

# CO<sub>2</sub> activation and reaction with hydrogen on Ni(110): formate formation

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Upon adsorption of CO<sub>2</sub> at  $T \approx 90$  K on Ni(110), the molecule weakly chemisorbs and undergoes a geometrical distortion, i.e. it bends into a nonlinear geometry. This geometrical distortion is triggered by electron transfer from the substrate to the molecule, accompanied by formation of an anionic CO<sub>2</sub><sup>δ-</sup> molecule. It is shown via HREELS spectra that CO<sub>2</sub><sup>δ-</sup> reacts with adsorbed H atoms in low concentration ( $\leq 0.1 \ell$ ) via a Langmuir-Hinshelwood mechanism to form the formic acid anion, i.e. formate, which remains adsorbed on the surface. Hydrogen coverages, which allow the surface to reconstruct, inhibit CO<sub>2</sub> chemisorption.

## 1. Introduction

Recently, several groups have started to investigate the adsorption of CO<sub>2</sub> on metallic substrates [1–29]. After very early studies by Eischens and Pliskin [29] via IR-spectroscopy in 1957, Wedler and his co-workers [5,6,25–27] took up CO<sub>2</sub> adsorption in order to unravel the elementary steps of the Fischer-Tropsch reaction. Even in those early studies, there are indications of an intermediate chemisorbed species, which was identified later to be a bent, anionic CO<sub>2</sub><sup>δ-</sup> species. This species has been identified subsequently on several metal surfaces. Parallel to the investigations on clean metal single-crystal surfaces [1–8], investigators have studied CO<sub>2</sub> adsorption on modified metal surfaces, i.e. alkali [9–15] and oxygen predosed systems [16–19], as well as polycrystalline simple [20–22] and noble-metal surfaces [23–27]. In the case of Cu, the study of CO<sub>2</sub> adsorption appears to be particularly relevant in view of the possible role of CO<sub>2</sub> in the methanol synthesis using ZnO/Cu catalysts. On the basis of CO<sub>2</sub> adsorption experiments on copper surfaces, Copperthwaite et al. [7] have claimed that a CO<sub>2</sub><sup>δ-</sup> intermediate may be active in the latter case.

After we had identified the formation of CO<sub>2</sub><sup>δ-</sup> on Ni(110) applying angle-resolved ultraviolet photoemission spectroscopy (ARUPS) [1], high resolution electron energy loss spectroscopy (HREELS)

[1], X-ray photoelectron spectroscopy (XPS) [2], near-edge X-ray absorption spectroscopy (NEXAFS) [2] and theoretical cluster calculations [30], we present in this study the reaction of adsorbed CO<sub>2</sub><sup>δ-</sup> with coadsorbed H<sub>2</sub> and follow the formation of formate on the surface. Adsorbed formate may be formed independently by dosing the surface with formic acid followed by thermal treatment, and the properties of such adsorbates have been studied in recent years applying electron spectroscopic techniques [20,31–40]. We shall dwell on those results for comparative purposes in our work. In the present study, we give conclusive evidence for the formation of HCOO<sup>-</sup> via reduction of CO<sub>2</sub> with H<sub>2</sub> from vibrational spectroscopy and discuss the reaction pathway in terms of a Langmuir-Hinshelwood mechanism. We show in addition that the reactivity of CO<sub>2</sub> in the adsorbed state depends on the bonding of the chemisorbed CO<sub>2</sub><sup>δ-</sup> towards the surface.

## 2. Experimental

The experiments were performed within an ultra-high-vacuum apparatus described in detail elsewhere [41]. It consists of two chambers, one which contains the HREELS spectrometer (ELS 22, Leybold AG) and another one equipped with LEED/AES and temperature programmed desorption (TPD) (with

a Feulnercup), as well as a gas-dosing system. The base pressure in the system was below  $1 \times 10^{-10}$  Torr. The sample was welded to two tungsten rods which were attached to a sample manipulator; it could be moved between the measurements positions in both chambers. The gases ( $\text{CO}_2$  and  $\text{H}_2$ ) were admitted to the system with all filaments off and the ion pump disconnected. While dosing, the sample surface was held at a temperature between 90 K and room temperature. Low temperatures were achieved by cooling with liquid nitrogen. Spectra as a function of temperature were taken using the following procedure: The sample was removed from the electron scattering position. Then the surface temperature was changed by heating against the liquid-nitrogen bath for a given time. While the surface was cooling off, the sample was repositioned within the measuring position and spectra were taken again at low temperature. The single crystal was cut and polished two within  $1^\circ$  of the (110) plane. It was cleaned in situ by sputter-anneal cycles as reported earlier [1,2,41]. The (110) crystal was mounted in such a way that the electron scattering plane was within the (100) azimuth.

