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In situ FT-IR spectroscopic studies on the mechanism of the catalytic oxidation of carbon monoxide over supported cobalt catalysts

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Three types of supported cobalt catalysts (5% as metal Co loading on SiO_2, Al_2O_3 and TiO_2) were prepared by incipient wetness impregnation with aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution. Then, all catalysts were calcined in air at 400 °C (assigned as 5Co/Si C400, 5Co/Al C400 and 5Co/Ti C400). Their catalytic activities towards the CO oxidation were studied in a continuous flow micro-reactor. Adsorption of carbon monoxide (CO) and the co-adsorption of CO/O_2 over cobalt oxide were further tested under *in situ* FT-IR. The results showed that both 5Co/Si C400 and 5Co/Al C400 had higher activity than 5Co/Ti C400. The T_{50} (50% conversion) for both 5Co/Si C400 and 5Co/Al C400 was reached at temperatures as low as ambient temperature. According to the *in situ* FT-IR analysis, the variation in oxidation of CO was interpreted with different mechanisms, i.e., the reaction between adsorbed CO and lattice oxygen of cobalt oxide, and part of CO_2 formation via carbonates on 5Co/Si C400; both types of carbonates are formed on 5Co/Al C400 to promote the CO oxidation; while both strong adsorption of CO on TiO_2 and CO_2 on cobalt oxide for 5Co/Ti C400 leads to affect the activity.

KEY WORDS: cobalt oxide; FT-IR; CO oxidation; adsorption.

1. Introduction

There are several reports describing the use of noble metals (Pt, Pd) for CO oxidation [1–7]. However, the high cost of noble metals and their sensitivity to sulfur poisoning have stimulated the search for substitute catalysts. Avoid the price and limited availability of previous metals, considerable attention has been paid to various transition metal oxides and mixed metal oxides. Owing to the importance of cobalt oxide as a catalyst for complete oxidation [8], cobalt oxide is one of the versatile materials among the transition metal oxides. In recent years, the research on CO oxidation is flourishing in the use of catalysts which contain bulk and supported metal oxides [9–15]. Our previous studies on bulk cobalt oxide [16–18] indicate that the relative activity decreased significantly with the oxidation state of cobalt and increased with the surface area of cobalt oxide. Loading a catalyst on high surface area support can modify the activity. Therefore, three kinds of supports (SiO_2 Al_2O_3 and TiO_2) are chose to detail studies of the catalytic oxidation of CO over supported cobalt catalysts.

The catalytic oxidation of CO over transition metal oxides is known to be accompanied by the formation of surface carbonate complexes, then interaction with the surface oxygen to evolve CO_2. Therefore, surface carbonates are regarded as intermediates [19,20]. However, others suggest that the high thermal stability of surface carbonates can deactivate the catalyst [21,22], thus raising doubt about their role as intermediates. In order to understand the relationship of formation of various surface species, in this study, *in situ* FT-IR has been used to demonstrate how CO reacts on the surface of supported cobalt catalysts.

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 °C for 4 h, hereafter named 5Co/Si C400, 5Co/Al C400 and 5Co/Ti C400, respectively.

2.2. 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 room temperature to 300 °C. The reaction products were analyzed on-line using a Varian 3700 gas chromatograph with a

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carbosphere column. Before reaction, the catalyst was activated in flowing 10% O_2/He at 500 °C for 3 h.

2.3. In situ *FT-IR study*

A self-supporting wafer (1.3 cm diameter) was prepared by compressing an 80 mg sample and was mounted in a self-designed high temperature IR quartz cell with a KBr window. One set of stainless steel gas lines was built and connected to the cell that allowed *in situ* measurement of the spectra of CO and CO/O_2 probe gases. Prior to adsorption of the probes, the wafer was first pre-treated in vacuum ($< 10^{-4}$ torr) at 500 °C for 30 min and then cooled to the desired temperature. At each temperature, the background spectrum was recorded and was subtracted from the sample spectrum that was obtained at the same temperature.

