Reaction of CO_2 on Pd(111) activated via promotor action of alkali coadsorption

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We present CO_2 adsorption studies on a Pd(111) surface as a function of Na precoverage using high resolution electron energy loss spectroscopy. For low Na coverage we find dissociation of CO_2 into CO and O even at 90 K. At high Na coverage as well as on oxygen contaminated Pd surface, formation of surface carbonates can be observed. At intermediate Na coverage the reaction proceeds via a bent anionic $CO_2^{\delta-}$ species which dissociates at higher temperatures into CO and O.

1. Introduction

In recent years alkali promotion effects have attracted some attention in the catalytic activation of inert molecules[1,2]. Such an inert molecule is CO_2, which is of increasing interest in view of the search for new catalytic processes that may lead to the conversion of this cheap chemical into organic compounds.

Several investigations concerning the adsorption and reaction of CO_2 on alkali precovered Pd(111) and Pd(100) surfaces lead to different results although they should be comparable to a certain extent.

In a previous paper, Wambach *et al*[3] have reported results of angle resolved photoemission investigations (ARUPS) on the system CO_2–Na–Pd(111). Their results are in good agreement with Berkó and Solymosi[4], who studied the system, CO_2 on a potassium precovered Pd(100) surface, using temperature programmed desorption (TPD) and electron energy loss spectroscopy in the electronic range. Both investigations showed that while CO_2 does not chemisorb on clean Pd(111) and Pd(100) surfaces, it chemisorbs on alkali precovered surfaces.

However, in contrast to Solymosi and Berkó[4], Matsushima[5] found no indication for the adsorption of CO_2 on a fully potassium covered Pd(111) surface. He studied the system CO_2–K–Pd(111), including CO_2 + O and CO + O co-adsorption using angle resolved TPD. Only in the presence of preadsorbed oxygen on the potassium covered surface did he observe CO_2 adsorption and formation of surface carbonate. Wambach *et al*[3] have found clear evidence from the photoelectron spectra for the formation of surface carbonate at high Na coverage, but the authors could not exclude conclusively the presence of oxygen on the fully alkali covered Pd(111) surface.

In this paper we present high resolution electron energy loss spectra for the system CO_2–Na–Pd(111) depending on alkali coverage and temperature.

As discussed in a previous paper[6] we find at intermediate Na coverages the formation of a bent $CO_2^{\delta-}$ species, previously identified as a precursor for CO_2 dissociation on clean Ni(110)[7] and Fe(111)[8] surfaces. At high Na coverages as well as on oxygen contaminated Pd(111) surfaces[6] we observe formation of surface carbonates. A further reaction channel was provided for low Na coverages where spontaneous dissociation of CO_2 into CO and O occurs even at lowest available temperature.

2. Technical details

The experiments were performed in a magnetically shielded uhv system with a base pressure below 10^{-8} Pa. The uhv system was equipped with 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). The HREEL spectra were recorded using a commercial Leybold–Heraeus ELS 22 spectrometer, operated at 5 eV primary energy with a resolution of, typically, 72 cm^{-1}. The spectra were taken in specular reflection at an angle of 60° to the surface normal.

The Pd(111) crystal was spotwelded between two tungsten wires which were spotwelded 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. Sodium was deposited onto the Pd(111) surface at room temperature by heating a commercial SAES getter* situated 1 cm from the sample. As reported earlier[3] at $\theta_{Na} = 0.4$ we observe a LEED-pattern with $(\sqrt{7/3} \times \sqrt{7/3})$ R10.9° symmetry. After CO_2 exposure no LEED pattern in addition to the substrate spots was observed. In order not to influence the adsorption behaviour all filaments in the uhv-chamber were turned down or off upon admission of CO_2.

The data were fitted by distribution functions. We have chosen Student functions because they include both the Lorentzian and Gaussian distribution as limiting cases[9]. Their contributions to the actual Student distribution are given by a so called form parameter[9]. This parameter together with amplitude, half-width and position of peak maximum comprise a physically meaningful set of parameters for fitting. We obtain a mainly Gaussian character for the presented data.

