

PROMOTER ACTION OF ALKALI IN THE ACTIVATION OF CO₂ ON Pd(111): A HREELS CASE STUDY

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Dedicated to Professor Dr. G. Wedler on the occasion of his 60th birthday

We study the adsorption and reaction of CO₂ as a function of temperature between 100 and 700 K in the presence of Na on a Pd(111) surface using high resolution electron energy loss spectroscopy. While CO₂ does not react with a clean Pd(111) surface, we find various reaction channels on the Na precovered Pd(111) surface depending on the Na coverage. At intermediate coverage a bent CO₂^{δ-} species with characteristic vibrational bands can be unambiguously identified. This species is stable up to 200 K, and dissociates into CO and oxygen similar to its behaviour on other surfaces, and as reported in a previous photoemission study [Wambach et al., Surface Sci. 209 (1989) 159]. In case the surface has been oxygen contaminated before Na and CO₂ exposure surface carbonates can be observed.

1. Introduction

Promoter effects play an important role in the catalytic activation of inert molecules [1,2]. CO₂ is particularly interesting in view of the search for new catalytic processes that may lead to the conversion of this cheap chemical into organic compounds. In a previous paper [3] we have reported on the adsorption and reaction of CO₂ with a Pd(111) surface in the presence of coadsorbed Na applying angle resolved photoemission as the spectroscopic method to identify the chemical nature and the electronic properties of the adsorbed species.

Matsushima [4], on the other hand, has studied angle resolved temperature programmed desorption for the system CO₂ on K/Pd(111), including CO₂ + O and CO + O coadsorption investigations. Berkó and Solymosi [5] reported temperature programmed desorption and electron energy loss (in the electronic regime) results for the system CO₂ on potassium precovered Pd(100) surfaces which should be comparable with the above mentioned studies to a certain extent. The studies by Solymosi and Berkó [5] and by Wambach et al.

[3] showed that, while CO₂ does not chemisorb on the clean Pd(100) and Pd(111) surfaces, CO₂ chemisorbs on an alkali precovered surface. However, in contrast to Berkó and Solymosi [5], Matsushima [4] found no evidence of CO₂ adsorption on the fully potassium covered Pd(111) surface as long as the surface was free of adsorbed oxygen. In case of oxygen preadsorption he has found indications for the formation of surface carbonate. Wambach et al. [3] have found clear evidence from photoelectron spectra for the formation of surface carbonate at high Na coverage, but the authors could not exclude conclusively the presence of surface oxygen on the fully alkali covered Pd(111) surface. In the present paper we present high resolution electron energy loss spectra for the system CO₂ on Na/Pd(111) as well as for CO₂ + O on Na/Pd(111) for intermediate alkali precoverages.

At intermediate coverages ($\theta = 0.25-0.7$) there is clear evidence from the spectra that a bent CO₂^{δ-} species, previously identified as a precursor for CO₂ dissociation on clean Ni(110) [6] and Fe(111) [7] surfaces, is formed on the alkali dosed Pd(111) surface. In very recent ion scattering experiments direct indications have been found that CO₂^{δ-} species are formed on clean Ni(110) and potassium precovered Ni(111) [8]. If the alkali precovered surface is contaminated with small amounts of oxygen we observe, in addition to the above reaction channel, the formation of surface carbonate.

2. Experimental

The experiments were performed in a magnetically shielded ultrahigh vacuum system containing facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), residual gas analysis with a quadrupole mass spectrometer, and high resolution electron energy loss spectroscopy (HREELS) (LH ELS 22). The electron analyser is rotatable in one plane. The resolution was typically 9 meV. The base pressure in the system was below 10⁻⁸ Pa.

The Pd(111) crystal was spot-welded between two tungsten wires which were spot-welded to two tungsten rods mounted on a sample manipulator. With liquid nitrogen the crystal could be cooled to 85 K. Heating was possible by electron impact onto the reverse side of the crystal. The surface was cleaned by argon ion bombardment. After annealing the cleanliness was checked with HREELS and surface order and geometry were established by LEED. Na was provided by a commercial SAES getter [9].