3. Results and discussion

3.1. *Catalytic activities towards the CO oxidation*

The catalytic oxidation of CO by O_2 over supported cobalt catalysts is investigated at temperatures within the range of 0–300 °C. The results are presented in figure 1. The light-off temperature, denoted T_{50}, is here defined as the temperature where the conversion of CO reaches 50%.

The better active catalysts are achieved over 5Co/Si C400 and 5Co/Al C400, where T_{50} are reached at temperatures as low as ambient temperature. That is lower than the noble metals (Pt, Pd) for CO oxidation [1–7]. At lower temperature, the activity increases with the temperature for both catalysts. However, when the temperature rose above 50 °C, the 5Co/Si C400 catalyst lost its activity and then, the activity recovered as the temperature rises to 100 °C. From TPO experiments, Jansson *et al.* [22] 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 [14] also confirms that the gas phase CO_2 can react with the oxide surface to form a carbonate species. Konova *et al.* [23] suggests that the deactivation of a gold catalyst for CO oxidation is the capability to adsorb CO and accumulate it as carbonate. The deactivation found over 5Co/Si C400 in the range of 50–100 °C may therefore be attributed to the coverage of carbonates on catalyst surface. The carbonates may desorb as CO_2 again when the temperature rise to 100 °C. Consider the relationship of deactivation and 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 progressive deactivation with temperatures, while the 5Co/Al C400 exhibits progressive increase of activity with temperature. Maybe, the increase in surface carbonates coverage on 5Co/Si C400 is accompanied by the blocking of the active sites to deactivate the catalyst. On the 5Co/Al C400 catalyst, the cycle of CO_2 evolution (activation) and re-adsorption (deactivation) may proceed in the range of 50–100 °C. Further experiments must be explored with *in situ* FT-IR to elucidate the difference.

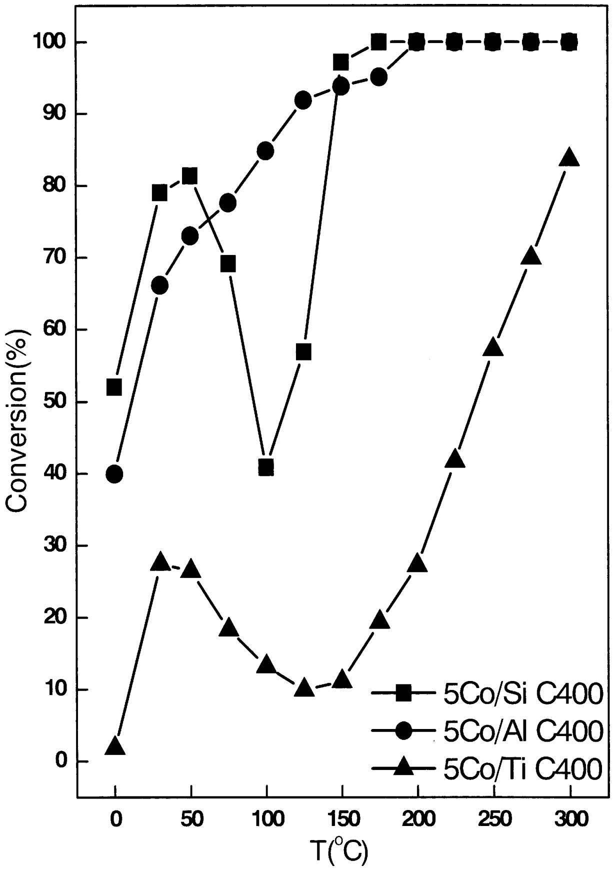

Figure 1. Conversion profiles for CO oxidation over supported cobalt catalysts: (■), 5Co/Si C400; (●), 5Co/Al C400; (▲), 5Co/Ti C400.

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. Apparently, the variation of T_{50} with the supported cobalt catalysts suggests that the kinds of support play an important role on their activity towards CO oxidation.

