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Water gas shift reaction in a catalytic bubbling fluidized bed reactor

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Abstract−The water gas shift reaction in a catalytic bubbling fluidized bed reactor was investigated by using simulated syngas (40% H_2, 40% CO and 20% CO_2) for the pre-combustion CO_2 capture and hydrogen production application. A commercial low temperature shift (LTS) catalyst with particle sizes of 200-300 μm was used to investigate the promotion effect by exchanging the fixed bed reaction with the fluidized bed reactor. The effects of the reactor temperature (180-400 °C), space velocity (800-4,800 $cm^3/h\cdot g$), and steam/CO ratio (1.0-2.5) on the CO conversion and syngas composition were determined, and the highest CO conversion was 86.8% at 300 °C with the LTS catalyst at a space velocity of 800 $cm^3/h\cdot g$ and steam/CO ratio of 2.5. The experiments exhibited an improvement in activity and a conversion reached that given by equilibrium at temperatures over 300 °C. Also, the performance was much improved than that when a fixed bed system was used.

Keywords: Water Gas Shift, Fluidized Bed, Catalyst, Hydrogen, CO Conversion

INTRODUCTION

Around the world, the need for clean energy is increasing, and so gasification processes with pre-combustion CO_2 capture and sequestration (CCS) have been developed as a means to maximize energy efficiency and minimize climate change. Specifically, hydrogen production and separation techniques have been employed to create a pre-combustion route for CCS from fossil-fuel fired power stations and to convert syngas into clean fuels and chemicals [1,2]. Although the demand for hydrogen is expected to continue to grow as the demand for clean transportation and power generation increases, hydrogen is still mostly produced from fossil fuels, including natural gas, liquid hydrocarbons and oil. Although most of the global H_2 production relies on steam methane reforming to produce syngas, coal gasification may replace steam methane reforming to meet the increased need for H_2 since coal is an abundant, low-cost substance [1-3].

Hydrogen production via gasification with CCS processes has attracted an increasing amount of attention in recent years. Gasification both offers a greater potential for CCS than other hydrogen production methods and also reduces the presence of other pollutants, such as NOx and SOx, when compared with conventional electricity production [4-7]. The CO in syngas obtained from gasification, for which the concentration can be higher than that of the reforming processes of natural gas by 35 to 65 vol%, should be converted into H_2 and CO_2 to maximize H_2 production and CO_2 capture. Also, the increase in CO_2 concentration due to the conversion of CO makes the CO_2 capture process more economically viable, both from a technological and an economic standpoint [1].

The water-gas shift reaction (WGSR) is an important step in the production of H_2 and CO_2 from syngas obtained from coal gasification. The hydrogen concentration can be enriched through further WGSR procedures after syngas has been produced from coal gasification, and currently a series of two fixed-bed reactors has been used as a commercial system with two different types of catalysts. The high-temperature shift (HTS) reaction operates at 320 to 450 °C, and the low-temperature shift (LTS) reaction operates at 200 to 250 °C [8-10]. Cu-promoted Fe-Cr oxides are conventional HTS catalysts, which are the most widely used, and copper-zinc-based catalysts are applied for the LTS reaction [11-14].

Conventional fixed-bed reactors were developed for the hydrocarbon reforming process, which produced less CO than coal gasification, so reactors with a larger volume and an increase in the amount of catalysts might be required to convert the large amount of CO obtained during coal gasification. However, conventional fixed bed reactors have a serious limitation in that they are poor at heat transfer and have a low catalyst particle effectiveness because of severe diffusional limitations associated with the size of the catalyst particles that are used. A smaller particle size is not feasible for fixed-bed systems due to the pressure drop [15]. Therefore, another type of WGSR catalytic reactor should be devised to convert CO obtained from coal gasification. There are a number of advantages to using fluidized bed reactors, such as automatic operation, ease of use, the presence of isothermal conditions throughout the reactor, rapid mixing of solid particles, a large margin of safety in avoiding temperature runaways for highly exothermic reactions, and higher heat and mass transfer. As a result, fluidized bed reactors have been widely used in industrial processes, including combustors, gasifiers, fluid catalytic cracking (FCC), polymerization, and trichlorosilan (TCS, intermediate raw material of polysilicon) synthesis [16-19]. Specifically, the isothermal conditions and rapid heat transfer might be useful for WGSR.

