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Quantitative mass analysis of N₂, CO₂ and N₂O reaction products in the NO-CO reaction at Pt(100)

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Abstract

The NO-CO reaction on Pt(100) was examined using temperature programmed reaction methods. The platinum surface was precovered at -80°C with various amounts of both NO and CO and then heated to 370°C. In this case the reaction occurs within a very narrow temperature range around 120°C exhibiting sharp reaction peaks at the mass numbers 28 (N₂/CO) and 44 (CO₂/N₂O). The reaction products were detected by a quadrupole mass analyzer scanning complete mass spectra of 50 amu width at a speed of 15 spectra per second. Thus the course of the reaction was recorded within a single measurement.

A subsequent analysis of the data using a modified least-squares fit method was applied to the mass spectra in order to gain information on the true composition of the desorbing gas mixture. To this end isotope and cracking patterns were evaluated. This analysis revealed that beside the major reaction products N₂ and CO₂ also minor amounts of N₂O appear on Pt(100).

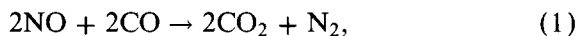
1. Introduction

Platinum is known as a catalyst for a series of reactions, such as the oxidation of hydrogen and carbon monoxide and the reaction between NO and CO, which is of special interest in environmental sciences. Investigations at different platinum single crystal surfaces showed that there are differences in the catalytic activity. Concerning the NO-CO reaction, the (100) and the (410) plane in particular are highly active [1].

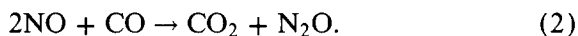
The catalytic reaction of NO and CO on Pt(100) shows two peculiarities. Firstly, in temperature programmed reaction (TPR) experiments, NO and CO coadsorbed on the surface react with sharp desorption peaks of the reaction products when the crystal is heated to temper-

atures above 100°C [2-5]. Secondly, the CO₂ production, monitored by mass spectrometers, exhibits kinetic oscillations under steady flow conditions [6-8]. In recent investigations even the spatial distributions of the adsorbate covered surface areas were studied using the photoelectron emission microscope (PEEM) [9,10], which is based on work function differences for the different adsorbates.

The reaction is known to proceed according to the equation



but another reaction channel is also possible:



Both N₂O and CO₂ correspond to mass number 44 and therefore cannot be distinguished by a mass spectrometer. Production of N₂O has been

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reported for Pt(110) and Pt(111) single crystal surfaces [11] and partly for Pt(410) [12], found by using the ^{13}C and ^{15}N isotopes.

2. Experimental

The experiments were carried out in a standard UHV chamber at a base pressure of 2×10^{-10} mbar. The platinum crystal was cleaned by Ar^+/Ne^+ sputtering, heating for 5 min at 350°C in 5×10^{-8} mbar O_2 and subsequent flashing to 700°C . After this treatment the (hex) reconstruction of the clean Pt(100) surface was clearly visible in LEED investigations. The cleaning procedure is completely computer-controlled regulating the crystal temperature and the gas dosages within an accuracy of 1%.

For coadsorption and TPR studies the crystal surface was covered with both NO and CO sequentially in various amounts and ratios. Additionally, the sequence of precoverage was varied. For that purpose the crystal was cooled down to -80°C and then exposed to the two gases using computer control for the exposures to obtain reproducibilities of 0.05 L.

The results presented here are extracted from measurements applying the method of multi-mass thermal desorption spectroscopy (MTDS) [13] which was developed for monitoring reaction products in a single measurement. It consists of a commercial quadrupole mass analyzer (QMA) [14] detecting all adsorbates and reaction products desorbing from the surface, a transient recorder [15] converting the QMA signal for computer processing and two power supplies [16,17] to operate the electron impact heating for the sample. After preparation of the precovered surface the crystal is heated to 370°C at a selectable heating rate between 2 and 40 K/s. The mass spectrometer continuously scans the mass range of 1 to 50 amu (where all reaction products and their cracking patterns appear) at a scan rate of 850 amu/s thus resulting in 15 complete mass spectra per second. All hardware components are controlled by a computer program in which the entire measurement is a single subroutine call.

