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REACTION CHARACTERISTICS OF TWO WATER GAS SHIFT CATALYSTS IN A BUBBLING FLUIDIZED BED REACTOR FOR SEWGS PROCESS

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ABSTRACT

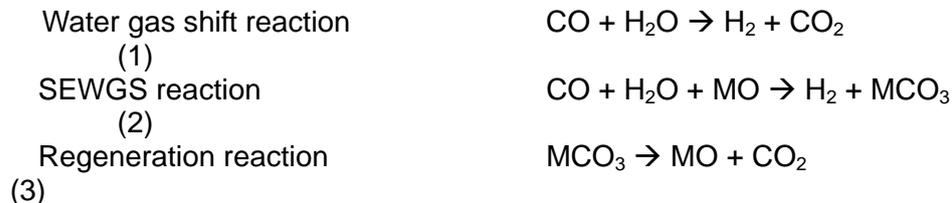
Reaction characteristics of two WGS catalysts for SEWGS process were investigated in a bubbling fluidized bed reactor. The commercial low temperature WGS catalyst produced by Süd-chemie and new catalyst produced by spray-drying method were used as bed materials. Reaction temperature, steam/CO ratio, and gas velocity were considered as experimental variables. Moreover, long-term operation results of two WGS catalysts were compared as well.

INTRODUCTION

Hydrogen production is the most fundamental part of the hydrogen energy system, and has always been the object of intense and vigorous research and development. World hydrogen production has been growing rapidly at 8-10% per annum for many years (1). At present, hydrogen is produced mainly from fossil fuels, water and biomass. However, more than 90% of the hydrogen is produced from fossil fuels (2).

Series of gasification of coal, water gas shift, and CO₂ separation is the predominant production route to hydrogen from coal for commercial scale application. However, this process needs multiple-steps such as high- and low-temperature water gas shift reaction as shown in eq. (1) to improve hydrogen yield, and CO₂ separation process to separate almost pure hydrogen from the gas mixture of CO, CO₂, and H₂. To separate CO₂ from the exhaust gas, additional energy and equipments are required. More than 22% of hydrogen generation cost comes from CO₂ separation process for purifying hydrogen (3). Although the previous process has been used for many years, there are some areas for improvement. The previous process requires many reactors and many kinds of catalysts and/or sorbents. Therefore, it will be extremely desirable if new concepts can be developed which can reduce the capital and operating cost of the conventional process (4). To overcome these disadvantages, SEWGS (Sorption Enhanced Water Gas Shift) system has been developed. Equation (2) and (3) explain concept of SEWGS system. The thermodynamic equilibrium in the shift reaction can be enhanced to give more hydrogen yield by adding a CO₂ absorbent into the shift reactor. Carbon dioxide is then captured as a solid carbonate as soon as it formed, shifting the reversible water-gas shift reactions beyond their conventional thermodynamic limits as shown in eq. (2). Regeneration of the sorbent releases pure CO₂ suitable for sequestration as shown in eq. (3) (4). It is important that the gas composition of the exhaust gas from the SEWGS reactor

contains only highly concentrated H₂ and excess water vapor. Therefore, H₂ can be easily recovered by cooling the exhaust gas without any extra energy consumption for H₂ separation. Moreover, the exhaust gas from the regeneration reactor contains only carbon dioxide and water vapor if we use steam as fluidization gas. After water condensation, almost pure carbon dioxide can be obtained with little energy loss for component separation.



where, MO: metal oxide, MCO₃: metal carbonate

In this study, the reaction characteristics of two WGS catalysts for SEWGS have been investigated in a bubbling fluidized bed reactor, as a preliminary research. The commercial low temperature WGS catalyst (MDC-7) produced by Süd-chemie and new WGS catalyst (PC) produced by KEPRI (Korea Electric Power Research Institute) by means of spray-drying were used as bed materials. Reaction temperature, steam/CO ratio, and gas velocity were considered as experimental variables. Moreover, long-term operation results of two WGS catalysts were compared as well.

