Increase in stability of BaCo/CeO₂ catalyst by optimizing the loading amount of Ba promoter for high-temperature water-gas shift reaction using waste-derived synthesis gas

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1. Introduction

New and renewable energy is a topic of tremendous research interest owing to pressing global environmental and energy concerns [1]. Waste is one of the most abundant renewable resources in earth and it has been reported that thermochemical treatment processes such as incineration and gasification are essential for the management of municipal solid waste [2–4]. In particular, the gasification of this waste is attracting a lot of attention and is being considered as an economically viable alternative to conventional natural gas reforming to produce synthesis gas (CO + H₂) [5]. In addition, this would help avoid several adverse environmental effects such as contamination of ground water and pollution of the air and allay concerns related to the early combustion technologies of the waste [3].

The water-gas shift (WGS) reaction is a CO cleaning step (CO + H₂O ≒ CO₂ + H₂) and is a key stage in the utilization of waste-derived synthesis gas, since this gas contains a higher concentration of CO (ca. 38°, dry basis) as compared to that in general synthesis gas (ca. 9%, dry basis) produced by the steam reforming of hydrocarbons [6–10]. The waste-derived synthesis gas can be utilized as a source of valuable chemical products such as hydrogen, ammonia, and methanol by controlling the H₂/CO ratio through the WGS reaction [3,11–13].

The conventional WGS reaction process exhibits two distinct temperature ranges due to its exothermic nature: a high-temperature shift (HTS; 350–500 °C), which uses an Fe-Cr catalyst because of the kinetics aspects, and a low-temperature shift (LTS; 190–250 °C), which uses a Cu-Zn-Al catalyst, considering the...
thermodynamic equilibrium [14–16]. When we use the WGS reaction for waste gasification, the HTS is preferable because of the high temperature of the outlet gas from the waste gasification process [17].

The commercial HTS catalyst typically consists of Fe2O3 (88–92%) and Cr2O3 (8–12%) [18]. In this Fe-Cr catalyst, magnetite (Fe3O4) is the active phase, which requires a partial reduction of Fe2O3 [19]. However, the Fe2O3 can form metallic iron (Fe0) through the over-reduction of Fe3O4, which loses its activity for the HTS. As a result, extreme care should be taken to maintain the active phase during the reduction process and reaction also [20]. Cr2O3 is used as a promoter to prevent the thermal sintering of Fe2O3 and a loss in the surface area of the catalyst during the reaction [21]. In spite of the advantages to using Cr in Fe-based catalysts, dissolution of hexavalent chromium induces potential environmental concerns, which must be eliminated [22]. In addition, commercial Fe-Cr catalysts are produced with the general synthesis gas in mind, which is generated by the steam reforming of hydrocarbons. Therefore, the development of novel catalysts which do not contain both Fe and Cr, and target the waste-derived synthesis gas is necessary. Several works about the development of HTS catalysts have been reported that do not contain either Fe or Cr. Liang et al. developed a mixed La2-xCe xO3 nanorods supported Au-based catalyst and showed that the reducibility of the nanorods is determined by the preferential exposure of the highly active planes as well as the La/Ce ratio [23]. Yamamura et al. developed a Pd/K/Co3O4 catalyst and investigated the effects of the K and Pd loading amounts on Co3O4 catalyst [24]. Gonzalez Castano et al. compared the behaviors of Pt- and Au-based catalysts during the HTS reaction and elucidated the effect of additives in alumina-based supports [25]. However, most of these studies used expensive noble metals. Considering their cost, our group had tried to develop non-noble metal based HTS catalysts that contain neither Fe nor Cr. We propose Co/CeO2 as a catalyst since Co3O4 is reported that it is effective for oxidizing CO to CO2 through catalysis [26]. By comparing this Co/CeO2 catalyst with a bare Co3O4 catalyst, we discovered the potential of Co-based catalysts as HTS catalysts and performed additional studies. The effect of the redox properties of the support (CeO2, ZrO2, TiO2, and Al2O3) was compared, and it was observed that the CeO2 support showed the best performance with respect to the HTS reaction [27]. Subsequently, we optimized the Co loading amount (15 wt%), which is directly related to the catalyst stability [28]. Based on the optimal loading amounts of Co and CeO2, we studied the effects of promoters, which can be divided into two categories: alkali metals including Na and K, and alkaline earth metals including Ca and Ba [29]. Among them, CaCo/CeO2 and BaCo/CeO2 catalyst exhibited stable performance owing to the strong resistance to the sintering of metallic Co [29]. In addition, it has also been reported that the deactivation of the un-promoted Co/CeO2 catalyst is due to the sintering of CoO and not due to coke formation [29]. It is well known that the promoter strongly affects the performance of the catalyst even when present in a very small amount, which means that even a small change in the loading amount of the promoter directly affects the catalytic performance. In case of Co-based catalysts, Morales et al. studied the effect of manganese oxide as a promoter on Co/TiO2 catalyst for the Fischer-Tropsch synthesis [30]. Further, Shimura et al. employed 13 different metals as promoters on the Co/Al2O3 catalyst and optimized the loading amounts of the promoters for the improvement the catalytic performance [31]. Moreover, the loading amounts of Ru, K, and Cs which were used as promoters for Co-based catalysts have also been studied [32,33]. From these studies, it is clear that even a small change in the amount of promoter loading directly affects the catalytic performance.

