In situ observation of methoxide hydrogenation on the Ni(111) surface

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The surface chemistry of methoxide (CH_3O–) on the Ni(111) surface has been studied in the presence of hydrogen pressures up to 2 Torr. During heating in vacuum methoxide decomposes to H_2 and CO, which desorb at 380 and 445 K, respectively. The CH_3O– decomposition process is rate limited by C–H bond breaking and exhibits a strong deuterium kinetic isotope effect in CD_3O–. In the presence of ambient hydrogen pressures of 0.02–2.0 Torr both CH_3O– and CD_3O– are hydrogenated directly to methanol at ≈ 310 K. Methoxide is hydrogenated by adsorbed hydrogen, which nearly saturates the surface at these pressures and temperatures.

Keywords: Methoxide hydrogenation; Ni(111) surface; catalysis

1. Introduction

A number of experimental methods have been developed over the past few years to allow the study of chemistry on well defined surfaces at modest to high pressures. The intent of these methods is to provide the same quality of information as is available in vacuum surface science investigations and to approach the conditions of catalytic environments [1,2]. Of these the method that has been available for the longest period of time is the Kelvin probe measurement of surface work function. Although the work function measurement is incapable of identifying surface species spectroscopically, it is a relatively fast measurement and is compatible with use in high ambient pressures [3,4]. When used to study reactions of adsorbed species that are otherwise well characterized the work function provides an excellent measurement of surface reaction kinetics. We have used the approach of preparing adsorbed species in vacuum and then studying adsorbate reactions in the presence of high ambient

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hydrogen pressures. Recently we have made in situ observations of the displacement of CO from the Ni(111) surface in the presence of ambient hydrogen [5]. In this letter we describe observations of reactions between adsorbed methoxide and ambient hydrogen to produce methanol.

At low temperatures ($T < 100$ K) methanol adsorbs molecularly on the Ni(111) surface. Heating past 160 K results in the formation of adsorbed methoxide, which has been identified by a number of techniques [6–8]. In ultra-high vacuum the decomposition of adsorbed methoxide is initiated by C–H bond breaking and results in the formation of adsorbed H_2 and CO, which desorb during heating. Self-hydrogenation of methoxide to methanol is not observed in vacuum.

It is important to note that methoxide hydrogenation to methanol has been observed in scanning kinetic spectroscopy (SKS) experiments monitoring product desorption from the Ni(111) surface during heating in a steady flux of methanol [9]. Methanol desorbs at ≈ 290 K as the result of recombination of methoxide and adsorbed hydrogen atoms. The source of adsorbed hydrogen in that case is methanol decomposition which is rate limited by C–H bond dissociation. In similar experiments in which hydrogen was added to the ambient at 2.5×10^{-6} Torr the threshold temperature for this desorption process is shifted to slightly lower temperatures (276 K). Adsorption of hydrogen on the Ni(111) surface prior to methanol exposure resulted in a shift of the methoxide hydrogenation process by ≈ 20 K to lower temperatures. These experiments indicate that methoxide can in fact be hydrogenated by hydrogen atoms from the surface.

2. Experimental

The apparatus used for this work has been described in a previous publication [5]. Briefly it consists of an ultra-high vacuum (UHV) chamber for surface preparation and analysis which is attached to a small high pressure (HP) chamber. The HP chamber contains the Kelvin probe used for the work function measurements. The Ni(111) sample was attached to a small sample module that could be transferred between manipulators in both chambers. The sample could be heated resistively and cooled with liquid nitrogen in both chambers.

The Ni(111) surface was cleaned by sputtering followed by annealing at 1000 K in the UHV chamber. Methoxide was produced on the surface by a saturation exposure to methanol at 180 K. TPD measurements were then made in the UHV chamber by heating the sample in front of a mass spectrometer using a computer to control the sample temperature. The work function measurements were made by transferring the sample to the HP chamber, pressurizing with purified hydrogen (0.02–2.0 Torr) and then heating in front of the Kelvin probe. Hydrogen has very little influence on the work function of the Ni(111) surface.