As reported earlier [3] at $\theta_{\text{Na}} = 0.4$ coverage we observed a LEED pattern with $(\sqrt{7}/3 \times \sqrt{7}/3)\text{R}10.9^\circ$ symmetry. After CO₂ exposure no LEED pattern in addition to the substrate spots were observed. In order not to influence the adsorption behaviour all filaments in the UHV chamber were turned down or off upon admission of CO₂.

3. Results and discussion

In fig. 1 we show a series of HREEL spectra of a CO₂ dosed Na precovered ($\theta = 0.25$) Pd(111) surface as a function of temperature. This series is taken as a representative example for the adsorption behaviour in the intermediate coverage region. At the lowest available temperature, which is close to 90 K, we find three species on the surface, namely:

(i) Physisorbed CO₂ which shows characteristic losses at 645 cm⁻¹ (bending mode), 1298 cm⁻¹/1368 cm⁻¹ (symmetric stretch split by Fermi Resonance with the first overtone of the bending mode), and 2340 cm⁻¹ (asymmetric stretch),

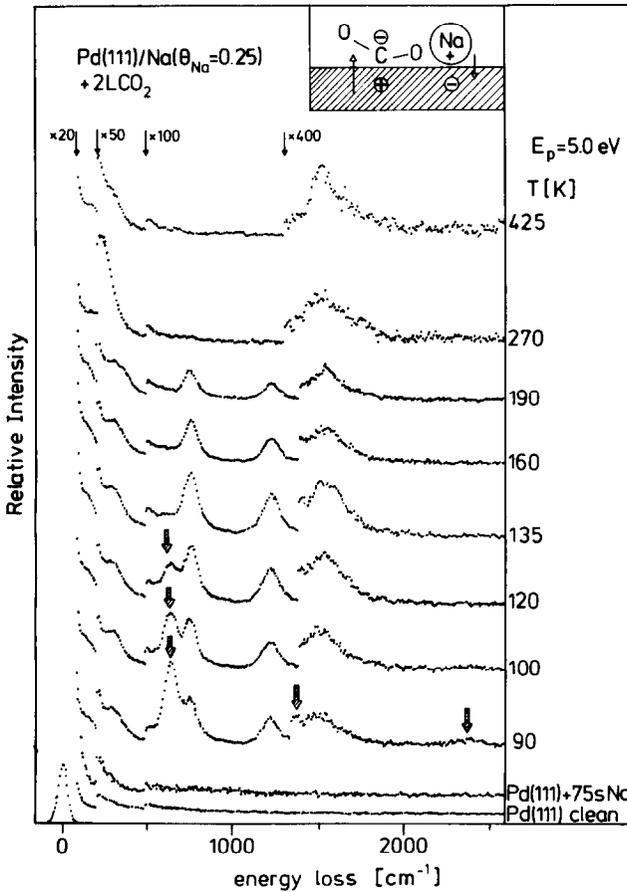


Fig. 1. Series of HREEL spectra (specular) of CO₂/Na+Pd(111) as a function of temperature. The inset shows a schematic structure that explains the observed loss energies and intensities.

Table 1

Comparison of vibrational loss energies (cm⁻¹) in CO₂/Ni(110) and CO₂/Na + Pd(111) (specular scattering)

System	Me-CO ₂	δ _s	ν _s	ν _a
CO ₂ /Ni(110)	410	750	1130	1620 (off spec.)
CO ₂ /Na + Pd(111)	282	744	1210	1530

(ii) CO adsorbed in the vicinity of the alkali exhibiting a loss at 1530 cm⁻¹, and

(iii) a bent CO₂^{δ-} species with characteristic losses at 282 cm⁻¹ (metal-CO₂ stretch), 744 cm⁻¹ (bending mode) and 1210 cm⁻¹ (symmetric stretch). The asymmetric stretch probably contributes to the peak at 1530 cm⁻¹.