In the present work, we focused on the effect of the loading amount of Ba as a promoter on the Co/CeO2 catalyst and, in particular, analyzed how it affects the catalytic stability in HTS reaction using waste-derived synthesis gas. The BaCo/CeO2 catalyst with different Ba loading were characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) measurements by N2 adsorption/desorption, CO—chemisorption, H2—temperature programmed reduction (H2—TPR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) and were correlated with the HTS reaction results.

2. Experimental

The experimental details related to the synthesis of the BaCo/CeO2 catalyst with different Ba loading and their reactions as well as their characterizations are summarized in Scheme 1, while the details are described in the sections that follow.

2.1. Synthesis of catalysts

BaCo/CeO2 catalysts containing different loading amounts of Ba promoter (1, 2, and 3 wt%) as well as Co (15 wt%) and supported on different amounts of CeO2 (82, 83, and 84 wt%) were prepared by
the incipient wetness co-impregnation method. Ahead of the co-impregnation, the support (CeO2) was prepared by a precipitation method. In detail, Ce(NO3)3·6H2O (99%, Aldrich) was dissolved in distilled water and the temperature was raised to 80 °C. The precipitation agent, 15 wt% KOH (95%, Samchun) solution was added to the Ce(NO3)3·6H2O solution under constant stirring until it reached the pH of 10.5. Digestion process (80 °C, 24 h) was followed and the resulting precipitate was filtered with 2 L of distilled water to remove any impurities. The precipitate was dried in an oven (100 °C in air, 12 h) after filtration. Calcination process (500 °C in air, 6 h) in a furnace was followed. The resulting material (CeO2) was co-impregnated with Co(NO3)2·6H2O (98%, Aldrich) and Ba(NO3)2·6H2O (99%, Aldrich). The cobalt (15 wt%) and barium (1–3 wt%) nitrate precursors were dissolved together in distilled water. The Ba precursor and Co precursor mixed solution was impregnated over 0.82–0.84 g (82–84 wt%) of the calcined CeO2 support. After the obtained mixtures were dried in an oven (100 °C in air, 12 h) and calcined in a furnace (500 °C in air, 6 h) before being used for the activity tests and characterization measurements.

