

# Changes in microstructure of a reduced cobalt catalyst during performing FT synthesis from syngas determined by in situ high-pressure syngas adsorption

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## Abstract

Syngas adsorptions at 1.2 MPa and room temperature on a precipitated cobalt catalyst reduced by H<sub>2</sub> and on that used for high-pressure FT synthesis were studied by diffuse reflectance FTIR spectroscopy. The syngas adsorption on the freshly reduced sample gives rise to two weak bands at 2013 and 2033 cm<sup>-1</sup>, which are assigned to linear adsorption of CO on metallic cobalt particles. The bands at 2013 and 2033 cm<sup>-1</sup> sharply increase by heating the sample after performing syngas adsorption for over 1 h, up to 100 °C in the high-pressure syngas flow. However, the intensities of the bands begin to reduce once the temperature remained constant. The increase of the bands during the heating may be attributed to recombination of the dissociated CO on the catalyst. High ability of the sample for CO dissociation indicates that fine metallic cobalt particles have been formed on the surface. Syngas adsorption on the sample after use for FT synthesis gives rise to two strong bands at 1999 and 2021 cm<sup>-1</sup>, and several weak bands at 2150, 2025, 1897 and 1822 cm<sup>-1</sup>. These bands do not increase while heating the sample to 100 °C in the high-pressure syngas flow, indicating low ability of the sample for CO dissociation; so large particles have been formed on the surface. The bands at 1999, 2021 and 1897 cm<sup>-1</sup> are assigned to CO adsorption on cobalt carbides; the bands at 2025 and 1822 cm<sup>-1</sup> may be associated with sintered metallic cobalt species and the band at 2150 cm<sup>-1</sup> due to Co<sup>2+</sup> species. The features of the high-pressure syngas adsorption indicate that, during FT synthesis, fine metallic cobalt particles on the surface are gradually transformed to a mixture of cobalt carbides, sintered metallic cobalt and small amount of cobalt oxides. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* FTIR; Syngas adsorption; Cobalt catalyst; FT synthesis; Microstructure

## 1. Introduction

Iron and cobalt-based catalysts are FT synthesis catalysts most commonly used. The morphological changes of the catalysts have been well studied for the purpose of understanding the catalytic property-structure relationship. It is now widely accepted that the composition of iron-based catalysts undergoes significant changes during the reactions, and that the formation of iron carbides always occurs

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to constitute the active sites for FT synthesis [1–4]. On the other hand, cobalt has a lesser tendency to produce carbides than Fe. The active components on cobalt catalysts are usually considered to remain in metallic states during FT synthesis [5–8].

Recently, however, Ducreux et al. [9] observed the formation of cobalt carbides on a supported cobalt catalyst during FT synthesis by in situ XRD, which was also related with the deactivation process of the sample. These observations have been supported by Tihay et al. [10], who reported that when an Fe–Co-based catalyst is used for FT synthesis, metallic Co particles on the surface are partly transformed to carbides, as revealed by high-resolution transmission electron microscopy (HRTEM) observations.

Cobalt species are usually observed to exist as the metallic phase during FT synthesis; those observations may suggest small sizes and low concentration of the cobalt carbide particles formed during the reaction. It was also found [9,10] that those cobalt carbides are unstable, which were decomposed to metallic cobalt and polymeric carbon easily, so that they have rarely been observed by ex situ techniques. Therefore, it may be favorable to identify cobalt carbides by using some surface-sensitive experimental techniques and by in situ investigations of the catalysts after performing FT synthesis.

We have recently investigated the high-pressure syngas adsorption on reduced and used iron catalysts by in situ diffuse reflectance FTIR [11]. The adsorption of CO on metallic iron particles and that on iron carbides can be clearly distinguished. Syngas adsorption on the cobalt species may be comparable to that on the iron species. Although the adsorption properties of oxidized and freshly reduced cobalt-based catalysts have been widely investigated [12–19], regarding to the cobalt catalyst used for high-pressure FT synthesis; however, nearly no infrared data are available. In order to elucidate the morphological changes during high-pressure FT synthesis, including whether or not cobalt carbides are formed, we characterized in the present work the processes of high-pressure syngas adsorption on freshly reduced cobalt catalyst and on that used for FT synthesis from syngas at different temperatures. In situ diffuse reflectance FTIR spectroscopy is applied to investigations of the syngas adsorption. The characterizations after catalytic test give information about the transfor-

mation of fine metallic cobalt phase into a mixture of cobalt carbides, sintered metallic particles and small amount of cobalt oxides.

## 2. Experimental

The precipitated cobalt oxide sample used in this work was prepared in the usual batch-wise manner by adding ammonia solution into a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The obtained precipitates were washed with deionized water, followed by drying at  $120^\circ\text{C}$  for 12 h and calcination in air at  $350^\circ\text{C}$  for 4 h.

The diffuse reflectance FTIR spectra were recorded with a resolution of  $4\text{ cm}^{-1}$  and accumulation of 20 on a Bio-Rad FTS 6000 FTIR spectrometer supplied with a MCT detector and a diffuse reflectance attachment. The infrared cell with ZnSe windows (Spectra-Tech Inc.) can be performed at high pressures and high temperatures. One set of stainless steel gas lines was connected to the cell, which allows in situ reduction and FT synthesis followed by high-pressure syngas adsorption.

