

METHANOL DECOMPOSITION ON Pd(111) STUDIED WITH XPS AND PM-IRAS

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A good knowledge of the physico-chemical processes taking place on metal surfaces during catalytic reactions is highly desirable for many technological applications, but still far from being attainable in many cases. Even simple and paradigmatic cases are, unfortunately, not fully understood. One of the several concerns is the difference in pressure usually existent between surface science studies and real catalytic reactions.

Methanol adsorption and decomposition on metal surfaces has traditionally being the subject of many studies in the past. Since it is a model simple molecule with three kinds of bonds, it can be regarded as a model hydrocarbon, convenient for basic research. Moreover, attention towards the interaction of this molecule with metal surfaces has considerably increased in the last years due to the fact that it is being currently used in direct methanol fuel cells as a hydrogen reservoir. Anyhow, as mentioned before, many aspects of the methanol-surface interplay are unknown, such as the mechanisms responsible for the C-O bond breaking, which may lead to the catalyst poisoning and further deactivation [1].

Methanol decomposition on metal surfaces may proceed via dehydrogenation to CO and hydrogen or via C-O bond scission to carbonaceous species (CH_x), CH_4 and H_2O . In this work we have studied the possible reaction pathways and molecular species on Pd(111) by combining X-ray photoelectron spectroscopy (XPS) and polarization-modulation infrared reflection-absorption spectroscopy (PM-IRAS). PM-IRAS is able to identify adsorbed species under high-pressure conditions. Thus, we have studied this system for either pressures in the UHV range and for high pressures as well.

During methanol desorption (from 110 K to 400 K), the complete molecule dehydrogenation was observed. Only small amounts of CO remained, while no carbon or CH_x deposits were detected. In contrast, in the 10^{-7} - 10^{-4} torr methanol pressure range and at temperatures between 300 and 450 K, significant amounts of CH_x species were detected, suggesting a considerable activity of Pd(111) for methanolic C-O bond scission. Methoxy, formaldehyde and formyl were also identified as intermediate decomposition products by PM-IRAS. A continuous deactivation of the surface was observed. The influence of surface defects (created by ion-bombardment) was also addressed.

In the high pressure range, methanol decomposition was examined by in-situ PM-IRAS, gas chromatography (GC) and post-reaction XPS analysis. Equivalent intermediates species as in the low-pressure range were observed. Furthermore, PM-IRAS spectra of CO adsorption on Pd(111) up to 128 Torr, acquired using a UHV-high pressure cell, did not show any indications of CO dissociation. Consequently, CH_x species must originate from C-O bond scission within CH_xO species and not from the dissociation of the final dehydrogenation product, CO.

Methanol oxidation to CO_2 and H_2O was also monitored with PM-IRAS, allowing a simultaneous detection of adsorbed and gas phase species. Products of methanol

decomposition were rapidly reacted away and only CO was observed during the reaction, which may be a surface spectator species.

References:

[1] O. Rodríguez de la Fuente, M. Borasio, P. Galletto, G. Rupprechter and H.-J. Freund, *Surface Science*, **566-568** (2004), 1024.

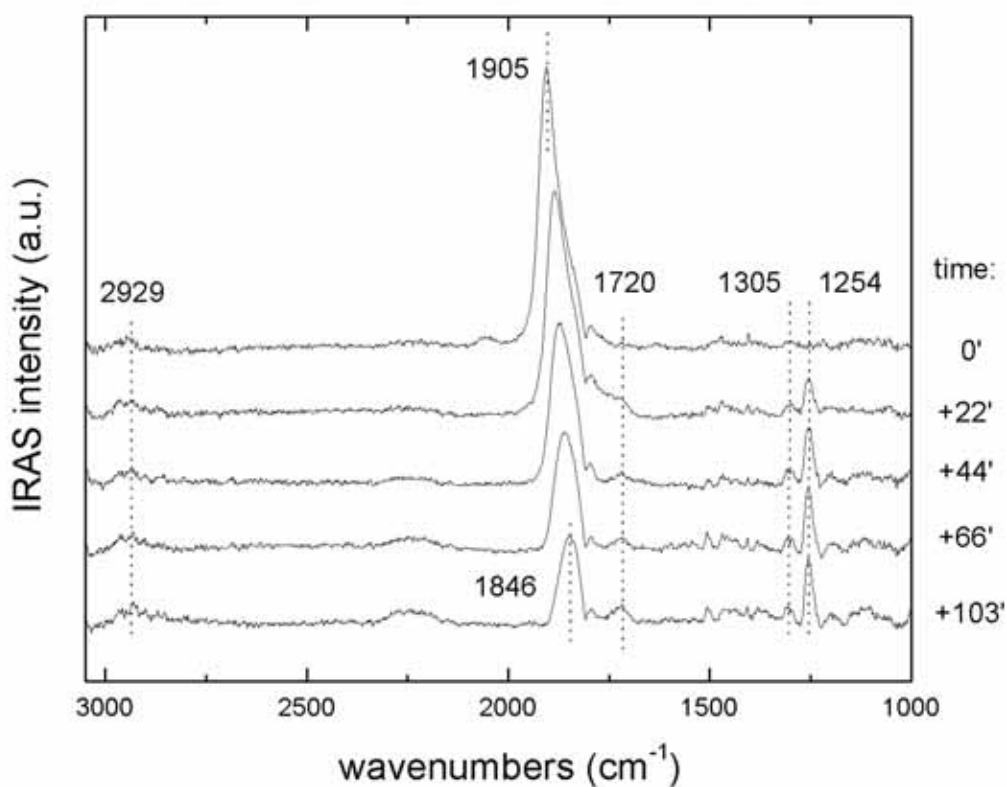


Figure 1: PM-IRAS spectra of the Pd(111) surface during continuous methanol exposure at 7×10^{-5} torr and 300 K after increasing times. The most relevant absorption bands indicate the existence of CO (1905-1846 cm^{-1}) and formaldehyde species (1305-1254 cm^{-1}). The decreasing CO band intensity (together with other experimental evidences) suggest a surface deactivation mechanism is taking place.