4 and N_2 were fed into the reactor with the flow rates of 1.5 and 13.5 $\text{cm}^3(\text{STP})/\text{min}$, respectively. The temperature of the reactor was increased from room temperature to 1273 K according to the programmed ramp rate. Effluent gas from the reactor was analyzed using two gas chromatographs, by injecting the gas samples through the sampling valves at 4-min intervals. One gas chromatograph was equipped with a Carboxen 1006 column (Supelco, US) held at the oven temperature of 313 K and a thermal conductivity detector (TCD); Ar was used as the carrier gas. This gas chromatograph was used for the analysis of H_2 , N_2 , CO, and CH_4 . The other was equipped with a Hayesep Q column (Supelco, US) held at the oven temperature of 333 K and a TCD; He was used as the carrier gas. This gas chromatograph was used for the analysis of (N_2+CO) , CH_4 , and CO_2 . H_2 , N_2 , CO, CH_4 , and CO_2 were determined from calibration data collected by employing N_2 as an internal standard.

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