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# The effect of adsorbed CO on the surface chemistry of CH<sub>3</sub> on Rh(1 1 1)

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## Abstract

The adsorption and reaction of methyl groups on clean and CO-modified Rh(1 1 1) have been studied using reflection absorption infrared spectroscopy and thermal desorption spectroscopy. It was found that co-adsorbed CO markedly stabilized CH<sub>3</sub> on Rh(1 1 1) and increased its stability above 100 K. In harmony with the stabilization effect, new high-temperature hydrogen and methane desorption states are observed. Co-adsorbed CO, however, did not influence the reaction pathway of the methyl group, dehydrogenation and hydrogenation were the dominant reaction routes. The observed CH<sub>3</sub> stabilization is explained by site blocking and electronic effects.

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## 1. Introduction

Alkyl fragments are believed to be important intermediates in a number of technological applications. In these processes, such as combustion, Fischer–Tropsch synthesis and oxidative coupling of methane, the alkyl groups are unstable and are expected to react with high probability. Recently, the surface chemistry of alkyl moieties has been well documented on a number of metal surfaces [1–3]. On the Rh(1 1 1) surface it was found that a fraction of CH<sub>3</sub> is hydrogenated to CH<sub>4</sub> above 150 K, another fraction exists on the surface up to 325 K and decomposes through the formation of CH<sub>x</sub> species to hydrogen and surface carbon [4,5].

Surface modifiers are often added intentionally in order to regulate the reaction pathway. Recently, the effect of potassium and other adatoms (Zn, I and O) on the chemistry of adsorbed CH<sub>3</sub> on the Rh(1 1 1) surface was examined [5]. The stability and reaction pathway of adsorbed CH<sub>3</sub> are only slightly influenced by the presence of co-adsorbed Zn and I atoms. Potassium, however, increased the stability of adsorbed CH<sub>3</sub> above 100 K. Adsorbed O atoms reacted with gaseous CH<sub>3</sub> to give methoxyl, CH<sub>3</sub>O species.

Co-adsorption of CO with hydrocarbon moieties is also of technical interest. In an earlier study, it was shown that CO may assist in the formation of an ordered structure of hydrocarbon species on various metal surfaces [6,7]. It has also been found that CO is capable of stabilizing C<sub>2</sub>-hydrocarbon fragments on Ni(1 0 0) [8] and Ru(0 0 1) [9]. In previous studies, Winograd et al.

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found that adsorbed  $\text{CH}_3$  produced by thermal decomposition of  $\text{CH}_3\text{I}$  was stabilized by CO on  $\text{Pd}(111)$ . Depending upon the initial coverage of CO, the hydrogenation of  $\text{CH}_3$  occurs at temperatures which are up to 80 K higher than for the clean surface [10].

## 2. Experimental

The two-level ultrahigh vacuum chamber is equipped with a single pass CMA, a quadrupole mass spectrometer for TPD and a single beam Fourier transform infrared spectrometer (Mattson Research Series) for reflection absorption infrared spectroscopy (RAIRS). The  $\text{Rh}(111)$  single crystal was cleaned by cycled heating in oxygen followed by argon ion bombardment and annealing at 1270 K. Gas phase methyl radicals were generated by the pyrolysis of azomethane ( $\text{CH}_3\text{N}_2\text{CH}_3$ ) in a heated quartz tube as described previously [11]. Methyl groups were adsorbed on the surface at 110 K by line-of-sight adsorption from the quartz tube. Adsorbed  $\text{CH}_3$  and  $\text{CD}_3$  were also produced by the low-temperature decomposition of the corresponding iodo compounds.  $\text{CH}_3\text{I}$  (Aldrich, 99.7%) and  $\text{CD}_3\text{I}$  (Cambridge Isotope, 99.7%) were kept in the dark to avoid photo-induced dissociation, and were purified by cycles of liquid nitrogen freeze-pump-thaw to remove gaseous impurities before dosing. The CO was obtained from Matheson (99.997%) and used without further treatment.

