# On the use of infrared spectroscopy in the study of carbon dioxide decomposition on copper containing methanol synthesis catalysts

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Infrared spectroscopy has been used to study the possible adsorption and decomposition of $CO_2$ on a copper containing methanol catalyst. It is demonstrated that the spectra from in situ infrared studies of the methanol synthesis can be complicated by many $CO_2$ combination bands in the 2200–1900 $cm^{-1}$ region. A comparison with previously published DRIFTS spectra from studies of copper catalysts exposed to $CO_2$ shows that nearly all of the bands assigned as CO adsorbed on copper originate from gas phase $CO_2$.

**Keywords:** infrared spectroscopy, DRIFTS, methanol synthesis, supported copper catalyst, CO, $CO_2$, adsorption

## 1. Introduction

Methanol is synthesised industrially from a CO, $CO_2$ and $H_2$ gas mixture at pressures of 5–10 MPa and temperatures of 490–510 K over catalysts consisting of copper, zinc oxide and alumina. The reaction mechanism for the methanol synthesis, the active sites and states of copper and the effect of ZnO are still subject to considerable controversy, even though the process has been extensively investigated for several decades [1–9, and references therein].

The majority of recent in situ work related to methanol synthesis seem to support the view that $CO_2$ is the main precursor to methanol in the commercial process [3–5,10–12]. However, the possible interconversion of $CO_2$ and CO through the so-called water–gas shift reaction [13] has led to much argument on whether $CO_2$ or CO is the main precursor [1,12,14]. The adsorption and possible decomposition of $CO_2$ on copper surfaces has therefore been studied by several groups [7,8,15–25, and references therein]. According to Elliott et al. [8] there is a general agreement that $CO_2$ dissociates on stepped copper surfaces as opposed to planar surfaces where the situation seems less clear. Upon adsorption the $CO_2$ is claimed to decompose to CO and oxygen atoms, and infrared spectroscopy has been used to detect this decomposition by observing bands of adsorbed CO.

Recently, the $CO_2$ adsorption on several model catalysts consisting of 5 to 20 wt% copper supported on silica has been investigated by standard infrared transmission spectroscopy [22–25]. The experimental conditions in the different studies vary, but a major band was observed between 2130 and 2105 $cm^{-1}$ after $CO_2$ exposure and assigned to CO adsorbed on either partially oxidised copper or on high index copper planes. In addition, a weak band at 2077 $cm^{-1}$ was reported in one of the studies [25] and assigned to CO adsorbed on a low index plane of copper.

Contrary to the above studies of model systems, two diffuse reflectance infrared studies (DRIFTS) of typical commercial catalysts, $Cu/ZnO/Al_2O_3$, report several bands in the spectral region between 2200 and 1900 $cm^{-1}$ upon exposure to $CO_2$ [7,8]. Elliott et al. [8] observed bands centred at 2115, 2092 and 2077 $cm^{-1}$ immediately after the introduction of 0.1 MPa $CO_2$ at room temperature, and assigned the bands to CO adsorbed on Cu(211), Cu(110) and Cu(111) respectively. The band at 2092 $cm^{-1}$ disappeared with time, while the intensity of the band at 2115 $cm^{-1}$ increased slightly. The authors explained this observation by an activated reconstruction of the surface under oxidising conditions. A broader band at 2060 $cm^{-1}$ was not assigned. Bailey et al. [7] observed similar bands at 2132, 2105, 2092 and 2076 $cm^{-1}$ when their catalyst was exposed to a gas mixture of $H_2$ and $CO_2$ at 3 MPa and 493 K. The bands were assigned to CO adsorbed on $Cu^+$, Cu(311), Cu(755) and Cu(111), respectively. Their intensities increased with the partial pressure of $CO_2$, but did not change with temperature. As opposed to Elliott et al. [8], the authors therefore concluded that no adsorbate induced surface restructuring occurred. Additional bands at 2060 and 1932 $cm^{-1}$ were also present in their spectra, but were not assigned.

Both DRIFTS studies relied the assignment of the observed bands on the extensive work by Pritchard and coworkers [26,27, and references therein]. However, several of the bands observed were remarkably narrow compared to bands previously reported in most studies of CO adsorption on heterogenous surfaces.

