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Surface Science 454–456 (2000) 273–279

surface science

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The effects of surface additives on the chemistry of CH_3 on Rh(111) as studied by reflection absorption infrared spectroscopy

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Abstract

The adsorption of gaseous CH_3 on clean and modified Rh(111) has been studied using reflection absorption infrared spectroscopy and thermal desorption spectroscopy. It was found that preadsorbed K adatoms markedly stabilized the CH_3 on Rh(111) and increased its stability by >100 K. This stabilization effect was attributed to the formation of a surface compound between CH_3 and K. In contrast, coadsorbed Zn and I adatoms caused only very slight stabilization of CH_3 on Rh due to the site blocking effect. The formation of methoxy species was observed in the CH_3+O coadsorbed layer on Rh(111). The reaction pathways of surface complexes were also determined. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alkali metals; Alkynes; Chemisorption; Rhodium; Surface chemical reaction; Vibrations of adsorbed molecules

1. Introduction

The study of the chemistry of hydrocarbon fragments on metal surfaces is strongly related to the hydrocarbon catalysis. Recently, several methods have been elaborated for the production of hydrocarbon species (CH_2, CH_3, C_2H_5 etc.) on metal surfaces, which allowed to examine their bonding, reactivities and reaction pathways on different metals. The results obtained are well documented in several reviews [1–3]. In the present paper the effects of potassium and other adatoms (Zn, I and O) on the chemistry of adsorbed CH_3 on the Rh(111) surface will be examined. The study of the chemistry of CH_3 fragment on a clean Rh(111) has been the subject of several recent works [4–6], the results of which will be mentioned as appropriate.

2. Experimental

The two-level ultrahigh vacuum chamber is equipped with a single pass CMA, a quadrupole mass spectrometer and a single beam Fourier transform infrared spectrometer (Mattson Research Series) for reflection absorption infrared spectroscopy (RAIRS). The 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 ($CH_3N_2CH_3$) in heated quartz tube as described previously [7].

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PII: S0039-6028(00)00118-7

Methyl groups were adsorbed on the surface at 110 K by direct, line-of-sight adsorption from the quartz tube. Potassium was deposited on Rh(111) at room temperature by resistively heating a getter wire source (SAES getter) located 2 cm from the sample. The K coverage was calibrated using low energy electron diffraction, Auger electron spectroscopy and thermal desorption spectroscopy yield. One monolayer of potassium on Rh(111) corresponds to a surface density of 5.8×10^{14} atoms cm^{-2} or $\theta_K=0.36$ [2]. The Zn adlayer was produced by the adsorption of $(C_2H_5)_2Zn$ at 100 K followed by the decomposition of the adsorbed layer by heating up to 500 K: this thermal treatment removed all the hydrocarbons from the surface [2]. Iodine was deposited on Rh(111) by annealing adsorbed CH_2I_2 at 600 K [4].

3. Results and discussion

3.1. Effects of potassium

The deposition of potassium lowered the work function of Rh by ca. 3.6 eV. Fig. 1A shows the RAIR spectrum obtained following CH_3 adsorption on a clean Rh(111) at 110 K. Absorption bands were detected at 2918 cm^{-1} [$\nu_a(CH_3)$], 1353 cm^{-1} [$\delta_a(CH_3)$] and 1141 cm^{-1} [$\delta_s(CH_3)$]. These bands can be attributed to the vibration of adsorbed CH_3 [4–6], which basically differ from those characteristic for adsorbed azomethane. Adsorption of CH_3 radicals on K-promoted Rh(111) surface produced very similar spectra with only a slight variation in their position (Fig. 1A).

In the next step the saturated layer was heated up to different temperatures, then cooled back and the spectral changes were registered at 100 K. During annealing the attenuation of all the bands occurred even at 150 K. The development of new absorption features was not observed. The extent of the reduction of the intensities as well as the temperature of the elimination of the bands, sensitively depended on the potassium content. For comparison in Fig. 1B we plotted the intensities of the asymmetric stretch of CH_3 species as a function of annealing temperature. In the case of clean Rh(111), this band completely disappeared at 300–320 K. At $\theta_K=0.14$ this temperature was ca. 375 K, while at $\theta_K=0.36$ it was 410 K. This indicates a considerable stabilization of adsorbed CH_3 by potassium.