For performing FTIR measurements, the oxidized samples were in situ reduced at  $300^\circ\text{C}$  and atmospheric pressure in a flow of ultrahigh purity ( $>99.999\%$ )  $\text{H}_2$  used as supplied. In situ high-pressure FT synthesis on the reduced sample was performed in a syngas flow ( $\text{H}_2/\text{CO} = 2.0$ ) at 1.2 MPa, 200 and  $240^\circ\text{C}$ , respectively. High-pressure syngas adsorption on the reduced and used samples was performed in the syngas flow at 1.2 MPa and room temperature. The syngas was also an ultrahigh purity one ( $>99.999\%$ ), which was used as supplied. He ( $>99.999\%$ ) used for flushing and thermal desorption of the adsorbed species was further purified by passing it through a deoxy trap. The gas flows were maintained at  $60\text{ ml min}^{-1}$  by mass flow control meters. Approximately 25 mg of powder sample was used for each experiment.

Powder XRD patterns of the catalyst samples were obtained on a Miniflex diffractometer (Rigaku) using  $\text{Cu K}\alpha$  radiation with a Ni filter. Cobalt phases were detected by comparing diffraction patterns with those in the standard powder XRD file compiled by the Joint Committee on Powder Diffraction Standards published by the International Center for Diffraction Data. The reduced and used samples were passivated

in a stream of 1% O<sub>2</sub>/He at room temperature before being transferred from the reactor for XRD measurements.

### 3. Results and discussion

#### 3.1. High-pressure syngas adsorption on freshly reduced cobalt catalyst samples

Freshly in situ H<sub>2</sub>-reduced cobalt sample was subjected to the adsorption experiment in a syngas flow (H<sub>2</sub>/CO = 2, 60 ml min<sup>-1</sup>) at 1.2 MPa and room temperature. Fig. 1A shows the spectra recorded with time after raising pressure to 1.2 MPa, from which only very weak bands can be observed until syngas adsorption for 15 h. The spectrum attached in the Fig. 1A is the amplified one of Fig. 1A(d), referencing to the spectrum recorded at the initial 15 s of the syngas adsorption. From which two bands at 2013 and 2033 cm<sup>-1</sup> can be clearly observed. According to the literature [12,16,18,19], the bands in the region of 2050–1980 cm<sup>-1</sup> are usually associated with the stretching modes of linear carbonyl on zero-valent Co. Therefore, the bands at 2013 and 2033 cm<sup>-1</sup> can be assigned to linearly adsorbed CO on tops of metallic cobalt particles. Since the adsorption is performed at the high pressure of 1.2 MPa, any bands due to CO adsorption on Co<sup>δ+</sup> (0 < δ ≤ 2), which should appear in the region of 2050–2180 cm<sup>-1</sup> [12,15,17,20], would be hidden in the very strong bands of gaseous CO and therefore difficult to detect.

The adsorption experiment was reproduced and after syngas adsorption was performed for 1 h, the sample was quickly heated up to 100 °C in the high-pressure syngas flow. The spectra recorded after the temperature reached 100 °C are shown in Fig. 1B. By increasing the temperature up to 100 °C, the bands at 2013 and 2033 cm<sup>-1</sup> become very stronger. The spectrum attached on Fig. 1B is the amplified one of Fig. 1B(a), referencing to the same spectrum as used for the amplified spectrum attached in Fig. 1A. It is seen that the bands become about 10 times as strong as those on the amplified spectrum shown in Fig. 1A. The spectra in Fig. 1B also indicate that, with remaining temperature at 100 °C, however, the intensities of the bands at 2013 and 2033 cm<sup>-1</sup> gradually decrease in the syngas flow. By a careful inspection, it