3.2. In situ *FTIR study*

We have performed *in situ* measurements of infrared spectra of CO and CO/O_2 adsorption on the surface of supported cobalt catalysts. Figures 2–4 show the FT-IR spectrum of the 5Co/Si C400, 5Co/Al C400 and 5Co/Ti C400 samples for CO adsorbed under a 0.5 torr CO pressure and different temperatures. The spectra of 5Co/Si C400 (figure 2) contained bands at 2349, 2166, 2143, 1610 and 1395 cm^{-1} between ambient temperature and 300 °C. These can be assigned to gaseous CO_2 (2349 cm^{-1}) and CO (2143 cm^{-1}), weakly linear adsorbed CO on cobalt oxide (2166 cm^{-1}, which is desorbed

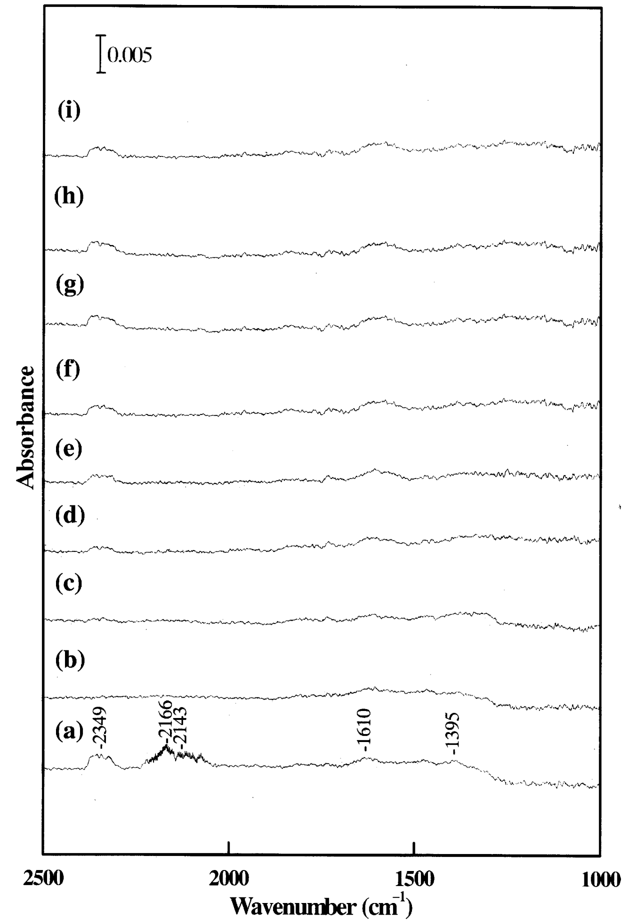

Figure 2. *In situ* FT-IR spectra of 5Co/Si C400 sample for 0.5 torr CO adsorbed at various temperatures: (a) R. T.; (b) evacuation; (c) 50 °C; (d) 100 °C; (e) 150 °C; (f) 200 °C; (g) 250 °C; (h) 300 °C; (i) cooling to R. T.