## 3. Results and discussion

Fig. 1A shows the RAIR spectrum in the CH stretching region registered following  $\text{CH}_3$  adsorption produced by pyrolysis of azomethane on clean  $\text{Rh}(111)$  surface at 110 K. An absorption band was detected at  $2918\text{ cm}^{-1}$  [ $\nu_a(\text{CH}_3)$ ]. Deformation modes (not shown) appeared at  $1353\text{ cm}^{-1}$  [ $\delta_a(\text{CH}_3)$ ] and  $1141\text{ cm}^{-1}$  [ $\delta_s(\text{CH}_3)$ ]. These bands can be attributed to the vibrations of adsorbed  $\text{CH}_3$  [4,5,12,13], which basically differ from those characteristics of adsorbed azomethane [14]. Adsorption of  $\text{CH}_3$  radicals on a CO pre-dosed

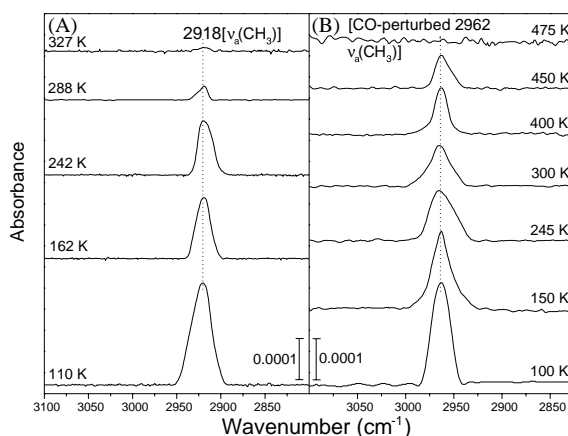


Fig. 1. RAIR spectra of adsorbed  $\text{CH}_3$  at saturation coverage at 110 K and annealed to different temperatures: (A) clean  $\text{Rh}(111)$ , and (B) pre-saturated with CO, CO coverage was 1 ML.

$\text{Rh}(111)$  surface produced similar spectra (Fig. 1B). In this case one monolayer CO coverage was used, which corresponds to  $1.2 \times 10^{15}$  CO molecules/ $\text{cm}^2$ . The positions of  $\text{CH}_3$  vibrations shifted to higher wave numbers by about  $40\text{ cm}^{-1}$  indicating certain interactions between adsorbed species. The frequency shift was proportional to CO coverage.

In the next step the saturated layer was heated up to different temperatures. The resulting spectral changes were registered at 100 K. The intensities of the bands started to attenuate due to vacuum treatment in the temperature range 100–150 K. The development of new absorption features was not observed. The intensities of the asymmetric stretching vibrations of  $\text{CH}_3$  species as a function of annealing temperature are plotted in Fig. 2. In the case of clean  $\text{Rh}(111)$  this band completely disappeared at 300–320 K. On the CO presaturated surface this temperature was ca. 475 K. This indicates a considerable stabilization of adsorbed  $\text{CH}_3$  by co-adsorbed CO.

A strong mutual interaction between adsorbed species is revealed in the RAIR spectra of linearly bonded CO (Fig. 3). When gas phase  $\text{CH}_3$  radicals were introduced to a CO presaturated  $\text{Rh}(111)$  surface, the band due to linearly bonded CO shifted from  $2076$  to  $2020\text{ cm}^{-1}$ . Its position

