A COMPARATIVE STUDY OF THE CATALYTIC DECOMPOSITION OF METHANOL ON RHODIUM AND NICKEL

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Received 17 September 1988; accepted 11 October 1988

Pulsed field desorption mass spectrometry shows that decomposition of methanol on Rh and Ni occurs via step-wise hydrogen abstraction from an adsorbed methoxy. Contrary to previous suggestions, an alternative mechanism through adsorbed methyl was not observed on Ni for pressures up to 3×10^{-3} Pa and temperatures up to the desorption of CO.

1. Introduction

The catalytic decomposition of methanol, CH_3OH, to carbon monoxide, CO, and hydrogen, H_2, has been widely investigated on Rh and Ni [1–7]. On Rh, the mechanism has been examined in detail by Pulsed Field Desorption Mass Spectrometry (PFDMS) [7]. The decomposition was observed to occur readily at room temperature and to proceed via step-wise hydrogen abstraction from an adsorbed methoxy species. On Ni, the same mechanism has generally been proposed [1–5], however results of Steinbach and Spengler [3] led them to conclude that an alternate decomposition mechanism to adsorbed methyl and hydroxyl species is also important. Their conclusion has recently been challenged [4,5]. The subject of this letter is to address this question by comparing results from the previous study of CH_3OH decomposition on Rh [7] with recent work on Ni using PFDMS.

2. Experimental details

The principle of PFDMS and details of the vacuum system have been described elsewhere [8], and the application of the technique for the study mechanisms of heterogeneous catalytic reactions has been documented [7–11]. In brief,

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short pulses of high electric field strengths with repetition frequencies up to 10 kHz are produced in front of field emitter tips used as the sample in an ongoing heterogeneous catalytic reaction. The pulses initiate field desorption of adsorbed species and intermediates that were formed in the intervals between pulses (down to 0.1 ms duration). The species desorbed (as ions) are then chemically identified by means of time-of-flight mass spectrometry.

The samples in this study were Rh and Ni field emitter tips prepared by etching high purity wires (99.995% from Goodfellow Metals) using standard procedures [12]. The tips were mounted with a thermocouple junction on a heating loop and cleaned by field evaporation and heating in hydrogen or oxygen. Methanol (99.8% purity from Merck) or deuterated methanol (98% isotopic purity from MSD isotopes) attached to a gas inlet manifold were purified by several freeze-thaw-pump cycles prior to the first use.

3. Results and discussion

METHANOL ON Rh

A representation of the results from the decomposition of methanol (CHD_2OH in this case) on Rh at 313 K is shown in fig. 1a for a gas pressure of 2.6×10^{-4} Pa and a pulse frequency of 5 kHz. Ions in the form $CH_xD_yO^+$ ($x = 0, 1$ and $y = 1, 2$) (labelled as methoxy) are seen in the spectrum from the reacting methanol, CHD_2OH. In an analysis with undeuterated methanol, specific ions of the type CH_3O^+ can be identified [7] and are recognizable as arising from an adsorbed methoxy species, $*\text{-}OCH_3$ (where $*$- represents the surface bond). Adsorbed methoxy has been identified on Rh(111) as an intermediate in CH_3OH decomposition by thermal desorption spectroscopy [6], and observation of CH_3O^+ with PFDMS is in agreement with these findings.

The methoxy group of ions also contains the parent methanol ion, CHD_2OH^+, and a range of protonated (and deuterated) analogs, such as $CHD_2OH_2^+$. Protonation is observed in PFDMS when hydrogen or polar, hydrogen containing molecules are present on the surface. Some dehydrogenated species of the methoxy are also included in the methoxy group and others are shown separately in the spectrum, as for example CHO^+ and CDO^+. They arise from surface intermediates formed during the decomposition of methoxy to $*$-CO through step-wise abstraction of the hydrogen (or deuterium) atoms [7].