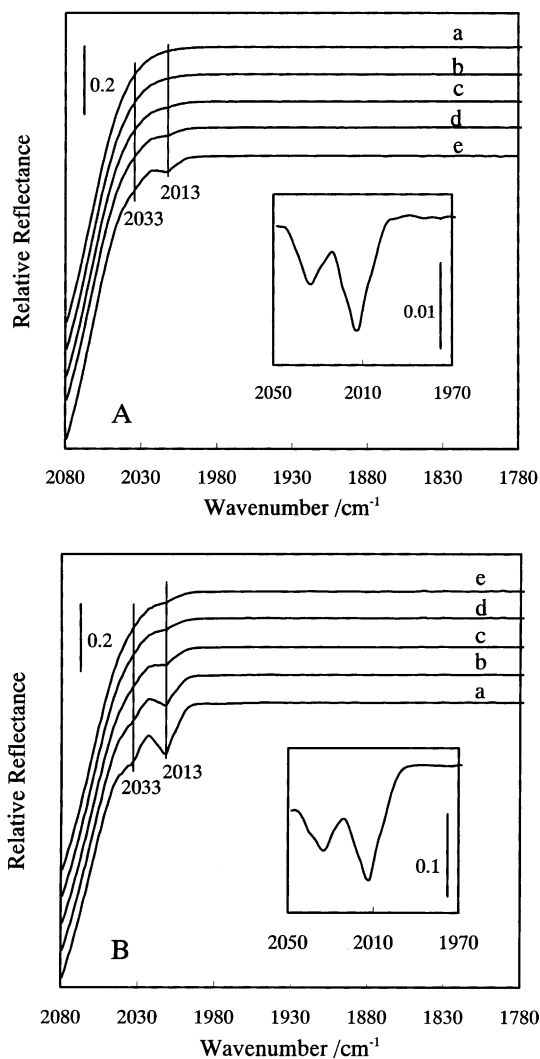


Fig. 1. Infrared spectra recorded from syngas adsorption on H<sub>2</sub>-reduced Co catalyst at 1.2 MPa and room temperature for 1 min (a), 20 min (b), 1 h (c), 3 h (d) and 15 h (e) (A); and those recorded after heating the reduced Co sample, which previously adsorbed syngas at 1.2 MPa and room temperature for 1 h, in the high-pressure syngas flow up to 100 °C (a), and then remaining at 100 °C for 1 min (b), 5 min (c), 1 h (d) and 3 h (e) (B).

is found that raising temperature in the range of about 50–130 °C will lead to obvious increase in intensities of the bands at 2013 and 2033 cm<sup>-1</sup>; whereas the intensities of the bands become reduced once the temperature is remained constant. These results suggest that the tremendous increases of the bands during

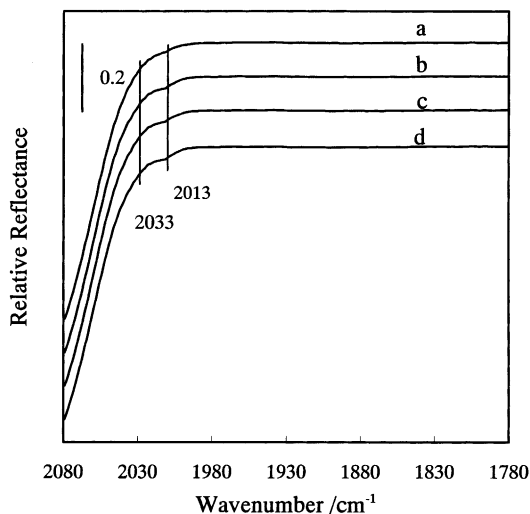


Fig. 2. Infrared spectra recorded from syngas adsorption on H<sub>2</sub>-reduced Co catalyst 1.2 MPa and 100 °C for 1 min (a), 20 min (b), 1 h (c) and 3 h (d).

the raising temperature should not be due to further adsorption of gaseous CO molecules on the catalyst surface.

To further elucidate the cause for the significant increase in intensities of the bands at 2013 and 2033 cm<sup>-1</sup> by raising temperature in the high-pressure syngas flow, more investigations have been performed. It is found that, as displayed in Fig. 2, while the syngas adsorption is performed at 1.2 MPa and 100 °C, only two weak bands are evolved at 2013 and 2033 cm<sup>-1</sup> after syngas adsorption for 3 h. The intensities of the bands are even lower than those of the bands in Fig. 1A.

As shown in Fig. 3, it is also found that heating the sample up to 100 °C in the high-pressure syngas flow, after performing syngas adsorption at room temperature for 20 min, produces a small increase of the bands at 2013 and 2033 cm<sup>-1</sup>. On the other hand, while the sample is heated after syngas adsorption at room temperature for 15 h, a tremendous increase in intensities of the bands at 2013 and 2033 cm<sup>-1</sup> is observed. These results clearly indicate that the increases of the bands at 2013 and 2033 cm<sup>-1</sup> during raising temperature have close correlation with the previous high-pressure syngas adsorption at room temperature.

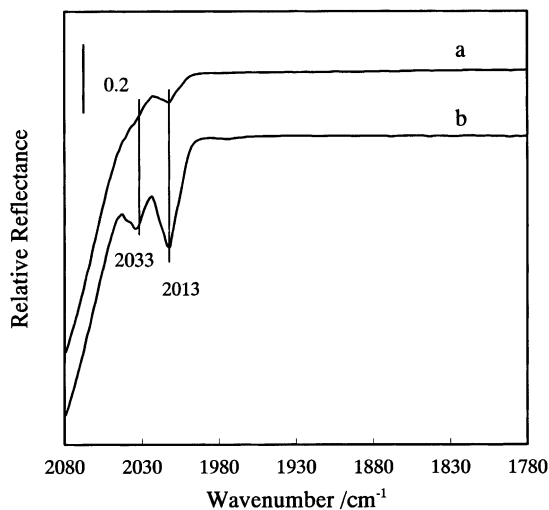


Fig. 3. Infrared spectra recorded after heating the H<sub>2</sub>-reduced Co sample up to 100 °C in the high-pressure syngas flow; the sample previously adsorbed syngas at 1.2 MPa and room temperature for 20 min (a) or 15 h (b).

The above results may be explained as that, during the syngas adsorption at room temperature, large amounts of CO molecules are dissociatively adsorbed on the reduced cobalt sample, which can not be detected by FTIR; with raising temperature, the surface carbon and oxygen atoms from dissociated CO recombine to form CO molecules, which are thereafter molecularly adsorbed on the surface and can be detected by FTIR. When the syngas adsorption is performed at room temperature for longer times, more CO molecules become adsorbed on the catalyst surface; therefore, larger increases in intensities of the bands at 2013 and 2033 cm<sup>-1</sup> are observed by raising temperature up to 100 °C.

