

The influence of calcination temperature on catalytic activities in a Co based catalyst for CO₂ dry reforming

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Abstract—The carbon dioxide dry reforming of methane (CDR) reaction could be thermodynamically favored in the range of 800 to 1,000 °C. However, the catalyst in this reaction should be avoided at the calcination temperature over 800 °C since strong metal support interaction (SMSI) in this temperature range can decrease activity due to loss of active sites. Therefore, we focused on optimizing the temperature of pretreatment and a comparison of surface characterization results for CDR. Results related to metal sintering over support, re-dispersion by changing of particle size of metal-support, and strong metal support interaction were observed and confirmed in this work. In our conclusion, optimum calcination temperature for a preparation of catalyst was proposed that 400 °C showed a higher and more stable catalytic activity without changing of support characteristics.

Keywords: Dry Reforming, CO₂ Utilization, Sintering, Metal-support Interaction, Synthesis Gas, Pre-treatment Effect

INTRODUCTION

The excessive use of fossil fuels in industrial activities has caused serious environmental problems. Recently, many scientists have paid much attention to global warming from the greenhouse gas effect, and several efforts to solve this problem are now being made. Carbon dioxide dry reforming of methane (CDR) has been one of the most promising technologies for the utilization of carbon dioxide and methane as greenhouse gases [1]. The synthesis gas produced by CDR has high CO content, which is effective for the synthesis of valuable oxygenated chemicals. Although CDR has economical and environmental advantages, it has not yet been commercialized. This is because of its deactivation due to the undesirable carbon deposition and oxidation on the surface of the catalyst during the process [1-3].

Supported nickel has been commonly studied for its low cost and high availability, but it has major problems, such as carbon deposition, which possibly forms on the catalyst surface and/or on the tubes of the reactor and leads to deactivation of the catalyst and/or a plugging of the tubes. For this reason, it is impossible to avoid carbon formation using nickel catalyst [4, 5].

Recently, it has been revealed that the supported cobalt catalyst shows better activity and stability than supported Ni for CDR [6,7]. The mechanism of carbon deposition on cobalt metal is different from nickel metal. Cobalt catalyst, especially over silica and alumina supports, is also reported to have a good stability [7]. These results

suggest that cobalt catalyst has potential as a good candidate in commercial use with a small amount of carbon deposition.

Conventional supports such as SiO₂ and Al₂O₃ have been reported having good stability over cobalt-based catalyst. SiO₂ can be reduced at low temperature and has more reduction degree and active metal site dispersion on support than Al₂O₃ [8]. Compared to alumina, silica has lower activity because it is an acidic support, which is not suitable to activate acid gas like CO₂. But the stability for CDR of SiO₂ is better than Al₂O₃ [7,9-11,27].

The supported metal catalysts are activated by changing to a stable metal oxide species. So, the calcination in air flow for a stable metal is generally set higher than the reaction temperature. In this process, the catalyst is maintained without structural changes of catalyst. The carbon dioxide dry reforming of methane (CDR) reaction could be thermodynamically favored in the range from 800 to 1,000 °C. However, the catalyst in this reaction should be avoided at the calcination temperature over 800 °C since strong metal support interaction (SMSI) in this temperature range can decrease activity due to a loss of active sites. Among these aspects, we focused on changes of structural and surface characteristics with some phenomena for various calcination temperatures of Co/SiO₂ catalyst.

MATERIAL AND METHODS

1. Preparation of the Catalysts

The Co/SiO₂ catalysts were prepared by impregnating them with SiO₂ (Sigma-Aldrich; BET surface area: 300 m²/g) and aqueous Co nitrate [Co(NO₃)₂·6H₂O]. The precursors were added to de-ionized water to yield the desired weight ratio of Co : SiO₂ (20 : 80). The mixed materials were evaporated using a vacuum evaporator

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at 60 °C. And after evaporated materials were dried at 80 °C, it was calcined at different temperatures for 6 hrs in the air flow. This catalysts were designated as Co/SiO₂(T), with the T denoting the calcination temperature such as 300, 400, 500, 600, 700 and 900 °C.

2. Characterization

Thermo-gravimetric analysis (TGA) of the Co/SiO₂ catalysts was carried out in an air flow at a heating rate of 1 °C/min using a DSC-TGA SDT 29S thermal analyzer.

The BET surface area of the pretreated catalysts was measured via nitrogen adsorption at -196 °C using the Micromeritics ASAP 2020 adsorption apparatus. Before the surface area measurement, the samples were pretreated under He for 4 hrs at 300 °C to clean the catalyst surface.

