

## Oxidation of CO by O<sub>2</sub> over ZnO Studied by FTIR Spectroscopy

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**Summary:** The adsorption of CO at room temperature on finely divided ZnO surfaces, studied by FTIR, shows reversible bands (2250-2050 cm<sup>-1</sup>) and irreversible absorption bands (1800-600 cm<sup>-1</sup>). The irreversible absorption bands (1800-600 cm<sup>-1</sup>) are assigned to various species such as *bi*- and monodentate carbonates. The band position of the reversibly adsorbed species depends on the extent of the surface carbonates, formed by the oxidation of CO. The order of introduction of CO and O<sub>2</sub> and whether the ZnO surface is oxidised or reduced, gave significantly different results in terms of species formed from irreversible adsorption. The strongest carbonate formation occurred on heating to 185 °C after O<sub>2</sub> was added to the pre-adsorbed CO on an oxidised ZnO surface at room temperature followed by heating to 185 °C in the presence of the two-gas mixture.

### Introduction

The structure of CO chemisorbed on metals is closely related to that of metal carbonyl compounds [1], so adsorption of CO on different metals [2-4] has been investigated by different techniques [5, 6]. CO is also known as a convenient molecule for studying surface sites present in oxides [7, 8] and the oxidation states of metals [9, 10]. Newly prepared samples of supported catalysts can hence be characterised by adsorption of CO [11] using the infrared spectroscopy. CO oxidation is an interesting reaction of practical importance concerning CO toxicity and the necessity to purify industrial and exhaust gases [12, 13]. ZnO is an integral part of highly active and selective catalysts for the production of CH<sub>3</sub>OH [14, 15] and also used for the oxidation of CO to CO<sub>2</sub> [16] in presence of oxygen or N<sub>2</sub>O [17] which is considered as an intermediate in the NO/CO reaction [18-20]. Because of the interaction of different carbonaceous species present on the surface of catalyst due to CO, O<sub>2</sub>/C O<sub>2</sub>, adsorption acts as a chain initiator for a defined catalytic reaction. The source of ZnO is also very important as the oxide can be obtained by the combustion of zinc metal (known as Kadox type), or the decomposition of ZnCO<sub>3</sub>, ZnNO<sub>3</sub> etc. and such alternatively prepared samples can behave differently [21] and are not suitable for the use in IR spectroscopy as the transmittance is significantly lost at lower wave numbers.

In this communication, adsorption of CO, CO+O<sub>2</sub> and CO<sub>2</sub> on oxidised and reduced ZnO surfaces of the Kadox type studied by infrared spectroscopy is reported.

### Results and Discussion

#### (a) The adsorption of CO over ZnO (oxid.)

The transmission mode spectra of the species resulting from the adsorption of CO (40 torr) at room temperature over a disc of ZnO (oxid.) are shown in Fig. 1. These and all other spectra were obtained by ratioing the single beam spectra with that of the gas-phase in contact with it as obtained by removal of the catalyst disc from the infrared beam. In comparison with the spectrum of the clean surface (Fig. 1a) after twenty minutes contact of the gaseous CO with the disc, produced spectrum 'b' with a sharp band at 2185 cm<sup>-1</sup> along with weak absorption bands at 1610, 1567, 1340 and 1290 cm<sup>-1</sup>. The sharp band at 2185 cm<sup>-1</sup> can be assigned [17, 22-25] to the reversibly adsorbed, sometimes called physisorbed, CO molecules [1, 26]. The additional bands in the region 1650-1200cm<sup>-1</sup> are from irreversibly adsorbed surface carbonate species formed from oxidation of CO [14, 17, 25-29] and adsorption upon ZnO non-polar faces [30]. Spectra 'c' and 'd' were recorded after the disc remained in CO for 3 and 21 hours, respectively. The sharp band at 2185 cm<sup>-1</sup> gradually shifted to 2188 cm<sup>-1</sup> and a separate strong shoulder at 2197 cm<sup>-1</sup> was observed after 21 hours.

