

FORMATION OF Ru SUBCARBONYLS BY REACTION OF CO WITH STEPPED Ru SINGLE CRYSTAL SURFACES

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The interaction of CO with Ru field emitter surfaces has been studied by pulsed field desorption mass spectrometry (PFDMS) at a pressure of 1.3×10^{-4} Pa CO and temperatures $T_1 = 328$ K and $T_2 = 458$ K. Probing the stepped region in the vicinity of the (001) pole of the Ru field emitter, various ionic species have been detected, including singly and doubly charged species $\text{Ru}(\text{CO})_x^{n+}$ ($x = 1-4$). The intensities of the Ru subcarbonyl species as well as their relative abundances depend on the field strength, the repetition rate of the field pulses (10^4 to 10 Hz) or field free reaction time, t_R (10^{-4} to 0.1 s), and the surface temperature. A consecutive reaction is considered involving chemisorbed Ru subcarbonyl molecules. These $\text{Ru}(\text{CO})_x$ species reach steady surface concentrations at different relaxation times, τ_R , the values of which depend on the temperature. $\text{Ru}(\text{CO})_2$ is formed during an activated process. A reaction model is presented which describes the removal of Ru lattice atoms and their diffusion into the adsorbed layer via $\text{Ru}(\text{CO})_2$ formation as part of a process inducing morphological changes of the Ru emitter apex.

1. Introduction

It has been shown in a large number of investigations that metal catalyst particles undergo changes of their crystallographic structure and morphology during the course of a chemical reaction. However, relatively little is known about the elemental processes leading to the observed changes. In order to improve the knowledge it is necessary to perform studies on geometrically well defined particles by means of in situ experimental techniques.

In the study reported here, a Ru field emitter has been analysed during the reaction with CO. Such a field emitter with its hemispherical apex can be regarded as an excellent model of a catalyst particle. The interaction of CO with Ru field emitter surfaces was already studied by other authors using field electron emission [1,2] or field desorption [3], however, the objective of these studies was different. The motivation for our studies is the partly contradictory results during investigations of CO on supported Ru [4–14], with a recent study showing significant morphology changes of the particles [14].

Pulsed field desorption mass spectrometry (PFDMS) has been used in order to obtain kinetic data about chemical processes occurring at the emitter

surface and changing the micromorphological properties of the emitter apex. PFDMS was already applied in similar investigations on CO/Ni [15,16].

2. Experimental

The experimental technique of PFDMS and its applications to kinetic studies of surface reactions have been described in detail elsewhere [16,17]. The principle of operation is to field desorb adsorbed species by means of high-voltage pulses and to chemically identify the respective ions by time-of-flight mass spectrometry. The field pulses (repetition frequencies up to 100 kHz, amplitudes up to ≈ 19 kV, half widths some 100 ns) are applied to a counter electrode (with a hole, 1 mm diameter) in front of the Ru field emitter. A channel plate image intensifier with a probe hole is mounted at the entrance of the flight tube and allows field electron microscopy at reversed fields. The emitter can be tilted so that ions desorbing from different surface planes can enter the flight tube through the probe hole. The size of the monitored area is calculated from the calibrated onset voltage for krypton field ionization.

Tip temperatures are measured by means of a thermocouple spotwelded to the emitter tip.

The Ru emitter surface is cleaned from carbon and oxygen contaminants by combined cycles of heat treatment (1500 K) and field evaporation.

Pulsed field desorption experiments are performed with a continuous impact of CO (99.995% purity, Messer-Griesheim GmbH) from the gas phase. The impinging molecules accumulate at the Ru surface during the time interval, t_R , between the pulses (fig. 1). The next high-field pulse desorbs the adlayer and analyses its composition in a quantitative manner. Adsorption proceeds as t_R increases. The adsorbing particles can undergo a chemical reaction so that various intermediates and products form in the adsorbed layer. Kinetic information on these processes are obtained by varying t_R . Usually a range $t_R = 100 \mu\text{s} \cdots 1 \text{ s}$ is scanned.