The above speculation is confirmed by flashing measurement in a helium flow as well. After the reduced cobalt sample was subjected to the high-pressure syngas adsorption at room temperature for 1 h, pressure was reduced to atmospheric pressure and then syngas was replaced by helium. The bands of gaseous CO disappear by simple helium flushing for about 0.5 min. The flashing was carried out after helium flushing for 3 min; at this moment no gaseous CO exists in the system. The spectra presented in Fig. 4 are those recorded before and after flashing the sample in the helium flow. The spectra shown are

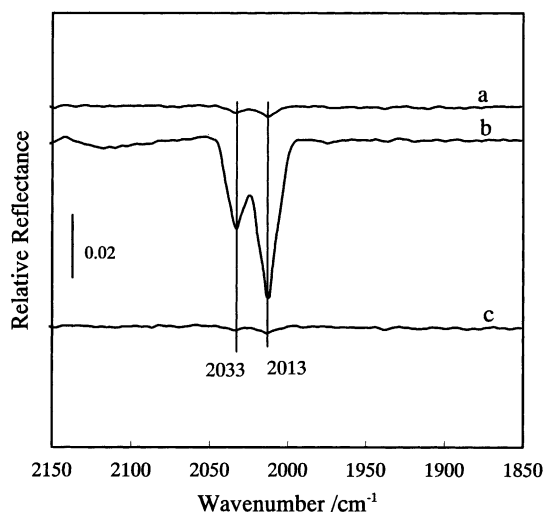


Fig. 4. Infrared spectra recorded from syngas adsorption on reduced Co catalyst at 1.2 MPa and room temperature for 1 h, followed by helium flushing at atmospheric pressure for 3 min (a), flashing the sample in the helium flow up to 100 °C (b) and remaining at 100 °C for 2 min (c).

referencing to the spectrum recorded at the end of hydrogen reduction before sample is exposed to syngas. From Fig. 4, it is observed that flashing to 100 °C in the helium flow results in an obvious increase in intensities of the bands at 2013 and 2033  $\text{cm}^{-1}$ . It is also observed that these bands thereafter quickly diminish and almost disappear in about 2 min.

Combining the results from quickly raising temperature in the high-pressure syngas flow and the results from He flashing, it can be concluded that, during desorption from the surface, parts of the dissociative CO molecules may go through the molecularly adsorption states, in this step increasing in the C–O bond strength and, therefore, being detected by FTIR with the same frequencies as the molecularly adsorbed CO molecules [21]. The recombined CO molecules are slowly desorbed in the high-pressure syngas flow. Upon helium flashing at atmospheric pressure the desorption becomes very fast. The recombination of dissociated CO has rarely been observed in literature, which may be due to the fact that CO adsorption on cobalt catalysts are usually performed at low pressures, such as <100 Torr, and therefore, desorption of the recombined CO occurs very faster.

It has been reported from X-ray photoelectron spectroscopy analyses [22–24] that, on crystalline iron surface, CO adsorbs molecularly at low temperatures such as –150 °C. The adsorbed CO molecules desorb sequentially at elevated temperatures and dissociate on the sample at above 100 °C. The dissociated carbon and oxygen atoms will recombine to CO molecules and desorb from the surface at above 500 °C. On this work, the temperatures for CO dissociation and for the dissociated carbon and oxygen atoms to recombine to CO molecules are both greatly reduced in comparison with the results for crystalline iron. Therefore, the catalyst samples have relatively higher capability for CO dissociation; which indicate that those metallic cobalt particles formed on the surfaces are fine ones.

On the spectra shown in Fig. 4, which were recorded after syngas was adsorbed for 1 h and then high pressure syngas was replaced by a helium flow at atmospheric pressure, no bands due to CO adsorption on  $\text{Co}^{2+}$  and  $\text{Co}^{1+}$  species are observed, therefore, most of the cobalt species on the surface have been converted to metallic phase by the hydrogen reduction. This result is in agreement with the data from X-ray photograph spectroscopy [25]. Jiang et al. [18] reported that while the cobalt sample is reduced in hydrogen at 300 °C and 1.2 MPa, syngas adsorption on the reduced sample gives bands at 2080 and 2050  $\text{cm}^{-1}$ , which are assigned to CO adsorption on  $\text{Co}^{\delta+}$  ( $0 < \delta < 2$ ) and oxygen-rich  $\text{Co}^0$  sites, respectively. Therefore, hydrogen reduction at low pressure, as used in this work, favors to complete reduction of the oxidized cobalt species.

### 3.2. High-pressure syngas adsorption on the reduced cobalt catalyst used for FT synthesis at 200 °C

To investigate the morphological changes of the reduced cobalt catalyst during FT synthesis, the sample used for in situ FT synthesis from syngas was also subjected to the experiment of high-pressure syngas adsorption. The FT synthesis was performed for 6 h at 1.2 MPa, 200 and 240 °C, respectively. After the reactions, the samples were cooled to room temperature in the high-pressure syngas flow.