In the 1650-1200 cm<sup>-1</sup> region, the bands at 1610, 1567, 1340 and 1290 cm<sup>-1</sup> increased their intensities on standing in CO but the rate of growth of the pair of bands at 1567 and 1340 cm<sup>-1</sup> was greater than that of the pair of bands at 1610 and 1290 cm<sup>-1</sup>. The later pair of bands only grew in the first three hours whereas the former pair continued growing even after 20 hours. In the region below

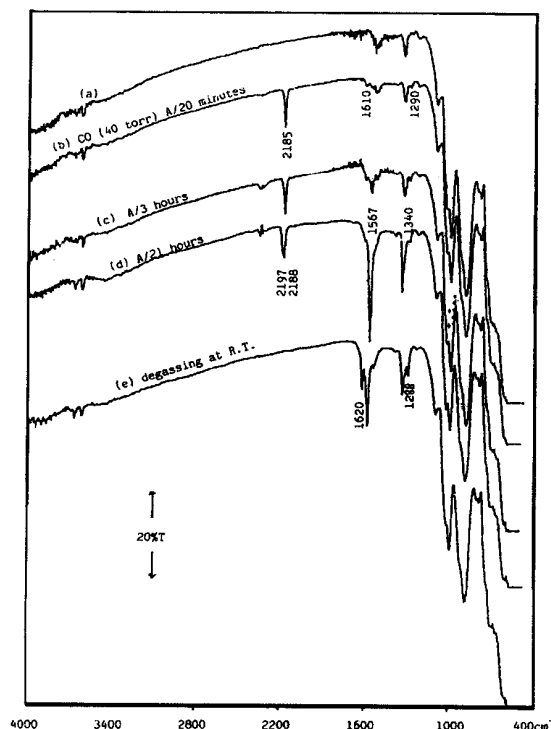


Fig. 1: I.R. spectra from the adsorption of CO on ZnO (oxid.).

- ZnO background spectrum;
- 40 torr CO at room temperature after 20 minutes;
- After 3 hours;
- After 21 hours; and
- After evacuation at room temperature.

1100  $\text{cm}^{-1}$  very weak bands, masked in Fig. 1 by the multiphonon ZnO absorptions [22], also continued to grow. A pair of bands at 1015 and 857  $\text{cm}^{-1}$ , shifted after evacuation, can be clearly seen from the ratio-mode spectrum e/d shown in Fig. 2.

Evacuation at room temperature for 30 minutes (spectrum 1e) completely removed the bands in the 2400-2100  $\text{cm}^{-1}$  region, showing their reversible behaviour. In the region 1650-800  $\text{cm}^{-1}$  the following changes were observed (Fig. 2).

- The set of bands originally at 1610, 1290, 985 and 845  $\text{cm}^{-1}$  increased their intensities and shifted to 1620, 1288, 980 and 843  $\text{cm}^{-1}$ .
- The set of bands at 1567, 1340, 1015 and 857  $\text{cm}^{-1}$  decreased their intensities and shifted to 1580, 1330, 1003 and 853  $\text{cm}^{-1}$ .

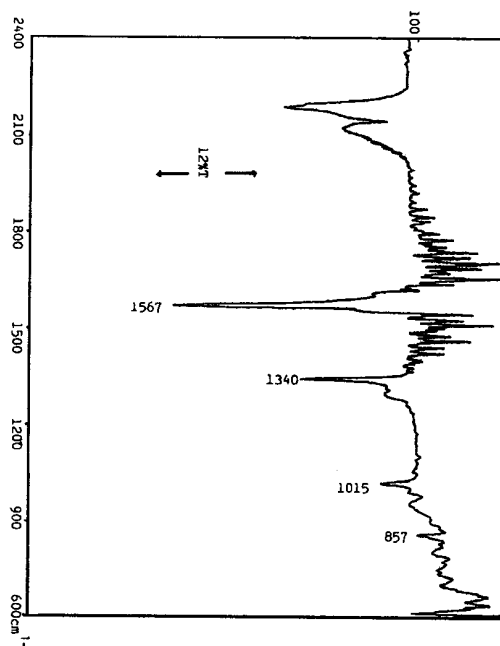


Fig. 2: The ratio-mode spectrum e/d of Fig. 1.

Spectra recorded at increasing pressures of CO from 20 to 100 torr, applied for a relatively short period of time, showed a general pattern of behaviour similar to those observed in Fig. 1; however, very lower -wavenumber bands at 2150 and 2100  $\text{cm}^{-1}$  were also discernable at higher pressures of CO as earlier reported by Rais [31].