An arbitrary field strength, F_R , between the pulses can be applied in order to investigate the influence of the electrical field on the surface processes.

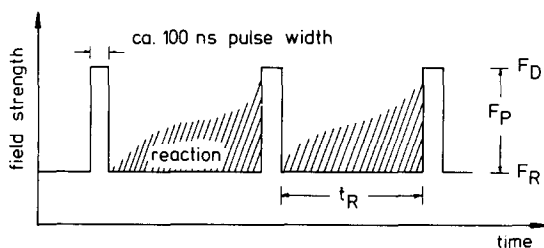


Fig. 1. Time scheme of the field pulses leading to desorption at a field strength F_D which is the sum of F_R (steady field, also called "reaction" field) and F_P (pulsed field).

3. Results

3.1. Mass spectra and steady field influence

The interaction of CO with Ru has been studied by probing the stepped surface region in the vicinity of the (001) pole of the Ru field emitter. The size of the monitored area is 8.8 nm², containing about 140 atomic sites of the Ru(001) plane.

Various ionic species are detected. Besides CO⁺ and Ru⁺, Ru²⁺, singly and doubly charged subcarbonyl species Ru(CO)_xⁿ⁺ (*x* = 1–4) are observed. Also C⁺, C²⁺, O⁺ and various Ru oxides up to RuO₃²⁺ can be seen in the mass spectra. The chemical nature of these ionic species indicates CO dissociation to take place. It has been observed that the C–O bond scission is promoted by the steady field strength, F_R . Higher Ru oxides are only formed during long time exposure to CO at elevated temperatures $T \geq 458$ K. For the experimental conditions applied in the present study the ion intensities of carbidic and oxidic species are always small. Details will be published elsewhere.

The ionic intensities of the subcarbonyl species, Ru(CO)_xⁿ⁺, are found to depend on F_R . This dependence is shown in fig. 2. For $F_R = 0$, the mass spectrum contains the subcarbonyl species up to Ru(CO)₄²⁺ (fig. 2a). When increasing F_R at constant desorption field strength, F_D , the ionic intensity of Ru(CO)₄²⁺ decreases. At $F_R \geq 7$ V/nm it drops to zero (fig. 2b). A decreasing trend is also observed for the CO⁺ intensity, whereas the Ru(CO)₃²⁺ intensity

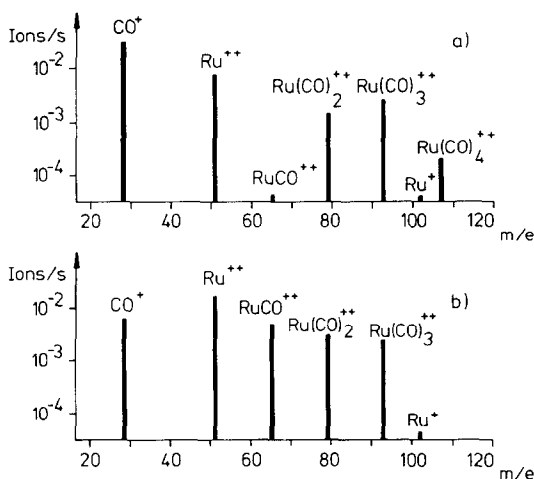


Fig. 2. Time-of-flight mass spectra containing doubly charged ¹⁹²Ru subcarbonyl ions. The plotted intensities consider the Ru isotope distribution. Experimental parameters: $t_R = 10$ ms, $T = 328$ K, $p_{CO} = 1.3 \times 10^{-4}$ Pa, $F_D = 29$ V/nm. (a) $F_p = 29$ V/nm, $F_R = 0$; (b) $F_p = 22$ V/nm, $F_R = 7$ V/nm.

remains constant, and the smaller homologs, RuCO^{2+} and Ru(CO)_2^{2+} , become more abundant with increasing F_R .