Powder X-ray diffraction (XRD) was measured with a Rigaku D/MAX-IIIIB X-ray diffractometer using Cu K α radiation with an Ni filter. The average Co₃O₄ crystallite size was calculated using Scherrer's equation, with the most intense diffraction peak at 36.8 of the 2 θ value.

Surface chemical analysis of the catalysts was carried out via X-ray photoelectron spectroscopy (XPS) using ESCALAB MK-II. During the experiments, the Al K α monochromatized line (1486.6 eV) was adopted and the vacuum level was around 10⁻⁷ Pa. The pretreated sample was previously pressed into a thin pellet, and the binding energy (BE) was corrected with the reference BE of C1s (284.4 eV).

H₂-chemisorption was carried out using Micromeritics ASAP 2020 to identify the dispersion, metal surface area and size of the metallic Co particles. Before each measurement, the sample was purged for 1 hr at 400 °C under He flow and subsequently reduced for 6 hrs at 400 °C in H₂. The catalyst was purged for 1 hr at 400 °C, and the H₂ adsorption isotherms were measured at 100 °C. The dispersion and the particle size of the metallic Co were calculated from the amount of the adsorbed H₂ under the assumption that the ratio of the adsorption stoichiometry of the hydrogen atom to that of the surface Co atom (H/Co) was 1 : 1 [12]. The O₂ titration was also carried out on the same instrument to identify the reduction degree of the metallic Co. The catalyst was reduced via H₂ chemisorption and analyzed in flowing 5% O₂/He at 100 °C. The reduction degree was calculated using [amount of O₂ consumption (mmol O₂; 3Co+2O₂→Co₃O₄)]/[theoretical amount of H₂ consumption with the assumption of fully reduced Co oxides (mmol H₂; Co₃O₄+4H₂→3Co+4H₂O)]×100.

Transmission electron microscope (TEM) analysis was performed on an FEI Tecnai G2-20 S-Twin instrument to measure the morphology and the Co₃O₄ particle size.

3. Activity Test of the Catalysts

CDR was performed with the prepared catalysts in a fixed-bed tubular reactor (9.5 mm inlet diameter) at atmospheric pressure. The prepared catalyst was loaded into a heat group of the reactor and heated to the reaction temperature of 850 °C with a heating rate of 10 °C/min under the flow of mixed gas (CH₄ : CO₂ : N₂=40 : 40 : 20, atmospheric pressure and GHSV=20,000 ml/g_{cat}/h). The activity test was performed for 25 hrs. A cold-trap was placed before the TCD to remove trace water in the product gases. Only H₂, CO, CH₄ and CO₂ were detected, and the carbon balance was maintained in the range of 100±5%. The conversions of the reactants and H₂/CO ratio were defined as follows, Eqs. (1), (2) and (3).

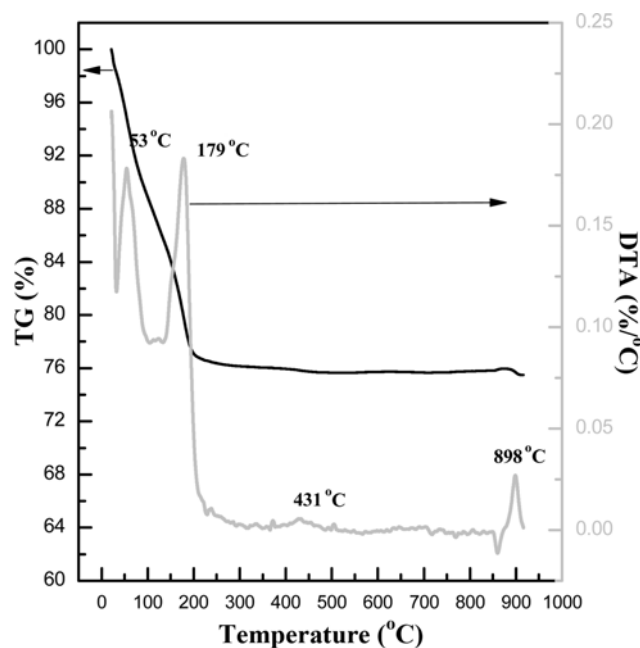


Fig. 1. TG-DTA curve for 20 wt% Co/SiO₂ at the range of 30-900 °C and at a constant heating rate of 10 °C·min⁻¹ in a flow of air.