The photoemission measurements were performed using the AT&T Bell Laboratories Dragon beamline at the National Synchrotron light source. The magnetically shielded UHV system was equipped with a VSW 150 mm hemispherical electron-energy analyzer with multianode detection, an ion gun and a backview LEED system. The beamline and apparatus are described in detail elsewhere [42,43]. The overall instrumental resolution was 0.5 eV, using a photon energy of 360 eV.

### 3. Results and discussion

Fig. 1 shows a thermal desorption spectrum of coadsorbed  $\text{CO}_2$  and  $\text{H}_2$  on Ni(110). Thermal desorption begins immediately with heating, starting at 90 K. The peak at 100 K is due to desorption of physisorbed  $\text{CO}_2$  leaving the surface. We attribute the small shoulder at 150 K to those linear  $\text{CO}_2$  molecules that solvate the  $\text{CO}_2^{d-}$  formed on the surface as we know from earlier studies by Bartos et al. [1]. The latter authors have shown that  $\text{CO}_2^{d-}$  itself is stable up to about 200 K, and dissociates into CO

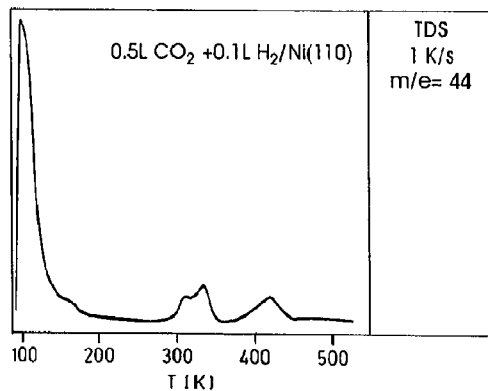


Fig. 1. Thermal desorption spectra of  $m/e=44$  for 0.5  $\mu\text{L}$   $\text{CO}_2$  + 0.1  $\mu\text{L}$   $\text{D}_2$  exposure to clean Ni(110) at 90 K.

and oxygen quantitatively at more elevated temperatures. The formed CO and oxygen recombine and desorb at temperatures between 400 and 500 K leading to the broad peak in this temperature region. The feature with shoulder peaking at 330 K is due to hydrogenation of formate formed on the surface via reaction of  $\text{CO}_2^{d-}$  with adsorbed hydrogen. We know from the work of Campbell and co-workers [34] for  $\text{HCOOH}$  on O/Cu(110) that one desorption channel is due to disproportionation of formate according to



We are not certain that such a process may happen on a Ni(110) surface but it would explain the shoulder slightly above 300 K. At the position of the shoulder, we do, indeed, observe desorption of formic acid.

We find the interpretation of our TPD traces corroborated by the HREELS results which we will discuss in the following: The HREELS data for the reaction of  $\text{CO}_2$  with hydrogen are shown in fig. 2. The energetic positions of the loss features are collected in table 1. The table shows that there are basically three sets of loss features. One is associated with physisorbed  $\text{CO}_2$ , a second one with chemisorbed  $\text{CO}_2^{d-}$  as identified earlier [1,2], and a third one due to chemisorbed formate  $\text{HCO}_2^{d-}$ . Formate may be assigned on the basis of results by Richardson and co-workers [31] who have published a set of detailed EELS studies on the system  $\text{HCO}_2^-(2 \times 2)/\text{Ni}(110)$  where the formate, how-

