Characterization and catalytic oxidation of carbon monoxide over supported cobalt catalysts

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Three types of supported cobalt catalysts (CoO_x/SiO_2, CoO_x/TiO_2 and CoO_x/Al_2O_3) were prepared by incipient wetness impregnation with aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution. The phase composition and the interactions of cobalt with supports under different calcined temperatures were investigated using thermogravimetry (TG), N_2-adsorption at -196 °C, X-ray diffraction (XRD), temperature-programmed reduction (TPR) and diffuse reflectance spectroscopy (DRS). Their catalytic activities towards the CO oxidation were further studied in a continuous flow micro-reactor. The results showed that the interaction of cobalt oxide with supports was much stronger in the kinds of Al_2O_3 and TiO_2, while no conclusive evidence of any interaction was found for SiO_2. Besides the crystalline Co_3O_4 which was formed in three supported catalysts, both high-temperature phases $CoAl_2O_4$ and $CoTiO_3$ spinel were also detected under XRD, DRS and TPR analysis. The degree of interaction between cobalt oxide and the support not only affected the surface area and reduction behavior of the catalysts, the catalytic activity toward the CO oxidation also affected simultaneously. As the $CoAl_2O_4$ and $CoTiO_3$ spinel formed, both the surface area and catalytic activity decreased significantly.

KEY WORDS: cobalt oxide; supported cobalt catalysts; surface area.

1. Introduction

The catalytic oxidation of carbon monoxide is one of the most important reactions in environmental protection. Both platinum group metals and transition metal oxides have been found to catalyze the oxidation. The high cost of previous metals and their sensitivity to sulfur poisoning have motivated the search for substitute catalysts. In recent years, the research on CO oxidation is flourishing in the use of catalysts which contain bulk and supported metal oxides [1–8]. Metal oxides are widely used in the field of heterogeneous catalysis, both as catalysts and as supports. In such applications the performance is determined by some parameters like bulk metal oxide, surface area and the surface oxide structure. Accordingly, metal oxides must have high stabilities as well as high surface areas under conditions of their use both as catalysts and as support materials [9]. Among the transition metal oxides, cobalt oxide is one of the versatile materials that is of interest to this study.

The types of cobalt oxide and surface area can affect the activity of CO oxidation. Our previous studies [8] indicated that the relative activity decreased significantly with the oxidation state of cobalt and increased with the surface area of cobalt oxide. Besides cobalt, the supports for such catalysts, e.g. Al_2O_3, SiO_2 and TiO_2, are indispensable. Loading a catalyst on an inert but high surface area support improves the accessibility of the active phase. Therefore efforts are plunged to detail studies the structural and chemical properties of these supported cobalt catalysts. During the course of our work, the emphasis is placed on the heat treatment of supported catalysts to express the relationship of the metal–support interactions and the activity of CO oxidation.

Based on the above, we modified supported catalysts by calcinations under different temperatures and studied the characterization of these catalysts by TG, BET measurements at liquid nitrogen temperature, XRD, DRS and TPR. Their catalytic activities towards the CO oxidation were further studied in a continuous flow micro-reactor.

2. Experimental

2.1. Sample preparation

Supported cobalt catalysts (5% as metal Co) were prepared by incipient wetness impregnating the supports (Al_2O_3 (Merck, 150 m^2 g^{-1}), SiO_2 (Aerosil, 200 m^2 g^{-1}) and TiO_2 (Degussa P25, 55 m^2 g^{-1})) with cobalt nitrate solutions. Then, samples were dried at 110 °C and

calcined in air (represented as T_C) at 400, 550 and 700 °C, respectively, for 4 h, hereafter named 5Co/Al C400, 5Co/Al C550, 5Co/Al C700 (for CoO_x/Al_2O_3 catalysts), 5Co/Si C400, 5Co/Si C550, 5Co/Si C700 (for CoO_x/SiO_2 catalysts), 5Co/Ti C400, 5Co/Ti C550, 5Co/Ti C700 (for CoO_x/TiO_2 catalysts), respectively.

2.2. Techniques of characterization

Thermal gravimetric analysis (TG/DTG) was carried out using a Seiko TG/DTA 300 system. The rate of heating was maintained at 10 °C min^{-1} and the mass of the sample was ~10 mg. The measurement was carried from RT to 800 °C under nitrogen flowing with a rate of 100 ml min^{-1}.

Nitrogen adsorption isotherms at −196 °C were determined volumetrically with Micrometritics ASAP 2010. The catalysts were pre-outgassed at 5×10^{-5} Torr for 3 h at 110 °C. The surface area was determined from the nitrogen adsorption isotherm.

The XRD analyses of the samples were carried out using a Siemens D5000 diffractometer. The patterns were run with a Ni-filtered $CuK_{\alpha 1}$ radiation (40 kV, 30 mA, $\lambda = 1.5405$ Å).

The DRS spectra were measured at room temperature on a Hitachi U3410 spectrophotometer equipped with an integration sphere. The spectra were recorded against a $BaSO_4$ standard in the region 200–2000 nm.