$$X_{CH_4}(\%) = \left(\frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \right) \times 100 \quad (1)$$

$$X_{CO_2}(\%) = \left(\frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \right) \times 100 \quad (2)$$

$$H_2/CO = \frac{n_{H_2,out}}{n_{CO,out}} \quad (3)$$

RESULTS AND DISCUSSION

The weight loss of the 20 wt% Co/SiO₂ catalysts at various temperatures was measured via TG-DTA analysis, as shown in Fig. 1. The used sample for TG-DTA was dried at 80 °C without calcination. At 100 and 200 °C, the weight loss occurred at 10% and 15%, respectively, which was caused by remaining water and desorbed precursors in a catalyst. Over this temperature, there was no more weight loss. The y axis at the right side of the figure shows the DTA results. Exothermic peaks were observed at 53, 179, 431 and 898 °C. The 53 °C and 179 °C peaks were assumed the partially remaining water of dried catalyst at 60 °C and the NO_x decomposition by nitration of the cobalt nitrate and air. There was no further weight change; the 431 °C and 898 °C peaks were due to sintering of cobalt particle over SiO₂ and SMSI of Co with SiO₂. Sintering is well-known as a physical phenomenon via the solid-solid reaction of cobalt particles [8]. Also, Kogelbauer et al. [13,14] reported that metal silicates were formed with an interaction between metal and silica, namely SMSI. A high calcination temperature caused a structural or textural change which could be affecting the surface area or the pore size distribution [8,13,14]. Thus, a study on an evidence and activity resulted in the background of the TG-DTA results for the phenomena was performed.

The BET surface area of the support was gradually decreased

Table 1. Summaries of BET, XRD, H₂-chemisorption and CDR activity for the 20 wt% Co/SiO₂ at various calcination temperatures

Notation	BET surface area (m ² /g)	Pore diameter (nm)	Particle size of Co ^{0a}	Particle size of Co ₃ O ₄ ^b	Degree of reduction (%) ^c	CH ₄ conversion (%)	CO ₂ conversion (%)	CO/H ₂ ratio
Co/SiO ₂ (300)	274	228	27	29	80	12	31	0.24
Co/SiO ₂ (400)	275	227	24	25	98	22	46	0.39
Co/SiO ₂ (500)	256	273	145	80	10	2	8	0.17
Co/SiO ₂ (600)	253	214	26	29	80	21	44	0.37
Co/SiO ₂ (700)	230	131	18	21	-	16	40	0.31
Co/SiO ₂ (900)	176	143	1458	39	-	2	9	0.14

^aParticle size of Co⁰ that was calculated using Sherrer's equation from XRD

^bParticle size of Co₃O₄ measured via H₂-chemisorption

^cDegree of reduction measured via O₂ titration

with an increasing of calcination temperature, as shown in Table 1. The decrease in the surface area of the support could be explained with three groups: Group 1 (300-400 °C), Group 2 (500-600 °C) and Group 3 (700-900 °C), depending on calcination temperature. The surface area and the pore diameter in Group 1 had constant values. In this group, the catalysts did not influence the physical characteristics of the BET results. Group 2 had a smaller surface area than Group 1, and the pore diameter sharply increased to 273 nm at 500 °C but decreased to 214.1 nm at 600 °C. From this phenomenon, it could be assumed that the calcination temperature influences the structural variation of active metals by sintering them at 500 °C and by rearranging the catalyst structure at 600 °C. In Group 3, a BET characteristic with a higher temperature decreased to about 50% through the strong interaction of the active metal and the support.

The calcined Co at 500 °C is known to lead to the formation of the Co₃O₄ phase [15-17]. Rathousky et al. [18,19] and Lira et al. [20] reported that the calcination conditions affected the performance of the Co/Al₂O₃ and Co/SiO₂ catalysts. Severe sintering phenomena have also been reported on Co/SiO₂ at an oxidation and reduction temperature of above 500 °C by forming cobalt silicates [21]. Ernst et al. [22] suggested that the cobalt oxide structure on the catalyst could be formed into two types: Co₃O₄ and/or Co₂SiO₄. Potoczna-Petru and Jablonski et al. [23,24] found the presence of small crystallites of Co₃O₄ on the particle size of a catalyst that was pretreated in air flow at 550 °C. From these reports, it could be assumed that the formation of cobalt oxide at various calcination temperatures depends on the Co concentration and the nature of the support.