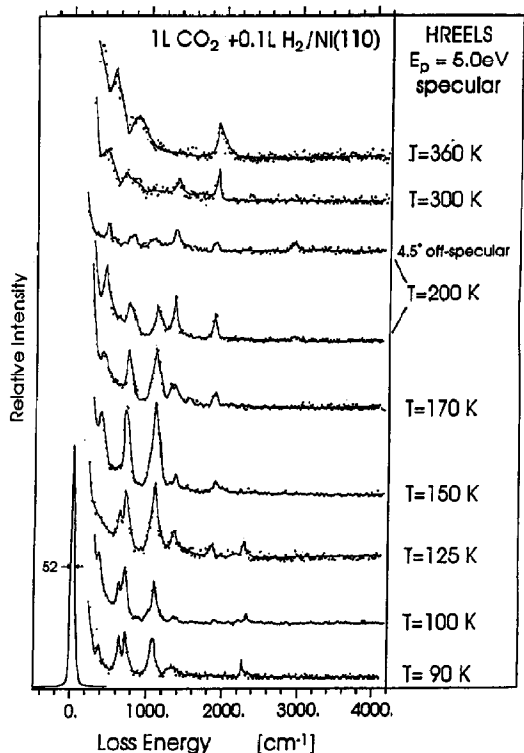


Fig. 2. Series of HREEL spectra of 1 l  $\text{CO}_2 + 0.1$  l  $\text{H}_2/\text{Ni}(110)$  as a function of temperature measured at specular scattering geometry. The spectrum at  $T = 200$  K was detected at  $4.5^\circ$  off-specular scattering geometry.

ever, was formed via saturation exposure of  $\text{Ni}(110)$  at 310–340 K. In the following, we shall discuss the data of fig. 2 going from low to high temperature.

At 90 K, the strong band at  $636\text{ cm}^{-1}$  indicates the presence of undistorted  $\text{CO}_2$  and has been assigned to the  $\text{CO}_2$  bending mode. The loss feature at  $2337\text{ cm}^{-1}$  is due to the asymmetric stretch of linear  $\text{CO}_2$

and exhibits little but appreciable intensity. The dynamic dipoles of the two mentioned  $\text{CO}_2$  vibrations behave differently, i.e. the stretching mode is polarized along the molecular axis, the bending mode perpendicularly with respect to the molecular axis. Therefore, if the molecular axis were oriented parallel to the metal surface, the stretching mode should be completely screened, and if the molecular axis were oriented perpendicular to the metal surface the bending mode should be screened. Both modes are active, however, with the bending mode strongly dominating, which indicates that  $\text{CO}_2$  is oriented not quite but almost parallel to the surface.

As has been shown previously by Bartos et al. [1], in addition to linear  $\text{CO}_2$  there is a bent  $\text{CO}_2^{2-}$  species present on the surface which leads to losses at 727, at 1103, and at  $403\text{ cm}^{-1}$ . These losses have been assigned to the bending mode, the symmetric stretch and the molecule–substrate stretching mode of  $\text{CO}_2^{2-}$ , respectively. The loss feature at  $1353\text{ cm}^{-1}$  has been observed in earlier work [1] and has been attributed to the presence of carbonate. We shall provide conclusive evidence that it is due to the formate symmetric stretch.

If the adsorbate is heated (from 90 K to a temperature close to 200 K, we observe characteristic changes of the loss intensities.

Firstly, between 120 and 170 K, the features due to linear  $\text{CO}_2$  disappear indicating the transformation to  $\text{CO}_2^{2-}$  of this surface species. Note that upon elevating the temperature, the relative intensities of  $\text{CO}_2$  bending and stretching modes change, i.e. the stretching vibration gains intensity. This may indicate a slightly different average adsorbate geometry of linear  $\text{CO}_2$  with its axis assuming a smaller incli-

Table 1  
Loss energies and binding energies of  $\text{CO}_2$ ,  $\text{CO}_2^{2-}$  and  $\text{HCOO}^-$

		Species		
		$\text{CO}_2$	$\text{CO}_2^{2-}$	$\text{HCOO}^-$
VIB ( $\text{cm}^{-1}$ )	$\nu(\text{Ni-O})$	–	403	403
	$\delta(\text{OCO})$	636	727	727
	$\nu_s(\text{OCO})$		1103	1353
	$\nu_a(\text{OCO})$	2337		
	$\nu(\text{C-H, C-D})$	–	–	2904, 2274
$E_{\text{bin}}$ (eV)	$\text{C}_{1s}$	291.2	286.6	287.0

nation with respect to the surface normal at higher surface temperature.

Secondly, while the  $\text{CO}_2$  features disappear, the  $\text{CO}_2^{\delta-}$  losses gain intensity suggestive of the earlier finding that  $\text{CO}_2$  is partly transformed into bent  $\text{CO}_2^{\delta-}$ . As discussed in detail by Bartos et al. [1] before, the asymmetric stretch of the  $\text{CO}_2^{\delta-}$  is missing on Ni(110) due to the  $\text{C}_{2v}$  symmetry of the adsorbed species.

