Study of Water-splitting on Carbothermally Reduced Wüstite for Solar/Chemical Energy Conversion

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Abstract —The possibility of the incorporation of solar energy by solar thermochemical water-splitting with wüstite, which is the 2nd step H₂ production in Fe₃O₄/coal redox process for solar/fossil energy mixing, was studied kinetically. The reaction formed efficiently molecular hydrogen and cation-excess magnetite. The reaction rate was greatly dependent on reaction temperature and H₂O steam flow rate. The H₂ volume generated by the reaction gave the maximum value (76 % of theoretical value) at 873K.

I. INTRODUCTION

Solar thermochemical process has been the current subjects for introducing the solar energy into the primary energy system. Several thermochemical systems have been studied for harnessing the concentrated sun light as the process heat. They include carbothermal redox process by Steinfeld et al.[1-2], methane reforming with CO₂ producing the syngas[3], and ammonia decomposition [4].

The carbothermal redox process uses fossil fuels such as coal and natural gas. Coal will be primarily important from long-term strategy consideration instead of relatively high-quality natural gas, i.e., CH₄.

Coal-magnetite redox process is the first step of the overall solar carbothermal process:

where x is the mole ratio of hydrogen to carbon content in the coal. This is highly endothermic and involves the mixing[5-7] of fossil energy (coal) and solar energy as a process heat.

Solar reactor experiments using a high-flux irradiation of 300W/cm² using a PSI solar system showed that the carbon decreased rapidly within only 1 sec of exposure, suggesting efficient heat transfer and chemical conversion by direct absorption of concentrated solar energy at the reaction site. The water-splitting is the

second solar step, producing H₂ and Fe₃O₄. The latter material is recycled to the first solar process. The proposed solar thermochemical process offers the possibility of performing simultaneously gasification of coal and reduction of iron oxide and also producing a fuel with an upgraded calorific value.

The above process needs to be fast enough to follow the first step (1) to perform effectively the overall solar gasification and water-splitting. Thus, the objective of

the present study was to investigate the reaction kinetics of Eq.(2).

II. EXPERIMENTAL

A. Specimens

The non-stoichiometric wüstites used in this investigation were prepared from Fe₃O₄. The samples prepared and reacted with water were identified by X-ray diffractometry with FeK α radiation (Rigaku X-ray diffractometer, model RAD-2A). Thermogravimetry (TG) was used to determine the oxygen content of the wüstite samples.

B. Water splitting by H₂O-wüstite system

The reaction cell was set in an infrared furnace (Shinku-Riko, model RHL-E45P). The sample feeder was fixed on the top of the reaction cell via a flexible silicone tube connector. H₂O/Ar diluent gases were introduced through the sample feeder and the reaction cell. The concentrations of the H₂ gas in the outlet gases were determined by gas chromatography with thermal conductivity detector (GC-TCD) (Shimadzu GC-8A) and a stainless steel column packed with 60/80 mesh Molecular Sieve 13X.

III. RESULTS AND DISCUSSION

A. Kinetics of water splitting by H₂O-wüstite system

The chemical composition and the observed lattice constants of all prepared samples were in good agreement with reported values[8].

Average rate of H₂ evolution R_{H_2} was calculated by:

$$R_{\text{H}_2} = [\text{H}_2] / \Delta t \quad (3)$$

where [H₂] is the total amount of hydrogen in a sampling bottle and Δt is a time interval for sampling. To obtain the total amount of H₂ evolved at each temperature, the area under the corresponding curve was integrated. The largest amount of H₂ evolved at 873K was 76 % of the

theoretical value calculated on a stoichiometry basis of the reaction (2). The reaction was completed in less than three minutes. With decreasing H₂O gas flow rate, the rate of H₂ evolution decelerated and also, the peak of the H₂ evolution rate appeared later. At lower temperatures (573 and 673K) the rates of H₂ evolution are hardly under the influence of H₂O gas flow rate. This indicates that cation migration did not follow H₂O gas flow rate at low temperatures. On the other hand, at higher temperatures (873 and 1073K) the rate of H₂ evolution was under the great influence of the H₂O gas flow rate. This suggests that the rate of cation migration did not follow the H₂O gas flow rate at high temperature. The water-splitting with wüstite completed approximately within 2 min. at high temperature. Coal-magnetite redox reaction completed approximately within 5 min. at 1373K. Regarding that the water-splitting completed faster than coal-magnetite redox reaction at lower temperature, the water-splitting can be considered to be incorporated in the 2nd step in Fe₃O₄/coal redox process for solar/energy mixing.

Fig. 1. The rate of H₂ evolution vs time at H₂O gas flow rate of 1.16 ml/sec at temperatures: ●, 1073K; △, 873K; ▲, 673K; □, 473K

B. Solid phase analysis

Wüstite samples were changed to cation-excess magnetite by the water-splitting reaction at higher temperatures (873 and 1073K), while below the eutectic point of wüstite (843K) two distinct wüstite phases were formed in addition to cation-excess magnetite. One of the wüstite phases had a lattice constant which was equal to that for the sample prior to water splitting. The other showed a larger lattice constant and corresponded to a more iron-rich composition. When temperature was below the eutectic point of wüstite and the H₂O gas flow rate was 17.4 and 69.6 ml/min, iron-deficient wüstite was observed in addition to iron-rich wüstite and cation-excess magnetite.

IV. CONCLUSION

Fig. 2. XRD pattern of the sample before and after the water-splitting with wüstite. ○ : original wüstite, □ : cation-excess magnetite, △ : iron-rich wüstite, ◇ : iron-deficient wüstite

The H₂ volume generated by the reaction of the wüstite with H₂O gave a maximum value (76 % of theoretical value) at 873K (0.1 MPa). The wüstite phase formed a cation-excess magnetite phase after the water splitting. Iron-rich wüstite or a mixture of iron-deficient wüstite and iron-rich wüstite phase were formed below the eutectic point. The H₂ evolution reaction completed approximately within 2 min. at temperatures of 873K and 1073K. This H₂ evolution rate was high enough to produce H₂ in a mass-production (2.6×10^{-5} m³ H₂/sec.g of wüstite) above 873K. These results led to the conclusion that the water splitting by H₂O and wüstite can be incorporated in the Fe₃O₄/Coal redox process for solar/fossil energy mixing.

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