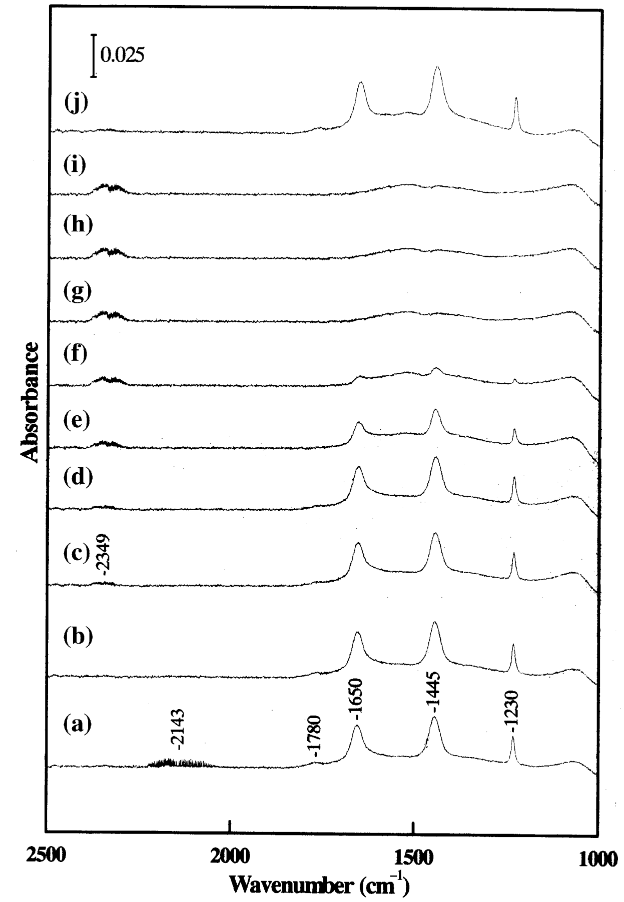

Figure 3. *In situ* FT-IR spectra of 5Co/Al C400 sample for 0.5 torr CO adsorbed at various temperatures: (a) R. T.; (b) evacuation; (c) 50 °C; (d) 75 °C; (e) 100 °C; (f) 150 °C; (g) 200 °C; (h) 250 °C; (i) 300 °C; (j) cooling to R. T.

after evacuation [figure 2(b)]) [10] and carbonates formed on cobalt oxide surface (1610 and 1395 cm^{-1}), respectively. The formation of CO_2 under room temperature simultaneous with the admission of 0.5 torr CO (figure 2(a)) indicates that the activity comes from the adsorbed CO and lattice oxygen of cobalt oxide.

$$*{-}\mathrm{CO} + *{-}\mathrm{O_L} \rightarrow \mathrm{CO_2} + * + *_\mathrm{L} \tag{1}$$

where * denotes an adsorption site on cobalt oxide surface, O_L represents lattice oxygen of cobalt oxide, $*_L$ is the escaping lattice oxygen resulted vacancy. Also, some of the adsorbed CO might migrate to form stable surface carbonates which remain present after evacuation (figure 2(b)). The effect of rising the temperature up to 300 °C for the surface carbonates has been studied (figure 2(c)–(h)). It is worthwhile notice that both the intensity of gaseous CO_2 and carbonates increases with the temperature. Until the temperature reaches 300 °C (figure 2(h)), their intensities are constant. On FT-IR study for CO oxidation on cobalt oxides at 80 K, *Lokhov et al.* [24] suggests that the re-adsorption of CO_2 leads to the formation of stable carbonate complexes. Also, in Finocchio *et al.* [25] experimental finds that a strong adsorption is produced after exposed 50 torr CO_2 on Co_3O_4 at RT. The observed tendency may therefore result from part of CO_2 formation via carbonate and part of carbonates is formed via gaseous CO_2 re-adsorption. The dynamic equilibrium also exists after the temperature cooling to room temperature.

$$*{-}\mathrm{carbonate} \rightarrow \mathrm{CO_2} + * \tag{2}$$

$$\mathrm{CO_2} + * \rightarrow *{-}\mathrm{carbonate} \tag{3}$$

The spectra of 5Co/Al C400 (figure 3) contained bands at 2143, 1780, 1650, 1445 and 1230 cm^{-1} between ambient temperature and 300 °C. Which assigned to gaseous CO (2143 cm^{-1}), carbonate formed via the interface oxygen (assigned as O_I) and cobalt oxide (1780 cm^{-1}), and other carbonates formed on cobalt oxide surface (1650, 1445 and 1230 cm^{-1}), temporarily. Excluding gaseous CO and carbonates, no adsorbed CO and gaseous CO_2 are observed (figure 3(a)) under room temperature. Meanwhile, two types of carbonates can be