The transmission mode spectra from adsorption of CO (40 torr) at room temperature over a disc of ZnO (oxid.), pre-treated with water and followed by evacuation for one hour, did not show any band due to CO adsorption (physisorbed or chemisorbed) showing that the sites responsible for CO adsorption were blocked by water adsorption similar to the blockages observed by Bocccuzzi *et al.* from pyridine [32] and Bowker *et al.* from hydrogen [34].

#### (b) The adsorption of CO over ZnO (red.)

Introduction of CO (40 torr) at room temperature over the ZnO (red.) surface produced the spectrum 'b' in Fig. 3. A pair of bands at 2185 and 2105  $\text{cm}^{-1}$  was obtained, which were replaced by a weak band at 2057 after 14 hours in CO as shown in the spectrum 'c'. The CO band at 2185  $\text{cm}^{-1}$  is

weaker compared to that in Fig. 1 showing that physical adsorption of CO on the ZnO (red.) surface is weaker (33). In the region  $1650\text{--}1200\text{ cm}^{-1}$  no bands developed but one at  $1350\text{ cm}^{-1}$  decreased its intensity. Evacuation at room temperature for 30 minutes (spectrum 3d) again completely removed the weak band at  $2057\text{ cm}^{-1}$ .

Adsorption of CO on the surfaces of ZnO (red) which have been in contact with 40 torr of  $\text{O}_2$  for one hour at room temperature, or at  $200^\circ\text{C}$  followed by cooling to room temperature and after evacuation for 30 minutes, did not show much difference to the spectra in Fig. 3 except that the bands in the region  $1600\text{--}800\text{ cm}^{-1}$  from carbonate-type products became visible.

(c) The adsorption of CO followed by  $\text{O}_2$  over ZnO (oxid.)

When 20 torr of CO followed by 20 torr of  $\text{O}_2$  were introduced at room temperature on the

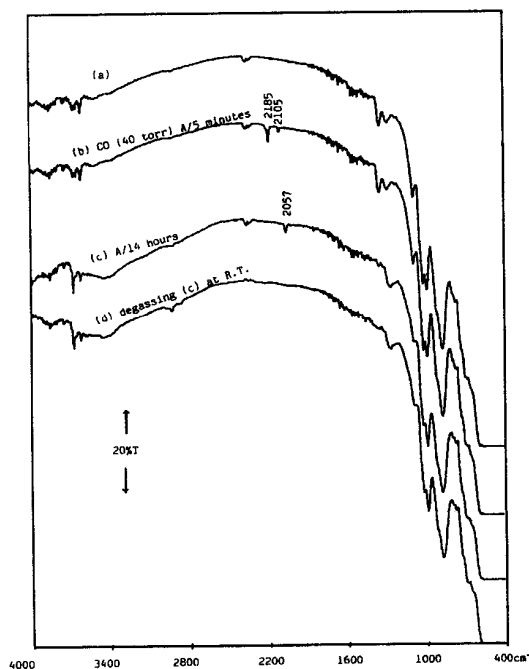


Fig. 3: I.R. spectra from the adsorption of CO on ZnO (red.).

- ZnO background spectrum;
- 40 torr CO at room temperature after 5 minutes;
- After 14 hours; and
- After evacuation at room temperature.

oxidised surface of ZnO, the infrared spectra in Fig. 4 were observed. The bands in the region  $1600\text{--}1200\text{ cm}^{-1}$  relative to the background spectrum of ZnO were comparatively stronger than in Fig. 1. A doublet at  $2200$  and  $2187\text{ cm}^{-1}$  from adsorbed CO was seen along with the usual new bands at  $1610$ ,  $1567$ ,  $1338$  and  $1290\text{ cm}^{-1}$ . Heating at  $185^\circ\text{C}$  in the presence of the resulting  $\text{CO}+\text{O}_2$  mixture, followed by cooling to room temperature showed the spectrum 4c. The doublet at  $2200$  and  $2187\text{ cm}^{-1}$  was replaced by a sharp band at  $2225\text{ cm}^{-1}$ . In the lower frequency region of  $1650\text{--}800\text{ cm}^{-1}$  the following changes were observed as can be very clearly seen from the ratio mode spectrum c/b, shown in Fig. 5:

- The set of bands at  $1567$ ,  $1338$ ,  $1010$  and  $855\text{ cm}^{-1}$  increased their intensities and shifted to