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*SAES getters Gmbh, Model No Na/NF/35/25/T14 + 14.

3. Results and discussion

3.1. Adsorption and reaction of CO$_2$ at intermediate Na coverage.
Figure 1 illustrates a series of HREEL spectra of a CO$_2$ dosed Na precovered ($\theta_{Na} = 0.25$) 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, which have been discussed in a previous paper[6]. Therefore we only briefly summarize the main results.

By comparison with already published HREELS investigations for the system CO$_2$ on Ni(110)[7], as well as with available ir-data for CO$_2$ in the gas phase[10], CO$_2$-transition metal complexes[11] and CO$_2^-$-alkali salts[12], we identify two species at the lowest temperature on the surface, namely physisorbed CO$_2$ and chemisorbed CO$_2^{\delta-}$. The physisorbed CO$_2$ (marked with arrows in the spectra) shows characteristic losses at 645 cm^{-1} (bending mode), 1298/1368 cm^{-1} (symmetric stretch split by Fermi resonance with the first overtone of the bending mode), and 2340 cm^{-1} (asymmetric stretch).

The chemisorbed bent CO$_2^{\delta-}$ is characterised by vibrational losses at 282 cm^{-1} (metal-CO$_2$ stretch), 744 cm^{-1} (bending mode) and 1210 cm^{-1} (symmetric stretch). Since in electron dipole scattering the intensities of the vibrational losses are determined by the dynamic dipole moment, it is not surprising
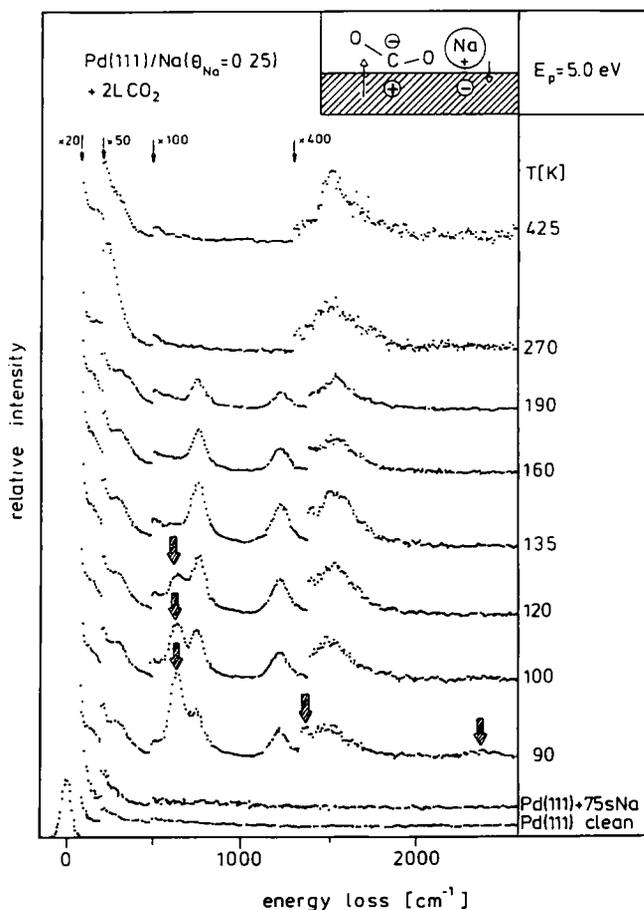
Figure 1. Series of HREEL spectra (specular) of 2L CO$_2$-Na(Θ_{Na} = 0.25)-Pd(111) as a function of temperature. The inset shows a schematic structure that explains the observed loss energies and intensities.