Since not only the known reaction products (see Eqs. (1) and (2)) with mass numbers 28 and 44 but also their fragments generated in the QMA as well as unexpected reaction products with mass numbers below 50 are recorded, the data gained from one measurement contain complete information on the course of the reaction. Evaluation of the true composition of the desorbing gas mixture is possible, as will be described in the following section.

3. Mathematical methods

Two gases that appear at the same place in a mass spectrum can only be distinguished if their isotope and cracking patterns are considered. Since the ionization process inside the spectrometer also produces fragments of the incoming molecules with a specific relative intensity, each single gas can be recognized by its characteristic peaks in a mass spectrum [18]. When several gases consisting of a few basic components are present in one mass spectrum, the analysis becomes more difficult and can only be performed by numerical evaluation algorithms. In the case presented here, the compounds of interest are NO, CO, N_2 , CO_2 and N_2O with overlapping major peaks at mass numbers 28 and 44. Taking the ion currents of C^+ , N^+ , O^+ and CO_2^+ as additional parameters, an equation system can be formed which is overdetermined. Its solution yields the partial pressures of the five gases involved. Isotopes may also be considered but often the signals are too small compared to the noise level. The equation can be written as

$$\begin{aligned} C \cdot p &= \begin{pmatrix} C_{11} & \cdots & C_{1g} \\ \vdots & & \vdots \\ C_{m1} & \cdots & C_{mg} \end{pmatrix} \cdot \begin{pmatrix} p_1 \\ \vdots \\ p_g \end{pmatrix} \approx \begin{pmatrix} i_1 \\ \vdots \\ i_m \end{pmatrix} \\ &= i, \end{aligned} \quad (3)$$

where C contains in matrix form the cracking patterns of the gases concerned, i.e. C_{mg} is the peak height at mass number m for the gas g , p is the vector of partial pressures to be found and i is a vector of ion currents taken from a measured mass spectrum. A similar approach to