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[‡] This article is dedicated to Prof. Seong Ihl Woo on the occasion of his retirement from KAIST.

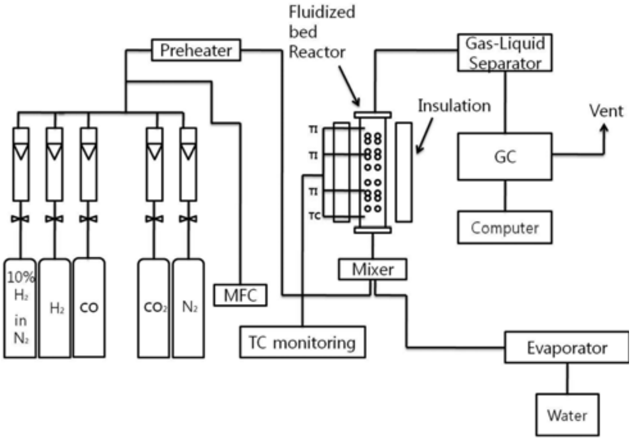

Fig. 1. Schematic of the fluidized bed reactor system.

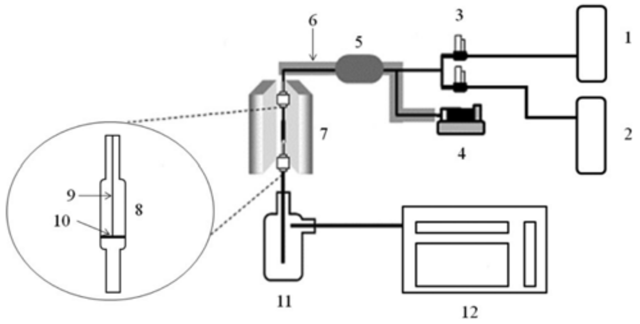

Fig. 2. Schematic of the fixed bed reactor system.

1. H_2/CO
2. CO_2
3. Mass flow controller
4. Water inject pump
5. Mixer
6. Heating tape
7. Furnace
8. Quartz reactor
9. Thermocouple
10. Catalysts
11. Trap
12. Gas chromatograph

Studies on WGSR in a catalytic bubbling fluidized bed reactor are relatively sparser than those on WGSR in fixed bed reactors. To this end, we investigated the effects of the reactor temperature (180-400 °C), space velocity (800-4,800 cm^3/h·g), and steam/CO ratio (1.0-2.5) on the CO conversion and syngas composition in a catalytic bubbling fluidized bed reactor. Simulated syngas similar to syngas obtained from entrained flow gasifiers was used to carry out the gasification processes with precombustion CO_2 capture. Also, the possibility of utilizing a fluidized bed reactor instead of fixed bed reactor was investigated based on the result of the WGSR performance.

EXPERIMENTAL

1. Experimental Setup

The experiments on the water-gas shift reaction involved using the catalytic bubbling fluidized bed reactor system shown in Fig. 1. This system consists of a preheater, evaporator, mass-flow controllers, catalytic bubbling fluidized bed reactor (i.d.=35 mm, o.d.=43 mm, height=1.2 m), gas-liquid separator, gas chromatograph, and computer. As shown in Fig. 1, the feed gases were controlled by using properly calibrated mass-flow controllers (Brooks, 5850E) to adjust the gas composition of CO, H_2, and CO_2. Water was dosed into the evaporator by an isocratic water pump and a syringe pump (KD Scientific, KDS 100). The water was heated, transformed into steam, and then uniformly mixed with the dry feed gas. The gas line was preheated to 200 °C to avoid water condensation before entering into the reactor.

A catalytic bubbling fluidized bed reactor with a sintered metal plate was used to convert the CO in the simulated syngas into H_2 and CO_2. An electric furnace heated the catalytic bubbling fluidized bed reactor to operating conditions, and only catalysts were used in the fluidized bed materials in this study. Shifted syngas was injected from two ice-cooled condensers that had been employed to trap water before the GC analysis.

The water gas shift reaction was performed in a fixed bed reactor as well to provide a comparison. The fixed bed reactor consisted of the experimental reactor system shown in Fig. 2. The measurements of the catalytic activity were at atmospheric pressure using a fixed-bed quartz reactor (i.d.=12 mm), and the reaction temperature was monitored with a K-type thermocouple inserted into the reactor through a quartz tube.