EXPERIMENTAL

The reactivity tests were carried out in a bubbling fluidized bed reactor. A schematic of the reactor is provided in Figure 1. The major components consist of a gas input system, a fluidized bed, a condenser, a hot gas filter, a gas sampling/analyzing unit, and water feeding pump. The fluidization column is 0.7 m high with an internal diameter of 0.05 m. A perforated gas distributor plate separates the fluidization column and air box. Reactant gas was fed to the air box. An electric heater could be controlled by a thermocouple and a heater controller. Temperature and pressure data were recorded by a data acquisition system. The exit stream from the fluidized bed reactor was sampled at the outlet of the reactor. The CH₄, CO, CO₂, H₂, NO, and O₂ concentrations were monitored using an on-line gas analyzer and recorded by a data acquisition system. Further details of the reactor system are available in our previous paper (5).

Two water gas shift catalysts, the commercial low temperature WGS catalyst (MDC-7) produced by Süd-chemie and new WGS catalyst (PC) produced by KEPRI (Korea Electric Power Research Institute) were used. MDC-7 catalyst had pellet shape and we crushed the pellets to 106–212 μm. However, PC catalyst has spherical shape and the same particle size range was prepared. Figure 2 shows photos of two WGS catalysts. The PC catalyst shows spherical shape and the MDC-7 catalyst shows irregular shape.

The static bed height was 0.4 m in all cases, and initial solid masses were 0.57 kg for PC catalyst (ρ_b=724.7 kg/m³) and 0.88 kg for MDC-7 catalyst (ρ_b=1117 kg/m³), respectively. The fluidized bed reactor operated with a total inlet gas flow of 2.0 Nl/min in all cases, except for tests to check effect of gas velocity. The total inlet gas

contained 50% of syngas and 50% of nitrogen. The syngas composition was 60.5% of CO, 27.2% of H₂, 9.9% of CO₂ and N₂ as a balance.

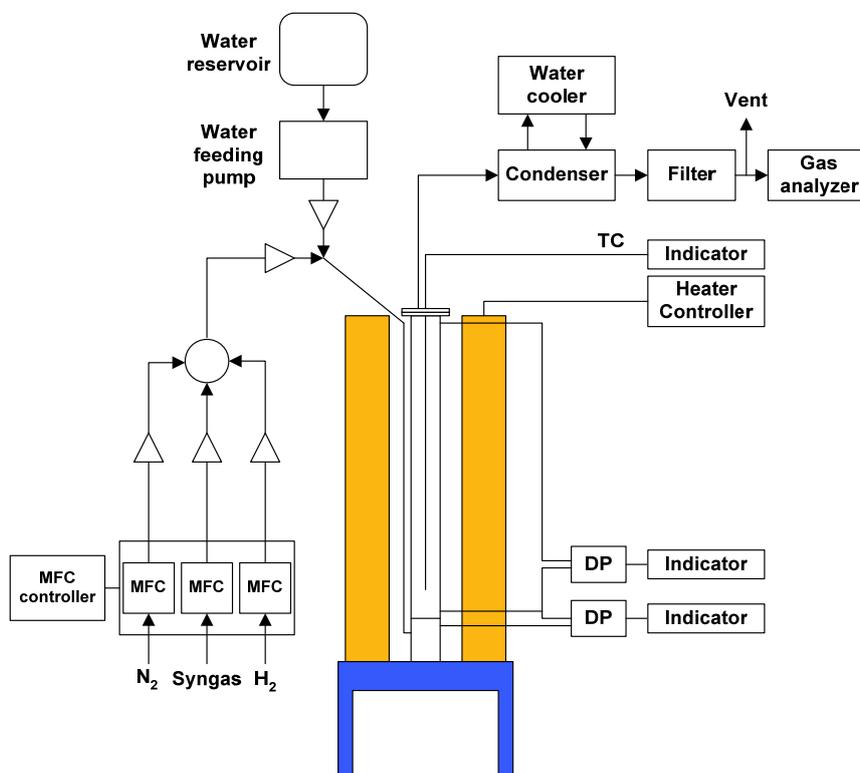


Figure 1. Schematic of a bubbling fluidized bed reactor.