Because of the incomplete spectral assignments and the discrepancies between the recent in situ infrared studies of copper-based catalysts exposed to $CO_2$

[7,8,22–25], we decided to undertake a detailed investigation of similar systems. We are in this study able to show that all, but one, of the bands previously reported in the spectral region from 2200 to 1900 $cm^{-1}$ [7,8] are due to gas phase $CO_2$ and not to CO adsorbed on the copper component of the catalyst.

## 2. Experimental

All spectra were recorded with a Perkin Elmer System 2000 FTIR spectrometer. The spectra of pure gas phase $CO_2$ were collected using a room temperature deuterated-triglycine-sulfate (DTGS) detector and a standard 10 cm transmission gas cell equipped with KBr windows. The spectral range from 6000 to 400 $cm^{-1}$ was investigated averaging 32 scans at a nominal resolution of 1 or 4 $cm^{-1}$.

The DRIFTS experiments were carried out using a diffuse reflectance attachment and a high vacuum reaction chamber (HVC-DR2), both supplied by Harrick Scientific. The chamber is connected to a standard gas handling system and can be operated at pressure up to 0.1 MPa and at temperatures from ambient to 873 K. The optical pathlength in the chamber is approximately 3 cm. A spectral range from 6000 to 600 $cm^{-1}$ was routinely investigated by averaging 64 scans at a nominal resolution of 8 $cm^{-1}$ with the use of an mercury–cadmium–telluride (MCT) detector. All DRIFTS spectra reported in this study are ratioed against that of pure KBr.

A standard methanol synthesis catalyst, $Cu/ZnO/Al_2O_3$, supplied by Haldor Topsøe A/S (PRL 435-2), was diluted with 90 wt% KBr before use. The samples were reduced in situ overnight at 493 K in a flow of 10% $H_2$ in $N_2$ (0.1 MPa, 30 $cm^3/min$) and subsequently cooled in an $N_2$-flow. After cooling to room temperature the $N_2$-flow was switched to a $CO_2$-flow (0.1 MPa, 30 $cm^3/min$) and the spectra collected. An identical procedure was followed in the reference experiments with pure KBr.

The gases supplied by AGA A/S, were of 99.9995% ($N_2$ and $H_2$) and 99.998% ($CO_2$) purity, and were used without further purification.

## 3. Results and discussion

The infrared spectrum obtained after exposing the reduced catalyst to 0.1 MPa $CO_2$ at room temperature is shown in figure 1a. The bands at 2077 and 2060 $cm^{-1}$ appeared shortly after switching from an $N_2$- to a pure $CO_2$-flow, and their intensity increased with time until all $N_2$ had been flushed out of the system. The spectrum shown was collected after 30 min, when a steady situation was obtained. The bands observed at 2077 and 2060 $cm^{-1}$ are in accordance with the recent FTIR results of Bailey et al. [7] and Elliott et al. [8] who assigned the 2077 $cm^{-1}$ band to CO adsorbed on a Cu(111) plane relying on studies of CO adsorption on copper single crystal planes [26]. The band at 2060 $cm^{-1}$ have not been reported in earlier studies of CO adsorption on copper systems, except for the two recent DRIFTS studies where the band was left unassigned [7,8].

As in the two previous DRIFTS studies, our $Cu/ZnO/Al_2O_3$ catalyst was diluted with KBr before use. The infrared beam is strongly absorbed by most oxide containing catalysts, and to increase the signal-to-noise ratio in DRIFTS studies and minimise unwanted reflec-