The observed Ru(CO)_x^{2+} ions indicate a consecutive surface reaction to take place involving their neutral molecules. This reaction is connected with a change of the electrical moment, thus an influence of the electrical field is expected. It is found that the field F_R increases the intensities of the low-index Ru(CO)_x species.

3.2. Variation of the desorption field strength

Fig. 3 shows the results of a desorption field strength variation measurement (pulses only, no steady field, $F_R = 0$) at $t_R = 1$ ms, $p_{\text{CO}} = 1.3 \times 10^{-4}$ Pa and $T = 328$ K. Several interesting observations are made. Firstly, the onset values of the field strength are different for the various species. At low field strengths, F_p , only the CO^+ ion intensity is high. Ru(CO)_3^{2+} and Ru(CO)_4^{2+} appear next, Ru(CO)_2^{2+} rises subsequently. RuCO^{2+} is observed only at the highest field strength values. The different onset field strengths of the

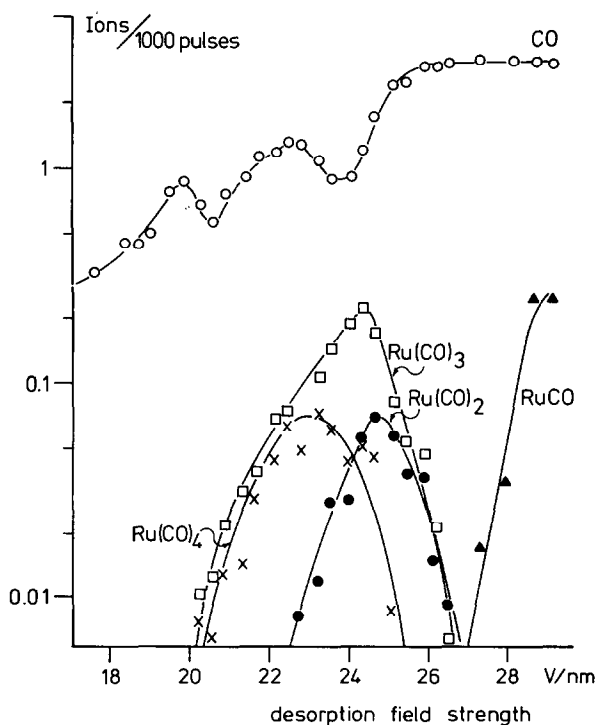


Fig. 3. Experimental intensities as function of the desorption field strength (pulses only, no steady field). Experimental parameters: $t_R = 1$ ms, $T = 328$ K, $p_{\text{CO}} = 1.3 \times 10^{-4}$ Pa.

$\text{Ru}(\text{CO})_x^{2+}$ species are determined by differing ionization potentials and variable surface binding energies of the neutral Ru subcarbonyls. The occurrence of RuCO^{2+} ions can be understood as field desorption of chemisorbed CO with the simultaneous removal of Ru atoms. Similar observations were made with other adsorption systems [15,18].

The intensities of the various ionic species follow different trends during variation of F_p . The CO^+ intensity curve does not rise continuously. Rather it shows considerable fluctuations until it levels off at high field strengths. The intensity fluctuations at low F_p are not unusual. Such observations can always be made if diffusion into or out of the monitored area takes place during t_R . A diffusion process of CO within a second physisorbed adlayer is considered here, since at low field strengths the concentration of chemisorbed CO is high and nearly unaffected by the pulses. At high field strengths the CO^+ curve does not increase any further. The intensity level corresponds to the amount of material impinging from the gas phase and adsorbing at the surface during t_R . Thus complete field desorption of CO_{ad} is achieved.

The field strength dependence of the $\text{Ru}(\text{CO})_x^{2+}$ ($x=2-4$) species is of special interest and differs considerably from RuCO^{2+} . Their intensities first reach maxima at medium F_p values before decreasing steeply later on. The maxima are due to diffusional supply from the shank. Similar observations have been made for Ni-subcarbonyls formed during interaction of CO with Ni [15,16]. At higher F_p values diffusion does not influence the measured ion intensities any longer since the migrating particles are field desorbed before entering the monitored area.