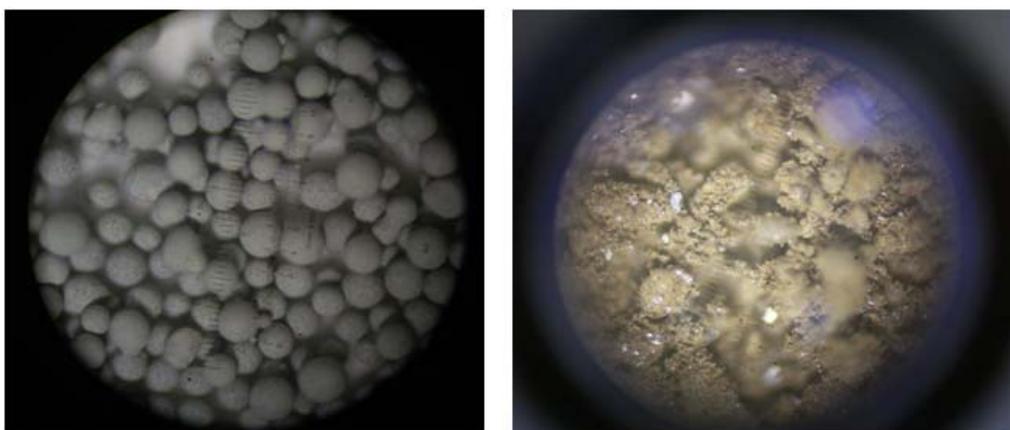


Figure 2. Photos of PC and MDC-7 catalysts.

RESULTS AND DISCUSSION

Prior to the start of each experiment, catalysts were reduced by H₂ gas (57%, N₂ balance) at 400°C. Figure 3 shows breakthrough curves of hydrogen concentrations during pretreatment (reduction) of catalysts. A breakthrough of hydrogen concentration marked the end of reduction. As shown in Figure 3, since MDC-7 catalyst showed sharper breakthrough curve than PC catalyst, and therefore, we could expect that the MDC-7 catalyst would show better reactivity than PC catalyst.

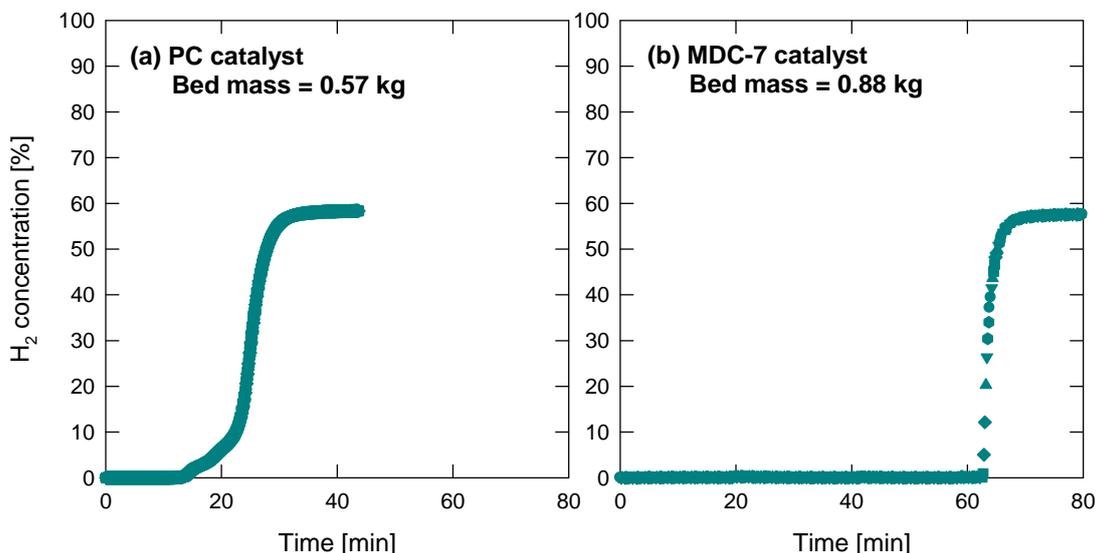


Figure 3. H₂ breakthrough curves during pretreatment of catalysts.

Figure 4 shows effect of temperature on CO conversion of catalysts. The CO conversion to H₂ and CO conversion to CH₄ were calculated by mass balance based on the output gas concentration and the tie component (N₂). For MDC-7 catalyst, high CO conversion up to 99.4% was observed in the range of 220~240°C at 4.0 of steam/CO ratio. For PC catalyst, lower CO conversion than MDC-7 catalyst was observed even at higher temperature (380~400°C) and at higher steam/CO ratio (=5).