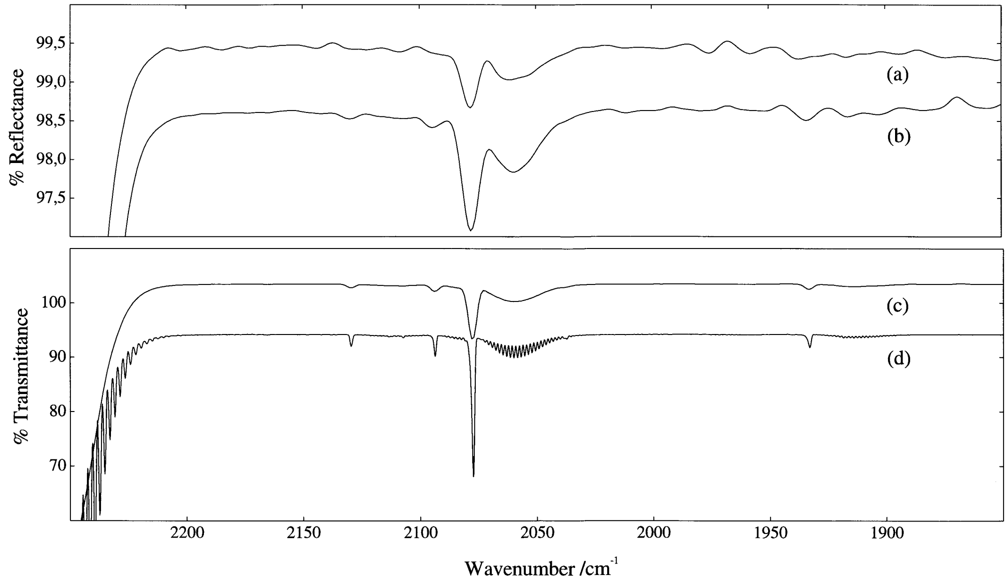

Figure 1. The infrared spectra of (a) 10 wt% $Cu/ZnO/Al_2O_3$ in KBr and (b) pure KBr exposed to 0.1 MPa $CO_2$-flow (30 $cm^3/min$) at 308 K studied by DRIFTS, and transmission spectra of 0.1 MPa of $CO_2$ at 298 K employing a resolution of (c) 4 $cm^{-1}$ and (d) 1 $cm^{-1}$.

tions effects [28, and references therein], it is common to dilute such samples with a non-absorbing matrix like KBr. KBr is one of the most commonly used materials in infrared spectroscopy, and it seems improbable that $CO_2$ should decompose to CO and oxygen atoms on a KBr sample, at least under the conditions employed in this study. Bailey et al. [7] claimed that DRIFTS experiments with KBr alone showed that none of the bands observed with the diluted catalyst derived from KBr. To establish if this assertion is true or if the 2060 $cm^{-1}$ band could be linked to KBr, we also used pure KBr instead of the diluted copper catalyst. The result is shown in figure 1b. Shortly after switching to a $CO_2$-flow, several bands were observed in the spectral region from 2200 to 1900 $cm^{-1}$. The bands at 2077 and 2060 $cm^{-1}$ are clearly seen, as in the experiment with the reduced copper catalyst, as are additional weaker bands around 2130, 2095 and 1930 $cm^{-1}$. In the light of these observations it is therefore unlikely that the bands presented in figure 1a should be assigned to CO adsorbed on different crystal planes of copper. The bands can neither be due to CO adsorbed on $K^+$ or $Br^-$ ions, because CO adsorbed on such species is unlikely to absorb at the wavenumbers observed in our study [29]. The only plausible explanation left is that the observed bands originate from $CO_2$ in the gas phase.

A standard transmission spectrum of gas phase $CO_2$ was therefore collected. The spectrum in figure 1c shows the well documented bands at 2129, 2107, 2077, 2060 and 1933 $cm^{-1}$. The bands are better defined due to a higher signal-to-noise ratio than in the DRIFTS spectra, but the similarities between the spectra in figures 1a–1c are obvious. Molecules in the gas phase can rotate freely, and by increasing the resolution from 4 to 1 $cm^{-1}$, the expected rotational fine structure becomes evident, as shown in figure 1d. The broad band at 2060 $cm^{-1}$ observed in all our spectra and in the earlier DRIFTS studies [7,8], is obviously due to unresolved rotational fine structure. With a resolution of 1 $cm^{-1}$, a weaker feature at 2037 $cm^{-1}$ becomes visible as well.

