열중량 분석에 의한 금속 산화물의 매체 순환식 수소 제조 반응성

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Reactivity of Metal Oxides for Chemical-Looping Hydrogen Generation by Thermogravimetric Analysis

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1. Introduction

Fossil fuels have many useful properties, but those are not renewable, emit pollutants, and are depleting nature. As hydrogen is one of the most important alternative energy resources, hydrogen generation from water is one of the most important long-term goals for future energy resources. Water splitting with reduction and oxidation (redox) of metal oxide, one of the hydrogen production methods, does not produce harmful pollutants, thereby it is an environment friendly process. Chemical-looping hydrogen generation (CLH), which is originated from chemical-looping combustion (CLC), is a water splitting process with redox of metal oxide [1, 2]. It is composed of two reactors, an oxidation and a reduction reactor. Reduction gas is introduced into the reduction reactor where it reduces metal oxide particle. The reduced metal oxide is circulated to the oxidation reactor where it split water with being oxidized. Hydrogen is generated from water in this reaction. The previous study for water splitting with redox of the metal oxide was operated at higher temperatures above 1500 K [3], namely thermochemical water splitting. Therefore, in this study, some metal oxides were selected for water splitting i. e., copper oxide (CuO) and manganese oxide (Mn_2O_3) supported on alumina, and silica, and the synthesis gas (H_2 + CO) was used for lower temperature reaction in the reduction. The reactivity of each metal oxide was determined by the thermal gravimetric analysis.

2. Experimental Method

2-1. Preparation of Metal Oxide Particles

Metal oxide particles were prepared by the solid phase method and two precipitation methods. Copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$, Aldrich] or manganese nitrate [$Mn(NO_3)_2 \cdot xH_2O$, Aldrich] aqueous solution was mixed with γ-Al_2O_3 (Fluka) or SiO_2 xerogel (Aldrich) particles for the first method of precipitation. Water in this mixture was evaporated in a vacuum evaporator, and it was calcined at 923 K for 40 minutes. The particles from 90 to 210 μm were prepared by sieving. For the solid phase method, copper oxide (CuO, Aldrich) was mixed with γ-Al_2O_3 in a ball mill for 18 h. The paste was made by adding distilled water to the mixed powders. The paste was dried at 383 K for 24 h, and calcined at 1173 K for 10 h. Then it was crushed and sieved to prepare
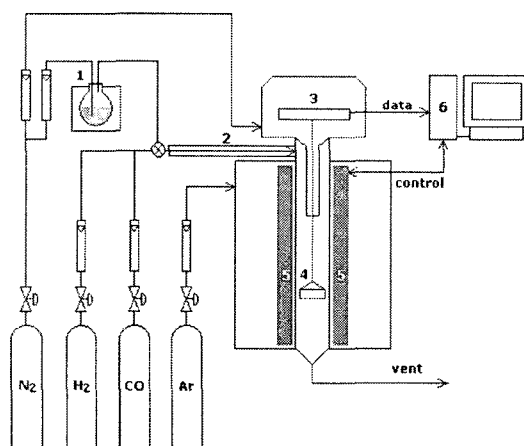
Fig. 1. Schematic diagram of a thermal gravimetric analyzer (TGA) system for the reactivity test; (1) water reservoir and bubbler, (2) gas pre-heater, (3) electric balance, (4) sample basket, (5) heater, (6) personal computer.

particle size in the range of 90-210 μm. Copper nitrate with aluminium nitrate [Al(NO$_3$)$_3 \cdot$9H$_2$O, Aldrich] aqueous solution was prepared for the second method of precipitation according to the method in a previous CLC study [4]. Solution of 2-propanol (Merck) was added and the mixture was dried at 373 K for 12 h at 423 K for 24 h and at 473 K for 5 h. At 773 K for 2 h, it was calcined and then pasted again. It was dried at 353 K for 30 min, and calcined at 1573 K for 6 h. Similarly, the particles from 90 to 210 μm were chosen by sieving. For all the particles, the weight ratio of CuO to Al$_2$O$_3$ was 1.5.