While the FT synthesis was performed at 1.2 MPa and 200 °C, the sample was less active and, according to FTIR observations, water and hydrocarbons were

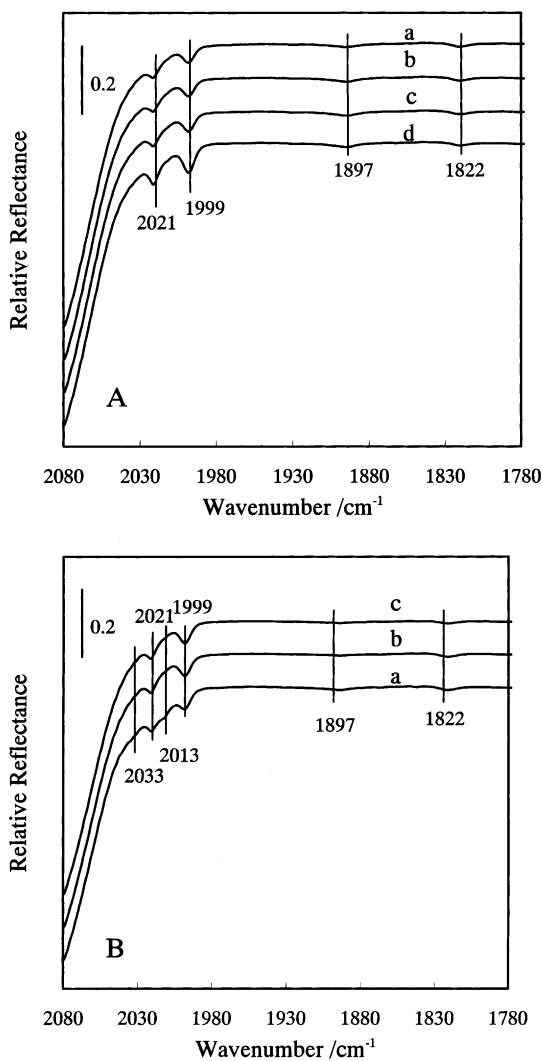


Fig. 5. Infrared spectra recorded from syngas adsorption on the reduced Co catalyst, after use for FT synthesis at 1.2 MPa and 200 °C for 6 h, at 1.2 MPa and room temperature for 1 min (a), 20 min (b), 1 h (c) and 3 h (d) (A); and those recorded after heating the used Co sample, which previously adsorbed syngas at 1.2 MPa and room temperature for 1 h, in the high-pressure syngas flow up to 100 °C (a), and remaining at 100 °C for 5 min (b) and 1 h (c) (B).

formed. The spectra recorded after cooling the sample to room temperature (<30 °C) are presented in Fig. 5A. It is observed that the syngas adsorption gives rise to two strong bands at 1999 and 2021  $\text{cm}^{-1}$  and two weak bands at 1897 and 1822  $\text{cm}^{-1}$ . The inten-

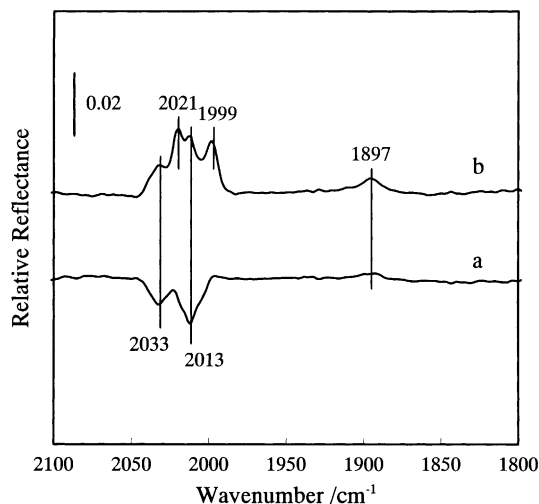


Fig. 6. Infrared spectra from the ratio of Fig. 5B(a) to Fig. 5A(c) (a), and the ratio of Fig. 5B(b) to Fig. 5B(a) (b).

sities of the bands slowly enhance with adsorption time.

The above experiment was reproduced and, after syngas adsorption for 1 h, the sample was quickly heated up to 100 °C in the high-pressure syngas flow. The spectra recorded after the temperature reached 100 °C are shown in Fig. 5B. Four bands at 1999, 2021, 2013, and 2033  $\text{cm}^{-1}$  are clearly observed. In comparison with the spectra recorded before raising temperature (Fig. 5A), two more bands at 2013 and 2033  $\text{cm}^{-1}$  appear. The ratio of Fig. 5B(a) to Fig. 5A(c) is presented in Fig. 6a, from which two minus bands at 2013 and 2033  $\text{cm}^{-1}$  can be clearly observed. However, the intensities of the bands become obviously reduced compared to those for the freshly reduced sample (attached of Fig. 1B). The spectrum shown in Fig. 6b is the ratio of Fig. 5B(b) to Fig. 5B(a), on which apparently four plus bands at 1999, 2021, 2013, and 2033  $\text{cm}^{-1}$  are observed. Therefore, adsorbed CO species are gradually desorbed from the surface at the elevated temperature. For correctly assigning the weak bands at 1897 and 1822  $\text{cm}^{-1}$ , it is useful to note that the adsorbed species responsible for the broadband at 1897  $\text{cm}^{-1}$  are also desorbed during heating and remaining the sample at 100 °C, whereas the adsorbed species responsible for the broadband at 1822  $\text{cm}^{-1}$  do not desorb from the surface.