Subsequent temperature programmed desorption (TPD) measurements showed that in harmony with former measurements adsorbed CH_3 is self-hydrogenated into CH_4, which desorbed after its formation at a peak temperature of 150 K (Fig. 2). The transformation of CH_3 into CH_4 very likely consists of the decomposition steps of CH_3 to CH_x or to C and the hydrogenation of them into CH_4. As in other cases, we can count with the participation of the background hydrogen in the hydrogenation reaction. The peak temperature for H_2 was 360 K, which agreed well with the T_P for H_2 desorption from Rh(111) [4], suggesting that the evolution of H_2 is a desorption limited process. The reaction pathway of adsorbed CH_3 remained the same on K-dosed surfaces: neither the formation of C_2H_6, nor C_2H_4 was detected. A desorption peak at 150 K for CH_4 observed for clean Rh(111) appeared for the K-promoted surface, too. A new shoulder developed, however, at 200 K, particularly at $\theta_K=0.36$. As a result of the stabilization of adsorbed H by potassium, a shift in the T_P for H_2 to higher temperatures also occurred, at $\theta_K=0.14$ it was 380 K, and at $\theta_K=0.36$ it was 402 K. Note that while RAIRS still shows the presence of adsorbed CH_3 above 250 K, no release of hydrocarbons was experienced either from clean or K-promoted Rh(111) above this temperature.

In order to establish the primary reason of the stabilizing effect of potassium in the subsequent measurements we examined the influence of the Zn and I overlayers. In contrast to K, work function measurements showed that Zn adlayer decreases the work function of Rh(111) only by ca. 0.3–0.4 eV. The RAIR spectrum of adsorbed CH_3 on Zn-covered Rh(111) is presented in Fig. 1A. The asymmetric stretch of adsorbed CH_3 on Rh sites appeared in this case at 2928 cm^{-1}. On heating up the coadsorbed layer the intensity of the peak at 2928 cm^{-1} decreased even at 155 K, and practically disappeared at the same temperature as on the clean surface. During the adsorption, however, new peaks were observed