Scanning electron microscope (SEM, Philips) provides whole and micro structure of particles. Crystalline phase change of the particles was analyzed by X-ray diffraction (XRD, Rigaku D/MAX-III, Cu Kα radiation) before and after each reaction. Nitrogen adsorption was used to determine surface area of the particles by the BET method (NOVA-4200, v.7.10).

2-2. Reactivity of Metal Oxide Particles

Reactivity of reduction and water splitting were determined in a thermal gravimetric analyzer (TGA, Setaram 92). The prepared particles (10 mg) in a quartz basket were exposed under the atmosphere of 50% H$_2$ + 50% CO for reduction and 20% H$_2$O in N$_2$ for water splitting. The TGA was heated at a heating rate of 5 K/min to determine the temperature window for the reaction and at a heating rate of 30 K/min with N$_2$ injection at the isothermal reaction condition. The schematic diagram of TGA system is shown in Fig. 1. The selected reaction temperature was 623-1123 K for the reduction and 573-773 K for water splitting from the experimental data.

Table 1. Main crystalline phase and surface area of metal oxide particles

Specimen	Preparation method	Main crystalline phase	Surface area [m^2/g]
CuO/Al$_2$O$_3$	Precipitation (solution and support particles)	CuO	84.34
	Solid phase method	CuO, CuAl$_2$O$_4$	4.92
	Precipitation (solution mixture)	CuO, CuAl$_2$O$_4$	1.60
CuO/SiO$_2$	Precipitation (solution and support particles)	CuO	145.68
Mn$_2$O$_3$/Al$_2$O$_3$	Precipitation (solution and support particles)	Mn$_2$O$_3$	77.16
Mn$_2$O$_3$/SiO$_2$	Precipitation (solution and support particles)	Mn$_2$O$_3$	195.18

3. Results and Discussion

3-1. Properties of Metal Oxide Particles

The shape of particles was examined by SEM. Particles which were prepared by precipitation with the solution and the support particles are a little less than those by the solid phase method. Preparation by precipitation with the solution and support particles is the metal oxide deposition method on support particles (113-140 μm), and other two methods are the crushing calcined loaves so that more smaller particles size can be seen in precipitation with the supports. Though, the prepared particles are in the size range of 90-210 μm.

The chemical structures of the samples were characterized by using X-ray powder diffraction. Copper oxide particle by precipitation with the solution and support particles has only CuO crystal phase without phases related to Al$_2$O$_3$ and it is found that copper oxide was well deposited on the surface of γ-Al$_2$O$_3$. In the cases of other two methods, copper aluminate (CuAl$_2$O$_4$) phase can be seen, and it may be formed with CuO and Al$_2$O$_3$ at higher temperatures. Manganese oxide made from manganese nitrate solution has only Mn$_2$O$_3$ phase. The crystalline phases of the particles are illustrated in Table 1.

Surface area analyzed by the N$_2$-BET method is also listed in Table 1. Particle prepared by precipitation with the solution and support particles has much larger surface area than those by the solid phase method and precipitation with the solution mixture. It is found that original pore of γ-Al$_2$O$_3$ supports was kept in calcination in case of precipitation with the solution and support particles, while pore was seldom formed by melting or phase change at higher calcination temperature in case of the other two methods.

3-2. Reactivity of Metal Oxide Particles

Reduction and oxidation of the metal oxide particles can be characterized by the conversion as