Besides this mobility aspect of the $\text{Ru}(\text{CO})_x$ species, some kinetic features of their formation also become apparent from fig. 3. At the highest F_p values the intensities of the $\text{Ru}(\text{CO})_x^{2+}$ ions drop down. This behaviour can be easily understood by considering a consecutive formation mechanism which involves the successive addition of CO_{ad} to the respective precursor subcarbonyl species. However, the CO_{ad} concentration is relatively small at high field strengths and for $t_R = 1$ ms. Thus the rate of $\text{Ru}(\text{CO})_x$ formation cannot be high and the respective surface concentrations of these species must be small. The complete absence of high index $\text{Ru}(\text{CO})_x^{2+}$ ions must be explained by an initial (activated) step which needs much more time than $t_R = 1$ ms.

3.3. Reaction time variations

The results of fig. 3 indicate that a variation of t_R at high pulsed field strength, F_p , should provide information about the kinetics of $\text{Ru}(\text{CO})_x$ formation. Such measurements have been performed at $F_p = 29$ V/nm and temperatures $T_1 = 328$ K (fig. 4) and $T_2 = 458$ K (fig. 5). The plotted intensities are a measure of the surface concentrations of the respective species built up in the monitored area during t_R .

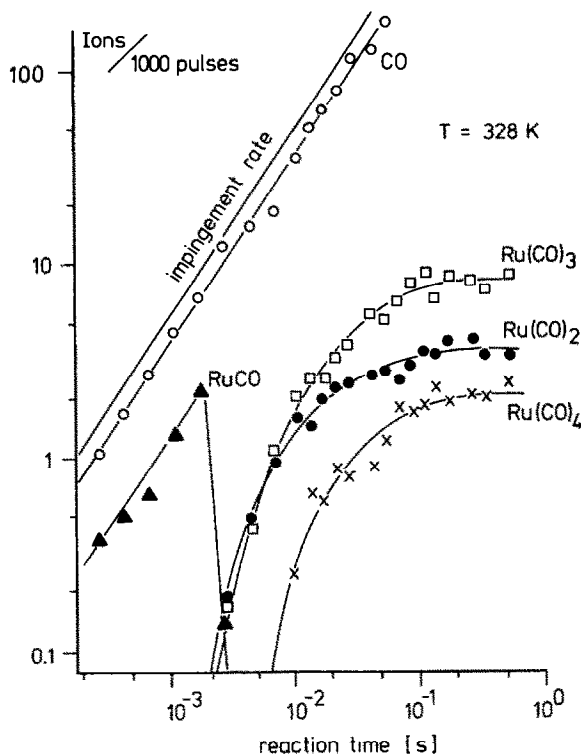


Fig. 4. Experimental intensities as function of the reaction time t_R , monitored at an area of about 140 surface sites (impingement rate ≈ 6.5 CO/s referring to a calibrated transmission of 18% for the mass spectrometer). Experimental parameters: $F_p = 29$ V/nm, $F_R = 0$, $T = 328$ K, $p_{CO} = 1.3 \times 10^{-4}$ Pa.

The various ionic species exhibit different time dependencies. Fig. 4 is inspected first. At short times, $t_R < 2$ ms, only CO^+ and $RuCO^{2+}$ are discernible. Their intensities are directly proportional to the impingement rate of CO_{gas} which has been determined by a separate field ionization experiment with a steady field. At $t_R > 2$ ms, however, $RuCO^{2+}$ disappears completely while CO^+ follows the same trend as before. By comparing the CO^+ intensity slope, i.e. the adsorption rate, with the impingement rate, sticking probabilities of $0.4 \cdots 0.9$ are obtained. These values are in reasonable agreement with $S_0 = 0.7$ as determined by Pfnür and Menzel [19] for adsorption on Ru(001) at the low-coverage limit. It must be concluded (within the margin of error of our measurements) that CO chemisorbs with an initial probability unaffected by the presence of steps.