that all losses caused by CO$_2^{\delta-}$ are rather intense. The peak around 1530 cm^{-1} might be either attributed to the asymmetric stretch of CO$_2^{\delta-}$ or to an alkali influenced CO stretch. In order to get more information we have fitted the observed spectra on the above mentioned Student functions as shown in Figure 2. Because all intensities have been normalized to the intensity of the primary elastic beam, they can be taken as a crude measure of the amount of each species on the surface. We plot the intensities of the all observed losses except the highest energy loss (2340 cm^{-1}) as a function of temperature in Figure 3. This figure supports the results of our previous investigation[6]. Upon heating, a decrease of the loss intensities of CO$_2$ together with an increase of the CO$_2^{\delta-}$ signal intensities can be observed. This behaviour indicates that CO$_2$ partly desorbs from the surface and partly transforms into CO$_2^{\delta-}$. In addition, this figure clearly demonstrates that the trend of intensity of the highest energetic loss follows the observed trends in intensities of the peaks at 744 and 1210 cm^{-1}, which were unambiguously attributed to CO$_2^{\delta-}$. Upon further heating ($T > 135$ K), CO$_2^{\delta-}$ obviously dissociates into CO and O as can be verified by the large increase of the high energy loss. Unfortunately, atomic oxygen cannot be observed at temperatures where transformation occurs because oxygen is known to migrate into the bulk of the solid at elevated temperature[13].

Since CO is the most stable species on the Na covered Pd(111) surface we have to expect a monotonic increase of CO induced signal intensity until rapid decrease indicates molecular CO desorption from this surface. Therefore we suggest that at low temperatures the high energy loss is due to the asymmetric stretching vibration of the CO$_2^{\delta-}$ moiety. Because of the fact that all losses of the anionic species are observed we conclude that the adsorption geometry of CO$_2^{\delta-}$ is of C$_s$— and not C$_{2v}$— symmetry as in the case of the free molecule and the CO$_2$-Ni(110) system[7].

At higher temperatures ($T > 135$ K), where CO$_2^{\delta-}$ can no longer be detected on the surface, the loss around 1530 cm^{-1} is now attributed to an alkali influenced CO stretching vibration[2]. The latter result is compatible with the photoemission study[3] where the transformation from CO$_2$ into CO had already been observed. However, identification of CO$_2^{\delta-}$ via photoemission is very difficult because the cross-section of the CO$_2^{\delta-}$ ionizations is known to be very small so that it has not been possible to detect the CO$_2^{\delta-}$ species on the Na covered Pd(111) surface with UPS.

Taking into account the fact that CO$_2$ does not chemisorb on the clean Pd(111) surface[3,14] we propose the following adsorption mechanism as discussed in our previous paper[6]: Na releases its electron to form a strong Na-Pd dipole[2]. The CO$_2$ molecule binds in the vicinity of this dipole and forms a second CO$_2^{\delta-}$-Pd dipole which is orientated 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 CO$_2^{\delta-}$-Pd dipole tries to become as large as possible to counterbalance the former[4]. Since the oxygen atoms carry most of the negative charge in the CO$_2^{\delta-}$ anion the CO$_2^{\delta-}$-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 Figure 1.