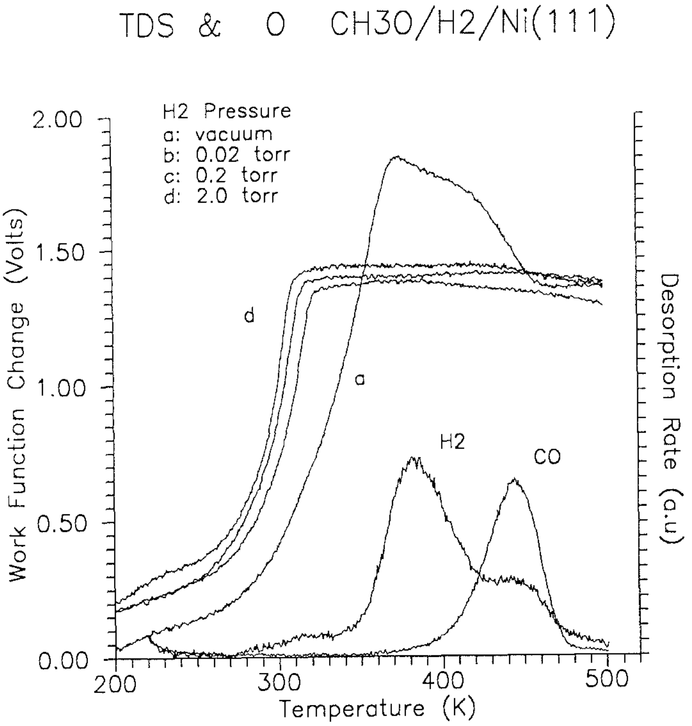

Fig. 1. Thermal desorption of H_2 and CO from the Ni(111) surface following CH_3O- decomposition in vacuum (right axis). CH_3O- was adsorbed by saturation exposure to CH_3OH at 120 K. Work function change during CH_3O- reactions on the Ni(111) surface in (a) vacuum, (b) 0.02, (c) 0.20, (d) 2.0 Torr of H_2 (left axis). CH_3O- was produced by CH_3OH adsorption at 180 K. The heating rate in all experiments was 5 K/s.

Heating in hydrogen over the temperature range used in these experiments (200–500 K) resulted in no change of the surface work function.

The reference surface of the Kelvin probe was a small gold mesh vibrating at a distance of ≈ 1 mm from the Ni(111) surface. The gold mesh does not adsorb hydrogen in the pressure range used [3,4], avoiding complications that might arise from changes of the reference surface work function during the course of an experiment. The sample was grounded through a small leaf spring positioned immediately in front of the Kelvin probe to provide a common ground with the reference surface and to avoid complications arising from the change in sample potential that occurs during sample heating.

3. Results and discussion

The results shown in this section illustrate decomposition and hydrogenation of both CH_3O- and CD_3O- on the Ni(111) surface. The lower portion of fig. 1 shows the thermal desorption of H_2 and CO resulting from methoxide decomposition on the Ni(111) surface. The methanol exposure ($T < 140$ K) was sufficient to saturate the monolayer and was followed by heating at 5 K/s. During heating some fraction of the methanol monolayer desorbs at 190 K while the rest decomposes to methoxide. Methoxide decomposes on the surface to CO and H_2, which then desorb at 380 and 445 K respectively. The appearance of CO and H_2 in the gas phase is rate limited by desorption and yields no information about the decomposition kinetics. The high temperature shoulder (445 K) on the 2 amu TPD trace is an artifact resulting from CO desorption. It is probably hydrogen displaced from the walls of the ionizer housing.

The high pressure work function measurements were made on Ni(111) surfaces prepared by adsorption of methanol at 180 K. Adsorption at this temperature results in the formation of a methoxide overlayer on the Ni(111) surface. The $\Delta\phi(T)$ curve (fig. 1, upper portion, curve a) obtained during heating in vacuum shows a sharp increase in the work function at 340 K indicating decomposition of methoxide which is then followed by hydrogen desorption. This temperature range for methoxide decomposition agrees with other data [6,9]. Hydrogen adsorption contributes very little to the work function of the surface and so the increase in the work function arises from conversion of the adsorbate from methoxide to CO. The surface work function then drops back to its clean surface value as CO desorbs at 445 K.

Also shown in the top panel of fig. 1 are the $\Delta\phi(T)$ curves obtained during heating of the methoxide overlayer in the presence of ambient hydrogen in the pressure range 0.02–2.0 Torr. These show single features in the temperature range 295–310 K in which the work function increases and then plateau's at its final value. There is no indication of a two-step process in which CO is produced on the surface at one temperature and then desorbs at another. One possible cause is that in the presence of hydrogen methoxide decomposition is accelerated and that the CO product is immediately displaced off the surface by hydrogen. In previous work we have studied the displacement of CO from the Ni(111) surface in the presence of hydrogen [5]. At $P_{H_2} = 2.0$ Torr CO is displaced from the Ni(111) in a desorption feature centered at 320 K and at $P_{H_2} = 0.02$ Torr the CO desorption feature is centered at 340 K. These features do not appear in the $\Delta\phi(T)$ curves shown for the reaction of methoxide in hydrogen.