$Ru(CO)_2^{2+}$ and $Ru(CO)_3^{2+}$ appear at nearly the same time, $t_R \approx 2$ ms, with equal intensities. $Ru(CO)_4^{2+}$ comes up somewhat later. As long as the inten-

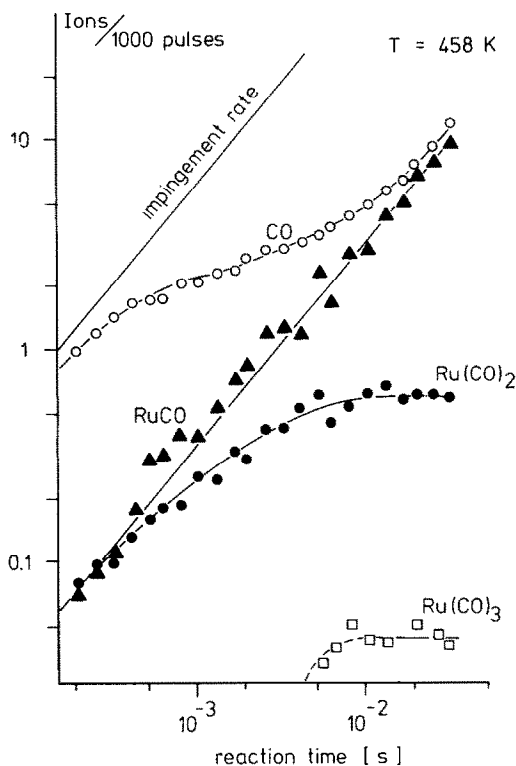


Fig. 5. Experimental intensities as function of the reaction time t_R . Same parameters as in fig. 4, except for $T = 458$ K here.

sities increase, the rates of formation and forward reaction dominate over the rates of back reaction of the respective neutral species. At long times, t_R , the intensities of the Ru(CO)_x level off and indicate steady surface concentrations. For the Ru(CO)_3 we find $c \approx 3 \times 10^{-4}$ molecules/site, which is higher than for the other subcarbonyl species at $T = 328$ K. The constant level portions of the concentrations indicate that the rates of formation, forward and backward reactions, counterbalance. It is observed that the Ru(CO)_2 concentration levels off first. The corresponding relaxation time, τ_R , which is the time to reach the $1 - 1/e$ value of the saturation concentration in a first order reaction, is $\tau_R \approx 30$ ms. This time is shorter than the respective times for Ru(CO)_3 and Ru(CO)_4 , which coincide and amount to ≈ 70 ms.

At a higher reaction temperature, $T_2 = 458$ K, the kinetic features of the Ru(CO)_x species are different and appear as follows (fig. 5). As compared to fig. 4 the steady Ru(CO)_3 concentration is drastically lower and only slightly above the detection limit, and Ru(CO)_4 is not seen at all. The steady Ru(CO)_2

concentration has also diminished substantially; however, it appears at short times t_R without any time lag. The relaxation time has shifted to shorter values and is found to amount to $\tau_R \approx 3$ ms. The observed temperature dependence indicates the Ru(CO)_2 formation to be associated with an activated process. It is likely that this process comprises the removal of a Ru atom from its lattice position. At $T_2 = 458$ K, CO_{ad} undergoes considerable thermal desorption from the Ru(001) terraces. Therefore, the CO_{ad} concentration is smaller than at $T_1 = 328$ K and high-index Ru(CO)_x species cannot form in significant amounts.