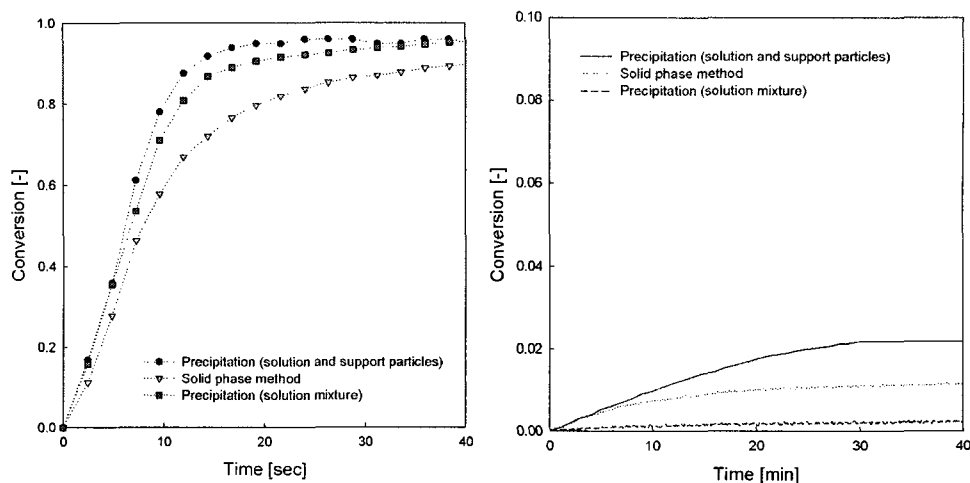$$X = \frac{m_{ox} - m}{m_{ox} - m_{red}} \qquad \text{for reduction} \qquad (1)$$

Fig. 2. Conversion of CuO/γ-Al_2O_3 with time by different particle preparation methods; (left) reduction, (right) water splitting.

$$X = \frac{m - m_{red}}{m_{ox} - m_{red}}$$ for water splitting   (2)

where m, m_{red} and m_{ox} are respectively weight of sample, weight of sample after fully reduced and weight of sample after fully oxidized. The values of m_{red} are determined to metallic Cu and MnO, as they can be reduced in strong reducing condition, respectively.

The reduction and water splitting conversion of CuO/γ-Al_2O_3 particles by different preparation methods are shown in Fig. 2. The reactivity of CuO/γ-Al_2O_3 particles prepared by the precipitation method with the solution and support particles is the best one compared with any other methods for both of reduction and water splitting. The reactivity of reduction is much faster than that of water splitting, and the conversion is also much higher. The reduction conversion of the particles prepared by the precipitation methods go over 0.9 within 20 s. The higher reactivity of the particle may be attributed to the initial crystal phase and higher surface area of pores. The crystalline of $CuAl_2O_4$ may have lower oxygen emissivity than that of CuO.

Each reaction conversion of different metal oxide particles on different supports are shown in Fig. 3. As can be seen, the reactivity of CuO is much higher than that of Mn_2O_3 regardless of the supports for reduction, and the reactivity of metal oxides supported on γ-Al_2O_3 is higher than that on SiO_2. Based on these results, CuO/γ-Al_2O_3 particle prepared by the precipitation method with the solution and the support particles was selected in the present kinetic study.