$CO_2$ is one of the most thoroughly studied molecules by infrared spectroscopy. As a triatomic, linear molecule it has three fundamental vibrations of which two are infrared active; the doubly degenerate bending mode at 667 $cm^{-1}$, and the asymmetric stretching mode at 2349 $cm^{-1}$. The totally symmetric stretching mode at 1388 $cm^{-1}$ is infrared inactive. In the full scale $CO_2$ gas phase spectrum shown in figure 2, a few bands are due to the 1% natural abundance of $^{13}CO_2$, but most of the additional bands arise from the combination bands and overtones of $^{12}CO_2$.

The assignment of the observed bands in the spectral region from 2200 to 1900 $cm^{-1}$ is given in table 1 and is in accordance with listings in the HITRAN92 database [30]. Each energy level is designated by the notation ($\nu_1$, $\nu_2$, $l$, $\nu_3$, $r$) in which ($\nu$) indicates a vibrational quantum number, ($l$) the vibrational angular momentum and ($r$) the sequence number of a Fermi resonance group. This notation was introduced by McClathey et al. [31] and adopted for the HITRAN database.

The integrated intensities of selected bands were calculated using the HITRAN92 database [30], and the intensity ratio between the $\nu_3$ fundamental and the bands in the region 2150–2000 $cm^{-1}$ is approximately 16000 : 1. The gas phase concentration of $CO_2$ must in other words be substantial before bands in the above mentioned region are observed, and it probably explains why these combination bands have not been considered before. However, the combination bands are not observed in all the recent infrared studies, despite the much higher applied $CO_2$ pressures [7,8,22–25]. This can be understood by considering the optical vapour phase pathlength employed in the different studies. According to the well known Beer–Lambert law ($A = \alpha c l$), the absorption of infrared radiation is proportional not only to the gas concentration (or partial pressure), but also to

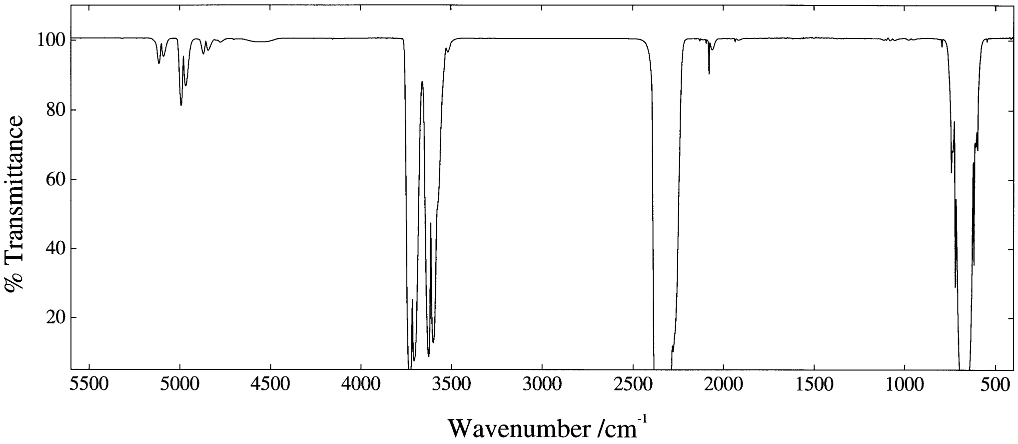

Figure 2. Infrared survey spectrum of gas phase $CO_2$ (0.1 MPa, 298 K, 10 cm pathlength).

Table 1
The assignment of $CO_2$ gas phase bands in the spectral region 2200–1900 $cm^{-1}$

| Observed frequency ($cm^{-1}$) | Reference [a] bandcenter $\nu_0$ ($cm^{-1}$) | Transition [b] upper ← lower vibrational state | | Isotope |
|---|---|---|---|---|
| 2129.5 | 2129.756 | 20001–01101 | | $^{12}C^{16}O_2$ |
| 2107.3 | 2107.084 | 13301–02201 | | $^{12}C^{16}O_2$ |
| 2093.6 | 2093.345 | 12201–01101 | | $^{12}C^{16}O_2$ |
| 2077.3 | 2076.856 | 11101–00001 | Q-branch | $^{12}C^{16}O_2$ |
| ~ 2060 | – | 11101–00001 | P-branch[c] | $^{12}C^{16}O_2$ |
| 1933.0 | 1932.470 | 11102–00001 | Q-branch | $^{12}C^{16}O_2$ |
| ~ 1920 | – | 11102–00001 | P-branch | $^{12}C^{16}O_2$ |
| 2037.2 | 2037.093 | 11101–00001 | | $^{13}C^{16}O_2$ |

[a] See ref. [30].