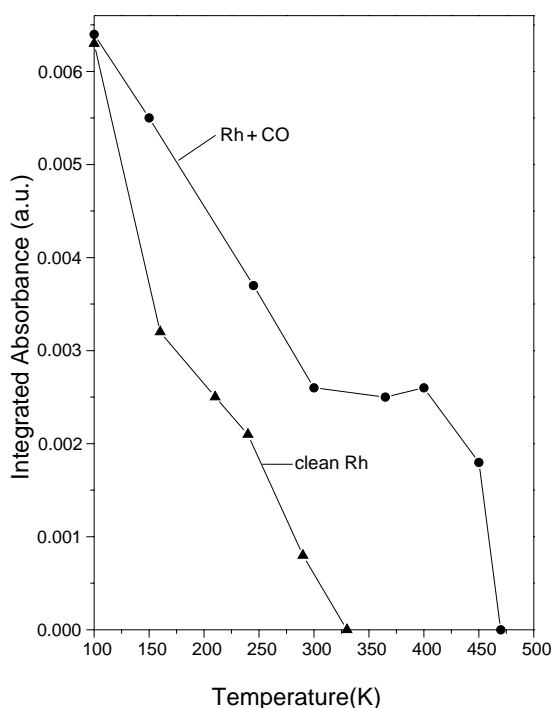


Fig. 2. Absorbance of the peak of  $\text{CH}_3$  at  $2918\text{--}2962\text{ cm}^{-1}$  after heating the adsorbed layer on clean and CO-covered Rh(111).

remained constant during thermal treatment, and the band disappeared at around 470 K, where CO desorbs from the surface.

Subsequent thermal desorption spectroscopic data showed that in harmony with former measurements adsorbed  $\text{CH}_3$  is self-hydrogenated into  $\text{CH}_4$ , which desorbed after its formation at a peak temperature of around 200 K [5]. The transformation of  $\text{CH}_3$  into  $\text{CH}_4$  very likely consists of the decomposition steps of  $\text{CH}_3$  to  $\text{CH}_x$  or to C and their hydrogenation to  $\text{CH}_4$ . As in other cases, we expect the participation of background hydrogen in the hydrogenation reaction. The peak temperature for  $\text{H}_2$  was around 300 K, which agreed with the  $T_p$  for  $\text{H}_2$  desorption from Rh(111) [5], suggesting that the evolution of  $\text{H}_2$  is a desorption limited process. In the presence of co-adsorbed CO, however, new, high-temperature  $\text{CH}_4$  and  $\text{H}_2$  formations were observed. These additional  $\text{CH}_4$  and  $\text{H}_2$  productions were observed between 420 and 480 K, where the CH frequencies for  $\text{CH}_3$  disappeared. Attempts to detect the

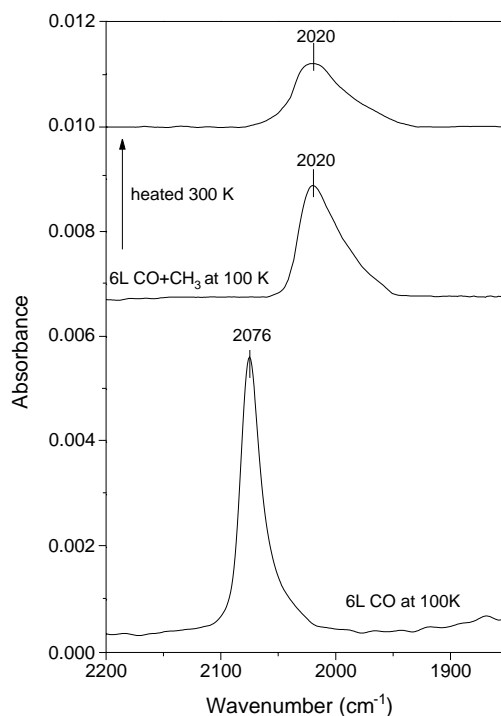


Fig. 3. RAIR spectra of adsorbed CO at saturation coverage on clean and  $\text{CH}_3$  postdosed Rh(111).

formation of other hydrocarbon products (acetylene, ethylene or ethane) failed.

In order to explain the origin of the high-temperature formation of methane and to exclude the role of background hydrogen, we performed detailed experiments with deuterated methyl groups produced by low-temperature thermal decomposition of  $\text{CD}_3\text{I}$  on the same Rh(111) surface.