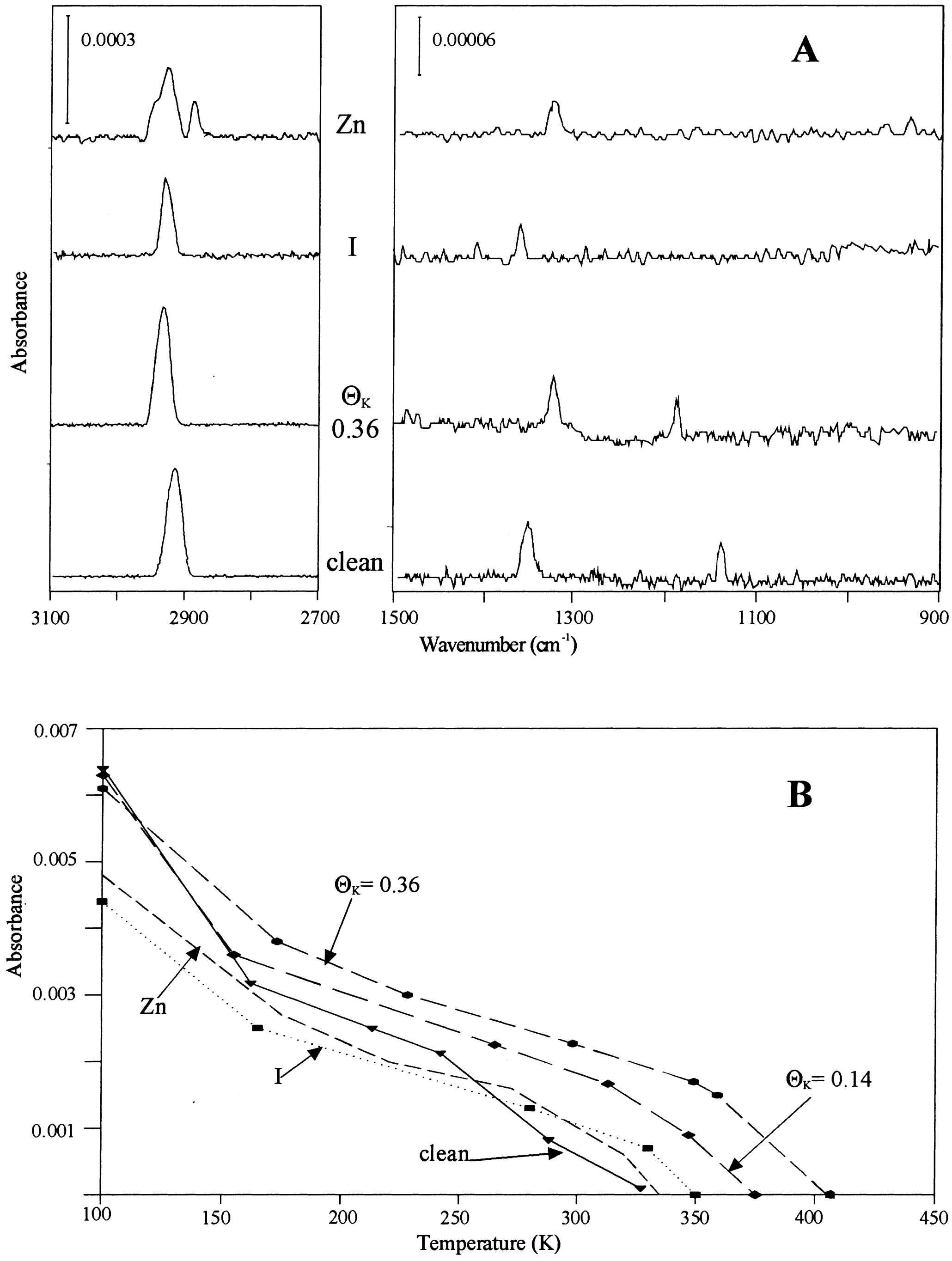

Fig. 1. (A) RAIR spectra of the adsorbed CH_3 at saturation on clean and doped Rh(111) at 100 K. (B) Absorbance of the peak of CH_3 at 2918–2926 cm^{-1} after heating the adsorbed layer on clean and doped-Rh(111). The coverage of I and Zn were ca. 0.3.