Summarizing so far we can state that at intermediate coverage Na acts as a promotor in CO$_2$ activation for dissociation, where the reaction proceeds via a bent, anionic CO$_2^{\delta-}$ precursor.
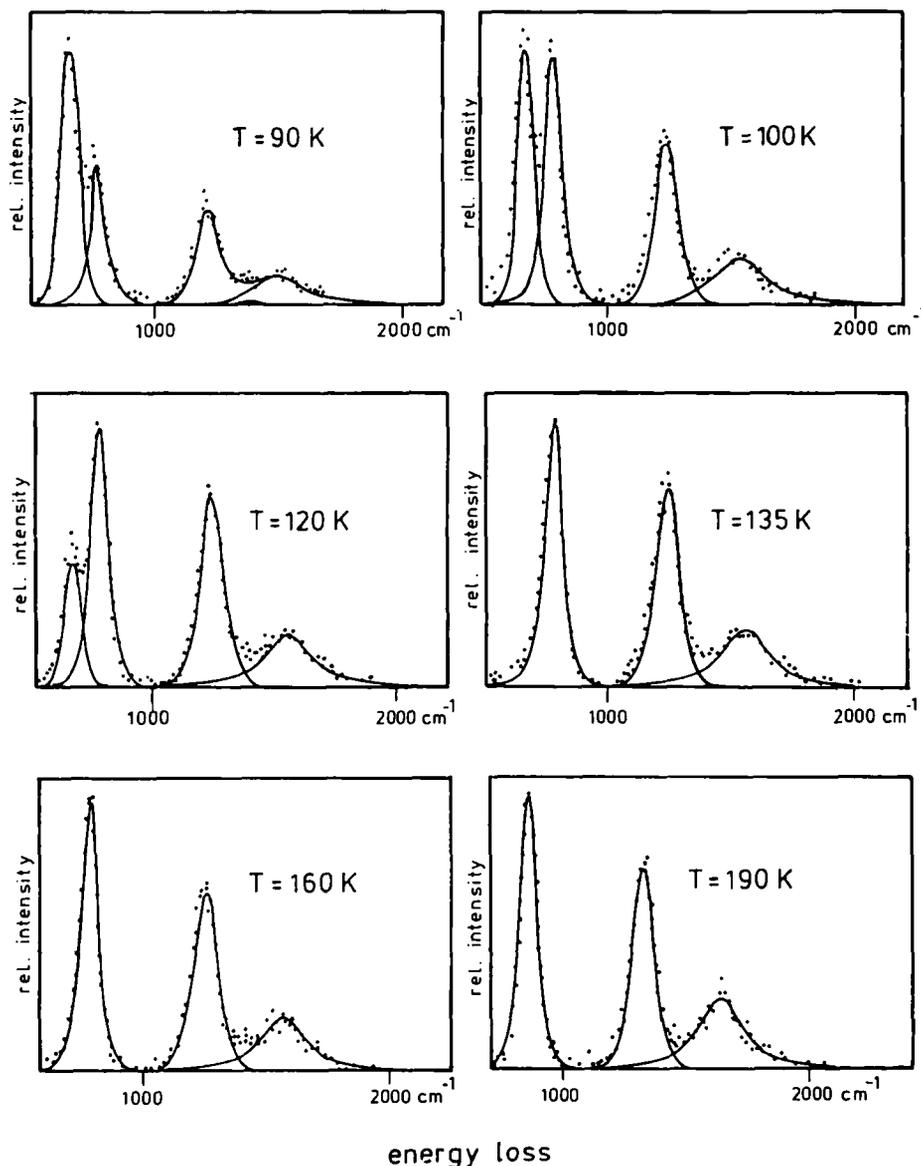
Figure 2. Series of HREEL spectra (specular) of 2L CO$_2$-Na(Θ_{Na} = 0.25)-Pd(111) as a function of temperature. The spectra up to 190 K has been fitted by a set of Student functions (... observed data; —— fitted data).
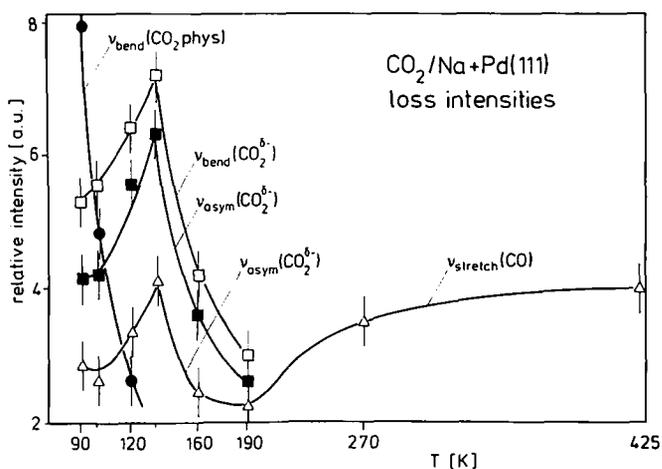
Figure 3. Variation of the loss intensities in the HREEL spectra shown in Figure 1 and Figure 2 with temperature.