2.2. Catalyst performance test

Performance tests of the prepared catalysts were performed in the temperature range of 350–550 °C and in the ambient pressure. Fixed-bed microtubular quartz reactor with an inner diameter of 4 mm was used, surrounded and heated in a furnace. 0.03 g of catalyst powder was used for the HTS reaction, positioned in the middle of the reactor with a quartz wool. To measure the exact temperature of the catalyst bed during the reaction, thermocouple was installed using T-junction which was inserted at the exit of the quartz reactor. The reaction temperature was programmed in 350–550 °C, increase in steps of 50 °C. The temperature and flow rate of the inlet gas were kept constant for approximately 30 min during each step to consider the time until the outlet gas reaches the micro gas chromatograph (Micro-GC, Agilent 3000) after the reaction. Next, the catalyst was tested five times at intervals of 3 min over a period of 20 min to check the reproducibility of the reaction result. The average CO conversion rates (XCO) were determined at each temperature, which are shown in Fig. 1. Each catalyst was reduced (400 °C in 5% H2/N2, 1 h) before the reaction. After the reduction process, the temperature was decreased to 350 °C and the reaction was initiated. The inlet gas is consisted of CO (38.2 vol %), CO2 (21.5 vol%), CH4 (2.3 vol%), H2 (29.2 vol%), and N2 (8.8 vol%); this composition is similar to that of the typical synthesis gas output after the gasification of the waste, which will enter the WGS reactor. The ratio of H2O/(CH4 + CO + CO2) was intentionally fixed at 2.0 to avoid coke formation, maintaining the gas hourly space velocity (GHSV) of 143,000 h−1. The water was injected by syringe pump and vaporized in the pre-heater (180 °C) upstream of the reactor. The outlet gas after the reaction was cooled down in the chiller and the residual water was trapped with a desiccant (Drierite®). The reactants and products were then analyzed online using a Micro-GC. The inlet and outlet gas composition is shown in Table S1. The catalytic stability test was conducted at 450 °C in order to evaluate the stability of the prepared catalysts. The conversion rate of CO and selectivities of CO2 and CH4 were calculated using the following formulas:

\[
\text{CO conversion rate (\%)} = \frac{\text{[CO]_{out} - [CO]_{in}}}{\text{[CO]_{in}}} \times 100
\]

\[
\text{CO2 selectivity (\%)} = \frac{\text{[CO2]_{out} - [CO2]_{in}}}{\text{([CH4]_{out} - [CH4]_{in})} + ([CO2]_{out} - [CO2]_{in})} \times 100
\]

\[
\text{CH4 selectivity (\%)} = \frac{\text{[CH4]_{out} - [CH4]_{in}}}{([CH4]_{out} - [CH4]_{in}) + [CO2]}
\]

2.3. Catalyst characterization

The XRD patterns of the reduced and used catalysts were recorded using Rigaku D/MAX-IIIC diffractometer (Ni-filtered Cu–Kα radiation, 40 kV, 100 mA) over 20 values of 20–80°. Scherrer equation was applied for the estimation of the crystallite size of the catalysts. The BET specific surface areas of the calcined samples were determined by the N2 adsorption/desorption method at −196 °C using a Micromeritics ASAP 2010 instrument. CO–chemisorption was conducted at 50 °C to determine the dispersion of the Co in the calcined catalysts using an Autochem 2920 instrument (Micromeritics). Before the analysis, in-situ reduction process (400 °C in 10% H2/Ar, 1 h) was conducted, and cooled down to 50 °C. After that, CO pulses with 10% CO/He were passed through the surface of the catalyst until it was saturated with CO. The adsorbed CO amount on the cobalt in the catalyst surface was determined by calculating the difference of peak area of CO which occurs due to the adsorption of CO on the catalyst. H2–TPR measurements using Autochem 2920 (Micromeritics) instrument were performed on the calcined catalysts. The H2–TPR measurement was performed by heating the sample (0.1 g) from 50 to 800 °C at a heating rate of 10 °C/min using 10% H2/Ar. Calibration of the detector sensitivity was conducted by using a known weight of NiO. XPS measurements using K-α (Thermo Scientific) spectrometer were performed on the reduced and used catalysts with a high-resolution monochromated Al–Kα X-ray source. The resulting spectra were corrected using the reference binding energy (C 1s, 284.6 eV). TEM analysis was conducted to check the morphologies of the prepared catalysts by using JEM-F200 (JEOL) instrument.