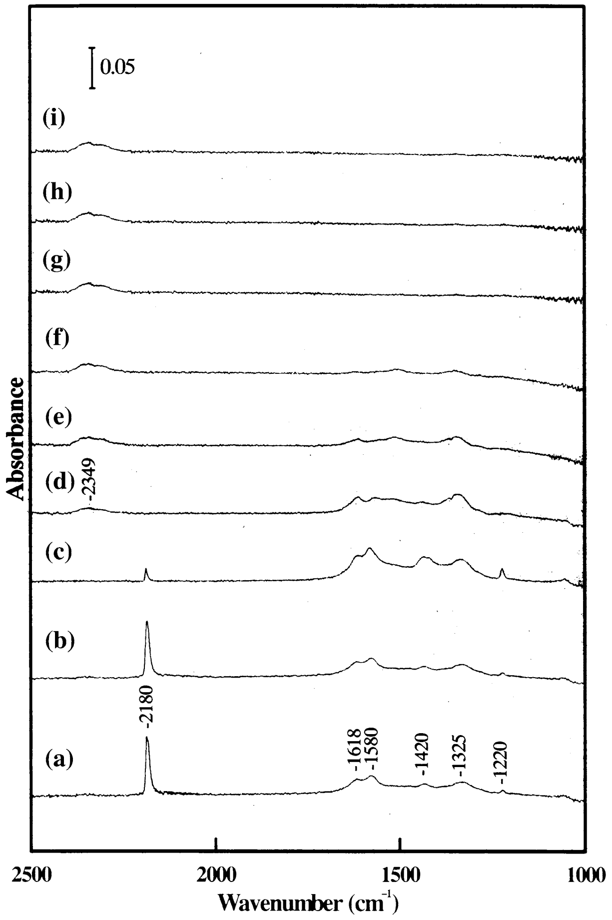

Figure 4. *In situ* FT-IR spectra of 5Co/Ti C400 sample for 0.5 torr CO adsorbed at various temperatures: (a) R. T.; (b) evacuation; (c) 50 °C; (d) 100 °C; (e) 150 °C; (f) 200 °C; (g) 250 °C; (h) 300 °C; (i) cooling to R. T.

distinguished on 5Co/Al C400 catalyst: one carbonate (1780 cm^{-1}) formed via the interface oxygen [assigned as carbonate$_{(I)}$] and three distinct bands (1650, 1445 and 1230 cm^{-1}) are other carbonates that formed on cobalt oxide surface [26]. The effect of the temperature up to 300 °C for the carbonates has been studied (figure 3(c)–(h)). It is notice that the intensity of gaseous CO_2 increases and the intensity of carbonates decreases with the temperature. Both types of carbonates can evolve CO_2 as temperature above room temperature as equations of (2) and (4).

$$*\text{–carbonate}_{(I)} \rightarrow CO_2 + *_{(I)} \qquad (4)$$

where $*_{(I)}$ denotes the interface adsorption site. In the range of RT –75 °C, the equation (4) is preferential. As the temperature raise above 75 °C, the equation (2) is preferential. Comparison with 5Co/Si C400 catalyst, the re-adsorption of CO_2 is not occurred at high temperatures (figure 3(c)–(i)) but re-adsorbs as the temperature back to room temperature on 5Co/Al C400 catalyst (figure 3(j)).

The spectra of 5Co/Ti C400 (figure 4) contained bands at 2349, 2180, 1618, 1580, 1420, 1325 and 1220 cm^{-1} between ambient temperature and 300 °C. These can be assigned to gaseous CO_2 (2349 cm^{-1}), linear adsorbed CO on TiO_2 (2180 cm^{-1}) [27] and carbonates formed on cobalt oxide surface and/or carbonate-like species on the support (1618, 1580, 1420, 1325 and 1220 cm^{-1}) [23], respectively. The variation of three supports is apparent. The adsorption of CO is not observed on both SiO_2 and Al_2O_3 supports (figures 2 and 3), while a strong adsorption of CO on TiO_2 (2180 cm^{-1}) is present at room temperature that is maintained after evacuation (figure 4(b)). According to the catalytic activity measurement (figure 1), the lower active of 5Co/Ti C400 may be ascribed to the strong adsorption of CO on TiO_2 (assigned as $*_s$–CO). Not only the $*_s$–CO, but the formation of carbonate is observed simultaneously (figure 4(a)). As the temperature increased, the $*_s$–CO migrates to the surface of cobalt oxide to form carbonates (figure 4(c)). The carbonates evolve CO_2 as temperature further increased (figure 4(d)–(h)) above 50 °C. The re-adsorption of CO_2, is not observed at high temperatures or the temperature back to room temperature.

$$*_s\text{–CO} + * \xrightarrow{T>R.T.} *\text{–carbonate} + *_s \xrightarrow{T>50\,^{\circ}C} CO_2 + * \qquad (5)$$

where $*_s$ denotes an adsorption site on TiO_2.