2. Experimental Procedure

Commercial low-temperature shift catalysts (LTSc, Sud-Chemie MDC-7) were used as fluidized bed materials and as a catalyst for the WGSR in this study. Catalysts with particle sizes of 200 to 300 μm for use as fluidized bed materials were produced by crushing commercial catalyst pellets and subsequently sieving the remains using stainless steel test sieves to achieve the desired particle size distribution. The catalyst components are shown in Table 1, and its surface area is 60.9054 m^2/g.

Pretreatment was carried out for the LTSc catalyst (30 g) at 350 °C for 12 h in 10% H_2/N_2. The reaction conditions consisted of reaction temperatures for the LTSc of 180-400 °C, steam/CO ratio of 1-2.5, and gas hourly space velocity (GHSV) of 800-4,800 cm^3/h·g. The detailed operating conditions are shown in Table 1, and the composition of the simulated syngas before reaching the catalytic bubbling fluidized bed reactor was 40% H_2, 40% CO and 20% CO_2 (2/2/1). This gas composition is similar to that of syngas from an entrained-flow coal gasifier with slurry feeding. The shifted syngas after WGSR was analyzed via gas chromatography (Agilent GC 6890, HP), and the CO conversion was calculated using the following formula:

Table 1. Components of the catalysts and operation conditions for the WGSR

Catalyst	Component (%)	Bulk density (kg/m^3)	Particle size (μm)	Apparent surface area (m^2/g)
MDC-7 (Sud-Chemie)	Copper oxide (43.1%) Zinc oxide (47.2%) Aluminum oxide (9.7%)	1137	200-300	60.9