In the measurements of XRD and XPS, the reduced catalysts were used instead of the calcined ones. The reduced catalysts were prepared through the reduction of the calcined samples, following the same condition which has conducted before the HTS reaction (400 °C in 5% H2/N2, 1 h) in order to ensure conditions similar to
those during the catalyst activation step. After the reduction, passivation process (room temperature in 10% air/N$_2$, 6 h) was followed to avoid explosive oxidation when the samples exposure to air. In the measurements of BET, H$_2$–TPR, CO–chemisorption, and TEM measurements, calcined catalysts were used. The samples subjected to the time-on-stream measurements (stability tests) were characterized by XRD, XPS, and TEM measurements.

3. Results and discussion

3.1. Catalytic activity and stability

The HTS reaction was performed over the various BaCo/CeO$_2$ catalysts, which contained Ba in different loading amounts (Fig. 1). The effect of Ba loading was apparent at low temperatures (\(<450^\circ\text{C}\)) during CO conversion. At 350$^\circ\text{C}$, 1% BaCo/CeO$_2$ showed the highest CO conversion rate, while the 3% BaCo/CeO$_2$ catalyst showed the lowest. However, all the prepared catalysts exhibited similar CO conversion rates at higher temperatures (\(\geq450^\circ\text{C}\)). The small decrement at the high temperatures was due to the limitation of thermodynamic equilibrium. The catalytic selectivities of the BaCo/CeO$_2$ catalysts with respect to CO$_2$ and CH$_4$ with the reaction temperature are shown in Fig. S1. All the prepared samples showed a CO$_2$ selectivity of almost 100%, indicating that the synthesized catalysts were selective with respect to the WGS reaction.

We had previously reported that as a promoter, Ba enhances the stability of the Co/CeO$_2$ catalyst [29]. Thus, the stabilities of the various catalysts containing Ba in different amounts were measured (Fig. 2). The 1% BaCo/CeO$_2$ catalyst showed the highest stability (86% $X_{\text{Co}}$, >50 h), with the 2% BaCo/CeO$_2$ catalyst also exhibiting a similar performance. On the other hand, the un-promoted Co/CeO$_2$ catalyst deactivated rapidly owing to the sintering of the metallic cobalt (Co$_0$). Thus, based on the stability test results, it is clear that the doping of Ba into Co/CeO$_2$ enhances the stability of the catalyst by improving its sintering resistance. However, 3% BaCo/CeO$_2$ deactivated rapidly, in a manner similar to the Ba-free sample (Co/CeO$_2$). To determine the optimal loading amount of Ba and investigate the underlying mechanism responsible for deactivation in the case of the Co/CeO$_2$ samples containing excessive Ba, various characterizations were performed.

3.2. XRD analyses

The XRD patterns of the reduced BaCo/Co$_2$ catalyst with different Ba loading amounts are shown in Fig. 3(A). The major diffraction peaks for all the samples are corresponding to the CeO$_2$ with a fluorite-type oxide structure. A relatively weak diffraction peak observed at 2$\theta$ = 44.2$^\circ$ corresponds to Co$_0$ (JCPDS 15-0806). Interestingly, the intensity of the Co$_0$ peak decreased after the doping of Ba, implying that the doping of Ba as a promoter probably increases the dispersion of Co$_0$ on the CeO$_2$ surface due to the smaller Co$_0$ crystallite size or causes Co$_0$ to enter the CeO$_2$ lattice [34].