Fig. 2 shows the XRD patterns of the Co/SiO₂ (T) catalysts. Other catalysts, except for Co/SiO₂(900), representing the characteristic peaks of Co₃O₄. Co/SiO₂(900) confirmed a typical peak, which is defined as Co₂SiO₄. The peak intensity increased in Group 3 with an increasing of calcination temperature. However, the peak intensity of Co/SiO₂(500) and Co/SiO₂(700) decreased. Fig. 3 shows the XRD patterns of the Co/SiO₂ (T) catalysts, as analyzed at the low scanning speed of 1.0°/min and within the range of 30-38° at 2θ value. The 36.7° at 2θ was the highest Co₃O₄ intensity in Group 1. The peak intensity increased with an increasing of a calcination temperature. The peak intensity of Co/SiO₂(500) in Group 2 decreased suddenly due to the sintering of the Co, while the peak intensity at Co/SiO₂(600) was increased rapidly. This was due to a re-dispersion followed by changing of particle size by Co and SiO₂ interaction after aggregating with the sintering of the Co metal at Co/SiO₂(500).

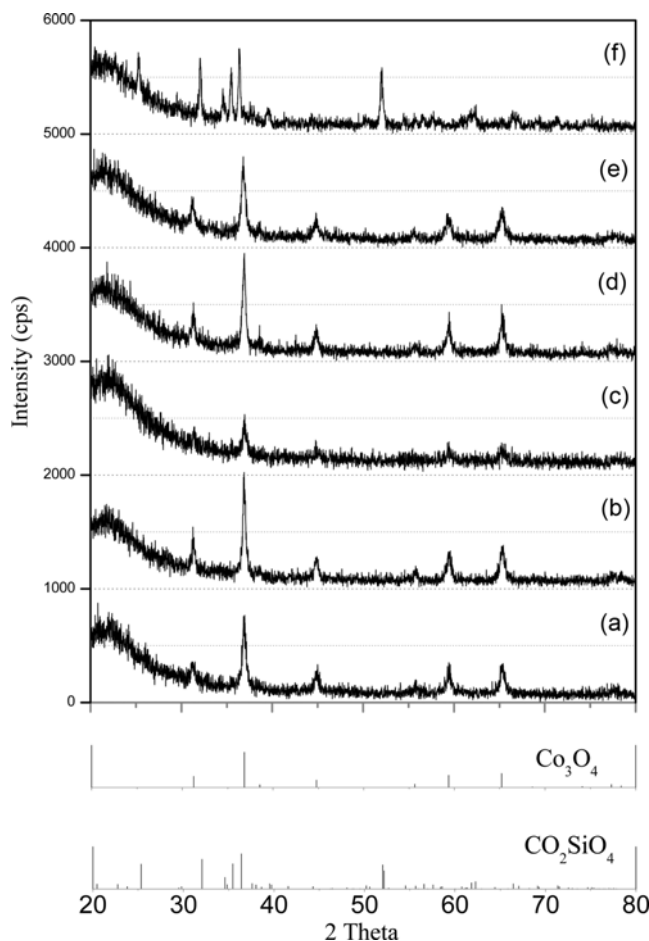


Fig. 2. XRD patterns of 20 wt% Co/SiO₂ at calcination temperature. (a) Co/SiO₂(300), (b) Co/SiO₂(400), (c) Co/SiO₂(500), (d) Co/SiO₂(600), (e) Co/SiO₂(700) and (f) Co/SiO₂(900).

The peaks in Group 3 showed a variation from a peak of Co₃O₄ to Co₂SiO₄ with a spectrum of peaks from Co/SiO₂(700) to Co/SiO₂(900). This confirmed the crystal deformation of the catalyst from Co₃O₄/SiO₂ to Co₂SiO₄.

The average Co₃O₄ particle size, as shown in Table 1, was calculated by using the Scherrer equation from the maximum peak of Co₃O₄. The particle sizes of the Co₃O₄ showed a variety within the range of 19-80 nm. In Group 1, the particle sizes decreased from