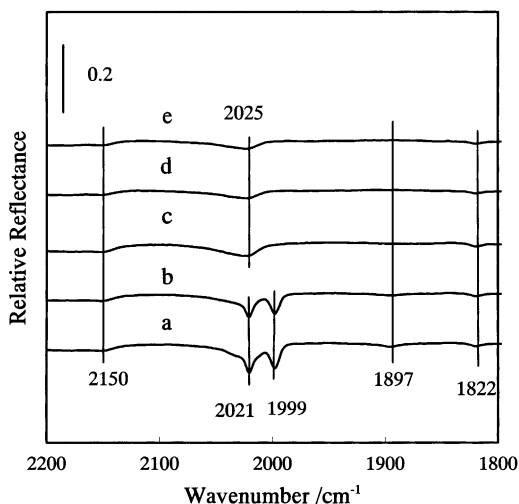


Fig. 7. Infrared spectra recorded after helium flushing of the Co catalyst, which was previously used for FT synthesis at 1.2 MPa and 200 °C for 6 h and syngas adsorption at 1.2 MPa and room temperature for 1 h, at atmospheric pressure for 3 min (a); and then heating the sample in the helium flow up to 100 °C (b), 150 °C (c); 200 °C (d) and 300 °C (e).

Helium flushing of the adsorbed species at atmospheric pressure followed by thermal desorption up to 300 °C was also performed after syngas adsorption for 1 h. A few spectra are shown in Fig. 7. Only a small decrease in intensities of the bands at 1999 and 2021  $\text{cm}^{-1}$  was observed after helium flushing for 3 min. With elimination of strong bands due to gaseous CO, a broad band at about 2150  $\text{cm}^{-1}$  is seen. The results from thermal desorption experiment indicate that nearly no increase is observed for the bands at 2013 and 2033  $\text{cm}^{-1}$  by raising temperature up to 100 °C; the bands at 1999, 2021 and 1897  $\text{cm}^{-1}$  begin to diminish at about 100 °C and disappear at about 150 °C. With elimination of the bands at 1999 and 2021  $\text{cm}^{-1}$ , a broad band at about 2025  $\text{cm}^{-1}$  can be observed. The bands at 2025 and 1822  $\text{cm}^{-1}$  do not disappear with raising temperature up to 300 °C.

Syngas adsorption on the used cobalt sample gives rise to a new set of bands, and the bands at 2013 and 2033  $\text{cm}^{-1}$  become very weaker compared with those for the freshly reduced sample. These results indicate that significant changes in microstructure have occurred during the reaction. Fine metallic cobalt particles formed by hydrogen reduction are

partially transformed during the FT synthesis; and the new-formed species exhibit significantly low ability for CO dissociation. According to the literature [12–14], the weak band at 2150  $\text{cm}^{-1}$  should be assigned to CO adsorption on  $\text{Co}^{2+}$  centers. These observations indicate that small amount of metallic cobalt species was oxidized, which may be due to the formation of water and  $\text{CO}_2$  on the surface during FT synthesis [26].

The bands in the region of 1900–1800  $\text{cm}^{-1}$  have been assigned to bridged CO on  $\text{Co}^0$  species [12,16]. As shown above, during the thermal desorption experiment in the helium flow, the broad bands at 2025 and 1822  $\text{cm}^{-1}$  do not disappear with raising temperature up to 300 °C, while the bands at 2021, 1999 and 1822  $\text{cm}^{-1}$  vanish with raising temperature up to 150 °C. Therefore, these bands may be assigned to two kinds of  $\text{Co}^0$  species, respectively. The surface species responsible for the bands at 2025 and 1822  $\text{cm}^{-1}$  exhibits high thermal stability and strong binding strength with the adsorbed CO. Therefore, it may be a new kind of sintered metallic cobalt phase formed during the reaction, which can connect with adsorbed CO to form stable sub carbonyl species. On the other hand, the strong doublet bands at 1999 and 2021  $\text{cm}^{-1}$  and the weak broad band at 1897  $\text{cm}^{-1}$  may be assigned to linear and bridging adsorption of CO on cobalt carbides, respectively.

The main reasons for assigning the bands at 1999, 2021 and 1897  $\text{cm}^{-1}$  to CO adsorption on cobalt carbides may be summarized below. (1) The formation of cobalt carbides during FT synthesis has been demonstrated by in situ XRD and HRTEM analyses [9,10]; it is probable that syngas adsorption on the used samples arise bands due to CO adsorption on cobalt carbides. (2) The bands in the region of 2040–1800  $\text{cm}^{-1}$  have been due to CO adsorption on  $\text{Co}^0$  species [12,16–19], cobalt carbides are  $\text{Co}^0$  species [10,27,28], so the bands of CO adsorption on cobalt carbides should appear in this region as well. (3) According to the literature [12,15–20,29], the features of CO adsorption on cobalt-based catalysts and those on iron-based catalysts are similar. For example, CO adsorption on  $\text{Fe}^{\delta+}$  or  $\text{Co}^{\delta+}$  ( $0 < \delta \leq 2$ ) gives bands in the region of 2200–2050  $\text{cm}^{-1}$ ; on  $\text{Fe}^0$  or  $\text{Co}^0$  species linear CO appears in 2050–1980  $\text{cm}^{-1}$  and bridged CO appears in 1900–1700  $\text{cm}^{-1}$ . It was revealed in our previous work [11] that on freshly  $\text{H}_2$ -reduced iron catalyst syngas