The XRD patterns of the used catalysts after the stability test are shown in Fig. 3(B). It is clear that the intensity of the Co$_0$ peak increases in the case of the un-promoted Co/CeO$_2$ sample. However, it is hard to discern the Co$_0$ peak in the Ba-promoted Co/CeO$_2$ samples, as was also the case for the reduced samples. This indicates that the doping of Ba inhibit the sintering of Co$_0$ on the catalyst surface owing to the interactions between Ba and Co$_0$, in keeping with our previous report [29]. The crystallite sizes of the catalysts were calculated by Scherrer equation based on the diffraction peak of Co$_0$ (2$\theta$ = 44.2$^\circ$), and the results are listed in Table 1. Only the un-promoted Co/CeO$_2$ catalyst exhibits a significant increase in the Co$_0$ crystallite size after the HTS reaction. The BaCo/CeO$_2$ catalyst with different Ba loading exhibit similar Co$_0$ crystallite sizes between the reduced and used samples. This indicates that the deactivation of the un-promoted Co/CeO$_2$ catalyst is due to the sintering of Co$_0$.

![Fig. 2. CO conversion rate with time-on-stream over BaCo/CeO$_2$ catalysts with different Ba loading amounts (H$_2$O/(CH$_4$ + CO + CO$_2$) = 2.0; T = 450$^\circ$C; GHSV = 143,000 h$^{-1}$).](image)

![Fig. 3. XRD patterns of BaCo/CeO$_2$ catalysts with different Ba loading amounts: (A) reduced samples and (B) used samples.](image)
display two well-resolved reduction peaks, one at 264 while the 2% and 3% BaCo/CeO₂ catalysts showed similar values. It is calcined samples, 1% BaCo/CeO₂ showed the highest Co₀ dispersion of Co₀ after the doping of Ba. However, it also implies that the rapid deactivation of the 3% BaCo/CeO₂ catalyst was not because of the sintering of Co₀.

3.3. BET and CO-chemisorption measurements

The BET specific surface areas (S_BET) of the BaCo/CeO₂ catalyst with different Ba loading are shown in Table 1. The S_BET value decreased after the doping with Ba. Among the BaCo/CeO₂ catalyst with different Ba loading, 1% BaCo/CeO₂ showed the highest value of 60 m²/g. The Co₀ dispersion values estimated from the CO-chemisorption measurements are also shown in Table 1. Although the loading amounts of Co were equal for all the samples, the dispersion value changed after the doping with Ba. Interestingly, the Ba-promoted catalysts showed higher Co₀ dispersions compared to that of the un-promoted Co/CeO₂ catalyst. This result was in keeping with the XRD results (including the trend in the crystallite size of Co₀) and confirmed that the doping of Ba improves the dispersion of Co₀ on the catalyst surface. Among the calcined samples, 1% BaCo/CeO₂ showed the highest Co₀ dispersion while the 2% and 3% BaCo/CeO₂ catalysts showed similar values. It is notable that, of the latter two, 3% BaCo/CeO₂ showed a higher Co₀ dispersion value after calcination and stability test. This further confirmed that the deactivation of 3% BaCo/CeO₂ was not related to the sintering of Co₀.

3.4. H₂-TPR measurements

H₂–TPR measurements were conducted to investigate the reducibility of the BaCo/CeO₂ catalyst with different Ba loading. The H₂–TPR profiles of the calcined samples are shown in Fig. 4. They display two well-resolved reduction peaks, one at 264–327 °C and the other at 333–390 °C; these can be attributed to the reduction of Co₃O₄ to CoO and that of CoO to Co₀, respectively [29]. The reduction temperatures of both cobalt oxide species decreased after doping with Ba in amounts of up to 2 wt%, indicating that Ba doping improves the reducibility of cobalt oxide species. This phenomenon means that the interactions between cobalt oxide and the CeO₂ support were weakened after the doping with Ba. The Ba promoter is probably interspersed between the support and the cobalt oxides and moderates the interactions between them. However, the reduction of cobalt oxide occurred at higher temperatures when the Ba loading amount was increased to 3 wt%. The extra Ba may partially cover the surface of the cobalt oxides, thus preventing their reduction. Similar observations have been reported for magnesia and manganese-modified Co₁₋ₓAlₓO₂ catalysts as well [35]. Further, Bao et al. observed a similar covering effect of Ba in a study on the influence of Ba on Co-based catalysts [36].