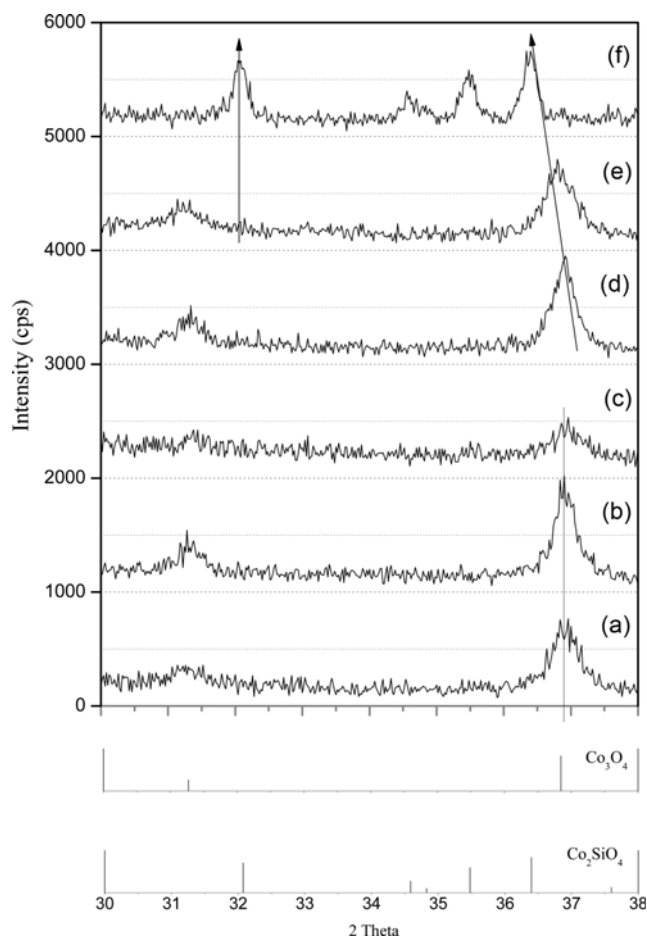


Fig. 3. XRD patterns in the $2\theta=30\text{--}38$ range of 20 wt% Co/SiO₂ at calcination temperature. (a) Co/SiO₂(300), (b) Co/SiO₂(400), (c) Co/SiO₂(500), (d) Co/SiO₂(600), (e) Co/SiO₂(700) and (f) Co/SiO₂(900).

29 to 25 nm with an increasing of calcination temperature. In Group 2 and Group 3, the particle size of Co/SiO₂(500) was larger (80 nm) than that of Co/SiO₂(400) due to the Co sintering. Based on the re-dispersion by interaction of Co₃O₄ and SiO₂ with an increasing of calcination temperature, Co/SiO₂(600) and Co/SiO₂(700) decreased to 29 nm and 21 nm, respectively. However, Co/SiO₂(900) increased to 39 nm due to the strong chemical bond between Co and SiO₂.

The Co⁰ particle size was detected via H₂ chemisorption of the reduced catalysts. The O₂ titration method was used to measure the reduction degree in the catalysts, which is shown in Table 1. The Co⁰ particle size of Co/SiO₂(T) was similar to that of Co₃O₄. Group 1 and Co/SiO₂(500) increased from 27 to 145 nm with increasing of calcination temperature. Co/SiO₂(600) and Co/SiO₂(700) was observed to have decreased to 26 and 18 nm, respectively. Moreover, Co/SiO₂(900) showed the highest value of 1,458 nm due to the low amount of the H₂ chemisorption. The degree of reduction in Group 1 increased from 80 to 98%. Because the active site of Co/SiO₂(400) was larger than that of Co/SiO₂(300) with increased Co₃O₄ dispersion over SiO₂ by decreasing Co₃O₄ particle size, which is calculated Co₃O₄ particle size in the XRD. In Group 2, the reduction degrees of Co/SiO₂(500) and Co/SiO₂(600) were 10 and 80%, respectively. No reduction was observed in Group 3. The variation