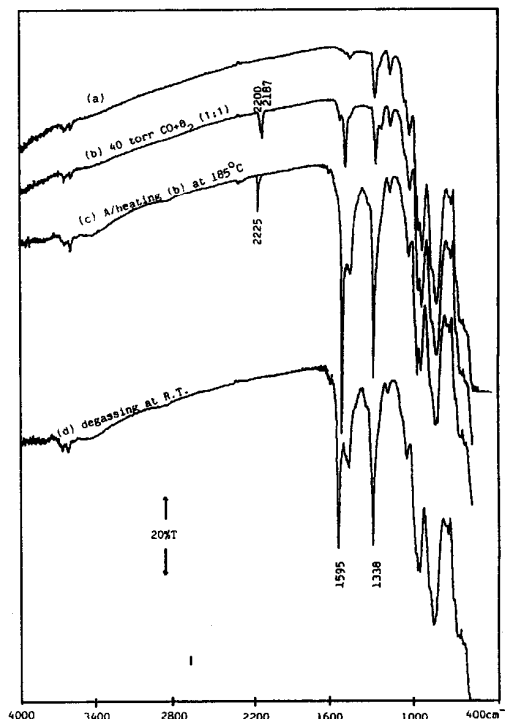


Fig. 4: I.R. spectra from the adsorption of CO followed by  $\text{O}_2$  on ZnO (oxid.).

- ZnO background spectrum;
- 20 torr CO followed by 20 torr  $\text{O}_2$  at room temperature after 5 minutes;
- After heating at  $185^\circ\text{C}$  for 30 minutes in the 1:1  $\text{CO}/\text{O}_2$  gas mixture followed by cooling to room temperature; and
- After evacuation at room temperature.

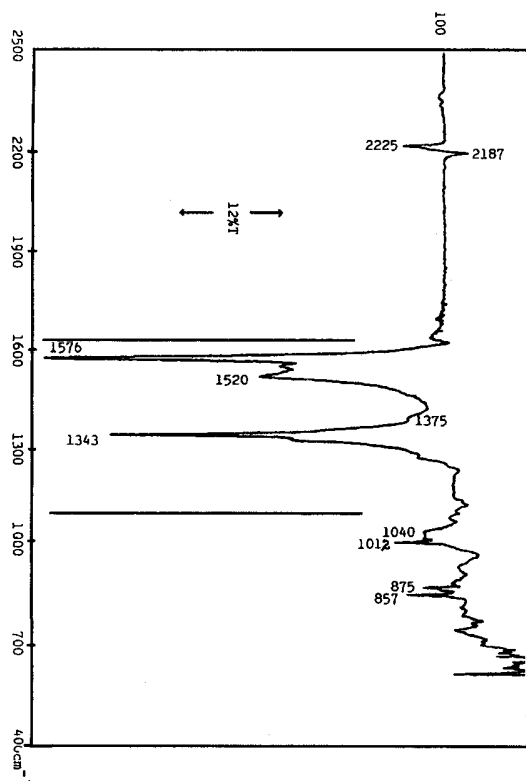


Fig. 5: The ratio-mode spectrum c/b of Fig. 4.

- 1576 (v.v.st), 1343 (v.st), 1012 and 857  $\text{cm}^{-1}$ .  
 ii) A strong new band at 1520  $\text{cm}^{-1}$ , along with weaker bands at 1375, 1040 and 875  $\text{cm}^{-1}$  appeared.

Evacuation at room temperature for 30 minutes (spectrum 4d) again completely removed the sharp band at 2225  $\text{cm}^{-1}$ . The changes, clearly seen from the ratio mode spectrum d/c (Fig. 6), were observed. The set of bands at 1576, 1343, 1012 and 857  $\text{cm}^{-1}$  decreased their intensities and in the process shifted to 1595, 1338, 1000 and 850  $\text{cm}^{-1}$ .

When 20 torr of  $\text{O}_2$  followed by 20 torr of CO was introduced at room temperature on the oxidised surface of ZnO, weaker bands due to CO and carbonates etc. were observed.