The products of methoxy decomposition, $*$-CO and $*$-H (solid bars), are seen in the mass spectrum in fig. 1a as CO^+ or Rh-monocarbonyl ions and H_x^+. Considerations made from PFDMS studies during reactions of CO with metals have reached the conclusion that metal carbonyl ions arise extensively, if not exclusively, from step or kink atom sites or from diffusing metal sub-carbonyls on the tip surface [10]. Formation of di-carbonyls, as seen by $Rh(CO)_2^{+2}$, has also been discussed elsewhere [10].

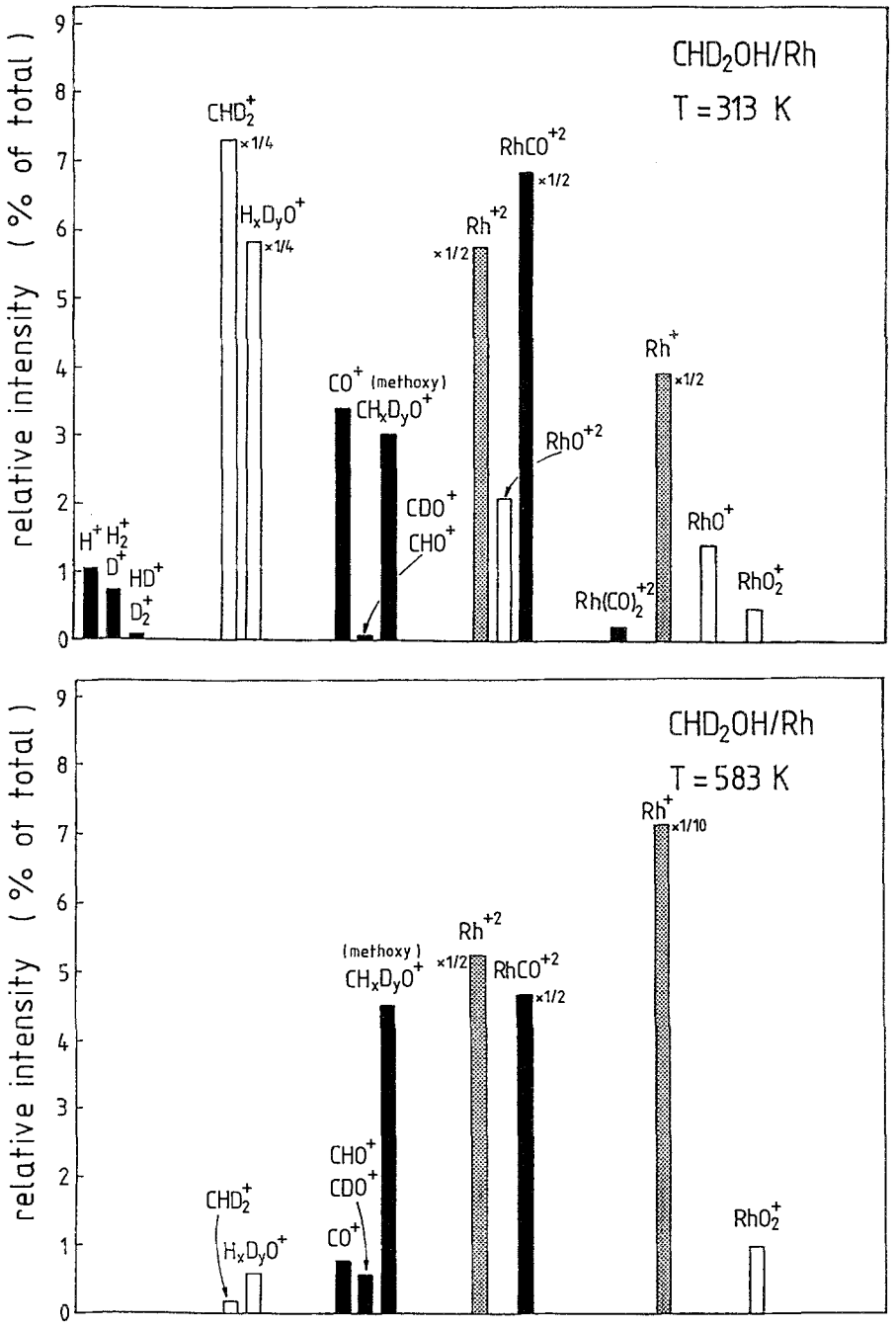

Fig. 1. A representation of the mass spectrum from the decomposition of methanol on rhodium at a pressure of 2.6×10^{-4} Pa and a pulse frequency of 5 kHz. The bars are solid, open, or dotted to aid in grouping, as discussed in the text. The temperatures are in (a) 313 K and in (b) 583 K.

The presence of ions of the type CHD_2^+ and OHD^+ or OH_2D^+ (open bars in fig. 1a) indicates that the intramolecular $*\text{-O-CH}_3$ (oxygen to carbon) bond has been broken in the adsorbed methoxy by the field pulse. Detailed examinations of pressure, reaction field, and reaction time dependences of the intensities of these ions confirm that field pulse rupture, not an alternative catalytic decomposition pathway, is exclusively responsible for cleaving the bond [7]. This removes CHD_2^+ (CH_3^+ in undeuterated methanol) and leaves behind $*\text{-O}$, which is subsequently removed as Rh-oxide or as hydroxide or water (after rapid hydrogenation) or which eventually diffuses out of the monitored area to the tip shank or thermally desorbs (as water) and is therefore not detected in the spectra.

The metal ions Rh^+ and Rh^{2+} in fig. 1a (dotted bars) arise from field evaporation of the metal substrate, most likely from kink or step sites on the surface, which is a commonly observed phenomenon in PFDMS [7,9–11]. The ratio of singly to doubly charged ion can vary from metal to metal and as a function of temperature, field strength, and reactive