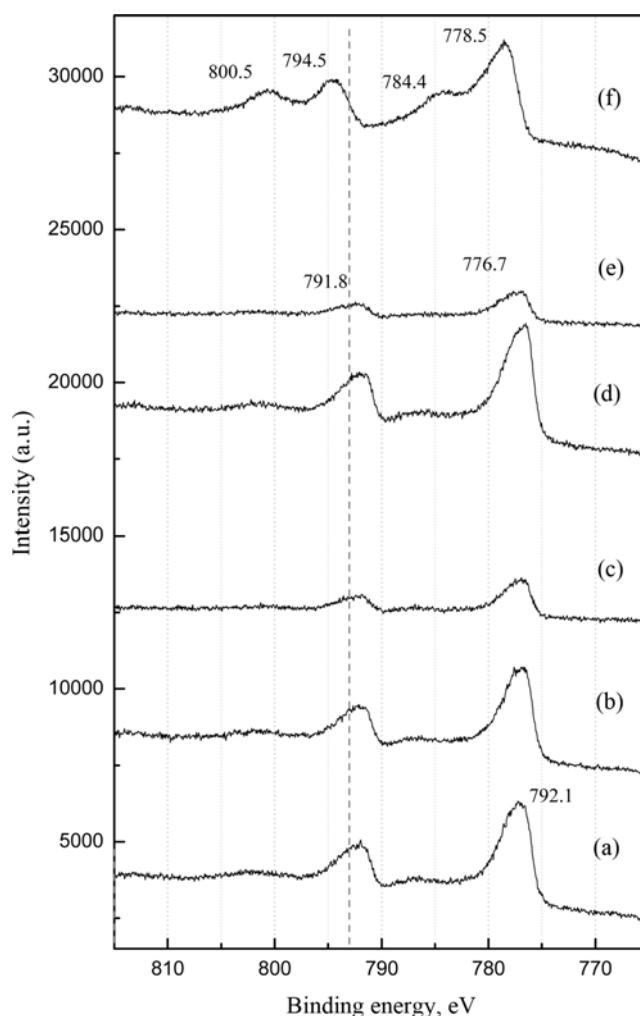


Fig. 4. Influence of calcination temperature on the XPS of Co 2p for 20 wt% Co/SiO₂. (a) Co/SiO₂(300), (b) Co/SiO₂(400), (c) Co/SiO₂(500), (d) Co/SiO₂(600), (e) Co/SiO₂(700) and (f) Co/SiO₂(900).

of particle size of Co⁰ obtained with the H₂ chemisorption and the reduction degree based on the O₂ titration explained well that active sites were decreased because of sintering at Co/SiO₂(500), an increase in the active site through the re-dispersion by changing of particle size of Co/SiO₂(600) and SMSI of the strong interaction of Co/SiO₂(900) with Co and SiO₂.

XPS was used to investigate the oxidation state of the atoms on the surface of the calcined catalysts. The Co 2p regions of CoSiO₂(T) was compared in Fig. 4. Co 2p had binding energies of 777.1 eV and 791.9 eV, respectively, for Co (2p_{3/2}) and Co (2p_{1/2}) [24]. All the binding energies were between 776.7 and 791.8 eV, except for Co/SiO₂(900). In Group 1, all the binding energies appeared with approximately the same peak intensity. In Group 2, Co/SiO₂(500) showed a low intensity via sintering. This was due to decreasing number of Co active sites on the catalyst surface with the Co agglomeration because of sintering. Co/SiO₂(600) showed the highest peak intensity with the re-dispersion by Co₃O₄ and SiO₂. This was due to increasing number of Co active sites on the catalyst surface with the Co rearrangement. In Group 3, peak intensity of Co/SiO₂(700) decreased, which is assumed to decrease from the partial interac-

tions of Co_3O_4 and SiO_2 , as a result of the high calcination temperature. Binding energy of $\text{Co}/\text{SiO}_2(900)$ was higher than others because of transformation of Co_2SiO_4 due to strong interaction with Co and SiO_2 . Moreover, new binding energy peaks of 784.4 eV and 800.5 eV were also appeared with its nature.

Fig. 5 shows TEM images of the pretreated catalysts to prove the phenomenon of sintering, re-dispersion by changing of particle size and interaction of the Co and SiO_2 (metal-support) of the catalyst. (a) $\text{Co}/\text{SiO}_2(400)$ showed a porous SiO_2 and Co_3O_4 size of ca. 100 nm. (b) $\text{Co}/\text{SiO}_2(500)$ could be confirmed the sintering phenomenon of Co with its significant increase of ca. 300 nm. (c) $\text{Co}/\text{SiO}_2(600)$ was dispersed again with the decrease of ca. 100 nm from the huge Co amount via sintering. (d) $\text{Co}/\text{SiO}_2(900)$ did not show the