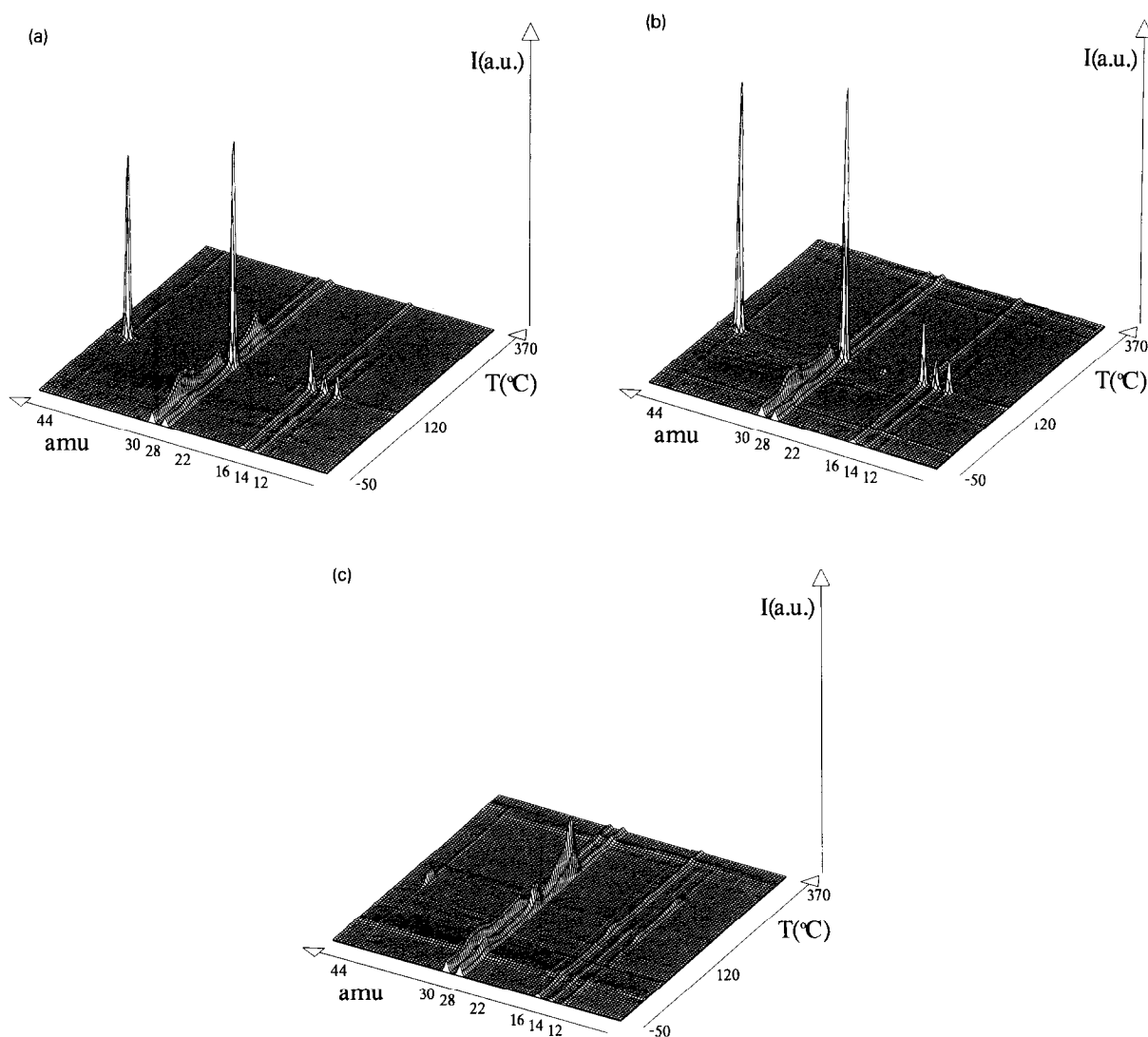


Fig. 1. MTDS spectra of the NO–CO reaction on Pt(100) with various pre-exposures of CO and a subsequent 10 L exposure of NO. CO pre-exposures are (a) 0.25, (b) 0.5 and (c) 1.5 L. The QMA signals are given as a function of mass number and temperature at a heating rate of 4.5 K/s.

the analysis of gas mixtures by matrix calculation is described in Ref. [19].

For the results reported here, Eq. (3) was solved by finding the absolute minimum of the error function

$$E(\mathbf{p}, \mathbf{i}) = \sum_m \left(\frac{\sum_g C_{mg} p_g - i_m}{i_m + c} \right)^2 \quad (4)$$

in an iteration process. The constant parameter c is introduced to vary the characteristics of this error function: If c is large compared to the values of i_m , the denominator becomes constant and E represents an absolute error. If c is small, the fraction represents a relative error, giving smaller peaks more statistical weight. A normal least-squares method (corresponding to

a large value of c in Eq. (4)) was found to be not suitable to distinguish between gases with equal mass numbers since the major peaks were dominating the error function E . The most plausible values with lowest deviations for the major peaks and highest resolving power for competing gases are obtained for a value of c in the region of the mean ion currents i_m .

The numerical procedure was tested by computer-simulated spectra including a generated statistical noise which were calculated from random gas mixtures. The analysis described above could reproduce the composition of the mixtures accurately within the error limits caused by the artificial noise.

Data for the cracking patterns can be found in literature (see for instance Ref. [20]) or may be supplied by the manufacturer of the spectrometer. However, for reliable results, the patterns have to be determined individually since the relative sensitivities and cracking probabilities also depend on the history of every single spectrometer head. Here, we calibrated the spectrometer by recording mass spectra of equimolar mixtures of one pure gas and argon. The argon peak at mass number 40 did not overlap with any other peak and served as a reference to determine the relative sensitivities of the spectrometer for the different gases. C was then compiled by taking the height of each peak appearing in the mass spectrum for a single gas divided by the height of the corresponding ^{40}Ar peak. Since C takes into account the fragmentation and related processes within the ionization region of the QMA and since gas-phase reactions between NO and CO induced by the ionization process are not observed, the results of the analysis reflect the true composition of the incoming gas mixture.