A TPR of supported cobalt catalysts was performed using 10% H_2 in Ar as a reducing gas. The gas flow rate was adjusted by a mass flow controller under 25 ml min^{-1}. The cell used for TPR was a quartz tube with an 8 mm inner diameter and the 80 mg catalyst was mounted on a quartz–wool. The hydrogen consumption in the experiment was monitored by a thermal conductivity detector (TCD) raising the sample temperature from RT to 800 °C at a constant rate of 10 °C min^{-1}.

2.3. Activity test

The catalytic activity of prepared samples towards CO oxidation was carried out in a continuous flow micro-reactor. A 25 ml min^{-1} stream of reactant gas (mixed 10%O_2/He with 4%CO/He) was catalyzed with 40 mg of freshly prepared catalysts. The reactor temperature was raised stepwise from a room temperature to 300 °C. The reaction products were analyzed on-line using a Varian 3700 gas chromatograph with a carbosphere column. Before reaction, the catalyst was activated in flowing 10% O_2/He at 300 °C for 3 h.

3. Results and discussion

3.1. Characterization of the supported cobalt catalysts

Understanding the interaction of cobalt nitrate with supports, TG/DTG is first used to investigate the thermal characterization of supported cobalt catalysts.

Figure 1 shows three DTG curves of as-synthesized catalysts in a dynamic nitrogen (100 ml min^{-1}) environment. There are three distinct mass-loss regions on increasing temperature which are also established. Both CoO_x/Al_2O_3 and CoO_x/SiO_2 catalysts show similar mass-loss regions (two kinds) except for CoO_x/TiO_2 (three kinds). The first region ($T \sim 100$ °C) is due to the departure of physisorbed water from the supports surface. The second region (T: 100–400 °C) is considered to the decomposition of a nitrate ion. In comparison with the DTG curves, the nitrate ion on both CoO_x/Al_2O_3 (figure 1b) and CoO_x/TiO_2 (figure 1c) catalysts are slowly decomposed. While, the decomposition of a nitrate ion is fast and continuous on CoO_x/SiO_2 (figure 1a), it can be deduced tentatively that the cobalt nitrate is more strongly interacted on both CoO_x/Al_2O_3 and CoO_x/TiO_2 catalysts. A smaller mass-loss region ($T \sim 665$ °C) is observed only on CoO_x/TiO_2 catalyst when compares with the bulk Co_3O_4 [8], this may be due to the decomposition of Co_3O_4 to CoO as following:

$$2Co_3O_4 \rightarrow 6CoO + O_2 \qquad (1)$$
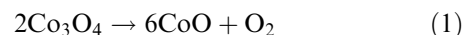
In order to further identify the cobalt species in these catalysts, the XRD, DRS and TPR of the as-synthesized and calcined samples are examined. Figures 2–4 show the XRD patterns of supported cobalt catalysts before and after calcinations. Although the peaks of Co_3O_4 overlap with those of anatase and rutile, the faint peak of (311) diffraction pattern can be observed on the as-synthesized CoO_x/TiO_2 catalyst (figure 4b) which is consistent with the diffraction peaks of cobaltic oxide with a spinel structure (Co_3O_4). The Co_3O_4 crystallite can deposit on titania support before calcinations. From the XRD patterns, it is clear that only Co_3O_4 species exist in all calcined temperatures on CoO_x/SiO_2 catalyst (figure 2). Since the silica is amorphous, the (311) diffraction pattern of Co_3O_4 crystallite is apparent whereby the particle size can be calculated according to the Scherrer equation. The order of 5Co/Si C400, 5Co/Si C550 and 5Co/Si C700 (figure 2c–e) is: 11.7, 12.6 and 14.1 nm, respectively. In contrast to CoO_x/SiO_2, in the XRD patterns of CoO_x/Al_2O_3 and CoO_x/TiO_2 catalysts cannot distinguish the signals originating from Co_3O_4 or other cobalt species. An explanation could be that Co_3O_4 signal is hidden behind the Al_2O_3 and TiO_2 signals. Only the Co_3O_4 species undergoes changes in its composition as the calcined temperature above 700 °C on both CoO_x/Al_2O_3 and CoO_x/TiO_2 catalysts. The 5Co/Al C700 sample (figure 3e) converts into cobalt aluminate spinel ($CoAl_2O_4$) with a blue color and 5Co/Ti C700 sample (figure 4e) converts into cobalt titanate spinel ($CoTiO_3$) with a green color.
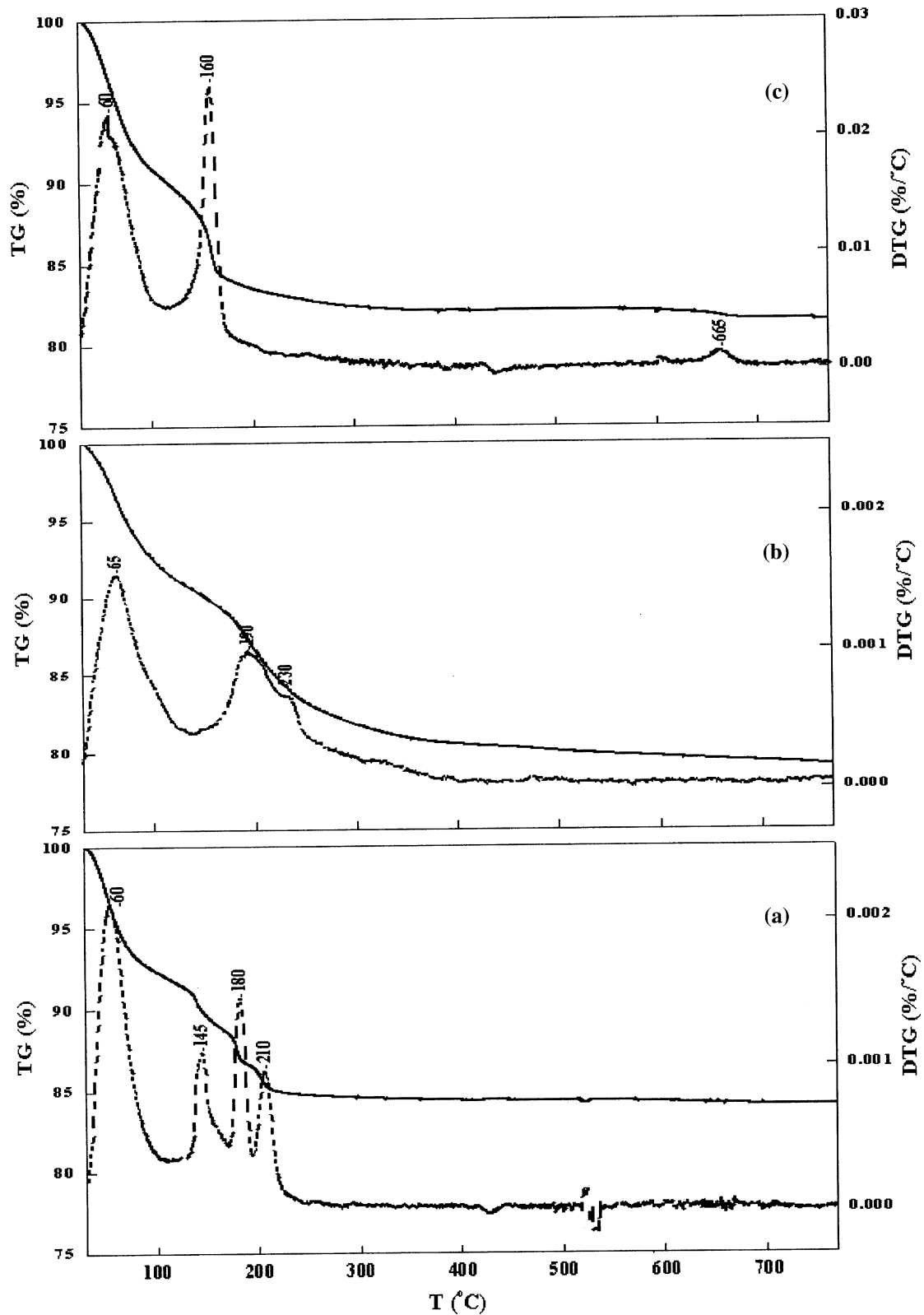
Figure 1. The TG/DTG profiles of supported cobalt catalysts in a dynamic nitrogen environment (a) CoO_x/SiO_2, (b) CoO_x/Al_2O_3, (c) CoO_x/TiO_2.