In contrast with the clean surface,  $\text{CD}_4$  desorption displayed two peaks (Fig. 4) on the CO presaturated surface; the amount of  $\text{CD}_4$  desorbed in the low-temperature peak ( $T_p = 200\text{--}220\text{ K}$ ) decreased, while that in the high-temperature peak ( $T_p = 470\text{--}480\text{ K}$ ) increased with increasing CO coverage.  $\text{CD}_3\text{H}$  desorbed at  $T_p = 208\text{--}218\text{ K}$  showing the role of background hydrogen in forming methane desorbed in the low-temperature peak. There was no detectable high-temperature  $\text{CD}_3\text{H}$  desorption, indicating that background hydrogen does not take part in this high-temperature methane formation. Additional

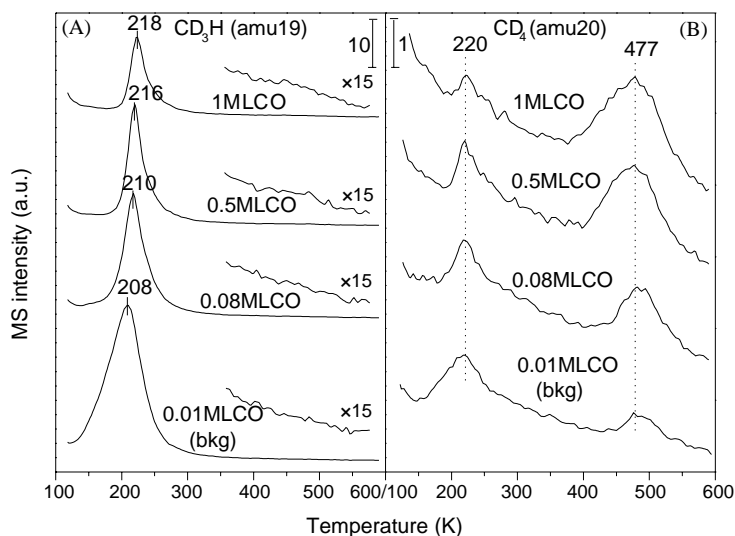


Fig. 4. Thermal desorption spectra of  $\text{CD}_3\text{H}$  and  $\text{CD}_4$  as a function of CO coverage. The heating rate was 5 K/s.

high-temperature  $\text{D}_2$  formation were observed at the same temperature, at which the bands due to  $\text{CH}_{3(\text{ads})}$  disappeared.

Two kinds of desorption states of methane and hydrogen indicate that the stability of a certain part of adsorbed methyl groups is not influenced by CO. The other fraction of methyl groups is strongly stabilized by CO. Probably a small part of stabilized methyl also dehydrogenates above 420 K forming carbon and hydrogen. We assume, however, that the main fraction of stabilized methyl undergoes a disproportionation-like reaction.

In the explanation of the effect of adsorbed CO, we consider two possibilities. One is the blocking of the free Rh atoms, and the other is the electronic effect. There is no doubt that the occupation of surface Rh atoms may inhibit the reaction of  $\text{CH}_3$ , which requires more adsorption sites. This effect may operate in the present system, but this could not be the dominant factor. As Zn and I adatoms with site blocking effects did not modify greatly the stability of  $\text{CH}_3$  on Rh(111) surface [5], the site blocking effect of adsorbed CO in the present case might also be minor. From the infrared shifts of the corresponding bands we may assume the occurrence of an enhanced charge transfer from  $\text{CH}_{3(\text{ads})}$  to the antibonding orbital of CO adsorbed on Rh sites (electronic effect). The

adsorbed  $\text{CH}_3$  will increase the density of states at the Fermi level and thus cause an increase of the  $\text{d-}2\pi^*$  back-donation from the metal to CO (red shift). This enhanced electron transfer makes C–H bonds stronger (blue shift), consequently the dehydrogenation of  $\text{CH}_{3(\text{ads})}$  would occur at higher temperature (i.e. its stability becomes higher), than in the absence of co-adsorbed CO.

#### 4. Conclusions

1. It was demonstrated that CO greatly enhanced the stability of adsorbed methyl groups on Rh(111). In harmony with the stabilization effect, new high-temperature hydrogen and methane peaks were detected.
2. Co-adsorbed CO, however, did not influence the product distribution of the reaction of the methyl groups. There was no detectable amount of desorbed  $\text{C}_2$  compounds.
3. The observed  $\text{CH}_3$  stabilization is explained by site blocking and electronic effects.

#### Acknowledgements

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