adsorption arises weak bands at 2013 and 2033  $\text{cm}^{-1}$ ; and that on the same sample used for high-pressure FT synthesis syngas adsorption gives two very strong bands at 1999 and 2021  $\text{cm}^{-1}$ , which are assigned to CO adsorption on iron carbides. So, in this work, the bands at 1999 and 2021  $\text{cm}^{-1}$  might be assigned to CO adsorption on cobalt carbides as well. (4) The another possible assignment of the surface species correlated with the bands at 1999, 2021 and 1897  $\text{cm}^{-1}$  may be some aggregated metallic cobalt phase transformed from the fine metallic cobalt particles. However, as described later in this paper, the surface species associated with the bands at 1999, 2021 and 1897  $\text{cm}^{-1}$  is unstable, which can be converted back to fine metallic cobalt species by helium treatment at 100 °C. Therefore, the assignment is denied because any aggregated metallic cobalt phase formed during the FT synthesis is more stable than those fine metallic particles on the freshly reduced sample.

### 3.3. High-pressure syngas adsorption on the reduced catalyst after use for high-pressure FT synthesis at 240 °C

While the freshly  $\text{H}_2$ -reduced sample was used for FT synthesis at 1.2 MPa and 240 °C, the sample was rather active. After reaction for 6 h, the sample was cooled to room temperature in the syngas flow to perform high-pressure syngas adsorption. The spectra recorded are displayed in Fig. 8.

As shown in Fig. 8, syngas adsorption on the used sample gives rise to two strong bands at 1999 and 2021  $\text{cm}^{-1}$ , and two weak bands at 1897 and 1822  $\text{cm}^{-1}$ . The spectra are similar to those from syngas adsorption on the sample after use for FT synthesis at 200 °C, but the intensities of the bands become significantly stronger.

The experiment was reproduced and after syngas adsorption for 1 h, the sample was quickly heated up to 100 °C in the high-pressure syngas flow. By this way, however, no bands are observed at 2013 and 2033  $\text{cm}^{-1}$  (the data are not shown). The data from thermal desorption experiment are shown in Fig. 9. The bands at 2013 and 2033  $\text{cm}^{-1}$  are not observed as well; and the bands at 1999 and 2021  $\text{cm}^{-1}$  remain unchanged by raising temperature to 100 °C. With further increasing temperature, the bands at 1999 and 2021  $\text{cm}^{-1}$  begin to diminish and vanish at about

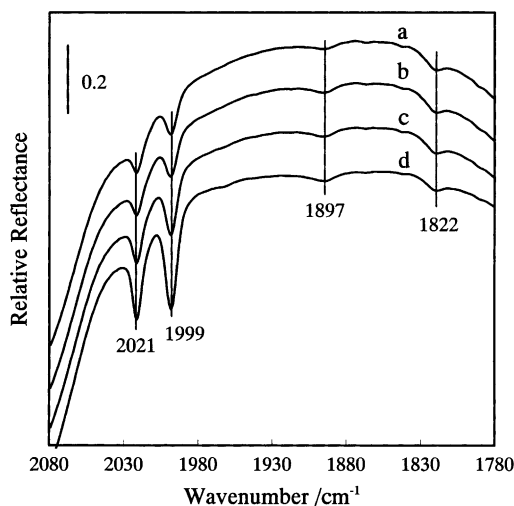


Fig. 8. Infrared spectra recorded from syngas adsorption on used Co catalyst at 1.2 MPa and room temperature for 1 min (a), 20 min (b), 1 h (c) and 3 h (d). The FT synthesis was performed at 1.2 MPa and 240 °C for 6 h.

200 °C; the band at 1897  $\text{cm}^{-1}$  disappears simultaneously. Therefore, the adsorbed CO molecules become more closely bound on the cobalt carbide particles in comparison with those on the sample after use

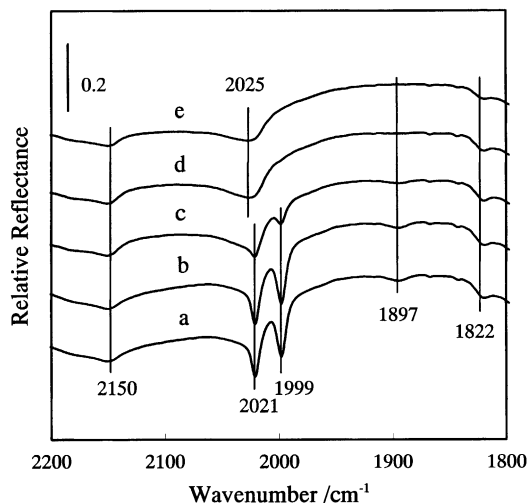


Fig. 9. Infrared spectra recorded from a helium flushing of the used Co catalyst, which was previously used for FT synthesis at 1.2 MPa and 300 °C for 6 h and syngas adsorption at 1.2 MPa and room temperature for 1 h, at atmospheric pressure for 3 min (a); and then heating the sample in the helium flow up to 100 °C (b), 150 °C (c), 200 °C (d) and 300 °C (e).



for FT synthesis at 200 °C. It is observed once again that the broad bands at 2150, 2025 and 1822  $\text{cm}^{-1}$  do not disappear until raising the temperature up to 300 °C.