The colors of the CoO_x/Al_2O_3 and CoO_x/TiO_2 catalysts after calcinations at 700 °C for 4 h in air turn into other species with blue and green, respectively, from black Co_3O_4 species. This is further confirmed by the DRS spectroscopy. The DRS spectra of 5Co/Al C400, 5Co/Al C550 and 5Co/Al C700 samples are shown in figure 5, while the spectra of 5Co/Ti C400, 5Co/Ti C550 and 5Co/Ti C700 samples are given in figure 6. The

DRS of 5Co/Al (C400 and C550) and 5Co/Ti (C400 and C550) (see figures 5a, b and 6a, b) display two characteristic bands at 720, 430 nm and 750, 505 nm, respectively, indicating that the formation of Co_3O_4 [10,11] is dominant at these temperatures. However, both the 5Co/Al C700 and 5Co/Ti C700 samples (figure 5c and 6c) show a distinguishing spectrum, which is dominated by characteristic triplet bands at 625, 580, 545 nm and 635, 600, 550 nm, respectively. According to these bands, the Co^{2+} in both samples should be tetrahedrally coordinated [10,12,13]. Such bands obviously correspond to a $^4A_2(F) \rightarrow T_1(P)$ transition of Co^{2+} ions in the tetrahedrally coordinated, as a surface $CoAl_2O_4$ and $CoTiO_3$ spinels. Therefore, we conclude that after the calcinations above 700 °C, the Co^{2+} ions can diffuse into the Al_2O_3 and TiO_2 lattice to form cobalt aluminate and cobalt titanate. These results are in good agreement with XRD results.

The BET surface area of the supports and the supported cobalt catalysts are given in table 1. The data show a gradual decrease in the surface area with an increase of the calcination temperature for the same support catalyst. Such behavior could be attributed to the increase in the crystalline of the formed CO_3O_4 or other spinels formed when raising the calcination

temperature. Especially for the spinels, the surface area decreased abruptly from 100 to 78 $m^2\ g^{-1}$ for $CoAl_2O_4$ and from 40 to 1.5 $m^2\ g^{-1}$ for $CoTiO_3$, respectively.