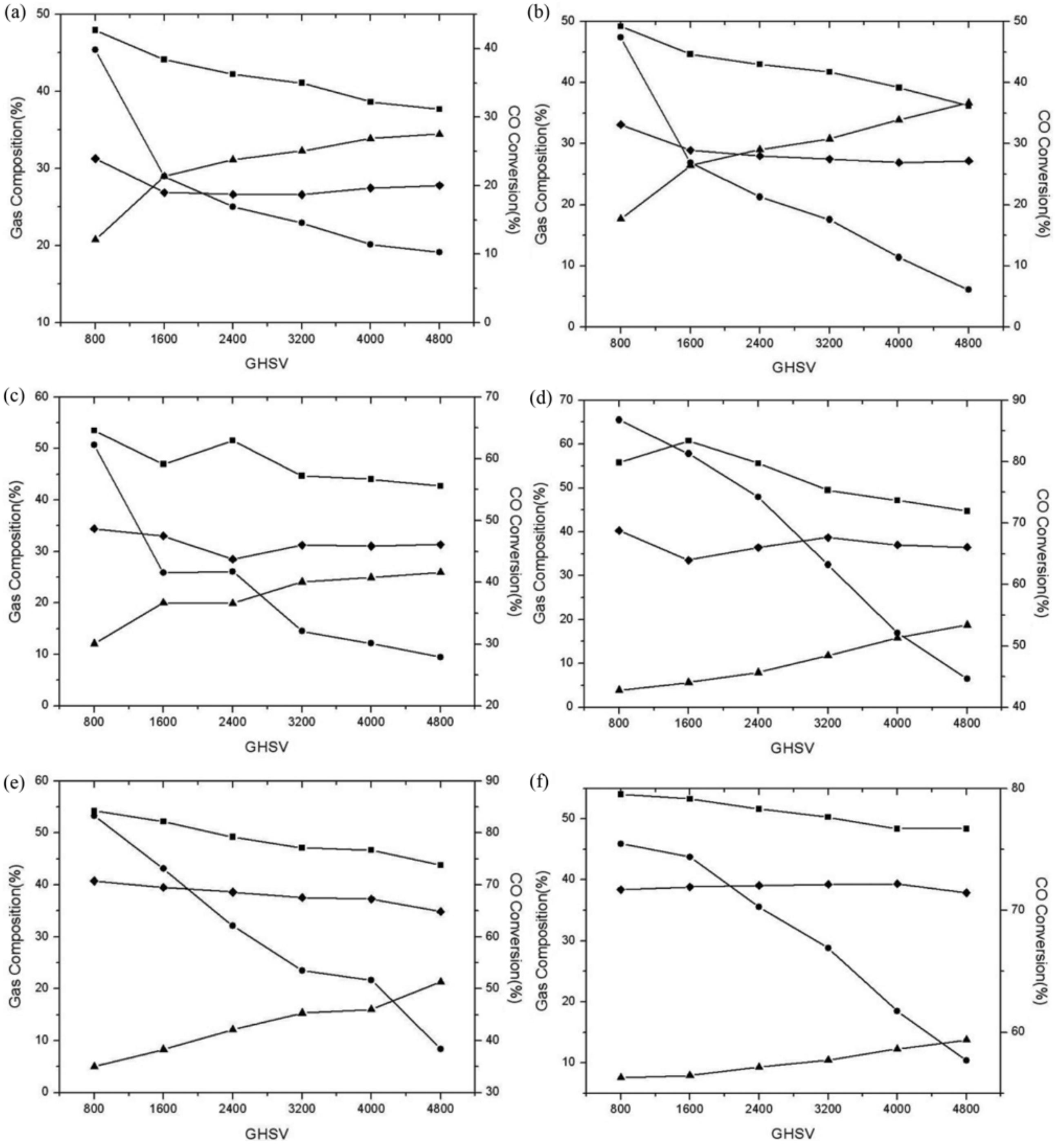

Fig. 3. Concentrations of H_2 (■), CO (◆) and CO_2 (▲) and CO conversions (●) under the effect of the LTSc with a steam/CO ratio of 2.5 at (a) 180 °C, (b) 200 °C, (c) 220 °C, (d) 300 °C, (e) 350 °C and (f) 400 °C.

Conversion of CO (X_{CO}) %

$$=(\text{moles of } CO_{in} - \text{moles of } CO_{out})/\text{moles of } CO_{in} \times 100$$

RESULTS AND DISCUSSION

1. Effect of WGSR Performance in the Catalytic Bubbling Fluidized Bed Rector

The CO in syngas had to be converted into CO_2 and H_2 to maximize the CO_2 capture and H_2 production in the gasification processes with precombustion CO_2 capture. Fig. 3 shows the concentration profiles for CO, CO_2 and H_2 from the WGSR with an LTS reaction in the catalytic bubbling fluidized bed reactor, where the reaction was carried out at various GHSV (800-4,800 $cm^3/h \cdot g$) over a wide range of temperatures (180-400 °C) while keeping the steam/CO ratio fixed at 2.5. In Fig. 3(a)-(f), the CO conversion and molar composition of hydrogen decreased as GHSV increased, regardless

Table 2. CO conversion at various GHSV at steam/CO=2.5

GHSV (cm^3/h·g)	CO conversion (%)					
	180 °C	200 °C	220 °C	300 °C	350 °C	400 °C
800	39.8	47.4	62.3	86.8	83.3	75.5
1200	21.4	26.9	41.5	81.3	73.1	74.4
2400	16.9	21.3	41.8	74.2	62.1	70.3
3200	14.6	17.6	32.1	63.21	53.5	66.9
4000	11.4	11.4	30.14	52.11	51.6	61.7
4800	10.3	6.1	27.9	44.7	38.4	57.7
Equilibrium conversion	99.4	99.1	98.6	94.9	91.6	86.8

of temperature.

As the temperature increased from 180 °C to 300 °C at a space velocity of 800 cm^3/h·g, the CO conversion increased gradually from 39.8% to 86.8%. The highest CO conversion was at 300 °C, and as the temperature increased over 300 °C, the conversion slowly decreased. Ruettinger et al. [20] reported that commercial copper catalysts lose their activity when exposed to temperatures above 280-300 °C due to the sintering of Cu crystallites. In our experiments, the CO conversion markedly increased at over 300 °C when compared to that at typical operating temperatures of the LTS reaction. Therefore, although LTSc catalysts are known to be suitable for use between 200 °C and 250 °C, the reactivity could improve even at over 300 °C by using a fluidized bed reactor. Also, the molar composition of hydrogen increased to 55% at 300 °C with a GHSV of 800 cm^3/h·g, maintained above 50% over 300 °C, and was slightly higher than that below 300 °C.