The influence of CO/O_2 co-adsorption is studied on the 5Co/Si C400, 5Co/Al C400 and 5Co/Ti C400 samples. In the CO/O_2 adsorption experiments (figures 5–7), first 0.5 torr CO is adsorbed on the catalysts at room temperature giving rise to absorption bands (figures 2–4(a)), and then 0.5 torr O_2 is introduced into the chamber (figures 5–7(a)).

Disappearance of weakly linear adsorbed CO on cobalt oxide and a significant band near 1427 cm^{-1} appears as O_2 is introduced on 5Co/Si C400 sample (figure 5(a)) at room temperature. This indicates that the CO_2 is formed immediately with the introduction of O_2 over the CO pre-adsorbed on cobalt oxide. Also, the introduced O_2 participates the irreversible CO adsorption (carbonates formation) that may be promoted the transformation of carbonates (i.e., from bidentate to monodentate carbonates). The new type carbonates is stable and increases with temperature up to 75 °C (figure 5(c)). As the temperature above 75 °C, the CO_2 (2349 cm^{-1}) intensity significantly increases and the carbonates intensity decreases. This indicates that the activity of 5Co/Si C400 sample comes from the adsorbed CO and lattice oxygen of cobalt oxide, and part of CO_2 formation via carbonates as equations (1) and (2). The consumed lattice oxygen ($*$–O_L) may be restored through adsorption of oxygen molecules on the resulted vacancy ($*_L$).

$$2\,*_L + O_2 \rightarrow 2\,*\,–O_L \qquad (6)$$

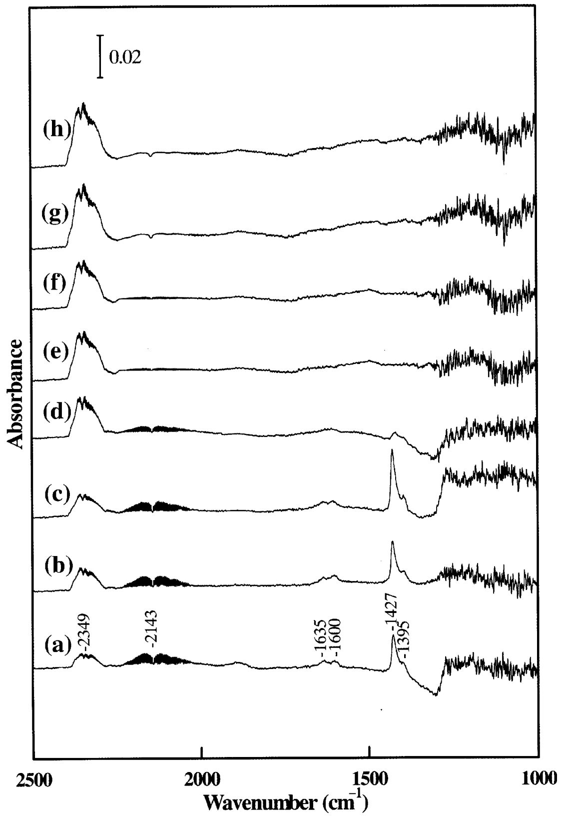

Figure 5. *In situ* FT-IR spectra of 5Co/Si C400 sample after exposure to 0.5 torr CO and 0.5 torr O_2 at various temperatures: (a) R. T.; (b) 50 °C; (c) 75 °C; (d) 100 °C; (e) 150 °C; (f) 200 °C; (g) 250 °C; (h) 300 °C.

The spectrum of CO/O_2 co-adsorption (figure 6(a)) is similar to CO adsorption on 5Co/Al C400 given in (figure 3(a)). As O_2 is introduced and temperature is elevated, there is no obvious band changed (figure 6(b)–(h)). It means that the CO oxidation on 5Co/Al C400 sample comes from the evolved of CO_2 on both types of carbonates as temperature above room temperature as equations of (2) and (4).