The reducibility of the cobalt species after the calcinations process on supported cobalt catalysts are studied by TPR. Figures 7–9 show the TPR profiles of the following catalysts: CoO_x/SiO_2, CoO_x/Al_2O_3 and CoO_x/TiO_2. In TPR measurements of CoO_x/SiO_2 (figure 7) catalysts, two reduction regions have been observed at around 200 °C (figure 7a and b) and 300–450 °C (figure 7c–e). These reduction regions are assigned to the residue of a nitrate (from cobalt precursor) ion and a CO_3O_4 crystallite. Apparently the nitrate ion can be removed completely by calcinations at ca. 400 °C (figure 7c) [14]. Reduction profiles of the CoO_x/SiO_2 catalyst shows two reduction peaks as the calcined temperature above 400 °C, which are similar to those observed in bulk Co_3O_4 [8,15–18]. These profiles point to a two-step reduction process: the first one is of low intensity at 350 °C and overlaps with the more intense second one whose maximum is placed at 370 °C according to the following equations:
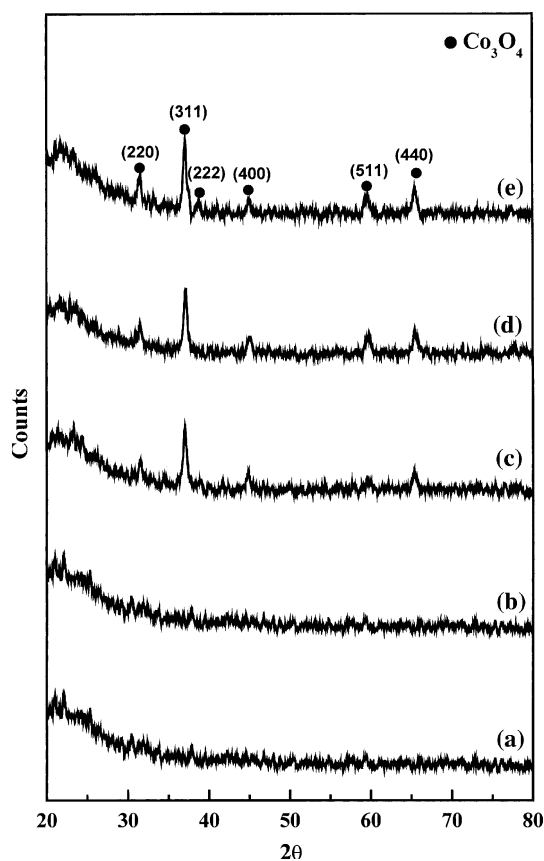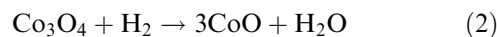
$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \qquad (2)$$

Figure 2. The XRD spectra of CoO_x/SiO_2 catalyst (a) SiO_2, (b) assyn, (c) T_C = 400 °C, (d) T_C = 550 °C, (e) T_C = 700 °C.
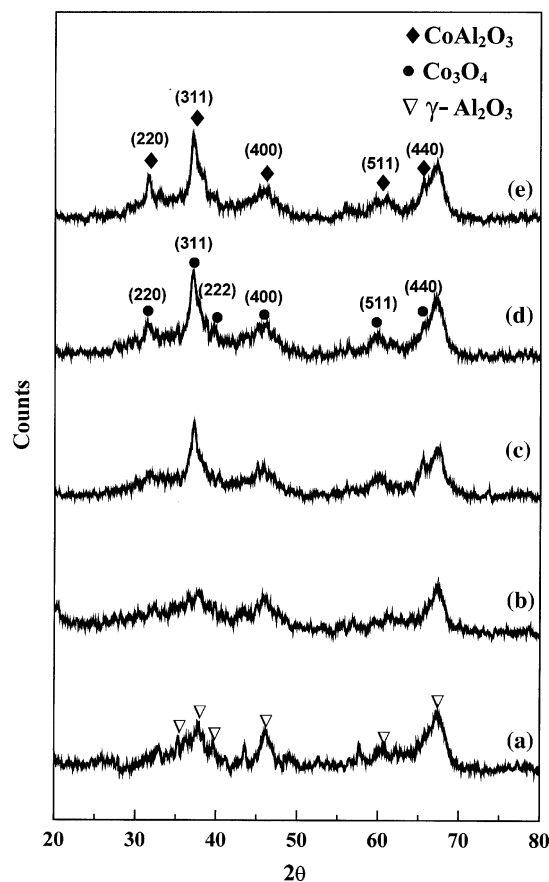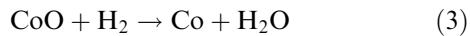

Figure 3. The XRD spectra of CoO_x/Al_2O_3 catalyst (a) Al_2O_3, (b) assyn, (c) T_C = 400 °C, (d) T_C = 550 °C, (e) T_C = 700 °C.

$$CoO + H_2 \rightarrow Co + H_2O \qquad (3)$$

In previous papers [15,19,20] it is shown that the particle size is a determining factor in the reduction process of oxidized cobalt catalysts. The slight shift of reductive peaks from 350, 370 °C to 360, 380 °C (figure 7c, e) indicates that a sintering of cobalt oxide at high temperatures may be possible.