3.2. CO$_2$ adsorption and reaction at high and low Na coverages.

In Figure 4 we show a series of HREEL spectra of CO$_2$-Na-Pd (111) adsorbates as a function of Na precoverage at lowest available temperature, i.e. 90 K. All spectra were taken with an exposure of 2L CO$_2$.

The two spectra in the middle of the figure (Θ_{Na} = 0.25; 0.4) represent the situation at intermediate Na coverage as already discussed in Section 1.

At high Na coverage (Θ_{Na} = 2.0) we find losses at 670 and 2363 cm^{-1} caused by physisorbed linear CO$_2$.The peak at 217 cm^{-1} is assigned to a metal–molecule loss. In the region between 850 and 1800 cm^{-1} we find several losses which we attributed to the vibrational modes of mono- and bidentate carbonate[15–17]. This observation is in good agreement with previous photoemission studies[3]. Investigations at an oxygen contaminated Na–Pd-surface[6] as well as Matsushima's studies[5] showed that formation of carbonate necessitates pre-adsorption of oxygen on the surface. The presence of oxygen on the surface at high Na
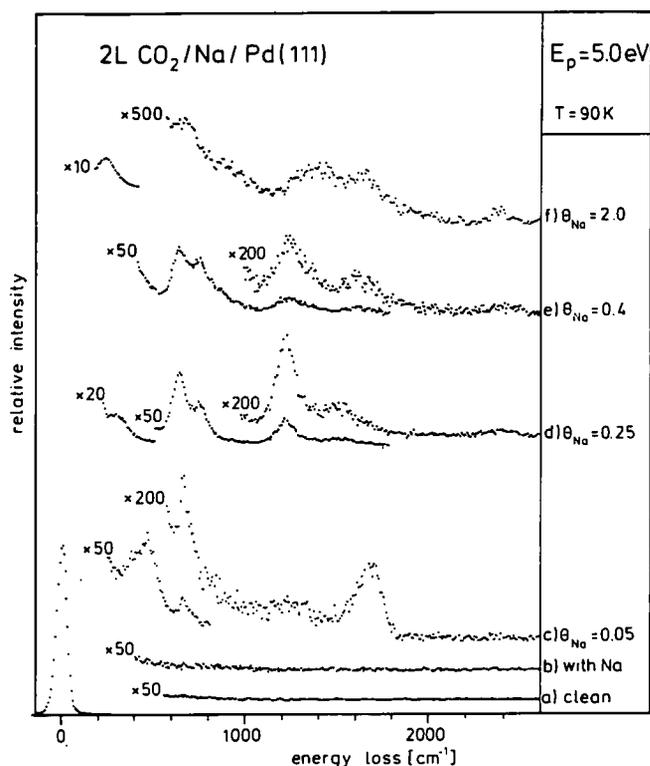
Figure 4. Series of HREEL spectra (specular) of CO_2–Na–Pd(111) as a function of sodium coverage; (b) is identical for all reported Na coverages.

coverages may be caused by CO_2 dissociation into CO and O or by contamination from residual gas phase oxygen during the long time of evaporation required for the preparation of this layer. Experiments with $^{12}C^{18}O_2$ may help to distinguish between these two possibilities.

At Na coverages of 0.05 ML we find that CO_2 dissociates into CO and O, even at 90 K. This can be verified by inspection of Figure 4. Bending mode of physisorbed CO_2 ($644\ cm^{-1}$), metal–O stretching vibration ($460\ cm^{-1}$) and an alkali influenced CO stretching mode ($1690\ cm^{-1}$) can be observed.

4. Summary

In the present study we have shown via high resolution electron energy loss spectroscopy that the adsorption of CO_2 on a surface which is inert with respect to CO_2 can be activated by co-adsorption of sodium. The experiments clearly demonstrate that the activation of CO_2 proceeds at intermediate Na coverages via a bent, anionic $CO_2^{\delta-}$ precursor[18], which leads, if no further reactant is provided, to dissociation into CO and chemisorbed oxygen. At high Na coverages we observe formation of surface carbonate whereas at low Na coverages spontaneous dissociation into CO and O occurs.

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