gas environment. In comparison to fig. 1a at 313 K for example, the Rh^+ and Rh^{2+} signals at 583 K in fig. 1b have increased since field evaporation is a thermally activated process. The Rh^+ intensity increased to a greater extent, in part due to different temperature dependencies for the two signals [12] and in part due to changes in the adsorbed layer composition [10,13].

Further qualitative changes in the spectra for CH_3OH decompositon on Rh in going from 313 K to 583 K reflect increases in decomposition and thermal desorption rates of the various surface species. For example, the intensity of ions arising directly from the field pulse rupture of the methoxy, CHD_2^+ and Rh-oxide ions (and hydroxide and water from eventual protonation reactions) decrease because the increased rate of decomposition acts to decrease the methoxy surface concentration and the approach to adsorption-desorption equilibrium of methanol, i.e., the decrease in sticking coefficient, act to limit the coverage of adsorbed methanol (methoxy). In addition, the amount of $*\text{-CO}$ (removed as CO^+ or $RhCO^{2+}$) decreases with increase in temperature. Peak thermal desorption temperatures for CO on Rh(100) and Rh(110) surfaces are about 520 K to 530 K [14,15]. The continued observation of ions from $*\text{-CO}$ at 583 K arises because the reaction time (0.2 ms at 5 kHz) is shorter than the mean residence time of $*\text{-CO}$ and because the ongoing decomposition of $*\text{-OCH}_3$ is a source of $*\text{-CO}$. This implies a greater increase in decomposition rate of $*\text{-OCH}_3$ than in thermal desorption rate of $*\text{-CO}$ with temperature increase. Detailed studies have also shown that thermal desorption of CO is a rate limiting step at lower temperatures [7]. The hydrogen signal, in contrast to that for CO, disappears by 583 K, consistent with lower thermal desorption temperatures of $*\text{-H}$, about 200 K to 350 K on Rh(111) and Rh(110) surfaces for example [16,17].