Figure 8 shows the TPR profiles of CoO_x/Al_2O_3. The results show more complexity than the CoO_x/SiO_2. The profiles consist of low temperature peak around 100–300 °C (figure 8a, b), a broad diffuse hydrogen consumption between 500 and 800 °C (figure 8a, b), a broad consecutive stages peaks around 350–500 °C and 510–750 °C (figure 8c, d), a broad peak around 500–650 °C (figure 8e) and a high temperature peak above 800 °C (figure 8e). These reduction regions are assigned to the residue of nitrate ions, trapped of a nitrate ion into the alumina micropore, Co_3O_4 crystallite, surface mixed Co^{3+}–Al^{3+} oxidic crystalline phase (which is difficult to be reduced), CoO crystallite and $CoAl_2O_4$ spinel. Since the strong interaction of cobalt nitrate with alumina, the nitrate ion can be trapped by alumina and resist reduction (figure 8a, b). As the calcined temperature arrives 400 °C (figure 8c), the nitrate ion can be

removed completely. Also, a distinct reduction of Co_3O_4 crystallite is observed (figure 8c, d).

In contrast to 5Co/Si C400 and bulk Co_3O_4, the reduction of Co_3O_4 on 5Co/Al C400 is actualized in only one-step. Arnoldy and Moulijn [21] also reported one broad peak spectrum for Co_3O_4 on CoO_x/Al_2O_3 catalyst. They ascribed this peak to the one-step reduction of Co_3O_4 to metallic Co. It might be argued that, since the diffusion limitation during a TPR system with smaller particles (CoO_x/Al_2O_3) is less severe, the stepwise peaks overlapped. While, the peak separation observed for the larger particles (unsupported material) does not diminish, it should enhance. As the calcined temperature arrives to 700 °C (figure 8e), some Co_3O_4 decomposed into CoO and some Co^{2+} ions diffused into the Al_2O_3 lattice to form a surface $CoAl_2O_4$ spinel. The $CoAl_2O_4$ spinel reduces at higher temperature than both CoO and Co_3O_4; obviously due to the existence of Al^{3+} ions. It is probable that the Al^{3+} ions polarize the covalent Co–O bonds that increase the effective charge of the Co ions [22], i.e., the lattice energy, resulting in an increase of reduction temperature is observed.

Figure 9 shows the TPR profiles of CoO_x/TiO_2. The profiles consist of low temperature peak around 100–300 °C (figure 9a, b), the broad consecutive stages peaks around 310–400 and 400–600 °C (figure 9a–d) and a high temperature peak around 550–700 °C (figure 9e).
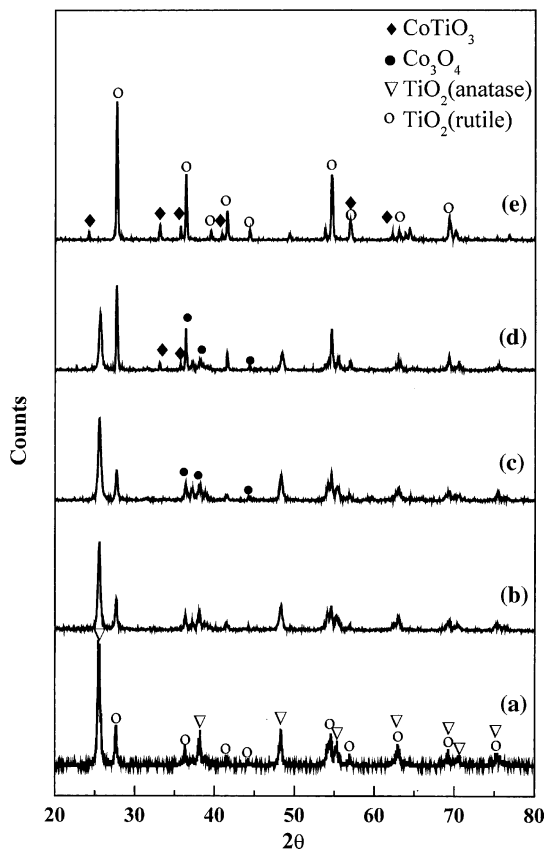

Figure 4. The XRD spectra of CoO_x/TiO_2 catalyst (a) TiO_2, (b) as-syn, (c) $T_C = 400$ °C, (d) $T_C = 550$ °C, (e) $T_C = 700$ °C.

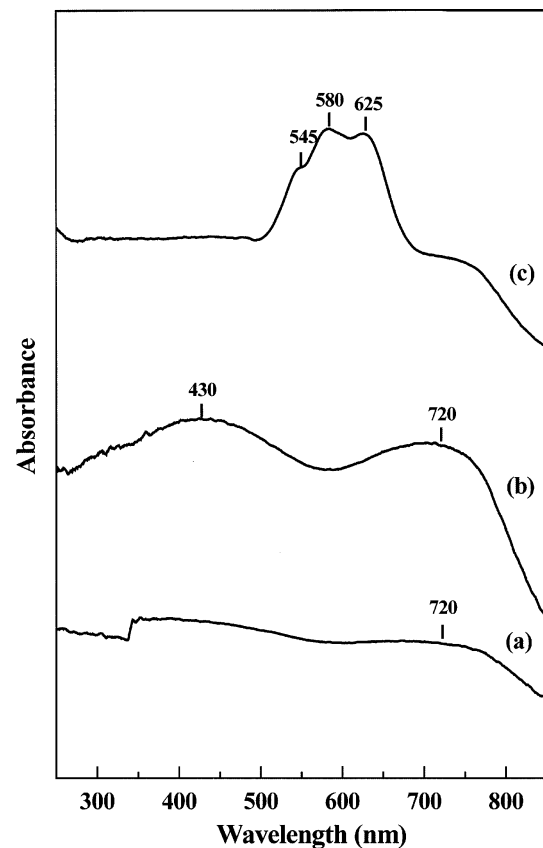Figure 5. The DRS spectra of CoO_x/Al_2O_3 catalyst (a) $T_C = 400$ °C, (b) $T_C = 550$ °C, (c) $T_C = 700$ °C.