However, the molar composition of CO_2 increased with an increase in GHSV, which was the opposite behavior to that of the molar composition of hydrogen. Since the products from WGSR are hydrogen and CO_2, WGSR can be assumed to not be the sole reaction, and some unknown side reaction occurred at the same time. The results of our experiment indicate that the molar composition of hydrogen decreased and that of CO increased as the CO conversion decreased. This suggests that CO hydrogenation can occur simultaneously with WGSR, as previously reported [21]. Methane, which can form from the hydrogenation of CO, was not detected during the reaction period. Nevertheless, further studies are necessary to understand and clarify these results.

The results for the CO conversion were compared to those of the WGS equilibrium constants obtained from the literature [22,23]. At less than 300 °C, the equilibrium constant is well-known to be over 98%, while the CO conversion is much lower than that of the equilibrium constant. Above 300 °C, the CO conversion in our fluidized bed system was over 85% of the equilibrium constants, which may be a result of an increase in the reaction rate due to enhanced mixing between the catalyst and reactant as well as the depression in the temperature gradient inside of the reactor of the fluidized bed system.

Ryu reported on the CO conversion characteristics of WGS with MDC-7 in a fluidized bed reactor [24]. The CO conversion decreased slightly as the reaction temperature increased below 300 °C with MDC-7, which was contrary to our results. The CO_2 composition was less than that obtained in our experimental conditions. A comparison with our results suggests that the reaction rate could be greatly influenced by the CO_2 concentration in the reactant gases at a relatively lower temperature and could be greatly increased by the reaction temperature. We observed a dramatic improvement in CO conversion by raising the reaction temperature, and equilibrium conversion was almost obtained at over 300 °C. Future studies will be conducted to determine the effect of the CO concentration in the reactant gases for WGS in the fluidized bed reactor.

2. CO Conversion with LTSc at Various Steam/CO Ratios

A GHSV of 800 cm^3/h·g and steam/CO ratios of 1, 1.5, 2 and 2.5 were employed to investigate the effect of the steam/CO ratio on the reactor performance, and the composition of the feed gas was 40% H_2, 40% CO, 20% CO_2 to investigate the reaction performance with a variation in the steam/CO ratios. The reaction temperature varied from 180 to 400 °C, and Fig. 4 and Table 3, respectively, show the reaction activity according to various steam/CO ratios and reaction temperatures in terms of the CO conversion. Water is a reactant in the water gas shift reaction, so the CO conversion increases as the steam to CO ratio increases.

The highest CO conversion was 97.1% at 300 °C with a steam/CO ratio of 2.5. As mentioned above, the performance improved at temperatures over 300 °C. Taking into consideration the experimental error, the CO conversion almost reached the equilibrium constants at temperatures over 300 °C for all steam/CO ratios. Thus, the use of the fluidized bed reactor as a water gas shift reactor is

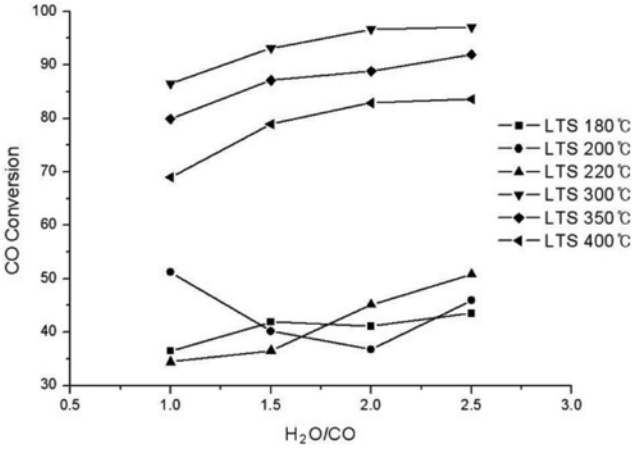

Fig. 4. Comparison of CO conversion at various steam/CO ratios and temperatures with the LTSc.