Elimination of the bands at 2013 and 2033  $\text{cm}^{-1}$  reveals complete disappearance of the fine metallic cobalt particles from the surface. In the meantime, it is also observed that more sintered metallic cobalt species and cobalt carbides are formed. Therefore, almost all of the fine metallic cobalt particles on the surface have been transformed to sintered metallic cobalt species, cobalt carbides and small amount of cobalt oxide by performing FT synthesis at elevated temperature. The temperatures for adsorbed CO molecules to desorb from the surface of cobalt carbide particles become significantly higher, which may indicate large sizes of the particles.

Syngas adsorption on the cobalt samples used for FT synthesis reveals the formation of cobalt carbides on the surfaces. However, in comparison with the data of syngas adsorption on used iron samples [11], the bands due to CO adsorption on cobalt carbides are obviously weaker than those due to CO adsorption on iron carbides. In addition, during syngas adsorption on used iron samples, no bands at 2025 and 1822  $\text{cm}^{-1}$  were observed. These results demonstrate that cobalt species have a lesser tendency to form carbides than the iron species.

It was also observed that, after the cobalt sample utilized for the FT synthesis at 1.2 MPa, 240 °C for 6 h is treated in a helium flow at 100 °C, syngas adsorption on the treated sample gives rise to weaker bands at 1999 and 2021  $\text{cm}^{-1}$ , and the bands at 2013 and 2033  $\text{cm}^{-1}$  appear again (the data are not shown). This result indicates that the surface species correlated to the bands at 1999 and 2021  $\text{cm}^{-1}$  are unstable, which might be decomposed to metallic cobalt and polymeric carbon easily. The observations that cobalt carbides are unstable are in agreement with the results from the literature [9,10].

#### 3.4. XRD patterns of the oxidized, reduced and used cobalt samples

Bulk cobalt phases of the samples were determined by XRD measurements. The results are shown in Fig. 10. The pattern of the oxidized cobalt sample has peaks at 31.3, 36.9, 44.7, 55.9, 59.3 and 65.4°,

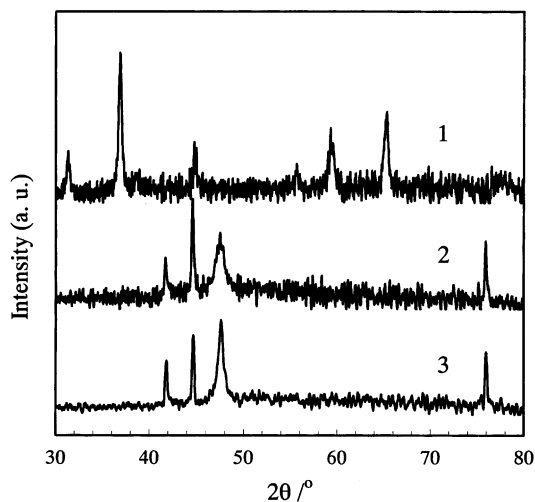


Fig. 10. XRD patterns of the cobalt catalyst samples: (1) oxidized, (2) after  $\text{H}_2$  reduction at 300 °C for 6 h, (3) after use for FT synthesis at 250 °C, 1.0 MPa for 6 h.

all of which are characteristics of  $\text{Co}_3\text{O}_4$  phase. The pattern of the catalyst sample reduced with hydrogen at 300 °C for 6 h has dominant peaks at 41.7, 44.6, 47.5 and 75.9°, which correspond to  $\text{Co}^0$  phase. The pattern of the reduced cobalt catalyst after use for FT synthesis at 1.0 MPa, 250 °C for 6 h shows same peaks as that of the freshly reduced sample.

XRD pattern of the freshly reduced sample reveals the formation of metallic cobalt species, which is in agreement with the results from high-pressure syngas adsorption. Syngas adsorption on the cobalt samples after use for FT synthesis at 1.2 MPa and 240 °C for 6 h indicates that noticeable amounts of cobalt carbides are formed; however, XRD pattern of the sample after use for FT synthesis at 1.2 MPa and 250 °C for 6 h shows that only metallic cobalt is present. These results indicate that only those cobalt species on the surface are transformed during the reaction. The observations that only metallic cobalt species are detected by XRD analysis are consistent with those in the literature [6–8]. Although bulk cobalt phase remains as metallic cobalt during the FT synthesis, the particles on the surface are gradually changed; the formation of cobalt carbides may have great effects on FT synthesis, which should be investigated in the future work.

#### 4. Summary

High-pressure syngas adsorption on freshly reduced cobalt sample gives rise to two weak bands at 2013 and 2033  $\text{cm}^{-1}$ , which are assigned to linear adsorption of CO on metallic cobalt particles. The bands at 2013 and 2033  $\text{cm}^{-1}$  sharply increase by heating the sample up to 100 °C in the high-pressure syngas flow after syngas adsorption for above 1 h. The increase of the bands during the heating may be attributed to recombination of the dissociated CO on the catalyst. High ability of the sample for CO dissociation indicates that fine metallic cobalt particles have been formed on the surface. The results of high-pressure syngas adsorption on the reduced sample after use for high-pressure FT synthesis from syngas indicate that fine metallic cobalt particles on the surface are gradually transformed to a mixture of cobalt carbides, sintered metallic cobalt and small amount of cobalt oxides. All the bands due to CO adsorption on the used sample do not increase by heating the sample to 100 °C in the high-pressure syngas flow, indicating low ability of the sample for CO dissociation. Therefore, the particles transformed from fine metallic particles during the FT synthesis are large ones.

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