These reduction regions are assigned to the residue of nitrate ion, Co_3O_4 crystallite and $CoTiO_3$ spinel. As the DTG and XRD results, the Co_3O_4 crystallite that deposited on titania support before calcinations proceeds two stages of reduction (figure 9a). As the calcined temperature arrives to 400 °C (figure 9c), the nitrate ion can be removed completely. Also, a distinct reduction of Co_3O_4 crystallite is observed (figure 9c, d). In contrast to the CoO_x/SiO_2 catalyst, the temperature ranges of consecutive reduction stages is broad for the CoO_x/TiO_2 catalyst. The signal due to the second stage of reduction for titania supported catalyst is well discernable and shifts to a higher temperature. This indicates that titania has a tendency to stabilize CoO and resist reduction. As the calcined temperature arrives to 700 °C (figure 9e), the reduction peak with a maximum at ca. 670 °C belongs to other species. According to XRD and DRS measurements, from this circumstantial evidence the peak at 670 °C might be ascribed to the reduction of surface $CoTiO_3$ spinel.

3.2. Catalytic activities towards the CO oxidation

The catalytic oxidation of CO by O_2 over supported cobalt catalysts is investigated at temperatures within the
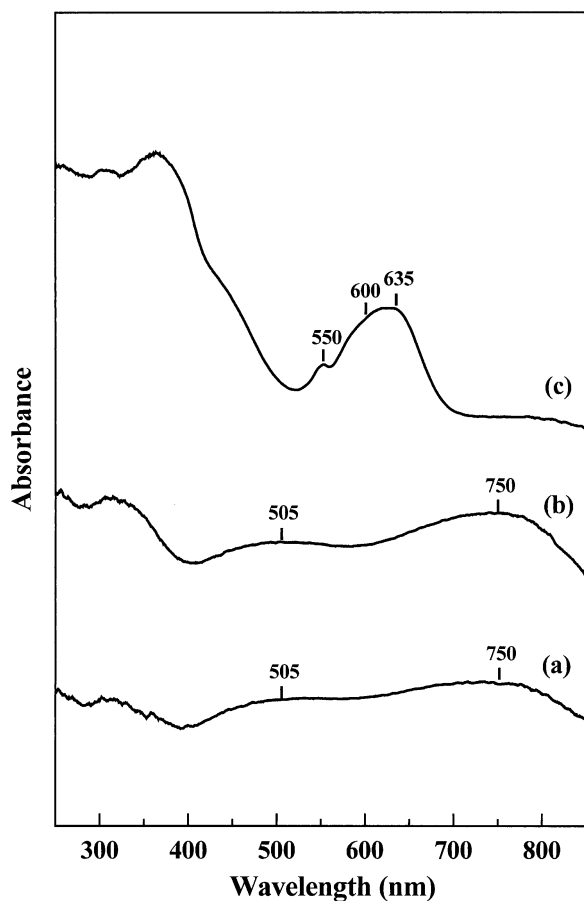
Table 1
Surface area and cobalt species of supported cobalt catalysts at different calcination temperatures

Sample	Calcination temperature (°C)	Surface area ($m^2\,g^{-1}$)	Cobalt species
5Co/SiC400	400	186	Co_3O_4
5Co/SiC550	550	177	Co_3O_4
5Co/SiC700	700	175	Co_3O_4
5Co/AlC400	400	102	Co_3O_4
5Co/AlC550	550	100	Co_3O_4
5Co/AlC700	700	78	$CoAl_2O_4$ (blue)
5Co/TiC400	400	43	Co_3O_4
5Co/TiC550	550	36	Co_3O_4
5Co/TiC700	700	1.5	$CoTiO_3$ (green)

range of 0–300 °C. The results are presented in figure 10. The light-off temperature, denoted T_{50}, is here defined as the temperature where the conversion of CO reaches 50%. Conceivably, the observed T_{50} decreased significantly with increasing the calcination temperature, i.e., 5Co/Al C400 ($T_{50} = 12$ °C) $\gg$ 5Co/Al C700 ($T_{50} = 232$ °C); 5Co/Si C400 ($T_{50} = 33$ °C) $\gg$ 5Co/Si C700 ($T_{50} = 202$ °C); 5Co/Ti C400 ($T_{50} = 160$ °C) $\gg$ 5Co/Ti C700 (T_{50} is larger than 300 °C).