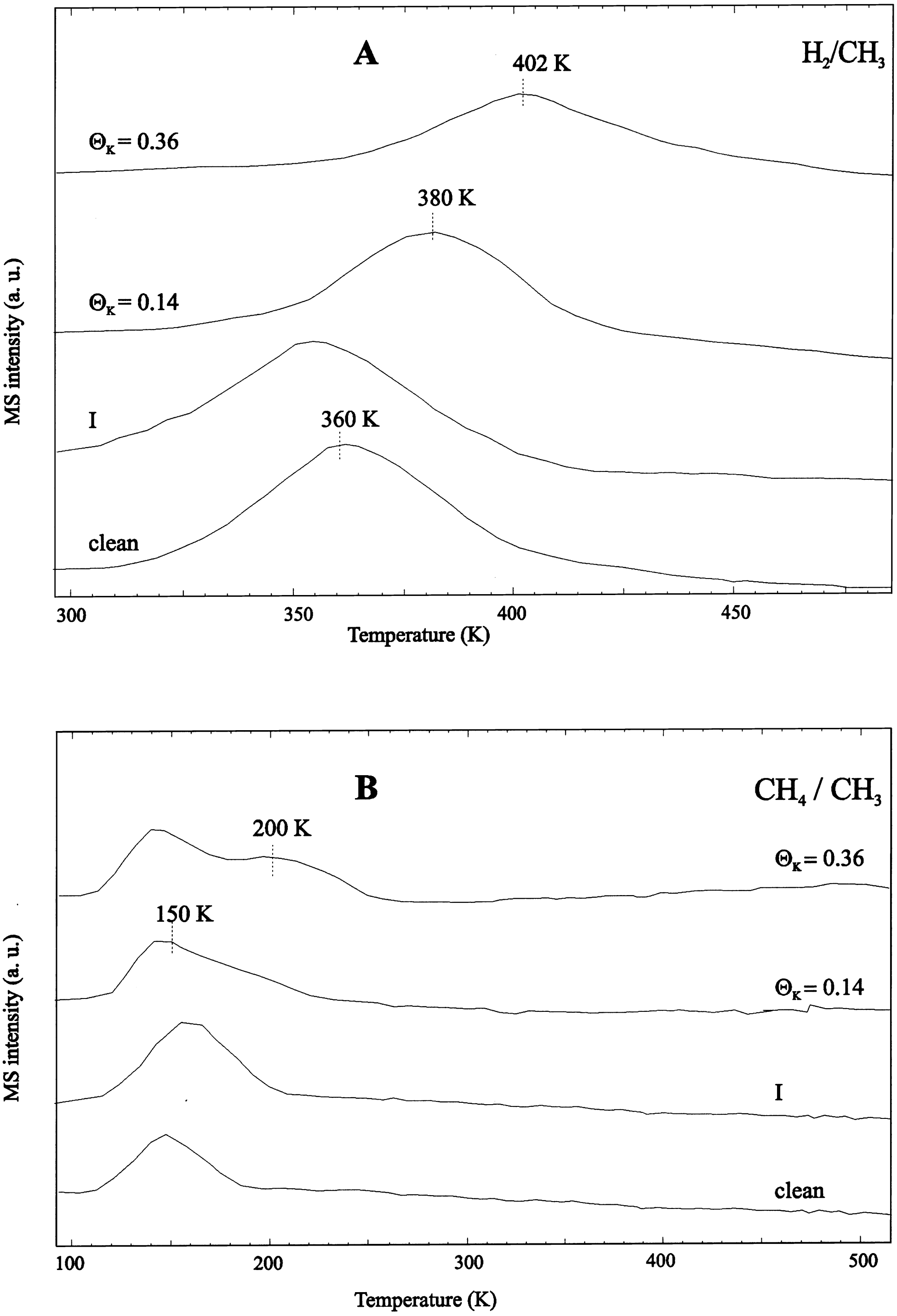

Fig. 2. Thermal desorption spectra of CH_4 (A) and H_2 (B) following the adsorption of the CH_3 radical on clean and doped-Rh(111).

at 2888 and 2950 cm^{-1}. The same peaks were found following the adsorption of $(CH_3)_2Zn$ on Pt(111) [8], therefore, it seems very likely, that these features belong to the vibrations of CH_3 bonded to Zn. As concerns these peaks, the 2888 cm^{-1} moved to 2905 cm^{-1} at 155 K, whereas the position of the 2950 cm^{-1} peak remained unaltered. Both peaks were eliminated at ca. 350 K, in harmony with the thermal stability of $(CH_3)_2Zn$ and CH_3-Zn on Pt(111) [8].

The work function of Rh(111) containing a saturated I adlayer was by 0.5 eV lower than that of clean Rh(111) [4]. Adsorption of CH_3 on I-covered surface gave the same RAIR spectrum as obtained for a clean surface. The most intense vibration band could be traced up to 340 K, which is higher by 25 K than for the clean surface (Fig. 1B). By means of TPD measurements we found only CH_4, $T_P=160$ K and H_2, $T_P=350$ K. These peak temperatures agree well with those determined on the clean surface. These results may answer the open question concerning the influence of coadsorbed I on the chemistry of adsorbed C_xH_y species. The adsorbed hydrocarbon fragments (CH_2, CH_3, C_2H_5, C_3H_7 etc.) have been produced in most cases by the adsorption and dissociation of the corresponding iodo compounds [1–3]. The drawback of this method of preparation is the presence of strongly adsorbed iodine, which might affect the reactions of C_xH_y species. The results presented in this study clearly show that the adsorbed iodine even at the highest coverage exerts only a slight influence on the stability of CH_3 and does not affect the reaction pathway of the CH_3 species.

In the explanation of the effect of potassium, we consider three possibilities:

1. blocking the free Rh atoms;
2. electronic effect; and
3. strong interaction between CH_3 and K.

