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Zirconia-supported tungsten oxides for cyclic production of syngas and hydrogen by methane reforming and water splitting

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ABSTRACT

ZrO₂-supported tungsten oxides were used for cyclic production of syngas and hydrogen by methane reforming (reduction) and water splitting (re-oxidation). The reduction characteristics of WO₃ to WO₂ and WO₂ to W were examined at various temperatures (1073–1273 K) and reaction times. Significant portions of the tungsten oxides were also reduced by the produced H₂ and CO. The extent of reduction by H₂ varied greatly depending on temperature and WO₃ content and also on the reduction of either WO₃ or WO₂, while that by CO was consistently low. When the overall degree of reduction became sufficiently high, methane decomposition started to proceed rapidly, resulting in considerable carbon deposition and H₂ production. Consequently, the H₂/(CO + CO₂) ratio varied from around 1 to higher than 2. During the repeated cyclic operations with a proper reduction time at a given temperature, the syngas and hydrogen yields decreased gradually while the H₂/(CO + CO₂) ratio remained nearly constant and the carbon deposition was negligible.

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1. Introduction

Conversion of solar heat to chemical energy is increasingly regarded as an important technology for sustainable energy [1,2]. For this purpose, various endothermic reactions have been studied for solar thermochemical processes. Among these, production of hydrogen from water is one of the most desirable long-term goals in solar fuel production. Applications of metal-oxide redox pairs to a thermochemical two-step water splitting cycle have been investigated extensively [3]. The first step is reduction of a metal oxide at a high temperature with liberation of oxygen, and the second step is re-oxidation of the reduced metal oxide or metal by water with liberation of hydrogen. This

cycle eliminates the need for H₂/O₂ separation and the material problems encountered at high temperatures (>2500 K) in direct one-step solar thermal splitting of water. Several redox systems have been investigated, but problems such as the requirement of very high temperatures (>2100 K) for thermal reduction [4–7] or too low H₂ yields in the re-oxidation step [5] have been reported. Some investigators have reported promising systems such as ZrO₂-supported ferrites [8,9] and cerium oxide mixed with ZrO₂, NiO, and Ta₂O₅ [10,11]; these systems show reasonable reactivity at 1673–1773 K and good repeatability during repeated cyclic operations.

To further lower the temperature of oxide reduction, a reducing agent can be used. The reducing agent may be coal

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[2,12], but methane is much more widely used [13–24]. When methane is used as the reducing agent, reduction can usually be achieved below 1300 K. The first step is reduction of the oxide by methane [20]:

Reduction by methane: Metal oxide + CH₄ → reduced metal oxide or metal + CO + 2H₂.

This desired reaction generates syngas at a H₂/CO ratio of 2, which is preferable for methanol synthesis. This is in contrast to the conventional catalytic methane reforming with steam, in which syngas with a H₂/CO ratio of higher than 4 is produced [25]. The reduced metal oxide or metal produced by this reaction is used to produce hydrogen in the next water splitting step [20]:

Water splitting: Reduced metal oxide or metal + H₂O → metal oxide + H₂.

This oxidation reaction may produce hydrogen that is uncontaminated with carbon monoxide, and the produced hydrogen can be safely used for fuel cells. The re-oxidized metal oxide can be reused in the first reaction. Hence, this two-step cyclic process has evident advantages for the production of syngas and carbon-free hydrogen [18,20,23].

However, other competing reactions can occur during the methane reforming step. Among several possible competing reactions, the major ones are listed below [18,20,24].

Metal oxide reduction by syngas: Metal oxide + H₂ or CO → reduced metal oxide or metal + H₂O or CO₂

Methane decomposition: CH₄ → C + 2H₂

Carbide formation: Metal + C → metal carbide.

These competing reactions can cause the H₂/CO ratio in the syngas to deviate from 2. In addition, the hydrogen produced during water splitting may be contaminated with carbon oxides due to the deposited carbon or metal carbide, although this can be avoided by controlling the operating temperature and time [20]. Another problem that may occur is sintering of metal oxides during repeated cycling, but sintering can be minimized by using supports such as ZrO₂, CeO₂, and ceria-zirconia composites [19,21,24].

Various metal oxides have been investigated for this two-step process: Fe₃O₄ [13], ZnO [6,14], CeO₂–ZrO₂ composite oxides [15], Ni-, Co-, Zn-, Mn- and Cu-ferrites [16–19], CeO₂ [20], and WO₃ [21–24]. Among these, WO₃ is interesting because it has been reported that WO₃ is more reactive and selective than other metal oxides such as Fe₃O₄, ZnO, SnO₂, In₂O₃, MoO₂, and V₂O₅ [21–23]. This may be because WO₃ is first reduced to WO₂, which is then further reduced to metallic W; furthermore, the high melting point of the system provides good resistance to sintering, which can provide stable repeated cyclic operations [24]. However, during the methane reforming of WO₃, carbon deposition and carbide formation are prone to occur [21–24], which need to be controlled. However, to the best of our knowledge, the extents of reduction of WO₃ by the desired reaction and by the other

competing reactions have not well been analyzed, and the operating temperature and time that minimize carbon deposition and carbide formation have not been well established.

In the present study, ZrO₂-supported WO₃ was investigated for cyclic production of syngas and hydrogen by methane reforming and water splitting. This study was focused on (1) examining the reactions that occurred during methane reforming, particularly the extents of WO₃ reduction to WO₂ and further to W by the main reaction and by the competing reactions, (2) determining the operating temperature and time that minimized carbon deposition and/or carbide formation, and (3) investigating the repeatability of the oxide system during cyclic operations. The oxide system was first investigated by temperature-programmed reduction (TPR) experiments, and the extents of reduction by the main reaction and by the competing reactions were preliminarily examined to get a quick overview of the reduction characteristics. Next, cyclic methane reforming and water splitting operations were performed at fixed temperatures to determine the extents of reduction by the main reaction and by the competing reactions and the optimal operating temperature and time to minimize carbon deposition and/or carbide formation.

2. Experimental

The overall experimental procedure was similar to that described in our previous study on the CeO₂/ZrO₂ system [20].

2.1. Preparation of ZrO₂-supported WO₃

ZrO₂-supported WO₃ samples (WO₃/ZrO₂) were prepared by following the procedure detailed in a previous study [22]. The ZrO₂ powder (Alfa Aesar, 99.5% purity) comprised monoclinic phase ZrO₂ with a particle size of 0.1–0.6 μm and a surface area of 6.4 m²/g. The ZrO₂ powder was added to an aqueous solution of (NH₄)₆H₂W₁₂O₄₀ (Fluka, 99% purity). The solution was evaporated to dryness while stirring at 343–353 K for one day, followed by calcination in air at 1173 K for 2 h. The calcined solid was crushed and sieved to obtain powder samples comprising 106–250 μm in size. The content of WO₃ in the samples was adjusted to 10, 30, or 50 wt% by using predetermined amounts of material.

2.2. TPR experiments

To determine the reactions that occurred during methane reforming, experiments were performed in the TPR apparatus shown in Fig. 1. The reactor comprised an 8-mm internal diameter quartz tube that was placed in a temperature-programmable electric furnace. The WO₃/ZrO₂ sample was packed between quartz wool in the middle of the reactor, and 1 g of sample was generally used unless noted otherwise. The feed gas flow rates of CH₄ and N₂ were 1.5 and 13.5 cm³(STP)/min, respectively. According to programmed ramp rates, the temperature of the reactor was raised from room temperature to 1273 K. The effluent gas from the reactor was analyzed with two gas chromatographs by injecting the gas samples through the sampling valves at 5-min intervals. One gas chromatograph

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