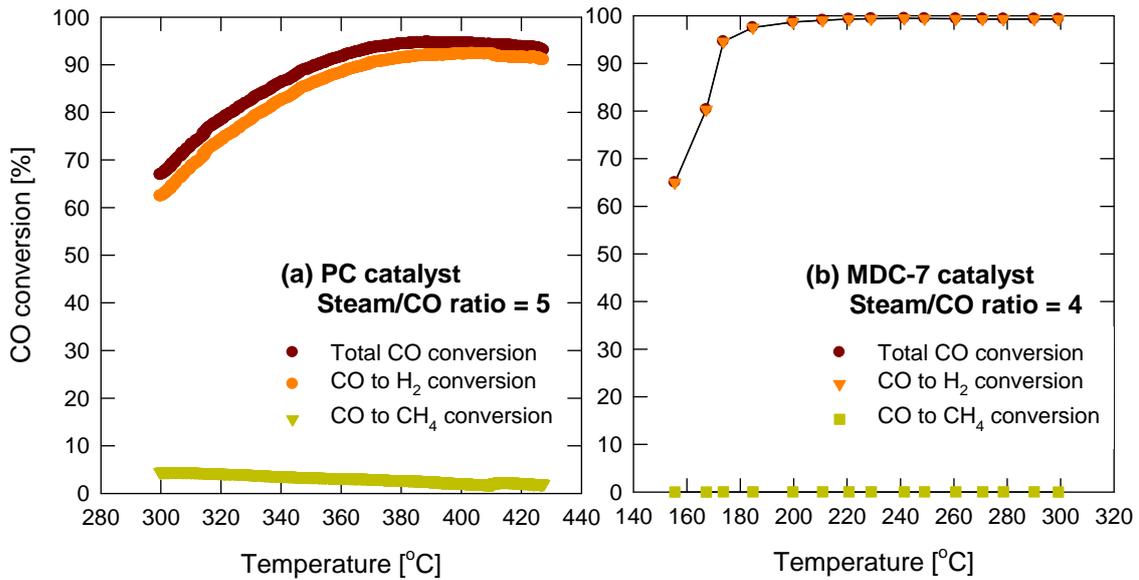


Figure 4. CO conversion versus reaction temperature.

Figure 5 shows effect of steam/CO ratio on CO conversion of two catalysts. For MDC-7 catalyst, CO conversion increased slightly as the steam/CO ratio increased up to 2.0, and maintained at high level thereafter. However, CO conversion of PC catalyst increased continuously as the steam/CO ratio increased up to 5.0. MDC-7 catalyst showed higher CO conversion at the same steam/CO ratio and at lower temperature. Moreover, PC catalyst generated higher CH₄ at lower steam/CO ratio.

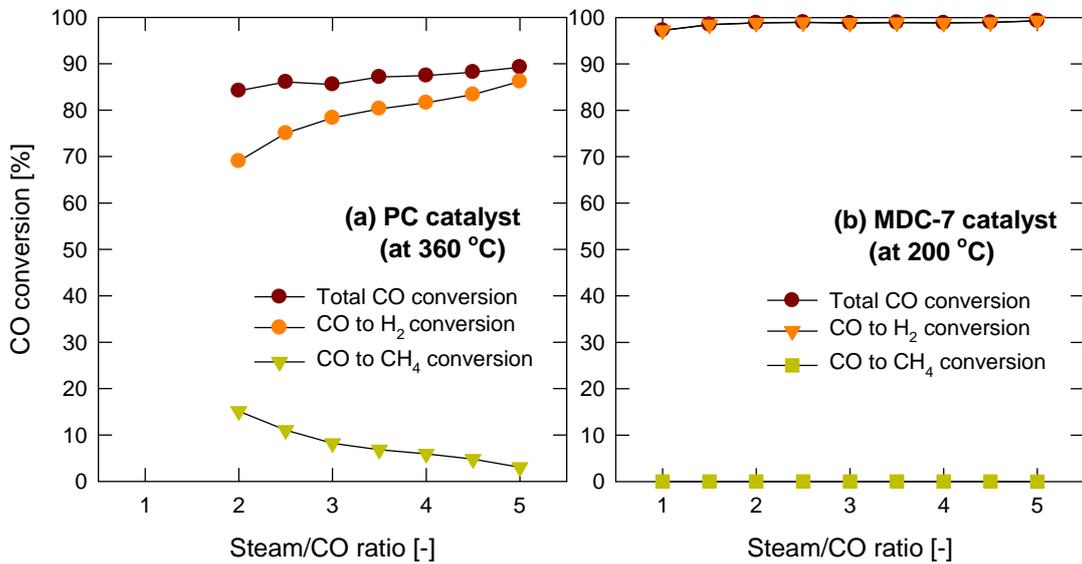


Figure 5. CO conversion versus steam/CO ratio.