There is no doubt that the occupation of surface Rh atoms may inhibit the reaction, which requires more adsorption sites. This effect may operate in the present system, but this could not be the dominant factor as in the other cases, when potassium exerted a dramatic stabilizing influence on the coadsorbed compounds. The fact that the influence of Zn and I adatoms, the adsorptions of which also block Rh sites, does not supports this conclusion as much. We may also assume the occurrence of a charge transfer from potassium directly or through the Rh to the antibonding orbital of the Rh—C bond, which would stabilize the C—H bond. A further development of this idea is the strong interaction between K and CH_3 , for example, the formation of a surface compound between the two adsorbed species. We believe this is the primary reason for the stabilization of CH_3 by K, as $K-CH_3$ is known to be a stable compound, even its structure has been determined [9].

Although potassium greatly enhanced the stability of adsorbed CH_3 on Rh(111), it did not influence the reaction pathway of CH_3: there was no detectable amount of C_2 compounds in the desorbing products. Analysis of RAIR spectra revealed no indication for the accumulation of any of its transient decomposition products, CH_2 or CH. Another remarkable feature is that no new CH_4 peak appeared in the TPD. This suggests that the hydrogenation of CH_3 is unfavourable on Rh(111) above 250 K, and the main pathway is its complete decomposition to carbon.

3.2. Effects of oxygen

Recently, two studies have been dealt with the reaction of adsorbed CH_3 and oxygen studied by high resolution electron energy loss spectroscopy (HREELS). In both works methoxy species was detected, but regarding the method of its formation opinions were divergent [5,6]. In the work of Bol and Friend [5] methoxy was produced when adsorbed O atoms reacted with gaseous CH_3; when the adsorption of reactants was reversed no methoxy species was detected. It was concluded that adsorbed CH_3 does not react with adsorbed oxygen to give CH_3O [5]. Somewhat contradictory of this conclusion are the spectroscopic evidences obtained for the formation of methoxy during the annealing of the CH_3I+O coadsorbed layer on Rh(111) [6]. As the low resolution of HREELS makes it sometimes very difficult to separate the vibrational losses and differentiate between coexisting hydrocarbon species, it was expected that RAIRS with high resolution provides a deeper