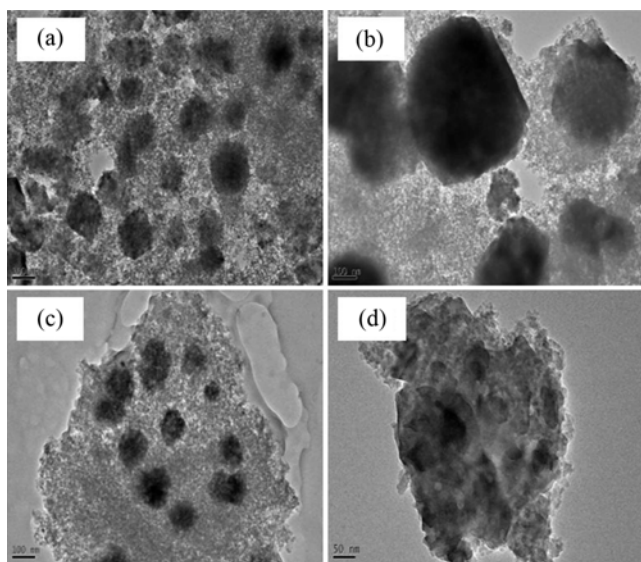


Fig. 5. TEM images of 20 wt% Co/SiO_2 at calcination temperature. (a) $\text{Co}/\text{SiO}_2(400)$, (b) $\text{Co}/\text{SiO}_2(500)$, (c) $\text{Co}/\text{SiO}_2(600)$ and (d) $\text{Co}/\text{SiO}_2(900)$.

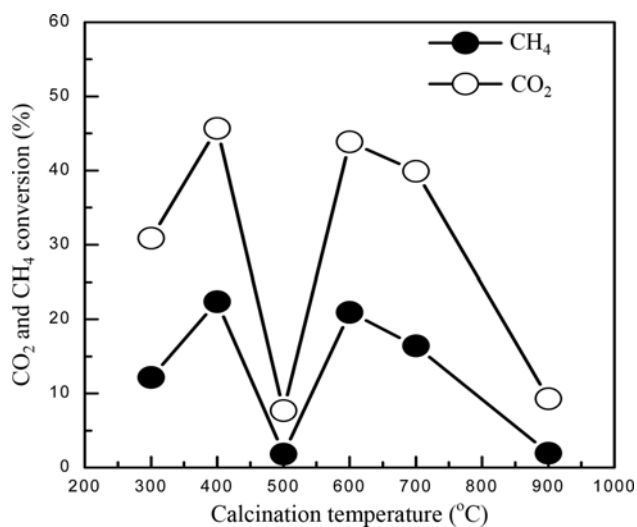


Fig. 6. Comparison of activities depend on various calcination temperature in CDR over 20 wt% Co/SiO_2 (Catalyst: 20.0 mg; flow rate: 66.7 ml/min ($\text{CH}_4/\text{CO}_2=1/1$); temperature: 850 °C; atmospheric pressure and space velocity: 20,000 $\text{mlh}^{-1}\text{g}^{-1}$).

Co particle. This was due to the strong interaction with the combined appearance of Co and SiO_2 .

In Fig. 6, (a) and (b) showed an activity at various calcination temperatures. In Group 1, the activity increased from 30 to 46% for the CO_2 conversion with an increasing of calcination temperature. The activity improved with the reduction degree and the increase in the crystallization degree, which is the intensity of Co_3O_4 in the XRD. In Group 2, the CO_2 conversion of sintered $\text{Co}/\text{SiO}_2(500)$ was decreased to 9% with respect to $\text{Co}/\text{SiO}_2(400)$ by decreasing in the BET characteristics, dispersion of active sites and reduction degree of Co via Co agglomeration. On the contrary, the CO_2 conversion of re-dispersed $\text{Co}/\text{SiO}_2(600)$ was increased to 45% by improving in the active sites, BET characteristics and reduction degree with rearrangement of the active metal. These results confirmed that the active site and reduction degree with cobalt particle size over SiO_2 have a major role in the activity of CDR.

In Group 3, the activities of $\text{Co}/\text{SiO}_2(700)$ and $\text{Co}/\text{SiO}_2(900)$ decreased to 40 and 10%, respectively. The calcined catalysts at a high temperature caused a decreasing in the active sites from the interaction of Co_3O_4 and SiO_2 . However, the activity of $\text{Co}/\text{SiO}_2(700)$