*(d) The adsorption of  $\text{CO}_2$  over ZnO (oxid.)*

A set of spectra were also recorded when 3 torr  $\text{CO}_2$  was introduced over ZnO (oxid.) at room temperature, shown in Fig. 7. A strong band at

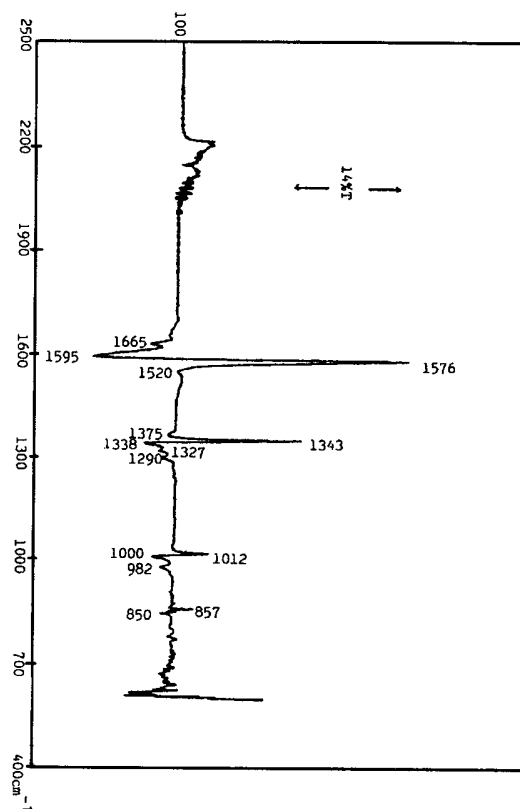


Fig. 6: The ratio-mode spectrum d/c of Fig. 4.

2355  $\text{cm}^{-1}$  along with a strong shoulder at 2365  $\text{cm}^{-1}$  and a much weaker band at 2290  $\text{cm}^{-1}$  was observed attributable to reversibly adsorbed  $\text{CO}_2$  species.. Evacuation at room temperature for 30 minutes completely removed these bands. The bands in the low frequency region 1800-800  $\text{cm}^{-1}$  were observed at 1652 (sh), 1617 (v.v.st), 1580 (sh), 1550 (st), 1422 (w), 1370 (sh), 1345 (v.st), 1228 (w), 1000, (m) and 845  $\text{cm}^{-1}$  which are seen from the ratio mode spectrum relative to the ZnO (oxid.) background shown in Fig. 8. These bands were also affected by evacuation at room temperature.

Carbon monoxide forms coordination compounds with transition metals in which the molecule is linked to metal via its carbon atom [34]. The strength of the CO bond depends upon the extent of the bonding between metal and carbon and electron back donation from metal. Adsorption of CO on oxides and metals has been widely studied. It has been pointed out that there are two distinct forms of CO adsorption:

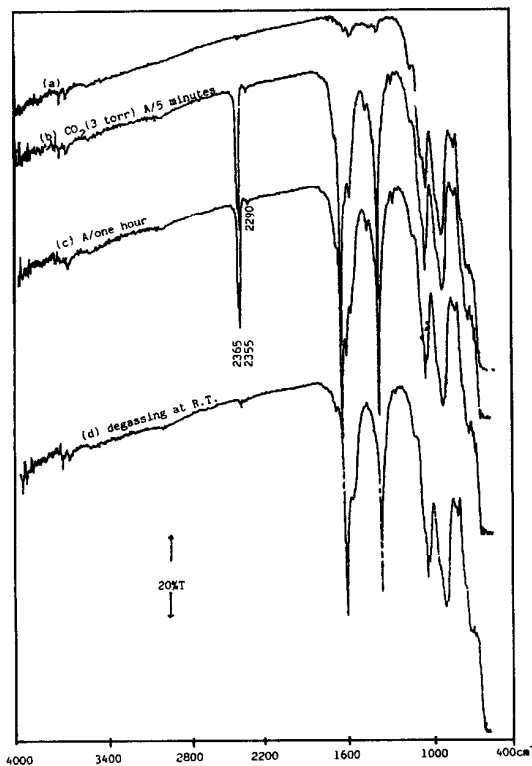


Fig. 7: I.R. spectra from the adsorption of CO<sub>2</sub> on ZnO (oxid.).

- a) ZnO background spectrum;
- b) CO<sub>2</sub> (3 torr) at room temperature after 5 minutes;
- c) After one hour;
- d) After evacuation at room temperature.