The best active catalysts are achieved over 5Co/Al C400 and 5Co/Si C400, where T_{50} are reached at temperatures as low as ambient temperature. At lower
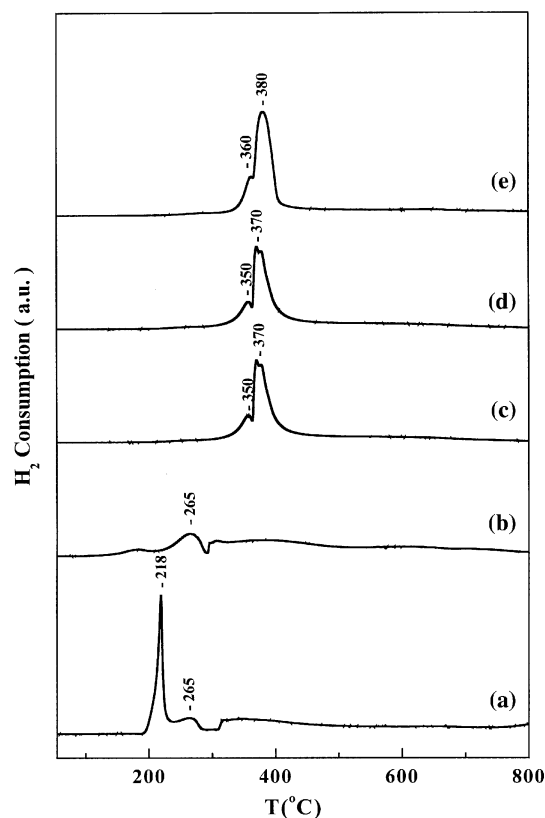

Figure 6. The DRS spectra of CoO_x/TiO_2 catalyst (a) $T_C = 400$ °C, (b) $T_C = 550$ °C, (c) $T_C = 700$ °C.

Figure 7. The TPR profiles of CoO_x/SiO_2 (a) as-syn, (b) $T_C = 200$ °C, (c) $T_C = 400$ °C, (d) $T_C = 550$ °C, (e) $T_C = 700$ °C.

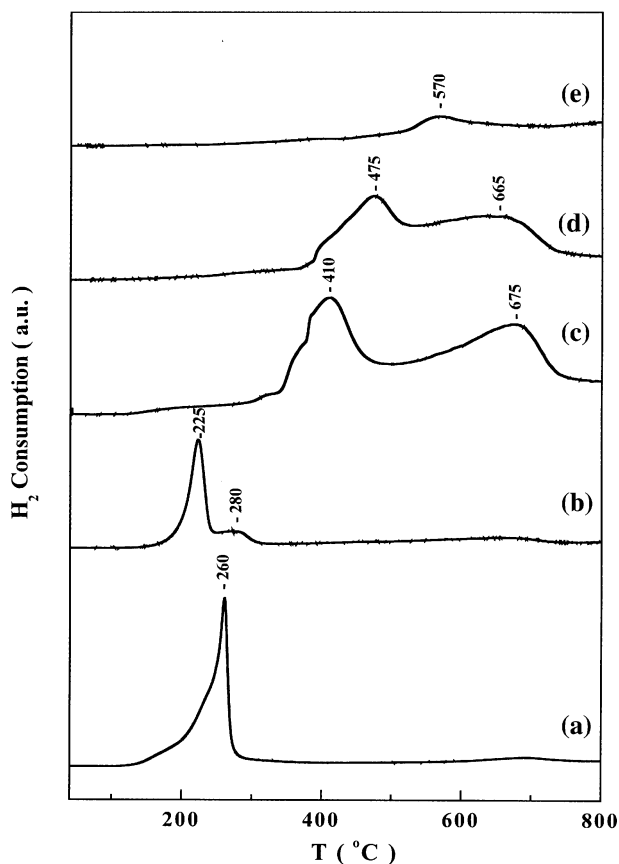Figure 8. The TPR profiles of CoO_x/Al_2O_3 (a) as-syn (b) $T_C = 200$ °C, (c) $T_C = 400$ °C, (d) $T_C = 550$ °C, (e) $T_C = 700$ °C.

Figure 9. The TPR profiles of CoO_x/TiO_2 (a) as-syn, (b) $T_C = 200$ °C, (c) $T_C = 400$ °C, (d) $T_C = 550$ °C, (e) $T_C = 700$ °C.

temperatures, the activity increases with the temperature for both catalysts. However, when the temperature above 50 °C, the catalysts have lost their activity and then, the activity recovered as the temperature raises to 100 °C. From TPO experiments, Jansson et al. [23] suggests that the presence of carbonates and surface carbon can deactivate the catalyst. This phenomenon can be eliminated by the regeneration of the deactivated catalyst in 10% O_2/Ar atmosphere. In the isotope study, Jansson [6] also confirms that the gas phase CO_2 can react with the oxide surface to form a carbonate species. The deactivation found over 5Co/Al C400 and 5Co/Si C400 in the range of 50–100 °C may therefore be attributed to the coverage of carbonates on catalyst surface. The carbonate may desorb as CO_2 again when the temperature raises to 100 °C. Consider the deactivation and the BET surface area of the catalysts (i.e., 102 m^2 g^{-1} for 5Co/Al C400, 186 m^2 g^{-1} for 5Co/Si C400), the high surface area of 5Co/Si C400 exhibits lower deactivation. In the same, the lower surface area of 5Co/Ti C400 (43 m^2 g^{-1}) exhibits lower activity than both 5Co/Al C400 and 5Co/Si C400 catalysts.