METHANOL ON Ni

A representation of a spectrum obtained for the decomposition of CH_3OH on Ni is shown in fig. 2a. These results were taken at 1.3×10^{-3} Pa and 298 K and

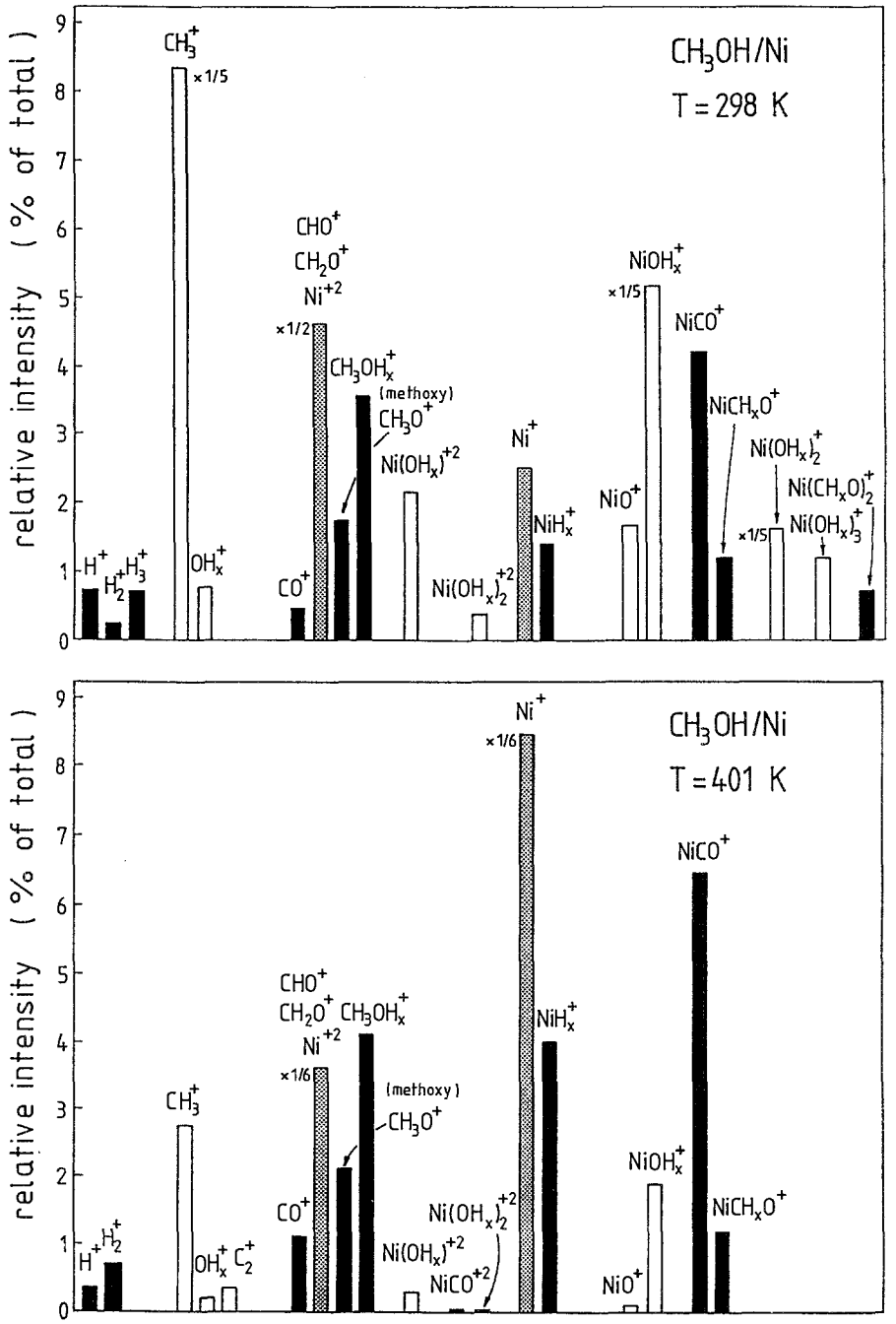

Fig. 2. A representation of the mass spectrum from the decomposition of methanol on nickel at a pressure of 1.3×10^{-3} Pa and a pulse frequency of 2 kHz. The bars are solid, open, or dotted to aid in grouping, as discussed in the text. The temperatures are in (a) 298 K and in (b) 401 K.