4. Results and discussion

Adsorption studies below room temperature [3] revealed that NO does not displace pre-adsorbed CO in a considerable amount and vice versa. This was confirmed after evaluation of all spectra recorded in this experiment. Since the preparation of the coadsorption systems

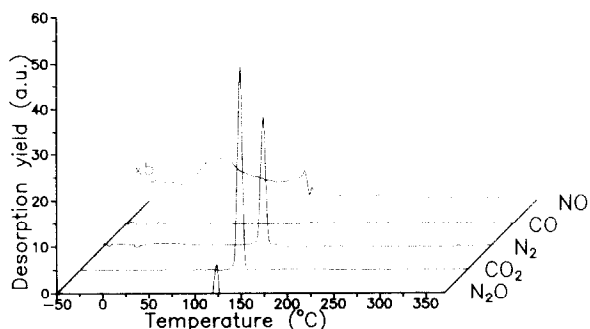


Fig. 2. Gas composition extracted from the spectrum of Fig. 1b. The partial pressures of NO, CO, N_2 , CO_2 and N_2O are given as a function of temperature.

was performed at -80°C and the gases were adsorbed sequentially, the CO and NO precoverages remained constant after postexposure to NO and CO, respectively.

Fig. 1 shows MTDS spectra for three different coadsorption systems of NO/CO/Pt(100) in a three-dimensional picture. To saturate the surface an exposure of 10 L NO was dosed onto the Pt(100) surface after precoverage with (a) 0.25, (b) 0.5 and (c) 1.5 L of CO. The QMA signal is plotted as a function of mass number and temperature. The “explosive” character of the reaction, resulting in sharp desorption peaks of the reaction products N_2 , CO_2 and N_2O (mass numbers 28, 44 and 44, respectively), is clearly visible in Figs. 1a and 1b. The temporal course of the reaction is equivalent to the temperature dependence since the heating rate was constant 4.5 K/s and can be divided into three parts: (1) *before* the reaction where no CO_2 or N_2O but mainly NO desorbs, occurring for temperatures below 120°C , (2) *during* the reaction where CO_2 and N_2O desorb at around 120°C in a narrow temperature range of typically 10 to 20 kelvin and (3) *after* the reaction (up to 370°C) where reaction products are no longer detected but surplus NO or CO molecules desorb.

The numerical analysis described above was applied to all spectra recorded in this experiment. Fig. 2 shows the results for a pre-exposure of 0.5 L of CO and a 10 L exposure of NO on Pt(100). The curves represent the partial pressures of NO, CO, N_2 , CO_2 and N_2O , calculated