Figure 7 shows the spectrum of CO/O_2 co-adsorption on 5Co/Ti C400 at various temperatures. The CO_2 adsorption on cobalt oxide (2350 cm^{-1}) is observed at room temperature [24]. The intensity of adsorbed CO_2 is decreased with raising temperature and disappears above 100 °C (figure 7(a)–(c)).

$$* + CO_2 + \xrightarrow{T<100\,^{\circ}C} * -CO_2 \xrightarrow{T>100\,^{\circ}C} * + CO_2 \qquad (7)$$

According to the catalytic activity measurement (figure 1), the less active of 5Co/Ti C400 and decreasing of activity with raising temperature up to 100 °C may be ascribed to both strong adsorption of CO on TiO_2 and CO_2 on cobalt oxide. As the temperature above 100 °C, not only the $*_s$–CO migrates to the surface of cobalt oxide to form carbonates but the desorbed of $*$–CO_2 is stimulated.

Accordingly, three different models of CO adsorbed and CO_2 desorbed over supported cobalt catalysts are assigned in figure 8. The major adsorbed species is listed in table 1. Excepting the carbonates formation, the CO adsorbed on 5Co/Si C400 sample (figure 8(a)) to promote the CO oxidation. The activity comes from the adsorbed CO and lattice oxygen of cobalt oxide, and part of CO_2 formation via carbonates as equations (1) and (2). Both types of carbonates are formed on 5Co/Al C400 sample (figure 8(b)) to promote the CO oxidation. The activity comes from the evolved of CO_2 on both types of carbonates as temperature above room temperature as equations of (2) and (4). The less active of 5Co/Ti C400 sample can be ascribed to both strong adsorption of CO on TiO_2 and CO_2 on cobalt oxide (figure 8(c)).

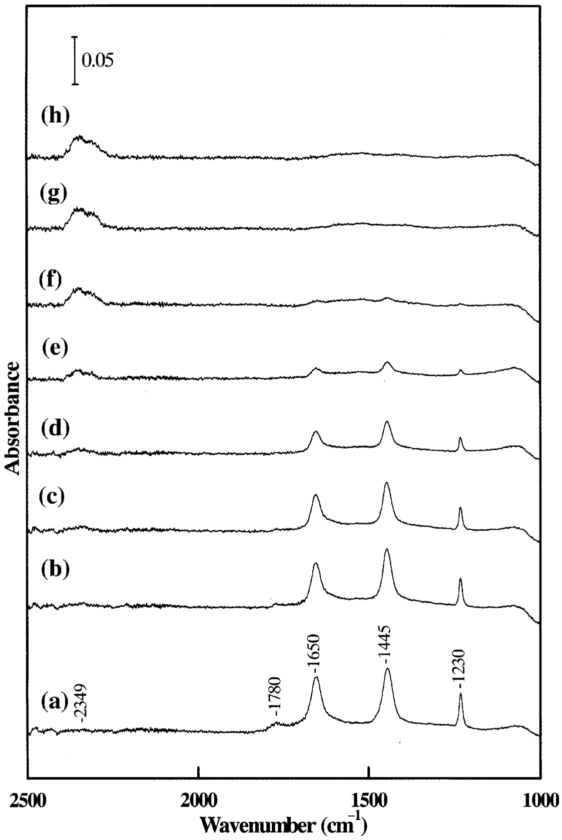

Figure 6. *In situ* FT-IR spectra of 5Co/Al C400 sample after exposure to 0.5 torr CO and 0.5 torr O_2 at various temperatures: (a) R. T.; (b) 50 °C; (c) 75 °C; (d) 100 °C; (e) 150 °C; (f) 200 °C; (g) 250 °C; (h) 300 °C.

4. Conclusion

Based on the CO catalytic oxidation activities and adsorption studies by *in situ* FT-IR over supported cobalt catalysts, we propose

1. The activity of 5Co/Si C400 sample comes from the adsorbed CO and lattice oxygen of cobalt oxide, and part of CO_2 formation via carbonates.

