INTERACTION OF METHANOL WITH RUTHENIUM

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The interaction of methanol with a clean (110) ruthenium surface has been studied using temperature programmed desorption methods. Methanol dissociates upon adsorption at 300 K and yields H₂(g) and chemisorbed CO as the dominant products. Randomization of evolved hydrogen was shown to occur during methanol adsorption and also upon subsequent thermal desorption using isotopically labeled methanol, CH₃OD. In addition to hydrogen and CO, small amounts of H₂CO, CH₃OH, CO₂, and H₂O, are also observed upon thermal desorption. In contrast with a previous study of formaldehyde on Ru(110), no detectable CH₄ product is found upon methanol desorption.

1. Introduction

The mechanism of the catalytic methanation reaction has been extensively studied and is of special current interest. Although the intermediate involved in the reaction is not known, oxygenated species derived from methanol and formaldehyde, i.e., HCO and CHO OH, have been suggested [1]. Recent studies in these laboratories have been concerned with the investigation of formaldehyde [2] and methyl formate [3] adsorption on tungsten as well as formaldehyde adsorption on ruthenium [4]. The rationale for these experiments is based on the assumption that adsorption of organic molecules which very closely resemble or can facilely rearrange to intermediate complexes present in the methanation reaction should then yield CH₄ upon desorption. Consequently, the methane yields observed upon desorption from surface layers produced by adsorption of various organic molecules may give valuable information as to the nature of the intermediate(s) present in CO hydrogenation. In addition, by use of deuterium substitution, the methods used here give basic information about the mode of decomposition of an organic molecule upon chemisorption. Here we wish to report the results of the interaction of methanol with Ru(110).

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2. Experimental

The ultrahigh vacuum system used for these experiments had a base pressure of 3 × 10⁻¹⁰ torr. A single crystal of Ru (0.6 cm average diameter, 0.02 cm thick) was polished to expose Ru(110) faces on both sides and mounted via W or Ru leads of 0.05 cm diameter; changing from W to Ru support leads in separate experiments did not alter desorption product yields, etc. The crystal was heated resistively and the temperature monitored with a 97% W/3% Re-74% W/26% Re thermocouple (0.0125 cm diameter wire).

Gas dosing of both faces of the crystal was accomplished using a symmetrical collimated molecular beam [4]. The orifices were constructed of microchannel plate capillary arrays consisting of multiple parallel capillaries 0.0025 cm diameter by 0.063 cm length. This crystal dosing technique gives a highly collimated incident flux which is 40 times the random flux and prevents a major gas load from being introduced into the ultrahigh vacuum chamber leading to unacceptable levels of residual gases. During adsorption and desorption, partial pressures were monitored with a quadrupole mass spectrometer.

The Ru(110) crystal was cleaned by heating at ≈1500 K repeatedly in O₂ at ≈1 × 10⁻⁵ torr O₂ beam pressure and then flashing clean in vacuum at 1515 K. Cleanliness was checked periodically by Auger electron spectroscopy.
3. Results and discussion

Fig. 1 illustrates what happens kinetically when a clean Ru(110) crystal at 300 K is rotated into a beam of methanol. Approximately 20% of the CH3OH molecules from the doser are directly incident upon the ruthenium surface. Upon interception of the beam by the crystal, the partial pressure of methanol (as monitored with the QMS) decreases. The lower trace (mass 31) corresponds to methanol uptake. As the coverage on the crystal increases, the rate of adsorption drops off until after 50–60 s the crystal becomes saturated. Simultaneously with the methanol uptake, H2 gas (mass 2) is evolved from the crystal as shown in the upper trace. A similar experiment monitoring mass 28 indicated no CO evolution. Therefore, at 300 K, a portion of the methanol dissociates upon interaction with the crystal to form CO(ads) and H2(g).

To test for the possible formation of significant amounts of adsorbed methoxy (CH3O) species during methanol adsorption, the same type experiment was carried out with CH3OD. Assuming that the methoxy species would be derived by the simple cleavage of the hydroxyl bond in methanol, the adsorption of the deuterated analog should give rise to a disproportionate yield of D2 during the period of the experiment in which the methoxy species is being formed. The evolution of H2, HD, and D2, uncorrected for QMS sensitivities, is shown in fig. 2. Above these traces is displayed a plot of the equilibrium constant calculated after proper corrections for the relative pumping speeds and QMS sensitivities to the isotopic species. Each point represents an equilibrium constant (K_eq) derived using the relative desorption flux of H2, HD, and D2 observed at various stages of the adsorption process. The dashed line represents K_eq for an equilibrated H2/D2/HD system at 300 K [5]. Within experimental error, complete scrambling of the hydrogens is seen at 300 K, implying that no significant amounts of adsorbed CH3O are formed via a simple breaking of the OH bond. Further evidence supporting the model for complete decomposition of CH3OD on Ru was found when the small amount of chemisorbed hydrogen remaining following CH3OD adsorption was studied mass spectrometrically. It was found to be the expected statistical mixture of H2, D2 and HD indicating complete isotopic scrambling and hence randomization of all hydrogens originating from CH3OD adsorption.