![Fig. 4. H₂-TPR profiles of calcined BaCo/CeO₂ catalysts with different Ba loading amounts.](image)

3.5. XPS analyses

XPS analyses on the Ba-promoted Co/CeO₂ catalyst were conducted to explore the phases of the cobalt species in the synthesized samples. The XPS Co 2p₃/₂ spectra of the reduced and used BaCo/CeO₂ catalyst with different Ba loading are shown in Fig. 5(A) and (B), respectively. The spectra of the cobalt species could be fitted to three peaks. Previous reports suggest that the cobalt peak can be deconvoluted into the following three peaks: Co₀ (778.1 eV), CoO (780.0 eV), and Co₃O₄ (779.6 eV) [37]. The spectral contribution of the active phase (Co₀) was estimated using the following equation:

\[
\text{Co₀ (%)} = \frac{[\text{Area under Co₀ peak}] - \text{[Area under overall peak]}}{100}
\]

The concentrations of Co₀ in the BaCo/CeO₂ catalyst with different Ba loading are listed in Table 1. The results show that the addition of Ba aided the formation of Co₀. However, this effect became less pronounced when the doping amount of Ba was increased. The 1% BaCo/CeO₂ sample contained the highest amount of Co₀ in both the reduced and used states, while the 3% BaCo/CeO₂ sample contained the lowest. These results indicate that the stability of the active phase (Co₀) directly determined the catalyst stability in the case of the BaCo/CeO₂ catalyst with different Ba loading. The XPS analysis results were in keeping with the H₂–TPR measurements results, showing that the formation and maintenance of Co₀ in 3% BaCo/CeO₂ did not occur as readily as in the other samples. This means that the stability of the Co₀ phase was lower in 3% BaCo/CeO₂, which probably led to the deactivation of the sample. The XPS Ce 3d spectra of the reduced and used BaCo/CeO₂ catalysts...

### Table 1

<table>
<thead>
<tr>
<th>Catalyst sample</th>
<th>S_BET (m²/g)</th>
<th>Crystallite size of Co₀ (nm)</th>
<th>Dispersion of Co₀ (%)</th>
<th>Co₀ concentration (%)</th>
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<td></td>
<td>Calcd</td>
<td>Reduced</td>
<td>Used</td>
<td>Calcd</td>
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<tr>
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<td>27.0</td>
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<tr>
<td>1% BaCo/CeO₂</td>
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<td>0.63</td>
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<tr>
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<td>N.A.</td>
<td>0.47</td>
</tr>
<tr>
<td>3% BaCo/CeO₂</td>
<td>55</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.49</td>
</tr>
</tbody>
</table>

* a Estimated from N₂ adsorption measurements at –196 °C.
* b Estimated from XRD analysis.
* c Estimated from CO-chemisorption measurements.
* d Estimated from XPS Co 2p spectra.
* e Not available due to very broad and weak XRD peak.
catalyst with different Ba loading are shown in Fig. S2 (A) and (C), respectively. Five sets of spin-orbit doublets were used for the fitting of the spectra of the reduced samples. The peaks labeled with ′v′ refer to the 3d_{5/2} states, while the ′u′ refer to the 3d_{3/2} states. The peaks labeled v_o, ′v′, u_o, and ′u′ were attributable to Ce^{3+} ions, while other peaks are corresponding to the Ce^{4+} ions [22,38]. The XPS O 1s spectra of the reduced and used BaCo/CeO_2 catalyst with different Ba loading are shown in Fig. S2 (B) and (D), respectively. Each spectrum was deconvoluted into three peaks: which are corresponded to the lattice oxygen (528.9 eV), oxygen that is closer to the oxygen vacancy sites (530 eV), and adsorbed oxygen species from hydroxyl group or water on the surface (532 eV) [22,39].