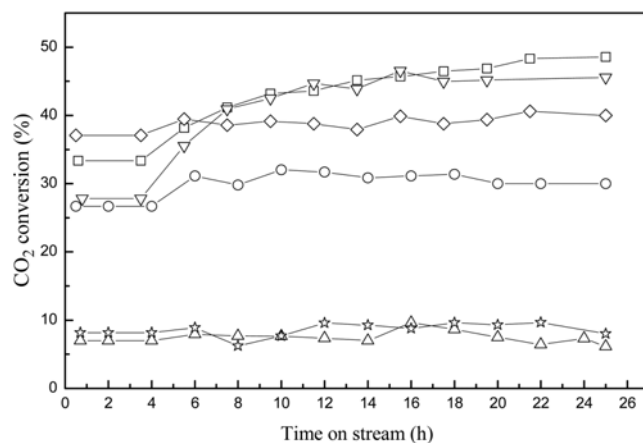
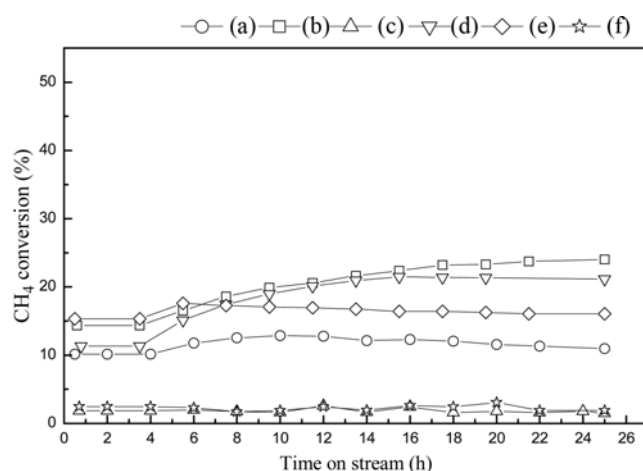


Fig. 7. Time on streams of the catalytic activities depend on various calcination temperature in CDR over 20 wt% Co/SiO_2 for 25 hr (Catalyst: 20.0 mg; flow rate: 66.7 ml/min ($\text{CH}_4/\text{CO}_2=1/1$); temperature: 850 °C; atmospheric pressure and space velocity: 20,000 $\text{mlh}^{-1}\text{g}^{-1}$). (a) $\text{Co}/\text{SiO}_2(300)$, (b) $\text{Co}/\text{SiO}_2(400)$, (c) $\text{Co}/\text{SiO}_2(500)$, (d) $\text{Co}/\text{SiO}_2(600)$, (e) $\text{Co}/\text{SiO}_2(700)$ and (f) $\text{Co}/\text{SiO}_2(900)$.

with the partial interaction of Co₃O₄ and SiO₂ was higher than that by completed interaction of Co/SiO₂(900), which had an overall strong interaction by formed Co₂SiO₄ with Co₃O₄ and SiO₂. In Table 1, CO/H₂ ratio shows similar trends to conversion. Co/SiO₂(400), which had the best conversion, was the highest to 0.39 and Co/SiO₂(900) was the lowest to 0.14. Fig. 7 shows the time on stream for the stability of an activity. The activity level of Co/SiO₂(500) and Co/SiO₂(900) remained at ca. 10%. The activity of others increased more ca. 5 and 10% after 4 hrs in the CH₄ and CO₂ conversion, respectively. The time on stream was stabilized after 24 hrs.

The results confirmed that sintering by Co₃O₄ particles, re-dispersion of partial interaction and Co₂SiO₄ of strong interaction with Co₃O₄-SiO₂ were occurring with the influence of calcination temperature. Despite the many studies on sintering and metal-support interaction [12,25,26], the re-dispersion of active sites after the sintering phenomenon improved active metal dispersion was confirmed in this study. Therefore, the rearrangement of active sites by re-dispersion of the catalyst at 600 °C newly occurred, whereby the activity increased. It effected improvement in the physical and chemical characteristics of the catalyst. Since the role of support as carbon dioxide decomposition is very important as one elementary step of CDR for preventing coke formation [27], we confirmed that calcined catalysts at 400 °C, which formed without changing of support characteristics, was the best condition of calcination temperature.

CONCLUSION

The crystallinity of prepared catalyst with highest activity in this CDR was obtained at a temperature of 400 °C from the result of XRD pattern. A metal sintering over support which could occur by aggregation of metallic particles around 500 °C and strong metal support interaction, which was revealed with a transformation of metal oxide species to metallic silicate around 900 °C, are also confirmed to be an influence as already well known. So that, the activities ranging those temperatures are lower than 400 °C. A re-dispersion of active metal by changing of particle size for metal-support at a calcination of 600 °C is especially observed and the activity was elevated than around 500 °C at which a metal sintering was found.

Eventually, we propose that 400 °C becomes the optimum calcination temperature for getting more higher and stable catalytic activity of carbon dioxide reforming without changing of support characteristics. These results could be an important guideline for optimizing the preparation process of catalyst in CDR.

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