- i) A weak reversible adsorption giving absorption bands in the region 2250–1950 cm<sup>-1</sup>. This can be removed by evacuation at room temperature.
- ii) A strong irreversible adsorption occurring in the region 1700–500 cm<sup>-1</sup>. Temperatures of more than 200 °C are required to remove this type of adsorbed CO which mainly desorbs as CO<sub>2</sub> above that temperature [35, 36].

The spectra in Fig. 1 show these two types of CO adsorption. The sharp band at 2185cm<sup>-1</sup> is assigned to the reversible type adsorption [14, 17, 22, 24]. This band shifted to 2188cm<sup>-1</sup> and a strong shoulder at 2197cm<sup>-1</sup> was also observable after 21 hours in CO at room temperature. A similar shift has been observed previously [12, 27]. Lavalley *et al.* [27] observed a similar high frequency shift when

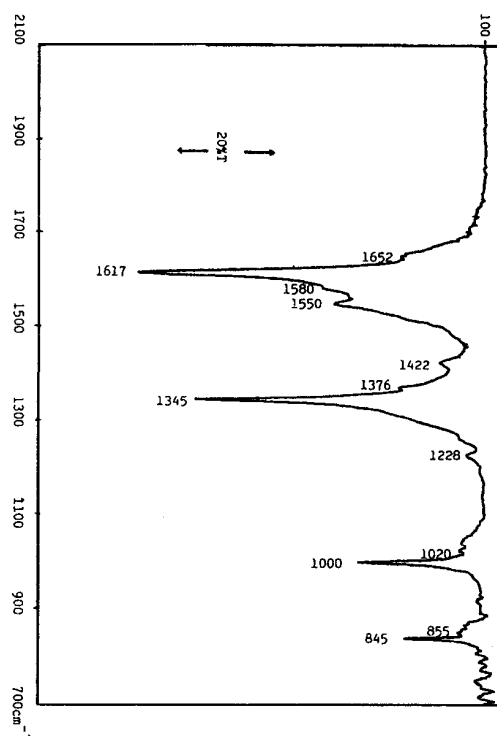


Fig. 8: The ratio-mode spectrum b/a of Fig. 7.

CO<sub>2</sub> was introduced to preadsorbed CO. They explained this shift as due to an increase in Lewis acidity of the surface zinc ion through the formation of adjacent carbonates. The rise in frequency of CO with time, in the spectra in Fig. 1, can also be related to the strength of carbonate bands in the lower region of 1700–600 cm<sup>-1</sup>.

In the case of adsorption from CO+O<sub>2</sub>, the band due to weakly adsorbed CO was observed as high as 2225cm<sup>-1</sup> (Fig. 4). A corresponding shift to lower frequency was also observed when a reduced ZnO was used (Fig. 3) presumably as the Lewis acidity of zinc ion has decreased. The band at 2057cm<sup>-1</sup> (Fig. 3c) from adsorption on particles of zinc metal (Zn<sup>0</sup>) could be related to a darkening of the oxide sample.

#### *The Region of 1800–500 cm<sup>-1</sup>*

In the region of 1800–500 cm<sup>-1</sup> two sets of bands from the chemisorption of CO at room temperature, appeared at 1610, 1290, 985, 845 cm<sup>-1</sup> shifting to 1620, 1288, 980, 843 cm<sup>-1</sup> and 1567, 1340,

1015, 857  $\text{cm}^{-1}$  shifting to 1580, 1330, 1003 and 853  $\text{cm}^{-1}$ . The first set of bands which appeared at the start of the adsorption has been assigned to a bidentate carbonate [17, 37]. The bands from this bidentate carbonate became stronger and shifted after evacuation. The second set has also been assigned [17, 38] to a less strongly adsorbed bidentate carbonate of a different type which on evacuation reduces its intensity and shifts. Saussey *et al.* [39] have proposed 4 types of bidentate carbonate from the adsorption of  $\text{CO}_2$ . However few of the bidentates in the current study are observed at slightly different frequencies. Oxidation of CO by  $\text{O}_2$  at 185 °C also produced the above two types of bidentate species which were affected by evacuation in a similar way *i.e.* the highest frequency band shifts upward while the other bands shift downward. However a new strong band was observed at 1520  $\text{cm}^{-1}$ , with weaker bands at, 1375, 1040 and 875  $\text{cm}^{-1}$ . These are assigned to monodentate carbonates [17] which are not affected by evacuation. Saussey *et al.* [39] has assigned these bands with a band at 1327  $\text{cm}^{-1}$  to polydentate carbonates and the band at 1375  $\text{cm}^{-1}$  was related to the gaseous  $\text{CO}_2$ . However spectra (Fig. 6) show that the band at 1375  $\text{cm}^{-1}$  behaves similar to the band at 1520  $\text{cm}^{-1}$  after evacuation when the bands from gaseous  $\text{CO}_2$  have disappeared. The spectra obtained from the adsorption of  $\text{CO}_2$  (Fig. 8) were similar to those observed by Saussey *et al.* [39].