with a pulse frequency of 2 kHz. The spectrum for methanol decomposition on Ni shows Ni^+ and Ni^{2+} signals from the substrate, as was seen for Rh. The spectra on Ni were generally much richer in detail though due to the abundance of Ni containing ions with no analogous counterparts in the case of Rh. This is due in part to the lower field desorption strength for Ni (36 V/nm) than for Rh (41 V/nm) [12]. Consideration was made for the isotopic abundances of Ni for all ions containing Ni.

The spectrum in fig. 2a shows hydrogenated and dehydrogenated methanol ions of the type CH_xO^+ and $NiCH_xO^+$ ($x = 1$–4) (solid bars). In comparison with the results on Rh, such ions indicate that the same decomposition pathway via step-wise hydrogen abstraction from $*$-OCH_3 must also exist on Ni. This is in agreement with and supports the work by a range of other spectroscopic techniques [1–5].

The overriding intensity in fig. 2a is in CH_3^+ and OH_x^+ or $NiOH_x^+$ ($x = 0$–3) signals (open bars). In consideration of similar results on Rh, they arise from field pulse rupture of the carbon-oxygen bond in $*$-OCH_3. Whether on Ni they also indicate formation of surface species from catalytic breaking of the carbon-oxygen bond in $*$-OCH_3 is an important question. Results from a molecular beam study of Steinbach and Spengler [3] led them to propose that on stepped or more open Ni surfaces such an alternate catalytic decomposition path of $*$-OCH_3 to $*$-CH_3 and $*$-OH opens at high methanol flux conditions (1×10^{16} molecules cm^{-2} s^{-1}, corresponding to pressures of about 1×10^{-2} Pa) and in the temperature range of 140 K to 440 K. This conclusion has been challenged by Russell, Chorkadorff, and Yates [4] from studies on Ni(111) using scanning kinetic spectroscopy, who propose for example that impurities may have led to a misinterpretation of the results. That the presence of steps may be a significant factor for the alternate pathway appears to be yet unresolved in these two views [5].

Direct proof from PFDMS of the alternate decomposition pathway of CH_3OH to $*$-CH_3 and $*$-OH would be the appearance of ions of the form $NiCH_3^+$ in the mass spectra. Under a range of experimental conditions of pressures between 1×10^{-5} Pa to 5×10^{-3} Pa, temperatures between 298 K to about 450 K, and pulse fequencies from 100 Hz to 10 kHz, such ions were not seen in any *significant* amounts (above 10–100 ppm concentrations) in the spectra. The observation of ions such as $NiCH_xO^+$ (from CH_xO species) and of occasional, though not statistically significant, quantities of $NiCH_3^+$ argues in favour of the appearance of $NiCH_3^+$ rather than CH_3^+ from $*$-CH_3 if the concentration were actually significant. The appearance of C^+ or NiC^+ alone (without $NiCH_3^+$) is not direct proof of an alternate decomposition path in this case, since carbon might also arise from the chemical decomposition of CO.

We believe based on the above discussion that the results in fig. 2a (and later in fig. 2b) show that CH_3OH decomposition on Ni occurs mainly through $*$-OCH_3 via a stepwise hydrogen abstraction mechanism in the above described range of conditions. We note especially that this conclusion applies for stepped

Ni surfaces. Because complete field desorption was not obtained readily on Ni, extensive kinetic studies on a continually cleaned surface were difficult, especially at higher pressures where gas phase ionization of the methanol in the high fields above the tip also occurred. Therefore a definitive conclusion that completely excludes the alternate decomposition pathway to $*\text{-}CH_3$ as kinetically insignificant, for example at higher pressures or temperatures than in this work, is not possible.