Figure 6 shows long-term test results of two catalysts. The reactivity of MDC-7 catalyst was maintained more than 8 hours but that of PC catalyst decreased as the reaction time increased. As a conclusion, MDC-7 catalyst showed better reactivity than PC catalyst from the viewpoints of reaction temperature, seam/CO ratio, CO conversion, and long-term durability.

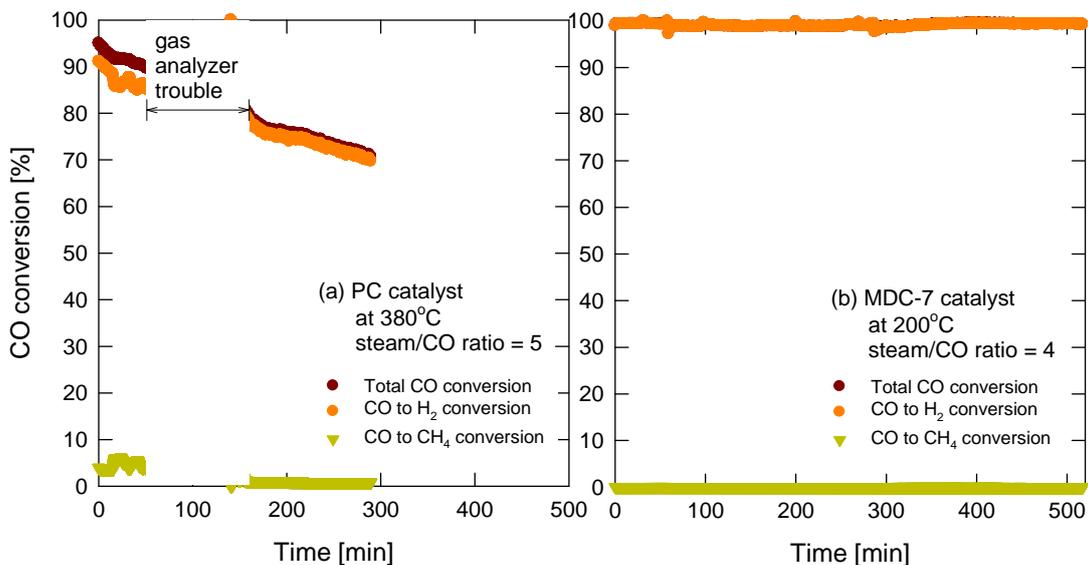


Figure 6. CO conversion versus time.

To check effects of syngas concentration and gas velocity, supplementary tests were performed using MDC-7 catalyst in the same reactor and the results are provided in Figure 7. The CO conversion of MDC-7 catalyst decreased slightly as the syngas concentration increased, but increased as the gas velocity decreased. However, these values are much higher than the results from the fixed bed with the same catalyst (6).

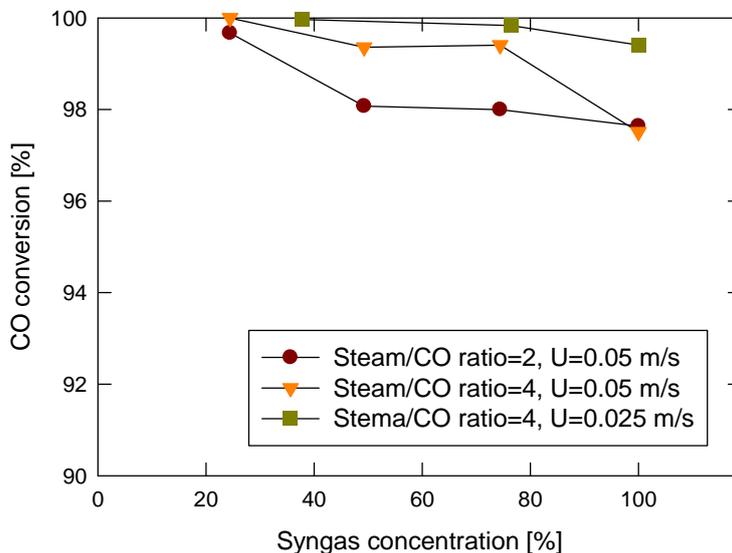


Figure 7. CO conversion to H₂ versus syngas concentration (MDC-7 catalyst).

CONCLUSIONS