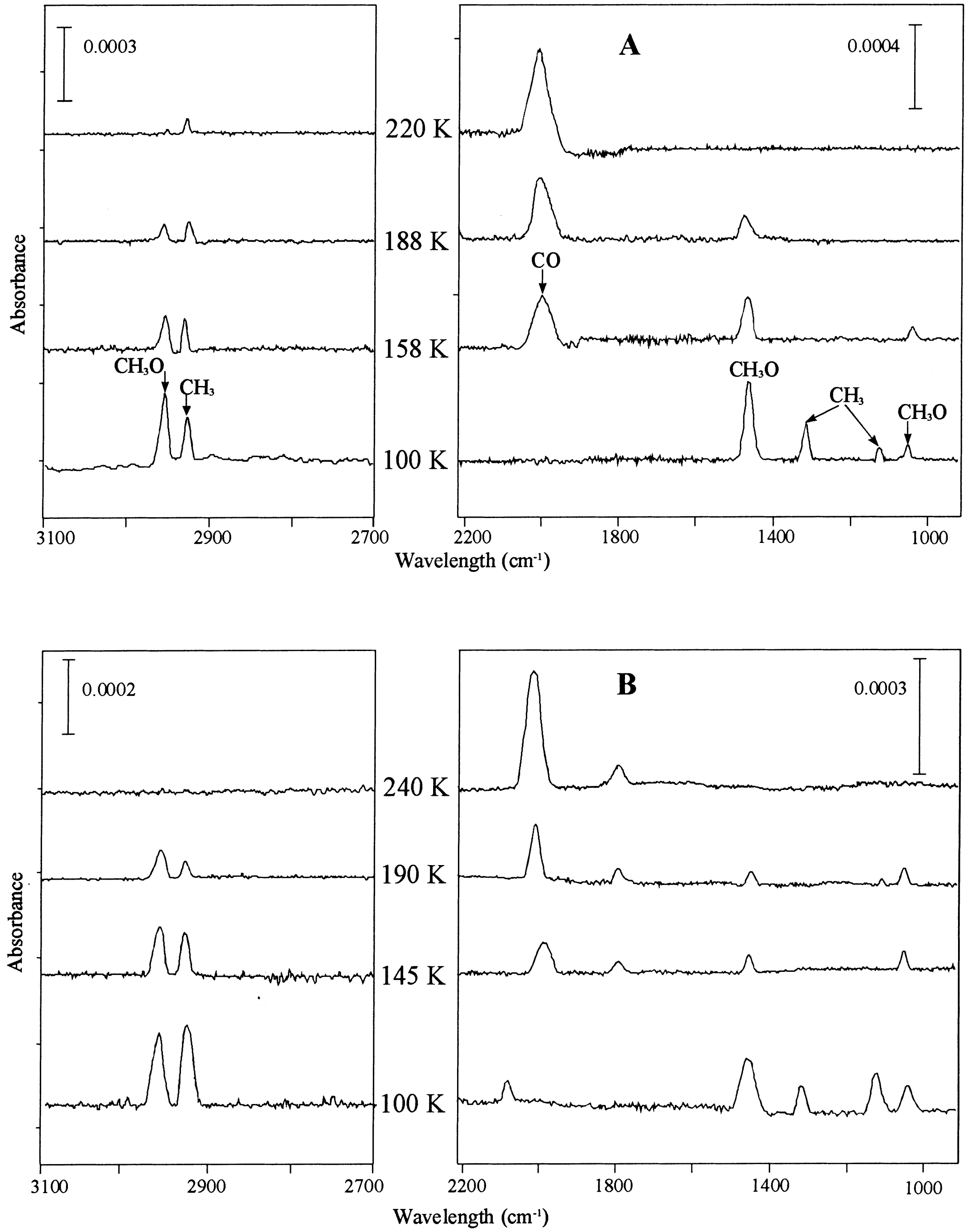

Fig. 3. RAIR spectra of Rh(111) (A) following the adsorption of CH_3 on O-covered surface ($\Theta_O=0.5$), and (B) following the adsorption of oxygen on the CH_3-saturated surface. Both compounds were adsorbed at 100 K.

insight into the nature of the interaction between adsorbed CH_3 and O atoms.

Following the exposition of the O-containing Rh(111) at 100 K to CH_3 we also observed the peaks of the adsorbed CH_3 (Fig. 3A). In addition, several new bands were produced at 2960, 1440 and 1040 cm^{-1}, which are the characteristic vibrations of methoxy species [5,6]. Annealing the adsorbed layer the intensities of these bands gradually decreased and disappeared at 220 K. At the same time a CO band developed at 2020 cm^{-1}. The same features were observed when CH_3 was adsorbed first on the Rh(111) at 100 K and this surface was exposed to O_2 at 100 K (Fig. 3B). As a result of annealing a CO peak at 2020 cm^{-1} also appeared. We should mention that there was no sign of these new peaks when the coverage of CH_3 was only one-third of the saturation and θ_O was <0.3. By means of TPD measurements we found the following desorption products: CO ($T_P=395$ K), H_2O ($T_P=160$ and 250 K), CO_2 ($T_P=320$ K).

The low thermal stability of the surface complex formed in the interaction between adsorbed CH_3 and O and its decomposition products correspond well to the behaviour of CH_3O on Rh(111) established before the adsorption of methanol on this surface [10], and support the conclusion drawn from RAIR spectra. The results presented in Fig. 3 clearly show that the CH_3O species is formed independently on the sequence of the adsorption of reacting species. Accordingly, we can count with certain migration of adsorbed species on Rh(111) even at 100 K. It is true that the intensities of CH_3O peaks are less when CH_3 is adsorbed first. In this case the surface concentration of both species is important: at low coverages, when the adsorbed species may be located far away from each other, the interaction is limited, if it occurs at all.

4. Conclusions

1. The stability and reaction pathway of adsorbed CH_3 on Rh(111) are only slightly influenced by the presence of coadsorbed Zn and I atoms.
2. Potassium, however, increased the stability region of adsorbed CH_3 by >100 K.
3. Adsorbed O atoms reacted with gaseous CH_3 to give methoxy, CH_3O species. Its formation also occurred when adsorbed CH_3 was exposed to oxygen at 100 K.

Acknowledgement

This work was supported by the Hungarian Academy of Sciences and OTKA T23023.

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