# Summary Abstract: Adsorption and decomposition of formic acid on clean and potassium-dosed Rh(111) surfaces

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## I. INTRODUCTION

It has emerged that adsorbed formate is an important surface species in several reactions catalyzed by supported rhodium, such as the water–gas shift reaction, the synthesis and decomposition of $CH_3OH$, and the hydrogenation of CO and $CO_2$.[1,2] In this work, which has a strong link with the above studies, we have investigated the interaction of HCOOH with clean and potassium-dosed Rh(111) surfaces by means of various spectroscopic methods: Auger electron spectroscopy (AES), ultraviolet photoemission spectroscopy (UPS), energy loss spectroscopy (ELS) (in the electronic range), and thermal desorption spectroscopy (TDS). Potassium was deposited on the Rh(111) sample from a SAES getter.

## II. CLEAN Rh(111) SURFACE

The thermal desorption spectra of HCOOH following its adsorption at 100–150 K indicate that HCOOH adsorbs strongly and dissociatively on Rh(111) up to 0.4 L. This process was accompanied by the development of a weak loss at 11.3 eV in the ELS (in the electronic range). Further exposure resulted in a desorption peak at 203 K ($\beta_1$) and the appearance of losses at 8.2 and 14.2–14.8 eV attributed to adsorbed HCOOH. A low-temperature peak, which did not saturate with exposure, was observed in TDS at 170 K ($\alpha$) (Fig. 1). This peak can be attributed to the desorption of a multilayer. The adsorption of HCOOH resulted in peaks at 6.2, 8.9, 10.0, 11.5, and 16.0 eV in He II spectra characteristic of molecularly adsorbed HCOOH.[3] Changes observed in the spectra occurred at 150–160 K: the peak associated with the 10*a* and 2*b* orbitals of HCOOH, initially centered at 6.2 eV, broadened and shifted to lower binding energy, to 5.3 eV. An additional photoemission peak, at 13.2 eV, indicative of formation of formate anion,[3] was clearly detected above 158 K.

The decomposition of formate species starts above 200 K (Fig. 1), as indicated by the evolution of $H_2$ ($T_P = 293$ and 385–323 K) and $CO_2$ ($T_P = 277$–$300$ K). The onset of decrease in the intensity of the 11.3-eV loss and the photoemission peaks also occurs at this temperature. These spectral features were entirely eliminated at 250–300 K, suggesting that the decomposition of formate is completed. In addition to $H_2$ and $CO_2$, CO is also formed in the surface reaction. The lowest temperature at which adsorbed CO was detected with UPS was 240 K. The desorption of CO occurred in one peak, with $T_p = 530$ K.

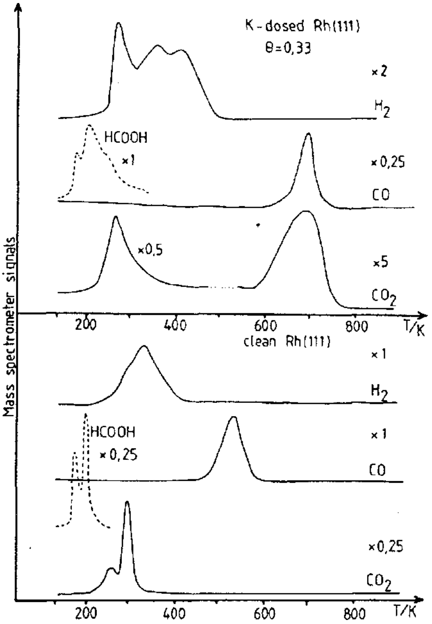

FIG. 1. Thermal desorption spectra following HCOOH adsorption on clean and K-dosed Rh(111) surfaces at 100 K.

## III. POTASSIUM-DOSED Rh(111) SURFACE

Preadsorbed potassium significantly altered the adsorption and reactions of HCOOH on this Rh surface. It led to the transformation of weakly held HCOOH to a more stable adsorbed formate, induced a new adsorption state ($\beta_2$) with $T_p = 253$ K (Fig. 1), and increased the surface concentration of the most stable adsorbed formate. The amount of weakly adsorbed HCOOH ($\alpha$) gradually decreased with the increase of the potassium concentration. The appearance of this state at monolayer K coverage ($\theta_K \approx 0.36$) required a three times larger HCOOH exposure than on the clean surface.

The intensity of the photoemission peak at 13.2 eV increased from 172 up to about 230 K, and started decreasing above 240 K. This peak disappeared only at 422 K. Intense new broad peaks appeared at 11.8 and 9.8 eV, due to adsorbed CO, with a weak one at 8.1 eV. This latter very probably corresponds to a carbonatelike species.[4] These peaks vanished only around 700 K. Thermal desorption studies showed that the amounts of $CO_2$ and $H_2$ slightly increased up to $\theta_K = 0.15$–$0.18$, then decreased. With the increase of the $\theta_K$ value, the absolute amount of CO and its ratio to $CO_2$ were gradually enhanced. At the same time, the peak temperature for the desorption of CO was shifted from 530 to 706 K ($\theta_K \sim 0.3$), which is a result of the stabilizing effect of potassium on the adsorbed CO (Fig. 1). From $\theta_K = 0.21$, a new high-temperature desorption peak of $CO_2$ appeared, at 693 K, which is indicative of the formation of a carbonatelike species.[5]

All these results suggest that preadsorbed potassium promotes the dissociation of HCOOH and increases the surface concentration of the more stable formate anion. This effect can be attributed to the enhanced electron donation from the K/Rh surface. However, the considerable stabilization of the formate species on the K/Rh surface leads us to assume a direct interaction between potassium and HCOOH, resulting in the formation of potassium formate. This interaction is supported by the observed shift in K (3*p*) level to lower binding energy in the He II difference spectra, which was considered to be an indication of a local interaction between K and the other adsorbed species.[6]

[1] F. Solymosi, A. Erdöhelyi, and T. Bánsági, J. Catal. 68, 371 (1981); 72, 166 (1981).

[2] A. Deluzarche, J. P. Hindermann, R. Kieffer, and A. Kiennemann, Rev. Chem. Intermed. 6, 255 (1985).

[3] R. W. Joyner and M. W. Roberts, Proc. R. Soc. London Ser. A **350**, 107 (1976).

[4] J. A. Connor, M. Considine, and I. H. Hillier, J. Chem. Soc. Faraday Trans. 2, 1285 (1978).

[5] F. Solymosi and L. Bugyi, Faraday Symp. Chem. Soc. (to be published).

[6] M. Kiskinova, G. Pirug, and H. P. Bonzel, Surf. Sci. 133, 321 (1983).