The assignments are given in the following Table 1:

Table-1: Assignment of various carbonate species.

| bidentate carbonate (a) | bidentate carbonate(b) | bidentate carbonate (b')* | bidentate carbonate (c) | Monodentate carbonate* |
|-------------------------|------------------------|---------------------------|-------------------------|------------------------|
| 1610(1620)              | 1567(1580)             | 1576(1595)                | 1665                    | 1520 (v.s)             |
| 1290(1288)              | 1340(1330)             | 1343(1338)                | 1303                    | 1375 (s)               |
| 985(980)                | 1015(1003)             | 1012(1000)                |                         | 1040                   |
| 845(843)                | 857(853)               | 856(850)                  |                         | 875                    |

The numbers in brackets corresponds to the bands after evacuation. These bands were obtained after heating at 185 °C in  $\text{CO}+\text{O}_2$ . The carbonates 'b' and 'b'' may be in different environment.

## Experimental

Zinc oxide used (Kadox 15) was obtained from the New Jersey Zinc Company and had a stated surface area of 10  $\text{m}^2\text{g}^{-1}$ . For infrared studies it was made into thin discs of 25-35  $\text{mg}/\text{cm}^2$  under a pressure of 1 ton  $\text{cm}^{-2}$  (*ca.*  $1 \times 10^7 \text{N}/\text{m}^2$ ). Infrared

spectra were recorded at 4  $\text{cm}^{-1}$  resolution using either a Digilab FTS14 or FTS20 spectrometer. The infrared cell has been described previously [22]. Two types of ZnO surfaces termed oxidised, ZnO (oxid.) and reduced, ZnO (red) were prepared by standard oxidation/reduction treatments used previously [22, 23]. In this treatment the oxide disc was cleaned by a three-times repeated cycle of oxygen treatment (40 Torr; 1Torr =  $133.3 \text{N}/\text{m}^2$ ) for 20 min at 400-410 °C followed by evacuation for 1 hour at  $5 \times 10^{-5}$  to  $10^{-5}$  Torr; and finally by heating in oxygen at 400 °C. A sample cooled to room temperature in oxygen and then evacuated, is termed an 'oxidised' surface, ZnO (oxid.). When the oxygen is evacuated at 400 °C and the sample then cooled to room temperature during evacuation, the resulting sample is termed a 'reduced' surface, ZnO (red.).

$\text{CO}$  gas (research grade) was obtained from Mason Ltd (UK).

## Conclusion

The following conclusions can be drawn from the infrared adsorption of CO and  $\text{CO}+\text{O}_2$  on ZnO:

1. Adsorption of CO on ZnO (Oxid.) surfaces shows bands in the region 2050-2250  $\text{cm}^{-1}$  due to reversibly adsorbed CO and bands in the region 1800-500  $\text{cm}^{-1}$  due to irreversibly adsorbed carbonate-type species from the oxidation of CO. Similar reversibly adsorbed bands in the 2350  $\text{cm}^{-1}$  region occur from the adsorption of  $\text{CO}_2$ . In general bands in the region 1800-500  $\text{cm}^{-1}$  are assigned to bi or monodentate carbonates. In most cases the formation of substantial amounts of carbonate is a slow process extending over several hours at room temperature in CO. However, addition of  $\text{O}_2$  on pre-adsorbed CO on the oxidised surface enhances this process, in particular when the sample is heated to 185 °C.
2. Adsorption of CO on ZnO (red.) surfaces shows weaker bands from reversibly adsorbed CO but, as expected, no appreciable formation of carbonates.
3. The order of introduction of  $\text{O}_2$  and CO and the stoichiometry of ZnO are important factors. The better room temperature conditions for CO oxidation are when  $\text{O}_2$  is added to pre-adsorbed

CO on an oxidised surface of ZnO, even more oxidation occurs at higher temperatures.

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