3.6. TEM analyses

TEM analyses were carried out to determine the particle sizes and shapes of the calcined and used catalysts. The TEM images of the catalysts are shown in Fig. 6. The calcined catalysts suggest a mixed rounded/cubic shape, and the used catalysts indicate that the physical structure of the catalyst did not change after the HTS reaction. The particle size of the un-promoted Co/CeO_2 catalyst increased slightly after the HTS reaction. However, the Ba-promoted Co/CeO_2 samples exhibited similar particle sizes and shapes. This result also indicates that the doping of Ba as a promoter enhances the sintering resistance while also confirming that the deactivation of 3% BaCo/CeO_2 was not due to sintering.

3.7. Relationship between catalytic performance, sintering resistance of Co^0, and phase stability of Co^0

The relationship between the catalytic performance, sintering resistance of Co^0, and phase stability of Co^0 is shown in Fig. 7. The X_CO value was obtained from time-on-stream measurements after 20 h. The numeric value of the sintering resistance of Co^0 and the phase stability of Co^0 were calculated using the following equation:
The Co dispersion of used sample and phase concentration in used sample were determined from the CO–chemisorption measurements, while the Co phase concentration of the reduced and used samples were calculated from the XPS Co 2p spectra (Table 1). The phase stability of Co in box (A) is similar to that in box (B); however, the sintering resistance of Co showed the lowest value in box (A). On the other hand, the phase stability of Co is the lowest in box (C) while the sintering resistance of Co is the highest. Both box (A) and box (C) show extremely lower XCO value after 20 h during the time-on-stream study compared to the box (B). This highlights the low stability of the corresponding catalyst. However, both the sintering resistance of Co and its phase stability are relatively high in box (B), in which the value of XCO is also high. This indicates that both the sintering resistance of Co and its phase stability are the primary factors deciding the stability of BaCo/CeO2 catalysts and that the catalyst stability can be tailored based on the loading amount of Ba promoter. Box (B) also shows that 1–2 wt% was the optimal loading amount for Ba for improving the catalytic performance of the BaCo/CeO2 catalyst. According to the stability test result, 1% BaCo/CeO2 catalyst showed slightly higher catalytic activity than 2% BaCo/CeO2 catalyst, showing that the 1 wt% is the optimum Ba loading in this system.

4. Conclusions

The effect of the loading amount of Ba promoter for the BaCo/CeO2 catalyst system was studied, and the optimal loading amount was determined to be 1 wt% in 15 wt% Co/CeO2. The doping of Ba on the Co/CeO2 catalyst in the optimal amount enhances the sintering resistance of Co. In addition, it also improves the reducibility of the catalyst, thus aiding the formation and maintenance of the active phase (CoO). However, the doping of an excessive amount of Ba (≥3 wt%) lowers the reducibility of the cobalt oxide species because Ba partially covers their surface and prevents their reduction. This retards the formation and maintenance of the active phase (CoO) during the HTS reaction, leading to the deactivation of the catalyst. In conclusion, both the sintering resistance of Co and its phase stability are critical factors determining the stability of the Ba-promoted Co/CeO2 catalyst system. The optimal range of Ba promoter loading in the Co/CeO2 catalyst was found to be 1–2 wt%. The optimized catalyst (1% BaCo/CeO2) showed excellent catalytic activity (ca. 90%) and stability (>50 h) even in a severe condition (Co conc. = 38%, GHSV = 143,000 h−1). This was owing to the enhanced sintering resistance and high stability of the Co species in the catalyst.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.renene.2019.08.050.

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