The CO^+ trace in fig. 5 shows a non-linear behaviour. At small t_R the measured CO^+ intensities are relatively high, and correspond to the amount of gaseous CO which adsorbs during t_R . Again, comparison with the impingement rate yields high sticking probabilities. The CO^+ intensities in this time range correspond to surface coverages $c_{\text{CO}} \leq 10^{-4}$ monolayer. Thus the measured S values refer to the zero-coverage limit. In addition, the apparent temperature independence of S_0 values indicates initial CO adsorption to be non-activated. These results agree with those of Pfnür and Menzel [19] on macroscopic Ru(001) surfaces. At times $t_R > 0.5$ ms the CO^+ intensity is considerably smaller than expected from the impingement rate of gaseous CO. This deviation indicates thermal desorption occurring during t_R . Such an interpretation would be in accord with the results of Klein [1] and Kraemer and Menzel [2] who also used Ru field emitter tips and observed the main part of the CO_{ad} layer to desorb thermally between 350 and 500 K. However, it comes as a surprise that thermal desorption occurs in the millisecond time scale. In fact, a longer time constant would have been expected in view of the results obtained by Pfnür et al. [20] for desorption from flat Ru(001). The PFDMS technique always samples the most stable (longest lifetime) adsorption states of the equilibrated layer and it is likely that these states are located at the step sites of the field emitter surface. It is believed that detailed equilibrium measurements at various temperatures must be performed in order to arrive at conclusions about the observed behaviour of the CO trace in fig. 5. This applies also to the increasing trend of the CO_{ad} concentration at long reaction times which so far can only be understood in terms of higher-order processes involved in the equilibration of the adsorbed layer.

The RuCO^{2+} ions indicate field desorption of chemisorbed CO by Ru_n -Ru bond breaking. The desorption process occurs preferentially at step sites where n is small.

4. Discussion

The interaction of CO with a stepped Ru surface, comprising (001)-oriented terraces, has been studied by means of PFDMS. The ionic species Ru(CO)_x^{2+}

up to $x = 4$ are formed. A field-induced formation of these species can be excluded on account of the dependencies of the ion intensities on the field strengths, F_R and F_p (fig. 2 and 3), on the reaction time and on the surface temperature (figs. 4 and 5). From the absence of $\text{Ru}(\text{CO})_4^{2+}$ at high F_R we must conclude that the corresponding neutral species is a product of the field-free surface reaction. In fact, the observed influence of the reaction field leads to the assumption that during the rising part of the pulse the electrical field forces the reaction to run *backward* so that the observed amount of $\text{Ru}(\text{CO})_4^{2+}$ ions may be even smaller than the concentration of $\text{Ru}(\text{CO})_4$ before the pulses.

The dependence of the $\text{Ru}(\text{CO})_x^{2+}$ ($x > 2$) intensities on the pulsed field strength gives strong evidence for surface mobility of the respective neutrals. Thus, these species must be weakly chemisorbed on the $\text{Ru}(001)$ terraces.

The kinetics of the $\text{Ru}(\text{CO})_x$ formation have been studied by reaction time variations. It might be suspected that surface diffusion from the shank of the Ru emitter into the monitored area perturbs the true reaction kinetics. The longer the time t_R the stronger this perturbation should be. However, diffusion cannot change the steady surface concentrations of $\text{Ru}(\text{CO})_x$ at long t_R . A shift of the relaxation times τ_R towards shorter values is conceivable.

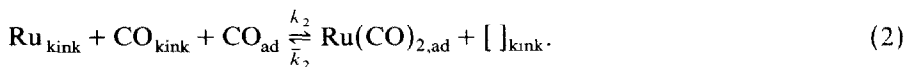
The occurrence of RuCO^{2+} has been attributed to field desorption from steps. A direct competition of RuCO^{2+} field desorption and $\text{Ru}(\text{CO})_2$ formations can be envisaged in order to account for the observed time dependence of RuCO^{2+} intensities at different temperatures. If the CO_{ad} concentration is small the change for RuCO^{2+} ion formation is high. Thus, only at short t_R or high temperatures such that CO_{ad} desorbs thermally, the RuCO^{2+} intensities follow a straight line t_R dependence.