The assignments to CO₂ and CO₂^{δ-} can be made on the basis of previous HREELS investigations for the system CO₂ on Ni(110) [6], where we find comparable vibrational spectra. The large intensities of the peaks at 282, 744, and 1210 cm⁻¹ are characteristic for the partly ionic species. We can use these frequencies to deduce the geometry of the adsorbate by comparison with the case of CO₂/Ni(110). Such a comparison between the observed frequencies is given in table 1. The bending mode (δ_s) on the Na/Pd(111) surface is shifted by only 6 cm⁻¹, the symmetric stretching mode (ν_s) by 80 cm⁻¹ to higher energy, while the metal-molecule vibration (Me-CO₂) is shifted down in energy by 128 cm⁻¹. It is important to consider a possible contribution of the asymmetric stretch (ν_a) of CO₂^{δ-} to the 1530 cm⁻¹ peak in the alkali coadsorbate. In order to differentiate the CO₂^{δ-} asymmetric stretch from the alkali influenced CO loss we had to fit the observed spectra [10] for all temperatures shown in fig. 1. The conclusion is that the change in intensity of the broad 1530 cm⁻¹ loss as a function of temperature can only be reproduced if two components contribute to this loss. We assign one of the components to the asymmetric stretch of CO₂^{δ-} and the other one to an alkali influenced CO loss.

The observation of the asymmetric stretch implies that the symmetry of the bound CO₂^{δ-} is C_s, i.e. lower than on the Ni(110) surface where it was C_{2v}. For CO₂ bound in C_s symmetry one usually expects mixed carbon and oxygen metal coordination. If we assume that the structure of the molecule is basically the same as in the case of CO₂/Ni(110), i.e. C-O bond lengths and O-C-O bond angle [11], which we feel is justified on the basis of the overall similarity of the relative energy positions and intensities of the symmetric stretch and bending modes we can propose a structure model shown in the inset of fig. 1. The expected moderate shifts with respect to the situation on Ni(110) are revealed by inspection of table 1. Taking into account the fact that CO₂ does not chemisorb on the clean Pd(111) surface [3,12] the following adsorption mechanism may be considered: The Na releases its electron to form a strong

Na–Pd dipole [2]. The CO₂ molecule binds in the vicinity of this dipole, and forms a second CO₂^{δ-}–Pd dipole which is oriented antiparallel with respect to the Na–Pd dipole, thus partly compensating each other and thereby minimizing the total energy. Since the Na–Pd dipole is rather large, as judged by the strong work function decrease (3 eV), the CO₂^{δ-}–Pd dipole tries to become as large as possible to counterbalance the former (see e.g. ref. [5b]). Since the oxygen atoms carry most of the negative charge in the CO₂^{δ-} anion the CO₂^{δ-}–metal dipole is largest if the oxygen atoms are turned away from the surface. Such a configuration leads to the lowest total energy favouring an adsorption geometry as shown in the inset of fig. 1. In light of these arguments, the configuration chosen for the CO₂/Ni(110) system [6] becomes even more plausible, because in this case the system tries to minimize the CO₂^{δ-}–Ni dipole and thus prefers to position the oxygen atoms close to the surface [13].

As stated above, at low temperature we find a coadsorbate containing physisorbed CO₂ as well as the bent CO₂^{δ-} species. If such a coadsorbate is heated the physisorbed CO₂ partly desorbs from the surface. Also, physisorbed CO₂ is transformed into CO₂^{δ-} as is shown in fig. 1 by the increase of the CO₂^{δ-} signals. The intensities have been normalized to the intensity of the primary elastic beam, and can thus be taken as a measure of the amount of bent CO₂^{δ-} on the surface. If we plot the CO₂(phys), CO₂^{δ-}, and CO intensities as a function of temperature we get fig. 2. It is clear that around 130–140 K the coverage of the CO₂^{δ-} is largest and decreases rapidly as we increase the temperature. At the same time the CO signal, which is already present at low temperature, increases and is at room temperature the only adsorbate signal observed. Unfortunately, the signal from chemisorbed oxygen is very low at the temperature where the transformation occurs, because oxygen is known to migrate into the bulk of the solid [14]. This result is compatible with the photoemission study [3] where the dissociation of CO₂ into CO and O had already been observed. However, in photoemission the cross-sections of the CO₂^{δ-} ionizations are known to have very low intensity so that it has not been possible in the latter case to detect the CO₂^{δ-} species. Fortunately, in electron dipole scattering the intensities of the losses are determined by the dynamic dipole moment of the compound. Consequently, CO₂^{δ-} gives rise to very intense losses, as stated above. Once again, only by combining various surface analytical tools it is possible to approach a complete characterization of chemical processes on solid surfaces. Summarizing so far we can state that Na acts as a promoter in CO₂ activation for dissociation, where the reaction proceeds via a bent, anionic CO₂^{δ-} precursor, similar to the situation on Ni(110).