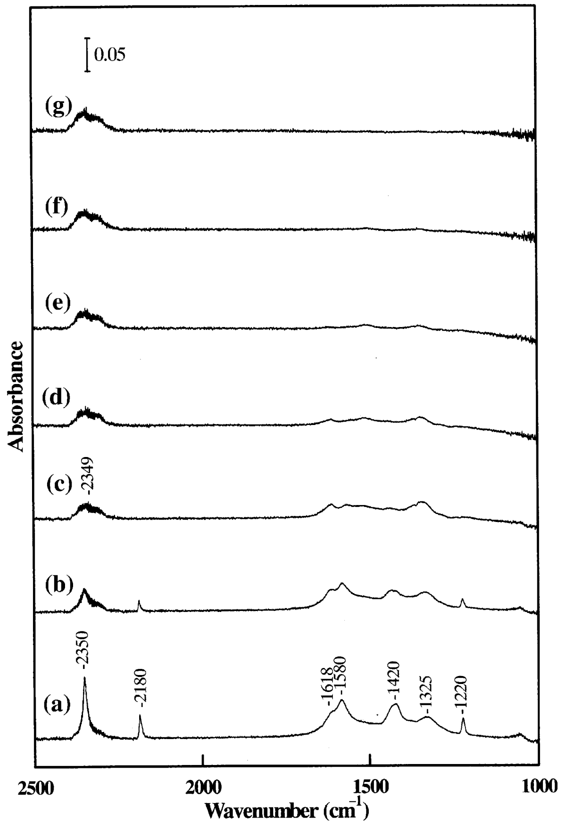

Figure 7. *In situ* FT-IR spectra of 5Co/Ti C400 sample after exposure to 0.5 torr CO and 0.5 torr O_2 at various temperatures: (a) R. T.; (b) 50 °C; (c) 100 °C; (d) 150 °C; (e) 200 °C; (f) 250 °C; (g) 300 °C.

2. The activity of 5Co/Al C400 sample comes from the evolved of CO_2 on both types of carbonates.
3. The less active of 5Co/Ti C400 sample can be ascribed to both strong adsorption of CO on TiO_2 and CO_2 on cobalt oxide.

Table 1

Types of adsorbed species over supported cobalt catalysts

Catalysts	Adsorbed species (cm^{-1})				
	*–CO[a]	$*_s$–CO[b]	$*_s$–CO_2[c]	*–Carbonate$_{(\mathrm{I})}$[d]	*–Carbonates
5Co/Si C400	2166	–	–	–	1610, 1427, 1395
5Co/Al C400	–	–	–	1780	1650, 1445, 1230
5Co/Ti 07400	–	2180	2350	–	1420, 1325, 1220

[a] Linear CO adsorbed on cobalt oxide.

[b] CO adsorbed on TiO_2.

[c] CO_2 adsorbed on cobalt oxide.

[d] Interface oxygen to form carbonate.

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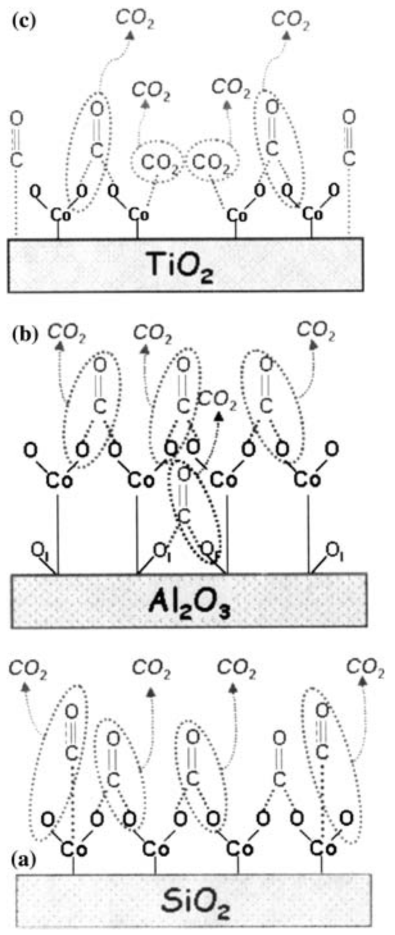

Figure 8. Proposed models of CO adsorbed and CO_2 desorbed over supported cobalt catalysts: (a) 5Co/Si C400; (b) 5Co/Al C400; (c) 5Co/Ti C400.

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