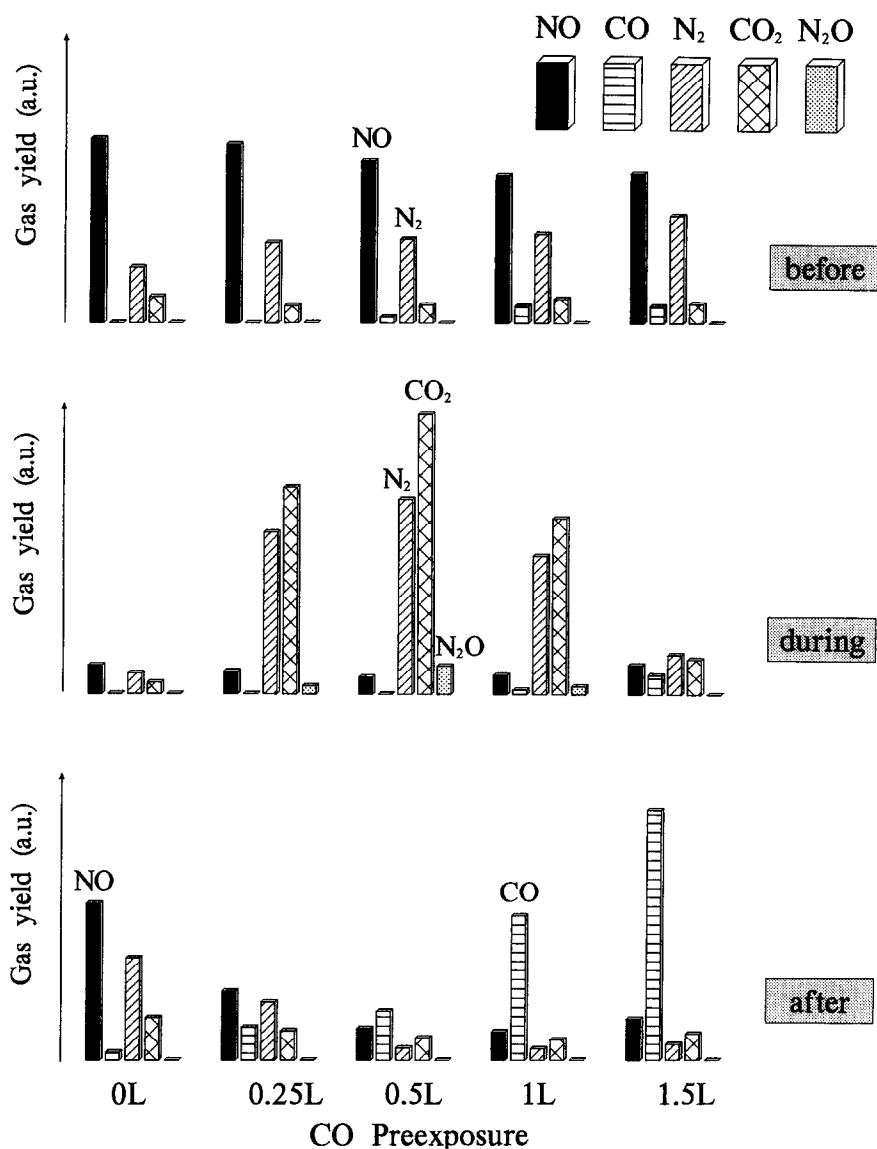


Fig. 3. Summary of the NO, CO, N₂, CO₂ and N₂O desorption yields for a series of CO pre-exposures and a subsequent 10 L exposure of NO. The bars represent the time integrated partial pressures without background correction. The three rows denote the temperature regions *before*, *during* and *after* the reaction.

from the measured ion currents. Since none of the spectra showed peaks at mass number 32 below 370°C, O₂ was not considered here. For a more compact presentation of the results, the areas *before*, *during* and *after* the reaction are integrated representing the total desorption yield for the corresponding temperature regions for each

individual gas. In Fig. 3 a summary of desorption yields for a series of CO pre-exposures is given. Since background subtraction was not applied to the partial pressures prior to integration, the yields may include an offset for the regions *before* and *after* the reaction where many data points contribute. This can be seen in the case of

no CO precoverage where CO desorbs *after* the reaction.

In each case, adsorbed NO is seen to desorb *before* the reaction takes place, accompanied by N₂ desorption due to NO dissociation. This is in agreement with Refs. [2,3,21]. Co-adsorbed CO seems to raise the NO dissociation probability at lower temperatures thus increasing the N₂ desorption yield. The sum of desorbing nitrogen atoms (either as NO or as N₂) is almost constant, indicating that the amount of weakly bound NO is independent of pre-adsorbed CO, at least for CO exposures below 2 L. N₂O is formed *during* the reaction according to Eq. (2), to an extent of 5 to 10% of the amount of CO₂. This occurs at optimum reaction conditions (for CO pre-exposures between 0.25 and 1 L). Obviously, more N₂ is produced than would be expected from the stoichiometry of Eq. (2). No atomic or molecular oxygen is detected since it is tightly bound to the surface and does not desorb at temperatures up to 370°C. *After* the reaction NO or CO molecules not participating in the reaction desorb. The maximum yield of CO₂ and N₂ is therefore to be expected at a CO precoverage for which the desorption of CO and NO molecules is balanced. This is the case for a CO exposure between 0.25 and 0.5 L.

5. Conclusion

By application of MTDS to several coadsorption systems of NO/CO/Pt(100) the NO–CO reaction was studied. Numerical evaluation of the measured ion currents yielded the partial pressures of the desorbing reaction products. N₂O was found to appear among the major products CO₂ and N₂ in the range of 5 to 10% of the corresponding yield of CO₂. The amount of N₂ desorption exceeds the value according to Eq. (1) indicating that part of the oxygen produced by NO dissociation does not react with

CO but remains adsorbed on the surface.

Acknowledgement

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