The following reaction scheme can be derived from the experimental data. Reversible adsorption occurs with high initial sticking probabilities, S_0 . Different states, associated with adsorption at step sites, $[\]_{\text{step}}$ (including ledges and kinks), and at terrace sites, $[\]_{\text{ad}}$ can be occupied.



Direct adsorption at step sites can also occur. Since the terrace sites dominate, the pathway (1b) is more likely.

$\text{Ru}(\text{CO})_2$ is formed during an activated process. This process is likely to be associated with the removal of a Ru atom from a kink step site position and its diffusion into the (001) terrace region.



$[\]_{\text{kink}}$ must not necessarily be reproduced as will be discussed below.

The formation of the higher index $\text{Ru}(\text{CO})_x$ species occurs on the (001)-oriented terraces by successive addition of CO_{ad} to the respective precursor species. A consecutive reaction mechanism is in accord with the $t_{\text{R}}(T)$ dependence of $\text{Ru}(\text{CO})_x$.

A similar kinetic mechanism was derived for the formation of $\text{Ni}(\text{CO})_x$ ($x \leq 3$) from Ni and gaseous CO after PFDMS studies [16]. In addition, field ion microscopy (FIM) was employed [21] and direct evidence could be obtained for the removal of kink site nickel atoms from the lattice during the interaction with CO. Similar measurements are currently being performed for CO/Ru. It is interesting that PFDMS results on Ni showed that step (2) does not occur before the chemisorbed layer is saturated by CO_{ad} . It was concluded that the compression structure which forms on low-index Ni planes is a prerequisite for the formation of $\text{Ni}(\text{CO})_2$. In the present study, $\text{Ru}(\text{CO})_2$ species are detected also at CO_{ad} concentrations far below the monolayer limit.

Determination of the rate-controlling step during the $\text{Ru}(\text{CO})_x$ formation is not straightforward. Reaction time variation measurements at $T_1 = 328$ K show the $\text{Ru}(\text{CO})_2$ formation to be associated with an incubation time, whereas the forward reaction to $\text{Ru}(\text{CO})_3$ is fast. At $\tau_{\text{R}} \approx 30$ ms, $\text{Ru}(\text{CO})_2$ reaches its steady concentration. The longer relaxation time for achieving a steady $\text{Ru}(\text{CO})_3$ concentration must then be due to a small rate of the backward reaction towards $\text{Ru}(\text{CO})_2$. Further measurements at different temperatures and various CO gas pressures will address this point.

It has been observed during the present study that CO_{ad} may decompose on the Ru field emitter surface. The decomposition most likely takes place at step sites. Shincho et al. [22] arrive at the same conclusion from studies on macroscopic $\text{Ru}(1,1,10)$ single crystal surfaces. Once dissociation took place, further CO adsorption may be blocked by carbon and oxygen. However, during PFDMS experiments neither species can accumulate at the surface. Consequently, a poisoning effect of the $\text{Ru}(\text{CO})_x$ formation is not observed here.

Step (2) of the outlined mechanism considers the concentration of $[\]_{\text{kink}}$ to be stationary. This is a good approximation for our experimental conditions, where continuous field evaporation of the Ru substrate preserves the kink sites. However, in studies on supported Ru [4–14] or Ru films [23] these sites are irreversibly consumed. Clearly, this will lead to smoothening [23] and faceting of the surface and to morphological changes of the metal particles as observed by Park et al. [14].

The results of the present study confirm the multiple adsorption model as suggested from IR results of CO on supported Ru [6,7,10–12]. $\text{Ru}(\text{CO})_x$ absorption is observed predominantly on small particles [7]. According to our results $\text{Ru}(\text{CO})_x$ formation must be regarded as a general phenomenon for stepped Ru surfaces. The absence of $\text{Ru}(\text{CO})_x$ IR absorption at large particle sizes is presumably a sensitivity problem and caused by too few steady state kink sites and $\text{Ru}(\text{CO})_x$ species on these crystallite surfaces.

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