The reduction and oxidation conversions of CuO/γ-Al_2O_3 particle prepared by the precipitation method with the solution and support particles with different reaction temperature are shown in Fig. 4. The reactivity increases with increasing reaction temperature for the reduction, and the conversion is slow in the early stage and faster in the later stage. The division of stages may be caused by phase change steps from CuO to Cu_2O and from Cu_2O to metallic Cu. This is disappeared with increasing
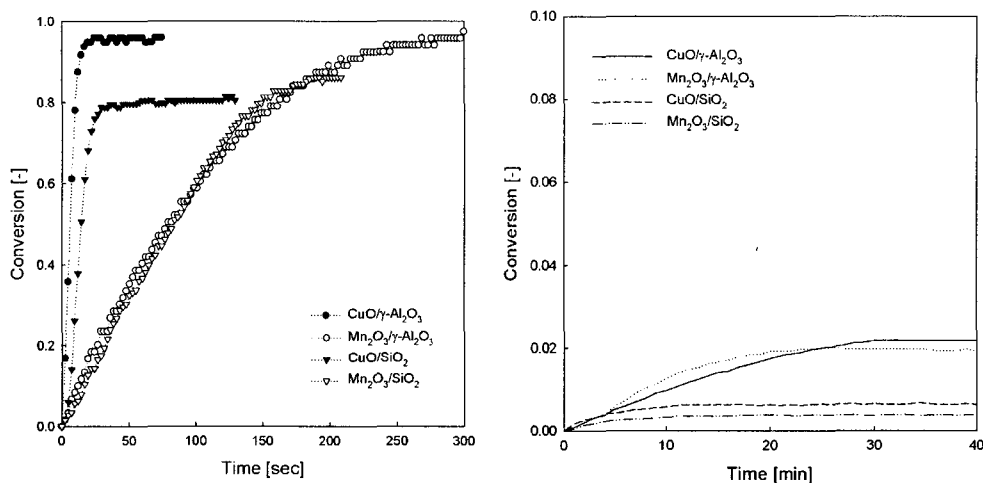
Fig. 3. Conversion of the metal oxides with time; (left) reduction, (right) water splitting.
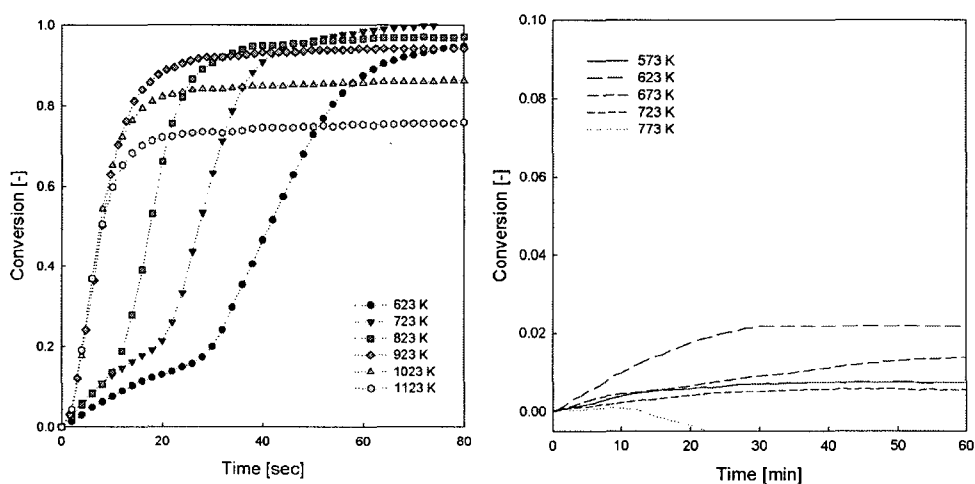

Fig. 4. Conversion of CuO/γ-Al₂O₃ with time at different reaction temperature; (left) reduction, (right) water splitting.

temperature as the conversion is increased. At higher temperatures (> 923 K), the final conversion is lower at higher reaction temperatures. It may be caused by the side reactions of H₂ and CO by themselves. Therefore, the optimum of reduction temperature would be around 923 K. For the water splitting, the optimum temperature exhibits at 623 K. At lower temperatures (< 623 K), water splitting activates with increasing reaction temperature, while at higher temperatures free oxygen atoms can be produced by thermal reduction of the metal oxide. The free oxygen atoms by thermal reduction may bond together as an oxygen molecule, or react with H₂ from H₂O split, so that weight of the metal oxide may decrease and the reactivity also decreases at higher temperatures.

For these reactivity test, copper oxide particle by the precipitation with the solution and γ-Al_2O_3 support particles would be the best looping material for CLH system at the reduction temperature of 623 K and the water splitting temperature of 923 K.

4. Conclusion

For the looping material of CLH system, CuO and Mn_2O_3 particles were prepared by two precipitation methods and the solid phase method. The reactivity of the metal oxides with different supports (γ-Al_2O_3 and SiO_2) was determined in TGA at the alternating reduction and oxidation conditions. The reactivity of CuO is higher than that of Mn_2O_3, and the particle supported on γ-Al_2O_3 produces higher reactivity than that of SiO_2. With these results, copper oxide particle by the precipitation with the solution and γ-Al_2O_3 support particles is found to be the best looping material for CLH system. The reduction reactivity of the metal oxide particles increases with increasing temperature, and the conversion is slow in the early stage and faster in the later stage. The optimum reduction temperature is found to be around 923 K. For the water splitting, the optimum temperature exhibits at 623 K.

5. References

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