It is now interesting to compare the above reaction with the chemical behaviour of an oxygen contaminated Na/Pd(111) surface. The result of such a study is shown in fig. 3. At lowest temperature we find the characteristic

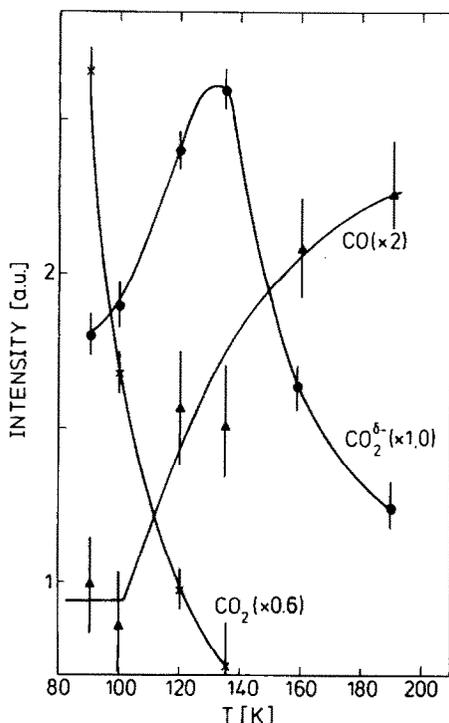


Fig. 2. Variation of the amount of adsorbed CO_2 (physisorbed) (crosses), chemisorbed CO_2 (circles) and CO (triangles) as a function of temperature as measured by the intensities in fig. 1. Separate intensity scales are associated with each species.

losses of physisorbed CO_2 marked with arrows in the spectrum. In addition, we find six losses which are tabulated in the first row of table 2. Two of these six losses can be identified in comparison with table 1 as due to $\text{CO}_2^{\delta-}$. The shift of the $\text{CO}_2^{\delta-}$ losses in table 2 to higher energies as compared with table 1 is a consequence of the high CO_2 coverage [15]. Two of the four remaining losses are situated in the region of carbonate (CO_3) losses [16–18]. The loss at about 1610 cm^{-1} is either due to adsorbed CO [15] or an intermediately present bidentate carbonate [16]. It becomes clear from the temperature dependence of the spectra, where two additional losses are found, that the carbonate losses must be due to a combination of several chemical species, e.g. carbonates with different chemical bonding as in mono-, bi- and tridentate carbonates. A tridentate carbonate should cause a single loss between 1420 and 1470 cm^{-1} due to the degenerate stretching vibration. Upon reducing the number of coordination points to two (bidentate) or one (monodentate) this stretching mode is split into a symmetric and an asymmetric component. The splitting depends in a characteristic fashion on the coordination: While in a

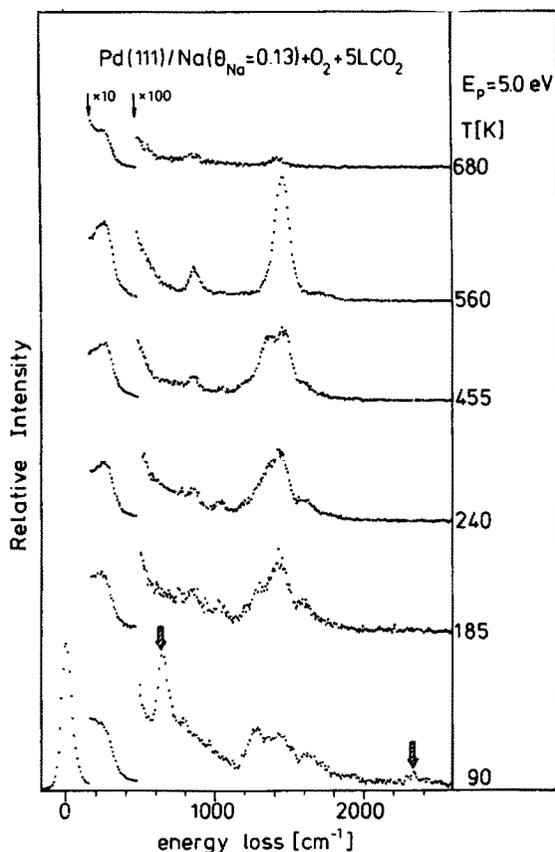


Fig. 3. Series of HREEL spectra (specular) of CO₂/Na+Pd(111) as a function of temperature. Before exposure the surface was contaminated with oxygen. Fig. 3 should be contrasted with fig. 1.