Table 3. Effect of steam/CO ratio of the LTS on the CO conversion at GHSV of 800 cm^3/h·g

Steam/ CO ratio	CO conversion (%)/Equilibrium conversion					
	180 °C	200 °C	220 °C	300 °C	350 °C	400 °C
1	36.5/91.1	51.2/89.0	34.4/86.6	86.5/75.2	79.9/68.7	68.9/61.1
1.5	41.9/98.3	40.2/97.4	36.5/96.2	93.1/88.2	87.1/82.4	78.9/75.2
2.0	41.1/99.1	36.7/98.7	45.1/98.0	96.7/92.8	88.8/88.5	82.8/82.6
2.5	43.5/99.4	46.0/99.1	50.8/98.6	97.1/94.9	91.9/91.6	83.6/86.8

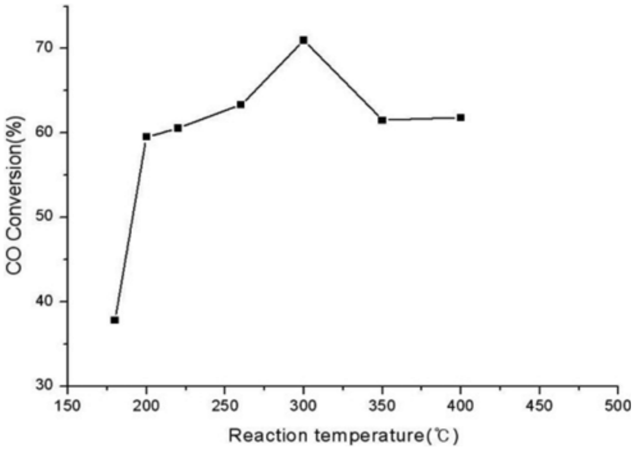

Fig. 5. CO conversion of the LTSc at 180-400 °C in the fixed bed reactor.

shown to be much more effective at temperatures over 300 °C. In our system, a commercial LTS catalyst was also effective above 300 °C, and a higher steam/CO ratio was observed to result in an improvement in the activity of the LTSc.

3. CO Conversion of the LTS Catalyst in a Fixed Bed Reactor

Fig. 5 shows the results obtained for the LTSc in the temperature range from 180 to 400 °C at a GHSV of 800 cm^3/h·g with steam/CO ratio of 2.5. For comparison, the results of the LTSc in the fixed bed reactor obtained under the same operating conditions are also included. The highest CO conversion was 71.0% at 300 °C, and this tendency is similar to that of the bubbling fluidized bed reaction, but with a lower CO conversion. Also, the performance of the LTSc decreases above 300 °C in the fixed bed reactor due to the sintering of Cu, as reported by Vanden Bussche [25]. A higher CO conversion was observed in the fixed bed than in the fluidized bed at 200 °C and 220 °C, and the highest CO conversion was at 300 °C in our fluidized bed reactor.

These results indicate that the bubbling fluidized bed system offers advantages over the fixed bed system due to effective temperature management, vivid solid mixing, etc., especially at high temperatures beyond 300 °C even though the catalyst was designed for the LTS reaction. In the case of tri-reforming processes with NiO-Mg/Ce-ZrO_2/Al_2O_3 catalyst, Khajeh et al. [26] proposed that a catalytic fluidized bed reactor is superior to a fixed bed one, and this is considered as a promising configuration for syngas production. Also, Laan and Beenackers [27] indicated that a fluidized bed reactor is a good candidate for highly exothermic reactions due to its excellent heat management ability, appropriate mixing, excellent temperature control, small pressure drop, and removal of diffusion limitations.

CONCLUSIONS

A WGSR system in conjunction with commercial LTSc was used to investigate the CO conversion in the water gas shift reaction with a bubbling fluidized bed system. The activity of the LTS catalyst in the WGS reaction was confirmed to be heavily influenced by the reaction temperature, steam/CO ratio and GHSV in the fluidized bed reactor. The highest activity of the LTSc was of 86.8% at 300 °C with a steam/CO ratio of 2.5 in the fluidized bed reactor. An increase in the steam/CO ratio resulted in an increase in CO conversion, reaching the equilibrium constant at temperatures over 300 °C. Also, the CO conversion of the catalytic bubbling fluidized bed reactor was higher than that of the fixed bed reactor. In the catalytic bubbling fluidized bed reactor, the LTSc exhibited substantially different behavior from that in a fixed bed reactor. Thus, the catalytic bubbling fluidized bed reactor can be conclusively determined to have potential for use in WGSR.

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