The decomposition of methoxide on the Ni(111) surface is initiated by C–H bond breaking and exhibits a deuterium isotope effect [9]. The lower portion of fig. 2 shows the desorption of D_2 and CO from the Ni(111) surface following decomposition of CD_3O–Ni. The CD_3O– layer was produced by saturation of the surface with CD_3OD at 120 K. D_2 desorbs at 390 K and CO at 435 K, roughly the same temperature as observed during CH_3O– decomposition. The kinetic isotope effect is apparent in the $\Delta\phi(T)$ curve obtained during CD_3O– decomposition in vacuum (upper portion, fig. 2). The increase in the work function associated with CD_3O– decomposition occurs at 370 K, which is 30 K

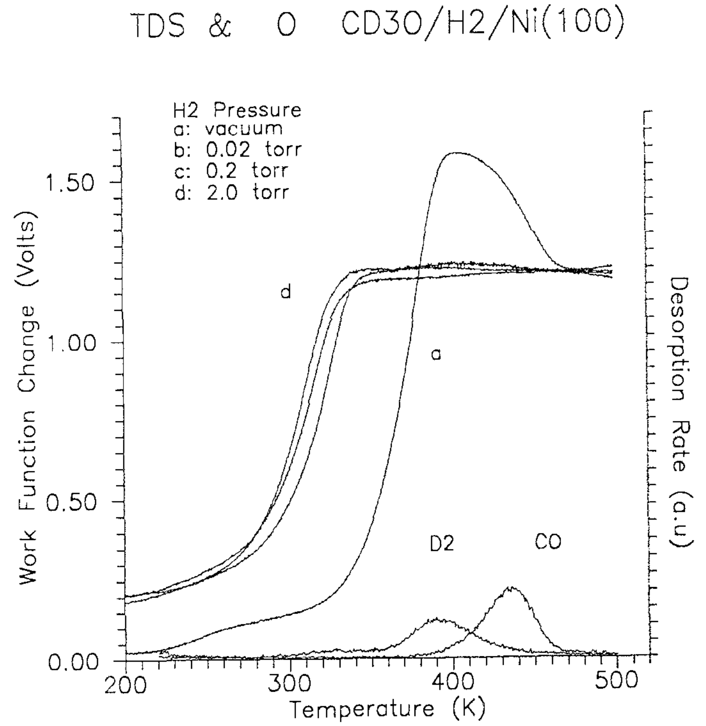

Fig. 2. Thermal desorption of D_2 and CO from the Ni(111) surface following CD_3O- decomposition in vacuum (right axis). CD_3O- was adsorbed by saturation exposure to CD_3OD at 120 K. Work function change during CD_3O- reactions on the Ni(111) surface in (a) vacuum, (b) 0.02, (c) 0.20, (d) 2.0 Torr of H_2 (left axis). CD_3O- was produced by CD_3OD adsorption at 180 K. The heating rate in all experiments was 5 K/s.

higher than in the case of CH_3O-. The $\Delta\phi(T)$ curves for reaction of CD_3O- in ambient hydrogen are also shown in fig. 2 and are virtually identical to those obtained with CH_3O-. They do not exhibit the large deuterium isotope effect observed for the decomposition reaction in vacuum. The deuterium isotope effect at high pressures is relatively small, shifting the $\Delta\phi(T)$ curves to higher temperatures by less than 10 K. The lack of an isotope effect is indicative of a reaction other than one involving C–H (C–D) bond breaking or formation. A second possibility that should be noted is that at high pressures hydrogen may exchange with deuterium in CD_3O- and that the species decomposing is in fact CH_3O-.

Our data are consistent with completely different reaction mechanisms in vacuum and in the presence of hydrogen,

$$CH_3O-_{(ad)} \xrightarrow[\text{vac.}]{} CO_{(ad)} + 3H_{(ad)} \rightarrow CO_{(g)} + \tfrac{3}{2}H_{2(g)},$$

$$CH_3O-_{(ad)} \xrightarrow[H_2]{} CH_3OH_{(g)}.$$

Methoxide decomposition by β-H elimination in vacuum shows a large, expected deuterium isotope effect. Our observations of the reaction occurring in the presence of hydrogen are consistent with direct hydrogenation of methoxide to methanol. Methanol desorption is fast at 300 K and hence it is not a stable intermediate on the surface. The reaction in hydrogen shows no evidence for CO production on the surface and does not exhibit the deuterium isotope effect that would be expected if the reaction involved C–H (C–D) dissociation. Finally, the temperature range in which this process is observed is consistent with that observed using scanning kinetic spectroscopy in which methoxide hydrogenation to methanol was observed using mass spectrometry [9].

The hydrogenation of methoxide to methanol implies the presence of hydrogen on the surface. The increase of the reaction rate with hydrogen pressure indicates a weak positive order dependence on hydrogen pressure. This is consistent with our observations of the CO displacement process on the Ni(111) surface, which showed that at these pressures (≈ 1 Torr) hydrogen comes close to saturating the surface. In that case increasing the hydrogen pressure past 1 Torr does not result in any further increase in the rate of CO displacement, indicating that at this pressure and $T < 320$ K the surface is saturated with hydrogen.

The use of the Kelvin probe to measure surface work function changes during the reaction of methoxide with ambient hydrogen has clearly shown that the reaction is much different from that observed in vacuum. The reaction rates are much faster than those observed for methoxide decomposition and do not exhibit the large isotope effect observed in CH_3O- and CD_3O- decomposition. Our results suggest that rather than observing methoxide decomposition, as in vacuum, methoxide is hydrogenated to methanol in the presence of ambient hydrogen.

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