A representation of the spectrum at 401 K on Ni is shown in fig. 2b. The increase in and change in ratio of Ni^+ and Ni^{2+} signals with temperature increase are due to thermal activation of the field evaporation process and influences of the adlayer composition, as was the case on Rh. Decomposition of CH_3OH through $*\text{-}OCH_3$ is still the main pathway at this temperature, as evidenced by the continued observation of CH_xO^+ and $NiCH_xO^+$ signals. The intensity of the OH_x^+, Ni-oxide ions, and Ni-hydroxide ions and of CH_3^+ from the field pulse rupture of $*\text{-}OCH_3$ have decreased extensively at 401 K due to an increased consumption of $*\text{-}OCH_3$ by decomposition and to a decrease in sticking probability of CH_3OH.

The CO^+ and $NiCO^+$ signals at 401 K have somewhat increased in intensity, in part from thermal activation of $*\text{-}CO$ field desorption. Peak thermal desorption temperatures of $*\text{-}CO$ from Ni(111) and Ni(110) are about 425 K to 450 K [18,19], so that it also remains for the most part still adsorbed on the Ni surface at 401 K. Thermal desorption of $*\text{-}CO$ appears therefore to be a rate-limiting step for the reaction on Ni under these conditions. The signal from adsorbed hydrogen (mainly seen in NiH_x^+) has increased with temperature for the same reasons as that from adsorbed CO. Peak thermal desorption temperatures of $*\text{-}H$ are about 350 K to 390 K from various planes of Ni [20], just below the temperature of 401 K investigated, and in this regard thermal desorption of $*\text{-}H$ may also be a slow step in the decomposition reaction on Ni under these conditions.

No significant evidence was seen in spectra at 401 K for ions of the type $NiCH_x^+$, although a signal for C_2^+, which appears in fig. 2b, was seen to increase with increasing temperature after about 350 K. This could arise from the onset of thermal decomposition of CO, which has been proposed to occur on polycrystalline Ni foils at about 400 K [21] and on sputter-damaged Ni(111) surfaces at about 450 K [22], for example. Stepped Ni surfaces, as are likely examined in this work, have also been shown to be especially active for CO dissociation [9,23].

4. Conclusions

The decomposition of methanol has been studied with PFDMS on Rh and Ni surfaces for temperatures below and at or just above thermal desorption of CO. On Rh, the spectra show ions which can be ascribed to an adsorbed methoxy

intermediate, $*\text{-}OCH_3$. Field pulse rupture of the $*\text{-}O\text{-}CH_3$ bond in the methoxy leads to the appearance of CH_3^+ and oxide ions. The chemical decomposition of $*\text{-}OCH_3$ occurs exclusively through step-wise hydrogen abstraction to $*\text{-}CO$ and $*\text{-}H$.

During methanol dcomposition on Ni, a variety of ions containing reaction intermediates attached to a Ni atom are observed. No significant direct evidence is however seen for the existence of a decomposition pathway to $*\text{-}CH_3$ and $*\text{-}OH$ on Ni in the form of ions as $NiCH_3^+$ under the given experimental conditions. Instead, the results on Ni compare well to those on Rh and lead to the conclusion that the overriding decomposition pathway is also through step-wise hydrogen abstraction from $*\text{-}OCH_3$.

For both metals, a qualitative comparison of signals arising from CH_3OH decomposition products, adsorbed CO and hydrogen, shows that the trends with increasing temperature are well explained on the basis of expected increases in methoxy decomposition rate, approach to adsorption-desorption equilibrium of methanol, and established thermal desorption temperatures for CO and H_2. In addition, thermal desorption of CO appears to be a slow step in the decomposition reaction on both metals under the conditions studied.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 6-81). Financial support from the Max-Planck Society (JJW) and from the National University of Singapore (GKC) is also recognized.

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