monodentate the splitting amounts to about 130 cm⁻¹, it is about 350 cm⁻¹ in a bidentate [16]. The observed frequencies are compatible with a mixture of mono- and bidentate carbonates, the relative abundance of which changes as a function of temperature. Note that on the basis of the present data it is very difficult to differentiate between mono- and bidentate carbonates. However, at highest temperature the observed losses are rather characteristic of a monodentate species. This conclusion can be verified if we look at the loss intensities: The loss at 1452 cm⁻¹ is very likely to be due to a $\nu_s(\text{OCO})$ vibration of a monodentate species which is found on the surface at all temperature studies. The same species causes the loss at 860 cm⁻¹ ($\pi(\text{CO}_3)$ vibration). The relative intensities of the two latter vibrations remains constant over the full temperature range. Also, the monodentate carbonate contributes

Table 2
Observed vibrational loss energies and assignment for an oxygen contaminated CO₂/Na+Pd(111) system as a function of temperature (the observed losses are marked)

T(K)	Assignment	ν (cm ⁻¹)	$\delta(\text{CO}_2)_{\text{phys}}$	$\delta(\text{CO}_2^{\text{f-}})$	$\pi(\text{CO})_{\text{mono}}$	$\pi(\text{CO}_3)_{\text{bi}}$	$\nu(\text{OCO})_{\text{bi}}$	$\nu(\text{CO})_{\text{mono}}$	$\nu_a(\text{CO}_2^{\text{f-}})_{\text{bi}}$	$\nu_a(\text{OCO})_{\text{mono}}$	$\nu_a(\text{OCO})_{\text{mono}}$	$\nu(\text{CO})_{\text{mono}}$	$\nu(\text{CO})_{\text{bi}}$	$\nu_a(\text{CO}_2)_{\text{phys}}$
262	X	645	X	800	860	X	1040	1040	1290	1370	1452	1613	2340	
90	X		X			X			X		X	X	X	X
185	X		X			X	X		X		X	X	X	
240	X					X	X		X		X	X	X	
455	X					X	X		X		X	X	X	
560	X					X	X		X		X	X	X	
680	X					X	X		X		X	X	X	

significantly to the metal–molecule loss at 262 cm⁻¹. If the peak at 1613 cm⁻¹ is not due to a CO contaminant, then it must be due to a bidentate species, i.e. a $\nu(\text{CO})$ stretching vibration. For such a species we would expect to observe a loss around 1020–1040 cm⁻¹. Close to this energy we find a loss after heating the surface to 185 K. At this temperature the concentration of the species has increased such that the loss at 1040 cm⁻¹ can be observed. After heating the surface to 450 K another carbonate loss is found at 1370 cm⁻¹. A final assignment of this loss cannot be given at present.

4. Summary and outlook

We have shown in the present study via high resolution electron energy loss spectroscopy that by the presence of alkali the adsorption of CO₂ can be activated on a surface which is inert with respect to CO₂ exposure without alkali promotion. The experiments clearly demonstrate that the activation of CO₂ proceeds via a bent, anionic CO₂^{δ-} precursor [13], which leads, if no further reactant is provided, to dissociation into CO and chemisorbed oxygen. In case the Na/Pd(111) system is contaminated with oxygen before CO₂ is dosed we still do find CO₂^{δ-} at intermediate temperature (up to 180 K) but then this species does not seem to dissociate but rather to react to form carbonates. We argue that mono- and bidentate carbonates are present on the surface, the relative abundance of which changes as a function of temperature.

It is now near at hand to try to react the intermediate CO₂^{δ-} species with other chemicals rather than oxygen. In view of the importance to form organic compounds from CO₂ it would be interesting to form C–H and C–C bonds. The former, namely the formation of a surface formate from adsorbed CO₂ and hydrogen, has been observed on a Na precovered Al(111) surface [19]. To achieve the latter goal we proposed to study the reaction of methyl radicals with the adsorbed CO₂^{δ-} radicals. A way may be to prepare CO₂^{δ-} on a Na/Pd(111) system and to react it with methylchloride to form NaCl and acetic acid [20].

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