[b] $(\nu_1, \nu_2, l, \nu_3, r)$, see ref. [31].

[c] Main contribution to rotational fine structure.

the optical pathlength. No information is given about the cell used by Millar and co-workers [22,23], but Burch et al. [24] report an extremely short gas phase pathlength of less than 1 mm in their high-pressure transmission infrared cell. Even the fundamental $CO_2$ asymmetric stretching mode at 2349 $cm^{-1}$ is not completely absorbing in their spectra, as it is in our study. The combination bands in the spectral region from 2200 to 1900 $cm^{-1}$ are therefore too weak to be observed. The transmission infrared cell used by Clarke and Bell [25] has a reported cell dead volume of 0.4 $cm^3$. The importance of the gas phase on the infrared spectra will expectedly be small in this study as well, but a weak band at 2077 $cm^{-1}$ is assigned to CO adsorbed on a low index copper plane. It seems more reasonable to assign this band to the (11101 ← 00001) transition of $CO_2(g)$, because this band does apparently not change with the temperature of the catalyst surface in contrast to the other bands that were assigned to CO adsorbed on different copper species. From the spectrum in figure 1d it is clear that the 2077 $cm^{-1}$ band is the most intense of the combination bands in that region, so it is expected to be the first additional band to appear as the amount of $CO_2(g)$ increases. Contrary to the above mentioned infrared transmission cells, the reaction chambers used in the DRIFTS studies have longer pathlenghts of approximately 1 [7] and 3 cm [8], respectively. The chamber used by Elliott et al. [8] is identical to the one used in our study.

All bands reported by Bailey et al. [7] in the 2200–1900 $cm^{-1}$ region can be assigned to gas phase $CO_2$. Their experiments were conducted in a combined $CO_2$ and $H_2$ atmosphere at elevated temperatures. At 473 K gas phase CO was observed, but it apparently did not adsorb. This is not surprising because CO is known to bind weakly to copper [27, and references therein], and Elliott et al. [8] have reported that the CO produced during decomposition of $CO_2$ on a $Cu/ZnO/Al_2O_3$ sample, desorbed above 400 K.

The only band reported in the 2200–1900 $cm^{-1}$ region in the previous DRIFTS studies [7,8] which cannot be assigned to gas phase $CO_2$ is the 2115 band observed by Elliott et al. [8] when a commercial catalyst was exposed to $CO_2$ at room temperature. When this is compared with the results of the other recent infrared studies [22–25] where no $CO_2$ combination bands are observed, it seems reasonable to assign this band to CO adsorbed on the copper component. The authors claim that the 2115 $cm^{-1}$ band correspond to CO adsorbed on a high index metallic copper surface, but according to Hollins [32], it is not possible to determine the various copper planes exposed on the catalyst based on $\nu_{CO}$ resulting from high coverage due to the existence of intensity transfer from low to high frequency bands. Hollins also claims that a small percentage of CO molecules adsorbed on sites influenced by oxygen will give rise to abnormally strong bands as a result of dipolar coupling, and the copper surface in Elliotts experiment [8] is probably partially oxidised by $CO_2$ which is the only reactant present.

## 4. Conclusion

The in situ infrared studies of CO adsorption on the surface of catalysts can be complicated by the presence of gas phase $CO_2$, as several combination bands of gas phase $CO_2$ appear in the spectral region from 2200 to 1900 $cm^{-1}$.

In light of the present work the interpretations of the spectra of Bailey et al. [7] and of Elliott et al. [8] appear questionable. We have been able to assign all, but one, of their bands observed in the spectral region from 2200 to 1900 $cm^{-1}$ to gas phase $CO_2$ instead of CO adsorbed on different crystal planes of copper on the commercial catalyst. It is therefore obvious that the discussion about the morphology of the copper surface and possible changes therein during catalytic reaction, is still in need of conclusive evidence.

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