Thirdly, starting with a surface temperature of  $T=125$  K, the intensity of the feature at the  $1353$   $\text{cm}^{-1}$  loss energy starts growing. Concomitantly a peak at  $1880$   $\text{cm}^{-1}$  loss energy, which is due to adsorbed CO, starts to grow.

Above temperatures of  $T=200$  K, the spectrum is very simple. It is characterized by three losses (except the CO loss at  $1880$   $\text{cm}^{-1}$ ) at  $403$ ,  $727$  and  $1353$   $\text{cm}^{-1}$ , and a very weak loss at  $2904$   $\text{cm}^{-1}$ . The last one becomes clearly visible at off-specular scattering angles (see fig. 2). Clearly this is the loss spectrum of adsorbed formate as reported by Richardson and co-workers [31], who also observed the unusual high intensity of the C-H stretch under off-specular conditions. (Note that we are able to reproduce their results by adsorption of formic acid and subsequent heating to room temperatures.) The formate species formed on the surface is stable up to temperatures between  $300$  and  $340$  K. The only species stable on the surface close to  $360$  K appears to be adsorbed CO.

The above analysis of the reaction is also corroborated by the set of XP spectra taken with synchrotron radiation shown in fig. 3. The spectrum at the top reflects the relatively high concentration of physisorbed  $\text{CO}_2$  (binding energy  $291.2$  eV) with respect to  $\text{CO}_2^{\delta-}$  (at  $286.6$  eV). The binding energies are very similar to those reported by Illing et al. [2] earlier. At  $T=120$  K, physisorbed  $\text{CO}_2$  has been widely attenuated, but  $\text{CO}_2^{\delta-}$  remains on the surface. At the same time, a small CO-induced feature grows in at  $285.6$  eV. At  $180$  K, a new feature has developed at binding energy  $287.0$  eV and the CO-induced peak has grown in intensity. A surface temperature of  $320$  K leaves CO as the only remaining surface species. The feature at  $287.0$  eV observed between  $180$  and  $300$  K must be connected with the formate species. As is shown in the inset of fig. 3 (top spectrum), which presents an XP spectrum of a surface exposed to formic acid at low temperature and heated to

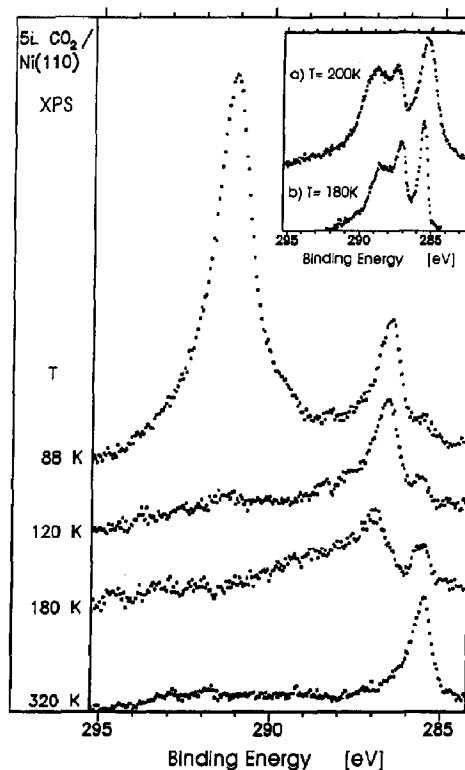


Fig. 3. Series of high-resolution XPS ( $\text{C}_{1s}$ ) of  $5$  l  $\text{CO}_2/\text{H}_2/\text{Ni}(110)$  as a function of temperature. The inset compares formate species formed (a) (in the top spectrum) out of formic acid by heating to  $200$  K with formic acid as solvent, and (b) after reaction of  $\text{CO}_2$  and  $\text{H}_2$  at  $180$  K solvated with readsorbed  $\text{CO}_2$ .

$T=200$  K, a peak at  $287.0$  eV is observed indicating the formation of the formate species together with CO. According to the work of Illing [44], we know that the additional feature at  $288.5$  eV is due to formic acid solvating the formed formate in the monolayer. The lower trace in the inset of fig. 3 is taken after  $\text{CO}_2/\text{H}_2$  adsorption, heating to  $T=180$  K and allowing  $\text{CO}_2$  to readsorb at low temperature. As for the formic acid, the  $\text{CO}_2$  solvating the formate leads to an additional feature at higher binding energy, a trace of which is also seen in the spectrum shown in fig. 3.