In fig. 3, the H2 observed in thermal desorption from a methanol layer is compared with that observed from a pure H2 layer. The H2 desorption spectra from chemisorbed CH3OH when compared to the desorption from a pure hydrogen-layer shows a shift in the peak maximum to higher temperatures. These results are consistent with the observation of a positive H–CO interaction found previously for coadsorbed hydrogen + CO mixtures on Ru(110) [4]. Less
Fig. 3. A comparison of $H_2$ desorption from an $H$ monolayer and from a saturated $CH_3OH$ layer.

$H_2$ is observed to desorb from the crystal following methanol adsorption as compared to a fully-covered hydrogen layer. In previous studies of formaldehyde on Ru(110), more $H_2$ was seen to evolve after $H_2CO$ chemisorption than after the adsorption of $H_2$. Results for mass 28 evolution after $CH_3OH$ adsorption indicate a reduction ($\approx 10\%$) in CO evolution compared to CO measured after CO adsorption. A similar small reduction of CO capacity was found for formaldehyde on Ru(110).

Recent results have shown no detectable organic species are formed upon desorption of coadsorbed hydrogen and CO on Ru(110) nor were any observed in dynamic experiments at $H_2 + CO$ pressures of $10^{-3}$ torr in the temperature range 300–1400 K [4]. Desorption from a layer produced by $CH_3OH$ adsorption, however, gives rise to products ($H_2CO$, $CH_3OH$, $CO_2$ and $H_2O$) other than $H_2$ and CO. These results indicate that small amounts of other species are present on the crystal following $CH_3OH$ adsorption which are not present when $H_2 + CO$ mixtures are adsorbed. Although the relative yields of $H_2CO$, $CH_3OH$, $CO_2$, and $H_2O$ are 1–0.1% of the CO evolved, their presence is significant since no detectable amounts of any of these compounds were observed for coadsorbed mixtures of hydrogen and CO (detection limit $\leq 0.01\%$ of CO evolved).

Fig. 4a shows the normalized yields of the thermal desorption products as a function of methanol dosing time using a lower $CH_3OH$ flux than used in figs. 1 and 2. Each plot represents the fractional yield normalized to the saturation yield. The hydrogen and CO (solid line) rise smoothly together until the crystal saturates at about 1000 s beam dosing time. The buildup of $H_2CO$ (dashed line) follows very closely that of hydrogen and CO implying a monotonic rise in the surface population of the precursor complex(es) with the hydrogen + CO coverage. This result is consistent with a unimolecular decomposition mechanism of complex formation rather than one necessitating high surface coverages, i.e., a bimolecular surface reaction.

Normalized yields of masses 15 and 31 are plotted versus beam dosing time in fig. 4b. These results show that these fragments arise from a common origin. This, with the fact that the relative intensities of the mass 15/mass 31 QMS signal are the same as observed in the $CH_3OH$ cracking pattern, indicate that any contribution to the mass 15 signal by methane is insignificant. We estimate that less than 0.05% of a mono-
layer of CH\textsubscript{4} is produced by saturation of a Ru(110) crystal with CH\textsubscript{3}OH at 304 K. Thus the results for methanol differ from those of formaldehyde on Ru(110) in that the formaldehyde leads to detectable methane formation upon desorption whereas methanol does not. The inference can be made that the chemisorption of H\textsubscript{2}CO, in contrast to CH\textsubscript{3}OH, results in a surface population of methane-precursor sufficient to produce detectable methane upon desorption.

In addition to H\textsubscript{2}CO and CH\textsubscript{3}OH, small amounts of H\textsubscript{2}O and CO\textsubscript{2} are observed to desorb following CH\textsubscript{3}OH chemisorption. The desorption curves of these products are shown in fig. 5 to illustrate their relative size and thermal desorption profiles. The vertical axis represents the QMS ion current and is uncorrected for pumping speed and QMS sensitivity.

4. Summary

(1) No evidence has been obtained for the produc-
tion of appreciable surface concentrations of CH\textsubscript{3}O(ads) on Ru at 300 K at any stage of surface coverage, using CH\textsubscript{3}OD as an adsorbate.

(2) At 300 K, the primary products from CH\textsubscript{3}OH adsorption on Ru(110) are CO(ads) and H\textsubscript{2}(g).

(3) Small quantities of H\textsubscript{2}CO, CH\textsubscript{3}OH, CO\textsubscript{2} and H\textsubscript{2}O (<1% monolayer) can be desorbed thermally following adsorption of CH\textsubscript{3}OH to saturation coverage on Ru(110) at 300 K.

(4) The adsorption of CH\textsubscript{3}OH by Ru(110) at 300 K, followed by thermal desorption does not lead to the production of CH\textsubscript{4} at levels above 0.05% of a monolayer. This observation suggests that the methanation reaction on Ru does not proceed via surface intermediates derivable from CH\textsubscript{3}OH.

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References

M.A. Vannice, J. Catalysis 44 (1976) 152;