The catalysts via the high temperatures calcination increases the strength of interaction between cobalt oxide and supports that may produce some species, i.e.,
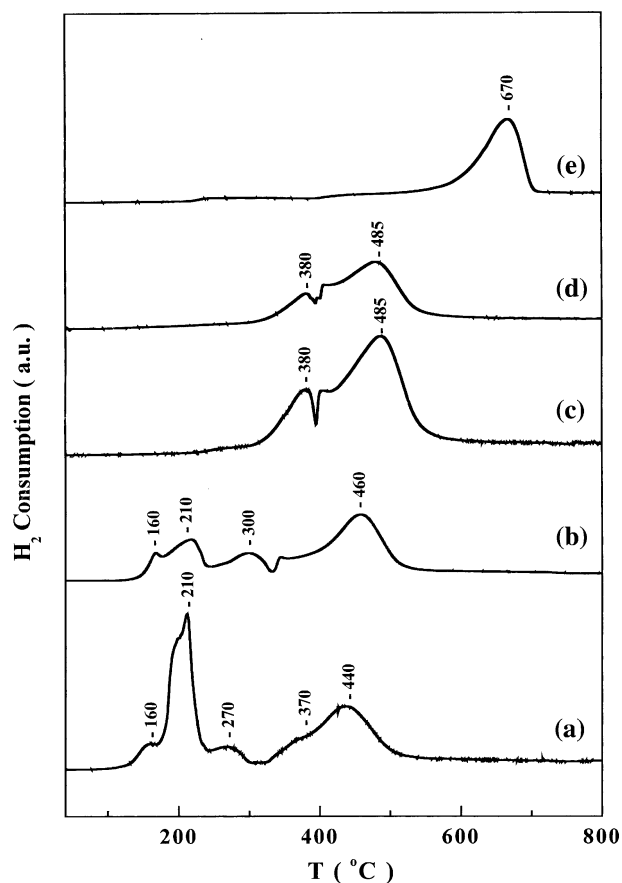
cobalt aluminate spinel ($CoAl_2O_4$) for 5Co/Al C700 and cobalt titanate spinel ($CoTiO_3$) for 5Co/Ti C700. The increase in T_{50} for high temperatures calcination catalysts is clear. As the spinel formed, both the surface area and catalytic activity decreased significantly. Apparently, the variation of T_{50} with the supported cobalt catalysts suggests that the kinds of support and the calcination temperature play an important role on their activity towards CO oxidation.

4. Conclusion

According to what has been shown and discussed above, the following results are found:

1. With a calcined temperature increase, only the Co_3O_4 species exists on a CoO_x/SiO_2 catalyst surface which sinters slightly with a change in temperature.
2. With a calcined temperature increase, Co_3O_4 ($T_C \sim 400$ °C), surface interaction of Co_3O_4–Al_2O_3 ($T_C \sim 400$ °C), sub-surface interaction of Co_3O_4–Al_2O_3 ($T_C \sim 550$ °C) and $CoAl_2O_4$ ($T_C \sim 700$ °C) become the dominant species on a CoO_x/Al_2O_3 catalyst.
3. With a calcined temperature increase, Co_3O_4 ($T_C \leq 400$ °C), sub-surface interactions of Co_3O_4–
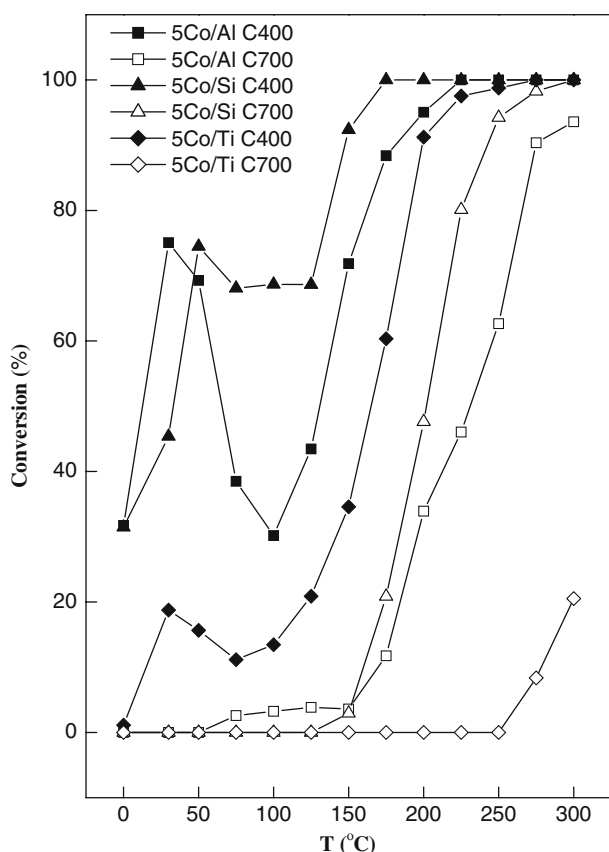
Figure 10. Conversion profiles for CO oxidation over supported cobalt catalysts.

Al_2O_3 ($T_C \sim 550$ °C) and $CoTiO_3$ ($T_C \sim 700$ °C) become the dominant species on a CoO_x/TiO_2 catalyst.

4. The catalytic activities towards the CO oxidation are decreased significantly with the calcination temperature and depends on the kinds of support.

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