We have shown before [1,2], that without the presence of hydrogen, only  $\text{CO}_2^{\delta-}$  forms on the surface which above  $200$  K dissociates into adsorbed CO and oxygen. Only with the presence of hydrogen (or deuterium) do we observe formate formation. Fig. 4 shows in the three upper traces spectra of deu-

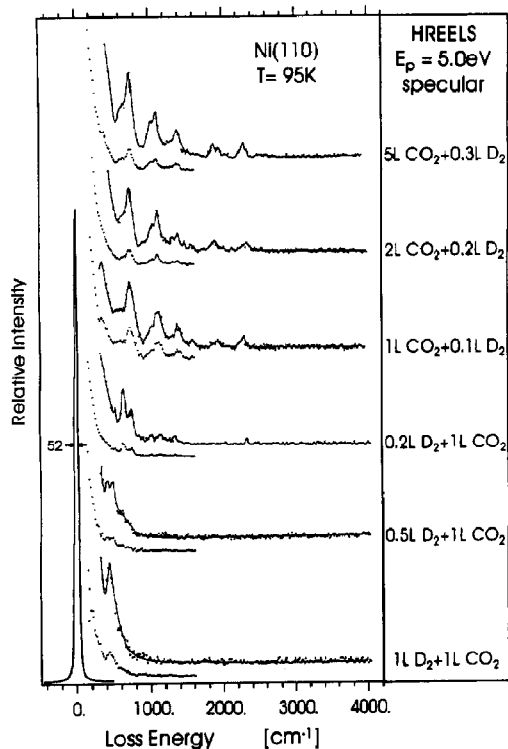


Fig. 4. Series of HREEL spectra of  $\text{CO}_2$  and  $\text{D}_2$  on Ni(110) at  $T=95$  K as a function of dosing measured at specular scattering geometry. In the three upper spectra, the crystal was heated to 140 K after dosing of  $\text{CO}_2$ . With exception of the very top spectrum, where  $\text{D}_2$  was dosed at 180 K, the dosing of  $\text{D}_2$  took place at 95 K.

terated formate which is indicated by the C–D vibration at  $\approx 2200$  cm. It should be kept in mind that  $\text{CO}_2$  exhibits the asymmetric stretch in the same region. However, the tendency for formate formation is a rather complex function of the hydrogen coverage (see fig. 4). Clearly, if we preadsorb hydrogen (or deuterium) at 95 K to saturation coverage (1 l),  $\text{CO}_2$  adsorption and even  $\text{CO}_2$  physisorption at low temperature is suppressed. Note that at saturation coverage, the Ni(110) surface undergoes a  $(2 \times 1)$  reconstruction, which was monitored using LEED. We have to go to low  $\text{H}_2$  doses (0.2 l) before we see  $\text{CO}_2$  physisorption.  $\text{CO}_2^{\delta-}$  formation appears to be suppressed by higher coverages of hydrogen but favored by low hydrogen precoverages. It is not clear at present what causes the effect but we have noted earlier [9] that  $\text{CO}_2^{\delta-}$  formation appears to be correlated with the substrate workfunction for typical  $\delta$ -

type substrates. Hydrogen is known to increase the workfunction by about 0.5 eV (from 4.5  $\rightarrow$  5.0 eV) for saturation coverage [45–49]. It is not unreasonable to assume that it is the increase in workfunction that quenches  $\text{CO}_2^{\delta-}$  formation and its further reaction.

The question now is, what is the mechanism for  $\text{HCO}_2^-$  formation? Are we dealing with a Langmuir–Hinshelwood or an Eley–Rideal mechanism? The fact that large  $\text{H}_2$  precoverages suppress  $\text{CO}_2$  adsorption points to an Eley–Rideal mechanism. The observations, however, that small precoverage of hydrogen induce formate formation, clearly support the idea that the reaction follows a Langmuir–Hinshelwood mechanism. The temperature dependence of the formation of the formate species points towards an activated process. We know that  $\text{CO}_2^{\delta-}$  establishes two O–metal bonds. We also know that the formate is bound in a similar way to the surface. The way to form a C–H bond without breaking the oxygen–metal interaction is for the carbon atom of the  $\text{CO}_2^{\delta-}$  to bind a hydrogen by using the wagging mode in which the whole molecular plane bends with respect to the surface plane. The activation of this vibration would then be the trigger for formate formation.

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